STATISTICAL MECHANICS

The Theory of the Properties of Matter in Equilibrium

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STATISTICAL MECHANICS

The Theory of the Properties of Matter in Equilibrium

Based on an Essay awarded the
Adams Prize in the University of Cambridge
1923–24

by

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NOTE

For permission to reproduce the following figures thanks are due to Dr Diecke and the Editor of *Physica* (Fig. 3); to the Council of the Cambridge Philosophical Society (Figs. 5, 6, 25); to Herr S. Hirzel, Leipzig (Fig. 7); to Prof. M. Born and the Massachusetts Institute of Technology (Fig. 8); to Herr Julius Springer, Berlin (Figs. 9, 21, 22, 23); to Messrs Ernest Benn, Ltd. (Fig. 10); to Messrs Longmans, Green and Co. Ltd. (Fig. 11); to the Council of the Royal Society (Figs. 14, 15, 16, 17, 18); to the Editor of *Science*, U.S.A. (Fig. 20); and to the Council of the Royal Astronomical Society (Figs. 24, 27, 28).

PREFACE

My reasons for expanding the Adams Prize Essay for 1923–1924 into the present book are set forth in the introductory chapter. Now that the book is finished it will be found I hope to be developed on a plan not too discreditable for 1926, but hardly one which would be adopted to-day. This is a fault hard to avoid, and I still hope that a systematic exposition of Statistical Mechanics, such as this book attempts to give, even if its tone is antiquated, may be of some value to students. I have therefore been at some pains to provide a reliable index of subjects. I hope that any matter which is treated in the book can be traced via the index with no more searching than is reasonable.

There remains only the pleasant task of thanking those who have helped me. The task is a heavy one, for without a number of collaborators the book could never have been finished. The greatest assistance has been given me by Prof. J. E. Lennard-Jones who has contributed Chapter x on a subject of which he is a master, and has also read many chapters in manuscript and proof. I could not have otherwise achieved a Chapter x of this completeness. Dr D. R. Hartree undertook for me the whole of the laborious calculations on which Chapter xvi is based, and provided similar material elsewhere in the book. Mr J. A. Gaunt wrote for me the greater part of the more elaborate discussion and development of Debye and Hückel's theory of strong electrolytes, and has read the whole book in proof. Mr W. H. McCrea has in the same way provided for me most of the material for the analysis of the specific heats of gases. To him also and to Dr L. H. Thomas I am grateful for reading proofs. I am deeply conscious that such merit as the book may have is largely due to the original work of these collaborators, started with the object of helping me. The contributions that I have gratefully taken from Mr H. D. Ursell and Dr D. M. Dennison stand in the same category. I have also benefited by Dr P. A. M. Dirac's criticisms of the last chapter, and Prof. J. E. Littlewood's mathematical assistance. Besides these primary helpers I have been generously given valuable information on various subjects by Dr S. Dushman, Prof. O. W. Richardson, Prof. A. Fowler, Prof. N. Bjerrum and Mr A. Egerton, to whom I offer my best thanks.

Of my obligations to Prof. C. G. Darwin I can make no adequate acknowledgment. The whole book is the outcome of my collaboration with him in which the revised method of approaching statistical theory was worked out.

Finally I must express my gratitude to the Cambridge University Press for their unfailing helpfulness and patience with a somewhat ruthless proof corrector.

R. H. F.

September 1928

TABLE OF THE VALUES IN C.G.S., CENTIGRADE AND ELECTROSTATIC UNITS OF THE COMMONER PHYSICAL CONSTANTS USED IN THIS MONOGRAPH

Charge on the electron, $-\epsilon$	$\epsilon = 4{\cdot}774 \times 10^{-10}$
Planck's Constant, h	$h = 6{\cdot}547 \times 10^{-27}$
Boltzmann's Constant, k	$k = 1{\cdot}372 \times 10^{-16}$
Loschmidt's Number [molecules per gram-molecule]	$6{\cdot}062 \times 10^{23}$
Avogadro's Number [molecules per cc. in a perfect gas at 0° C. and 1 atmosphere]	$2{\cdot}705 \times 10^{19}$
Mass of an atom of atomic weight 1	$1{\cdot}650 \times 10^{-24}$
Mass of H-atom [atomic weight 1·0077]	$1{\cdot}662 \times 10^{-24}$
Mass of electron	$8{\cdot}98 \times 10^{-28}$
Mechanical Equivalent of Heat, J	$J = 4{\cdot}184 \times 10^{7}$
Gas Constant, R (in Calories)	$R = 1{\cdot}988$
Velocity of light, c	$c = 2{\cdot}999 \times 10^{10}$
Electron-volt or volt	$1{\cdot}591 \times 10^{-12}$

These values are mainly taken from Millikan, *Phil. Mag.* vol. XXXIV, p. 1 (1917). They should not be regarded as all necessarily correct or even self-consistent to the *last* figure.

CHAPTER I

INTRODUCTION

§ 1·1. In attempting to study the physical state of matter at high temperatures on the lines suggested by the notice for the Adams Prize Essay for 1923–1924, it was at once apparent that the problem demanded all the available resources of present-day statistical mechanics. These have been somewhat increased in recent years, and the whole aspect of the kinetic theory of matter, at least in full statistical equilibrium, has been steadily altered by the development of the Quantum Theory. As a result there is no recent systematic exposition of the equilibrium theory of statistical mechanics*, envisaging throughout both classical and quantized systems, to which one may appeal in the further applications that it is proposed to make here. Prof. Darwin and I have been fortunate enough in recent years to have developed a method (new in this connection) which enables a systematic exposition to be undertaken with, we would submit, a sufficient degree of elegance. It has, at the same time, been possible to apply the results to a problem more immediately related to that proposed —that is to a theoretical study of the state of matter in stellar reversing layers and in the interior of gaseous stars.

These were of course the main problems with a view to which the essay was first written, but, for the reasons just given, it was thought best not to concentrate entirely on applications in the essay itself but to begin instead with the systematic survey of the equilibrium theory which was then needed and perhaps is still not superfluous. The essay, accordingly, from the first took the form of a monograph on the Equilibrium Theory of Statistical Mechanics. Originally the applications of the theory were mainly astrophysical, but it has been a simple matter to expand their scope. My object was to include all types of application of the equilibrium theory, so that, however inadequately, the monograph should cover the whole field. In the end, however, I have made no attempt to apply the theory to surfaces, or to liquids beyond the theory of dilute solutions; my knowledge of these branches of the theory is still too meagre to justify an exposition of them.

The standard results of the equilibrium theory have long been classical. They are here derived from the fundamental hypotheses in the systematic

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* More accurately, no such exposition existed in 1924. There are now at least two which should be mentioned: Herzfeld, "Kinetische Theorie der Wärme" (*Müller-Pouillets Lehrbuch der Physik*, vol. III, part 2), and Smekal, "Allgemeine Grundlagen der Quantenstatistik und Quantentheorie" (*Encyclopädie mathematischen Wissenschaften*, vol. V, part 3, No. 28).

way mentioned above. The presentation here has been revised and to some extent remodelled, and now forms, I hope, a connected account of the greater part of the equilibrium theory of statistical mechanics, so far as this has yet been developed. In general, the theory and its simpler practical applications have been developed concurrently to avoid too continuous a sequence of unapplied theorems. The more complicated applications form the subject-matter of the later chapters.

At every stage the theory is developed for classical and quantized systems indiscriminately. It is therefore necessary from the start to be absolutely clear what is to be regarded, for the purposes of the theory, as the present logical position of the quantum theory. Though the quantum theory had its origin in Planck's statistical discussion of the laws of temperature radiation and in the breakdown of the theorem of equipartition, it should be regarded as a purely "atomic" theory—that is, a theory applying directly to individual atoms and other connected systems, but not *primarily* connected with the statistical behaviour of large collections of such systems. It is founded on the theory of spectra, and its laws must primarily be sought for by the study of the properties of individual atoms and molecules, and the interactions of pairs of such, or rather in those phenomena which can most certainly be referred back to such individual systems and interactions. Among these phenomena spectra stand first. The laws so derived for individual atoms, just as the laws for classical systems, are then at our disposal to use in discussing the statistical behaviour of large collections of such atoms and systems. If we can make use of them thus, the derived laws of temperature radiation and specific heats are then available for comparison with experiments on radiation or material systems in bulk. We thus ascertain whether the laws of atomic systems and the general hypotheses of statistical mechanics are adequate to account for such molar properties as we are able to compute. This complete divorce of the quantum theory from its historical setting seems to me to be essential to a grasp of its present logical position and to a properly proportioned view of the theory of statistical mechanics.

The theory has been written out at a difficult moment. So much was completed before the changes required by the new mechanics were established that these changes have not been incorporated in the body of the work but are discussed instead in the last chapter. This has the additional justification that it is only in exceptional cases that the primary changes are *practically* significant in comparisons with experiment in spite of their *theoretical* importance. Secondary consequences of the new mechanics appear in modifications of the weights and energies of the stationary states. These are often important or indeed essential in applications and have been incorporated, at least as alternatives, throughout. In the body of the monograph, then, it is assumed that the reader is fully acquainted with the classical quantum theory of atomic systems as formulated by Bohr*, which is really independent of all statistical results, but this is corrected by inserting the results of the newer theory when necessary. The bearing and development of the quantum theory *on the statistical side* are treated in detail.

In these developments we have deliberately used a non-historical deductive method. So far as possible the theory has been presented as a finished structure, with some attempt at logical completeness, not visibly constructed to fit the facts. Results have been deduced at each stage from the general theory, and checked by comparison with experiment.

Conforming to this method, the distribution laws for classical systems are derived by a limiting process from the similar laws for quantized systems. It is not difficult, I believe, to justify this somewhat unusual procedure, in which the laws for Planck's oscillator are fundamental, and the rest of the theory, quantized and classical, a generalization from this starting point. In the first place it is undesirable in a systematic exposition to regard both classical and quantized systems as fundamental. If we are so to regard one only it must be the latter, for we cannot derive the laws of quantized systems from those of classical systems. Secondly, it may at least be claimed that there is a gain in elegance and physical reality, for classical systems are the exception rather than the rule in atomic physics. This is not to say (of course) that we do not use classical mechanics, so far as we can, to derive the quantum mechanics of atomic systems by a process of generalization. But once the laws of quantum mechanics have thus been guessed, as they largely must be *before* we can discuss the theorems of statistical mechanics, quantized systems naturally come first. An apparent exception is the guessing process in the preliminary discussion of "weight". The conception of weight is certainly more important in statistical discussions than in atomic problems, but in the latest versions of the quantum theory the weights have already taken their place as atomic constants determined by the laws of atomic mechanics.

§ **1·2**. *The generality of statistical theorems.* The equilibrium theory of statistical mechanics, as presented here or in any similar manner, is strictly a theory of the distribution of energy, and occasionally also of momenta, and derives these and other distribution laws by general arguments, making no reference whatever to the particular mechanisms of interaction which bring about the equilibrium between the individual systems. If the fundamental hypotheses of the theory are accepted, there seems no escape from this conclusion. Thus, for example, Maxwell's law

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* Bohr, *Proc. Camb. Phil. Soc. Suppl.* 1924, or *Zeit. für Phys.* vol. XIII, p. 117 (1923). Alternatively, see Van Vleck, "Quantum principles and line spectra," *Nat. Res. Council Bull.* (1926), or Born, *Vorlesungen über Atommechanik* (1925).

for the distribution of velocity among the molecules of a gas in statistical equilibrium must be true *whatever be the laws of collisions between these and any other types of molecule in the gas.* The theorems of statistical mechanics thus appear to have something of the same generality as the laws of thermodynamics. They have necessarily less than the full generality of the latter, for they contemplate and refer to a particular molecular structure; granted this limitation, however, it seems that they must be granted also the universal character of thermodynamical theorems, with its advantages and disadvantages. It is impossible to argue that the fact that a particular mechanism leads to a state of complete equilibrium in agreement with experimental facts is any evidence for the particular mechanism discussed. It is merely evidence that the laws of this mechanism have been correctly and consistently written down! Any other mechanism would give the same result.*

Particular mechanisms of interaction first become relevant in the study of *non-equilibrium* states, such as states of steady flow. Finally, of course, it is these mechanisms of interaction, for example between atoms and radiation or atoms and atoms in collision, that are of supreme interest; it must be regretfully admitted that the study of complete statistical equilibrium cannot by *itself* provide any information as to any particular process. It does, however, provide a rigid form to which all possible mechanisms whatever must conform; that is to say, any possible mechanism, left to act by itself, must set up and preserve the laws of statistical equilibrium. This idea, which is well known in the classical theory of radiation, has recently proved of great importance in general statistical mechanics, following a line of thought opened up by Klein and Rosseland†. It appears in general that a particular process can never be supposed to be able to act alone, unaccompanied by a corresponding reverse process; only the two together form a possible single mechanism. The next step forward from the purely equilibrium theory of statistical mechanics is obviously a systematic survey of possible mechanisms, working out the laws that they must observe in order to fit into the equilibrium theory and preserve, as they must, its distribution laws. We attempt to sketch such a survey in the concluding chapters of this monograph.

§ 1·3. *Scope of the monograph.* The scope of the monograph may now be more exactly indicated. At the close of this chapter we specify the

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* This is perhaps an overstatement. In the theory of imperfect gases, for example, we assume a mutual potential energy for each pair of particles and derive an equation of state depending on that potential energy. If the laws of classical mechanics are obeyed by the encounter then the potential energy suffices to determine all its details as a mechanism for the exchange of energy and momentum. But these details are not relevant to the study of the equilibrium state itself and might conceivably be different without affecting it.

† Klein and Rosseland, *Zeit. für Phys.* vol. IV, p. 46 (1921).

fundamental assumptions on which the theorems of statistical mechanics are to be based. These are in general those commonly accepted, previous to the recent speculations of Einstein*, and no serious critical discussion is attempted; but it is desirable to put on record the precise assumptions made in the theory that is to follow. In Chapters II–IV we develop the equilibrium theory for all the types of matter commonly treated in this way—such as perfect gases, crystals, and any general body obeying classical laws. We include also a similar treatment of radiation, but exclude all cases in which dissociation or evaporation occur. Chapter III contains applications to the specific heats of gases, and the latter part of Chapter IV applications to the properties of simple crystals. The theory is generalized in Chapter V to include all types of dissociation and evaporation, and in Chapter VI the connection between the equilibrium theory of statistical mechanics and the laws of thermodynamics is considered in detail. We point out the close analogies between them which allow of the proper interpretation of certain functions of the state of the bodies we discuss as the temperature and entropy of thermodynamics. This chapter concludes with criticisms of the commoner ways of introducing entropy into statistical mechanics, which, it is claimed, are either obscure or misleading, and certainly unnecessary.

Chapter VII returns to applications, now in the region of very low temperatures. Its subject is Nernst's heat theorem and the chemical constants—entropy at the absolute zero. It is possible to obtain a clearer understanding of this theorem and of the chemical constants from the standpoint of statistical mechanics than in any other way. A comparison with experiment is also desirable at this stage of the theory, and can be most conveniently obtained in this field. The present state of the theory leaves Nernst's heat theorem and the chemical constants at a most interesting stage. Definite discrepancies between observation and those forms of Nernst's theorem which make the more comprehensive assertions appear to be established and to fit in a most suggestive way into the general equilibrium theory. In Chapter VIII we extend the general theory to include, so far as is possible, imperfect gases, allowing also for the possibility of electrostatic charges, and in Chapter IX apply the theory to a discussion of theoretical and semi-empirical equations of state. Chapter X, which has been contributed by Dr Lennard-Jones, gives a general numerical survey of intermolecular forces so far as these can be derived by analysis of the equations of state of imperfect gases† and from the properties of allied crystals. It is interesting to find that one and the same law of force will account satisfactorily for so wide a range of properties.

Chapter XI attempts to cover the whole field of thermionic phenomena,

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* Einstein, *Berl. Berichte*, p. 261 (1924), pp. 3, 18 (1925). See also Chapter XXI.

† Evidence from viscosity is also used.

so far as these can be related to states of equilibrium. The most important part is the theoretical formula for the vapour density of free electrons in equilibrium with a hot metal, including the effect of the space charge. This is of primary importance for further applications, because it involves the chemical constant of the electron and experiment confirms the theoretical value. Chapter xii deals with the magnetic and dielectric phenomena of matter in bulk, the most important application being to the paramagnetism of gases. Chapter xiii attempts to carry the theory on to describe the properties of liquids, but nothing is achieved beyond a development of the theory of dilute solutions including the theory of strong electrolytes. Chapters ix–xiii inclusive and the greater part of Chapter viii are additions to the scope of the original essay.

Chapters xiv–xvi deal with applications of the theory at high temperatures to the insides and outsides of stars, the applications proposed by the examiners for the Adams Prize. In Chapter xiv the equilibrium theory of a gas of highly ionized atoms is developed as far as the methods available permit, including the effects of the sizes of the ions and their electrostatic fields. For many purposes approximate forms are necessary which may be expected to be qualitatively valid over wide ranges of conditions. These are provided. These approximations are mainly required for Chapter xvi, which makes a start on the study of the properties of stellar material in the interior of a star. It would be out of place to carry these calculations to great detail or to trace their repercussions on Eddington's work in this monograph. In general they confirm the values of the physical constants of stellar matter which he uses, particularly for the larger stars, while suggesting that certain modifications in his calculations may be required. These may prove interesting. Chapter xv, meanwhile, has dealt with such problems of the atmosphere of a star as can be treated by means of the formulae of the equilibrium state—the more important are the theory of the rise and decay of absorption lines with the rising temperature of the reversing layer and the theory of the rate of escape of molecules from an atmosphere. A summary is given of some of Milne's beautiful work on the calcium chromosphere, but here our connection with the equilibrium theory is getting very weak. The outward flux of radiation, which is an entirely trivial perturbation of complete equilibrium in the stellar interior, is now becoming the controlling feature.

The next group of three chapters, xvii–xix, contains detailed studies of the laws to which actual mechanisms of interaction must conform in order to preserve the equilibrium laws. The laws of material collision processes between free atoms and molecules and free atoms and solid surfaces are discussed in Chapter xvii and applied in Chapter xviii to the kinetics of homogeneous gas reactions. The laws of radiative processes are discussed in Chapter xix. Modifications to these chapters required by the new mechanics are noted as usual in Chapter XXI. Chapter XX contains for completeness an account of the formal calculus of fluctuations, and the last, Chapter XXI, as we have said, some account of the changes of form in the whole of the foregoing required by the new mechanics.

It will be seen that the content of this monograph is not *strictly* confined to equilibrium states of matter. We have ventured outside into regions dealing with steady rates of change (states of flow), but only where the application of the laws of the equilibrium state is immediate. When the changes are such, or the accuracy required is so great that the equilibrium laws can no longer be used without modification, as in the grand theory of transport phenomena in gases, we must be silent. Nor can we do justice here to the phenomena of very high vacua. But where the direct application of the equilibrium laws themselves is relevant or sufficient, as in the study of unit mechanisms or in thermionics, we have endeavoured to press the theory forward.

§ **1·4**. *The fundamental assumptions of statistical mechanics.* It has been pointed out above that it is not the purpose of this monograph to attempt a critical discussion of the fundamental basis of statistical mechanics. But it is desirable, by way of introduction, to consider shortly the usual bases, and to specify as clearly as possible the one selected, indicating shortly the reasons for its choice.

There are two distinct starting points from which we may build up with equal success a theoretical model to represent the material systems of our more or less direct experience—the Gibbsian ensemble and the general conservative dynamical system. Of these the Gibbsian ensemble has perhaps the advantage in logical precision, in that the whole of the necessary assumptions can be explicitly introduced in the initial formulation of the "canonical" ensemble. For this reason it should perhaps be preferred, and is preferred by some theoretical physicists. But to others something more than success and logical rigour appears to be necessary for the acceptance of a model which is to account to our aesthetic satisfaction for the properties of matter. A certain "sanity", or physical reality, may be demanded in the initial postulates and in the details of the model, particularly in so far as they are to reproduce the well-known properties of matter. To these others the Gibbsian ensemble appears to be weak from this aspect, and they are led—in spite of logical and analytical incompleteness—to prefer the conservative dynamical system of many degrees of freedom as the more satisfactory model from which to derive (or attempt to derive) the properties of matter. This is the model, generalized to include quantized systems, which will be used in this monograph.

We have of course to deal in general with dynamical systems which are collections of large numbers of similar atoms, molecules, or electrons.

It is convenient to introduce a consistent nomenclature for the whole collection and its constituent parts. We call the collection which composes the complete dynamical system *an assembly*. We call its constituent atoms etc., or any part of it which for the greater part of time has practically an independent existence, *a system*. The model we propose to use will then be called *an assembly of systems*. The motions and interactions of these systems are controlled by the laws of dynamics modified by the quantum theory, and the assembly as a whole is *conservative*.

The first object of statistical mechanics is to determine all the "normal" properties* of such an assembly and correlate them with the properties of matter in bulk as we know it, when the assembly is in complete equilibrium. This section, which may be called the *equilibrium theory*, will form the main subject of this monograph. We may define the "normal" properties of the equilibrium theory in the manner of Jeans, or perhaps more naturally as *all those properties which the assembly possesses on a time average*. In order for this to have practical significance they must be properties true for times of the order of those in which the ordinary observations of physics and chemistry can be made.

We have naturally no means of deriving such time averages with full logical rigour short of a sufficiently detailed solution of the general dynamical equations of the assembly. Equally naturally we lack this information even in the classical case. It remains necessary to assume the general form that the solution will take—the best known such assumption is that of Maxwell, the assumption of quasi-continuity of path. It is extremely probable that this assumption is always untrue; it is, moreover, insufficient and at the same time unnecessarily restrictive for the purpose in hand. But some similar assumption must be made in its place. Its object is to entitle us to assert that the required time average properties may be correctly calculated as if they were averages over the whole phase space† of the assembly subject to the condition that the assembly has the proper energy, and perhaps momenta, and provided that the different elements of the phase space are "weighted" in the proper way. Even then it is necessary, by an extra assumption or investigation (but no such has yet been given), to identify the "long-time average" so calculated with the "short-time averages" which are of physical significance. It is only thus that the "normal" properties, in the sense of Jeans, become physically significant.

The usual arguments by which our choice of weights is guided for a classical assembly are developed in rather more detail in the following section.

This assignment of the "weight" of each element of the phase space

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* Jeans, *Dynamical Theory of Gases*, ed. 3, p. 74 *sqq.*

† See § 1·5.

of the assembly is fundamental to the whole problem. Once these weights are agreed on, and it is further agreed as above that the "normal" properties of the assembly are the properties of the assembly averaged on this basis over the whole phase space (subject to the energy and other similar conditions), the rest of the derivation of these properties requires merely straightforward mathematics, which can be carried through with rigour. It is therefore desirable to look closely into this critical step. The assignment of the weights is frequently spoken of in this connection as an assignment of *a priori* probabilities. If this is taken at its face value the behaviour of the systems in our assembly must be according to the laws of chance, and cannot be controlled by dynamical (or any other determinate) laws in ordinary space and time. This is a possible hypothesis, but in the end hardly a satisfying one. To avoid an appearance of definitely accepting this hypothesis we use the neutral word "weight" instead of the commoner "*a priori* probability", although in effect (though not in origin) they become synonymous terms. For the purpose of the ensuing calculations we require to know or assume the relative times (out of a long interval) during which the representative point of the assembly remains in two given elements of the phase space. It is these which determine the relative weights. It is customary to assume, and we assume here, that in dealing with classical systems these times are proportional to the extensions of the corresponding elements of the phase space, and therefore also that the weight to be assigned to any element in calculating normal properties is proportional to the element's extension. This is consistent with, though by no means a deduction from, Liouville's theorem.

It is usual to proceed from this basis by the calculation of values of maximum frequency of occurrence (most probable values) rather than average values. The results are, of course, identical—the mathematical machinery is not. Average values are, as naturally as, if not more naturally than, most probable values, taken to be the normal properties of the assembly. They have besides an overwhelming advantage in ease and rigour of mathematical presentation; in particular the usual indiscriminate use of Stirling's theorem for large factorials can be entirely avoided.

Most of this is an old story; on the proposed basis all the ordinary equilibrium distribution laws of assemblies of classical systems can be derived by averaging over the phase space included between the energy surfaces E and $E + dE$ and letting $dE \to 0$. In any general discussion, however, we must treat not only classical but quantized systems, in which only discrete values of the energy are permissible. For reasons already specified we formulate everything from the quantum point of view and include the classical case by a limiting process.

No attempt has been made in these paragraphs to minimize the logical incompleteness of this development of statistical theory from the chosen starting point. It will be only too painfully apparent, and is of course the same for all variants of this development. I confess to a belief that it is unavoidable and may continue so for a long time. It can only be said that the assumptions made have a certain inherent plausibility and are justified by their success, and that, in spite of these lacunae, this starting point is physically preferable to the Gibbsian ensemble.

One further step can be made, which, while it does not fill the logical gaps indicated above, yet goes a long way towards giving us confidence in our conclusions and warranting the belief that the average properties we calculate are really normal properties of the assembly, which it will always to our senses possess. This step is the calculation of *fluctuations*. Just as we calculate the average value of any quantity P, say, and find it s $\bar{P}$, so we can calculate the average value of $(P-\bar{P})^2$, or $\overline{(P-\bar{P})^2}$. If we do this, we find that in all cases $\overline{(P-\bar{P})^2} \leqslant \bar{P}$. It follows that the average deviation of P from its average, and therefore normal, value $\bar{P}$ is of the order $\sqrt{\bar{P}}$, and if $\bar{P}$ itself is large the deviation is insignificant. We can interpret this by saying that out of any time interval only an insignificant fraction in general can be spent in states in which P differs effectively from its normal value $\bar{P}$. This very greatly consolidates the whole theory.

§ 1·5. *Conservative dynamical systems.* It will be convenient at this stage to enumerate briefly the chief properties of conservative systems, which suggest the hypotheses of statistical mechanics. The state of the assembly, which is the conservative system here in question, is fully defined by specifying the necessary N Hamiltonian coordinates q and N conjugated momenta p. It can be conveniently represented geometrically by a point in space of $2N$ dimensions, whose rectangular cartesian coordinates are the Np's and Nq's. This space is called the *phase space* of the assembly and the point its *representative point*. The equations of motion of the assembly are

$$\dot{p}_s = -\frac{\partial H}{\partial q_s}, \quad \dot{q}_s = \frac{\partial H}{\partial p_s} \quad (s = 1, \ldots N), \qquad \ldots\ldots(1)$$

where H is the Hamiltonian function. It is usually only necessary to consider assemblies in the formulation of which the time does not occur explicitly, so that H is the total energy E expressed as a function of the p's and q's. Through every point of the phase space passes a definite *trajectory* of the assembly satisfying (1), and confined of course to the surface $H = E$, constant, and perhaps to other surfaces defined by constant momenta as well.

We have mentioned above that no logical justification has ever been attempted for the assumption that the average values concerned in observations are equivalent to the long-time average properties of the assembly. Attempts, however, to justify identifying these long-time averages with averages over the phase space, though far from successful, have led to interesting investigations, which throw light on the proper choice of the weight for each element of phase space in this process of averaging. As the first of these we may cite Liouville's theorem.

Let τ be the density of a "fine dust" of representative points in any element of phase space. Then Liouville's theorem states that $D\tau/Dt = 0$, where D/Dt is the mobile operator of hydrodynamics (generalized), giving the rate of variation of τ for a given group of points as we follow them along their trajectories. Consider a fixed volume element in the phase space bounded by $p_1,\ p_1 + dp_1, \ldots q_N,\ q_N + dq_N$, of extension $d\Omega\ (= dp_1 \ldots dq_N)$. The representative points crossing the face p_s, of area dS, have a component velocity $\dot{p}_s$ normal to that face, and so the rate of increase in $\tau d\Omega$ due to motion across this face is

$$(\tau\dot{p}_s dS)_{p_s}.$$

There is a similar rate of loss

$$(\tau\dot{p}_s dS)_{p_s+dp_s}$$

due to motion across the opposite face, and so a net rate of increase for this pair of faces

$$-\frac{\partial}{\partial p_s}(\tau\dot{p}_s)\,dp_s dS = -\frac{\partial}{\partial p_s}(\tau\dot{p}_s)\,d\Omega.$$

Summing for all the $2N$ pairs of faces, it follows that

$$\frac{\partial\tau}{\partial t} + \sum_1^N \left\{\frac{\partial}{\partial p_s}(\tau\dot{p}_s) + \frac{\partial}{\partial q_s}(\tau\dot{q}_s)\right\} = 0. \qquad \ldots\ldots(2)$$

Hence

$$\frac{D\tau}{Dt} = \left\{\frac{\partial}{\partial t} + \sum_1^N \left(\dot{p}_s\frac{\partial}{\partial p_s} + \dot{q}_s\frac{\partial}{\partial q_s}\right)\right\}\tau, \qquad \ldots\ldots(Def.)$$

$$= -\tau\sum_1^N\left(\frac{\partial\dot{p}_s}{\partial p_s} + \frac{\partial\dot{q}_s}{\partial q_s}\right) = 0. \qquad \ldots\ldots(3)$$

This is Liouville's theorem. If we consider it in terms of an element of phase space moving with the dust of representative points, it states that the extension of any such element is constant throughout the motion. This is of course easily proved directly. The rate of increase of volume is

$$\int_S \sum_1^N (l_s\dot{p}_s + \lambda_s\dot{q}_s)\,dS,$$

where dS is any element of the bounding surface and (l_s, λ_s) the direction cosines of its "normal". But this is equal to

$$\int_\Omega \sum_1^N \left(\frac{\partial\dot{p}_s}{\partial p_s} + \frac{\partial\dot{q}_s}{\partial q_s}\right) d\Omega$$

by Green's theorem, and so vanishes.

The content of Liouville's theorem relevant to the basis of statistical mechanics is that the density of a group of representative points remains constant along their trajectories. If at any time they are distributed with uniform density in the phase space, they will for ever have uniform density. There can therefore be no eventual crowding together of the points into favoured regions of the phase space. If "normal" properties are to be determined by averaging over the phase space, they must be properties true of almost all the phase space, and not properties of special regions, unless various regions are selectively weighted in this averaging. Again, the theorem suggests that no such selective weighting can be legitimate, for there is no natural crowding into one region rather than another, and therefore no excuse for selective weighting. In short, it suggests that the only reasonable choice of weight is the one actually made in statistical mechanics, namely a weight proportional to the extension of the region.

We can perhaps make this choice of weight clearer by a rather different presentation (of essentially the same argument). To each element of phase space $d\Omega$ we can certainly assign a time t_Ω during which the representative point will lie in $d\Omega$ out of a total interval T, and can thereby define a function of position in the phase space

$$W(p_1 \dots q_N) = \left\{ \operatorname*{Lt}_{T\to\infty} \frac{t_\Omega}{T} \right\}. \qquad \dots\dots(4)$$

It seems reasonable to assert that this limit exists. It represents the "probability", defined as a limiting frequency ratio, that the representative point lies in $d\Omega$ at any specified epoch t, and is from its definition independent of t. This fits in with our physical preconception that such "probabilities" cannot depend on the epoch of observation.

The function W might be expected to depend on the particular trajectory chosen. No doubt it does so depend for any dynamical system, but it clearly cannot do so in any way which would make any difference to observable quantities, or consistency would vanish from physics. We therefore assume that there is some W, a definite one-valued function of position in the phase space, such that for any trajectory, or at least on the average for all trajectories,

$$KW\,d\Omega \quad (K \text{ constant})$$

represents the frequency ratio with which the representative point lies in $d\Omega$ for an arbitrary choice of epoch t. On this basis the frequency ratio with which the assembly has the property P is

$$\int_{\Omega_1} W\,d\Omega \Big/ \int_{\Omega} W\,d\Omega, \qquad \dots\dots(5)$$

where Ω_1 is that part of the whole phase space Ω in which P holds. Normal properties of the assembly are those for which (5) is effectively unity.

That such a W really exists is largely a pious hope, but granted its existence its form can be fixed, and we can show that for any Hamiltonian assembly W may be taken to be independent of the coordinates and therefore may be put equal to unity. For since $KW\,d\Omega$ is the frequency ratio for the falling of the representative point in $d\Omega$, the total number in $d\Omega$ out of a "fine dust" of representative points will be effectively $K'W\,d\Omega$. This is the τ of Liouville's theorem, and by repeating his argument we find that

$$\frac{\partial W}{\partial t} + \sum_1^N \left\{\frac{\partial}{\partial p_s}(W\dot{p}_s) + \frac{\partial}{\partial q_s}(W\dot{q}_s)\right\} = 0.$$

Therefore $$\sum_1^N \left\{\frac{\partial}{\partial p_s}\left(-W\frac{\partial H}{\partial q_s}\right) + \frac{\partial}{\partial q_s}\left(W\frac{\partial H}{\partial p_s}\right)\right\} = 0. \qquad \ldots\ldots(6)$$

This is the general partial differential equation which any possible W must satisfy. Obviously a solution is $W = 1$.

The form of (6) shows that W is a *last multiplier** of the system of differential equations (1) which specify the trajectory, and it can be shown that the actual choice of last multiplier satisfying (6) can make no difference in statistical calculations. For if M and N are two last multipliers and a function f is defined by $f = N/M$, then $f = a$ is a uniform integral of the equations of motion (e.g. the energy integral itself), and N/M will be constant throughout the whole of the phase space to which our calculations extend. The function f can therefore be absorbed into K and ignored in all calculations. Since $W = 1$ is one solution of (6) and the simplest, we may legitimately take

$$K\,d\Omega \quad (K \text{ constant})$$

to be the weight to be attached to the element $d\Omega$ in all statistical calculations. Since in any contact transformation the extension of any element of phase space remains unaltered,† the constant K is genuinely invariant and independent of the system of coordinates, provided only that they are Hamiltonian.‡

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* See, for example, Forsyth, *Differential Equations*, ed. 3, § 174.

† See, for example, Boltzmann, *La théorie des Gaz*, vol. II, p. 64. This invariance under a contact transformation is the most general assertion we have made about $d\Omega$. It includes its constancy during the motion, since the motion of any Hamiltonian system may be regarded as a succession of infinitesimal contact transformations. This alternative proof of Liouville's theorem is that used by Boltzmann, *loc. cit.*

‡ Some further discussion will be given in § 21·3, by way of introduction to the modifications imposed by the new mechanics.

CHAPTER II

THE RULES FOR WEIGHTS, AND THE THEOREMS OF STATISTICAL MECHANICS FOR ASSEMBLIES OF PERMANENT SYSTEMS

§ **2·1.** We shall establish in this chapter all the usual theorems of statistical mechanics for assemblies of permanent (non-combining and non-dissociating) systems, quantized or classical, which are in the highest possible degree independent of one another. These are, of course, the assemblies most amenable to exact treatment, about which most is known. They naturally include perfect gases and crystals, but it is convenient to postpone the actual calculations for crystals (and temperature radiation) to Chapter IV, though they are fully covered by the methods here developed.

The highest degree of independence is attained when it is sufficiently accurate to assume throughout the calculations that the energy of the assembly is the sum of the energies of the individual systems and contains no part depending on the coordinates of more than one such system. On this assumption, universally if sometimes tacitly made, some comment is needed. Such an assembly is, of course, an ideal limit to which an actual assembly may approximate but can never attain. For it is essential to the whole idea of an assembly that it should form a connected dynamical system with a single energy integral but not a number of separate ones. If, indeed, the energy were really entirely independent of such cross terms, which represent the interactions of the systems, the systems would never interact and the assembly would not be connected. We have therefore to assume that some such interactions do occur, but in this limiting case so rarely that their contribution to the total energy of the assembly may be neglected. They still suffice to preserve connection and ensure that only a single energy integral exists. This is an example, of course, of the general assertion underlying the whole theory that, while there must exist mechanisms of interaction, their mere existence is sufficient, their nature being irrelevant to the laws of equilibrium.

§ **2·2.** *The classical theory of weight.* We have agreed to attach a weight

$$K\,dp_1 \dots dq_N, \qquad \dots\dots(7)$$

where K is an absolute constant, to the element of phase space or cell $dp_1 \dots dq_N$. This means that the average value $\overline{Q}$ of any quantity Q is to be calculated by the equation

$$\overline{Q}\int_{\Omega} dp_1 \dots dq_N = \int_{\Omega} Q\,dp_1 \dots dq_N, \qquad \dots\dots(8)$$

the region Ω of integration being the whole relevant phase space. If our assembly consists of N similar systems each of s degrees of freedom, then the cell is

$$(dp_1 \ldots dq_s)_1 \ldots\ldots (dp_1 \ldots dq_s)_N,$$

and the weight

$$K\,(dp_1 \ldots dq_s)_1 \ldots\ldots (dp_1 \ldots dq_s)_N. \qquad \ldots\ldots(9)$$

The N systems are by hypothesis exactly similar, so that the weight remains the same for any interchange of systems. We can thus attach the required weight to a cell of the assembly by attaching a weight

$$K'\,(dp_1 \ldots dq_s) \qquad \ldots\ldots(10)$$

to a cell of the phase space in which the state of a single system can be represented. We may set up a *convention* by which we attach weights in this way to cells of systems. But it must always be remembered that such weights have a meaning *only when re-combined by multiplication over all systems in the assembly*. It is strictly only for the cells of the assembly itself that we have attached any meaning to weight. But for convenience and clarity it is legitimate to think of these as decomposed into cells for each system and to attach conventional weights to these—posterior re-multiplication being tacitly assumed.

The conventional weight which we attach to the cell of a *system* cannot be interpreted as proportional to the time which the representative point of the system lies in this cell, as can the weight attached to a cell of the assembly. Interpreted so it is definitely wrong. For if the weight for the cell of the assembly is given by (9), and if for simplicity we suppose that the energy function contains only square terms, then the average time spent by a selected system in a selected cell can be shown by integration to be

$$K'' e^{-2jE_1}\,(dp_1 \ldots dq_s)_1,$$

where E_1 is the energy of the system in $(dp_1 \ldots dq_s)_1$, and K'' and j are constants. The conventional weight applied in this sense is wrong. We could if desired take this accurate value instead of the conventional weight, and on re-combining for the cell of the assembly we should obtain

$$K' e^{-2j\Sigma E_1}\,(dp_1 \ldots dq_s)_1 \ldots\ldots (dp_1 \ldots dq_s)_N,$$

or

$$K\,(dp_1 \ldots dq_s)_1 \ldots\ldots (dp_1 \ldots dq_s)_N$$

as before, since $\Sigma E_1 = E$, a constant. The factors e^{-2jE_1} are thus irrelevant. This digression should make clearer the extremely conventional meaning of the weight attached to a system's cell.

It may be agreed then that the weight $K'\,(dp_1 \ldots dq_s)_1$ shall be attached to the system's cell, where K' is an invariant, the same for all similar systems. It is not yet clear, however, how K' varies from system to system.

If in the course of the motion of the assembly one system A can change into another B then obviously $K_A' = K_B'$. (The number of degrees of freedom of a classical system cannot change.) Again if, for example, system A can dissociate into systems B and C then $K_A' = K_B' K_C'$. There are a series of similar relations. Such relations as these are necessary and sufficient to preserve the equality of weights for equal cells of the assembly, since by Liouville's theorem, applied to the practically independent system or pair of systems, the cells of these systems must have invariant extensions so long as they remain independent. If, however, two kinds of systems exist which can never change into one another, then no relation can be established or needs to exist between the assigned weight factors K_A' and K_B'. We shall see later that this independence has a physical significance and is in accord with classical thermodynamics.

More complicated cases arise if the weights are taken to include as factors the so-called symmetry numbers*. This is the most convenient course, but it is not necessary here to do more than mention how these arise in the simplest case. Consider an assembly in which both atoms A and molecules AA exist and dissociate and re-combine. As above, the weights to be assigned to the phase space of atoms and molecules will naturally be connected by the relation $K_{AA}' = K_A'^2$. It is necessary, however, when dissociation and re-combination are going on, to consider also all possible ways of forming the molecules AA out of the atoms A, all of which correspond to possible phases of the assembly. This is best done by calculating the permutations of all the atoms to form specified numbers of free atoms and molecules. If this is done in the most straightforward way it will be found that the arrangements AA' and $A'A$ in a single molecule are counted as distinct. But during the free motion of this molecule the exchange of AA' into $A'A$ can take place by a simple rotation.† The separate cells of the assembly corresponding to AA' and $A'A$, other coordinates being unaltered, are therefore counted twice over by the later permutation of the atoms. The number of repetitions due to this permutation is called the symmetry number of the molecule and denoted by σ. The repetitions may be eliminated by dividing all the weights of the cells of these molecules by σ. It is sometimes convenient to suppose that these divisors are absorbed in the weights instead of leaving them to be introduced at a later stage. In the simple case we should then take

$$K_{AA}' = K_A'^2/2,$$

and in general

$$K'_{\text{mol}} = \Pi \{K'_{\text{atom}}\}/\sigma.$$

The divergences from the formulae of the last paragraph here introduced are convenient in practice and of course purely formal. Weights which are modified by the symmetry numbers in this way may be called *prepared weights* when it is desired to distinguish them.

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* Ehrenfest and Trkal, *Proc. Sect. Sci. Amsterdam*, vol. XXIII, p. 169 (1920). A full discussion is undertaken in Chapter V.

† The new mechanics requires that such exchanges of similar atoms in a molecule (or electrons in an atom) can and do always take place by internal motions, not only by rotations like a rigid body. See Chapter XXI.

§ 2·3. *The weights of quantized systems.* We are certain from non-statistical evidence that individual systems exist which do not obey the laws of classical dynamics and electrodynamics, but obey instead a set of laws not yet fully formulated which are commonly called the laws of the quantum theory*. It remains to discuss here how our fundamental assumptions, especially the rules for assigning weight, must be modified so that we may be able to include assemblies containing quantized systems in the general equilibrium theory of statistical mechanics.

Let us start by considering the simple case of an ideal linear harmonic oscillator. If it were a classical system, its element of phase space $dpdq$ would have a weight $K'dpdq$, where K' is constant. If its mass is m and its frequency ν, its Hamiltonian function is

$$H = \frac{1}{2m} p^2 + (2\pi\nu)^2 \frac{m}{2} q^2 = \alpha_1, \qquad \text{......(11)}$$

$\omega = 2\pi\nu$

and

$$\oint p\,dq = \oint \{2m\alpha_1 - (2\pi\nu)^2 m^2q^2\}^{\frac{1}{2}} dq,$$

$$= \frac{2m\alpha_1}{2m\pi\nu} \int_0^{2\pi} \sin^2 \phi\, d\phi,$$

$$= \alpha_1/\nu, \qquad \text{......(12)}$$

where $\oint$ denotes integration round one complete cycle of values of p, q. Thus the standard rule of the older quantum theory

$$\oint p\,dq = nh \qquad \text{......(A)}$$

is equivalent here,† as of course it must be, to $\alpha_1 = nh\nu$.

Consider further the geometrical meaning of $\oint p\,dq$. It is the area enclosed by the curve

$$\frac{1}{2m} p^2 + (2\pi\nu)^2 \frac{m}{2} q^2 = \alpha_1 = nh\nu \qquad \text{......(13)}$$

in the phase plane (p, q) of the oscillator, which represents the orbit of the oscillator, and by (A) has the area nh. Thus while the classical theory permits any such orbit, the quantum theory selects an enumerable sequence of discrete orbits which in fact cut up the phase plane into equal areas h. An essential part of the postulates of the quantum theory of atomic systems is a correspondence in detail between classical and quantized systems,

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* Bohr or Born or Van Vleck, *loc. cit. ante.*

† These and similar arguments are unaffected by modifications made by the new mechanics which give here $\alpha_1 = (n + \frac{1}{2})\, h\nu$, for the arguments are concerned with asymptotic forms for large n and these are unaffected.

by which the two become indistinguishable in the limit for large quantum numbers. Symbolically

$$\operatorname*{Lt}_{n\to\infty} \text{(Quantized system)} = \text{Classical system.}$$

It is convenient to refer to this as *the limiting principle**. By this principle it is easy to see that for large n, when the permitted orbits are close together and still separate off areas h, the weight belonging to an area h of the classical phase plane must be attached to each single orbit. More strictly, if ϖ_n is the weight of the nth orbit,

$$\operatorname*{Lt}_{n\to\infty} \varpi_n = K'h.$$

There is no reason to expect different weights for different orbits, and in fact, as we shall see later, another line of argument shows in analogous cases that ϖ_n is independent of n. It follows that $\varpi_n = K'h$. This was the original assumption made by Planck from which he derived the correct law of temperature radiation.

The generalization $\varpi_n = K'h$ for the linear harmonic oscillator is thus (as we shall see) amply justified by success and is the first step in the necessary rational generalization of the classical rules for weights.

We shall find that it is immaterial what value we attach to any one weight, provided all relative weights are unaltered. We shall therefore make the simplest possible convention and assume that the weight of any permitted state of a (quantized) simple linear harmonic oscillator is 1. We must therefore put $K' = 1/h$ and so assign a weight

$$dp\,dq/h$$

to any cell of a classical system of one degree of freedom. A slight additional advantage of this convention is that the weights are (as they should be) all pure numbers. It follows at once that the weight of any cell of a classical system of s degrees of freedom is

$$\frac{1}{h^s}(dp_1 \ldots dq_s), \qquad \ldots\ldots(14)$$

subject to the possible presence of the indeterminable factors already mentioned.

Further progress depends on finding some connection between the weights of other quantized systems and those of a simple linear harmonic oscillator. This is provided by the theory of *adiabatic invariants*†. The general form of the quantum conditions may be written

$$J_r(a_1, a_2, \ldots) = n_r h \quad (r = 1, \ldots s),$$

where the a's determine the values of any external parameters. Though the proof is not complete, it is believed that if, while the motion is in

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* The content of this principle is quite distinct from that of the wider Correspondence Principle which has arisen from it. This latter is to be regarded strictly as a postulate of the quantum theory without reference to the classical limit. The limiting principle persists in the new mechanics, which replaces the Correspondence Principle by precise dynamical relations.

† Bohr or Born, *loc. cit. ante*. The theory was begun by Ehrenfest.

progress, the values of the a's are changed sufficiently slowly over any range in which the degree of periodicity of the system, and so the number of quantum conditions, does not alter permanently, then the J's remain constant throughout the change.* Indeed, if the quantum conditions are to have any physical reality this property of permanence is essential. Now the invariant quantum conditions determine the extension of the elements into which the phase space is cut up by the permissible orbits. For, for any non-degenerate system,

$$\int dp_1 \dots dq_s = \int dJ_1 \dots dw_s,$$

where the J's are constant along any orbit and the w's (angle variables) all range from 0 to 1. Hence the extension enclosed by a single orbit is $J_1 J_2 \dots J_s$. In the general case this extension is $n_1 n_2 \dots n_s h^s$. If the J's are precluded from taking the value zero there would then be $n_1 n_2 \dots n_s$ orbits, with each of which in the limit may be associated an extension h^s. As, however, the J's may sometimes be zero the actual number of orbits lies between $n_1 n_2 \dots n_s$ and $(n_1 + 1)(n_2 + 1) \dots (n_s + 1)$.†

Moreover, since the J's are invariants for adiabatic changes, the cells into which the orbits dissect the phase space are also invariant. It follows that we must attach the same weight to any two orbits or to orbits of any two systems which can be transformed into one another adiabatically without passing through a degenerate system, or, in short, that the weights also are adiabatic invariants. In particular, since any non-harmonic linear oscillator can be adiabatically transformed into a harmonic one, the weight of any possible state of any linear oscillator must be unity. Further, in conformity with (14) and the limiting principle, it is natural to suppose that the weight of any possible state of any non-degenerate system of any number of degrees of freedom is also unity.

The theory of adiabatic invariants takes us yet a stage further. For Bohr‡ has shown that for systems of more than one degree of freedom one may expect to be able to connect by an adiabatic change two different stationary states of the same system with different values of the quantum numbers. He has given as an example an actual process which applies to a Keplerian ellipse. It follows that in such cases the weights of the different stationary states are necessarily equal. And although such transformations are not always possible, in particular for systems of one degree of freedom, it

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* Burgers, *Com. Phys. Lab. Leiden*, Nos. 145–156, Suppl. 41 *c*, *d*, *e*, or *Proc. Sect. Sci. Amsterdam*, vol. xxv, pp. 849, 918 (1916), and p. 1055 (1917); Dirac, *Proc. Roy. Soc.* A, vol. cvii, p. 725 (1925).

† Or in the new mechanics there is the possibility that some of the J's may take half odd integer values and some integer values. It is also possible that some of the J's may take both positive and negative values giving an extra factor 2 in the number of possible orbits for each such J, but at the same time an extra factor 2 in the extension of the phase space, so that the argument is unaffected.

‡ Bohr, *Danske Vid. Selsk. Skrifter IV* vol. xi, p. 24 (1918).

is hardly possible to avoid concluding that the weights must always be equal. The weight unity which we have assigned is then the natural value to take.

It will appear at a later stage* that the adiabatic invariance of the weights is a necessary premise for the second law of thermodynamics for such assemblies. This is, of course, a still more cogent reason for this invariance than the above analysis.

The foregoing arguments break down if the systems are degenerate, and so possess fewer adiabatic invariants than their number of degrees of freedom. In such cases we start by considering a non-degenerate system which has the given system as a limit under adiabatic transformation. A definite number of different states of the non-degenerate system will coalesce to form each state of the degenerate system. It is clear that the only reasonable generalization will be to take the weight of any state of the degenerate system as equal to the number of separate states of the non-degenerate system which have this state as their limit. This generalization seems to prove successful, but no proof exists that the weight so defined is unique, and no general rule for enumerating the coalescing states. Each case has to be treated separately.

A simple example will illustrate the working of this rule for calculating degenerate weights. Consider a two-dimensional harmonic oscillator. If the two fundamental frequencies are equal then

$$J = \oint p_x dx + \oint p_y dy = nh$$

is the only quantum condition. If, however, the frequencies are independent the system is non-degenerate and

$$J_x = \oint p_x dx = n_1 h,$$

$$J_y = \oint p_y dy = n_2 h.$$

When the two frequencies tend to equality we get the former case as the limit and obviously $n_1 + n_2 = n$. The total number of states which coalesce to form the degenerate state is $n + 1$. This must, by the rule, be the weight of the degenerate state. It is easily verified by direct calculation that this weight agrees with the limiting principle. For the whole phase space (x, y, p_x, p_y) enclosed by the orbits for which $E = nh\nu$ is

$$\iiiint dx\,dy\,dp_x\,dp_y,$$

extended over the region for which

$$\frac{1}{2m}(p_x^2 + p_y^2) + (2\pi\nu)^2 \frac{m}{2}(x^2 + y^2) \leqslant E.$$

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* See also Bohr, *Proc. Camb. Phil. Soc. Supplement*, p. 17 (1924).

This is a familiar Dirichlet's integral, whose value is

$$\frac{\pi^2 E^2}{\Gamma(3)} \frac{4m}{m(2\pi\nu)^2} = \frac{E^2}{2\nu^2}.$$

The region enclosed between the orbits for which $E = nh\nu$ and $E = (n+1)h\nu$ is therefore

$$\tfrac{1}{2}h^2\{(n+1)^2 - n^2\} = h^2(n+\tfrac{1}{2}),$$

in agreement with the limiting principle.

In the same way the total number of states which coalesce to form the degenerate state $J = nh$ of a three-dimensional isotropic oscillator is $\frac{1}{2}(n+1)(n+2)$, which is taken by the rule to be the weight of the degenerate state. It may again be verified by direct calculation of

$$\int^{(6)} \cdots \int dx\,dy\,dz\,dp_x\,dp_y\,dp_z$$

over the region for which

$$\frac{1}{2m}(p_x{}^2 + p_y{}^2 + p_z{}^2) + (2\pi\nu)^2 \frac{m}{2}(x^2+y^2+z^2) \leqslant E = nh\nu,$$

or of

$$\int^{(6)} \cdots \int dr\,d\theta\,d\phi\,dp_r\,dp_\theta\,dp_\phi$$

over the region for which

$$\frac{1}{2m}\left(p_r{}^2 + \frac{1}{r^2}p_\theta{}^2 + \frac{1}{r^2\sin^2\theta}p_\phi{}^2\right) + (2\pi\nu)^2\frac{m}{2}r^2 \leqslant E = nh\nu,$$

that this weight satisfies the limiting principle.

It cannot be maintained that the rules for the weights of degenerate systems are as yet in a final form, and there are difficulties in connection with apparently permissible orbits, transformable adiabatically into orbits which are mechanically impossible, which have been discussed at length by Bohr.*

In summary of this discussion we may say that

(i) *To each element of the phase space of a classical system we attach a weight*

$$\frac{dp_1 \ldots dq_s}{h^s}.$$

(ii) *To each mechanically possible stationary state of a non-degenerate quantized system we attach the weight*

$$1.$$

(iii) *To each such state of a degenerate system we attach a weight equal to the number of different stationary states of some non-degenerate system which coalesce in the limit to form the given state of the degenerate system.*

(iv) *Weights are adiabatic invariants.*

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* These difficulties disappear in the light of the new quantum mechanics. See Chapter XXI.

(v) *They are significant only when combined by multiplication over the whole assembly.*

We are now in a position to undertake the study of the equilibrium properties of the general assembly on the basis laid down in this chapter. It is to be remembered that the idea of temperature—particularly absolute temperature—and the laws of thermodynamics are initially entirely foreign to statistical mechanics. They must be introduced by analogy as we proceed.

§ 2·4. *A simple case. An assembly of two sets of simple harmonic linear oscillators.* For simplicity of exposition we consider first this special case which will serve to bring out all the distinctive features of the problem and the method. Let us suppose that the assembly consists of two large sets of linear harmonic oscillators A and B, obeying the laws of the quantum theory. They will each have a series of stationary states of weight unity in which their energies take the values $nh\nu_1$ or $n\epsilon$, and $nh\nu_2$ or $n\eta$. We may emphasize once again that in assigning individual stationary states and energies to the systems separately we tacitly assume that they are practically independent systems, each pursuing its own motion undisturbed for the greater part of time. This is essential to the energy specification and therefore essential to the treatment of assemblies composed of large numbers of practically independent systems. At the same time we must assume that exchanges of energy between the oscillators are possible and do occasionally take place, otherwise the systems will not form a connected assembly and obviously cannot possess unique equilibrium distribution laws. In the present very special case we may think of the exchanges of energy as effected by a few free atoms in an enclosure containing the oscillators—so few in number compared with the oscillators that we may ignore their energy altogether. (Later on we shall be able to include the energy of any number of such atoms or molecules in our discussion, as well as the energy of temperature radiation. The latter can then also be regarded as an agent of energy exchange.)

For the purposes of the proposed proof we must suppose that ϵ and η are commensurable and shall therefore suppose that they are integers with no common factor. This amounts to making a special choice of the unit of energy. The removal of this restriction by a limiting process will be considered at a later stage.

We will suppose that the total numbers of oscillators of types A and B are M and N.

It is our object to determine the distribution laws of this assembly, that is, the equilibrium or average distribution of the oscillators among the various states of which they are capable. This is its only normal property of importance. A specification of this distribution—equilibrium or not—

is frequently referred to as a specification of the *statistical state of the assembly.* This conveys correctly the idea that it is only the macroscopic state of the assembly that really interests us and not the microscopic state. If, for example, 47 systems A have the energy 5ϵ, it makes no difference statistically which of the M systems these 47 may be.

A possible statistical state of the assembly can be specified by any set of positive integers* (a_r, b_s) subject to the conditions

$$\Sigma_r a_r = M,\ \Sigma_s b_s = N,\ \Sigma_r r a_r \epsilon + \Sigma_s s b_s \eta = E. \qquad \ldots\ldots(15)$$

It is understood that a_r denotes the number of systems of type A in the rth state of energy $r\epsilon$ and b_s the number of type B in the sth state of energy $s\eta$. The conditions (15) express the facts that there are MA's and NB's in all and that the total energy is E. Now more than one cell of the phase space of the assembly corresponds to this statistical state. In fact, since the systems of each set are identical, the number of cells must be the number of distributions of MA's into sets $a_0, a_1, \ldots$, and simultaneously NB's into sets $b_0, b_1, \ldots$, that is

$$\frac{M!}{a_0!\,a_1!\ldots}\,\frac{N!}{b_0!\,b_1!\ldots}. \qquad \ldots\ldots(16)$$

We call each such distribution a *complexion.* To any complexion, which corresponds to a cell of the phase space, we must attach the proper weight, which here is

$$1^{a_0} \times 1^{a_1} \times \ldots \times 1^{b_0} \times 1^{b_1} \times \ldots = 1.$$

When the complexions have all been multiplied by the proper weight they are called *weighted complexions*—a distinction which is of course unnecessary in this example. The number of weighted complexions representing this statistical state is therefore given by (16) and the total number of weighted complexions C by the equation

$$C = \Sigma_{a,b}\,\frac{M!}{a_0!\,a_1!\ldots}\,\frac{N!}{b_0!\,b_1!\ldots}, \qquad \ldots\ldots(17)$$

summed for all $a, b \geqslant 0$ subject to (15).

The equilibrium distribution laws for the assembly are to be obtained by averaging over the phase space—that is, over all complexions. We can therefore find at once an expression for the average value $\overline{a_r}$ of a_r, or of any similar quantity, for we have

$$C\overline{a_r} = \Sigma_{a,b}\,\frac{a_r M!}{a_0!\,a_1!\ldots}\,\frac{N!}{b_0!\,b_1!\ldots}. \qquad \ldots\ldots(18)$$

The most important such quantity is $\overline{E_A}$, the average energy of the systems A. This is given by

$$C\overline{E}_A = \Sigma_{a,b}\,\frac{(\Sigma_r r\epsilon a_r)\,M!}{a_0!\,a_1!\ldots}\,\frac{N!}{b_0!\,b_1!\ldots}. \qquad \ldots\ldots(19)$$

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* I.e. positive or zero. We shall make this convention throughout.

Both these summations are of course over the same range of values as (17).

A rapid and powerful method of evaluating these sums is essential to the elegance of this development, and is provided by expressing these summations as contour integrals and evaluating the integrals by the method of steepest descents.

Now the general term of

$$(1 + z^\epsilon + z^{2\epsilon} + \dots)^M$$

expanded in powers of z is

$$\frac{M\,!}{a_0\,!\,a_1\,!\,\dots}\, z^{\Sigma_r r\epsilon a_r} \quad (\Sigma_r a_r = M), \qquad \dots\dots(20)$$

and similarly of

$$(1 + z^\eta + z^{2\eta} + \dots)^N,$$

$$\frac{N\,!}{b_0\,!\,b_1\,!\,\dots}\, z^{\Sigma_s s\eta b_s} \quad (\Sigma_s b_s = N).$$

By multiplying these series together it follows that the coefficient of z^E in

$$(1 + z^\epsilon + z^{2\epsilon} + \dots)^M\,(1 + z^\eta + z^{2\eta} + \dots)^N$$

is

$$\Sigma_{a,b}\,\frac{M\,!}{a_0\,!\,a_1\,!\,\dots}\,\frac{N\,!}{b_0\,!\,b_1\,!\,\dots},$$

summed for all positive values of the a's and b's subject to $\Sigma_r a_r = M$, $\Sigma_s b_s = N$ and also $\Sigma_r r\epsilon a_r + \Sigma_s s\eta b_s = E$, in short the conditions (15). *Thus C is the coefficient of z^E in*

$$(1 - z^\epsilon)^{-M}\,(1 - z^\eta)^{-N}. \qquad \dots\dots(21)$$

Similarly, observing the extra factor in (19), we find at once that $C\overline{E_A}$ is the coefficient of z^E in

$$(1 - z^\eta)^{-N}\, z\,\frac{d}{dz}\,(1 + z^\epsilon + z^{2\epsilon} + \dots)^M, \qquad \dots\dots(22)$$

for operation with $z\,d/dz$ introduces in the terms (20) just the required extra factor $\Sigma_r r\epsilon a_r$. The expression (22) can be put in the alternative forms

$$\left\{z\,\frac{d}{dz}\,(1 - z^\epsilon)^{-M}\right\}(1 - z^\eta)^{-N}, \qquad \dots\dots(23)$$

$$(1 - z^\epsilon)^{-M}\,(1 - z^\eta)^{-N}\left\{-\,Mz\,\frac{d}{dz}\log\,(1 - z^\epsilon)\right\}. \qquad \dots\dots(24)$$

It thus appears that the required sums are the coefficients in certain simple power series, and, as we shall see, this conclusion is capable of immediate extension to general quantized systems. Now the most convenient expressions for such coefficients are complex integrals taken round a contour enclosing the origin $z = 0$. Thus we find

$$C = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}\,\frac{1}{(1 - z^\epsilon)^M\,(1 - z^\eta)^N}, \qquad \dots\dots(25)$$

$$C\overline{E_A} = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}\,\frac{-\,Mz\,\dfrac{d}{dz}\log\,(1 - z^\epsilon)}{(1 - z^\epsilon)^M\,(1 - z^\eta)^N}. \qquad \dots\dots(26)$$

The contour γ may of course be any contour lying within the circle of convergence of these power series (radius unity) and circulating once counter-clockwise round $z = 0$.

We can determine a similar formula for $C\overline{a_r}$. We have

$$C\overline{a_r} = \Sigma_{a,b} \frac{a_r M\,!}{a_0\,!\, a_1\,! \ldots} \frac{N\,!}{b_0\,!\, b_1\,! \ldots},$$

$$= M\Sigma_{a,b} \frac{(M-1)\,!}{a_0\,!\, a_1\,! \ldots} \frac{N\,!}{b_0\,!\, b_1\,! \ldots},$$

summed over all positive a, b subject to

$$\Sigma_r a_r = M - 1,\ \ \Sigma_s b_s = N,\ \ \Sigma_r r\epsilon a_r + \Sigma_s s\eta b_s = E - r\epsilon.$$

This reduces at once to

$$C\overline{a_r} = \frac{M}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}} \frac{z^{r\epsilon}}{(1-z^\epsilon)^{M-1}(1-z^\eta)^N}. \qquad \ldots\ldots(27)$$

These integrals are exact and hold for all values of M, N and E. They are, however, only physically significant when M, N and E are very large, since all assemblies that we can observe contain a very great number of systems. We therefore require primarily the asymptotic values of these integrals when M, N and E tend to infinity in fixed ratios. This means, physically, that we require the limiting properties of the assembly when its size tends to infinity without alteration of its *intensive* properties (constitution, etc.). The properties of the finite assembly will be shown to deviate only trivially from these limiting properties. These asymptotic values can be rigorously established here and in the general case by the method of steepest descents. It will tend to clarity first to sketch this method and the results, and to compare the results with those of other developments.

Consider the integrand on the positive real axis. It tends to infinity as $z \to 0$ and $z \to 1$, and somewhere between, at $z = \vartheta$, there is a unique *minimum*. For γ take the circle of radius ϑ and centre the origin. Then for values of z on γ, $z = \vartheta e^{i\alpha}$ say, $z = \vartheta$, $\alpha = 0$ is, when M, N and E are large, a strong *maximum* of the modulus of the integrand. Owing also to the fact that the differential coefficient of the integrand vanishes at $\alpha = 0$ the complex terms there are trivial and the whole effective contribution to the integral comes from very near this point. This remains true so long as there are no equal maxima elsewhere, which cannot occur when ϵ and η have no common factor. It remains true, moreover, when there are extra factors such as $-Mz\dfrac{d}{dz}\log(1-z^\epsilon)$, and in effect such extra factors may be taken outside the sign of integration if in them we replace z by ϑ.

The result is that ϑ is the unique positive fractional root of

$$\frac{d}{dz}\{z^{-E}(1-z^{\epsilon})^{-M}(1-z^{\eta})^{-N}\}=0, \qquad \text{......(28)}$$

or

$$E=\frac{M\epsilon}{\vartheta^{-\epsilon}-1}+\frac{N\eta}{\vartheta^{-\eta}-1}. \qquad \text{......(29)}$$

By comparing (25) and (26) we find

$$\overline{E_A}=-M\vartheta\frac{d}{d\vartheta}\log(1-\vartheta^{\epsilon}),$$

$$=\frac{M\epsilon}{\vartheta^{-\epsilon}-1}. \qquad \text{......(30)}$$

Similarly,

$$\overline{E_B}=\frac{N\eta}{\vartheta^{-\eta}-1}, \qquad \text{......(31)}$$

which satisfies the essential equation $E=\overline{E_A}+\overline{E_B}$. These equations determine the partition of energy among the two sets of oscillators in a large assembly.

It is already suggested by these formulae that ϑ is a function of the state of the assembly with the properties of *temperature*, and it turns out later that ϑ may be taken to represent the temperature on a special scale. It bears the relation

$$\vartheta=e^{-1/kT} \qquad \text{......(32)}$$

to the absolute temperature T, where k is Boltzmann's constant. If we use this result in advance then

$$\overline{E_A}=\frac{M\epsilon}{e^{\epsilon/kT}-1}, \qquad \text{......(33)}$$

which is the familiar result due to Planck. In the same way, by comparing (25) and (27), we find

$$\overline{a_r}=M\vartheta^{r\epsilon}(1-\vartheta^{\epsilon}),$$

$$=Me^{-r\epsilon/kT}(1-e^{-\epsilon/kT}). \qquad \text{......(34)}$$

This result, in the more usual form

$$\frac{\overline{a_r}}{\overline{a_{r'}}}=\frac{e^{-r\epsilon/kT}}{e^{-r'\epsilon/kT}}, \qquad \text{......(35)}$$

is also classical and due to Planck.*

Logically the relation (32) must be deduced from the second law of thermodynamics, by which alone the *absolute* temperature scale can be defined. But we may anticipate this, if it is preferred, by asserting that in the limit in which $\nu \to 0$ and so $\epsilon \to 0$ the mean energy of a simple linear oscillator must be kT. This assertion then defines T on the basis of the

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* In the new mechanics with energies $(n+\frac{1}{2})\epsilon$ instead of $n\epsilon$ there are purely formal alterations, which may be entirely obliterated by a change of the energy zero. Since the zero of energy must always be fixed by a convention, we may say that no change is made in these formulae. This is easily verified directly.

theorem of equipartition of energy for classical systems which we have not yet proved (see § 2·7). It then follows from (30) that

$$kT = \mathop{\mathrm{Lt}}_{\epsilon \to 0} \frac{\epsilon}{\vartheta^{-\epsilon} - 1} = \frac{1}{\log 1/\vartheta},$$

which is (32).

We give the mathematical theorems in the next section, and shall there see that the full proof of (33)–(35) avoids all the apparatus of factorials approximated to by Stirling's theorem which disfigure the usual proofs. This apparatus is both cumbersome and, at least superficially, lacking in rigour, for Stirling's theorem is often there applied to 0 ! and 1 !.

§ 2·5. *Application of the method of steepest descents.* We base the proof of the foregoing results on the following:

Theorem 2·5. *If*

(i) $\phi(z)$ *is a regular analytic function of* z *expressible in the form*

$$\phi(z) = z^{-\alpha_0}\{f_1(z)\}^{\alpha_1}\{f_2(z)\}^{\alpha_2}\ldots,$$

where the α*'s are positive constants, integral after multiplication by* E*, and the* $f(z)$ *are power series in* z *which start with non-zero constant terms and have real positive integral coefficients and radii of convergence unity;*

(ii) *Not all the indices in all the* $f(z)$ *contain a common factor other than unity;*

(iii) $F(z)$ *is a regular analytic function with no singularity in the unit circle except perhaps a pole at* $z = 0$;

(iv) γ *is a contour circulating once counter-clockwise round* $z = 0$;

then

$$\frac{1}{2\pi i}\int_\gamma F(z)[\phi(z)]^E \frac{dz}{z} = \frac{[\phi(\vartheta)]^E}{[2\pi E \vartheta^2 \phi''(\vartheta)/\phi(\vartheta)]^{\frac{1}{2}}}\{F(\vartheta) + O(1/E)\}, \quad \ldots\ldots(36)$$

where ϑ *is the unique positive fractional root of*

$$\frac{d\phi(z)}{dz} = 0. \quad \ldots\ldots(37)$$

We have aimed not at maximum generality, only at a theorem sufficient for the purpose in hand. For example, the coefficients of the $f(z)$ need not be integers. It is sufficient to suppose that $f(z) \to \infty$ as $z \to 1$. Nor need the radius of convergence be unity for the purpose of the proof. But both these conditions are always satisfied by quantized systems.

Consider the function $\phi'(z)$ for real positive z. The equation

$$\frac{\phi'(z)}{\phi(z)} = \frac{-\alpha_0}{z} + \frac{\alpha_1 f_1'}{f_1} + \frac{\alpha_2 f_2'}{f_2} + \ldots \quad \ldots\ldots(38)$$

determines $\phi'(z)$. Consider the behaviour of $y = zf_1'/f_1$. This function y

by (i) takes the value 0 for $z = 0$ and steadily increases to $+\infty$ as z increases to 1. For if $f_1(z) = \Sigma\varpi_n z^n$ we have

$$y = \frac{\Sigma n\varpi_n z^n}{\Sigma\varpi_n z^n}, \quad zy' = \frac{(\Sigma\varpi_n z^n)(\Sigma n^2\varpi_n z^n) - (\Sigma n\varpi_n z^n)^2}{(\Sigma\varpi_n z^n)^2}.$$

The numerator of zy' is $\Sigma\Sigma\,(n-n')^2\,\varpi_n\varpi_{n'}z^{n+n'}$, which is always positive. Therefore either $y \to \infty$ or $y \to A$, a finite limit, as $z \to 1$. But the latter is impossible as it implies that $f_1(z)$ is bounded as $z \to 1$, which is contrary to hypothesis. Thus the expression

$$\frac{a_1 z f_1'}{f_1} + \frac{a_2 z f_2'}{f_2} + \dots$$

is zero for $z = 0$ and steadily increases to $+\infty$ as $z \to 1$. It therefore takes the value a_0 once and once only, for $z = \vartheta$ say, which is then the unique root of (37). It follows also that $\phi''(\vartheta) > 0$.

The method of steepest descents proceeds by making the contour γ pass through the col, $\phi'(z) = 0$, in such a direction that the value of the integrand falls off *along* γ from a maximum value at the cól at the greatest possible rate. This is here achieved (since $\phi(z)$ is real for positive real z) by taking for γ the circle $|z| = \vartheta$. On this circle (or any other) the maximum modulus of the integrand must occur for positive real z on account of (ii). It is easy to show rigorously that when E is large all parts of the contour except that in the immediate neighbourhood of $z = \vartheta$ make contributions exponentially small compared to this critical region. If we put $z = \vartheta e^{i\alpha}$, then when α is small

$$[\phi(z)]^E = [\phi(\vartheta)]^E \exp\{-\tfrac{1}{2}E\alpha^2\vartheta^2\phi''(\vartheta)/\phi(\vartheta) + KE\alpha^3 + O(E\alpha^4)\},$$

where K is some function of ϑ. When E is large we may suppose that $E^{\frac{1}{2}}\alpha$ ranges effectively from $-\infty$ to $+\infty$, while α and all terms such as $E\alpha^3$ remain small. Thus

$$\frac{1}{2\pi i}\int_\gamma F(z)\,[\phi(z)]^E\,\frac{dz}{z} = \frac{1}{2\pi}[\phi(\vartheta)]^E$$
$$\times \int_{-\infty}^{+\infty}\{F(\vartheta) + i\alpha F'(\vartheta) + O(\alpha^2) + KE\alpha^3 + O(E\alpha^4)\}\,e^{-\frac{1}{2}E\alpha^2\vartheta^2\phi''(\vartheta)/\phi(\vartheta)}\,d\alpha,$$

the error in taking the range of integration with respect to α infinite instead of some small number such as $kE^{-\frac{3}{8}}$ being exponentially small. Odd terms in α vanish on integration and

$$\int_{-\infty}^{+\infty} e^{-\frac{1}{2}E\alpha^2\vartheta^2\phi''(\vartheta)/\phi(\vartheta)}\,d\alpha = \left\{\frac{2\pi}{E\vartheta^2\phi''(\vartheta)/\phi(\vartheta)}\right\}^{\frac{1}{2}}; \qquad \dots\dots(39)$$

$$\int_{-\infty}^{+\infty} \alpha^2 e^{-\frac{1}{2}E\alpha^2\vartheta^2\phi''(\vartheta)/\phi(\vartheta)}\,d\alpha = O(E^{-\frac{3}{2}}),$$

$$\int_{-\infty}^{+\infty} E\alpha^4 e^{-\frac{1}{2}E\alpha^2\vartheta^2\phi''(\vartheta)/\phi(\vartheta)}\,d\alpha = O(E^{-\frac{3}{2}}).$$

Hence the theorem.

The theorem applies at once to the assembly of two sets of linear oscillators with

$$\phi = z^{-1}(1 - z^{\epsilon})^{-M/E}(1 - z^{\eta})^{-N/E} \quad (M/E,\ N/E \text{ constant}).$$

All our conclusions hold with, in particular,

$$C = \frac{\vartheta^{-E}(1 - \vartheta^{\epsilon})^{-M}(1 - \vartheta^{\eta})^{-N}}{\{2\pi E\vartheta^2\phi''(\vartheta)/\phi(\vartheta)\}^{\frac{1}{2}}}\left[1 - O\left(\frac{1}{E}\right)\right]. \qquad \ldots\ldots(40)$$

Since we always suppose that the assembly is very large (E large) we shall in all formulae omit the factor $[1 - O(1/E)]$ which is always present, and preserve only the limiting asymptotic form, which gives us all our results. We must be careful, however, not to overlook its presence in any formula in which the leading terms cancel.

The expression $E\vartheta^2\phi''(\vartheta)/\phi(\vartheta)$ can be simplified. Since $\phi'(\vartheta) = 0$ it is equal to

$$\begin{aligned} E\left(\vartheta\frac{d}{d\vartheta}\right)^2 \log\phi(\vartheta) &= E\vartheta\frac{d}{d\vartheta}\left[-1 + \frac{(M\epsilon/E)\,\vartheta^{\epsilon}}{1 - \vartheta^{\epsilon}} + \frac{(N\eta/E)\,\vartheta^{\eta}}{1 - \vartheta^{\eta}}\right], \\ &= \vartheta\frac{dE}{d\vartheta}, \qquad \ldots\ldots(41) \end{aligned}$$

if E is regarded as a function of ϑ determined by the relation (29), that is,

$$E = \frac{M\epsilon}{\vartheta^{-\epsilon} - 1} + \frac{N\eta}{\vartheta^{-\eta} - 1}.$$

This relation (41) is valid generally.

Finally, it is of some importance to observe that the condition (ii) in the theorem of this section is inessential. If it fails the only difference is that *all* integrals such as C and $C\overline{E_A}$ are β times as great as before, where β is the common factor in the indices of the $f(z)$, and no physical result is altered. This is, of course, only true because the function $F(z)$ is always composed of a selection of terms from the series in $\phi(z)$. From each of the β equal maxima of $|\phi(z)|$ on the circle $|z| = \vartheta$ we always get a dominant contribution which is real, positive and equal to the contribution from the main maximum on the positive real axis.

§ 2·6. *Generalization to an assembly of any quantized systems and to any number of types of system. Simple examples.* Nothing in the preceding work depends essentially on the fact that we are discussing simple harmonic linear oscillators. Suppose instead we have two sets of quantized systems A and B. Systems A are M in number; their sequence of stationary states has energies $\epsilon_0, \epsilon_1, \ldots, \epsilon_r, \ldots$, weights $\varpi_0, \varpi_1, \ldots, \varpi_r, \ldots$, and a statistical distribution specified by $a_0, a_1, \ldots, a_r, \ldots$. Systems B are N in number; their sequence of stationary states has energies $\eta_0, \eta_1, \ldots, \eta_s, \ldots$, weights $\rho_0, \rho_1, \ldots, \rho_s, \ldots$, and a statistical distribution specified by $b_0, b_1, \ldots, b_s, \ldots$. We assume for the present that all the ϵ's and η's are expressible as integral multiples of one basic unit of energy (and for simplicity not all expressible in the form $\alpha + r\beta$, $\beta > 1$). Then in this case the total number of weighted complexions representing this statistical state of the assembly is

$$C = \Sigma_{a,b} \frac{M\,!\,N\,!\,\varpi_0^{a_0}\varpi_1^{a_1}\dots\rho_0^{b_0}\rho_1^{b_1}\dots}{a_0\,!\,a_1\,!\dots b_0\,!\,b_1\,!\dots}, \qquad \dots\dots(42)$$

summed for all positive a, b subject to

$$\Sigma_r a_r = M,\ \Sigma_s b_s = N,\ \Sigma_r \epsilon_r a_r + \Sigma_s \eta_s b_s = E. \qquad \dots\dots(43)$$

We have here to form the functions

$$f(z) = \varpi_0 z^{\epsilon_0} + \varpi_1 z^{\epsilon_1} + \varpi_2 z^{\epsilon_2} + \dots, \qquad \dots\dots(44)$$

$$g(z) = \rho_0 z^{\eta_0} + \rho_1 z^{\eta_1} + \rho_2 z^{\eta_2} + \dots, \qquad \dots\dots(45)$$

which from their special properties in the development of the theory we call *partition functions*. They are equivalent to the functions introduced by Planck under the name *Zustandsumme*, and are the transcription into the quantum theory of Gibbs' phase integrals.

Just as in § 2·4 it follows from the multinomial theorem that C is the coefficient of z^E in $[f(z)]^M [g(z)]^N$. It follows at once that

$$C = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}} [f(z)]^M [g(z)]^N, \qquad \dots\dots(46)$$

and, similarly, that

$$C\overline{E_A} = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}} \left\{z\frac{d}{dz}[f(z)]^M\right\} [g(z)]^N, \qquad \dots\dots(47)$$

$$C\overline{a_r} = \frac{M}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}} \varpi_r z^{\epsilon_r} [f(z)]^{M-1} [g(z)]^N. \qquad \dots\dots(48)$$

Theorem 2·5 applies to these integrals with $\phi = z^{-1}[f(z)]^{M/E}[g(z)]^{N/E}$, provided that the partition functions converge for $|z| < 1$. If the sequence of energies can be expressed as here supposed and does not terminate the series must converge for $|z| < 1$. For if the system is of s degrees of freedom and non-degenerate, the ϖ's are all unity and the radius of convergence must be unity. If the system then degenerates until it has only $u\ (< s)$ independent frequencies, the new partition function can be formed from the old by the grouping together of sets of terms whose energies are no longer distinct. This cannot alter the radius of convergence. We find, therefore, that ϑ is determined as the unique root of

$$E = M\vartheta\frac{d}{d\vartheta}\log f(\vartheta) + N\vartheta\frac{d}{d\vartheta}\log g(\vartheta), \qquad \dots\dots(49)$$

and

$$\overline{E_A} = M\vartheta\frac{d}{d\vartheta}\log f(\vartheta), \qquad \dots\dots(50)$$

$$\overline{a_r} = M\varpi_r\vartheta^{\epsilon_r}/f(\vartheta). \qquad \dots\dots(51)$$

There are similar formulae for systems B.

Obviously the restriction to two types of system is trivial. With any number of types of system the arguments are unaltered. We find for the total number of weighted complexions

$$C = \frac{1}{2\pi i}\int_{\gamma} \frac{dz}{z^{E+1}} \Pi_{\tau} \left[f_{\tau}(z)\right]^{M_{\tau}}. \qquad \text{......(52)}$$

There is a unique ϑ determined by

$$E = \Sigma_{\tau} M_{\tau} \vartheta \frac{d}{d\vartheta} \log f_{\tau}(\vartheta), \qquad \text{......(53)}$$

and

$$\overline{E_{\tau}} = M_{\tau} \vartheta \frac{d}{d\vartheta} \log f_{\tau}(\vartheta), \qquad \text{......(54)}$$

$$(\overline{a_r})_{\tau} = M_{\tau} (\varpi_r)_{\tau} \vartheta^{(\epsilon_r)_{\tau}}/f_{\tau}(\vartheta). \qquad \text{......(55)}$$

The partition function $f(z)$ is presumed to refer to the whole motion of a quantized system. It should be observed that, in the important special case in which the motion splits up into two or more parts entirely independent of one another, the partition function $f(z)$ must factorize into functions of the same type, which refer separately to the independent motions. A particular case of this is the translatory motion and the internal motions and rotations of a free molecule. The translatory is of course classical, but partition functions can still be constructed as will be shown in § 2·7.

We may properly comment at this stage on the properties of the parameter ϑ which, while mathematical in origin, is obviously fundamental in describing the state of the assembly, and should be identifiable by analogy with some physical property of the assembly. We have already stated in advance that ϑ measures the temperature. We can now see reason to justify this identification, though not of course the particular relation between ϑ and T. For ϑ *is a parameter helping to define the state of our assembly which must have the same value for all sets of systems in the assembly*. This is the precise property which distinguishes the temperature from other parameters and justifies the identification.*

It is natural at this stage to consider a few examples of special systems and construct their partition functions.

§ **2·61**. *Two- and three-dimensional isotropic harmonic oscillators.* These are degenerate systems with only one fundamental frequency. The two-dimensional oscillator has (we have seen) $\varpi_n = n + 1$, $\epsilon_n = nh\nu = n\epsilon$, and therefore

$$f(z) = 1 + 2z^{\epsilon} + 3z^{2\epsilon} + \dots,$$

$$= (1 - z^{\epsilon})^{-2}. \qquad \text{......(56)}$$

The three-dimensional oscillator also has $\epsilon_n = n\epsilon$ and ϖ_n equal to the

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* See, for example, Born, *Phys. Zeit.* vol. XXII, pp. 218, 249, 282 (1921).

number of partitions of n into three positive or zero integers. Thus $\varpi_n = \frac{1}{2}(n+1)(n+2)$,

$$f(z) = 1 + 3z^{\epsilon} + 6z^{2\epsilon} + \dots + \tfrac{1}{2}(n+1)(n+2)z^{n\epsilon} + \dots,$$
$$= (1-z^{\epsilon})^{-3}. \qquad \text{......(57)}$$

These are simple examples of the rules for assigning weights. Thus in these two cases

$$\overline{E_A} = \frac{2M\epsilon}{\vartheta^{-\epsilon}-1}, \frac{3M\epsilon}{\vartheta^{-\epsilon}-1}, \qquad \text{......(58)}$$

which fit in exactly with the expected requirements of two and three times the mean energy of a linear harmonic oscillator respectively.

This could be generalized to show that a harmonic oscillator of s degrees of freedom has a partition function

$$f(z) = (1-z^{\epsilon})^{-s}, \qquad \text{......(59)}$$

and a mean energy s times that of a linear harmonic oscillator. In fact, for most purposes it is precisely equivalent to s independent simple harmonic linear oscillators.

§ **2·62**. *Rotations of a rigid solid of revolution (diatomic molecule) without axial spin.* This provides a rather more complicated example in weight counting and has important applications to the specific heats of gases. It is a degenerate system of one independent frequency.*

Let A be the transverse moment of inertia of the molecule, and θ, ϕ the usual spherical polar coordinates. Then

$$p_\theta = A\dot{\theta}, \quad p_\phi = A\sin^2\theta\,\dot{\phi},$$
$$H = \frac{1}{2A}\left(p_\theta{}^2 + \frac{1}{\sin^2\theta}p_\phi{}^2\right). \qquad \text{......(60)}$$

The Hamilton-Jacobi partial differential equation is

$$\frac{1}{2A}\left\{\left(\frac{\partial S}{\partial\theta}\right)^2 + \frac{1}{\sin^2\theta}\left(\frac{\partial S}{\partial\phi}\right)^2\right\} = \alpha_1,$$

which has the general solution

$$S = \alpha_2\phi + \int(2A\alpha_1 - \alpha_2{}^2/\sin^2\theta)^{\frac{1}{2}}\,d\theta. \qquad \text{......(61)}$$

The equation of the orbit is

$$\frac{\partial S}{\partial\alpha_2} = \beta_2 = \phi - \int\frac{\alpha_2\,d\theta}{\sin^2\theta\,(2A\alpha_1 - \alpha_2{}^2/\sin^2\theta)^{\frac{1}{2}}},$$
$$= \phi - \cos^{-1}\frac{\alpha_2\cot\theta}{(2A\alpha_1 - \alpha_2{}^2)^{\frac{1}{2}}}, \qquad \text{......(62)}$$

or $$\alpha_2\cot\theta = (2A\alpha_1 - \alpha_2{}^2)^{\frac{1}{2}}\cos(\phi - \beta_2). \qquad \text{......(63)}$$

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* We give these classical calculations with a detail foreign to our general practice, since they are not readily accessible in a correct form elsewhere.

The actual orbit is of course uniform rotation in a plane whose normal is defined by the angles λ, σ. Thus the orbit is

$$\cos\lambda\cos\theta + \sin\lambda\sin\theta\cos(\phi - \sigma) = 0. \qquad \text{......(64)}$$

By comparison of (63) with (64) it follows that

$$\sigma = \pi + \beta_2, \quad \tan\lambda = \frac{(2A\alpha_1 - \alpha_2{}^2)^{\frac{1}{2}}}{\alpha_2}, \quad \cos\lambda = \pm\frac{\alpha_2}{(2A\alpha_1)^{\frac{1}{2}}}. \qquad \text{......(65)}$$

Except when $\lambda = \frac{1}{2}\pi$, $\cos\lambda = 0$, $\alpha_2 = 0$, ϕ increases or decreases steadily from 0 to 2π according as $\alpha_2 > 0$ or $\alpha_2 < 0$, and θ goes from $\frac{1}{2}\pi - \lambda$ to $\frac{1}{2}\pi + \lambda$ and back during one period.

The single actual quantum condition is

$$J = \oint p_\phi d\phi + \oint p_\theta d\theta = nh, \qquad \text{......(66)}$$

or

$$nh = 2\pi \mid \alpha_2 \mid + (2A\alpha_1)^{\frac{1}{2}} \oint \left(1 - \frac{\cos^2\lambda}{\sin^2\theta}\right)^{\frac{1}{2}} d\theta.$$

The substitution $\cos\theta = \sin\lambda\cos u$ evaluates the integral and we find

$$nh = 2\pi \mid \alpha_2 \mid + (2A\alpha_1)^{\frac{1}{2}}\, 2\pi\, (1 - \mid \cos\lambda \mid).$$

Using (65) this reduces to*

$$\alpha_1 = \frac{n^2h^2}{8\pi^2A}. \qquad \text{......(67)}$$

To determine the weights we may suppose that the system is so disturbed that the periods in θ and ϕ are no longer equal—for example, by a slow procession of the orbital plane. There are then two quantum conditions in place of (66), which reduce to

$$n_\phi h = 2\pi \mid \alpha_2 \mid, \quad n_\theta h = (2A\alpha_1)^{\frac{1}{2}}\, 2\pi\, (1 - \mid \cos\lambda \mid).$$

We then find eventually that

$$\cos\lambda = \pm\frac{\alpha_2}{(2A\alpha_1)^{\frac{1}{2}}} = \pm\frac{n_\phi}{n_\theta + n_\phi}, \quad \alpha_1 = \frac{(n_\theta + n_\phi)^2 h^2}{8\pi^2A}.$$

The separate states that coalesce to form the degenerate state of quantum number n are all those for which $n_\theta + n_\phi = n$. There are $2n$ of these for which $\cos\lambda \neq 0$, and $\cos\lambda = 0$ gives a single possible state in which the orbit passes through the pole. There are thus $2n + 1$ states in all, $\varpi_n = 2n + 1$, and

$$f(z) = 1 + 3z^\epsilon + \ldots + (2n + 1)\, z^{n^2\epsilon} + \ldots \left(\epsilon = \frac{h^2}{8\pi^2A}\right). \qquad \text{......(68)}$$

We have assumed that all the states are possible ones and that none of

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* This result can be obtained more simply from the general relation $\omega = dE/dJ$. For the action variable J for a rigid rotator is $J = A\omega$. Hence $dE/dJ = J/A$, $E = J^2/2A = n^2h^2/8\pi^2A$, as in the text. There is, however, no such short cut to the counting of the weights. The modifications made by the new mechanics are noted at the end of this section.

them, for example those for which $n_\phi = 0$, must be ruled out for some cause not here specified.*

The contribution of molecular rotations to the energy of the assembly will therefore be

$$\overline{E_A} = M\vartheta \frac{d}{d\vartheta} \log f(\vartheta),$$

where $f(\vartheta)$ is given by (68). The contribution to its *specific heat*, C_{rot}, is

$$C_{\text{rot}} = \frac{d\overline{E_A}}{dT} = Mk\,(\log \vartheta)^2 \left(\vartheta \frac{d}{d\vartheta}\right)^2 \log f(\vartheta). \qquad \text{......(69)}$$

If

$$\sigma = \frac{h^2}{8\pi^2 AkT} = \frac{h^2}{8\pi^2 A} \log 1/\vartheta,$$

and M refers to one gram-molecule so that $Mk = R$, the gas constant, then

$$C_{\text{rot}} = R\sigma^2 \frac{d^2}{d\sigma^2} \log \{\Sigma_n\, (2n+1)\, e^{-n^2\sigma}\}. \qquad \text{......(70)}$$

Practical applications of this formula are made in §§ 3·3, 3·4. The modification made by the new mechanics is to replace $n^2\epsilon$ by $n\,(n+1)\,\epsilon$ so that the partition function becomes†

$$f(\vartheta) = \sum_{n=0}^{\infty} (2n+1)\, \vartheta^{n(n+1)\epsilon}, \qquad \text{......(71)}$$

$$= \sum_{n=0}^{\infty} (2n+1)\, e^{-n(n+1)\sigma}. \qquad \text{......(72)}$$

§ **2·63**. *Rotations of a rigid solid of revolution with axial spin.* We have here a degenerate system of three degrees of freedom and two frequencies. Let A and C be the transverse and axial moments of inertia, and θ, ϕ and ψ the usual Eulerian coordinates. The angles θ and ϕ must be taken to fix a definite direction in space independent of any directions of rotation since the two ends of the solid may be different. Then

$$p_\theta = A\dot{\theta},\ p_\phi = A\sin^2\theta\,\dot{\phi} + C\cos\theta\,(\dot{\psi} + \dot{\phi}\cos\theta),\ p_\psi = C\,(\dot{\psi} + \dot{\phi}\cos\theta),$$

$$H = \frac{p_\theta{}^2}{2A} + \frac{(p_\phi - p_\psi\cos\theta)^2}{2A\sin^2\theta} + \frac{p_\psi{}^2}{2C} = \alpha_1. \qquad \text{......(73)}$$

The Hamilton-Jacobi partial differential equation has the solution

$$S = \alpha_2\phi + \alpha_3\psi + \int \frac{d\theta}{\sin\theta} \left\{ \left(2A\alpha_1 - \frac{A\alpha_3{}^2}{C}\right) \sin^2\theta - (\alpha_2 - \alpha_3\cos\theta)^2 \right\}^{\frac{1}{2}}. \qquad \text{...(74)}$$

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* Such exceptions were of course a common and unsatisfactory feature of the old quantum theory. They are no longer necessary in the new.

† Schrödinger, *Ann. der Phys.* vol. LXXIX, p. 520 (1926).

The θ, ϕ equation of the orbit is

$$\frac{\partial S}{\partial \alpha_2} = \beta_2 = \phi - \int \frac{d\theta}{\sin\theta} \frac{\alpha_2 - \alpha_3 \cos\theta}{\left\{\left(2A\alpha_1 - \dfrac{A\alpha_3{}^2}{C}\right)\sin^2\theta - (\alpha_2 - \alpha_3\cos\theta)^2\right\}^{\frac{1}{2}}} \quad \text{.......(75)}$$

The actual motion in θ and ϕ is of course a uniform rotation of the axis OP (Fig. 1) at a fixed angular distance ϵ about the invariable line OI of coordinates λ and σ. The invariable line OI is the axis of constant resultant angular momentum of the system. The direction of OI is unrestricted, but $\epsilon \leqslant \frac{1}{2}\pi$. The actual (θ, ϕ)-equation of the orbit must therefore be

$$\cos\theta\cos\lambda + \sin\theta\sin\lambda\cos(\phi - \sigma) = \cos\epsilon. \quad \text{......(76)}$$

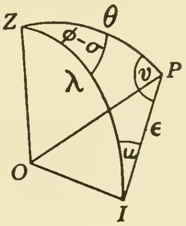

Fig. 1.

Let α be the resultant angular momentum about OI. Then

$$\left.\begin{aligned} \alpha_2 &= p_\phi = \alpha\cos\lambda \quad (0 \leqslant \lambda \leqslant \pi), \\ \alpha_3 &= p_\psi = \alpha\cos\epsilon, \\ \alpha_1 &= \tfrac{1}{2}\left(\frac{\alpha^2\sin^2\epsilon}{A} + \frac{\alpha_3{}^2}{C}\right). \end{aligned}\right\} \quad \text{......(77)}$$

We have already discussed the case of zero axial spin, which will therefore be omitted here, and we have $0 < \cos\epsilon \leqslant 1$, $\cos\epsilon = 0$ being excluded. Since p_ψ can obviously be of either sign, so can α, but we confine ourselves at first to $\alpha > 0$.

We may start by verifying that (75) gives (76) with $\sigma = \beta_2$ by using (77) to eliminate α_1, α_2 and α_3 and making the substitution

$$\cos\theta = \cos\lambda\cos\epsilon + \sin\lambda\sin\epsilon\cos u. \quad \text{......(78)}$$

The motion in ψ can be established similarly. The integral derived from S can be evaluated by the substitution (78) and the analogous formula in v. The sign of $\dot\psi$, however, is constant throughout the motion and depends on that of α. Greater detail is unnecessary here.

Case I. The axis OP rounds the pole OZ if $\epsilon > \lambda$ or $\epsilon > \pi - \lambda$. The motion in ϕ is then a rotation through 2π in one or other direction and the quantum conditions are

$$\oint p_\theta d\theta + \oint p_\phi d\phi = \oint p_\theta d\theta + 2\pi\alpha\,|\cos\lambda\,| = n_1 h,$$

$$\oint p_\psi d\psi = 2\pi\alpha\cos\epsilon = n_\psi h.$$

The integral $\oint p_\theta d\theta$ can be rationalized by the substitution (78) and has the general value

$$\oint p_\theta d\theta = 2\pi\alpha\,\{1 - \tfrac{1}{2}\,|\cos\lambda - \cos\epsilon\,| - \tfrac{1}{2}\,|\cos\lambda + \cos\epsilon\,|\}, \quad \text{......(79)}$$

which in this case reduces to $2\pi\alpha\,(1 - |\cos\lambda|)$. Therefore the quantum conditions are

$$\alpha = \frac{n_1 h}{2\pi}, \quad \alpha\cos\epsilon = \alpha_3 = \frac{n_\psi h}{2\pi}\ (0 < n_\psi \leqslant n_1). \qquad \ldots\ldots(80)$$

The energy of the rotation is then

$$\alpha_1 = \frac{h^2}{8\pi^2}\left\{\frac{n_1^2}{A} + \left(\frac{1}{C} - \frac{1}{A}\right)n_\psi^2\right\}. \qquad \ldots\ldots(81)$$

In order to determine the weight, we must, as before, remove the degeneracy by supposing the periods in θ and ϕ to become slightly unequal. Then the first quantum condition is replaced by two,

$$\alpha\,(1 - |\cos\lambda|) = \frac{n_\theta h}{2\pi}, \quad \alpha\,|\cos\lambda| = \frac{n_\phi h}{2\pi},$$

so that

$$\cos\lambda = \pm\frac{n_\phi}{n_\theta + n_\phi} = \pm\frac{n_\phi}{n_1}.$$

The value $n_\phi = 0$ is not here permissible, since then $\lambda = \frac{1}{2}\pi$ and the condition $\epsilon > \lambda$ is not fulfilled. There are therefore $2n_1$ states, and this number is the contribution to the weight.

Case II. The axis OP does not round the pole OZ if $\epsilon < \lambda$ and $\epsilon < \pi - \lambda$. The motion in ϕ is then an oscillation, and since p_ϕ is constant $\oint p_\phi d\phi = 0$. The quantum conditions now become

$$\left.\begin{aligned} \oint p_\theta d\theta + \oint p_\phi d\phi &= 2\pi\alpha\,(1 - \cos\epsilon) = n_\theta h, \\ \oint p_\psi d\psi &= 2\pi\alpha\cos\epsilon = n_\psi h \quad (n_\psi \neq 0), \end{aligned}\right\} \qquad \ldots\ldots(82)$$

and the energy
$$\alpha_1 = \frac{h^2}{8\pi^2}\left\{\frac{(n_\theta + n_\psi)^2}{A} + \left(\frac{1}{C} - \frac{1}{A}\right)n_\psi^2\right\}. \qquad \ldots\ldots(83)$$

There can only be one state of this type.

We can now write down the contribution to the partition function made by all states for which $n_\psi \neq 0$ and $\alpha > 0$. It is

$$\sum_{n_1=1}^{\infty}\ \sum_{n_\psi=1}^{n_1} (2n_1 + 1)\,\vartheta^{\frac{h^2}{8\pi^2}\left\{\frac{n_1^2}{A} + \left(\frac{1}{C} - \frac{1}{A}\right)n_\psi^2\right\}}. \qquad \ldots\ldots(84)$$

In the doubly degenerate case, in which $C = A$, this reduces still further to

$$\sum_{n_1=1}^{\infty} n_1\,(2n_1 + 1)\,\vartheta^{\frac{h^2 n_1^2}{8\pi^2 A}}. \qquad \ldots\ldots(85)$$

To these expressions we have to add the contributions from (i) the states for which $\alpha < 0$, $n_\psi \neq 0$, and (ii) the states without axial spin for which

$n_\psi = 0$. Adding the former just doubles (84) and (85) and the latter adds (68). Thus the complete partition functions are

$$f(\vartheta) = \sum_{n_1=1}^{\infty} \sum_{n_\psi=1}^{n_1} 2(2n_1+1)\, \vartheta^{\frac{h^2}{8\pi^2}\left\{\frac{n_1{}^2}{A} + \left(\frac{1}{C} - \frac{1}{A}\right) n_\psi{}^2\right\}} + \sum_{n_1=0}^{\infty} (2n_1+1)\, \vartheta^{\frac{h^2 n_1{}^2}{8\pi^2 A}},$$

$$= \sum_{n_1=1}^{\infty} \sum_{|n_\psi| \leqslant n_1} (2n_1+1)\, \vartheta^{\frac{h^2}{8\pi^2}\left\{\frac{n_1{}^2}{A} + \left(\frac{1}{C} - \frac{1}{A}\right) n_\psi{}^2\right\}}, \qquad \text{......(86)}$$

$$f(\vartheta) = \sum_{n_1=0}^{\infty} (2n_1+1)^2\, \vartheta^{\frac{h^2 n_1{}^2}{8\pi^2 A}}. \qquad \text{......(87)}$$

In the latter case the formula for the rotational specific heat is

$$C_{\text{rot}} = R\sigma^2 \frac{d^2}{d\sigma^2} \log\{\Sigma\,(2n_1+1)^2\, e^{-n_1{}^2\sigma}\}, \qquad \text{......(88)}$$

with the same σ as (70). This formula also is applied in § 3·6.

A still more general model can be discussed—namely, a rigid body with three unequal moments of inertia containing an internal spinning gyroscope representing electronic moment of momentum,* which we shall not refer to further here.

The formula replacing (86), according to the new mechanics, is†

$$f(\vartheta) = \sum_{(n_1)} \sum_{|n_\psi| \leqslant n_1} (2n_1+1)\, \vartheta^{\frac{h^2}{8\pi^2}\left\{\frac{n_1(n_1+1)}{A} + \left(\frac{1}{C} - \frac{1}{A}\right) n_\psi{}^2\right\}}. \qquad \text{......(89)}$$

The values of n_1 and n_ψ must be either integral, $n_1 = 0, 1, \ldots$, or half odd-integers, $n_1 = \frac{1}{2}, \frac{3}{2}, \ldots$. It reduces, when $A = C$, to

$$f(\vartheta) = \sum_{(n_1)} (2n_1+1)^2\, \vartheta^{\frac{h^2}{8\pi^2 A} n_1(n_1+1)}, \qquad \text{......(90)}$$

The limiting forms when C is small are

$$(a) \quad n_1 = 0, 1, \ldots \quad f(\vartheta) = \sum_{(n_1)} (2n_1+1)\, \vartheta^{\frac{h^2}{8\pi^2 A} n_1(n_1+1)}, \qquad \text{......(91)}$$

$$(b) \quad n_1 = \tfrac{1}{2}, \tfrac{3}{2}, \ldots \quad f(\vartheta) = \sum_{(n_1)} 2(2n_1+1)\, \vartheta^{\frac{h}{8\pi^2 A} n_1(n_1+1)}. \qquad \text{......(92)}$$

In all cases constant terms are omitted from the set of energy values. They depend of course on the definition of zero energy and do not affect any physical result.

§ 2·7. *Assemblies containing free molecules* (*or other classical systems*). If we are to introduce classical systems into the assembly and discuss them by the foregoing method, it is clear that some limiting process is essential,

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* Kramers, *Zeit. für Phys.* vol. XIII, p. 343 (1923).

† Dennison, *Phys. Rev.* vol. XXVIII, p. 318 (1926), ignoring constant terms in the energy.

for they must be introduced initially as quantized systems. As in fact all motions are subject to the laws of quantum mechanics and all systems are really quantized systems, we are concerned in this limiting process only with questions of technical convenience. We shall now show that this can be done very simply. Questions as to the validity of this limiting process are postponed to the next chapter. For simplicity we shall suppose that the assembly consists of M quantized systems of any type, partition function $f(z)$, and N atoms of mass m moving freely in a volume V whose energy is solely kinetic energy of translation. The whole discussion applies equally well to any number of types of classical and quantized systems; internal motions and rotations of the free atoms or molecules can be included among the latter.

The phase space for a free atom is specified by the six coordinates $p_1, \ldots, q_3$, and is divided up into small cells 1, 2, ..., t, ..., of extension

$$(dp_1 \ldots dq_3)_t$$

and, by the rules of § 2·3, weight δ_t given by

$$\delta_t = \frac{(dp_1 \ldots dq_3)_t}{h^3}. \qquad \ldots\ldots(93)$$

In the preceding problems we have dealt with assemblies whose state depends only on a single parameter ϑ. Here we have a new independent parameter V to take into account, and this is best done by starting with atoms in an external field of force of potential Q which may finally be reduced to the local boundary field of the walls. Then there is an energy ζ_t associated with the tth cell given by

$$\zeta_t = \frac{1}{2m}(p_1{}^2 + p_2{}^2 + p_3{}^2)_t + Q_t; \qquad \ldots\ldots(94)$$

Q is a function of q_1, q_2, q_3 only.

Consider an *artificial* assembly in which the cells are small and the energy anywhere in a cell constant and equal to ζ_t. Then all the ζ's and ϵ's can be supposed chosen so that they are commensurable and expressible as integers with the proper unit of energy. The artificial assembly is effectively composed of quantized systems only, and can be made to represent the actual one to any assigned standard of approximation. In the artificial assembly we have at once the partition function

$$h(z) = \Sigma_t \delta_t z^{\zeta_t}, \qquad \ldots\ldots(95)$$

and the distribution laws are given at once by the old formulae. To obtain the distribution laws for the actual assembly we must proceed to the limit by making the extension of every cell tend to zero. We construct in fact any sequence of artificial assemblies for each of which we can determine the distribution laws, and which has the actual assembly as a limit ($\delta_t \to 0$ for all t). We must then *prove* that these laws have a unique limit, and that this limit represents the distribution laws of the actual assembly, evaluated, that is to say, after we have proceeded to the classical limit. This point is postponed to § 3·7. We really carry out some such process in discussions of the classical distribution laws by any method whatever.*

Now by the definition of an integral, when

$$\delta_t \to 0, \quad (all\ \ t),$$

$$h(z) \to H(z),$$

$$= \frac{1}{h^3}\int \ldots \int e^{-\frac{\log 1/z}{2m}[p_1^2+p_2^2+p_3^2+2mQ]}\, dp_1 \ldots dq_3, \qquad \ldots\ldots(96)$$

the integration being extended over all values of $p_1, \ldots, q_3$. For an assembly in a volume V we may represent the walls by supposing that $Q = 0$ in V and that $Q \to \infty$ rapidly near the wall. Then provided that the real part of $\log 1/z$ is positive ($|z| < 1$),

$$H(z) = \frac{V}{h^3}\iiint e^{-\frac{\log 1/z}{2m}(p_1^2+p_2^2+p_3^2)}\, dp_1 dp_2 dp_3,$$

$$= \frac{(2\pi m)^{\frac{3}{2}}\, V}{h^3 (\log 1/z)^{\frac{3}{2}}}. \qquad \ldots\ldots(97)$$

In the formulae for the distribution laws of the artificial assembly $h'(z)$ and perhaps other differential coefficients occur. It is easily proved directly that $h'(z)$ has the limit $H'(z)$, etc. Thus the laws for the sequences of artificial assemblies have a unique limit which will be the laws given by the formulae of the preceding sections if we use (97) for the partition function of the free motion of the atoms. For example,

$$\overline{E_B} = N\vartheta \frac{\partial}{\partial\vartheta} \log H(\vartheta) = N\vartheta \frac{d}{d\vartheta} \log [\log 1/\vartheta]^{-\frac{3}{2}},$$

$$= \tfrac{3}{2}N/\log 1/\vartheta = \tfrac{3}{2}NkT. \qquad \ldots\ldots(98)$$

$$\overline{b_t} = \frac{N\vartheta^{\zeta_t}\delta_t}{H(\vartheta)} = \frac{N}{V}\left(\frac{\log 1/\vartheta}{2\pi m}\right)^{\frac{3}{2}} e^{-\frac{1}{2}m(\log 1/\vartheta)(u^2+v^2+w^2)}\, dp_1 \ldots dq_3,$$

$$= \frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m}{2kT}(u^2+v^2+w^2)}\, du \ldots dz. \qquad \ldots\ldots(99)$$

This is Maxwell's Law.

Finally we observe that it is possible to replace $h(z)$ by $H(z)$ formally in C and the other integrals, if γ is fixed as the circle $|z| = \vartheta$, although the interpretation of the integral as a coefficient in a power series now fails, and the integrand is no longer single-valued. If $H(z)$ is taken to be real for real positive z these formal integrals give all the correct results. It will be shown in § 3·7 that this is always true.

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* Cf. Jeans, *loc. cit.* chaps. III, V *passim.*

§ **2·71**. *Maxwell's distribution law with mass motion.* It is easy to extend the argument to the case of mass motion by introducing an extra variable for each of the additive integrals of our systems which is conserved in every interaction in the assembly. Consider for simplicity an assembly of any number of types of classical systems. Let ζ_t be the energy, and μ_t any component of the momentum, associated with the tth cell of the first set of systems. Then

$$C = \Sigma_{a,b} \frac{M\,!\, \delta_0{}^{a_0} \delta_1{}^{a_1} \dots}{a_0\,!\, a_1\,! \dots} \times \dots, \qquad \dots\dots(100)$$

summed over all positive values of $a, b, \dots$ subject to

$$\Sigma_t a_t = M, \;\; \Sigma_t b_t = N, \dots, \qquad \dots\dots(101)$$

$$\Sigma_t a_t \zeta_t + \dots = E, \qquad \dots\dots(102)$$

and

$$\Sigma_t a_t \mu_t + \dots = G, \qquad \dots\dots(103)$$

where G is the total component of momentum of the assembly. There is a similar extra limitation for each component of momentum or angular momentum which is conserved.

Now just as we introduced a *selector variable* z to select all the terms of $\Sigma_{a,b}$ which satisfy (102) from the simple expression in which (102) is not obeyed, so we may also introduce another variable x to select further those terms which obey (103) in addition. For this purpose we introduce the partition function

$$h\,(z, x) = \Sigma_t \delta_t z^{\zeta_t} x^{\mu_t}, \qquad \dots\dots(104)$$

and the proper value of C will be the coefficient of $z^E x^G$ in the double series $[h\,(z, x)]^M\,[j\,(z, x)]^N \dots$. This is given by the double integral

$$C = \frac{1}{(2\pi i)^2} \iint \frac{dz\,dx}{z^{E+1} x^{G+1}} [h\,(z, x)]^M [j\,(z, x)]^N \dots. \qquad \dots\dots(105)$$

Similarly, it is easily shown that we must have

$$C\overline{a_t} = \frac{M}{(2\pi i)^2} \iint \frac{dz\,dx}{z^{E+1}\,x^{G+1}} (\delta_t z^{\zeta_t} x^{\mu_t})\,[h\,(z,x)]^{M-1}[j\,(z,x)]^N \dots, \quad \dots(106)$$

$$C\overline{E_A} = \frac{1}{(2\pi i)^2} \iint \frac{dz\,dx}{z^{E+1}\,x^{G+1}} \left\{z \frac{\partial}{\partial z} [h\,(z, x)]^M\right\} [j\,(z, x)]^N \dots, \quad \dots(107)$$

$$C\overline{G_A} = \frac{1}{(2\pi i)^2} \iint \frac{dz\,dx}{z^{E+1} x^{G+1}} \left\{x \frac{\partial}{\partial x} [h\,(z, x)]^M\right\} [j\,(z, x)]^N \dots, \quad \dots(108)$$

where $\overline{E_A}$ and $\overline{G_A}$ are the energy and component of momentum of the first set of systems. These double (and similar multiple) integrals can all be evaluated by a simple extension of Theorem 2·5, which we shall discuss in Chapter v. The resulting distribution laws can be reduced to those of the actual assembly by the limiting process of § 2·7.

The formal deduction of Maxwell's distribution law with mass motion by this method is very simple. We treat the case in which G and μ_t are the momenta, in the direction of q_1, of free molecules in a volume V, so that $\mu_t = (p_1)_t$. Then

$$h(z,x) \to H(z,x) = \frac{V}{h^3} \iiint \exp\left[-\frac{\log 1/z}{2m}(p_1^2+p_2^2+p_3^2) + (\log x)\, p_1\right] dp_1 dp_2 dp_3,$$

$$= \frac{(2\pi m)^{\frac{3}{2}}\, V}{h^3 (\log 1/z)^{\frac{3}{2}}} \exp\left\{\frac{m\,(\log x)^2}{2\log 1/z}\right\}. \quad \text{......(109)}$$

The distribution laws depend on *two* parameters ϑ and ξ which form the unique relevant root of the simultaneous equations

$$\frac{\partial}{\partial z}(z^{-E} h^M j^N \ldots) = \frac{\partial}{\partial x}(x^{-G} h^M j^N \ldots) = 0,$$

reducing in the limit to

$$E = M\vartheta \frac{\partial}{\partial \vartheta} \log H(\vartheta, \xi) + N\vartheta \frac{\partial}{\partial \vartheta} \log J(\vartheta, \xi) + \ldots, \quad \text{......(110)}$$

$$G = M\xi \frac{\partial}{\partial \xi} \log H(\vartheta, \xi) + N\xi \frac{\partial}{\partial \xi} \log J(\vartheta, \xi) + \ldots. \quad \text{......(111)}$$

We derive from (107) and (108)

$$\frac{\overline{E_A}}{M} = \vartheta \frac{\partial}{\partial \vartheta} \log H(\vartheta, \xi),$$

$$= \tfrac{3}{2}\frac{1}{\log 1/\vartheta} + \frac{m\,(\log \xi)^2}{2\,(\log 1/\vartheta)^2}, \quad \text{......(112)}$$

$$\frac{\overline{G_A}}{M} = \xi \frac{\partial}{\partial \xi} \log H(\vartheta, \xi) = \frac{m \log \xi}{\log 1/\vartheta}. \quad \text{......(113)}$$

Since $\overline{G_A}/M$ is the mean q_1-momentum per molecule of the first set, equal to mu_0 say, it follows from (113) and its analogues that the bulk-velocity u_0 must be the same in equilibrium for every set of systems in the assembly, and from (112) that the mean kinetic energy of translation per molecule is

$$\tfrac{3}{2}kT + \tfrac{1}{2}mu_0^2.$$

Finally, from (109)

$$H(\vartheta, \xi) = \frac{(2\pi m)^{\frac{3}{2}}\, V}{h^3 (\log 1/\vartheta)^{\frac{3}{2}}} \exp\{\tfrac{1}{2} m\,(\log 1/\vartheta)\, u_0^2\}. \quad \text{......(114)}$$

From (106) we find $\quad \overline{a_t} = M\delta_t \vartheta^{\zeta_t} \xi^{\mu_t}/H(\vartheta, \xi),$

$$= \frac{M}{V}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} dx \ldots dw \exp\left\{-\frac{m}{2kT}(u^2+v^2+w^2) + mu\log\xi - \frac{1}{2kT}mu_0^2\right\},$$

$$= \frac{M}{V}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} dx \ldots dw \exp\left\{-\frac{m}{2kT}[(u-u_0)^2+v^2+w^2]\right\}, \quad \text{......(115)}$$

which is Maxwell's Law for this case. We may observe that the parameter ξ

which arises from the second selector variable has a simple physical interpretation, for

$$\log \xi = u_0/kT,$$

where u_0 is the common bulk-velocity of all sets of systems in the assembly.

§ 2·72. *The theorem of equipartition.* The most important classical distribution law which we have not yet included is the theorem of equipartition. This is often stated as follows—*if we have any set of M classical systems in the assembly each of s degrees of freedom, whose energy (in Hamiltonian form) consists of the sum of t square terms ($s \leqslant t \leqslant 2s$), then in equilibrium the mean energy of the set is Mt ($\frac{1}{2}kT$), or $\frac{1}{2}kT$ for each square term in the energy.* The present method enables us to give a very simple proof of this theorem, and to indicate its full range of validity, including, for example, the rotations of a rigid body, which some current proofs do not.

Suppose the equations of motion of the system do not contain the time explicitly. Then its Hamiltonian function is the energy and is the sum of (a) a homogeneous quadratic function of the p's whose coefficients are functions of the q's, and (b) a function of certain of the q's (the potential energy). We will now suppose (1) *that the potential energy is a homogeneous quadratic function of $t - s$ of the q's whose coefficients may be functions of the other ($2s - t$) q's,* (2) *that the coefficients of the quadratic p-terms are functions only of these ($2s - t$) q's which do not contribute directly to the potential energy under* (1). We can then show that *the mean energy of the set is Mt ($\frac{1}{2}kT$), which is the theorem of equipartition in its most general form.*

The partition function for these systems is

$$H(z) = \frac{1}{h^s}\int^{(2s)}\cdots\int e^{-(\log 1/z)\epsilon}\, dp_1 \ldots dq_s, \qquad \text{......(116)}$$

where ϵ is the energy in Hamiltonian form. The limits of integration of the ($2s-t$) q's which provide no square terms in ϵ will be determined by the geometry of the system. Local boundary fields such as those defining the walls of a containing vessel can be regarded alternatively as geometrical constraints defining the limits of integration of certain q's. The other variables are to be integrated from $-\infty$ to $+\infty$. The homogeneous quadratic function of the p's can be expressed by a linear transformation as a sum of s squares with positive coefficients,

$$\alpha_1 r_1^2 + \ldots + \alpha_s r_s^2.$$

We change the variables from $p_1, \ldots, p_s$ to $r_1, \ldots, r_s$ and integrate with respect to these from $-\infty$ to $+\infty$. Then

$$H(z) = \frac{1}{h^s}\int^{(s)}\cdots\int \left(\frac{\pi}{\log 1/z}\right)^{\frac{1}{2}s} \frac{\mu}{(\alpha_1 \ldots \alpha_s)^{\frac{1}{2}}}\, e^{-(\log 1/z)W}\, dq_1 \ldots dq_s,$$

where μ is the Jacobian of the $(p—r)$ transformation, and W the potential energy. We can now find a linear transformation of $q_1, \dots, q_{t-s}$ which casts W into the form

$$\beta_1 w_1^2 + \dots + \beta_{t-s} w_{t-s}^2.$$

We change the variables from $q_1, \dots, q_{t-s}$ to $w_1, \dots, w_{t-s}$. By hypothesis μ, the α's and the β's do not depend on the w's and are functions of the "geometrical" variables only. Integrating with respect to the w's we find therefore

$$H(z) = \left[\frac{\pi}{\log 1/z}\right]^{\frac{1}{2}t} \frac{1}{h^s} \int^{(2s-t)} \dots \int \frac{\mu}{(\alpha_1 \dots \alpha_s)^{\frac{1}{2}}} \frac{\mu'}{(\beta_1 \dots \beta_{t-s})^{\frac{1}{2}}} \, dq_{t-s+1} \dots dq_s, \quad \dots\dots(117)$$

where μ' is the Jacobian of the $(q—w)$ transformation. The integral in $H(z)$ depends only on the geometrical limits, and is independent of z.

The mean energy for a set of M of these systems is

$$\begin{aligned} \overline{E} &= M\vartheta \frac{\partial}{\partial \vartheta} \log H(\vartheta), \\ &= -M\vartheta \frac{d}{d\vartheta} \log [\log 1/\vartheta]^{\frac{1}{2}t}, \\ &= \tfrac{1}{2}Mt/\log 1/\vartheta = Mt\,(\tfrac{1}{2}kT), \qquad \dots\dots(118) \end{aligned}$$

which is the theorem stated. It is clear that the theorem cannot be true for non-relativistic Hamiltonian functions under conditions wider than those given here.

§ **2·73**. *Classical rotations.* A special case included in this proof is that of the rotations of a rigid body. General molecular rotations must therefore contribute $3\,(\frac{1}{2}kT)$ to the mean molecular energy, and transverse rotations only of a body with an axis of symmetry and no axial spin $2\,(\frac{1}{2}kT)$. These results are in common use, and we shall refer in the next chapter to the classical value $Mk\ (= R)$ here obtained for C_{rot}. We shall later want the complete expressions for these two partition functions, and it is convenient to insert the calculations here.

For the transverse rotations, moment of inertia A,

$$\epsilon = \frac{1}{2A}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right);$$

$$\begin{aligned} H(z) &= \frac{1}{h^2}\iiiint \exp\left\{-(\log 1/z)\left(\frac{p_\theta^2}{2A} + \frac{p_\phi^2}{2A\sin^2\theta}\right)\right\} dp_\theta\, dp_\phi\, d\theta\, d\phi, \\ &= \frac{1}{h^2}\frac{2\pi A}{\log 1/z}\int_0^\pi \int_0^{2\pi} \sin\theta\, d\theta\, d\phi, \\ &= \frac{8\pi^2 A}{h^2 \log 1/z}. \qquad \dots\dots(119) \end{aligned}$$

For the general rotations of a rigid body, moments of inertia A, B, C,

$$\epsilon = \frac{1}{2A\sin^2\theta}\{(p_\phi - \cos\theta\, p_\psi)\cos\psi - \sin\theta\sin\psi\, p_\theta\}^2$$

$$+\frac{1}{2B\sin^2\theta}\{(p_\phi - \cos\theta\, p_\psi)\sin\psi + \sin\theta\cos\psi\, p_\theta\}^2 + \frac{1}{2C}p_\psi{}^2;$$

$$H(z) = \frac{1}{h^3}\int^{(6)}\cdots\int \exp(-\epsilon\log 1/z)\, dp_\theta\, dp_\phi\, dp_\psi\, d\theta\, d\phi\, d\psi,$$

the limits of integration for θ, ϕ, ψ being $(0, \pi)$, $(0, 2\pi)$, $(0, 2\pi)$. The energy can be expressed in the integrable form

$$\tfrac{1}{2}\left(\frac{\sin^2\psi}{A}+\frac{\cos^2\psi}{B}\right)\left\{p_\theta + \left(\frac{1}{B}-\frac{1}{A}\right)\frac{\sin\psi\cos\psi}{\sin\theta\left(\frac{\sin^2\psi}{A}+\frac{\cos^2\psi}{B}\right)}(p_\phi - \cos\theta\, p_\psi)\right\}^2$$

$$+\frac{1}{2AB\sin^2\theta}\,\frac{1}{\frac{\sin^2\psi}{A}+\frac{\cos^2\psi}{B}}(p_\phi - \cos\theta\, p_\psi)^2 + \frac{1}{2C}p_\psi{}^2.$$

Integrating with respect to p_θ, p_ϕ, p_ψ in that order, we find

$$H(z) = \frac{1}{h^3}\frac{(8\pi^3 ABC)^{\frac{1}{2}}}{(\log 1/z)^{\frac{3}{2}}}\int_0^\pi\int_0^{2\pi}\int_0^{2\pi}\sin\theta\, d\theta\, d\phi\, d\psi,$$

$$= \frac{8\pi^2}{h^3}\frac{(8\pi^3 ABC)^{\frac{1}{2}}}{(\log 1/z)^{\frac{3}{2}}}. \qquad \text{......(120)}$$

§ **2·74**. *External fields of force.* In addition to these formulae for the distribution laws we shall require formulae for the average values of the forces exerted by the assembly or its sets of systems on the bodies which control the external fields. The most important example is the formula for the pressure of a gas. We suppose that the forces are derived from a potential defined by certain parameters $x_1, x_2, \ldots$. In the partition function $f(z) = \Sigma_r \varpi_r z^{\epsilon_r}$, therefore, the ϵ_r are functions of $x_1, x_2, \ldots$. In calculating the equilibrium values of the reactions, that is, the work done in small reversible changes of the x's, the weights ϖ_r are constant, since they are adiabatic invariants.

Now the reaction of a single system in its rth cell (or state) on the external bodies is a set of generalized forces

$$-\frac{\partial\epsilon_r}{\partial x_1},\ -\frac{\partial\epsilon_r}{\partial x_2},\ \ldots.$$

The total generalized force X_1 tending to alter the parameter x_1 will therefore be

$$\Sigma_r\, a_r\left(-\frac{\partial\epsilon_r}{\partial x_1}\right),$$

and its average value $\overline{X_1}$ will be given by

$$\overline{X_1} = \Sigma_r \overline{a_r} \left(-\frac{\partial \epsilon_r}{\partial x_1}\right). \qquad \text{......(121)}$$

Using (51) this becomes

$$\overline{X_1} = \Sigma_r M_r \varpi_r \vartheta^{\epsilon_r} \left(-\frac{\partial \epsilon_r}{\partial x_1}\right) \Big/ f(\vartheta),$$

$$= \frac{M}{\log 1/\vartheta} \frac{\partial}{\partial x_1} \log f(\vartheta). \qquad \text{......(122)}$$

In the special case of free atoms or molecules in an enclosure in which the sole external field is the local boundary field of the walls, giving a potential term Q in the energy, equation (122) reduces in the limit to

$$p = \frac{M}{\log 1/\vartheta} \frac{\partial}{\partial V} \log H(\vartheta) = \frac{MkT}{V}. \qquad \text{......(123)}$$

This is the standard equation for the partial pressure of any constituent of a perfect gas. It is most easily derived from (122) by regarding any small area ω of the boundary as a piston free to move normally, whose position is defined by the parameter x_1. Then $\overline{X_1} = p\omega$ by definition of p, and $\omega dx = dV$.

All this is quite straightforward for a potential energy term in the energy function of classical systems distributed over the cells of their phase space. It is, however, of great importance to realize that the argument establishing (122) is general and applies equally well to the variations in the permissible energies of quantized systems due to the reversible changes of parameters defining external fields.

Consider the case of any system whose Hamiltonian function expressed in terms of uniformizing variables (J, w) is

$$H_0(J_1, \ldots, J_n),$$

and is the energy of the system. Let this system be subjected to a variation of the external parameters giving rise to a new term $\delta\Omega$ in the potential energy. Then for the perturbed system

$$H_1 = H_0(J_1, \ldots, J_n) + \delta\Omega(J_1, \ldots, J_n, w_1, \ldots, w_n). \qquad \text{......(124)}$$

Then, by the general theorems of perturbations,

$$H_1 = H_0(J_1', \ldots, J_n') + \overline{\delta\Omega}, \qquad \text{......(125)}$$

where $J_1', \ldots, J_n'$ are the new uniformizing variables, and $\overline{\delta\Omega}$ is the time mean of $\delta\Omega$, which may be calculated (to the first order) for the unperturbed orbit. But since the J's are adiabatic invariants $J_1 = J_1'$, etc. for reversible variations, and therefore

$$\delta\epsilon_r = \overline{\delta\Omega},$$

where ϵ_r is the energy in this quantized state. We may assume that the form of Ω is such that to the first order

$$\overline{\delta\Omega} = \Sigma_s \frac{\overline{\partial\Omega}}{\partial x_s}\,\delta x_s,$$

that is, that the operations of time averaging and differentiation may be inverted; this assumption is formally

$$\frac{\partial}{\partial x}\frac{1}{\tau}\int_0^\tau \Omega dt = \frac{1}{\tau}\int_0^\tau \frac{\partial\Omega}{\partial x}\,dt.$$

Then $$\delta\epsilon_r = \Sigma_s \frac{\overline{\partial\Omega}}{\partial x_s}\,\delta x_s. \qquad \text{......(126)}$$

But $\overline{\partial\Omega/\partial x_s}$ is just the mean force exerted on the system by the body exerting the outside field, and $-\overline{\partial\Omega/\partial x_s}$ the mean force exerted by the system on the outside body. By (126) this mean force is exactly $-\partial\epsilon_r/\partial x_s$ as before, thus showing that (122) and (123) are of great generality. For example, for any set of M independent systems of partition function $H(\vartheta)$ or one complex system of partition function $K(\vartheta)$ we have

$$p = \frac{M}{\log 1/\vartheta}\frac{\partial}{\partial V}\log H(\vartheta), \qquad \text{......(127)}$$

$$p = \frac{1}{\log 1/\vartheta}\frac{\partial}{\partial V}\log K(\vartheta), \qquad \text{......(127)}'$$

respectively.

The importance of (126) can hardly be over-emphasized, as to it is due the obedience of these assemblies to the second law of Thermodynamics, and therefore their utility as models for actual matter. It is therefore perhaps worth while to consider in detail the simple example of a pendulum executing small oscillations in a uniform field of force (say gravity) whose intensity can be regarded as variable at will.

For the small coplanar oscillations of a pendulum

$$H_0 = \nu_0 J,$$

where ν_0 is the frequency of oscillation. Hence

$$H_1 = \nu_0 J + \overline{\delta\Omega}.$$

For gravity we may take $\Omega = gh^*$, $\delta\Omega = h^*\delta g$, where h^* is the height of the bob above some fixed datum level. Then

$$\overline{\delta\Omega} = \delta\Omega_0 + \frac{\delta g}{\tau}\int_0^\tau \tfrac{1}{2}l\theta^2\,dt,$$

where $\delta\Omega_0$ is the increase in potential energy of the bob in its position of rest, l is the length of the string and θ its angular displacement. We have at once

$$\overline{\delta\Omega} = \delta\Omega_0 + \tfrac{1}{4}l\,\delta g\,\theta^2_{\text{max}}.$$

Now since the mean kinetic and potential energies of a pendulum are equal

$$H_0 = \nu_0 J = \tfrac{1}{2} g l \theta^2_{\max}.$$

Hence
$$\overline{\delta\Omega} = \delta\Omega_0 + \tfrac{1}{2}\frac{\delta g}{g} J\nu_0,$$

and, since $\nu_0 \propto \sqrt{g}$, $\tfrac{1}{2}\delta g/g = \delta\nu/\nu_0$,

$$\overline{\delta\Omega} = \delta\Omega_0 + J\delta\nu.$$

This should be the change of energy. The first term gives at once the increase of potential energy of the bob in its mean position, and since J is invariant, the increase of vibrational energy in the rth state must be $J\delta\nu$. Thus $\delta\epsilon_r = \overline{\delta\Omega}$ in accordance with the general theorem.

We see, therefore, that the mean reactions of our systems and assemblies to external fields of force can be calculated at once from the partition function. For perfect gases, for example, the partition function gives at once C_v and p as functions of T and V, and these, with Maxwell's distribution law, are all the equilibrium properties of the perfect gas. The partition function contains in itself the whole of the equilibrium properties. This, as we shall see later, is a consequence of the fact that the partition function is equivalent to a thermodynamic potential. When we have established this equivalence it will be legitimate and sometimes convenient to appeal to thermodynamic theorems instead of direct calculation when examining thermo-mechanical or thermo-electrical relations.

§ **2·75.** *Analogies with Gibbsian phase integrals.* The analogy with Gibbs development can be clearly seen at this stage. The partition function for a molecule of a perfect gas in an external field of force of potential W is, in terms of T,

$$H\,(T) = \frac{1}{h^3}\int^{(6)}\!\!\cdots\int e^{-\left\{\frac{1}{2m}(p_x{}^2+p_y{}^2+p_z{}^2)+W\right\}/kT}\,dp_x dp_y dp_z dx\,dy\,dz,$$

and the partition function for N such molecules is this integral N times repeated, or $[H\,(T)]^N$.

Now this integral N times repeated is exactly Gibbs' integral* for this assembly of N molecules of a perfect gas over "an ensemble of such assemblies canonically distributed in phase". Gibbs defines a function ψ by the equation

$$e^{-\psi/\Theta} = \int_{\text{phases}}^{\text{all}}\!\!\cdots\int e^{-\epsilon/\Theta}\,dp_1 \ldots dq_n, \qquad \ldots\ldots(128)$$

so that here $\psi = -N\Theta \log H\,(T)$. Gibbs' Θ is proportional to T, and his ψ is shown eventually to be equivalent to the thermodynamic potential $U - TS$, an equivalence established directly for our partition functions in Chapter VI. What we have done here may, if it is preferred, be regarded

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* Gibbs, *Elementary Principles in Statistical Mechanics*, p. 33, eq. 92.

as a generalization of the Gibbsian phase integral so as to include quantized systems in the assembly. Our semi-logical dynamical foundation can be discarded, without altering the results, for the hypothesis of canonical distribution in phase.

We may observe here that whatever be the form of W the p_x, p_y, p_z integrations can be effected, giving

$$H(T) = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \int^{(3)} \cdots \int e^{-W/kT}\, dx\,dy\,dz. \qquad \ldots\ldots(129)$$

Thus the partition function or phase integral splits into two factors for the kinetic and potential energies, which can always be discussed separately for classical systems. When $W = 0$ except for boundary fields the factor for the potential energy reduces to the volume V. The form of both factors remains essentially Gibbsian.

§ **2·76**. *Boltzmann's distribution law.* It remains to mention this law, which is the complement of Maxwell's for classical systems, and is naturally associated with the distribution in external fields of force. It can be stated generally as follows:

For any set of classical systems, the average numbers $\overline{a_1}$, $\overline{a_2}$ *in any two equal elements of their phase space are in the ratio*

$$\overline{a_1} : \overline{a_2} = e^{-\epsilon_1/kT} : e^{-\epsilon_2/kT}, \qquad \ldots\ldots(130)$$

where ϵ_1 *and* ϵ_2 *are the energies of the systems in these elements of their phase space.*

This law follows at once from previous theorems, for

$$\overline{a_1} = \delta_1 \vartheta^{\epsilon_1}/H(\vartheta), \quad \overline{a_2} = \delta_2 \vartheta^{\epsilon_2}/H(\vartheta), \quad \delta_1 = \delta_2.$$

It extends of course to quantized systems in the form

$$\overline{a_1} : \overline{a_2} = \varpi_1 e^{-\epsilon_1/kT} : \varpi_2 e^{-\epsilon_2/kT}, \qquad \ldots\ldots(131)$$

also a consequence of preceding theorems. The law contains nothing not already given, but is inserted here formally for completeness.

Boltzmann's law has, of course, numerous important applications and important specialized forms. If we consider two elements of the *physical* space accessible to the systems, in which their dynamical state is the same, so that the Hamiltonian energy function differs only in the different values of W, we can integrate over all possible momenta and obtain

$$n_1 : n_2 = e^{-W_1/kT} : e^{-W_2/kT}. \qquad \ldots\ldots(132)$$

In (132) n_1 and n_2 are the average total numbers of systems without regard to their kinetic energy in equal volume elements of physical space. This leads at once to the density law for an isothermal atmosphere of perfect gases. Since n is proportional to ρ, the mass density of the gas, equation (132) can be written

$$\rho = \rho_0 e^{-(W-W_0)/kT}. \qquad \ldots\ldots(133)$$

If V^* denotes the gravitational potential in the atmosphere per unit mass (including any field of "centrifugal force") and m is the mass of a molecule, then

$$\rho = \rho_0 e^{-m(V^*-V_0^*)/kT}. \qquad \text{......(134)}$$

This is the atmospheric density law, commonly known as Dalton's. Since V^* is the same for all molecules and m varies from molecule to molecule, equation (134) describes the well-known settling of the heavier molecules to the base of the atmosphere—the most prominent property of an atmosphere in statistical (i.e. isothermal) equilibrium.

The potentials here considered are primarily potentials due to bodies external to the assembly to which the systems of the assembly itself make no effective contribution. This restriction is removed in Chapter VIII.

We have no space to enter here into further atmospheric problems such as the nature of convective equilibrium and the rate of escape of molecules from the boundary of the atmosphere. Such problems belong more properly to the study of steady non-equilibrium states and require the explicit introduction of mechanisms of interaction, but escape is a border-line problem and of particular interest which we shall discuss in Chapter XV.

The validity of equations (130) and (131) is completely general, but that of (132) and (133) is not; they must be confined strictly to the field specified in their enunciation. For example, we cannot always apply (132) to elements of volume belonging to the system in different parts of the assembly which are different *phases* in the thermodynamical sense. More refined considerations are then necessary on which we embark in Chapter V. We must also be careful not to restrict in any way the range of the integrations with respect to the momenta. For example, if we apply Boltzmann's theorem to the number of *free* electrons in the neighbourhood of a fixed positive charge, we mean by free those which have sufficient kinetic energy to escape altogether. The relative numbers of these in two volume elements are not given correctly by (132). It is necessary to return to (130) and observe that the integration with respect to the momenta must be taken only over the region for which

$$(p_x^2 + p_y^2 + p_z^2)/2\,m \geqslant -W > 0.$$

Thus in this case the constant quantity is

$$\frac{e^{-W/kT}}{n}\iiint_{\Sigma p_x^2 \geqslant -2mW} e^{-(p_x^2+p_y^2+p_z^2)/2mkT}\, dp_x dp_y dp_z,$$

which reduces easily to give

$$n_1 : n_2 = e^{-W_1/kT}\int_{-W_1/kT}^{\infty} e^{-x} x^{\frac{1}{2}}\, dx : e^{-W_2/kT}\int_{-W_2/kT}^{\infty} e^{-x} x^{\frac{1}{2}}\, dx. \qquad \text{......(135)}$$

Equation (132) would of course continue to give the relative numbers of electrons *both bound and free*, were it not for the limitations imposed by the quantum theory on the bound electrons.

CHAPTER III

ASSEMBLIES OF PERMANENT SYSTEMS (*cont.*). THE SPECIFIC HEATS OF SIMPLE GASES

§ **3·1**. *The properties of perfect gases. Specific heats.* Further development of the general theory without some detailed application to experimental data would be somewhat arid. We pause here, therefore, to compare theory and experiment for perfect gases. Since actual gases are not perfect the properties of perfect gases cannot strictly be said to be observed. They must be obtained by extrapolation to zero concentration from the actual observations at ordinary concentrations. This presents no serious difficulty and introduces little uncertainty into the results. In this chapter we shall suppose that the necessary corrections have been made. The methods of doing this will be reviewed in Chapter IX.

The theory provides us with (1) the equation of state $pv = MkT = RT$; (2) Maxwell's velocity distribution law; (3) formulae for C_v, for any given molecular model. It is hardly necessary to discuss the field of validity of the equation of state of a perfect gas. It is sufficiently a commonplace that $pv = MkT$ is accurately the limit of the actual equation of state for all permanent gases or gas-mixtures at all temperatures except very near to the absolute zero.* For most of the simpler gases the equation of state is already very near to its limiting form at normal pressures of the order of one atmosphere even if the temperature is low. Maxwell's law enables us to calculate the numbers of events, such as collisions of a definite type, which occur per second per unit volume of the gas or per unit area of the surface of a wall. Results of this type are of great importance in surface phenomena and chemical kinetics and are obtained and used in Chapters XVII and XVIII. Here we shall be content to compare the present positions of the specific heats of perfect gases in theory and experiment.†

From the definitions‡ of C_v and C_p, namely

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v, \quad C_p = \left[\frac{\partial\,(E + pv)}{\partial T}\right]_p, \qquad \text{......(136)}$$

it follows at once that for perfect gases

$$C_p - C_v = R = 1{\cdot}98 \text{ cal./gm. mol.} \qquad \text{......(137)}$$

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* For this, see Chapter XXI.

† The more important general authorities for the experimental data used in these comparisons are: Partington and Shilling, *The specific heats of gases*, Benn (1924); Eucken, *Zeit. für Phys.* vol. XXIX, pp. 1, 36 (1924); Lewis, *A system of physical chemistry*, vol. III, chap. IV (ed. 1919); Jeans, *loc. cit.* chap. VII. These authors, especially the first two, contain a great quantity of well-digested information.

‡ See, for example, Planck, *Thermodynamik*, ed. 6, §§ 81, 82.

This relation is well known to be obeyed accurately so that it is only necessary to discuss C_v or γ $(= C_p/C_v)$ whichever is the more convenient. By (98) the contribution of the translational kinetic energy to C_v is $\frac{3}{2}R$ in all cases. Any excess of C_v over this value must come from internal motions of the atom or molecule, that is, from rotations of the molecule, from vibrations of the atoms in the molecule or from electronic rearrangements. Any defect of C_v below $\frac{3}{2}R$ must be due to the effective entry of translational quantum conditions ("degeneration") and only occurs at extremely low temperatures.

§ 3·2. *Monatomic gases.* A free atom possesses classical kinetic energy of translation and the internal energy of its electronic system. The energy step associated with the change from the normal state to the nearest excited state is very large, and the internal energy can contribute nothing to C_v except at very high temperatures. The energy required for this step varies for ordinary monatomic gases from 4 to 20 volts* (Hg, He), while kT in volts is $8{\cdot}60 \times 10^{-5}\,T$. Thus ϵ/kT is of the order $10^5/2T$, and $e^{-\epsilon/kT}$ is negligibly small for all terms in the partition function for the internal atomic energy, except the first (normal) term for which $\epsilon = 0$, unless T is at least 10,000° K.† The theory thus predicts $C_v = \frac{3}{2}R$, $C_p = \frac{5}{2}R$, $\gamma = C_p/C_v = \frac{5}{3}$ for all monatomic gases at ordinary temperatures. The experimental values of γ are in satisfactory agreement.

TABLE 1.

Observed values of γ for monatomic gases, corrected for deviation from the perfect gas laws.

Gas	Temp. ° C.	γ	Authority
He	18	1·660	Scheel and Heuse‡
	− 180	1·673	
Ne	19	1·64	Ramsay§
A	15	1·65	Scheel and Heuse‡
	− 180	1·69	
Kr	19	1·68	Ramsay§
Xe	19	1·66	
Hg	275–356	1·666	Kundt and Warburg§

‡ See Partington and Shilling, *loc. cit.* chap. xv.
§ Landolt and Börnstein, *Tabellen* (1923), No. 264.

§ 3·3. *Diatomic gases at moderate temperatures.* In addition to the types of motion and energy content which they share with free atoms, diatomic

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* A "volt" or "electron-volt" is here used as a measure of energy, denoting the energy acquired by an electron in falling freely through a potential difference of 1 volt. The "volt" is a convenient unit of energy in most problems concerned with atomic or molecular structure.

† As the partition function is an infinite series, the argument is here incomplete, without the construction and examination of the partition function in detail. This forms the theme of Chapter XIV, and the exact investigation confirms the result used here.

molecules possess further types of motion. The atomic nuclei can rotate about their centre of gravity to a first approximation like a rigid body, and can vibrate along the line joining them to a first appoximation like a simple harmonic oscillator. If the molecule is nearly rigid, so that the frequency of these vibrations is high, the rotations and vibrations are nearly independent of each other. Moreover, at fairly low temperatures the nuclear vibrations will not contribute to C_v for the same reason that the electronic structure does not contribute, and the whole extra motion reduces to the rotations of a rigid body. The non-vibrating molecule must indeed stretch under the centrifugal forces, but for stiff molecules of high vibrational frequency this effect will be small for moderate rotations—that is, at low temperatures.

Partition functions for such rotations were specified in §§ 2·62 and 2·63 according to the older quantum theory, and the slight modifications required by the new mechanics were also noted. Their classical form was given in § 2·73. It must be shown next that the quantum forms satisfy the limiting principle. The forms of (68), (72), (90) and similar functions for high temperatures ($T \to \infty$, $\sigma \to 0$), can be established by a variety of methods. Perhaps the simplest is to compare the sum with the corresponding integral

$$\int_0^\infty (2x+1)\, e^{-\sigma x^2}\, dx, \text{ or } \int_0^\infty (2x+1)\, e^{-\sigma x(x+1)}\, dx.$$

It is easy to show, by breaking up the sum and the integral into two parts at the maximum of the integrand which is then monotonic in each part, that they differ at most by a term of the order of the largest term in the series. This term occurs for the value of n nearest the root of the equation $n\,(2n+1) = 1/\sigma$ or $(2n+1)^2 = 1/2\sigma$ and is of order $\sigma^{-\frac{1}{2}}$. Hence

$$\sum_0^\infty (2n+1)\, e^{-n^2\sigma} = \int_0^\infty (2x+1)\, e^{-x^2\sigma}\, dx + O\left(\frac{1}{\sqrt{\sigma}}\right),$$

$$= -\left[\frac{e^{-x^2\sigma}}{\sigma}\right]_0^\infty + O\left(\frac{1}{\sqrt{\sigma}}\right) \sim \frac{1}{\sigma}, \qquad \ldots\ldots(138)$$

with a similar result for the other form.

A more exact treatment of this relationship is possible and not without importance. The series $\Sigma e^{-\sigma j^2}$ is a Θ-function and an exact discussion can be given by using the transformation theory of these functions. The series $\Sigma\,(2j+1)\, e^{-\sigma(j+\frac{1}{2})^2}$ is however not a Θ-function and the transformation theory does not apply. A special investigation* shows that

$$\sum_0^\infty (2j+1)\, e^{-\sigma(j+\frac{1}{2})^2} = \frac{1}{\sigma} + \frac{1}{12} + \frac{7}{480}\sigma + O(\sigma^2).$$

We find then that the limiting form of this partition function is

$$\frac{8\pi^2 AkT}{h^2},$$

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* Mulholland, *Proc. Camb. Phil. Soc.* vol. XXIV, p. 280 (1928).

in agreement with (119). By repetition of these arguments it is easily shown that this asymptotic relation may be differentiated any number of times. Thus

$$\sigma^2 \frac{d^2}{d\sigma^2} \log f(\sigma) = \sigma^2 \frac{f''f - f'^2}{f^2} \sim 1,$$

$$C_{\text{rot}} \to R \quad (T \to \infty), \qquad \text{......(139)}$$

again in agreement with the limiting principle. Using Mulholland's asymptotic expansion we find that the specific heat

$$C_{\text{rot}} = 1 + \tfrac{1}{45}\sigma^2 + O(\sigma^3),$$

for small σ. Thus the classical value is approached much more rapidly than one would have anticipated. It is obvious that

$$C_{\text{rot}} \to 0 \quad (T \to 0), \qquad \text{......(140)}$$

or more precisely that

$$C_{\text{rot}} = O(\sigma^2 e^{-2\sigma}) \quad (\sigma \to \infty).$$

Similar results are obtained from the more general expression (89) when C is very small compared with A. There is then a range of values of T for which σ is practically zero but σ' $(= h^2/8\pi^2CkT)$ still very large, so that only those terms of (89) are relevant for which n_ψ has its least value. The limiting form of the partition function is then either

$$\frac{8\pi^2AkT}{h^2}$$

as before, or

$$2\,\frac{8\pi^2AkT}{h^2}\,e^{-h^2/8\pi^2CkT} \qquad \text{......(141)}$$

according as the least value of $|n_\psi|$ is 0 or $\frac{1}{2}$. Equation (139) holds unaltered for this range of values of T. For all diatomic gases not containing a hydrogen atom A is at least as great as 10^{-39} gm. cm.^{2}, and $1/\sigma$ at least $\frac{1}{4}T$. All ordinary values of T are "large" for such gases so far as concerns σ and small for σ', since C is at most $A/10{,}000$, and we should always have $C_{\text{rot}} = R$. The extra factor 2 agrees with the limiting principle, for it allows of the two possible directions of axial spin.

The limiting forms of (89) and (90) for large T and normal values of both A and C can be established in the same way, using for (89) comparison with a double integral. They apply of course rather to polyatomic molecules (see § 3·6), and agree as they should with (120). For the rigid body with three effective rotational freedoms we therefore find

$$\left.\begin{aligned} C_{\text{rot}} &\to \tfrac{3}{2}R \quad (T \to \infty) \\ C_{\text{rot}} &\to 0 \quad\;\;\, (T \to 0) \end{aligned}\right\}. \qquad \text{......(142)}$$

§ **3·4.** *Rotational specific heat of* H_2 *at low temperatures.* The predicted variation in the rotational specific heat has been observed for hydrogen alone among diatomic gases. The best observations are shown plotted in

Fig. 2. The specific heat C_v has approximately the normal value for a diatomic gas ($\frac{5}{2}R$) at ordinary temperatures of 300° K. and above, but falls steadily to $\frac{3}{2}R$ ($C_{\text{rot}} = 0$) as T diminishes. For temperatures below 40° K. C_v and $\frac{3}{2}R$ are indistinguishable. This general behaviour is completely accounted for if we may identify the variable part of C_v with C_{rot} and apply the foregoing theory. The values of the temperature for which the change occurs fit in with independent evidence as to the moment of inertia of the hydrogen molecule. This explanation, originated by Ehrenfest, has long been universally accepted.

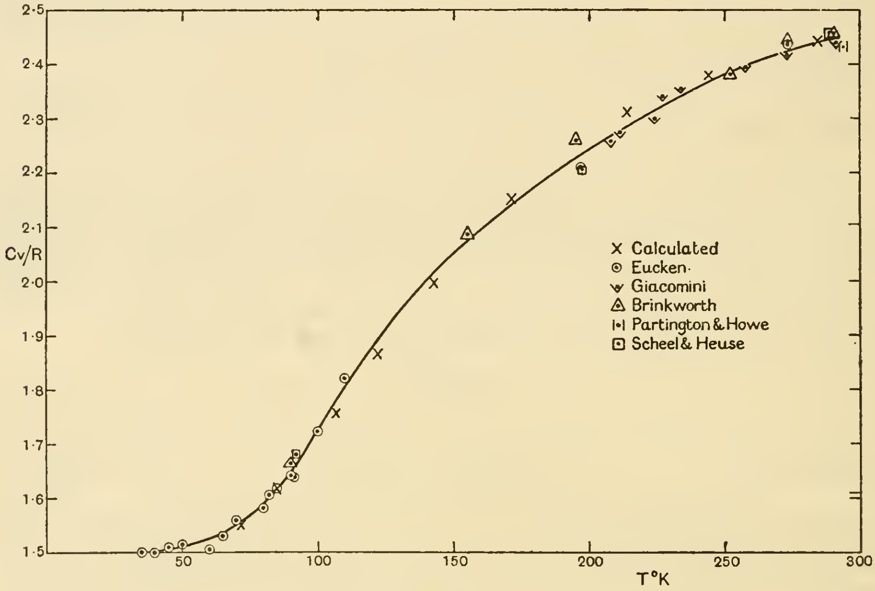

Fig. 2. The specific heat of hydrogen.

It is only recently, however, that complete agreement *in detail* between theory and observation has been obtained. Dennison* has shown that the data for the normal state of hydrogen, derived from the analysis of its band spectrum, yield precisely the observed values of C_v when properly applied.

As we have said, the first crude application of the new mechanics to the rotational states of a rigid rotator without axial spin yields the partition function

$$f(\vartheta) = \sum_{j=0}^{\infty} (2j+1)\, \vartheta^{(j+\frac{1}{2})^2\epsilon} \quad (\epsilon = h^2/8\pi^2 A). \qquad \ldots\ldots(143)$$

This set of weights and energies is undoubtedly confirmed by the analysis

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* Dennison, *Proc. Roy. Soc.* A, vol. cxv, p. 483 (1927). A full discussion of theories previous to the work of Dennison is given by Van Vleck, *Phys. Rev.* vol. xxviii, p. 980 (1926).

of simple infra-red band spectra such as those of HCl, HBr, CO and CN,* and no theoretical modification is possible. No sufficient agreement, however, can be obtained with the observed curve of Fig. 2 for any value of A. Choosing A to give a good fit at low temperatures, the best that can be done is shown in Fig. 3† by Curve A.

The mistake in this attempted application of the theory lies in applying the formula (143), which appears to be correct for a heteropolar molecule formed of two different atoms, to a homopolar molecule formed of two identical atoms, without examining whether the homopolar character is significant. It is now established in the new mechanics that the identical nature of the electrons in an atom or the atoms in a molecule is vital to its structure.‡ It is necessary to consider in detail the forms of the wave-functions of Schrödinger's theory which belong to the various energy values, with regard to their behaviour when any pair of identical members of the system are interchanged. This has been done in detail with special reference to hydrogen by Hund§. In such a case, in which there are two like nuclei to consider, the wave-functions for the rotation break up into two distinct groups, those which are symmetrical and those which are antisymmetrical in the nuclei.|| Wave-functions for a rigid rotator with-

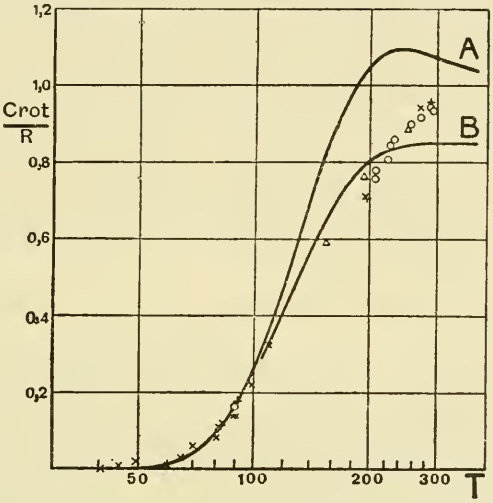

Fig. 3. The specific heat of a rigid rotator according to (143) (Curve A).

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* R. H. Fowler, *Phil. Mag.* vol. XLIX, p. 1272 (1925); Kemble, *Zeit. für Phys.* vol. XXXV, p. 286 (1925). The latter has numerous references to experimental data.

† Dieke, *Physica*, vol. V, p. 412 (1925). The points represent observations and Curve B theoretical modifications no longer of interest.

‡ Heisenberg, *Zeit. für Phys.* vol. XXXVIII, p. 411 (1926); *ibid.* vol. XLI, p. 239 (1927).

§ Hund, *ibid.* vol. XLII, p. 93 (1927).

|| The wave form is symmetrical when Schrödinger's ψ is unchanged by an interchange of nuclei and antisymmetrical when ψ is unaltered in magnitude but reversed in sign.

out axial spin are symmetrical for j even in (143) and antisymmetrical for j odd. Further, if the two nuclei are absolutely indistinguishable there is no interconnection whatever possible between the symmetrical and antisymmetrical states and only one or other, but not both, can be expected to present itself in this universe. This is in beautiful agreement with observations on the band spectrum of helium (emitter He_2) which has for some time been recognized to possess only half the expected number of lines in each band, alternate lines being completely absent. The symmetrical rotational forms do not occur.* The bands of H_2 on the other hand show alternating intensities and no missing lines. Both symmetrical and antisymmetrical rotational forms are present and the alternations are accounted for, as has been shown by Hori,† if the molecules with antisymmetrical wave-functions are three times as numerous as the symmetrical ones. This, however, is exactly what we should expect if the nuclei have spins like the electrons and if only wave-functions which are antisymmetrical for the nuclei can occur when account is taken both of their orientations and their rotations. Hori has also shown from the spectrum that the normal state of the molecule has no axial spin, so that the spin-free rotator is a legitimate model, and that its moment of inertia must be $4{\cdot}67 \times 10^{-41}$ gm. cm.^{2}.

These results require that we shall take for the partition function for the normal H_2-molecule not (143) but

$$f(\vartheta) = \sum_{j=0,2,4\ldots} (2j+1)\,\vartheta^{(j+\frac{1}{2})^2\epsilon} + 3\sum_{j=1,3,5\ldots} (2j+1)\,\vartheta^{(j+\frac{1}{2})^2\epsilon}. \quad \ldots\ldots(144)$$

Partition functions such as this were therefore examined by Hund,‡ but were found to give curves bearing no resemblance whatever to the observations of Fig. 2. To apply the theory properly one further point must be made. While Hori's work leaves no doubt whatever that the possible states are correctly enumerated in (144), it is also assumed in (144) that interchanges between all the states of (144) take place freely, so that the distribution laws of the equilibrium state are correctly given by (144) even at very low temperatures. But it is necessary to ask whether these interchanges can occur freely at ordinary and low temperatures; they must all be able to occur in a vacuum-tube discharge, but even then interchanges between the symmetrical and antisymmetrical rotational states are rare and no corresponding intercombination lines are observed in the spectrum of the discharge. They would *never* occur if the nuclei had no spin, and occur with a frequency proportional to the perturbation of the energy values by the nuclear spins—much less frequently than interchanges between the states of par- and ortho-helium. It is therefore reasonable

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* It is not yet established *by analysis of the observations* that it is the antisymmetrical and not the symmetrical forms which are found.

† Hori, *Zeit. für Phys.* vol. XLIV, p. 834 (1927).

‡ Hund, *loc. cit.*

to assume that in ordinary hydrogen gas interchanges between the symmetrical and antisymmetrical states only occur in times very long compared with the time of an experiment. These times are estimated to be of the order of a month. The specific heat measurements are therefore not made on a gas in the true equilibrium state governed by (144) but in a metastable equilibrium in which the gas behaves like a mixture of different gases, one of them the symmetrical and the other the antisymmetrical molecules.

We therefore proceed as follows. We introduce the functions

$$f_s(\sigma) = \sum_{j=0,2,4\ldots} (2j+1)\, e^{-(j+\frac{1}{2})^2\sigma}, \qquad \ldots\ldots(145)$$

$$f_a(\sigma) = \sum_{j=1,3,5\ldots} (2j+1)\, e^{-(j+\frac{1}{2})^2\sigma}. \qquad \ldots\ldots(146)$$

Then the rotational specific heat of the symmetrical gas (by itself) is given by

$$\frac{(C_{\text{rot}})_s}{R} = \sigma^2 \frac{d^2}{d\sigma^2} \log f_s(\sigma),$$

and of the antisymmetrical gas (by itself)

$$\frac{(C_{\text{rot}})_a}{R} = \sigma^2 \frac{d^2}{d\sigma^2} \log f_a(\sigma).$$

That of the actual 3 : 1 mixture will be

$$\frac{C_{\text{rot}}}{R} = \frac{\sigma^2}{4}\left\{3\frac{d^2}{d\sigma^2}\log f_a(\sigma) + \frac{d^2}{d\sigma^2}\log f_s(\sigma)\right\},$$

$$= \frac{\sigma^2}{4}\frac{d^2}{d\sigma^2}\log\{f_a^3(\sigma)\, f_s(\sigma)\}. \qquad \ldots\ldots(147)$$

We have to replace the $(3f_a + f_s)$ of the true equilibrium by $(f_a^3 f_s)^{\frac{1}{4}}$. The result of using (147) with $A = 4{\cdot}64 \times 10^{-41}$ is the set of points shown by crosses in Fig. 2. The agreement with observation is all that can be desired.

There is of course no doubt that (143) will yield the correct rotational specific heats of polar molecules such as HCl at very low temperatures. It is a great pity that this region is not accessible to observation as the vapour pressure of HCl is too low. The important region for HCl is below 60° K.

The temperature at which, on the theory, C_{rot} should have an assigned value is proportional to $1/A$ since A and T occur only in the combination AT. The moment of inertia of H_2 is obviously smaller than that of any other molecule and C_{rot}/R is effectively unity for H_2 above 300° K. and zero below 40° K. Refinements of the partition function will not affect the general comparisons that follow. For we now see more exactly that, for example in O_2, C_{rot}/R must be unity at least as soon as the temperature reaches 300/16 or 20° K. Observations of a variable C_{rot} are therefore impracticable for all diatomic molecules which contain no H-atom.

Even the halogen hydrides have moments of inertia too large, that of HCl, for example, being five times* that of H_2, and leading to the result just given above. The absence of other examples of this variation among diatomic gases is therefore in accordance with the theory.

This analysis requires a broadening of the classification of the states of a rotating homopolar molecule with which we shall be further concerned later on. We have hitherto treated our atoms, still more our atomic nuclei, as structureless points, a treatment which has just proved statistically inadequate. We may not even treat all nuclei as structureless mass points. The proton—the H-nucleus—has two possible orientations and so must be assigned a weight twice as great as that which we have hitherto used for structureless points. The hydrogen molecule has therefore a weight four times that of a structureless rotator (in the normal state no further factor is introduced by the orientations of the electrons). If we introduce the symmetry number σ, here 2, the prepared weight of the hydrogen molecule reduces to twice that of a structureless rotator. The classical partition function with the prepared weights is then such that (144) obeys the limiting principle. Both in the classical and in the new mechanics the nuclear structure introduces a factor 4, which in both is reduced to 2 by considerations of symmetry. These, however, are not entirely analogous in the two theories.

§ 3·5. *Diatomic gases. Vibrational energy.* The next approximation to a real molecule is to abandon the assumption of rigidity and allow for the vibration of the atomic nuclei along the line joining them. Besides the translations and rotations already dealt with no other motion can contribute effectively to the partition function at temperatures less than about 10,000° K.

Let $b(\vartheta)$ be the partition function for the vibrational and rotational energy, referred to its own state of least energy as zero of energy. If the binding forces are very strong so that the molecule is nearly rigid and the frequency of vibration high, we may suppose to a first approximation that the vibrations and rotations do not affect one another; to this approximation $b(\vartheta)$ will factorize into

$$b(\vartheta) = r(\vartheta)\, v(\vartheta),$$

the partition functions for the rotations and vibrations respectively. To the same rough approximation we may suppose that the vibrations are like those of a simple harmonic oscillator of frequency ν, but that as an energy χ will dissociate the molecule not more than p states are possible in which the molecule remains a molecule. Then

$$v(\vartheta) = \frac{1 - \vartheta^{ph\nu}}{1 - \vartheta^{h\nu}},$$

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* Imes, *Astrophys. J.* vol. L, p. 251 (1919). See also Table 13, p. 160.

where $ph\nu$ is of the order of χ. [Actually this form is some way from the truth. The energies of the vibrational states commonly appear to tend to χ as a limit.] If χ and $ph\nu$ are fairly large compared with $h\nu$, there will be a considerable range of values of ϑ or T for which $\vartheta^{ph\nu}$ is negligible compared with 1 even if $\vartheta^{h\nu}$ is not. For such temperatures

$$v(\vartheta) = (1 - \vartheta^{h\nu})^{-1} \qquad \text{......(148)}$$

approximately, and in this region (148) will be an equally good approximation to more exact forms of the vibrational partition function. The contribution to the specific heat is

$$C_{\text{vib}}/R = \left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}. \qquad \text{......(149)}$$

We shall write this $C_{\text{vib}}/R = P(\Theta/T) \quad (\Theta = h\nu/k).$ ......(150)

When $h\nu/kT$ is large the contribution is zero. If ν is so large that $h\nu/kT$ is large at room temperatures, then for such diatomic gases we shall have

$$C_v = \tfrac{5}{2}, \quad \gamma = \tfrac{7}{5}.$$

Otherwise C_v exceeds $\frac{5}{2}$ by the amount given by (149). These predictions are in good general agreement with the facts shown in Table 2.

TABLE 2.

Observed values of γ for diatomic gases.

Gas	Temp. ° C.	γ	Authority	Value of $h\nu/k$ from spectrum*
H_2	16	1·407	Scheel and Heuse†	6110
N_2	20	1·398		3360
	− 181	1·419		.
O_2	20	1·398		2240
	− 76	1·411		.
	− 181	1·404		.
CO	18	1·396		3080
	− 180	1·417		.
NO	15	1·38		2710
	− 45	1·39		.
	− 80	1·38		.
HCl	15	1·40	Partington‡	4150
HBr	—	—	—	3700
HI	—	—	—	[3500]§

* Authorities for $h\nu/k$ are Mecke, *Zeit. für Phys.* vol. XLII, p. 390, down to NO inclusive, and Imes, *loc. cit. ante*, for the halides. It is possible that the values for O_2 and N_2 may still be open to doubt.

† See Partington and Shilling, *loc. cit.*

‡ See *ibid.* Table B.

§ Extrapolated.

A proper study of the vibrational specific heat of any of these gases requires observations at rather high temperatures. A more accurate formula is then necessary than that provided by the separate contributions of $r(\vartheta)$ and $v(\vartheta)$. Apparently reliable observations are available for O_2, N_2 and CO up to 1000° C. and for H_2 up to 2000° C. A fairly satisfactory theoretical account of the specific heat of H_2 at high temperatures has been given by Kemble and Van Vleck, who discussed an elastic rotator with a particular law of force according to the classical quantum theory. They used values of A and ν_0, however, adjusted to fit the specific heat curve. From the point of view of *statistical* theory it is not necessary to go back to a mechanical model. It is sufficient to take the states of vibration and rotation of the normal H_2-molecule as enumerated directly from the band spectrum by Hori, to construct a semi-empirical partition function with their help and to use this function to evaluate C_{rot} and C_{vib}. This has been carried out successfully by McCrea.* At these higher temperatures the differences between symmetrical and antisymmetrical rotational states are unimportant, and we may use without serious loss of accuracy the one partition function

$$f(\vartheta) = \sum_{n=0}^{\infty} \sum_{j=0}^{\infty} (2j+1)\, \vartheta^{E(n,j)}, \qquad \text{......(151)}$$

where

$$\frac{E(n,j)}{hc} = A\,(n+\tfrac{1}{2}) + (j+\tfrac{1}{2})^2 B\,(n+\tfrac{1}{2}) + (j+\tfrac{1}{2})^4 \beta\,(n+\tfrac{1}{2}). \quad \text{...(152)}$$

The functions A, B, β are tabulated by Hori. It is easily verified that for our purpose β may always be neglected, and that at the temperatures concerned

$$\sum_{j=0}^{\infty} (2j+1)\, e^{-hcB(n+\frac{1}{2})(j+\frac{1}{2})^2/kT} = \frac{kT}{hcB\,(n+\frac{1}{2})}. \qquad \text{......(153)}$$

with sufficient accuracy. It remains, therefore, only to compute the series

$$\sum_{n=0}^{\infty} \frac{1}{B\,(n+\frac{1}{2})}\, e^{-hcA(n+\frac{1}{2})/kT} \qquad \text{......(154)}$$

and its first two differential coefficients. For the values of T concerned not more than four or five terms are required, so that observed values are available and no extrapolation is needed. The results are given in the following table. Partington and Shilling state that the best representation of the observed total specific heat between 273° K. and 2273° K. is given by

$$C_v = 4{\cdot}659 + 0{\cdot}00070\, T. \qquad \text{......(155)}$$

TABLE 3.

Specific heat C_v of H_2 at high temperatures.

Temp. ° K	C_v obs. (155)	C_v calc.
600	5·08	4·98
800	5·22	5·04
1000	5·36	5·16
1200	5·50	5·34
1600	5·78	5·72
1800	5·92	5·89
2000	6·06	6·05
2500	[6·41]†	6·37

† Extrapolated.

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* McCrea, *Proc. Camb. Phil. Soc.* vol. XXIV, p. 80 (1928).

The agreement is satisfactory especially at the higher temperatures where it would fail but for these theoretical refinements.

If it is desired to refer the energy values back to a model it is necessary to assume a definite law of force between the nuclei. Such calculations have been made by Fues,* for example, using the new mechanics. His result is quoted here for reference if required. For the law of force

$$E_{\text{pot}} = -E' + (2\pi\nu_0)^2 A \left\{\frac{1}{\rho} - \frac{1}{2\rho^2} + c_3(\rho - 1)^3 + c_4(\rho - 1)^4 \ldots\right\}, \quad \ldots(156)$$

where $\rho = r/r_0$, r_0 is the equilibrium distance apart, and ν_0 the classical fundamental frequency of small vibrations, the energy values (constant terms omitted) are

$$E(n,j) = h\nu_0 (n + \tfrac{1}{2}) [1 - \tfrac{3}{2}\kappa^2 (1 + 2c_3)(j + \tfrac{1}{2})^2] + \ldots$$
$$+ \frac{h^2}{8\pi^2 A}(j + \tfrac{1}{2})^2 [1 - \kappa^2 (j + \tfrac{1}{2})^2] - \frac{h^2}{8\pi^2 A}(n + \tfrac{1}{2})^2 [3 + 15c_3 + \tfrac{15}{2}c_3^2 + 3c_4], \quad \ldots\ldots(157)$$

where
$$\kappa = h/4\pi^2\nu_0 A. \quad \ldots\ldots(158)$$

It is natural to attempt to extend to other diatomic gases the construction of semi-empirical partition functions which has proved successful for H_2. The results are surprising and lead one to suspect grave inaccuracies either in the observed specific heat or in the band spectrum data. Errors in the latter would mean of course that we have taken data for a state that is not the normal state. This is impossible for CO which has an infra-red vibration-rotation absorption spectrum. Oxygen is the worst case. The observed value of the specific heat given by Partington is well reproduced by the simple theory using a Planck term if we use a value 5600 for $h\nu_0/k$ instead of 2240. These discrepancies are interesting and await further investigation, but this will require experimental work at high temperatures.

The specific heat variation takes place for the halogens Cl_2, Br_2 and I_2 in a convenient temperature range, but good observations seem never to have been made. Existing observations are consistent with values of $h\nu/k$ of about 1000, 450, and 300 respectively.† The value 300 for I_2 is well determined by the band spectrum.

§ 3·6. *Polyatomic molecules.* The only polyatomic molecules which could possibly show less than the classical rotational energy in accessible temperature ranges are those containing only one atom other than hydrogen, and of these only CH_4, NH_3, and OH_2 need be considered. Low temperature observations are only practicable for CH_4 (methane), and values of C_v/R

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* Fues, *Ann. der Phys.* vol. LXXX, p. 367 (1926).

† Cox, *Proc. Camb. Phil. Soc.* vol. XXI, p. 543 (1923); Eucken, *loc. cit.*

less than 3 have actually been recorded* and Urey† has tentatively analysed them. They seem in reasonable agreement with the partition functions of § 2·63. In view, however, of the extreme symmetry of CH_4 accurate data for C_{rot}/R and an accurate analysis might well prove of great interest.

Turning now to higher temperatures, it is of course useless at present to attempt the analysis for any but the simplest molecules, and as among these there are good observations for CO_2, H_2O, CH_4 and NH_3 we confine attention to them. Owing to the considerable number of vibrational freedoms a convincing analysis is only possible when the vibrational frequencies can be regarded as already known by other evidence, from the (infra-red) band spectra.

§ **3·61**. *Specific heat of ammonia gas* (NH_3). A satisfactory explanation of the infra-red band spectrum of the NH_3-molecule has been given by Dennison‡ on the assumption that the molecule has the form of a regular pyramid with the nitrogen nucleus at the apex. There are then four distinct fundamental frequencies of which two are double. There is one relation between them. The four frequencies can be correlated satisfactorily with the frequencies of important bands. We may therefore take the two single frequencies to be $1{\cdot}340 \times 10^{14}$ and $0{\cdot}281 \times 10^{14}$ and the two double ones $1{\cdot}009 \times 10^{14}$ and $0{\cdot}474 \times 10^{14}$. If we make the rough approximation of using Planck terms (150) for each vibration, then

$$\frac{C_{\text{vib}}}{R} = P\left(\frac{6370}{T}\right) + P\left(\frac{1346}{T}\right) + 2P\left(\frac{4810}{T}\right) + 2P\left(\frac{2330}{T}\right). \quad\text{......(159)}$$

These are derived from Dennison's theoretical frequencies which are slightly different from the observed ones given above. The molecule has a symmetry $3\,! = 6$ and the rotational terms divide up in an elaborate manner§ which, however, is of no importance at high temperatures. Taking

$$C_v/R = 3 + C_{\text{vib}}/R$$

the observed values are shown plotted against the theoretical curve in Fig. 4. The agreement is very satisfactory on the whole, but much higher temperatures are necessary to test the contributions of the first term in (159).

§ **3·62**. *Specific heat of methane* (CH_4). A variety of evidence (such as inertness and absence of electric moment) indicates a highly symmetrical structure for the nuclei of this molecule, in which the H-nuclei (in equilibrium) probably lie at the vertices of a regular tetrahedron with the

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* Partington and Shilling, *loc. cit.*

† Urey, *J. Amer. Chem. Soc.* vol. XLV, p. 1445 (1923).

‡ Dennison, *Phil. Mag.* vol. I, p. 195 (1926).

§ Hund, *Zeit für Phys.* vol. XLIII, p. 788 (1927).

carbon at the centre. The normal modes have been investigated by Dennison* and shown to consist of one single, one double, and two triple vibrations, nine in all of four independent frequencies. The band structure, so far as it is known (which is not in great detail), agrees well with the assignment to these modes in order of the following frequencies:

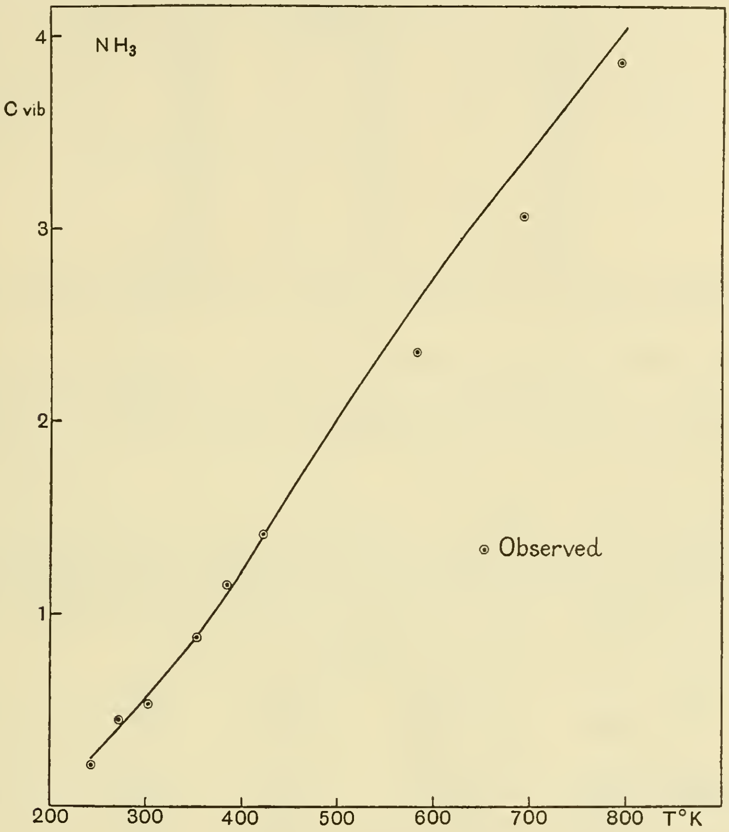

Fig. 4. The vibrational specific heat of ammonia.

Observations below 500° K. by Osborne, Stimson, Sligh and Cragoe, *Phys. Ber.* vol. v, p. 271 (1924); above 500° K. by Haber, *Zeit. für Elektrochem.* vol. xx, p. 597 (1914).

$12{\cdot}651 \times 10^{13}$, $4{\cdot}560 \times 10^{13}$, $9{\cdot}042 \times 10^{13}$, $3{\cdot}912 \times 10^{13}$. The resulting specific heat is, using observed frequencies,

$$\frac{C_{\text{vib}}}{R} = P\left(\frac{6040}{T}\right) + 2P\left(\frac{2180}{T}\right) + 3P\left(\frac{4310}{T}\right) + 3P\left(\frac{1870}{T}\right). \quad \ldots\ldots(160)$$

Observed and calculated values are given in Table 4. On the whole the two values are in good agreement and the excess of the observed values is certainly largely due to a stretching effect which has not yet been

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* Dennison, *Astrophys. J.* vol. LXII, p. 84 (1925).

investigated. But the observations even after Eucken's discussion are hardly certain enough for more serious comparison with theory.

TABLE 4.

Vibrational specific heats of CH_4.

Temp. ° K.	C_{vib}, observed	C_{vib}, calculated
193	0·07	0·04
218	0·09	0·10
243	0·16	0·20
278	0·45	0·42
373	1·85	1·42
473	3·45	2·81
573	4·9	4·17
673	6·3	5·46
773	7·6	6·64
873	8·8	7·70

Observations as reduced by Eucken and Fried, *Zeit. für Phys.* vol. XXIX, p. 41 (1924), except the first two from Heuse, *Ann. der Phys.* vol. LIX, p. 86 (1919).

§ **3·63**. *Specific heat of carbon dioxide* (CO_2). For this gas we have good and extensive observations of the specific heat summarized in Table 5. The theoretical explanation, however, presents peculiar difficulties, which have been fully discussed by McCrea*. Two models have been proposed to account for the band spectrum, one straight† and the other bent‡ in the equilibrium position. Both have symmetry about the carbon atom in the centre. There is no doubt that the bent model gives the best and simplest explanation, though the other is not impossible. Its normal modes are shown in Fig. 5. Its moments of inertia are $A = B = 5 \times 10^{-39}$, $C = 0{\cdot}5 \times 10^{-40}$. The resulting specific heat functions are

$$\textit{Bent} \quad \frac{C_v'}{R} = 3 + P\left(\frac{960}{T}\right) + P\left(\frac{3350}{T}\right) + P\left(\frac{5230}{T}\right); \quad \ldots\ldots(161)$$

$$\textit{Straight} \quad \frac{C_v''}{R} = \tfrac{5}{2} + 2P\left(\frac{960}{T}\right) + P\left(\frac{1750}{T}\right) + P\left(\frac{3290}{T}\right). \quad \ldots\ldots(162)$$

The two models must have the classical rotational specific heat for three and two rotational freedoms respectively. Table 5 and Fig. 6 compare the theory with observation. We may say at once that the specific heats at high temperatures are strong if not convincing evidence against the straight model. The neglected stretching effect must almost certainly increase the calculated specific heat and might bring C_v' into agreement with C_v, while it could not possibly bring C_v''. An estimate based on its value for H_2 indicates that it is of the right order of magnitude.

This acceptance of the bent model, which can hardly be questioned in view of all the evidence, leaves us with a discrepancy at low tem-

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* McCrea, *Proc. Camb. Phil. Soc.* vol. XXIII, p. 890 (1927), vol. XXIV, p. 290 (1928).

† Eucken, *Zeit. für Phys.* vol. XXXVII, p. 714 (1926).

‡ Dennison, *Phil. Mag.* vol. I, p. 195 (1926), and other authors there referred to.

peratures where its specific heat is too high. No escape is provided by the falling off of the rotational specific heat for the small moment of inertia C below its classical value, since the moment of inertia is too large by a factor about 10.* The only possibility seems to be that molecules in which the vibration ν_3 is not excited are straight—the rest bent. This idea is put forward by McCrea and leads to the specific heat shown by the

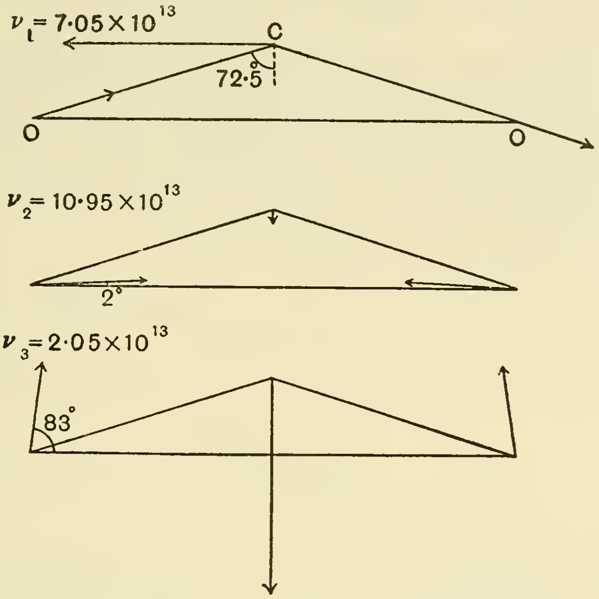

Fig. 5. The normal vibrational modes of the CO_2 molecule. The lengths of the arrows show roughly the relative amplitudes for the different particles.

TABLE 5.

Temp. °K.	C_v' calculated for bent model	C_v'' calculated for straight model	C_v observed
155	6·12	5·28	5·02±0·4 (1)
197	6·33	5·72	5·83 (2)
273	6·75	6·70	6·67 (3)
373	7·17	7·76	7·14
473	7·51	8·63	7·56
673	8·10	9·86	8·34
873	8·64	10·73	9·03
1073	9·15	11·25	9·65
1473	9·99	11·93	10·63
1873	10·59	12·33	11·29
2273	10·90	12·50	11·62

Authorities (1), (2) Eucken, *Zeit. für Phys.* vol. XXXVII, p. 714 (1928), quoting (1) Donath, (2) Heuse. (3) For this and higher temperatures Partington and Shilling, *loc. cit.*

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* The molecule is not symmetrical about the C axis, so that the moment of inertia required is smaller than for H_2 under otherwise corresponding conditions.

dotted line *ab* in Fig. 6, in reasonable agreement with observation at low temperatures, using only data from the band spectrum. McCrea also brings forward some other evidence in favour of this change of shape. There are then, however, difficulties with the specific heat at higher temperatures, and the question can hardly be regarded as settled.

§ **3·64**. *Specific heat of water vapour* (H_2O). Attempts have been made to account in a similar way for the specific heat of H_2O, but without success. A recent analysis by McCrea* shows, however, that the very large specific heat at high temperatures must be accounted for by dissociation of the molecules of water into H_2 and O_2. The observational material is therefore not suitable for illustrating specific heat theory.

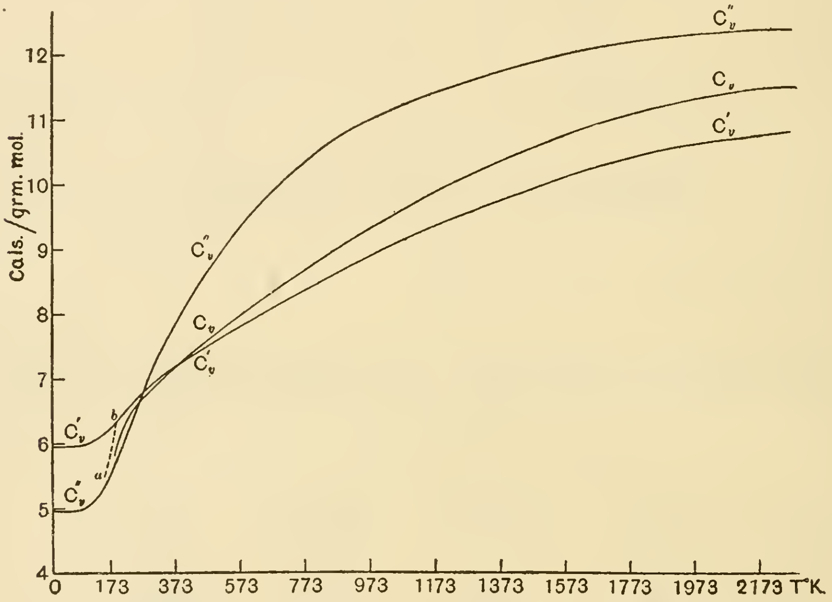

Fig. 6. The specific heat of CO_2; observed, C_v; calculated for the bent model, C_v'; for the straight model, C_v''.

§ **3·65**. Summing up this survey we may say that the general forms of the curves of specific heat for ordinary gases are well reproduced by the theory. Closer agreement, however, between theory and observation may require a knowledge of fine points in the theory of the structure of the molecule and in discussion of the observations. The final refinements have already been made in the discussion of the specific heat of H_2 at all temperatures, but not in any other case. In the light of this example we may expect such refined discussions to be valuable for other gases and hope that they will not be long delayed. Attention might well be paid to O_2, NH_3 and CH_4 in particular.

* McCrea, *Proc. Camb. Phil. Soc.* vol. XXIII, p. 942 (1927).

§ 3·7. *The formation of partition functions by limiting processes.* We postponed from the last chapter a closer discussion of the difficult points in the formation of partition functions for classical systems by a limiting process. It will be sufficient to consider the partition function for the translatory motion of free atoms in an enclosure of volume V, which is the typical and the most important case.

In the earlier discussion, where no limiting process was involved, it was convenient to choose a unit of energy to fit the assembly, so that all the energies were measured by integers without a common factor. Here this implies a continual change of the unit of energy as we proceed to the limit, which is apt to obscure essential features. We therefore fix the unit of energy once for all and assume that for the artificial assemblies of the sequence the ζ_t are chosen so that $\zeta_t = \xi_t/\tau$, where the ξ_t and τ are integers, and τ changes from one sequence to another. As we proceed to the limit $\tau \to \infty$.

The partition functions for the atoms in the artificial assembly may still be taken to be

$$h(z) = \Sigma_t \delta_t z^{\zeta_t},$$

and we require the coefficients of z^E in, say,

$$[h(z)]^M [j(z)]^N,$$

and similar expressions. The powers of z in $h(z)$ are now fractional and $[j(z)]^N$ represents the partition functions for the rest of the assembly. If we write $x = z^{1/\tau}$, $h(x) = \Sigma_t \delta_t x^{\xi_t}$, etc., these coefficients are the coefficients of $x^{\tau E}$ in

$$[h(x)]^M [j(x)]^N,$$

and therefore

$$C = \frac{1}{2\pi i}\int_\gamma \frac{dx}{x^{\tau E+1}} [h(x)]^M [j(x)]^N. \qquad \text{......(163)}$$

On changing back to the variable z we find

$$C = \frac{1}{2\pi i\tau}\int_{\tau\gamma} \frac{dz}{z^{E+1}} [h(z)]^M [j(z)]^N, \qquad \text{......(164)}$$

in which the contour $\tau\gamma$ means that the integral must now be taken τ times round the circle γ. We have to study the asymptotic form of (164) when $\tau \to \infty$.

The following arguments are incomplete in detail, but show how the use of $H(z)$ in place of $h(z)$ in all the integrals and the derived distribution laws may be justified. The details can be filled in without much trouble.

Let

$$h(z) = \Sigma_\xi \delta_\xi z^{\xi/\tau}, \qquad \text{......(165)}$$

where $h^3\delta_\xi$ is the extension of that set of points in 6 dimensions in which

$$\frac{\xi}{\tau} \leqslant \frac{1}{2m}(p_1^2 + p_2^2 + p_3^2) < \frac{\xi+1}{\tau} \quad \{(q_1, q_2, q_3) \text{ in } V\}.$$

Any other possible $h(z)$ will differ from this only by terms of order $1/\tau$. Then

$$h^3\delta_\xi = \frac{4\pi}{3}\{(\xi+1)^{\frac{3}{2}} - \xi^{\frac{3}{2}}\}\left(\frac{2m}{\tau}\right)^{\frac{3}{2}} V, \qquad \text{......(166)}$$

$$= 2\pi\left\{\frac{\Gamma(\xi+\frac{3}{2})}{\xi\,!} + \frac{a}{(\xi+1)^{\frac{1}{2}}} + O[(\xi+1)^{-\frac{3}{2}}]\right\}\left(\frac{2m}{\tau}\right)^{\frac{3}{2}} V. \qquad \text{......(167)}$$

It is found that the dominant contributions come from the first term in { }, and

$$\Sigma_\xi \frac{\Gamma(\xi+\frac{3}{2})}{\xi\,!} z^{\xi/\tau} = \tfrac{1}{2}\Gamma(\tfrac{1}{2})(1-z^{1/\tau})^{-\frac{3}{2}}.$$

Thus, approximately,

$$h(z) = \frac{(2\pi m)^{\frac{3}{2}} V}{h^3}\{\tau(1-z^{1/\tau})\}^{-\frac{3}{2}}, \qquad \text{......(168)}$$

and any other $h(z)$ will likewise approximate to (168). In (164) z^E and $j(z)$ are uniform functions of z, and so is $[h(z)]^M$ when it is summed for all the τ circles. Thus we can write

$$C = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}[j(z)]^N Q(M,\tau,z), \qquad \text{......(169)}$$

where $$Q(M,\tau,z) = \frac{1}{\tau}\sum_{r=0}^{\tau-1}[h(ze^{2\pi ri})]^M,$$

$$= \left\{\frac{(2\pi m)^{\frac{3}{2}} V}{h^3}\right\}^M \frac{1}{\tau}\sum_{r=0}^{\tau-1}\{\tau(1-z^{1/\tau}e^{2\pi ri/\tau})\}^{-\frac{3}{2}M}. \qquad \text{......(170)}$$

In (170) it is supposed for definiteness that $am(z) = 0$ for real z and that $am(z)$ lies between $\pm\pi$ on the circle γ. The series in (170) can be expanded in the form

$$\frac{\tau}{\tau^{\frac{3}{2}M}\Gamma(\frac{3}{2}M)}\left[1 + \frac{\Gamma(\frac{3}{2}M+\tau)}{\tau\,!}z + \frac{\Gamma(\frac{3}{2}M+2\tau)}{2\tau\,!}z^2 + \dots\right],$$

the other terms vanishing on summation. When $\tau \to \infty$

$$\frac{\Gamma(\frac{3}{2}M+r\tau)}{(r\tau)\,!} \sim (r\tau)^{\frac{3}{2}M-1}.$$

Therefore as $\tau \to \infty$

$$Q(M,\tau,z) \sim \frac{1}{\tau\Gamma(\frac{3}{2}M)}\left\{\frac{(2\pi m)^{\frac{3}{2}} V}{h^3}\right\}^M [z + 2^{\frac{3}{2}M-1}z^2 + \dots + r^{\frac{3}{2}M-1}z^r + \dots]$$

$$= \frac{1}{\tau}q(M,z). \qquad \text{......(171)}$$

The factor $1/\tau$ will be irrelevant, as it will occur similarly in all the integrals. It can then be shown that we can work out all the distribution laws using $q(M,z)$ in the ordinary integrals in place of $[h(z)]^M$. The unique distribution laws so obtained in terms of $q(M,z)$ will be those obtained by proceeding to the classical limit before calculating average values.

In order to see that this form is the same as that obtained by proceeding to the classical limit afterwards as in § 2·7, we examine the form of $q(M, z)$ for large M. For real z it can be shown at once by comparing the series $z + 2^{\frac{3}{2}M-1}z^2 + \dots$ with

$$\int_0^\infty x^{\frac{3}{2}M-1} z^x dx \left(= \frac{\Gamma(\frac{3}{2}M)}{(\log 1/z)^{\frac{3}{2}M}}\right),$$

that the difference is negligible for large M. It follows that as $M \to \infty$

$$q(M, z) \sim \left[\frac{(2\pi m)^{\frac{3}{2}} V}{h^3 (\log 1/z)^{\frac{3}{2}}}\right]^M = [H(z)]^M. \qquad \dots\dots(172)$$

A closer discussion of the series for complex z shows that, for the purpose of substitution in the integral (169), $q(M, z)$ can be replaced by (172) for all values of z provided that $\log(1/z)$ is real for real z and that $|\,am\,(z)\,| < \pi$. This argument, when the details are filled in, is the full justification of the procedure of § 2·7. It shows that the order of the operations $\tau \to \infty$ and $E \to \infty$ is indifferent, and that, with the proper convention as to z, $h(z)$ may be replaced by $H(z)$ in the integral for C. Similar arguments apply to the other integrals, to differential coefficients of $h(z)$ and $H(z)$, and to other classical systems.

A somewhat similar limiting process is required for sets of quantized systems when the energy quanta are incommensurable, but the arguments are simpler. We form a sequence of artificial assemblies with commensurable energies, whose limits are the actual energies of the real assembly. A procedure which uses the limiting partition functions with a properly defined range for $am\,(z)$ is justified by the same arguments. We shall not find it necessary to refer again to such limiting processes. We shall assume that, where necessary, they have all been carried out.

§ **3·8.** *Fluctuations.* We have hitherto ignored all questions of the fluctuations of a quantity P about its mean value $\bar{P}$. As we pointed out in the introductory chapter a proof that in general $\overline{(P - \bar{P})^2} = O(\bar{P})$ is essential to the completeness of the theory, to guarantee that an average property is one which the assembly may be expected actually to have. We shall show in Chapter XX that asymptotic formulae for the general fluctuations $\overline{(P - \bar{P})^s}$ can be calculated for all integral values of s by a simple extension of the analysis of this chapter. We shall not stay to consider these here, but content ourselves with proving that

$$\overline{(P - \bar{P})^2} = O(\bar{P}) \qquad \dots\dots(173)$$

in all the important cases that arise. We observe that

$$\overline{(P - \bar{P})^2} = \overline{P^2} - (\bar{P})^2. \qquad \dots\dots(174)$$

Consider a typical assembly for which

$$C = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}\,[f(z)]^M\,[g(z)]^N\,\dots, \qquad \dots\dots(175)$$

and consider the case $P = E_A$. Then, by the arguments of §§ 2·4, 2·6,

$$C\overline{E_A{}^2} = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}\left\{\left(z\frac{d}{dz}\right)^2 [f(z)]^M\right\}[g(z)]^N\,\dots. \qquad \dots\dots(176)$$

If we evaluate this we find

$$\overline{E_A{}^2} = [f(\vartheta)]^{-M}\left(\vartheta\frac{d}{d\vartheta}\right)^2 [f(\vartheta)]^M\left(1 + O\left(\frac{1}{E}\right)\right). \qquad \dots\dots(177)$$

We have also

$$\overline{E_A} = [f(\vartheta)]^{-M}\left(\vartheta\frac{d}{d\vartheta}\right)[f(\vartheta)]^M\left(1 + O\left(\frac{1}{E}\right)\right). \qquad \dots\dots(178)$$

It is here necessary to include the O-terms, for the leading terms in the fluctuation will cancel. Thus, combining (177) and (178),

$$\overline{E_A{}^2} = [f(\vartheta)]^{-M}\,\vartheta\frac{d}{d\vartheta}\{\overline{E_A}\,[f(\vartheta)]^M\}\left(1 + O\left(\frac{1}{E}\right)\right),$$

$$= \left\{(\overline{E_A})^2 + \vartheta\frac{d\overline{E_A}}{d\vartheta}\right\}\left(1 + O\left(\frac{1}{E}\right)\right).$$

It follows that

$$\overline{(E_A - \overline{E_A})^2} = O(\overline{E_A}^2/E) + O(\overline{E_A}),$$

$$= O(\overline{E_A}), \qquad \dots\dots(179)$$

which is the relation required.

The fluctuation of, say, $\overline{a_r}$ can be calculated in a similar way. We have

$$\overline{(a_r - \overline{a_r})^2} = \overline{a_r(a_r - 1)} + \overline{a_r} - (\overline{a_r})^2,$$

and $$C\overline{a_r(a_r - 1)} = \frac{M(M-1)}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}(\varpi_r z^{\epsilon_r})^2\,[f(z)]^{M-2}\,[g(z)]^N. \qquad \dots(180)$$

Evaluating this we find

$$\overline{a_r(a_r - 1)} = M(M-1)(\varpi_r\vartheta^{\epsilon_r})^2/(f(\vartheta))^2\left(1 + O\left(\frac{1}{E}\right)\right),$$

$$= \left(1 - \frac{1}{M}\right)(\overline{a_r})^2\left(1 + O\left(\frac{1}{E}\right)\right).$$

Thus $$\overline{(a_r - \overline{a_r})^2} = \overline{a_r} - (\overline{a_r})^2/M + O((\overline{a_r})^2/E),$$

$$= O(\overline{a_r}), \qquad \dots\dots(181)$$

which is the relation required. The method is quite general. We shall not usually refer to such questions again except in Chapter xx, but shall in all cases leave it to the reader to supply such proofs as are necessary to establish the genuine normality of the equilibrium properties of the assembly. The omitted proofs are always extremely simple.

There is, however, one point of some importance which should not be overlooked. All our arguments can be used to determine $\overline{P}$, even when $\overline{P}$ is not large for values of E which are large enough to make other mean values such as $\overline{Q}$ effectively normal properties of the assembly. This does not in any way invalidate the calculation of $\overline{Q}$ or $\overline{P}$. It merely means that $\overline{P}$ itself is not yet, owing to its smallness and relatively large fluctuations, an effectively normal property of assemblies of this size.

CHAPTER IV

PARTITION FUNCTIONS FOR TEMPERATURE RADIATION AND CRYSTALS. SIMPLE PROPERTIES OF CRYSTALS

§ **4·1.** *Temperature radiation.* In addition to the energy of the material systems in our assemblies, there will be energy of radiation in equilibrium with the matter. It is desirable therefore to construct a partition function for this energy, to enable us to include it in a general discussion of equilibrium laws. This will be especially true of very hot assemblies, in which the energy of radiation is comparable to the energy of the matter. It is not without interest to observe that, if we treat the aether in any enclosure as an approximately independent dynamical system, obeying the laws of the quantum theory, then Planck's well-known laws of temperature radiation follow at once from the equilibrium theory of statistical mechanics. This is in itself trivial, for of course the laws of the classical quantum theory were constructed to give it. What is of some importance is that we thus deduce Planck's law of temperature radiation as a theorem of the pure equilibrium theory, without appeal to any other fundamental principles or to the mechanisms of the processes of absorption and emission. Such an exposition was first attempted by Debye*.

§ **4·2.** *The normal modes of a continuous medium.* In order to construct a partition function for the energy of the motion of the aether, regarded as analogous to a material system, it is only necessary to find suitable coordinates by which to describe its motion and to apply the rules of the quantum theory. This is easily done. We must start by analysing the number of degrees of freedom of a *continuous medium*—for the sake of generality this may be the aether or idealized gases or elastic solids.† The gas, the aether, and the elastic solid are fundamentally merely continuous media capable of transmitting respectively compressional oscillations only, transverse oscillations only or oscillations of both types.

The possible motions all must satisfy the general wave equation

$$\frac{\partial^2\phi}{\partial t^2} = a^2\nabla^2\phi. \qquad \text{......(182)}$$

In (182) ϕ has various meanings in the various problems—a velocity potential, a component of electric or magnetic force, the dilation $\Sigma\partial u/\partial x$, or a component of the "molecular rotation" $\varpi_x = \frac{1}{2}(\partial w/\partial y - \partial v/\partial z)$, (u, v, w) being the velocity components of the medium. For compressional

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* Debye, *Ann. der Phys.* vol. XXXIII, p. 1427 (1910).

† Jeans, *Dynamical Theory of Gases*, chap. XIV. Some minor oversights are here corrected.

waves there is only one independent type of solution. For transverse aether waves if the components (X, Y, Z) of the electric vector all satisfy (182) then so do the components (A, B, C) of the magnetic vector and, moreover,

$$\Sigma \frac{\partial X}{\partial x} = 0.$$

There are therefore here just two independent types of solution. For the torsional transverse waves of an elastic solid

$$\Sigma \frac{\partial \varpi_x}{\partial x} = 0,$$

so that there are just two independent types here also, or three in all for an elastic solid including the compressional waves.

Consider for simplicity an enclosure of the shape of a rectangular box

$$x = 0,\ x = \alpha,$$
$$y = 0,\ y = \beta,$$
$$z = 0,\ z = \gamma,$$

and a solution ϕ of (182). Let ϕ_0 be the value of ϕ for $t = 0$. Then assuming the possibility of an expansion of ϕ_0 in multiple Fourier series we have

$$\phi_0 = \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} A_{lmn} \genfrac{}{}{0pt}{}{\cos}{\sin} \frac{l\pi x}{\alpha} \genfrac{}{}{0pt}{}{\cos}{\sin} \frac{m\pi y}{\beta} \genfrac{}{}{0pt}{}{\cos}{\sin} \frac{n\pi y}{\gamma}. \qquad \text{......(183)}$$

Similarly, if ϕ_0' is the value of $\partial\phi/\partial t$ for $t = 0$, we can write

$$\phi_0' = \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} A'_{lmn} \genfrac{}{}{0pt}{}{\cos}{\sin} \frac{l\pi x}{\alpha} \genfrac{}{}{0pt}{}{\cos}{\sin} \frac{m\pi y}{\beta} \genfrac{}{}{0pt}{}{\cos}{\sin} \frac{n\pi y}{\gamma}. \qquad \text{......(184)}$$

Then it follows that the solution of (182) is

$$\phi = \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \left\{A_{lmn} \cos pt + \frac{A'_{lmn}}{p} \sin pt\right\} \genfrac{}{}{0pt}{}{\cos}{\sin} \frac{l\pi x}{\alpha} \genfrac{}{}{0pt}{}{\cos}{\sin} \frac{m\pi y}{\beta} \genfrac{}{}{0pt}{}{\cos}{\sin} \frac{n\pi y}{\gamma}, \qquad \text{......(185)}$$

where
$$p^2 = \pi^2 a^2 \left\{\frac{l^2}{\alpha^2} + \frac{m^2}{\beta^2} + \frac{n^2}{\gamma^2}\right\}. \qquad \text{......(186)}$$

In each of (183)–(185) there are eight possible terms and eight independent coefficients A, A' for given l, m, n.

We must now consider more closely the boundary conditions. For sound waves in a gas (ϕ velocity potential) we must have $\partial\phi/\partial n = 0$ on every boundary; that is, $\partial\phi/\partial x = 0$ at $x = 0$ and $x = \alpha$, etc. This can only be effected by retaining only the cosine terms in ϕ, so that

$$\phi = \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \left\{A_{lmn} \cos pt + \frac{A'_{lmn}}{p} \sin pt\right\} \cos \frac{l\pi x}{\alpha} \cos \frac{m\pi y}{\beta} \cos \frac{n\pi y}{\gamma}. \qquad \text{......(187)}$$

Thus to each lmn there corresponds here just one possible normal mode of the system—one degree of freedom. For compressional waves in an elastic solid (ϕ the dilatation) we must have $\phi = 0$ over the boundary, only the sine terms can occur and there is just one normal mode as before.

The transverse aether waves and the torsional elastic solid waves are similar. For the former we may take $\phi = X$. We must then assume that the walls of our enclosure are perfect conductors, or energy will not be conserved in the assembly. Thus $X = 0$ at $y = 0$, $y = \beta$, $z = 0$, and $z = \gamma$, which leaves the two terms of type

$$\begin{matrix}\cos\\ \sin\end{matrix} \frac{l\pi x}{\alpha} \sin \frac{m\pi y}{\beta} \sin \frac{n\pi z}{\gamma}.$$

There are similar terms in Y and Z. In X, Y and Z, however, the pure sine terms are impossible, or else the condition

$$\Sigma \frac{\partial X}{\partial x} = 0 \qquad \text{......(188)}$$

cannot be satisfied. Of the one remaining term in each of X, Y, Z, two only remain independent when (188) is satisfied. There are thus 1, 2, or 3 normal modes per value of l, m, n in the three cases gas, aether, elastic solid.

We now return to (186), in which a can take different values for the different types of wave. Since $p = 2\pi a/\lambda$, where λ is the wave length, we have

$$\frac{4}{\lambda^2} = \frac{l^2}{\alpha^2} + \frac{m^2}{\beta^2} + \frac{n^2}{\gamma^2}. \qquad \text{......(189)}$$

The number of normal modes with wave lengths λ satisfying $\lambda \geqslant \lambda_0$ is equal to 1, 2, or 3 times the number of points with integral coordinates inside an octant of the ellipsoid (189) with $\lambda = \lambda_0$, which has the volume

$$\frac{4\pi}{3} \frac{\alpha\beta\gamma}{\lambda_0{}^3}.$$

The number of normal modes with wave lengths between λ and $\lambda + d\lambda$ is therefore

$$4\pi\alpha\beta\gamma \frac{d\lambda}{\lambda^4} (1, 2, 3) \qquad \text{......(190)}$$

in the three cases, or

$$4\pi V \frac{d\lambda}{\lambda^4} (1, 2, 3), \qquad \text{......(191)}$$

where V is the volume of the enclosure. This result is really independent of the shape of the enclosure.* For the aether the number of normal modes with frequencies between ν and $\nu + d\nu$ is

$$\frac{8\pi V}{c^3} \nu^2 d\nu, \qquad \text{......(192)}$$

where c is the velocity of light.

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* Weyl, *Math. Ann.* vol. LXXI, p. 441 (1911), or Courant, *Gött. Nachr.* (1919), p. 255; *Math. Zeit.* vol. VII, p. 14 (1920).

§ 4·3. *The partition function for temperature radiation.* We shall assume that the zero of energy for the vibrations of the aether is the state in which every normal mode has its lowest possible quantum number.* The energy in any other state is then on all versions of the quantum theory

$$h\,(n_1\nu_1 + \ldots + n_r\nu_r + \ldots),$$

and each such state is of weight unity. The partition function is then

$$\begin{aligned} R\,(z) &= \Sigma_{(n)}\, z^{h\,(n_1\nu_1 + \ldots + n_r\nu_r + \ldots)}, \\ &= \Pi_r\,(1 - z^{h\nu_r})^{-1}. \qquad \ldots\ldots(193) \end{aligned}$$

This factorization is typical of systems whose motions separate into independent parts, like the normal modes of a continuous medium controlled by linear partial differential equations. Convergency conditions are satisfied so long as $|\,z\,| < 1$. To obtain an intelligible form of (193) we apply (192). Then

$$\log R\,(z) = -\frac{8\pi V}{c^3}\,\Sigma\nu^2 d\nu \log\,(1 - z^{h\nu}). \qquad \ldots\ldots(194)$$

On proceeding to the limit $d\nu \to 0$ we obtain formally

$$\log R\,(z) = -\frac{8\pi V}{c^3}\int_0^\infty \nu^2 \log\,(1 - z^{h\nu})\,d\nu. \qquad \ldots\ldots(195)$$

To evaluate the integral we can use the logarithmic series and integrate term by term. Then

$$-\int_0^\infty \nu^2 \log\,(1 - z^{h\nu})\,d\nu = \frac{2}{h^3\,(\log 1/z)^3}\sum_1^\infty \frac{1}{n^4}. \qquad \ldots\ldots(196)$$

Since $\Sigma n^{-4} = \pi^4/90$, we find

$$\log R\,(z) = \frac{8\pi^5 V}{45 c^3 h^3\,(\log 1/z)^3}. \qquad \ldots\ldots(197)$$

Consider an assembly containing radiation and N material systems of partition functions $f\,(z)$. Then by the arguments of the last chapter

$$C = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}\,R\,(z)\,[f\,(z)]^N, \qquad \ldots\ldots(198)$$

$$C\overline{E_R} = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}\left\{z\frac{\partial}{\partial z}R\,(z)\right\}[f\,(z)]^N, \qquad \ldots\ldots(199)$$

where $\overline{E_R}$ is the average value of the energy of the radiation in the assembly. It follows that

$$\overline{E_R} = \vartheta\frac{\partial}{\partial\vartheta}\log R\,(\vartheta) \quad (\vartheta = e^{-1/kT}), \qquad \ldots\ldots(200)$$

or

$$\overline{E_R} = \frac{8\pi^5 V}{15 c^3 h^3\,(\log 1/\vartheta)^4} = \frac{8\pi^5 k^4}{15 c^3 h^3}\,VT^4. \qquad \ldots\ldots(201)$$

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* Any other choice of this zero introduces an infinite constant into the energy of the radiation which is without physical significance.

This is the Stefan-Boltzmann law of total radiation with the usual theoretical value of Stefan's constant. To find the energy associated with any particular range of frequencies we write

$$R(z) = R_1(z)\, R_2(z),$$

where
$$\log R_1(z) = -\frac{8\pi V}{c^3}\,\nu^2 d\nu \log(1 - z^{h\nu}).$$

Then by the usual arguments

$$C\overline{E_{R_1}} = \frac{1}{2\pi i}\int_{\gamma} \frac{dz}{z^{E+1}}\left\{z\frac{\partial}{\partial z}R_1(z)\right\} R_2(z)\,[f(z)]^N,$$

$$\overline{E_{R_1}} = \vartheta \frac{\partial}{\partial \vartheta}\log R_1(\vartheta),$$

$$= \frac{8\pi h V}{c^3}\,\frac{\nu^3 d\nu}{\vartheta^{-h\nu} - 1}. \qquad \text{......(202)}$$

In the usual notation $E_\nu d\nu$ is the energy *density* in this frequency range, and we find

$$E_\nu = \frac{8\pi h\nu^3}{c^3}\,\frac{1}{e^{h\nu/kT} - 1}, \qquad \text{......(203)}$$

which is Planck's law.

We can now introduce the energy of radiation by means of its partition function $R(z)$ into any discussion of equilibrium conditions. The limiting processes involved are of a simple type, for the final form of $R(z)$ is merely an analytical approximation to the partition function (193), which is that of a quantized system. No special investigation such as that of § 3·7 is necessary except to deal with incommensurable frequencies.

Though we do not take up thermodynamic relationships until Chapter VI, it is again convenient to record at once the thermodynamic consequences of the existence and form of the partition function $R(\vartheta)$. The radiation contributes $k \log R(\vartheta)$ to the characteristic function, and therefore by equation (399) we find

$$S_R = k\log R(\vartheta) + kT\,\frac{\partial \log R(\vartheta)}{\partial T},$$

$$= \frac{32\pi^5 k^4}{45 c^3 h^3}\,VT^3 = \frac{4}{3}\frac{\overline{E_R}}{T}, \qquad \text{......(204)}$$

$$p_R = kT\frac{\partial}{\partial V}\log R(\vartheta),$$

$$= \frac{8\pi^5 k^4}{45 c^3 h^3}\,T^4 = \frac{1}{3}\frac{\overline{E_R}}{V}, \qquad \text{......(205)}$$

for the entropy, S_R, and pressure, p_R, of radiation.

§ **4·4**. *Applications to crystals.* The partition function for a crystal can be similarly constructed, to the approximation with which we can determine the normal modes. The work is a transcription of the usual determination of the energy content.* It will not be possible here to enter in great detail into the equilibrium properties of crystals, in particular into the calculation of the necessary functions from assumed lattice structures and laws of force. For these the reader should refer to Born (*loc. cit.*). But some account of the very great successes of statistical mechanics in this field should be given, not entirely limited to specific heats. The field of application here is of course far richer than for the permanent perfect gas, whose equilibrium properties are summed up almost completely in $pv = NkT$ and the form of C_v.

A crystal may be supposed to be built up of a lattice of N congruent cells each of which contains s atoms, atomic ions or electrons. It is not normally necessary to include all the electrons in every atom in the cell. Those which are tightly bound to a particular atom belong to that atom just as in a gas, and a partition function can be assigned to each atom or atomic ion for its internal degrees of freedom. These, however, make no effective contribution to the properties of the crystal at relevant temperatures any more than to those of a gas and for the same reason (§ 3·2). But for the sake of full generality it is necessary to allow for some of the atoms being ionized and for some few of their electrons having an independent existence in the cell.

We regard the crystal as a single Hamiltonian system, and its motion as small oscillations about a configuration of equilibrium, which we analyse into its normal modes. To a first approximation these will all be simple harmonic oscillations, and will adequately represent the motion so long as the general run of the oscillations is small, that is, when the crystal is not too hot. At greater violence of oscillation terms in the potential energy of higher order than the squares of the displacements must be introduced. The effect of these on the energy and partition function can be treated by perturbation theory.

§ **4·5**. *The partition function for a crystal.* It has been shown by Born (*loc. cit.*) that there are, as one would expect, $3s$ distinct sets of normal modes for a crystal of s structural units per cell, and that the frequencies of each set ν_j $(j = 1, \ldots, 3s)$ N in number are distributed uniformly through a certain three-dimensional space in which spherical polar coordinates represent space frequency (i.e. wave number) and direction of wave normal for the corresponding wave. The $3s$ sets of frequencies divide necessarily into two groups, those whose frequencies tend to zero for long wave

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* Born, "Atomtheorie des festen Zustandes", § 27 (1923), *Encyc. Math. Wiss.* vol. v, part 3, No. 25, whose exposition we follow in the main here.

lengths of the normal mode, and those whose frequencies tend to a non-zero limit. In general if the unit cell of the crystal is properly chosen there are just three of the first type, for which

$$\nu_j = c_j/\lambda + \dots \quad (j = 1, 2, 3); \qquad \dots\dots(206)$$

the c_j are *the velocities of sound* and are functions of direction of the wave normal. The other $(3s - 3)$ sets of frequencies may be called by distinction *optical*, and for them we have

$$\nu_j = \nu_j^0 + c_j/\lambda + \dots \quad (j = 4, \dots, 3s). \qquad \dots\dots(207)$$

The ν_j^0 and c_j are functions of the crystal structure and the c_j again of direction of the wave normal. The ν_j^0 correspond to the frequencies peculiar to the crystal determining its anomalous reflections (*Reststrahlen*).

In applications of this analysis into normal modes it is usually sufficiently accurate to ignore the variation of ν_j with wave length in (207) for the optical modes, but for the acoustical modes this is inadequate. The more exact frequency distribution law is required. The analysis has been carried through by Born for the general lattice structure. It is clear that the result ought to approximate closely to the results obtained in the simpler problem of § 4·2 of fixing the acoustical frequencies of a continuous medium (elastic solid), and this is in fact the case. It can be shown that for the acoustical modes the number of the N frequencies of the jth set which lie in the frequency range $\nu, \nu + d\nu$ for wave normals in the solid angle $d\Omega$ is asymptotically equal for large N to

$$\frac{V}{c_j^3}\nu^2 d\nu d\Omega \quad (j = 1, 2, 3), \qquad \dots\dots(208)$$

where V is the volume of the crystal. Since there are N of these frequencies in all there will be a finite upper limit ν_j^* for these ν's in each $d\Omega$, such that

$$V\int\frac{d\Omega}{c_j^3}\int_0^{\nu_j^*}\nu^2 d\nu = \frac{V}{3}\int\frac{(\nu_j^*)^3}{c_j^3}\,d\Omega = N. \qquad \dots\dots(209)$$

Both ν_j^* and c_j are functions of direction. In general for frequencies not too near ν_j^*, the total number dN of acoustical frequencies in the range $\nu, \nu + d\nu$ is therefore

$$dN = 4\pi V\left(\frac{1}{c_1^3} + \frac{1}{c_2^3} + \frac{1}{c_3^3}\right)\nu^2 d\nu, \qquad \dots\dots(210)$$

in which the c's represent mean values for direction. For isotropic crystals or quasi-isotropic mixtures there is no dependence on direction, and this reduces accurately to

$$dN = 4\pi V\left(\frac{2}{c_t^3} + \frac{1}{c_l^3}\right)\nu^2 d\nu, \qquad \dots\dots(211)$$

where c_t and c_l are the velocities of torsional and compressional waves respectively—this is the result of § 4·2.

It is now easy to construct the partition function to this approximation. There is one new point that here first needs attention—the precise specification of the zero of energy. One might be tempted to define this to be either the state of lowest permissible energy in each normal mode, or the state for which the Hamiltonian H of the small oscillations is zero. With the latter definition the energy zero for the crystal is then the state of rest with every constituent particle in its position of equilibrium. [According to the new mechanics this is not a possible state of the system. There is an irreducible *nullpunktsenergie* $\frac{1}{2}h\nu$ in every normal mode.] This specification, however, of the energy zero hardly goes deep enough, if variations in the volume of the crystal are taken into account, for such variations which vary the length of edge of the unit cell must alter the potential energy of the state of rest itself. This ambiguity can be avoided by taking the energy zero as the state of infinite separation at relative rest of all the constituent particles of the crystal, each particle separately being in some specified normal state. The energy of the crystal in its state of rest is then, say, $F_0(V)$. $F_0(V)$ is of course negative; its argument can usually be safely omitted. It is, however, only in the simplest case of an isotropic crystal subjected only to isotropic pressures or tensions that the argument V sufficiently defines its state. We return to the more general case in § 4·9.

The energy of the state of the crystal specified by the quantum numbers $n_1, \ldots, n_r, \ldots$ is

$$F_0 + h(n_1\nu_1 + \ldots + n_r\nu_r + \ldots),$$

the weights unity (or at least all equal), and the partition function $K(z)$ given by

$$\log K(z) = F_0 \log z - \sum_{r=1}^{3sN} \log(1 - z^{h\nu_r}). \qquad \ldots\ldots(212)$$

according to the classical quantum theory. This must of course be approximated to by the foregoing analysis of the frequency distribution. We then find at once

$$\log K(z) = F_0 \log z - V\sum_{j=1}^{3}\int\frac{d\Omega}{c_j^3}\int_0^{\nu_j^*}\log(1 - z^{h\nu})\,\nu^2 d\nu - N\sum_{j=4}^{3s}\log(1 - z^{h\nu_j^0}). \qquad \ldots\ldots(213)$$

It is usually sufficiently accurate to ignore variations of ν_j^* and c_j with direction and to define mean values $\bar{\nu}_j$ and $\bar{c}_j$ by the equations

$$\int\frac{(\nu_j^*)^3}{c_j^3}\,d\Omega = \bar{\nu}_j^3\int\frac{d\Omega}{c_j^3} = \frac{4\pi\bar{\nu}_j^3}{\bar{c}_j^3}. \qquad \ldots\ldots(214)$$

In virtue of (209)

$$\bar{\nu}_j = \bar{c}_j\left(\frac{3N}{4\pi V}\right)^{\frac{1}{3}}. \qquad \ldots\ldots(215)$$

If we now define three new constants of the crystal by the equations $k\Theta_j = h\bar{\nu}_j$ ($j = 1, 2, 3$), and replace ν_j^* by $\bar{\nu}_j$ in (213), we find

$$\log K(z) = F_0 \log z - \frac{3N}{(\log 1/z)^3} \sum_{j=1}^{3} \frac{1}{k^3 \Theta_j^3} \int_0^{k\Theta_j \log 1/z} \log(1 - e^{-x})\, x^2 dx - N \sum_{j=4}^{3s} \log(1 - z^{h\nu_j^0}). \qquad \ldots\ldots(216)$$

According to the new mechanics we must replace $\log(1 - e^{-x})$ by $\log(1 - e^{-x}) + \frac{1}{2}x$ and $\log(1 - z^{h\nu_j^0})$ by $\log(1 - z^{h\nu_j^0}) - \frac{1}{2}h\nu_j^0 \log z$ in the formula (216).

Having constructed the partition function $K(z)$ we have at once the usual expression for the mean energy $\overline{E_K}$ of the crystal;

$$\overline{E_K} = \vartheta \frac{\partial}{\partial \vartheta} \log K(\vartheta). \qquad \ldots\ldots(217)$$

In terms of the absolute temperature T,

$$\log K(T) = \frac{-F_0}{kT} - 3N \sum_{j=1}^{3} \frac{T^3}{\Theta_j^3} \int_0^{\Theta_j/T} \log(1 - e^{-x})\, x^2 dx - N \sum_{j=4}^{3s} \log(1 - e^{-h\nu_j^0/kT}), \qquad \ldots\ldots(218)$$

$$\overline{E_K} = F_0 + 3NkT^4 \sum_{j=1}^{3} \frac{1}{\Theta_j^3} \int_0^{\Theta_j/T} \frac{x^3 dx}{e^x - 1} + N \sum_{j=4}^{3s} \frac{h\nu_j^0}{e^{h\nu_j^0/kT} - 1}. \qquad \ldots\ldots(219)$$

The last result has been simplified after differentiation by an integration by parts. These are the complete formulae, but the $3s - 3$ frequencies can be grouped again into two classes: $3(p - 1)$ infra-red frequencies not necessarily all different, and $3(s - p)$ ultra-violet, where p is the number of massive particles in the unit cell and $s - p$ the number of separated electrons. We can in most applications (always at low temperatures) ignore the ultra-violet frequencies of the electrons altogether, and so find in all in (218) just $3p$ terms, pN being the total number of atoms in the crystal.

This view of the part played by the "free" electrons in the lattice is somewhat old-fashioned and should probably be discarded altogether. In view of the work of Pauli† and Sommerfeld‡, which we can discuss more conveniently in Chapter XXI, we should now again rather regard these electrons as an electron gas in free movement among the positive ions of the lattice just as in the classical theory of metallic conduction which we owe to Drude. The only difference is that the gas is an almost completely degenerate one and does not contribute appreciably to the specific heat. The result is therefore the same as for a lattice of high frequency.

If in (219) we ignore the differences between Θ_1, Θ_2 and Θ_3, and neglect the terms arising from the infra-red frequencies, we find approximately

$$\overline{E_K} = F_0 + \frac{9NkT^4}{\Theta^3} \int_0^{\Theta/T} \frac{x^3 dx}{e^x - 1}. \qquad \ldots\ldots(220)$$

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† Pauli, *Zeit. für Phys.* vol. XLI, p. 81 (1927).

‡ Sommerfeld, *Naturwiss.* (1927), p. 825, and *Zeit. für Phys.* vol. XLVII, p. 1 (1928).

This is Debye's result, which we could recover directly by constructing a partition function according to Debye's theory. The complete *theoretical* result (219) is due to Born. The form was first suggested by Nernst.

The two types of term in (218) and (219) are often referred to as Debye's terms and Einstein's terms respectively. The latter name arises from the early investigation by Einstein of specific heats of crystals in which he treated their normal modes as Planck's oscillators all of the same frequency. Einstein's terms in (218) are obviously only significant when the ν_j^0 are effectively different from zero, so that it is allowable to ignore the terms c_j/λ. When $\nu_j^0 \to 0$ we must finally get an additional Debye's term. For example, in a two-atom lattice in which both types of atom are similarly situated and of approximately equal masses (e.g. KCl) it is obviously better to neglect Einstein's terms and treat the whole body as if it were built up of atoms of a single type. We shall thus get a better approximation to the corpus of normal modes.

§ **4·6**. *Debye's formula for C_v in theory and experiment.* The possible field of validity of Debye's formula for the partition function of a crystal can be defined fairly closely. The formula can only be expected to apply to crystals built up out of atoms of one type, all of which are similarly situated in the lattice—that is, for elements crystallizing in the regular system, with extensions perhaps to nearly regular crystals and to simple compounds of similar atoms like KCl. The unit cell of the lattice may then be thought of as containing a single atom, and N is the number of atoms in the crystal or conglomerate. An examination of the facts shows a remarkable agreement with the theory in the expected region, as will now be described. The quantity directly observed is C_p while the theory gives C_v. The derivation of C_v from C_p is effected by formula (250) of a later section.

Let us introduce for shortness the notation

$$D(x) = \frac{3}{x^3}\int_0^x \frac{\tau^3}{e^\tau - 1}\,d\tau; \qquad \text{......(221)}$$

$D(x)$ is frequently called Debye's transcendent. Then

$$\overline{E_K} = F_0 + 3NkTD(\Theta/T), \qquad \text{......(222)}$$

$$C_v = 3Nk\left\{D\left(\frac{\Theta}{T}\right) - \frac{\Theta}{T}D'\left(\frac{\Theta}{T}\right)\right\}. \qquad \text{......(223)}$$

For large values of x

$$D(x) = \frac{\pi^4}{5x^3} - 3e^{-x}\left\{1 + O\left(\frac{1}{x}\right)\right\}. \qquad \text{......(224)}$$

This is easily proved by replacing $\int_0^x$ by $\int_0^\infty - \int_x^\infty$, expanding $1/(e^\tau - 1)$ in the infinite integral and integrating term by term. For small values of x, by direct expansion of the integrand,

$$D(x) = 1 - \tfrac{3}{8}x + \tfrac{1}{20}x^2 + O(x^4).$$

These relations can be differentiated. Therefore we have approximately

$$\overline{E_K} = F_0 + 3NkT, \qquad C_v = 3Nk\left(1 - \frac{1}{20}\frac{\Theta^2}{T^2}\right) \quad (T \to \infty), \qquad \text{......(225)}$$

$$\overline{E_K} = F_0 + \frac{3\pi^4}{5}Nk\frac{T^4}{\Theta^3}, \quad C_v = \frac{12\pi^4}{5}Nk\frac{T^3}{\Theta^3}\left(1 - \frac{15}{4\pi^4}\frac{\Theta^4}{T^4}e^{-\Theta/T}\right) \quad (T \to 0). \qquad \text{......(226)}$$

We make the following observations: (1) The relation $C_v = 3Nk$ is an example of the theorem of equipartition of energy and expresses the well-known laws of Dulong and Petit and Neumann and Regnault. It should hold to within $\frac{1}{2}$ per cent. for $T/\Theta > 3$. The law of Dulong and Petit states that the specific heat per gram-atom has approximately the same value (6·4 for C_p, 6·0 for C_v after correction) for all elements in the solid state. The law of Neumann and Regnault states that the specific heat per gram-molecule of a simple compound in the solid state is approximately equal to the sum of the specific heats of the corresponding solid uncombined components. These laws, their region of validity and the nature of the exceptions to them are well known. (2) The relation (226) states that C_v and $\overline{E_K}$ vary as T^3 and T^4 at low temperatures, with deviations of at most 2 per cent. so long as $T/\Theta < 1/10$. (3) The general form of (223) shows that C_v obeys a law of "corresponding states", being a function of the single variable Θ/T. (4) Equation (215) and the following definition show that Θ can be calculated from the velocities of sound and so from the elastic constants of the crystal. These four deductions are borne out by experiment. The nature of the agreement will now be examined more closely for the last three.*

The T^3-law at low temperatures has been accurately verified for elements and simple compounds. Typical examples are shown in Table 6. The figures of the third column should be constant when the T^3-law holds.

The law of corresponding states has also been found true for elements and simple compounds. Fig. 7† shows the observed values of C_v for eighteen substances plotted as functions of T/Θ, the value of Θ for each substance being chosen to give the best fit for that substance with the continuous curve which represents equation (223). The agreement is eminently satisfactory. The substances and temperature ranges are specified in Table 7 overleaf.

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* The following statements of fact are based on Schrödinger, *Phys. Zeit.* vol. xx, pp. 420, 450, 474, 497, 523 (1919), except where otherwise stated. Full references to the original literature will be found in this paper.

† Schrödinger, *loc. cit.*

TABLE 6.

The T^3-law for C_v at low temperatures.

Copper (Cu)			Iron (Fe)		
Temp. ° K.	C_v	$10^2 C_v^{\frac{1}{3}}/T$	Temp. ° K.	C_v	$10^2 C_v^{\frac{1}{3}}/T$
14·51	0·0390	2·35	32·0	0·152	1·67
15·60	0·0506	2·37	33·1	0·177	1·70
17·50	0·0726	2·39	35·2	0·244	1·77
18·89	0·0930	2·40	38·1	0·288	1·73
20·20	0·1155	2·42	42·0	0·325	1·64
21·50	0·1410	2·42	46·9	0·522	1·71
23·5	0·22	2·57	Aluminium (Al)		
25·37	0·234	2·43			
27·7	0·32	2·47	19·1	0·066	2·12
			23·6	0·110	2·03
			27·2	0·162	2·01
Iron pyrites (FeS_2)			32·4	0·25	1·95
			33·5	0·301	2·00
27·5	0·1095	1·75	35·1	0·33	1·97
29·8	0·1385	1·74			
32·9	0·179	1·72	Beryl (BeO)		
35·8	0·232	1·72			
38·3	0·295	1·74	76·8	0·202	0·765
42·2	0·402	1·75	78·1	0·219	0·773
46·7	0·530	1·74	79·3	0·226	0·769
51·7	0·712	1·74	80·3	0·223	0·756
54·7	0·844	1·74	82·6	0·236	0·750
56·9	0·952	1·73	84·9	0·274	0·766

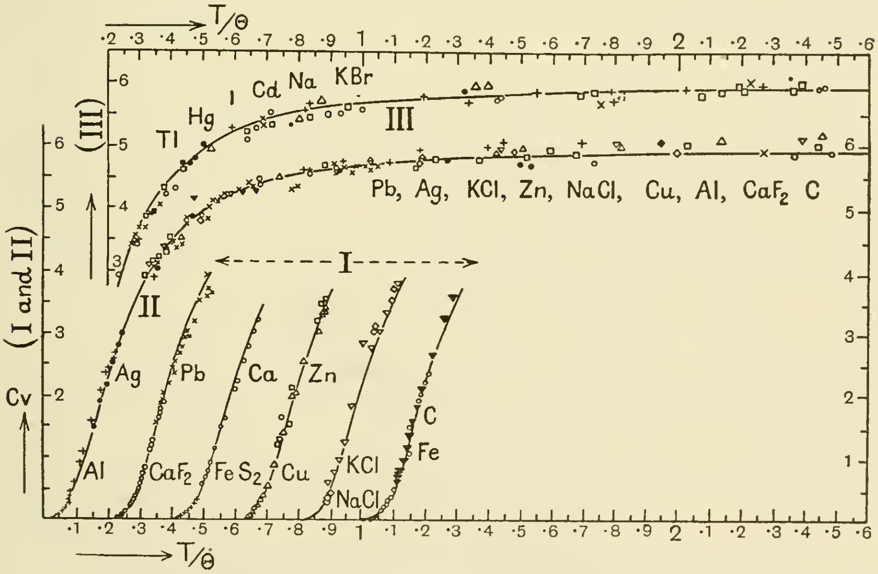

Fig. 7. The specific heats of various solids as functions of T/Θ.

TABLE 7.

Data for Fig. 7, studying the law of corresponding states.

Substance	Chemical symbol	Temperature range	Θ	Points in Fig. 7 Curves		
				I	II	III
Lead	Pb	14–573	88	×	×	
Thallium	Tl	23–301	96			○
Mercury	Hg	31–232	97			□
Iodine	I	22–298	106			×
Cadmium	Cd	50–380	168			+
Sodium	Na	50–240†	172			△
Potassium bromide	KBr	79–417	177			●
Silver	Ag	35–873	215		●	
Calcium	Ca	22–62	226	○		
Sylvine	KCl	23–550	230	▽	▽	
Zinc	Zn	33–673	235	□	□	
Rocksalt	NaCl	25–664	281	◊	◊	
Copper	Cu	14–773†	315	△	△	
Aluminium	Al	19–773	398		+	
Iron	Fe	32–95†	453	○		
Fluorspar	CaF_2	17–328	474	○	○	
Iron pyrites	FeS_2	22–57†	645	+		
Diamond	C	30–1169	1860	▼	▼	

† For Na, Cu, Fe, FeS_2 C_v rises *above* the curve after these temperatures.

The calculation of Θ from the elastic constants can be carried through very simply for isotropic solids and the value so calculated compared with the Θ of Table 7 which is chosen to give the best fit in Fig. 7. The elastic properties of an isotropic solid can be expressed in terms of two constants, the compressibility κ and Poisson's ratio σ. In terms of these the velocities of sound are*

$$c_l^2 = \frac{3(1-\sigma)}{(1+\sigma)\kappa\rho}, \quad c_t^2 = \frac{3(1-2\sigma)}{2(1+\sigma)\kappa\rho}, \qquad \text{......(227)}$$

where ρ is the density. Equation (211) shows that the required function is

$$\chi(\sigma)(\kappa\rho)^{\frac{3}{2}}, \quad \chi(\sigma) = \left\{\frac{1+\sigma}{3(1-\sigma)}\right\}^{\frac{3}{2}} + 2\left\{\frac{2(1+\sigma)}{3(1-2\sigma)}\right\}^{\frac{3}{2}}, \qquad \text{...(228)}$$

so that the theoretical mean value of Θ for use in Debye's formula is given by

$$\frac{1}{\Theta^3} = \tfrac{1}{3}\Sigma\frac{1}{\Theta_j^3} = \left(\frac{k}{h}\right)^3 \frac{4\pi V}{9N}\Sigma\frac{1}{c_j^3} = \left(\frac{k}{h}\right)^3 \frac{4\pi V}{9N}\chi(\sigma)(\kappa\rho)^{\frac{3}{2}}.$$

If V represents the volume of one gram-atom or gram-molecule, then $V\rho = M$, where M is the molecular weight, and

$$\Theta = \left(\frac{9N}{4\pi}\right)^{\frac{1}{3}} \frac{h}{k} \frac{V^{\frac{1}{6}}}{(M\kappa)^{\frac{1}{2}}\{\chi(\sigma)\}^{\frac{1}{3}}}, \qquad \text{......(229)}$$

$$= 3{\cdot}605 \times 10^{-3}\frac{V^{\frac{1}{6}}}{(M\kappa)^{\frac{1}{2}}\{\chi(\sigma)\}^{\frac{1}{3}}}. \qquad \text{......(230)}$$

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* Love, *Theory of Elasticity*, ed. 3, p. 301.

The following examples are given by Born:*

TABLE 8.

Comparison of the values of Θ from specific heat data and from direct calculation from the elastic constants.

Substance	ρ	$\kappa \,.\, 10^{12}$	σ	$\chi(\sigma)$	Θ Table 7	Θ Eq. (230)
Al	2·71	1·36	0·337	10·2	398	402
Cu	8·96	0·74	0·334	10·5	315	332
Ag	10·53	0·92	0·379	15·4	215	214
Pb	11·32	2·0	0·446	61·0	88	73

The agreement is excellent. There is, however, a difficulty that the calculations of Θ have been carried out with the values of the elastic constants determined at ordinary temperatures, whereas it has been argued† that it is the values of these constants at the absolute zero which are relevant, and the use of these would seriously damage the agreement. This objection, however, does not appear to me to be entirely valid. The elastic constants and Θ are of course functions of V for an actual crystal, and the values required for these calculations are those corresponding to the actual volume of the crystal. The theory proceeds by imagining the crystal units at rest in equilibrium in their mean positions corresponding to a given crystal volume; this may involve large negative pressures over the boundary, which are theoretically unobjectionable. On this is superposed without change of volume (but with change of pressure) the heat motion corresponding to any given temperature, and at this temperature the observed C_v and the C_v calculated from the elastic constants for this volume should agree.‡ The observed values of C_v do not in fact therefore correspond to a sequence of C_v's at a single constant volume, the volume at absolute zero, but to a sequence of varying volumes which are the actual volumes of the crystal at each stage at atmospheric (or other small) pressure. These are compared with C_v, calculated for a genuinely constant volume, the volume at normal temperatures. The agreement in the Θ will largely depend on how the various parts of the theoretical curve are weighted in fitting it to the observations. There is a tendency to fit so that the deviations are of roughly constant absolute magnitude all along the curve. This will weight heavily the normal temperatures for which C_v is largest and would explain the satisfactory agreement in the table.

There is, however, still left over an unsatisfactory point of divergence between theory and experiment, for the values of Θ derived from the T^3-law at low temperatures, equation (226), *should* agree with the values

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* Born, *loc. cit.* p. 643.

† Eucken, *Verh. der Deut. phys. Ges.* vol. xv, p. 571 (1913).

‡ It is tacitly assumed in the theory that the elastic constants depend *directly* only on the volume.

calculated from the elastic constants at low temperatures. There is some tendency for these Θ's to be larger than those derived from the whole curve, but the increase is far smaller than the calculations indicate, and the matter remains not fully cleared up.

TABLE 9.

Comparisons of Θ derived by various methods.

Substance	C	Fe	Al	Cu	Ag
Θ from C_v curve	1860	453	398	315	215
Θ from T^3-law	2230	455	385	321	—
Θ from elastic constants at 290° K.	—	—	402	332	214
Θ ditto, at low temperatures	—	—	488	344	235

§ **4·7**. *Applications of formulae for C_v more accurate than Debye's.* Debye's formula for C_v is admittedly derived by crude approximations from (219) or (213), and should only hold at all strictly for isotropic bodies. More accurate calculations are possible in the general case. Such calculations have been successfully carried out by Försterling†. When $|\,\xi\,| < 2\pi$ the function $\xi/(e^\xi - 1)$ can be expanded in the convergent power series

$$\frac{\xi}{e^\xi - 1} = 1 - \tfrac{1}{2}\xi - \sum_{n=1}^{\infty} (-1)^n \frac{B_n}{(2n)!}\,\xi^{2n}, \qquad \text{......(231)}$$

where the B_n are Bernoulli's numbers. If we now return to the original form of log $K(z)$ in (213) we see that the part giving rise to Debye's terms gives an exact contribution to $\overline{E_K}$ of the form

$$Vh \sum_{j=1}^{3} \int \frac{d\Omega}{c_j{}^3} \int_0^{\nu_j{}^*} \frac{\nu^3 d\nu}{\vartheta^{-h\nu} - 1}.$$

If $\Theta_j = h\nu_j{}^*/k$ as before, but now a function of direction, this becomes

$$kTV \left(\frac{kT}{h}\right)^3 \sum_{j=1}^{3} \int \frac{d\Omega}{c_j{}^3} \int_0^{\Theta_j/T} \frac{\xi^3 d\xi}{e^\xi - 1}.$$

If we expand by (231) and differentiate to obtain C_v we find an exact contribution

$$kV \left(\frac{k}{h}\right)^3 \sum_{j=1}^{3} \int \frac{d\Omega}{c_j{}^3} \left[\frac{\Theta_j{}^3}{3} + \sum_{1}^{\infty} \frac{(-1)^n B_n (2n-1)}{(2n)!\,(2n+3)} \frac{\Theta_j{}^{2n+3}}{T^{2n}}\right].$$

Let us now assume that $\nu_j{}^* \propto c_j$. Then

$$\nu_j{}^* = c_j \left(\frac{3N}{4\pi V}\right)^{\frac{1}{3}}, \quad \Theta_j = \frac{h}{k} c_j \left(\frac{3N}{4\pi V}\right)^{\frac{1}{3}};$$

We write

$$\sum_{j=1}^{3} \Theta_j{}^{2n} = \left\{\frac{h}{k}\left(\frac{3N}{4\pi V}\right)^{\frac{1}{3}}\right\}^{2n} \frac{1}{\rho^n} \sum_{j=1}^{3} \rho^n c_j{}^{2n}, \qquad \text{......(232)}$$

$$\gamma = \frac{1}{\rho}\frac{h^2}{k^2}\left(\frac{3N}{4\pi V}\right)^{\frac{2}{3}}, \quad \int \left(\sum_{j=1}^{3} \Theta_j{}^{2n}\right) d\Omega = 4\pi\gamma^n \mathrm{K}_n. \qquad \text{......(233)}$$

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† Försterling, *Ann. der Phys.* (4) vol. LXI, p. 577 (1920); *Zeit. für Phys.* vol. III, p. 9 (1920), vol. VIII, p. 251 (1922).

Then the contribution to C_v is

$$3Nk\left\{1+\sum_{1}^{\infty}(-1)^n\frac{B_n\,(2n-1)}{(2n)!\,(2n+3)}\frac{\gamma^n\,\mathrm{K}_n}{T^{2n}}\right\}. \qquad \ldots\ldots(234)$$

Formula (234) replaces Debye's term in C_v. The integrands of the coefficients K_n can be shown to be rational functions of the measurable elastic constants of the crystal, so that the K_n can be calculated. The full formula for C_v is then

$$C_v = 3Nk\left\{1+\sum_{1}^{\infty}(-1)^n\frac{B_n\,(2n-1)}{(2n)!\,(2n+3)}\frac{\gamma^n\mathrm{K}_n}{T^{2n}}\right\}+Nk\sum_{j=1}^{3p}\frac{(\Theta_j/T)^2\,e^{\Theta_j/T}}{(e^{\Theta_j/T}-1)^2}, \qquad \ldots\ldots(235)$$

valid when $T > \Theta/2\pi$.

Försterling has used this formula in the most accurate comparison of theoretical and observed specific heats yet attempted. Having calculated the first term entirely from elastic data, the correct number of extra terms of Einstein's type are introduced corresponding to the known lattice structure. The number of *different* Θ_j allowable is also known from the structure and symmetry. These are then fixed to give the best fit possible between the observed and theoretical C_v, and the whole theory is checked by comparing these Θ_j with the natural frequencies of the crystal determined by the method of *Reststrahlen*. Excellent representations of C_v are possible among other substances for NaCl, KCl, KBr, CaF_2 and SiO_2, and typical comparisons of the wave lengths of the natural frequencies derived from specific heats and optical measurements (*Reststrahlen*) are shown in the following table.

TABLE 10.

Comparisons of wave lengths of Reststrahlen *directly measured and deduced from specific heat curves.*

Substance	λ_0 optical 10^{-4} cm.	λ_0 from C_v
NaCl	66·7	64·5
KCl	78·0	77·0
CaF_2	53·1	51·0, 34·7*

* Optically inactive.

§ 4·8. *Equations of state for simple isotropic solids, as thermodynamic consequences of the form of the partition function.* It is convenient to discuss at this stage other properties of solids which follow from the general form of the partition function. We consider in this section the simplest case in which with sufficient accuracy

$$\log K\,(T) = -\frac{F_0\,(V)}{kT} - 9N\left\{\frac{T}{\Theta\,(V)}\right\}^3\int_0^{\Theta(V)/T}\log\ (1-e^{-x})\,x^2\,dx. \qquad \ldots\ldots(236)$$

In (236) we have shown Θ explicitly as a function of V; Θ must always vary with V according to the simple theory, unless $V^{\frac{1}{6}}\,\kappa^{-\frac{1}{2}}\,\{\chi(\sigma)\}^{-\frac{1}{3}}$ is independent of the volume. If the solid obeyed Hooke's law perfectly, so that for all displacements the stresses and strains were strictly proportional, this function would be independent of V, for Poisson's ratio σ would be an absolute constant, and the compressibility κ would be proportional to the linear dimensions. But this ideal case can never hold for actual solids, and a V-variation of Θ must be admitted.

By the general formula (127)′ which becomes $p = kT\dfrac{\partial}{\partial V}\log K(T)$ when rewritten in terms of T, it follows at once that

$$p = -F_0'(V) - 3NkT\frac{\Theta'}{\Theta}D\left(\frac{\Theta}{T}\right). \qquad \text{......(237)}$$

This is the *equation of state*. For many isotropic bodies it is sufficient to assume that

$$F_0(V) = -\frac{A}{V^{\frac{1}{3}m}} + \frac{B}{V^{\frac{1}{3}n}} \quad (n > m), \qquad \text{......(238)}$$

where A and B are constants. This is the form of $F_0(V)$ when the atoms in a regular crystal act on one another with central forces consisting of a strong repulsive field of short range of potential β/r^n, and a weaker attractive field of longer range of potential $-\alpha/r^m$. In the calculation of $F_0(V)$, by definition, the structural units are taken to be at rest in their mean positions. We cannot enter here into the calculation of A and B from the laws of force of individual atoms (see Chapter x). If V_0 is the natural volume of the solid at zero temperature and pressure, then

$$F_0'(V_0) = 0. \qquad \text{......(239)}$$

For the form (238) V_0 is therefore fixed in terms of the constants of the interatomic forces by the equation

$$\frac{mA}{V_0^{\frac{1}{3}m}} = \frac{nB}{V_0^{\frac{1}{3}n}}. \qquad \text{......(240)}$$

For small volume changes we may write

$$\begin{aligned} F_0'(V) &= F_0''(V_0)(V - V_0), \\ &= \frac{1}{9}\frac{n(n-m)B}{V_0^{\frac{1}{3}n+2}}(V - V_0), \qquad \text{......(241)} \end{aligned}$$

and
$$F_0(V) = F_0(V_0) + \frac{1}{18}\frac{n(n-m)B}{V_0^{\frac{1}{3}n+2}}(V - V_0)^2, \qquad \text{......(242)}$$

$$F_0(V_0) = -\frac{n-m}{m}\frac{B}{V_0^{\frac{1}{3}n}}. \qquad \text{......(243)}$$

We may now introduce the usual coefficients of thermal expansion α and compressibility κ by the equations (definitions)

$$3\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T. \qquad \text{......(244)}$$

Then
$$\frac{1}{\kappa V} = -\left(\frac{\partial p}{\partial V}\right)_T = F_0''(V) + 3NkT\frac{\partial}{\partial \Theta}\left\{\frac{\Theta'}{\Theta}D\left(\frac{\Theta}{T}\right)\right\}\Theta'. \qquad \text{......(245)}$$

At the absolute zero this reduces to

$$\kappa_0 = 1/V_0F_0''(V),$$

and by (241) and (243) we have the relation

$$F_0(V_0) = \frac{9V_0}{nm\kappa_0}. \qquad \text{......(246)}$$

This important relation between the compressibility and the lattice energy or heat of evaporation at zero temperature can be used to determine nm, or n when m is known as for an ionic lattice ($m = 1$). The actual comparisons are made with a calculated $F_0(V_0)$, after fixing B to give the right scale to the lattice. We shall take up the general question of the specification of interatomic forces in Chapter x.

On differentiating (237) with p constant we find that

$$\left[F_0''(V) + 3NkT\frac{\partial}{\partial\Theta}\left\{\frac{\Theta'}{\Theta}D\left(\frac{\Theta}{T}\right)\right\}\Theta'\right]\left(\frac{\partial V}{\partial T}\right)_p = -3Nk\frac{\Theta'}{\Theta}\left\{D\left(\frac{\Theta}{T}\right) - \frac{\Theta}{T}D'\left(\frac{\Theta}{T}\right)\right\}$$
$$= -\frac{\Theta'}{\Theta}C_v.$$

This can be reduced to the simple form

$$\frac{3\alpha}{\kappa} = \left\{-\frac{\Theta'}{\Theta}\right\}C_v. \qquad \text{......(247)}$$

We see at once that a body for which $\Theta' = 0$ should show no thermal expansion. Finally, from the thermodynamic relation

$$C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p, \qquad \text{......(248)}$$

and from
$$\left(\frac{\partial p}{\partial T}\right)_V = \left\{-\frac{\Theta'}{\Theta}\right\}C_v = \frac{3\alpha}{\kappa}, \qquad \text{......(249)}$$

obtained by differentiating (237) with V constant, we deduce

$$C_p - C_v = 9\alpha^2TV/\kappa. \qquad \text{......(250)}$$

This formula is of great practical importance in deducing C_v from observations of C_p. It is principally used in certain semi-empirical simplified forms.

These formulae appear to be in good agreement with observation for many solids. In particular (247) is satisfied if the value of $-V\Theta'/\Theta$ is about 2·3. A calculation of σ and κ in terms of the interatomic forces would allow this value to be interpreted as fixing a relation between m and n.

§ 4·9. *General equations of state of the general crystal.* We have hitherto, in discussing its equation of state, regarded a crystal as an isotropic solid, subjected only to changes of volume by isotropic (hydrostatic) pressures, which might be negative. The single geometrical variable necessary could then be the volume V as for a gas, and the single elastic constant the volume compressibility. This, however, is insufficient for even the simplest solid, since solids possess at least two independent elastic constants, say Young's modulus and Poisson's ratio, and crystals of lower symmetry may possess many more, 21 in all. We are therefore led to re-formulate the calculations, to include the symmetry of the crystal structure and the general mechanical and perhaps electrical stresses to which a rigid body can be subjected.*

We start by specifying more closely than in § 4·4 the basic cell, by repetitions of which the crystal is constructed. The cell is of course not unique, but we suppose a definite choice has been made. The cell is then a definite parallelopiped whose three concurrent edges are specified by the vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. The volume of this cell is

$$\Delta = \delta^3 = \begin{vmatrix} a_{1x} & a_{1y} & a_{1z} \\ a_{2x} & a_{2y} & a_{2z} \\ a_{3x} & a_{3y} & a_{3z} \end{vmatrix}, \qquad \ldots\ldots(251)$$

and δ is called the lattice constant. Choosing any origin O in the basic cell, let $\mathbf{r}$ be the vector from O to any other point, usually to one of the other atoms in the same cell. Then the vector distance from O to the congruent points in the other cells is written

$$\mathbf{r} + \mathbf{r}^l, \quad \mathbf{r}^l = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3, \qquad \ldots\ldots(252)$$

where l_1, l_2, l_3 are any integers positive, zero or negative. They are contracted to l and called the "cell-index".

The positions of the atoms or other units requiring separate consideration in the basic cell are denoted by the vectors from O,

$$\mathbf{r}_k \quad (k = 1, 2, \ldots, s). \qquad \ldots\ldots(253)$$

Any atom of the lattice is at a point specified by $\mathbf{r}_k{}^l$, where

$$\mathbf{r}_k{}^l = \mathbf{r}_k + \mathbf{r}^l. \qquad \ldots\ldots(254)$$

The vector distance between any two atoms of the lattice is

$$\mathbf{r}_k{}^l - \mathbf{r}_{k'}{}^{l'} = \mathbf{r}_k - \mathbf{r}_{k'} + \mathbf{r}^{(l-l')} = \mathbf{r}_{k,k'}{}^{(l-l')}. \qquad \ldots\ldots(255)$$

§ 4·91. *Crystal statics, or energies without heat motions.* We will next consider the form of the potential energy function when the atoms are at rest in their mean positions and act on one another with radial forces of

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* My knowledge of the atomic theory of crystals is derived almost entirely from Born, *Problems of Atomic Dynamics*, Cambridge, Mass. (1926), and "Atomtheorie des festen Zustandes", *loc. cit.*, *q.v.* The simple account, which I have tried to give here, not unnaturally follows Born's lectures closely.

potential energy $\phi_{k,k'}(r)$ for the pair of atoms of type k and k' at a distance r apart.

We require of course the potential energy per unit cell, which may be taken to be the basic cell, and have therefore to calculate the potential energy of each of the k units in this cell in the field of all the other units in the crystal, which is regarded as infinite in extent. We then obtain the total energy of the crystal, omitting surface effects, by summing these potential energies over the k units of the cell and multiplying by $\frac{1}{2}N$, where N is the number of cells in the actual crystal. Every term would be counted twice over by this summation, hence the factor $\frac{1}{2}$. We shall continue to call the total potential energy of the actual crystal F_0, and have therefore

$$F_0 = \tfrac{1}{2} N \Sigma_k \Sigma_{l,k'} \phi_{k,k'}(r^l_{k,k'}). \qquad \text{......(256)}$$

It is commonly convenient to use a different notation for the l and k summations, calling them S_l and Σ_k. We have therefore

$$F_0 = \tfrac{1}{2} N S_l \Sigma_{k,k'} \phi_{k,k'}(r^l_{k,k'}). \qquad \text{......(257)}$$

In (257) the summation S_l runs from $-\infty$ to $+\infty$ in each of the three indices and the summation $\Sigma_{k,k'}$ twice over the s units of the basic cell. All terms for which $r = 0$, that is, $k = k'$, $l = 0$, are omitted.

Methods of evaluating these sums in terms of given atomic forces for the simpler cases are sketched in Chapter x, and we shall not consider them further here.

We should observe in passing that the form chosen for the unit of summation as a term depending on two atoms only is by no means general. More general forms are to be expected and are required to account for the more intimate properties of crystals. For example, if we have in the basic cell three non-collinear ions 1, 2, 3 with appreciably polarizable electronic structures, their mutual potential energy can be reduced to the form

$$\phi_{123}(\mathbf{r}_{12}, \mathbf{r}_{23}, \mathbf{r}_{31}),$$

at least approximately, but is *not* expressible in the form

$$\phi_{12}(r_{12}) + \phi_{23}(r_{23}) + \phi_{31}(r_{31}),$$

which is the form assumed in (257). Summations more complicated than (257) are then required, which we shall not formulate here.

Let us now consider the requirements of the equilibrium state. If we suppose that the vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{r}_1, \ldots, \mathbf{r}_s$ as specified refer to the equilibrium state with all units at rest in their mean positions, then the first order variations of F_0 must vanish for any small variations in position of any one (or more) of the constituents. Since all the cells are the same these conditions of course are not all independent, and it is easy to see that the independent conditions reduce to those in which every cell is submitted to the same variations. Such variations may be called *homogeneous displacements* and are of special importance.

Let us now pause a moment to consider the complete specification of the geometrical variables which describe the crystal, and which are entitled to enter into thermodynamical or statistical equations. It is no longer possible conveniently to use the actual volume; again, the displacements from the equilibrium state with the atoms at rest and undisturbed by external fields of force are practically always small in an actual crystal. It is therefore convenient to take as standard the undisturbed state of rest, and to refer all other states to that state. In any other actual state of the crystal (preserving the lattice repetition) the mean positions of the structural units can be just specified exactly by specifying the general homogeneous displacement which transforms the standard state to the required state, and this disturbance may usually be regarded as small. When external forces are acting, mechanical or electrical, they must therefore be supposed to be uniform over the extent of the crystal. Since the actual space variation of external fields is very small on the molecular scale this apparent restriction is a trivial one.

The general homogeneous displacements, which we are thus led to regard as a suitable geometrical specification of the crystal, contain terms for the displacement of one set of atoms relative to another which are at first sight not accessible to direct observation and control for the crystal in bulk and so not permissible statistical variables. Ideally, however, one can regard these displacements as directly measurable by X-ray methods, which can already place all the atoms in the basic cell at least in simpler cases. Moreover, in ionic lattices some at least of these displacements can be varied independently by external electrostatic forces. They cannot therefore all be ignored, and it seems a legitimate generalization to include them all in the statistical description of the crystal. As we shall see, they can be eliminated later from the partition function by the usual thermodynamic process as soon as it is desired to do so.

Disturbances of the crystal other than homogeneous only enter with its thermal motion.

The general homogeneous displacement consists of small vector changes in $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{r}_1, \ldots, \mathbf{r}_s$, the lattice being rebuilt out of the cells so altered. In greater detail we write these changes as follows, where bars denote the new values. For the components of $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$

$$\overline{a_{t,x}} = a_{t,x} + \Sigma_y\, u_{x,y}\, a_{t,y} \quad (t = 1, 2, 3); \qquad \ldots\ldots(258)$$

for the components of $\mathbf{r}_k$

$$\overline{x_k} = x_k + u_{k,x} + \Sigma_y u_{x,y} y_k \quad (k = 1, \ldots, s). \qquad \ldots\ldots(259)$$

The displacements then consist of a homogeneous strain of the whole of each cell defined by the tensor $u_{x,y}$, and then a displacement of the s

elements of each cell by the vector $\mathbf{u}_k$. To exclude a rotation of the lattice as a whole as a rigid body the tensor $u_{x,y}$ must be symmetrical or

$$u_{x,y} = u_{y,x} \quad (all\ x, y), \qquad \ldots\ldots(260)$$

and to exclude a translation of the lattice as a whole as a rigid body the sum of the s displacement vectors must vanish or

$$\Sigma_k u_{k,x} = 0 \quad (all\ x). \qquad \ldots\ldots(261)$$

Let us now suppose that we can compute the value of F_0 given by (257) under this homogeneous displacement, retaining terms in the displacements up to the second order. Then

$$\overline{F_0} = F_0 + \Sigma_{k,x}\left(\frac{\partial \overline{F_0}}{\partial u_{k,x}}\right)_0 u_{k,x} + \Sigma_{x,y}\left(\frac{\partial \overline{F_0}}{\partial u_{x,y}}\right)_0 u_{x,y} + \frac{1}{2}\left\{\Sigma_{k,x}\Sigma_{k',y}\frac{\partial^2 \overline{F_0}}{\partial u_{k,x}\partial u_{k',y}} u_{k,x}u_{k',y}\right.$$

$$\left. + 2\Sigma_{k,x}\Sigma_{y,z}\frac{\partial^2 \overline{F_0}}{\partial u_{k,x}\partial u_{y,z}} u_{k,x}u_{y,z} + \Sigma_{y,z}\Sigma_{y',z'}\frac{\partial^2 \overline{F_0}}{\partial u_{y,z}\partial u_{y',z'}} u_{y,z}u_{y',z'}\right\},$$

$$= F_0 + F_1 + F_2. \qquad \ldots\ldots(262)$$

By the conditions of equilibrium in the specified standard state

$$\left(\frac{\partial \overline{F_0}}{\partial u_{k,x}}\right)_0 = 0, \quad \left(\frac{\partial \overline{F_0}}{\partial u_{x,y}}\right)_0 = 0. \qquad \ldots\ldots(263)$$

These equations are not all independent, for the change of potential energy must vanish identically when the crystal is moved as a whole or rotated as a whole in the absence of external forces. Thus

$$\Sigma_k\left(\frac{\partial \overline{F_0}}{\partial u_{k,x}}\right)_0 \equiv 0, \qquad \ldots\ldots(264)$$

and since in a pure rotation $u_{x,y} + u_{y,x} = 0$, etc.,

$$\left(\frac{\partial \overline{F_0}}{\partial u_{y,z}}\right)_0 \equiv \left(\frac{\partial \overline{F_0}}{\partial u_{z,y}}\right)_0. \qquad \ldots\ldots(265)$$

The independent conditions (263) thus reduce to $3s + 3$, which is the same as the number of independent displacements ($u_{x,y}$, $u_{k,x}$) subject to (260) and (261), and therefore just suffice to fix the standard equilibrium state. The numbers of independent variables and equations can of course be reduced by the crystal symmetry, but are reduced equally.

Suppose now that the crystal is again held in equilibrium but not in its standard state. This is possible if external mechanical or electrical forces exist, acting selectively on the different units of the crystal cell. We have then to consider a crystal element in a resultant state of homogeneous displacement. The selective forces on particular sets of atoms may naturally be thought of as being applied as body forces acting uniformly through the body of the crystal, but the ordinary mechanical stress tensor which primarily deforms the cell is in actual practice applied to the surface of the crystal. One may think at first sight that in a scheme which omits surface effects these surface applied stresses cannot be included, but this difficulty is only apparent. We find the same apparent difficulty in discussing imperfect gases in Chapters VIII and IX, which is considered in detail in § 5·71. We shall not go into details here, but by similar arguments the surface applied stresses can be seen to be transmitted uniformly through the solid by considering the actions across suitable sets of geometrical interfaces inside it, so that effectively the cells of the crystal are subjected to uniform body forces. In any such case of non-standard equilibrium under uniform homogeneous displacements we have therefore

$$(K_{x,y})_0 = -\frac{\partial \overline{F_0}}{\partial u_{x,y}}, \qquad \text{......(266)}$$

$$(K_{k,x})_0 = -\frac{\partial \overline{F_0}}{\partial u_{k,x}}, \qquad \text{......(267)}$$

where the functions so defined, vanishing in the standard state, are the external stress tensor and the s external selective force vectors respectively. This identification follows at once from the requirements of the conservation of energy.

§ **4·92**. *Crystals with thermal agitation.* It is now possible to superpose on the distorted crystal the usual general thermal agitation, and so to construct its partition function. Into the details of this calculation we need not go. It requires calculations of $\overline{F_0}$ to the third order in the displacements in order to get the frequency spectrum of the crystal correct to the first order terms in the homogeneous displacements. The calculations are complicated, but can be carried through. With approximations of the same type as before we arrive at

$$\log K(z) = (F_0 + F_2)\log z - \frac{3N}{(\log 1/z)^3}\sum_{j=1}^{3}\frac{1}{k^3\Theta_j{}^{*3}}\int_0^{k\Theta_j{}^*\log 1/z}\log(1-e^{-x})\,x^2dx$$
$$- N\sum_{j=4}^{3s}\log(1-z^{h\nu_j{}^*}), \qquad \text{......(268)}$$

corresponding to (216), but now $\Theta_j{}^*$ and $\nu_j{}^*$ refer to the displaced lattice. If we anticipate Chapter VI as before and write (268) in terms of T, like (218), we have

$$\log K(T) = -\frac{F_0 + F_2}{kT} - 3N\sum_{j=1}^{3}\frac{T^3}{\Theta_j{}^{*3}}\int_0^{\Theta_j{}^*/T}\log(1-e^{-x})\,x^2dx$$
$$- N\sum_{j=4}^{3s}\log(1-e^{-\Theta_j{}^*/T}), \qquad \text{......(269)}$$

where $$\Theta_j{}^* = \Theta_j\{1 - \Sigma_{k,x}B^j{}_{k,x}\,u_{k,x} - \Sigma_{x,y}B^j{}_{x,y}\,u_{x,y}\}. \qquad \text{......(270)}$$

Strictly speaking, the averaging for direction of equation (214) must be carried out remembering that $B^j{}_{k,x}$ and $B^j{}_{x,y}$ $(j = 1, 2, 3)$ are functions of direction. This will be indicated in the equations that follow.

The analysis is of course only carried through for small displacements, so that only the first order terms arising from the changes in the Θ's can be retained. When we expand (269) in powers of $u_{k,x}$ and $u_{x,y}$ and indicate the hitherto ignored directional averaging, the result can easily be reduced to the form

$$\log K\,(T) = -\frac{F_0+F_2}{kT} - 3N\sum_{j=1}^{3}\frac{T^3}{\Theta_j{}^3}\int_0^{\Theta_j/T}\log\,(1-e^{-x})\,x^2dx$$
$$-N\sum_{j=4}^{3s}\log\,(1-e^{-\Theta_j/T}) + \frac{1}{kT}\{\Sigma_{k,x}\,\mathbf{K}^{\circ}{}_{k,x}\,u_{k,x} + \Sigma_{x,y}\,\mathbf{K}^{\circ}{}_{x,y}\,u_{x,y}\}, \qquad \ldots\ldots(271)$$

where, the bars denoting averaging for direction,

$$\mathbf{K}^{\circ}{}_{k,x} = NkT\left\{3\sum_{j=1}^{3}\overline{B^j{}_{k,x}\frac{T^3}{\Theta_j{}^3}\int_0^{\Theta_j/T}\frac{x^3dx}{e^x-1}} + \sum_{j=4}^{3s}\overline{B^j{}_{k,x}\frac{\Theta_j/T}{e^{\Theta_j/T}-1}}\right\}, \qquad \ldots\ldots(272)$$

$$\mathbf{K}^{\circ}{}_{x,y} = NkT\left\{3\sum_{j=1}^{3}\overline{B^j{}_{x,y}\frac{T^3}{\Theta_j{}^3}\int_0^{\Theta_j/T}\frac{x^3dx}{e^x-1}} + \sum_{j=4}^{3s}\overline{B^j{}_{x,y}\frac{\Theta_j/T}{e^{\Theta_j/T}-1}}\right\}. \qquad \ldots\ldots(273)$$

To the specified order of accuracy this is the complete partition function, replacing (218), and depending on all the geometrical parameters $u_{k,x}$ and $u_{x,y}$ instead of only on V. The temperature dependent terms have only been given to a first approximation in these parameters.

§ **4·93**. *General applications*. By the general formula (122), which applies to the assembly we are here considering, we have in terms of T

$$\overline{K_{x,y}} = kT\frac{\partial}{\partial u_{x,y}}\log K\,(T), \qquad \ldots\ldots(274)$$

$$\overline{K_{k,x}} = kT\frac{\partial}{\partial u_{k,x}}\log K\,(T). \qquad \ldots\ldots(275)$$

These are the average reactions of the specified types which the assembly exerts on the outside world, or the forces exerted by the surroundings reversed in sign, so that the external work done by the crystal in any specified displacement at the given temperature is

$$\Sigma_{x,y}\overline{K_{x,y}}\,\delta u_{x,y} + \Sigma_{k,x}\overline{K_{k,x}}\,\delta u_{k,x}. \qquad \ldots\ldots(276)$$

The average energy $\overline{E_K}$ is given as before by

$$\overline{E_K} = kT^2\frac{\partial}{\partial T}\log K\,(T). \qquad \ldots\ldots(277)$$

The forms of the average reactions are found on combining (266), (267), (274) and (275) to be

$$\overline{K_{x,y}} = \mathbf{K}^{\circ}{}_{x,y} - \frac{\partial F_2}{\partial u_{x,y}}, \qquad \ldots\ldots(278)$$

$$\overline{K_{k,x}} = \mathbf{K}^{\circ}{}_{k,x} - \frac{\partial F_2}{\partial u_{k,x}}. \qquad \ldots\ldots(279)$$

Anticipating the results of Chapter VI we may of course apply all the processes of thermodynamics to our crystal. In particular we can evaluate the displacements $u_{k,x}$ and construct a new function of the other variables and $\overline{K_{k,x}}$ instead of the $u_{k,x}$ which has similar properties. This is a process of practical importance because all observable properties of a crystal are properties which it possesses for given values of the external forces $\overline{K_{k,x}}$ and not for given values of the displacements $u_{k,x}$. As appears in Chapter VI $k \log K(T)$ for the crystal is the thermodynamic function known as Planck's characteristic function, and $-kT \log K(T)$ is the more usual *work function*† A. The function we require here is

$$A^* = A + \Sigma_{k,x} \overline{K_{k,x}} u_{k,x}, \qquad \text{......(280)}$$

expressed as a function of T, $u_{x,y}$ and $\overline{K_{k,x}}$ after eliminating the $u_{k,x}$ from (280) by means of (279). It is as it were a partial transformation from the work function to the free energy. By the formation of the usual total variation we see that

$$u_{k,x} = \frac{\partial A^*}{\partial \overline{K_{k,x}}}. \qquad \text{......(281)}$$

We have still to define the strength of the electric doublet **p** induced in the crystal by the displacements of type $u_{k,x}$, whether they are due to external electric fields, to thermal agitation or to the other displacements $u_{x,y}$. We have at once

$$p_x = N \Sigma_k \epsilon_k u_{k,x}, \qquad \text{......(282)}$$

where ϵ_k is the charge on the kth unit of the basic cell. If an external electric field of components $\mathbf{E}_x$, $\mathbf{E}_y$, $\mathbf{E}_z$ is acting, the forces $\overline{K_{k,x}}$ are given by the equations

$$\overline{K_{k,x}} = -N\epsilon_k \mathbf{E}_x. \qquad \text{......(283)}$$

The $u_{k,x}$ may be supposed eliminated from (282) also, with the help of (279).

We cannot pursue the theory of crystal structure in detail any further, but must content ourselves with general remarks. The general equilibrium properties of crystals and their relationships may be illustrated by the following diagram.‡

The formal equations connecting these quantities can all be derived from the functions A or A^*, and can therefore be evaluated for given crystal structure and given atomic models by carrying through the calculations which we have indicated here. For example, the pyro-electric effect is a change of dipole strength in the crystal caused by heating it, and is of course coupled with the corresponding inverse electrocaloric effect which is a change of temperature following on the application of an external

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† This function is sometimes called the *free energy*, but not with strict accuracy, and it is well to distinguish it systematically from $F = A + pv$, the true free energy.

‡ Given by Born, *loc. cit.* after Heckmann.

electric field. The pyro-electric effect appears of course as the production of equal and opposite surface charges on opposite faces of the crystal. The best known example is tourmaline in which the charges separate along the trigonal axis. This effect can be calculated by evaluating p_x, p_y, p_z for zero external stress tensor and zero electric field. The pyro-electric moment so calculated corresponds to that observed, but it is not what may be called the *true pyro-electric moment* which would naturally be that for zero external electric field and zero displacements $u_{x,y}$. The actual displacements $u_{x,y}$ for zero stress tensor themselves involve non-zero values of $u_{k,x}$ (independently of the direct temperature effect), and so produce a piezo-electric moment which is superposed on the true pyro-electric moment to give the observed value.

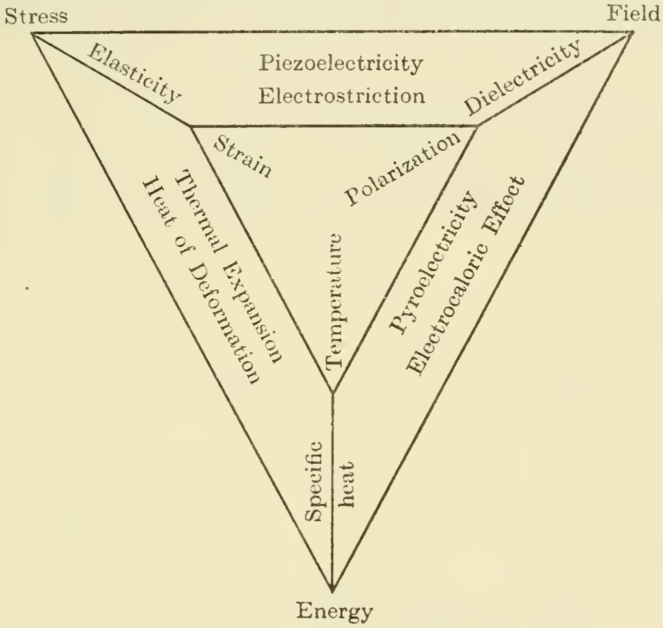

Fig. 8. The equilibrium properties of crystals.

The point of chief interest to statistical theory is the dependence of all these parameters on the temperature. It is not difficult to see that the interconnections between the pyro-electric moment, the thermal expansions and the temperature are fixed by the coefficients $B^j{}_{k,x}$ and $B^j{}_{x,y}$ of equations (272) and (273). At low temperatures only the Debye-terms, $j = 1, 2, 3$, are important, and we find in addition to (226) for the energy, the relations

$$\text{Thermal expansions} \propto T^4. \qquad \text{......(284)}$$

$$p_x, p_y, p_z \propto T^4. \qquad \text{......(285)}$$

The proportionality between the excess energy content over the zero point energy and the thermal expansions is in agreement with observation, and represents a law formulated on empirical grounds by Gruneisen, but the proportionality with the pyro-electric moment is not in agreement with observation. The observations suggest that p_x tends to zero rather like T or T^2. The explanation is still uncertain, but it is probably connected with certain other phenomena in crystals of low symmetry to which we shall now refer on account of their striking character.

§ **4·94**. *Some properties of strongly anisotropic crystals.* The investigations of Gruneisen and Goens* on single crystals of zinc and cadmium have shown that these hexagonal crystals are very strongly anisotropic,

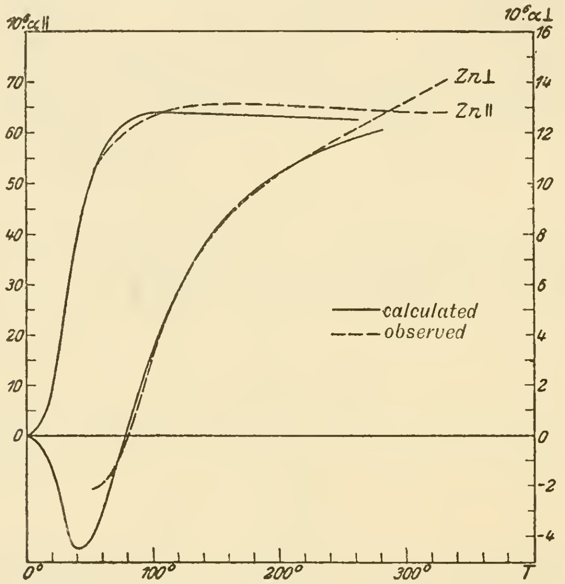

Fig. 9. The coefficients of thermal expansion $\alpha_{||}$ and $\alpha_{\perp}$ of zinc crystals along and across the hexagonal axis.

all their properties being markedly different along and across the hexagonal axis. In particular the frequencies of elastic vibration are very different in these directions. On following through the calculations for the coefficients of thermal expansion it is found that

$$\alpha_{||} = \gamma_{11} p_{||} + \gamma_{12} p_{\perp}, \qquad \text{......(286)}$$

$$\alpha_{\perp} = \gamma_{21} p_{||} + \gamma_{22} p_{\perp}, \qquad \text{......(287)}$$

where

$$p_{||} = f_1(T),\ p_{\perp} = f_2(T), \qquad \text{......(288)}$$

$$\gamma_{12} = \gamma_{21} < 0. \qquad \text{......(289)}$$

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* Gruneisen and Goens, *Zeit. für Phys.* vol. xxvi, pp. 235, 250 (1924), vol. xxix, p. 141 (1924), vol. xxxvii, p. 278 (1926).

To a first approximation f_1 and f_2 are of Debye's type, but with very different Θ's. The γ's are elastic moduli, so that the p's are of the nature of "thermal pressures". The Θ's are as usual fixed by the elastic constants and serve to determine successfully the specific heats.

The interesting special property of these crystals is that they show for certain temperatures a *negative* value of $\alpha_{\perp}$, that is a contraction across the hexagonal axis on heating. But this follows from the theory, for owing to the great difference in the Θ's f_1 at low temperatures has a sensible value while f_2 is still negligible. At higher temperatures both $\alpha_{||}$ and $\alpha_{\perp}$ become positive, for the functions f_1 and f_2 become comparable and $\gamma_{22} > | \gamma_{12} |$. The observations and theoretical calculations for zinc are shown in Fig. 9 and are in remarkable agreement.

In view of this result it seems possible that the observed variation of pyro-electric moment, which does not obey the T^4-law, arises from a combination of several rather different functions of the temperature which partly balance each other. The crystals concerned in pyro-electric effects are in general strongly anisotropic.

CHAPTER V

THE GENERAL ASSEMBLY. DISSOCIATION AND EVAPORATION

§ 5·1. *Introductory.* We now pass on to the general assembly in which gaseous atoms and molecules combine and dissociate, or evaporate from and recondense on crystals. Generally speaking we may say that we are now to investigate the equilibrium state of an assembly of practically independent systems, which no longer retain their individualities throughout the motion of the assembly, but are able to break up and recombine in such a way as to form any specified number of different types of independent systems. It will obviously be important to specify what we regard as the ultimate structural elements of the assembly—the indivisible systems which can combine, but never break up further. The formal exposition will be the same whatever the ultimate units are assumed to be, but the physical interpretation will be different. In the initial exposition we shall for definiteness suppose that the ultimate units are the atoms of chemistry. At a later stage the same formulae will be reinterpreted in terms of positive nuclei and electrons in the study of the properties of matter at very high temperatures. This interpretation is obviously the more fundamental. There are naturally outstanding difficulties in the picture of molecules built up from structureless atoms, which disappear when the electronic structure of the molecules is considered. We have already had an example (H_2) in § 3·4. This later interpretation will of course include the former as a special case, but in practice the two fields hardly overlap. In any assembly hot enough to contain an appreciable equilibrium concentration of atomic ions and free electrons, the number of molecular species effectively present will be found to be always very small and generally zero.

Recent discussion of the problems of dissociation from the standpoint of pure statistical mechanics adopted in this monograph has all been based on the work of Ehrenfest and Trkal*. These authors only discuss the dissociation problem on semi-classical lines; they assume, that is, that all degrees of freedom of a system are either "fully excited" so that the classical theory is adequate or "completely unexcited", in which case they may be ignored. This restriction is here removed so that the discussion is perfectly general, and subject only in its range of applicability to restrictions of a physical nature inherent in the problem. Actual matter (for example, imperfect gases) will not always be comparable to an assembly analysed

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* Ehrenfest and Trkal, *Proc. Sect. Sci. Amsterdam*, vol. XXIII, p. 162 (1920). I do not know o any earlier discussion of dissociation or the kindred matters of chemical constants, "thermodynamic probability" and absolute entropy on the hypotheses of Chapter I which can be regarded as logically convincing.

into practically independent systems. We shall make a first attempt in a later chapter towards the removal of this particular restriction.

For simplicity of exposition we begin by considering a gaseous assembly in which a single reaction $A^1 + A^2 \rightleftarrows A^1A^2$ can occur. This serves to bring out the essential points at which the analysis of Chapter II must be extended to take account of such reactions. We find that the expressions we require are still coefficients in certain expansions in multiple power series as in § 2·4; to sum them it is only necessary to use the exponential theorem instead of the multinomial theorem used there. The required coefficients can then be picked out by a multiple complex integral which can be evaluated by steepest descents. The new selector variables, over and above z, have their proper physical interpretation. Just as z corresponds to the temperature, so the new variables, one for each type of atom (or other structural unit) in the assembly, correspond to the partial potentials of thermodynamic theory.

After discussion of the simple case mentioned we give the analysis for the general gaseous assembly, and then the extension to assemblies containing crystals or other condensed systems for which we can construct partition functions. We include some simple examples of the interpretation of our formulae in terms of atoms, molecules and chemical reactions, but the main discussion of the results can only be profitably taken up after we have discussed the relationship between the equilibrium theory of statistical mechanics and the laws of thermodynamics.

§ 5·2. *The number of "examples" of a dissociating assembly, the number of weighted complexions of an example, and the total number of weighted complexions.* In conformity with our general principles we are to determine the equilibrium state of the assembly by averaging over all elements of the phase space, or all complexions representing possible states of the assembly. Let us denote by an *example* of the assembly that collection of states in which all the systems of the assembly retain their individualities. An example of the assembly is then exactly equivalent to an assembly in which no dissociation or recombination is going on, so that the numbers of each species present, and the particular atoms constituting each molecule, remain permanently fixed. The number of weighted complexions of any example of an assembly can therefore be directly calculated by the methods of Chapter II. The new feature in the enumeration of the total number of weighted complexions for a dissociating assembly consists solely in the enumeration of the number of examples.

In the simple case in which there are present in all X_1 atoms A^1 and X_2 atoms A^2 we may classify the examples of the assembly into *groups*, which are characterized by the specification of the numbers of free atoms and molecules which the assembly then possesses. For example, we may here specify a group of examples by the specification that there shall be M_1 free atoms A^1, M_2 free atoms A^2, and N molecules A^1A^2, these numbers being subject of course to the conditions

$$M_1 + N = X_1, \quad M_2 + N = X_2. \qquad \text{......(290)}$$

Each member of the group will be represented by the same number of weighted complexions calculated as in Chapter II. To determine the number of examples in the group we observe that every possible distribution of the X_1 atoms A^1 among the M_1 free atoms and N molecules is possible, and similarly for the X_2 atoms A^2. The total number of ways in which the atoms can be permuted is of course

$$X_1!\,X_2!,$$

but this counts separately permutations of the same M_1 free atoms A^1, M_2 free atoms A^2, and N molecules A^1A^2 among themselves. Such permutations do not correspond to separate examples of the assembly, for they are included in the count of weighted complexions for any one example. The count of the complexions for an example takes full account of all the possible positional interchanges of the systems of any species among themselves, for these interchanges are effected by the free motion of the one example *since all our systems are here atoms and molecules in a gaseous phase.* To avoid this reduplication we have therefore to divide by $M_1!\,M_2!\,N!$, so that the number of examples in the group is reduced to

$$\frac{X_1!\,X_2!}{M_1!\,M_2!\,N!}.$$

This however is not necessarily all. It may happen that certain rotations of the molecules as a whole will also be equivalent to a permutation of the constituent atoms of each type. In general, let there be σ different orientations of each of the N molecules which are equivalent to such a simple permutation. This will be called the *symmetry number* of the molecule. These interchanges, σ^N in all, will again be taken full account of by the count of weighted complexions for any one example, so that the number of independent examples in the group is finally reduced to

$$\frac{X_1!\,X_2!}{M_1!\,M_2!\,N!\,\sigma^N}. \qquad \text{......(291)}$$

In the special case under immediate consideration $\sigma = 1$.

The foregoing arguments are quite general. If there are in all $X_1, X_2, \ldots$ atoms $A^1, A^2, \ldots$ or other ultimate structural units, $M_1, M_2, \ldots$ free atoms $A^1, A^2, \ldots$ and $N_1, N_2, \ldots$ molecules of various types, with symmetry numbers $\sigma_1, \sigma_2, \ldots$, then the number of independent examples in a group will be

$$\frac{X_1!\,X_2!\ldots}{M_1!\,M_2!\ldots N_1!\,N_2!\ldots\sigma_1^{N_1}\sigma_2^{N_2}\ldots}. \qquad \text{......(292)}$$

An alternative presentation of this important point may be of value. During the natural motion of any example the centres of gravity of the M_1 free atoms A^1, the M_2 free atoms A^2 and N molecules A^1A^2 may interchange their M_1, M_2, N positions respectively, and each of the N molecules can independently assume any one of σ orientations. Each of the resulting changes, $M_1 !\, M_2 !\, N !\, \sigma^N$ in number, is a permutation. No one of these permutations must be allowed to count as a new example.*

Having enumerated the number of examples in a group the final count of the total number of weighted complexions is a simple matter. If c is the number of weighted complexions corresponding to a single example, then the number corresponding to the group in the simple case is

$$\frac{X_1 !\, X_2 !\, c}{M_1 !\, M_2 !\, N !\, \sigma^N}. \qquad \text{......(293)}$$

The total number will then be obtained by summing (293) over all possible values of M_1, M_2 and N—that is, all positive values subject to (290). There will be similar formulae in the general case.

Following Chapter II we suppose that the partition functions for the free atoms A^1 and A^2 are $f_1(z)$, $f_2(z)$, where

$$f_1(z) = \Sigma_u \varpi_u{}^1 z^{\epsilon_u{}^1}, \quad f_2(z) = \Sigma_u \varpi_u{}^2 z^{\epsilon_u{}^2}, \qquad \text{......(294)}$$

and for the molecules A^1A^2, $g(z)$, where

$$g(z) = \Sigma_v \rho_v z^{\eta_v}. \qquad \text{......(295)}$$

We shall suppose, further, that the statistical state of any example is specified by assigning the numbers $a_1{}^1, a_2{}^1, \ldots, a_u{}^1, \ldots, a_1{}^2, a_2{}^2, \ldots, a_u{}^2, \ldots,$ $b_1, b_2, \ldots, b_v, \ldots$ of atoms and molecules respectively to their various cells or quantum states. We may suppose for convenience that $g(z)$ is so specified that it includes both (classical) kinetic energy of translation and (quantized) internal and rotational energy. It is then actually the product of two separate partition functions.

In constructing these partition functions it is necessary to specify precisely a standard state of the assembly to which we assign by convention zero energy, and to measure all energies consistently relative to this state. In all cases of gaseous dissociation the most convenient state of zero energy to assume is that state in which all the molecules are dissociated, so that the assembly consists entirely of free atoms, at rest, sufficiently far apart to be entirely outside each other's fields of force.† On this convention the assembly can in certain states possess a negative energy, but of course there is no objection to this. If, then, in any state E is the total energy of

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* See for all this enumeration Ehrenfest and Trkal, *loc. cit.* p. 169. The corresponding formulation according to the new mechanics, which is, I think, completely satisfactory, and simpler than that of the classical theory, is given in Chapter XXI.

† This specification is that already used in § 4·5.

the assembly, it must be specified relative to this zero, and so must all the ϵ's and η's. For example, if χ is the heat of dissociation per molecule at the absolute zero—that is, the work required to separate a molecule at rest in its lowest permissible quantum state of vibration and rotation into two free atoms at rest—then the energy to be associated with this state of the molecule is $-\chi$, or, say, $\eta_1 = -\chi$.

It is necessary to go back to our original enumeration of the weighted complexions representing any specified statistical state of the assembly —here, of an example of the assembly. We found in § 2·6 that this number c was given by

$$c = \frac{M_1 !\, M_2 !\, N !\, (\varpi_1^1)^{a_1^1} \dots (\varpi_1^2)^{a_1^2} \dots (\rho_1)^{b_1} \dots}{a_1^1 ! \dots a_1^2 ! \dots b_1 ! \dots}. \qquad \text{......(296)}$$

This was eventually to be summed over all positive a's and b's subject to

$$\Sigma_u a_u^1 = M_1,\ \Sigma_u a_u^2 = M_2,\ \Sigma_v b_v = N, \qquad \text{......(297)}$$

$$\Sigma_u a_u^1 \epsilon_u^1 + \Sigma_u a_u^2 \epsilon_u^2 + \Sigma_v b_v \eta_v = E. \qquad \text{......(298)}$$

In view of (293) and (290) we here obtain a number of weighted complexions for each group of examples equal to

$$\frac{X_1 !\, X_2 !\, (\varpi_1^1)^{a_1^1} \dots (\varpi_1^2)^{a_1^2} \dots (\rho_1/\sigma)^{b_1} \dots}{a_1^1 ! \dots a_1^2 ! \dots b_1 ! \dots}; \qquad \text{......(299)}$$

in (299) each ρ_v can be taken to occur divided by σ, since $\Sigma_v b_v = N$. The expression (296) has here to be summed over all positive a's and b's subject to (297) and (298), and then over all positive M's and N's subject to (290). This is equivalent to summation of (299) over all positive a's and b's such that

$$\Sigma_u a_u^1 + \Sigma_v b_v = X_1, \qquad \text{......(300)}$$

$$\Sigma_u a_u^2 + \Sigma_v b_v = X_2, \qquad \text{......(301)}$$

$$\Sigma_u a_u^1 \epsilon_u^1 + \Sigma_u a_u^2 \epsilon_u^2 + \Sigma_v b_v \eta_v = E. \qquad \text{......(302)}$$

In view of the fact that the molecular weights ρ_v always occur divided by the symmetry number in the form ρ_v/σ, it is usually convenient, as we stated in § 2·2, to regard σ as absorbed into ρ_v, and to use always these prepared weights for the molecules. We shall in future suppose that this has been done.

The construction of integrals for C and $C\overline{P}$ proceeds here from (299) subject to (300)–(302) instead of (as in Chapter II) from (296) subject to (297) and (298). There will be similar formulae in the general case.

§ 5·3. *A gaseous assembly with two types of atom and one possible reaction.* We will now complete the analysis for the simple case, determining the equilibrium properties of the assembly. To conform to equations (300)–(302)

we introduce three selector variables x_1, x_2, z, and construct the multiple series

$$X_1\,!\,X_2\,!\,\Sigma_{a,b}\,\frac{(\varpi_1{}^1 x_1 z^{\epsilon_1{}^1})^{a_1{}^1}\ldots(\varpi_1{}^2 x_2 z^{\epsilon_1{}^2})^{a_1{}^2}\ldots(\rho_1 x_1 x_2 z^{\eta_1})^{b_1}\ldots}{a_1{}^1\,!\ldots a_1{}^2\,!\ldots b_1\,!\ldots}, \quad\ldots\ldots(303)$$

summed over all positive values of the a's and b's. Its sum is obviously

$$X_1\,!\,X_2\,!\exp\{x_1 f_1(z)+x_2 f_2(z)+x_1 x_2 g(z)\}. \quad\ldots\ldots(304)$$

It is evident that the total number of weighted complexions C, that is the sum (299) subject to (300)–(302), is the coefficient of $x_1{}^{X_1}x_2{}^{X_2}z^E$ in (304). This can be expressed as the triple complex integral

$$C=\frac{X_1\,!\,X_2\,!}{(2\pi i)^3}\iiint\frac{dx_1\,dx_2\,dz}{x_1{}^{X_1+1}x_2{}^{X_2+1}z^{E+1}}\exp\{x_1 f_1(z)+x_2 f_2(z)+x_1 x_2 g(z)\}. \quad\ldots\ldots(305)$$

The integral for each variable is taken round a circle in its own plane, with its centre at the origin. In the z-plane $|z|<1$, but $|x_1|$ and $|x_2|$ need not be restricted.

We must next construct similar integrals for quantities such as $C\overline{a_u{}^1}$. For this purpose we have to sum (299) with an extra factor $a_u{}^1$ under the sign of summation. Each term in (299) or (303) so modified can be obtained from the unmodified term by the operation $\varpi_u{}^1\partial/\partial\varpi_u{}^1$. Therefore

$$C\overline{a_u{}^1}=\varpi_u{}^1\frac{\partial C}{\partial\varpi_u{}^1}.$$

In (305) $\varpi_u{}^1$ occurs only in $f_1(z)$ and

$$\varpi_u{}^1\frac{\partial f_1}{\partial\varpi_u{}^1}=\varpi_u{}^1 z^{\epsilon_u{}^1}.$$

Therefore

$$C\overline{a_u{}^1}=\frac{X_1\,!\,X_2\,!}{(2\pi i)^3}\iiint\frac{dx_1\,dx_2\,dz}{x_1{}^{X_1+1}x_2{}^{X_2+1}z^{E+1}}(\varpi_u{}^1 x_1 z^{\epsilon_u{}^1})\exp\{x_1 f_1(z)+x_2 f_2(z)+x_1 x_2 g(z)\}. \quad\ldots\ldots(306)$$

Similarly,
$$C\overline{M_1}=C\Sigma\overline{a_u{}^1}=\Sigma_u\varpi_u{}^1\frac{\partial C}{\partial\varpi_u{}^1} \quad\ldots\ldots(307)$$

$$=\frac{X_1\,!\,X_2\,!}{(2\pi i)^3}\iiint\frac{dx_1\,dx_2\,dz}{x_1{}^{X_1+1}x_2{}^{X_2+1}z^{E+1}}\{x_1 f_1(z)\}\exp\{x_1 f_1(z)+x_2 f_2(z)+x_1 x_2 g(z)\}. \quad\ldots\ldots(308)$$

For $\overline{E_{A^1}}$, the mean energy of the free atoms A, we have

$$C\overline{E_{A^1}}=C\Sigma_u\overline{a_u{}^1}\epsilon_u{}^1=\Sigma_u\varpi_u{}^1\epsilon_u{}^1\frac{\partial C}{\partial\varpi_u{}^1}, \quad\ldots\ldots(309)$$

and the extra factor in the integrand is

$$x_1\Sigma_u\varpi_u{}^1\epsilon_u{}^1 z^{\epsilon_u{}^1},\ \text{or}\ x_1 z\partial f_1/\partial z.$$

For $C\overline{b_v}$ the extra factor in the integrand is $\rho_v x_1 x_2 z^{\eta_v}$, and for $C\overline{N}$, $x_1 x_2 g(z)$. For the mean energy $\overline{E_{A^1A^2}}$ of the molecules A^1A^2 the extra factor in the integrand of $C\overline{E_{A^1A^2}}$ is $x_1 x_2 z\partial g/\partial z$.

Let us assume for the moment (for a proof see § 5·5) that when the assembly is sufficiently large, integrals such as these can be approximated to, by the method of steepest descents, by making the contours pass through a unique set of positive real values ξ_1, ξ_2, ϑ of x_1, x_2, z, at which the first partial differential coefficients of the integrand all vanish. We shall then find by extensions of the arguments of Chapter II that

$$\overline{a_u{}^1} = \xi_1 \varpi_u{}^1 \vartheta^{\epsilon_u{}^1}, \qquad \overline{b_v} = \xi_1 \xi_2 \rho_v \vartheta^{\eta_v}, \qquad \text{......(310)}$$

$$\overline{M_1} = \xi_1 f_1(\vartheta), \qquad \overline{N} = \xi_1 \xi_2 g(\vartheta), \qquad \text{......(311)}$$

$$\overline{E_{A^1}} = \xi_1 \vartheta \frac{\partial f_1(\vartheta)}{\partial \vartheta}, \quad \overline{E_{A^1 A^2}} = \xi_1 \xi_2 \vartheta \frac{\partial g(\vartheta)}{\partial \vartheta}, \qquad \text{......(312)}$$

etc. The equations defining ξ_1, ξ_2, ϑ are

$$\xi_1 f_1(\vartheta) + \xi_1 \xi_2 g(\vartheta) = X_1, \qquad \text{......(313)}$$

$$\xi_2 f_2(\vartheta) + \xi_1 \xi_2 g(\vartheta) = X_2, \qquad \text{......(314)}$$

$$\xi_1 \vartheta \frac{\partial f_1(\vartheta)}{\partial \vartheta} + \xi_2 \vartheta \frac{\partial f_2(\vartheta)}{\partial \vartheta} + \xi_1 \xi_2 \vartheta \frac{\partial g(\vartheta)}{\partial \vartheta} = E. \qquad \text{......(315)}$$

Assuming that ξ_1, ξ_2, ϑ, which define the concentrations and temperature of the assembly, are thus uniquely determined, the complete form of the "equation of mass-action" follows at once from (311) by eliminating ξ_1, ξ_2. We find

$$\frac{\overline{M_1}\,\overline{M_2}}{\overline{N}} = \frac{f_1(\vartheta) f_2(\vartheta)}{g(\vartheta)}. \qquad \text{......(316)}$$

Thus the equilibrium constant of the laws of mass-action is expressible at once, in the simplest way, in terms of partition functions.

Integrals can obviously be constructed, which will enable us to evaluate fluctuations in these assemblies, and prove all such relations as $\overline{(P - \overline{P})^2} = O(\overline{P})$, which guarantee the effective possession of normality. We need not stop over these points further here; details will be found in Chapter XX.

Let us consider in rather more detail the physical meaning of (316), which is also called the reaction isochore. We may take

$$f_1(\vartheta) = \frac{(2\pi m_1)^{\frac{3}{2}}\, V}{h^3 (\log 1/\vartheta)^{\frac{3}{2}}}, \quad f_2(\vartheta) = \frac{(2\pi m_2)^{\frac{3}{2}}\, V}{h^3 (\log 1/\vartheta)^{\frac{3}{2}}},$$

$$g(\vartheta) = \frac{\{2\pi (m_1 + m_2)\}^{\frac{3}{2}}\, V}{h^3 (\log 1/\vartheta)^{\frac{3}{2}}}\, b'(\vartheta),$$

where $b'(\vartheta)$ is the partition function for the internal energy and rotational energy of the molecule. Relative to our assigned energy zero the normal state of lowest energy of the molecule has an energy $-\chi$. It is therefore convenient to write

$$b'(\vartheta) = \vartheta^{-\chi} b(\vartheta),$$

where $b(\vartheta)$ begins with a constant term, and is the partition function for the internal and rotational energy of the molecule referred to its own state of lowest energy as the zero of energy. If to the usual first approximation we suppose that the internal vibrations are unaffected by the rotations, the partition function $b(\vartheta)$ factorizes into

$$b(\vartheta) = r(\vartheta)\, v(\vartheta),$$

where $r(\vartheta)$ is the partition function for the rotations and $v(\vartheta)$ for the internal vibrations. If we express (316) in terms of average molecular densities, $\nu_1 = \overline{M_1}/V$, etc., we find

$$\frac{\nu_1 \nu_2}{\nu_{12}} = \left(\frac{2\pi m_1 m_2}{m_1 + m_2}\right)^{\frac{3}{2}} \frac{\vartheta^{\chi}}{h^3 (\log 1/\vartheta)^{\frac{3}{2}}} \frac{1}{r(\vartheta)\, v(\vartheta)}, \qquad \text{......(317)}$$

$$= \frac{1}{h^3}\left(\frac{2\pi k m_1 m_2}{m_1 + m_2}\right)^{\frac{3}{2}} T^{\frac{3}{2}} e^{-\chi/kT} \frac{1}{R(T)\, V(T)}. \qquad \text{......(318)}$$

It is convenient to collect the commoner approximate forms which (318) may be expected to assume. When $T \to 0$

$$R(T) \sim \rho_1/\sigma,$$

where ρ_1 is the weight of the lowest possible rotational state calculated from (91) or (92). When $T \to \infty$, if the moment of inertia A of the molecule is effectively constant we find from (119), allowing for the symmetry, that

$$R(T) \sim \frac{8\pi^2 A k T}{\sigma h^2}.$$

For the vibrational term one may suppose that to a similar rough approximation the vibrations are those of a simple harmonic oscillator of frequency ν_0. In discussing specific heats in Chapter III we have already seen the limitations of these simplifications. Then

$$v(\vartheta) = 1/(1 - \vartheta^{h\nu_0}).$$

When $T \to 0$, $V(T) \to 1$. When $T \to \infty$,

$$V(T) \sim \frac{kT}{h\nu_0}.$$

This form will only be valid if $kT \gg h\nu_0$ and at the same time $kT \ll \chi$, which is in general a limiting value of the sequence of vibrational energies. For values of kT comparable with χ no simplified form is available.

If we write $\epsilon = h^2/8\pi^2 A$ then in general, as we have seen in Chapter III, $h\nu_0 \gg \epsilon$, and the reaction isochore takes successively the following standard simplified forms:

$$\frac{\nu_1 \nu_2}{\nu_{12}} = \left(\frac{2\pi k m_1 m_2}{m_1 + m_2}\right)^{\frac{3}{2}} \frac{\sigma}{\rho_1 h^3} T^{\frac{3}{2}} e^{-\chi/kT} \quad (kT \ll \epsilon), \qquad \text{......(319)}$$

$$= \left(\frac{2\pi k m_1 m_2}{m_1 + m_2}\right)^{\frac{3}{2}} \frac{\sigma}{8\pi^2 h A k} T^{\frac{1}{2}} e^{-\chi/kT} \quad (\epsilon \ll kT \ll h\nu_0, \chi), \qquad \text{......(320)}$$

$$= \left(\frac{2\pi k m_1 m_2}{m_1 + m_2}\right)^{\frac{3}{2}} \frac{\sigma \nu_0}{8\pi^2 A k^2} T^{-\frac{1}{2}} e^{-\chi/kT} \quad (h\nu_0 \ll kT \ll \chi). \qquad \text{......(321)}$$

Equation (320) corresponds to the conditions considered by Ehrenfest and Trkal and agrees with their result, but only because we have taken the weights ϖ_n of the nth state of rotation of the molecule to satisfy $\varpi_n \sim 2n$ as $n \to \infty$. Weights such as n or $n+1$, which were sometimes suggested before the advent of the quantum mechanics, could even then only be maintained by very forced arguments, disagree here with the limiting principle, and are certainly wrong.

These formulae for the reaction isochore are of very well-known forms, of recognized validity. It is unnecessary to undertake a direct comparison of the whole of these and similar formulae with experiment, because, as we shall see in Chapter VI, these formulae and the general equation (316) really only differ from the formulae of thermodynamics by fixing the precise value of the constant factor—or, in other words, the "chemical constants". The ultimate test of the theory need therefore only be made by comparing observed and calculated values of these constants, and to this we shall return in connection with Nernst's heat theorem in Chapter VII.

§ 5·4. *Gaseous assemblies with any number of components and reactions.* In view of the preliminary formulation of the simple case above, it is now only necessary to specify a notation suitable for the general gaseous assembly. Let the different types of atoms be denoted by the affix r, molecules by the affix s. Then the energy, weight and number of free atoms of type r associated with their uth cell will be denoted by $\epsilon_u{}^r$, $\varpi_u{}^r$ and $a_u{}^r$. For molecules of type s the corresponding quantities are $\epsilon_v{}^s$, $\varpi_v{}^s$, and $a_v{}^s$, the weight $\varpi_v{}^s$ being taken to include the symmetry number σ_s. If A^r is the atomic symbol for the atom of type r the molecular symbol for the molecule of type s in the chemical form will be

$$\Pi_r A^r{}_{q_s{}^r}.$$

We have assumed here that the molecule of type s contains $q_s{}^r$ atoms of type r. All possible reactions may then be regarded as contained in the set

$$\Sigma_r q_s{}^r A^r \rightleftharpoons \Pi_r A^r{}_{q_s{}^r} \quad (s = 1, 2, \ldots),$$

or constructed out of members of the set. The actual sequence of reactions by which equilibrium is attained is without effect on that equilibrium.

Let the number of atoms of type r be X_r, there being j types in all, the free atoms of type r, M_r, and the molecules of type s, N_s. Then

$$X_r = M_r + \Sigma_s q_s{}^r N_s \quad (r = 1, 2, \ldots, j). \qquad \ldots\ldots(322)$$

To preserve the correct atomic and molecular totals we require

$$\Sigma_u a_u{}^r = M_r \quad (r = 1, 2, \ldots, j), \quad \Sigma_v a_v{}^s = N_s \quad (s = 1, 2, \ldots),$$

and therefore in general

$$\Sigma_u a_u{}^r + \Sigma_s \Sigma_v q_s{}^r a_v{}^s = X_r \quad (r = 1, 2, \ldots, j). \qquad \ldots\ldots(323)$$

To satisfy the energy equation we require also

$$\Sigma_r \Sigma_u a_u^r \epsilon_u^r + \Sigma_s \Sigma_v a_v^s \epsilon_v^s = E. \qquad \text{......(324)}$$

The total number of weighted complexions is therefore

$$(\Pi_r X_r\,!)\, \Sigma_{(a)}\, \Pi_r \Pi_u \frac{(\varpi_u^r)^{a_u^r}}{a_u^r\,!}\, \Pi_s \Pi_v \frac{(\varpi_v^s)^{a_v^s}}{a_v^s\,!}, \qquad \text{......(325)}$$

where the summation is extended over all positive a's satisfying (323) and (324). To sum (325) subject to these conditions we introduce the appropriate selector variables and form the expression

$$(\Pi_r X_r\,!)\, \Pi_r \Pi_u \left[\Sigma_{(a)} \frac{(\varpi_u^r x_r z^{\epsilon_u^r})^{a_u^r}}{a_u^r\,!}\right] \Pi_s \Pi_v \left[\Sigma_{(a)} \frac{(\varpi_v^s x_1^{q_s^1} x_2^{q_s^2} \dots z^{\epsilon_v^s})^{a_v^s}}{a_v^s\,!}\right], \qquad \text{......(326)}$$

where $\Sigma_{(a)}$ now means unlimited summation over all positive a's. To obtain (325) we must select the coefficient of $x_1^{X_1} x_2^{X_2} \dots z^E$ from (326), but the expression (326) reduces at once to

$$(\Pi_r X_r\,!) \exp \{\Sigma_r x_r f_r(z) + \Sigma_s x_1^{q_s^1} x_2^{q_s^2} \dots g_s(z)\},$$

where $f_r(z)$ and $g_s(z)$ are the partition functions for the atom of type r and molecule of type s. We observe that the exponential contains a single term of a very simple nature corresponding to each type of atom or molecule present. We obtain at once

$$C = \frac{(\Pi_r X_r\,!)}{(2\pi i)^{j+1}} \int^{(j+1)} \dots \int \frac{dz\, \Pi_r dx_r}{z^{E+1} \Pi_r x_r^{X_r+1}} \exp \{\Sigma_r x_r f_r(z) + \Sigma_s x_1^{q_s^1} x_2^{q_s^2} \dots g_s(z)\}. \qquad \text{......(327)}$$

For $C\overline{a_u^r}$ and similar expressions we obtain similar integrals. For example,

$$C\overline{a_u^r} = \varpi_u^r \frac{\partial C}{\partial \varpi_u^r} = \varpi_u^r z^{\epsilon_u^r} \frac{\partial C}{\partial f_r}. \qquad \text{......(328)}$$

The integrand therefore only differs from that of C by the extra factor $\varpi_u^r x_r z^{\epsilon_u^r}$. In other cases the extra factors are as follows:

For

$$\begin{array}{ll} C\overline{M_r}, & x_r f_r(z), \\ C\overline{a_v^s}, & \varpi_v^s x_1^{q_s^1} x_2^{q_s^2} \dots z^{\epsilon_v^s}, \\ C\overline{N}, & x_1^{q_s^1} x_2^{q_s^2} \dots g_s(z), \\ C\overline{E_r}, & x_r z \dfrac{\partial f_r(z)}{\partial z}, \\ C\overline{E_s}, & x_1^{q_s^1} x_2^{q_s^2} \dots z \dfrac{\partial g_s(z)}{\partial z}. \end{array}$$

Anticipating the results of § 5·5, a unique set of parameters $\xi_1, \xi_2, \dots, \vartheta$ are defined by the real positive solution of the equations

$$\xi_r f_r(\vartheta) + \Sigma_s q_s^r \xi_1^{q_s^1} \xi_2^{q_s^2} \dots g_s(\vartheta) = X_r \quad (r = 1, \dots, j), \qquad \text{...(329)}$$

$$\Sigma_r \xi_r\, \vartheta \frac{\partial f_r(\vartheta)}{\partial \vartheta} + \Sigma_s \xi_1^{q_s^1} \xi_2^{q_s^2} \dots \vartheta \frac{\partial g_s(\vartheta)}{\partial \vartheta} = E. \qquad \text{......(330)}$$

It then follows by the method of steepest descents that

$$\overline{a_u{}^r} = \varpi_u{}^r \xi_r \vartheta^{\epsilon_u{}^r}, \quad \overline{M_r} = \xi_r f_r(\vartheta), \quad \overline{a_u{}^r} = \overline{M_r}\varpi_u{}^r \vartheta^{\epsilon_u{}^r}/f_r(\vartheta), \qquad \text{...(331)}$$

$$\overline{a_v{}^s} = \varpi_v{}^s \xi_1{}^{q_s{}^1} \xi_2{}^{q_s{}^2} \ldots \vartheta^{\epsilon_v{}^s}, \quad \overline{N_s} = \xi_1{}^{q_s{}^1} \xi_2{}^{q_s{}^2} \ldots g_s(\vartheta), \quad \overline{a_v{}^s} = \overline{N_s}\varpi_v{}^s \vartheta^{\epsilon_v{}^s}/g_s(\vartheta). \qquad \text{......(332)}$$

The laws of mass-action follow from (331) and (332) in the form

$$\frac{\overline{N_s}}{\Pi_r(\overline{M_r})^{q_s{}^r}} = \frac{g_s(\vartheta)}{\Pi_r\{f_r(\vartheta)\}^{q_s{}^r}} \quad (s = 1, 2, \ldots). \qquad \text{......(333)}$$

We obtain also the energy distribution laws

$$\overline{E_r} = \xi_r \vartheta \frac{\partial f_r(\vartheta)}{\partial \vartheta} = \overline{M_r}\vartheta \frac{\partial}{\partial \vartheta} \log f_r(\vartheta), \qquad \text{......(334)}$$

$$\overline{E_s} = \xi_1{}^{q_s{}^1} \xi_2{}^{q_s{}^2} \ldots \vartheta \frac{\partial g_s(\vartheta)}{\partial \vartheta} = \overline{N_s}\vartheta \frac{\partial}{\partial \vartheta} \log g_s(\vartheta), \qquad \text{......(335)}$$

and, similarly, any other details of the equilibrium state. For the reaction of the assembly on external bodies which submit its systems to fields of force we find, as in § 2·74,

$$\begin{aligned} \overline{Y} &= \Sigma_r \Sigma_u \overline{a_u{}^r}\left(-\frac{\partial \epsilon_u{}^r}{\partial y}\right) + \Sigma_s \Sigma_v \overline{a_v{}^s}\left(-\frac{\partial \epsilon_v{}^s}{\partial y}\right), \\ &= \frac{1}{\log 1/\vartheta}\left\{\Sigma_r \xi_r \frac{\partial f_r}{\partial y} + \Sigma_s \xi_1{}^{q_s{}^1} \xi_2{}^{q_s{}^2} \ldots \frac{\partial g_s}{\partial y}\right\}, \qquad \text{......(336)} \\ &= \frac{1}{\log 1/\vartheta}\left\{\Sigma_r \overline{M_r}\frac{\partial}{\partial y}\log f_r + \Sigma_s \overline{N_s}\frac{\partial}{\partial y}\log g_s\right\}. \qquad \text{......(337)} \end{aligned}$$

In the case of local boundary fields this reduces of course to the ordinary equation of state for a "perfect" gaseous assembly (in which, however, the number of constituents is a function of the temperature),

$$p = \frac{kT}{V}\{\Sigma_r \overline{M_r} + \Sigma_s \overline{N_s}\}. \qquad \text{......(338)}$$

§ **5·5**. *Proof of the results of* §§ 5·3 *and* 5·4. We now give a proof of the results of §§ 5·3 and 5·4, parts of which for simplicity are written out for the case of three variables x, y, z. The proof, however, will be easily seen to be quite general.

The form of the integrand of C and the analogous integrals is that of a triple (in general multiple) power series

$$\Phi = \Sigma_{abc} Q_{abc} x^a y^b z^c, \qquad \text{......(339)}$$

in which the Q_{abc} are all positive, and the a, b, c (integers) start at negative values and run to $+\infty$. The domain of convergence of the series (339) in our actual problem is all values of x and y and all z's such that $|z| < 1$, but its actual form is immaterial. For our proof we require certain properties of this function which are obtained in the following

Lemma. For real positive values of x, y, z *the function* Φ *has an absolute minimum at* ξ, η, ϑ *which is the unique solution of the equations*

$$\frac{\partial\Phi}{\partial x}=\frac{\partial\Phi}{\partial y}=\frac{\partial\Phi}{\partial z}=0 \qquad \text{......(340)}$$

in this domain.

(i) Since Φ is always positive, and since it may be assumed from the physical origin of the Q_{abc} that $\Phi \to +\infty$ as x, y, z tend to their boundary values (i.e. 0, ∞ or 0, 1) in any manner, Φ must have an absolute minimum value Φ_0 which it assumes at some points of the domain of real positive values x, y, z. At such a point ξ, η, ϑ equations (340) must of course be satisfied.

(ii) That ξ, η, ϑ is the *unique* solution of (340) in the real domain will follow at once if it can be shown that *any* stationary value of Φ must be an absolute minimum—that is that, if Φ_0 is any stationary value,

$$\Phi - \Phi_0 \geqslant 0$$

for the whole domain, equality being only possible when $x = \xi$, $y = \eta$, $z = \vartheta$. If we write $x = e^{\lambda}$, $y = e^{\mu}$, $z = e^{\nu}$, then

$$\Phi = \Sigma_{abc}\, Q_{abc}\, e^{a\lambda + b\mu + c\nu},$$

and, by Taylor's theorem, for *any* stationary value Φ_0,

$$\Phi - \Phi_0 = \tfrac{1}{2}\left[(\lambda-\lambda_0)^2\frac{\partial^2\Phi}{\partial\lambda^2} + \dots + 2(\lambda-\lambda_0)(\mu-\mu_0)\frac{\partial^2\Phi}{\partial\lambda\partial\mu}\right], \qquad (341)$$

an expression in which all the partial differential coefficients are to be evaluated for some particular set of values of λ, μ, ν. It is therefore only necessary to prove that the expression on the right of (341) is a positive quadratic form.

(iii) The proof of the lemma reduces therefore to the proof of the essential inequalities

$$\frac{\partial^2\Phi}{\partial\lambda^2} > 0, \qquad \begin{vmatrix} \dfrac{\partial^2\Phi}{\partial\lambda^2} & \dfrac{\partial^2\Phi}{\partial\lambda\partial\mu} \\ \dfrac{\partial^2\Phi}{\partial\lambda\partial\mu} & \dfrac{\partial^2\Phi}{\partial\mu^2} \end{vmatrix} > 0, \qquad \begin{vmatrix} \dfrac{\partial^2\Phi}{\partial\lambda^2} & \dfrac{\partial^2\Phi}{\partial\lambda\partial\mu} & \dfrac{\partial^2\Phi}{\partial\lambda\partial\nu} \\ \dfrac{\partial^2\Phi}{\partial\lambda\partial\mu} & \dfrac{\partial^2\Phi}{\partial\mu^2} & \dfrac{\partial^2\Phi}{\partial\mu\partial\nu} \\ \dfrac{\partial^2\Phi}{\partial\lambda\partial\nu} & \dfrac{\partial^2\Phi}{\partial\mu\partial\nu} & \dfrac{\partial^2\Phi}{\partial\nu^2} \end{vmatrix} > 0.$$

[For more variables the series of inequalities is correspondingly extended.]

Firstly

$$\frac{\partial^2\Phi}{\partial\lambda^2} = \Sigma_{abc}\, Q_{abc}\, a^2 e^{a\lambda + b\mu + c\nu} > 0,$$

for every term is positive. Secondly

$$\begin{vmatrix} \dfrac{\partial^2\Phi}{\partial\lambda^2} & \dfrac{\partial^2\Phi}{\partial\lambda\,\partial\mu} \\ \dfrac{\partial^2\Phi}{\partial\lambda\,\partial\mu} & \dfrac{\partial^2\Phi}{\partial\mu^2} \end{vmatrix} = \begin{vmatrix} \Sigma_{abc}\,Q_{abc}\,a^2 e^{a\lambda+b\mu+c\nu} & \Sigma_{a'b'c'}\,Q_{a'b'c'}\,a'b'e^{a'\lambda+b'\mu+c'\nu} \\ \Sigma_{abc}\,Q_{abc}\,ab e^{a\lambda+b\mu+c\nu} & \Sigma_{a'b'c'}\,Q_{a'b'c'}\,b'^2 e^{a'\lambda+b'\mu+c'\nu} \end{vmatrix}.$$

If we collect together all terms containing $Q_{abc}\,Q_{a'b'c'}$ we see that this determinant reduces to

$$\Sigma'\,Q_{abc}\,Q_{a'b'c'}\,e^{(a+a')\lambda+(b+b')\mu+(c+c')\nu}\left\{\begin{vmatrix} a^2 & a'b' \\ ab & b'^2 \end{vmatrix} + \begin{vmatrix} a'^2 & ab \\ a'b' & b^2 \end{vmatrix}\right\}.$$

The terms { } are formed of all possible permutations of the dashed and plain letters, and reduce to

$$ab'\begin{vmatrix} a & a' \\ b & b' \end{vmatrix} + a'b\begin{vmatrix} a' & a \\ b' & b \end{vmatrix} = \begin{vmatrix} a & a' \\ b & b' \end{vmatrix}^2.$$

The summation Σ' is over all possible values of a, b, c, a', b', c', the specified permutations being excluded. Since every term in Σ' is positive the second condition is fulfilled. Finally, an exactly similar argument shows that

$$\begin{vmatrix} \dfrac{\partial^2\Phi}{\partial\lambda^2} & \dfrac{\partial^2\Phi}{\partial\lambda\,\partial\mu} & \dfrac{\partial^2\Phi}{\partial\lambda\,\partial\nu} \\ \dfrac{\partial^2\Phi}{\partial\lambda\,\partial\mu} & \dfrac{\partial^2\Phi}{\partial\mu^2} & \dfrac{\partial^2\Phi}{\partial\mu\,\partial\nu} \\ \dfrac{\partial^2\Phi}{\partial\lambda\,\partial\nu} & \dfrac{\partial^2\Phi}{\partial\mu\,\partial\nu} & \dfrac{\partial^2\Phi}{\partial\nu^2} \end{vmatrix} = J\left(\frac{\dfrac{\partial\Phi}{\partial\lambda} \quad \dfrac{\partial\Phi}{\partial\mu} \quad \dfrac{\partial\Phi}{\partial\nu}}{\lambda \qquad \mu \qquad \nu}\right)$$

$$= \Sigma'\,Q_{abc}\,Q_{a'b'c'}\,Q_{a''b''c''}\,e^{(a+a'+a'')\lambda+(b+b'+b'')\mu+(c+c'+c'')\nu}\begin{vmatrix} a & a' & a'' \\ b & b' & b'' \\ c & c' & c'' \end{vmatrix}^2,$$

$$> 0.$$

This completes the proof of the lemma which can obviously be extended to any number of variables.

The integrals which we desire to study asymptotically are all of the form

$$\frac{1}{(2\pi i)^3}\iiint \Phi\,\frac{dx\,dy\,dz}{xyz},$$

or combinations of integrals of the type

$$\frac{1}{(2\pi i)^3}\iiint R\Phi\,\frac{dx\,dy\,dz}{xyz},$$

where R is one of the terms in Φ. On the contours of integration the maximum value of the modulus of the integrand occurs when all the variables are real and positive, and, as we shall see, if the contours are arranged to go through the real-value minimum of Φ, it is only the contribution from this neighbourhood which need be considered.

To see that only this neighbourhood makes an effective contribution needs somewhat careful consideration. If certain relations are satisfied between the a, b, c, there may be other points on the contours at which the amplitudes of all the terms are again equal so that the same maximum value is repeated. The same difficulty comes in when z is the only selector variable (Chapter II), in which case we have shown that the repetitions of the maximum are without effect on the physical applications, and can in fact be avoided by proper choice of the unit of energy. In the case in which Φ takes the special form

$$\frac{\exp\{x_1 f_1 + x_2 f_2 + x_1 x_2 g\}}{x_1^{X_1} x_2^{X_2} z^E}$$

it is not difficult to see that no repetitions of the maximum can occur except those which are identical with the repetitions of Chapter II. To attain the maximum every term in $x_1 f_1 + x_2 f_2 + x_1 x_2 g$ must be real and positive. This will occur and occur only at points at which the amplitudes $\theta_{x_1}, \theta_{x_2}, \theta_z$ of x_1, x_2, z satisfy the relations

$$\theta_{x_1} + \epsilon_u^1 \theta_z \equiv 0 \ (\mathrm{Mod}\ 2\pi) \quad (\textit{all } u),$$
$$\theta_{x_2} + \epsilon_u^2 \theta_z \equiv 0 \ (\mathrm{Mod}\ 2\pi) \quad (\textit{all } u),$$
$$\theta_{x_1} + \theta_{x_2} + \eta_v \theta_z \equiv 0 \ (\mathrm{Mod}\ 2\pi) \quad (\textit{all } v).$$

The first of these equations is equivalent to the assertions (1) that ϵ_u^1 is of the form $\epsilon_0^1 + n\zeta_u^1$, where n and the ζ_u^1 are positive integers, and (2) that

$$\theta_z = \frac{2\pi r}{n}, \ \theta_{x_1} = -\frac{2\pi r}{n}\epsilon_0^1 \quad (0 \leqslant r < n).$$

The remaining equations add the information that

$$\epsilon_u^2 = \epsilon_0^2 + n\zeta_u^2, \ \eta_v = \eta_0 + n\zeta_v, \ \theta_{x_2} = -\frac{2\pi r}{n}\epsilon_0^2,$$
$$\eta_0 - \epsilon_0^1 - \epsilon_0^2 \equiv 0 \ (\mathrm{Mod}\ n/r).$$

It is easy to see that if $n > 1$ these relations may permit of a number of subsidiary maxima. It must be recalled, however, that f_1 and f_2 are necessarily partition functions for free atoms and therefore start with a cell of zero energy $\epsilon_0^1 = \epsilon_0^2 = 0$. Subsidiary maxima can therefore only occur for real values of the x's, that is to say, can only be strictly analogous to the subsidiary maxima of Chapter II, and can be removed by a change of the unit of energy.

It may be mentioned finally that, even if the most general type of subsidiary maximum could occur, it would not affect any physical result, for these depend only on the ratio of two of our integrals, and owing to the special forms of the integrands all such ratios are completely unaltered.

It is convenient at this point to recall the forms of the partition functions f and g. Each of them contains as a factor the partition function for the translatory motion of the atom or molecule as a whole, namely

$$\frac{(2\pi m)^{\frac{3}{2}}\, V}{h^3 (\log 1/z)^{\frac{3}{2}}}, \qquad \text{......(342)}$$

in which m is the mass of the molecule or atom and V is the volume of the assembly available to this particular species. We thus obtain for each partition function the factor V, the rest of the function depending only on z. It is convenient to recognize this structure explicitly, by writing $V_r F_r(z)$ for $f_r(z)$ and $V_s G_s(z)$ for $g_s(z)$. If there are semipermeable membranes to be considered the V_r and V_s need not all be equal. As we shall see directly, the asymptotic expansions, which we require when E and the X's are large, naturally involve also the corresponding largeness of the V_r and V_s.

Consider now the integral

$$C = \frac{X_1!\, X_2!}{(2\pi i)^3} \iiint \frac{dx_1\, dx_2\, dz}{x_1 x_2 z}\, \frac{\exp\{V_1 x_1 F_1 + V_2 x_2 F_2 + V x_1 x_2 G\}}{x_1^{X_1} x_2^{X_2} z^E},$$

whose integrand satisfies the conditions of the lemma. The unique minimum on the positive real axis is at ξ_1, ξ_2, ϑ, where ξ_1, ξ_2, ϑ is the unique relevant solution of the equations

$$V_1 \xi_1 F_1 + V \xi_1 \xi_2 G = X_1, \qquad \text{......(343)}$$

$$V_2 \xi_2 F_2 + V \xi_1 \xi_2 G = X_2, \qquad \text{......(344)}$$

$$V_1 \xi_1 \vartheta F_1' + V_2\, \xi_2 \vartheta F_2' + V \xi_1 \xi_2 \vartheta G' = E \quad (F_1' = \partial F_1/\partial\vartheta, \text{ etc.}). \quad \text{...(345)}$$

We observe that ξ_1, ξ_2, ϑ are *intensive* parameters. Their values are unaltered if E, the X's and the V's are made large in any fixed ratios. We may assume that, when the circles of integration are made to pass through ξ_1, ξ_2, ϑ, this point provides the unique relevant maximum value of the modulus of the integrand on the contours of integration. To show that its neighbourhood contributes the dominant part of the whole integral we write

$$x_1 = \xi_1 e^{i\alpha_1}, \; x_2 = \xi_2 e^{i\alpha_2}, \; z = \vartheta e^{i\beta},$$

$$V_1 x_1 F_1 + V_2 x_2 F_2 + V x_1 x_2 G = V\Psi(i\alpha_1, i\alpha_2, i\beta),$$

so that if the ratios of the V's are fixed Ψ is independent of V. Then for small values of α_1, α_2 and β the integrand takes the form

$$\frac{\exp\{V\Psi(0,0,0)\}}{\xi_1^{X_1} \xi_2^{X_2} \vartheta^E} \exp\left[-\tfrac{1}{2} V \left\{\alpha_1^2 \frac{\partial^2 \Psi}{\partial i\alpha_1^2} + \dots + 2\alpha_1\alpha_2 \frac{\partial^2 \Psi}{\partial i\alpha_1 \partial i\alpha_2}\right\}_0 + KV\alpha^3 + O(V\alpha^4)\right], \qquad \text{......(346)}$$

n which the differential coefficients are to be evaluated at $\alpha_1 = \alpha_2 = \beta = 0$. We have already shown in the proof of the lemma that this quadratic form is essentially positive. If V is large it follows by the arguments of § 2·5 that the variables $\alpha_1, \alpha_2, \beta$ in the quadratic terms may be supposed to range from $-\infty$ to $+\infty$ while all other terms remain small. By a linear transformation the quadratic form can be reduced to its principal axes, and the value of this exponential, integrated in all variables from $-\infty$ to $+\infty$, can be shown to be

$$\left(\frac{2\pi}{V}\right)^{\frac{3}{2}} \left\{ J \left(\frac{\frac{\partial \Psi}{\partial i\alpha_1}, \frac{\partial \Psi}{\partial i\alpha_2}, \frac{\partial \Psi}{\partial i\beta}}{i\alpha_1 \quad i\alpha_2 \quad i\beta} \right)_0 \right\}^{-\frac{1}{2}}. \qquad \text{......(347)}$$

The terms $KV\alpha^3$ vanish on integration. The terms $O(V\alpha^4)$ leave an error term $O(1/V)$. We have already shown in the lemma that $J > 0$. We therefore find ultimately for C the asymptotic form

$$C = \frac{X_1 ! \, X_2 !}{(2\pi V)^{\frac{3}{2}}} \frac{\exp \{V\Psi(0, 0, 0)\}}{\xi_1^{X_1} \xi_2^{X_2} \vartheta^E} \left[\{J_0\}^{-\frac{1}{2}} + O\left(\frac{1}{V}\right) \right] \text{......(348)}$$

Any other integral containing an extra factor R in the integrand can be discussed in exactly the same way. The leading term differs from C simply in the extra factor $R(\xi_1, \xi_2, \vartheta)$, and there is still an error term $O(1/V)$ as before. We are led at once to all the results obtained formally in §§ 5·3 and 5·4.

In conclusion it should be mentioned that it may often happen in actual cases that certain theoretically possible species may be exceedingly rare in the assembly; some term such as $\xi_r f_r(\vartheta)$ may be excessively small. This will not in any way invalidate our formulae. If we suppose that a certain species is *completely* absent we have merely to drop a single term from the main exponential. The arguments can then all be repeated unaltered, and it is clear from the form of the equations that the equilibrium laws which we so obtain differ only imperceptibly from their complete form. The general validity in fact of this proof of the laws of dissociative equilibrium is dependent solely on the sufficient size of the assembly as a whole and not on the effective presence of any particular possible species, except of course in so far as the laws explicitly refer to this particular species.

§ **5·6**. *Crystals*. It is easy to adapt the present methods to include in the assembly crystals for which we can construct partition functions (Chapter IV). Consider first an assembly of X molecules (or atoms) of which P compose a single crystal (or a small number of such crystals) and N its molecular vapour, so that only questions of evaporation and condensation, not of dissociation, arise. To enumerate the total number of weighted complexions, we observe first that the number of weighted complexions of the vapour of N molecules with energy F is by the principles of § 5·4 the coefficient of $x^N z^F$ in

$$N\,!\,\Sigma_a \frac{(\varpi_1 x z^{\epsilon_1})^{a_1} \ldots}{a_1\,! \ldots} = N\,! \exp\{xg(z)\},$$

where $g(z)$ is the partition function for the free molecules. The crystal (Chapter IV) has a partition function which is effectively of the form $[\kappa(z)]^P$, and is represented by weighted complexions in number equal to the coefficient of z^U in $[\kappa(z)]^P$, where U is its internal energy. If the energy zeros are suitably defined then $U + F = E$, where E is the total energy of the assembly, and the number of weighted complexions representing this example of the assembly, including all ways of dividing the energy between the crystal and the vapour, is the coefficient of $x^X z^E$ in

$$N\,!\,[x\kappa(z)]^P \exp\{xg(z)\}. \qquad \text{......(349)}$$

There is an essential difference in the enumeration of the number of examples in a group for crystals and for gaseous molecules. For during the motion of a single example the molecules in the crystal do not interchange their positions as do the molecules in a gas. When therefore we permute the molecules to obtain all possible examples of the assembly arising during the most general evaporations and condensations, we do not have to divide by $P\,!$ as we divide by $N\,!$ to avoid repetitions of the same configurations. Thus there are here $X\,!/(N\,!\,\sigma^N)$ examples in the group, where σ is the symmetry number of the gaseous molecule. We can suppose as usual that the symmetry number σ is included in the weights of the partition function $g(z)$. When therefore we sum for all values of N, we find that the total number of weighted complexions C is given by*

$$C = \frac{X\,!}{(2\pi i)^2} \iint \frac{dx\,dz}{x^{X+1} z^{E+1}} \exp\{xg(z) - \log[1 - x\kappa(z)]\}. \quad \text{...(350)}$$

Equation (350) leads at once to the usual formulae.† For example,

$$C\bar{P} = \frac{X\,!}{(2\pi i)^2} \iint \frac{dx\,dz}{x^{X+1} z^{E+1}} \frac{x\kappa(z)}{1 - x\kappa(z)} \exp\{xg(z) - \log[1 - x\kappa(z)]\}, \quad \text{...(351)}$$

leading to

$$\bar{P} = \frac{\xi\kappa(\vartheta)}{1 - \xi\kappa(\vartheta)}, \qquad \text{......(352)}$$

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* It should be observed that the form $[\kappa(z)]^P$ for the partition function of the crystal is only valid for large values of P. For small values there is of course a partition function $\kappa(z, P)$, but the deviation of this from $[\kappa(z)]^P$ will be without effect on the final equilibrium, provided that the crystal phase is effectively present.

† A strict view of equations (350) and (351) leads one to include the extra factor $1/[1 - x\kappa\ z)]$ in (351) in the exponential term, with an expectation that (351) may have to be evaluated at values of ξ and ϑ different from those for (350). It appears on a closer investigation that no effective difference is made by this inclusion, as a consequence of the particular values of ξ and ϑ concerned.

where
$$E = \xi\vartheta \frac{\partial g(\vartheta)}{\partial\vartheta} + \frac{\xi\vartheta \dfrac{\partial\kappa(\vartheta)}{\partial\vartheta}}{1-\xi\kappa(\vartheta)}, \qquad \text{......(353)}$$

$$X = \xi g(\vartheta) + \frac{\xi\kappa(\vartheta)}{1-\xi\kappa(\vartheta)}. \qquad \text{......(354)}$$

On evaluating (352) we find that to this approximation

$$\xi\kappa(\vartheta) = 1 \qquad \text{......(355)}$$

if the crystal phase is effectively present, so that $\overline{P}$ is large. From (352) and (354), or by the usual direct argument,

$$\overline{N} = \xi g(\vartheta), \qquad \text{......(356)}$$

which in virtue of (355) becomes

$$\overline{N} = g(\vartheta)/\kappa(\vartheta). \qquad \text{......(357)}$$

This in the present notation is the usual formula for the vapour-pressure of the crystal.

It is now clear how to include crystals in the general assembly. In the expression (327) for C the exponential factor in the absence of crystals is

$$\exp\left[\Sigma_r x_r f_r(z) + \Sigma_s x_1^{q_1^1} x_2^{q_1^2} \ldots g_s(z)\right].$$

If, for example, the molecule 1 is also present in crystal form, with partition function $\kappa_1(z)$, the exponential factor becomes instead

$$\exp\left[\Sigma_r x_r f_r(z) + \Sigma_s x_1^{q_s^1} x_2^{q_s^2} \ldots g_s(z) - \log\{1 - x_1^{q_s^1} x_2^{q_s^2} \ldots \kappa_1(z)\}\right]. \qquad \text{......(358)}$$

The equations (329) become

$$X_r = \xi_r f_r(\vartheta) + \Sigma_s q_s^r \xi_1^{q_s^1} \xi_2^{q_s^2} \ldots g_s(\vartheta) + \frac{q_1^r \xi_1^{q_1^1} \xi_2^{q_1^2} \ldots \kappa_1(\vartheta)}{1 - \xi_1^{q_1^1} \xi_2^{q_1^2} \ldots \kappa_1(\vartheta)}, \qquad \text{......(359)}$$

and the equation (330)

$$E = \Sigma_r \xi_r \vartheta \frac{\partial f_r(\vartheta)}{\partial\vartheta} + \Sigma_s \xi_1^{q_s^1} \xi_2^{q_s^2} \ldots \vartheta \frac{\partial g_s(\vartheta)}{\partial\vartheta} + \frac{\xi_1^{q_1^1} \xi_2^{q_1^2} \ldots \vartheta\partial\kappa_1(\vartheta)/\partial\vartheta}{1 - \xi_1^{q_1^1} \xi_2^{q_1^2} \ldots \kappa_1(\vartheta)}. \qquad \text{......(360)}$$

The equation for $\overline{P_1}$, the molecules in the crystal, is

$$\overline{P_1} = \frac{\xi_1^{q_1^1} \xi_2^{q_1^2} \ldots \kappa_1(\vartheta)}{1 - \xi_1^{q_1^1} \xi_2^{q_1^2} \ldots \kappa_1(\vartheta)}, \qquad \text{......(361)}$$

which leads ($\overline{P_1}$ large) to

$$\xi_1^{q_1^1} \xi_2^{q_1^2} \ldots \kappa_1(\vartheta) = 1. \qquad \text{......(362)}$$

The ordinary laws of mass-action in the vapour phase (333) all follow without modification

$$\frac{\overline{N_s}}{\Pi_r (\overline{M_r})^{q_s^r}} = \frac{g_s(\vartheta)}{\Pi_r \{f_r(\vartheta)\}^{q_s^r}}.$$

To these must now be added the vapour-pressure equation

$$\overline{N_1} = g_1(\vartheta)/\kappa_1(\vartheta), \qquad \text{......(363)}$$

which follows from (332) and (362) when this type of crystal is present. The analysis thus leads at once to the well-known modifications of the laws of mass-action for gas reactions due to the presence of a solid (crystalline) phase of any of the constituent molecules. The concentration $\overline{N_1}/V$ of the constituent which occurs in the solid phase must by (363) have a determinate value, a function only of T, which is unaffected by the presence of all other constituents and to which these other constituents must conform in the laws of mass-action.

The method of evaluating any other mean values connected with assemblies containing crystals should now be sufficiently clear. It may be observed, however, that a direct evaluation of $\overline{P_1}$ needs a second approximation to (361) and is better obtained if required from the residue of the X's when the requirements of the gaseous phase have been met.

An example of such extensions to assemblies with crystals (assemblies of more than one phase) is the generalization of (337). This is easily found to have the form

$$\overline{Y} = \frac{1}{\log 1/\vartheta}\left\{\Sigma_r \overline{M_r}\frac{\partial}{\partial y}\log f_r(\vartheta) + \Sigma_s \overline{N_s}\frac{\partial}{\partial y}\log g_s(\vartheta) + \overline{P}\frac{\partial}{\partial y}\log \kappa(\vartheta)\right\}. \qquad \text{......(364)}$$

The interpretation of this equation for local boundary fields is best postponed until we have introduced the idea of internal stresses in § 5·71.

In concluding these remarks on the most general assemblies which we have yet discussed we should include the energy of radiation in the assembly which we have not yet done explicitly for dissociating assemblies. We observe that it merely needs the inclusion of the factor $R(z)$ in every integrand to take complete account of the equilibrium temperature radiation in the assembly. The equation (330) determining ϑ in terms of E is of course altered, but obviously no property of the assembly expressed as a function of ϑ. So far as the laws of dissociative equilibrium are concerned, it makes no difference whether radiation is or is not explicitly included, and this is as it should be. The equilibrium will be the same whether exchanges of energy take place by radiation or by collisions alone; but of course this does not imply that the steady state remains unaltered when the assembly is subjected to radiation of a different temperature from outside. We must of course explicitly include $R(z)$ when the energy E of the assembly as a function of ϑ is under discussion.

Deeper discussion is required when the systems evaporating from the crystal are not the crystal molecules, for example, in thermionic phenomena. To this we return in § 5·9.

A further application obviously open to the methods so far developed is a study of the equilibrium theory of adsorbed films and surfaces phases in general, but this will not be taken up in this monograph.

§ **5·7**. *Interpretation of the vapour-pressure equation.* Equation (363) determines the vapour-pressure of the molecules in a gaseous phase in equilibrium with a crystal or other solid for which we can construct a partition function of the form $[\kappa(\vartheta)]^P$. It is desirable to interpret this equation. The standard state of zero energy can here conveniently be taken to be that in which all the molecules are condensed in the crystal, and the crystal is in its lowest quantum state, for we can ignore refinements connected with changes of volume of the crystal. Let χ be the work required to remove one molecule to rest (or its lowest quantum state) at infinity from the crystal in this standard state. (More strictly let $P\chi$ be the work required to separate the crystal of P molecules in this state into P free molecules at rest at infinite separation; for we are ignoring surface effects. Defined thus, χ will be independent of P for large P, but may depend effectively on P as the crystals get small, for then the ignored surface energy may become sensible.) Then, relative to the assigned zero of energy,

$$g(\vartheta) = \vartheta^{\chi} \frac{(2\pi m)^{\frac{3}{2}} V}{h^3 (\log 1/\vartheta)^{\frac{3}{2}}} r(\vartheta)\, v(\vartheta). \qquad \text{......(365)}$$

Moreover,

$$p = \overline{N}kT/V. \qquad \text{......(366)}$$

Thus

$$\log p = -\frac{\chi}{kT} + \tfrac{5}{2}\log T + \log\frac{(2\pi m)^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3} + \log R(T)\, V(T) - \log K(T). \qquad \text{......(367)}$$

The symmetry number σ may be taken most suitably in the weights of $R(T)$. This is the complete form of the vapour-pressure equation. For monatomic gases in which $R(T) = V(T) = 1$ it takes a well-known form, and a form hardly less well known when $R(T)$ has its classical value. But, as with the dissociative equilibria, only the additive constant in the equation need be discussed in relation to experiment, and this must be postponed until the thermodynamic relationships of (367) have been established in Chapter VI.

§ **5·71**. *Internal stresses.* We have so far defined the pressure only in such a way that $pdSdn$ is the average work done by the boundary field on the assembly when an element dS of the boundary is moved in a distance dn normal to itself. Thus the pressure so far refers entirely to the relationship of the assembly to the outside world. Pressures at points or across areas inside the assembly, or in general internal stresses, are as yet undefined. Definitions of these quantities will often be required.

The average *stress* per unit area across any imaginary surface inside the assembly is defined to be *the resultant force per unit area exerted by systems on side A on systems on side B, together with the momentum transferred per unit area per second from A to B by systems crossing the surface from A to B* and *B to A*. The stress exerted by side A on side B is necessarily equal and opposite to the stress exerted by B on A so long as the forces obey Newton's third law.

The stress so defined is of course in general a symmetrical tensor of the second rank of nine components $p_{xx}, p_{yy}, p_{zz}, p_{yz}\ (= p_{zy}), p_{zx}\ (= p_{xz}), p_{xy}\ (= p_{yx})$. For any gas (or fluid) in equilibrium it reduces necessarily to the simple form $p_{xx} = p_{yy} = p_{zz}, p_{yz} = p_{zx} = p_{xy} = 0$. This simple isotropic stress per unit area, always normal to the surface across which it acts, is defined to be *the pressure*. The verification of this simplification and the explicit calculation of the pressure across any internal surface is immediate for perfect gases. The forces between the systems are negligible, so that, for example, p_{xx} is the rate of transfer of x-momentum across a unit surface normal to the x-axis. Molecules with the x-component of velocity between u and $u + du$ carry x-momentum mu across the surface, and the number of such molecules crossing unit area in time dt is the number of such molecules in a volume udt. Both other velocity components are entirely irrelevant, merely fixing the shape of the volume udt. Thus by Maxwell's law the number is

$$\frac{Nudt}{V}\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{1}{2}mu^2/kT}\,du,$$

and

$$p_{xx} = \frac{Nm}{V}\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}}\int_{-\infty}^{+\infty} u^2 e^{-\frac{1}{2}mu^2/kT}\,du,$$

$$= \frac{Nm}{V}\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}}\left(\frac{2kT}{m}\right)^{\frac{3}{2}}\frac{\pi^{\frac{1}{2}}}{2} = \frac{N}{V}kT.$$

Similar values are found for p_{yy} and p_{zz}. For p_{zx}, which is the rate of transfer of z-momentum across unit area normal to the x-axis, we find similarly

$$p_{zx} = \frac{Nm}{V}\frac{m}{2\pi kT}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} uw\,e^{-\frac{1}{2}m(u^2+w^2)/kT}\,du\,dw,$$

$$= 0.$$

This calculation is of course merely one version of the classical pressure calculation of the Kinetic Theory.

We have so far considered the case of a single set of systems and calculated the "partial" stress which they cause. Obviously for perfect gases the stresses are additive, and reduce as above to an isotropic pressure given by the equation

$$p = \frac{kT}{V}\{\Sigma_r \overline{M_r} + \Sigma_s \overline{N_s}\}. \qquad \text{......(368)}$$

In (368) the values of $\overline{M_r}$ and $\overline{N_s}$ are *local* values in the neighbourhood of the internal point considered. If there are only boundary fields then the pressure is constant throughout the gas and equal to the pressure on the boundary previously otherwise defined. This result of course continues to hold generally, e.g. for imperfect gases, in which connection we return to it in Chapter VIII.

The surface across which we calculate the stress may be an interface between two phases. It follows at once that the pressure on a solid phase is equal to the pressure in the surrounding gas phase evaluated at its surface.

We are now in a position to examine the form of (364) for boundary fields. By definition of the external pressure p, $Ydy = pdV$, and from the geometry of the assembly $dV = dV_s + dV_g$, where V_s, V_g are the volumes of the solid and gaseous phases. Hence

$$Ydy = pdV_s + pdV_g.$$

But by (364) $$Ydy = p_s dV_s + p_g dV_g,$$

where p_s and p_g are the expressions obtained by applying the general pressure formulae of § 2·74 to the two phases in their average state as if they were separate assemblies. Such an application will therefore always give the correct equal pressures in the various phases.

We may notice also that the equilibrium state of statistical mechanics as calculated on our general hypotheses is a state of mechanical equilibrium of the matter in the assembly. No element of it has any mass motion relative to the enclosure containing the assembly, and in the absence of external fields the pressure is everywhere constant.

The final result of these paragraphs may be expressed by saying that the stresses on any volume element or any phase of the assembly may be calculated by applying the general laws to this element or phase with its average constitution and energy as if it were itself a separate assembly.

It is possibly more significant to start by *postulating* that the general laws of statistical mechanics apply not merely to the assembly as a whole but also to its constituent elements and phases as if they were separate assemblies with their average constitution and energy. We can then work backwards and deduce the constancy of the pressure and the existence of mechanical equilibrium.

§ 5·8. *Dissociative equilibrium in an external field of force.* The formulae of the preceding sections refer to gaseous (and other) assemblies subject to no external fields of force, except the local boundary fields. This restriction can easily be removed for the gaseous part of the assembly, for which alone it is of importance. We will suppose for simplicity that all the gaseous components are confined to the same volume V. Then the V-factor in their partition functions must be replaced by $V_\alpha(\vartheta)$, where

$$V_\alpha(\vartheta) = \iiint_V e^{-W_\alpha \log 1/\vartheta}\, dq_1 dq_2 dq_3; \qquad \text{......(369)}$$

W_α is the potential energy of the atom or molecule of species a in the field. The equilibrium laws for the *whole* gaseous part of the assembly are then unaltered in form. It is, however, now necessary to consider also the equilibrium laws for any physically small element, dV_u of the assembly, since the distributions are no longer uniform in space.

The function $V_\alpha(\vartheta)$ is strictly the partition function for the potential energy, and has all the properties of a partition function (see Chapter VIII). If $\overline{n_u{}^r}, \overline{n_u{}^s}$ are the average numbers of the atoms r or molecules s in the volume element dV_u, then, by general formulae, such as (331),

$$\overline{n_u{}^r} = \overline{M}_r e^{-W_r \log 1/\vartheta}\, dV_u / V_r(\vartheta), \qquad \text{......(370)}$$

$$\overline{n_u{}^s} = \overline{N}_s e^{-W_s \log 1/\vartheta}\, dV_u / V_s(\vartheta). \qquad \text{......(371)}$$

Besides being obtainable directly from the properties of $V_\alpha(\vartheta)$, these formulae can of course be obtained from (331) by summing or integrating for all variables except the positional coordinates q_1, q_2, q_3. For the whole gaseous part of the assembly the laws of mass-action (333) take the form

$$\frac{\overline{N}_s}{\Pi_r (\overline{M}_r)^{q_s{}^r}} = \frac{V_s(\vartheta)}{\Pi_r \{V_r(\vartheta)\}^{q_s{}^r}} \times \frac{G_s(\vartheta)}{\Pi_r \{F_r(\vartheta)\}^{q_s{}^r}} \quad (s = 1, 2, \ldots). \qquad \text{......(372)}$$

For the volume element dV_u they take the form, after reduction by (372),

$$\frac{\overline{n_u{}^s}/dV_u}{\Pi_r \{\overline{n_u{}^r}/dV_u\}^{q_s{}^r}} = \frac{G_s(\vartheta)}{\Pi_r \{F_r(\vartheta)\}^{q_s{}^r}}\, e^{-(W_s - \Sigma_r q_s{}^r W_r) \log 1/\vartheta} \quad (s = 1, 2, \ldots). \qquad \text{......(373)}$$

In general, therefore, the equilibrium constant might be expected to be a function of position in the gas, varying from place to place according to (373). In actual fact there is no such variation in any known conditions. For there will be no variation provided

$$W_s - \Sigma_r q_s{}^r W_r = 0, \qquad \text{......(374)}$$

that is, provided *the potential energy of any system or group of systems in the field is unaltered by dissociation or recombination.* But this proviso is in general satisfied in actual conditions. Actual fields are usually combinations of gravitational (including inertial) and electrostatic fields. Let Φ be the gravitational and Ψ the electrostatic potential. Then

$$W_s = m_s \Phi + \epsilon_s \Psi, \quad W_r = m_r \Phi + \epsilon_r \Psi, \qquad \text{......(375)}$$

where m_s, m_r and ϵ_s, ϵ_r are the mass and charge of the systems s, r. But total mass and total charge are conserved by dissociation and recombination. Therefore

$$m_s = \Sigma_r q_s{}^r m_r, \quad \epsilon_s = \Sigma_r q_s{}^r \epsilon_r,$$

and

$$W_s - \Sigma_r q_s{}^r W_r = \{m_s - \Sigma_r q_s{}^r m_r\}\, \Phi + \{\epsilon_s - \Sigma_r q_s{}^r \epsilon_r\}\, \Psi = 0.$$

Thus in all such cases

$$\frac{\overline{n_u{}^s}/dV_u}{\Pi_r\,\{\overline{n_u{}^r}/dV_u\}^{q_s{}^r}}=\frac{G_s\,(\vartheta)}{\Pi_r\,\{F_r\,(\vartheta)\}^{q_s{}^r}},\qquad\qquad \text{......(376)}$$

and the equilibrium constants for all volume elements of the gas are the same, and the same as that for the whole gas, *without* external fields.* The total amount of dissociation, however, in the whole gas will in general have been altered by the external field.

This constancy does not necessarily hold for magnetic systems in magnetic fields, which require further consideration (see § 11·8).

It is interesting to verify that the equilibrium laws of the assembly still contain the laws of mechanical equilibrium under the influence of external fields (gravitational, inertial, or electrostatic). Equation (368) still gives the pressure in the gas if $\overline{M_r}/V$ is replaced by $\overline{n_u{}^r}/dV_u$ and $\overline{N_s}/V$ by $\overline{n_u{}^s}/dV_u$. As functions of position $\overline{n_u{}^r}$ and $\overline{n_u{}^s}$ are given by (370) and (371) and W_r and W_s by (375). Hence

$$p=\frac{kT}{dV_u}\,(\Sigma_r\overline{n_u{}^r}+\Sigma_s\overline{n_u{}^s}),$$

$$dp=-\frac{1}{dV_u}\,(\Sigma_r\overline{n_u{}^r}\,dW_r+\Sigma\overline{n_u{}^s}\,dW_s),$$

$$=-\frac{1}{dV_u}\,\{(\Sigma_r m_r\overline{n_u{}^r}+\Sigma_s m_s\overline{n_u{}^s})\,d\Phi+(\Sigma_r\epsilon_r\overline{n_u{}^r}+\Sigma_s\epsilon_s\overline{n_u{}^s})\,d\Psi\},$$

$$=-\rho d\Phi-\sigma d\Psi.\qquad\qquad \text{......(377)}$$

Since ρ and σ are the density of mass and charge in the gas, equation (377) is the usual equation for fluid equilibrium.

§ **5·9**. *Evaporation of partial constituents from a crystal.* We have so far considered only the evaporation from a crystal of its complete structural unit, the crystal molecule, so that the vapour and the crystal have been always composed of systems of the same type. We can allow the unit cell of the crystal to consist of more than one molecule of the vapour phase, but that is all. Such a discussion is, however, insufficient in many applications, for example, in all applications to thermionics in which electrons and positive ions are evaporated separately and in different numbers from metallic crystals. The necessary *formal generalization* of the argument to include such cases is due to Schottky† and is very simple. The *practical evaluation* of the new partition function introduced is, however, impossible without a far deeper knowledge of solid structure, and we obtain little

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* For the independence of gravitational forces see Gibbs, *Collected Papers*, "Thermodynamics , pp. 144, 171; for the extension to electrostatic forces, Milne, *Proc. Camb. Phil. Soc.* vol. XXII, p. 493 (1924).

† Schottky, *Ann. der Phys.* vol. LXXVIII, p. 434 (1925).

more than by the usual thermodynamic discussion of the same problem. It is sufficient to consider a simple case of a crystal of two components evaporating separately without interaction in the gas phase. Such interaction can obviously be included at once when required.

We may formally suppose that we can construct a partition function, $\kappa_{P,P'}(z)$, for the crystal or solid containing P, P' systems of the two types. From this we form the function

$$\Sigma_{P,P'} x^P x'^{P'} \kappa_{P,P'}(z),$$

or

$$\mathrm{K}(x, x', z).$$

Actually of course only large values of P and P' will be relevant, and then only in very nearly some fixed normal ratio. For such an assembly, including also a vapour phase, we have

$$C = \frac{X\,!\,X'\,!}{(2\pi i)^3} \iiint \frac{dx\,dx'\,dz}{x^{X+1} x'^{X'+1} z^{E+1}} \mathrm{K}(x, x', z) \exp\{xg(z) + x'g'(z)\}. \qquad \text{......(378)}$$

The equilibrium state is then as usual fully specified by the parameters ξ, ξ', and ϑ which give the integrand of C its unique minimum for real values of the arguments, and we have as usual

$$\overline{P} = \xi \frac{\partial}{\partial \xi} \log \mathrm{K}, \quad \overline{P'} = \xi' \frac{\partial}{\partial \xi'} \log \mathrm{K}, \qquad \text{......(379)}$$

and similar equations. We can then apply the usual argument applicable to any substantial solid, that $\overline{P}$ and $\overline{P'}$ must be practically infinite so that to the first approximation (379) may be expected to be equivalent to relations of the type

$$\xi\kappa(\vartheta) = 1, \quad \xi'\kappa'(\vartheta) = 1. \qquad \text{......(380)}$$

For the vapour phase we shall have the normal relations

$$\overline{N} = \xi g(\vartheta), \quad \overline{N'} = \xi' g'(\vartheta). \qquad \text{......(381)}$$

Combining these with (380) we find

$$\overline{N} = g(\vartheta)/\kappa(\vartheta), \quad \overline{N'} = g'(\vartheta)/\kappa'(\vartheta). \qquad \text{......(382)}$$

These are of the same form as (357), but there is no obvious method by which $\kappa(\vartheta)$ and $\kappa'(\vartheta)$ can be constructed. Much more would be required than Born's analysis of normal modes for the normal crystal. The thermodynamic meaning of $\kappa(\vartheta)$ and $\kappa'(\vartheta)$ will be brought out further in § 6·5.

It is fortunate that the treatment of the evaporation of electrons from the condensed gas of free electrons in the metal, in the manner of Sommerfeld, avoids these difficulties and allows $\kappa(\vartheta)$ for the electrons to be exactly calculated, to the approximation to which this picture is valid.

CHAPTER VI

THE RELATIONSHIP OF THE EQUILIBRIUM THEORY TO CLASSICAL THERMODYNAMICS

§ **6·1**. In the preceding chapters we have obtained all the distribution laws of the equilibrium state of any assembly for which we can construct partition functions. Except for the extension to imperfect gases which is the subject of Chapter VIII, this includes all types of assembly commonly treated in statistical mechanics. We have obtained all these distribution laws without any reference to thermodynamical ideas except to specify the exact relation between ϑ and the absolute temperature, where it will be seen that such an appeal is logically essential. It is fair to claim this feature for a merit in the present method of exposition. The ideas of thermodynamics are entirely foreign to the foundations of statistical mechanics which are mainly dynamical. The proper course is to prove that the laws of thermodynamics are true for the assemblies of statistical mechanics if we use suitable analogies to interpret their properties.* Such proofs are given in the succeeding sections, and it will be seen that the direct introduction of the laws of thermodynamics in this way is satisfactorily simple. We definitely discard Boltzmann's hypothesis relating entropy to a probability too often ill-defined, and introduce the entropy in just the classical way in which it is introduced into ordinary thermodynamics.

When the true relationship between the equilibrium theory of statistical mechanics and thermodynamics has thus been made apparent by showing that our assemblies in equilibrium are thermodynamic systems, it is natural to enquire into other methods of exposition in which an early introduction of entropy plays a leading part. This is the more natural, since many writers have contributed such expositions, and it cannot be maintained that logical clarity has often been achieved. Detailed criticism is out of place, but for completeness a short survey is included.

§ **6·2**. *Temperature.* We have already in anticipation identified ϑ with the temperature on some empirical scale, but we may conveniently recapitulate the argument here. The legitimacy of the identification depends solely on the possession by ϑ of properties strictly analogous to those assigned to the "empirical temperature", in a rational formulation of the foundations of thermodynamics.† The basic fact of thermodynamics is that

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* This is made abundantly clear by Gibbs, *Elementary Principles in Statistical Mechanics*, chaps. IV and XIV.

† See, for instance, Max Born, *Phys. Zeit.* vol. XXII, pp. 218, 249, 282 (1921).

the state of any two bodies in thermal contact is determined by a common value of a parameter which is defined to be the empirical temperature, but of course on an arbitrary scale, and any convenient body may be chosen for thermometer. On the statistical side we have shown in Chapters II–IV that when two assemblies or sets of systems in an assembly can exchange energy, so that there is one common energy total for the whole, then their equilibrium states are defined in terms of a common value of a parameter ϑ. The analogy is exact, and we are therefore logically justified in identifying ϑ with the empirical temperature as defined in thermodynamics.

It was shown further that it was possible to prove that $\vartheta = e^{-1/kT}$ by postulating the properties of perfect gases, using a perfect gas for thermometer, and asserting that the temperature shall be proportional to the pressure of the perfect gas at a constant volume; but this appeal to the properties of an ideal substance is illogical (though often convenient) and inessential. In thermodynamical theory the *absolute temperature* is defined in connection with the second law, and can only be defined in this way. We wish to show that the assemblies of statistical mechanics obey the laws of thermodynamics (or from our assumptions to prove the laws of thermodynamics), and so we must not postulate a knowledge of the absolute temperature but define it in connection with entropy, just as we do in classical thermodynamics.

§ 6·3. *Entropy and absolute temperature.* In classical thermodynamics the "heat" dQ taken in in any small change is defined to be the increase in internal energy plus the external work done by the assembly.* Thus for our general assembly

$$dQ = dE + \Sigma_t Y_t dy_t. \qquad \text{......(383)}$$

The second law of thermodynamics asserts that *there exist functions T and S of the state of the assembly such that $T = f(\vartheta)$, where ϑ is the empirical temperature, and*

$$dQ = TdS. \qquad \text{......(384)}$$

Except for a certain arbitrarily assignable constant multiplier and an additive constant these functions are unique.

For the assemblies contemplated in § 5·4 Y and E are given by (336) and (330). On differentiating E we find that

$$\begin{aligned}\log 1/\vartheta\, dQ &= \log 1/\vartheta\ d\left\{\Sigma_r \xi_r \vartheta \frac{\partial f_r}{\partial \vartheta} + \Sigma_s \xi_1^{q_s^1} \xi_2^{q_s^2} \ldots \vartheta \frac{\partial g_s}{\partial \vartheta}\right\} \\ &\qquad + \Sigma_t \left\{\Sigma_r \xi_r \frac{\partial f_r}{\partial y_t} + \Sigma_s \xi_1^{q_s^1} \xi_2^{q_s^2} \ldots \frac{\partial g_s}{\partial y_t}\right\} dy_t, \\ &= d\left[\Sigma_r \xi_r \left\{f_r + \log 1/\vartheta \,.\, \vartheta \frac{\partial f_r}{\partial \vartheta}\right\} + \Sigma_s \xi_1^{q_s^1} \xi_2^{q_s^2} \ldots \left\{g_s + \log 1/\vartheta \,.\, \vartheta \frac{\partial g_s}{\partial \vartheta}\right\}\right] \\ &\qquad - \Sigma_r f_r d\xi_r - \Sigma_s g_s d\,(\xi_1^{q_s^1} \xi_2^{q_s^2} \ldots). \qquad \text{......(385)}\end{aligned}$$

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* Born, *loc. cit.*

With the help of (329) the last sets of terms in (385) reduce at once to

$$-\Sigma_r X_r d\xi_r/\xi_r.$$

It is therefore established that $\log 1/\vartheta \,.\, dQ$ is a perfect differential, and our assembly obeys the second law of thermodynamics. The postulated functions T and S exist and are defined by the equations

$$1/kT = \log 1/\vartheta, \qquad \ldots\ldots(386)$$

$$\begin{aligned}(S - S_0)/k = {} & \Sigma_r \xi_r \left\{ f_r + \log 1/\vartheta \,.\, \vartheta \frac{\partial f_r}{\partial \vartheta} \right\} \\ & + \Sigma_s \xi_1^{q_s^1} \xi_2^{q_s^2} \ldots \left\{ g_s + \log 1/\vartheta \,.\, \vartheta \frac{\partial g_s}{\partial \vartheta} \right\} - \Sigma_r X_r \log \xi_r, \qquad \ldots\ldots(387) \\ = {} & \Sigma_r \xi_r f_r + \Sigma_s \xi_1^{q_s^1} \xi_2^{q_s^2} \ldots g_s - E \log \vartheta - \Sigma_r X_r \log \xi_r. \qquad \ldots(388)\end{aligned}$$

The constant k, Boltzmann's constant, is of course fixed by fixing the scale interval between two standard temperatures, and S_0 is essentially undetermined. It is usually convenient to put $S_0 = 0$.

We may note here that S is closely connected to C, the total number of weighted complexions which represent all possible states of the assembly. It is not difficult to show if required that this total number of weighted complexions does not differ significantly from the number of weighted complexions which represent the approximately *average* state of the assembly. The value of C is given in a simple case by (348) which can at once be generalized. Doing this we find that approximately

$$\begin{aligned}\log C = \Sigma_r \log X_r\,! + \Sigma_r \xi_r f_r(\vartheta) + \Sigma_s \xi_1^{q_s^1} \xi_2^{q_s^2} \ldots g_s(\vartheta) \\ - \Sigma_r X_r \log \xi_r - E \log \vartheta. \qquad \ldots\ldots(389)\end{aligned}$$

In this equation terms of order $\log V$ have been neglected compared to the much larger V, X, E. Comparing (389) and (388) we find the relation

$$S - S_0 = k \log \frac{C}{\Pi_r X_r\,!}. \qquad \ldots\ldots(390)$$

If we agree to take $S_0 = 0$ and to retain only the variable part C_0 of C, omitting therefore the $X_r\,!$, we can write this relation in the form

$$S = k \log C_0, \qquad \ldots\ldots(391)$$

where k is Boltzmann's constant. We may also describe C_0 as "the integrand of C evaluated at (ξ, ϑ)".

It is instructive to cast (388) into a form in which the contributions to the entropy of each molecular species or each solid are separately in evidence. We have at once

$$\Sigma_r X_r \log \xi_r = \Sigma_r (\overline{M_r} + \Sigma_s q_s^r \overline{N_s}) \log \xi_r,$$

and therefore

$$\begin{aligned}S/k = \Sigma_r \{\xi_r f_r - \overline{M_r} \log \xi_r - \overline{E_r} \log \vartheta\} \\ + \Sigma_s \{\xi_1^{q_s^1} \xi_2^{q_s^2} \ldots g_s - \overline{N_s} \log (\xi_1^{q_s^1} \xi_2^{q_s^2} \ldots)\} - \overline{E_s} \log \vartheta.\end{aligned}$$

Thus a gas of simple systems contributes to S

$$k\,[\xi_r f_r(\vartheta) - \overline{M_r}\log\xi_r - \overline{E_r}\log\vartheta], \qquad \text{......(392)}$$

or a gas of composite systems

$$k\,[\xi_1^{q_s^1}\xi_2^{q_s^2}\ldots g_s(\vartheta) - \overline{N_s}\log(\xi_1^{q_s^1}\xi_2^{q_s^2}\ldots) - \overline{E_s}\log\vartheta]. \qquad \text{...(393)}$$

The contributions are of identical type and need not be separately discussed. In exactly the same way a crystal contributes

$$k\,[-\log\{1 - \xi_1^{q_s^1}\xi_2^{q_s^2}\ldots \kappa_s(\vartheta)\} - \overline{P_s}\log(\xi_1^{q_s^1}\xi_2^{q_s^2}\ldots) - \overline{E_{P_s}}\log\vartheta]. \qquad \text{......(394)}$$

These mixed forms may be made more valuable by eliminating either the ξ_r or the $\overline{M_r}$ and $\overline{N_s}$ by means of (331) and (332). Thus the contribution of a set of molecules in the gaseous state takes either of the forms

$$k\,[f(\vartheta)\{\xi - \xi\log\xi\} - \overline{E}\log\vartheta], \qquad \text{......(395)}$$

$$k\,[\overline{M}\{\log(f(\vartheta)/\overline{M}) + 1\} - \overline{E}\log\vartheta], \qquad \text{......(396)}$$

the contribution of a crystal, after reduction,

$$k\,[\overline{P}\log\kappa(\vartheta) - \overline{E}\log\vartheta]. \qquad \text{......(397)}$$

The crystalline form corresponding to (395) is necessarily illusory. These results can be embodied in the following

Theorem (6·3). *Any particular species of free molecule with partition function* $f(\vartheta)$, *present in the assembly to an average number* $\overline{M}$ *with average energy* $\overline{E}$ *contributes* (396) *or* (395) *to the entropy.*

Any crystal (*or other solid*) *containing molecules to an average number* $\overline{P}$ *with partition function* $[\kappa(\vartheta)]^P$ *and average energy* $\overline{E}$ *contributes* (397).

It is to be particularly noticed that the theorem determines explicitly the dependence on M.* This is because, for the assemblies discussed, M can be made (by dissociation, etc.) to vary reversibly—that is, a sequence of natural equilibrium states can be found, in which M varies. A great part of the controversies about entropy in statistical mechanics has centred round the determination of the variation of S with M, ignoring just this point, that such variations can only be relevant, and therefore determinable, when M can change reversibly. This has naturally led to great confusion of thought,† only avoidable in some way equivalent to the foregoing.

The forms of (395) and (397) suggest at once that the connection between partition functions and the functions of thermodynamics can be

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* Strictly $\overline{M}$. But since it never matters whether we are dealing with a fixed M or an average $\overline{M}$ we shall usually omit the bar in future over symbols representing numbers of systems of a given type unless the context requires it for clarity.

† See Ehrenfest and Trkal, *loc. cit.*, for a critical exposition of this confusion.

simplified by the use of *Planck's characteristic function* as the primary thermodynamic quantity. Ψ is defined in thermodynamics by the equation

$$\Psi = S - E/T; \qquad \text{......(398)}$$

it is thus merely a modification of the work function A.* It has the properties

$$E = T^2 \frac{\partial \Psi}{\partial T}, \; S = \Psi + T \frac{\partial \Psi}{\partial T}, \; Y_1 = T \frac{\partial \Psi}{\partial y_1}, \ldots . \qquad \text{......(399)}$$

In terms of Ψ the foregoing theorem can be rewritten as follows:

Theorem 6·31. *Any particular species of free molecule contributes to the characteristic function*

$$kM \{\log (f(\vartheta)/M) + 1\}; \qquad \text{......(400)}$$

any crystal or other solid

$$kP \log \kappa (\vartheta). \qquad \text{......(401)}$$

We may conveniently recall here the further property of Ψ as a thermodynamic potential, that for any assembly at given temperature and given volume (or generally given parameters y_r) the equilibrium state is determined by the equation

$$d\Psi = 0 \qquad \text{......(402)}$$

for all relevant variations. It is easily verified by differentiation of Ψ that the general laws of mass-action, *etc.*, which we have determined directly in Chapter v are equivalent to this equation.

§ **6·4**. *The increasing property of entropy.* We are now in a position to complete our account of the thermodynamic properties of our assemblies by showing that the function S which we have identified with the entropy possesses the characteristic *increasing property.* We have to show that, with such conventions for the arbitrary constants that $S' + S'' = S$ when an assembly in equilibrium is separated into two by an ideal workless process such as the closing of an ideal door, then on junction by a similar process

$$S' + S'' \leqslant S; \qquad \text{......(403)}$$

S' and S'' are the entropies of the two assemblies before junction or after separation and S the entropy of the combined assembly. Since the joining together of two gaseous assemblies is essentially irreversible only a convention can settle the values of the various entropy constants. A sufficient convention is to take $S_0 = 0$ in (388)—that is, to take S as given completely by theorem 6·3.

To establish (403) it is convenient to exhibit explicitly the dependence of the partition functions on the volume accessible to each free species of

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* See Planck, *Wärmestrahlung*, 5th ed. p. 127 (1923).

system. If, then, we distinguish all quantities referring to the two separate assemblies by single and double primes we have

$$S'/k = \Sigma_r \xi_r' V_r' F_r(\vartheta') + \Sigma_s \xi_1'^{q_s^1} \xi_2'^{q_s^2} \dots V_s' G_s(\vartheta') - E' \log \vartheta' - \Sigma_r X_r' \log \xi_r',$$

$$S''/k = \Sigma_r \xi_r'' V_r'' F_r(\vartheta'') + \Sigma_s \xi_1''^{q_s^1} \xi_2''^{q_s^2} \dots V_s'' G_s(\vartheta'') - E'' \log \vartheta'' - \Sigma_r X_r'' \log \xi_r'',$$

$$\begin{aligned} S/k &= \Sigma_r \xi_r (V_r' + V_r'') F_r(\vartheta) + \Sigma_s \xi_1^{q_s^1} \xi_2^{q_s^2} \dots (V_s' + V_s'') G_s(\vartheta) \\ &\qquad - (E' + E'') \log \vartheta - \Sigma_r (X_r' + X_r'') \log \xi_r, \\ &= S'(\vartheta, \xi_1, \xi_2, \dots,)/k + S''(\vartheta, \xi_1, \xi_2, \dots,)/k. \end{aligned}$$

But it was shown in § 5·5 that $\vartheta', \xi_1', \xi_2', \dots$ define the unique minimum of the function S', so that

$$S'(\vartheta', \xi_1', \xi_2', \dots) \leqslant S'(\vartheta, \xi_1, \xi_2, \dots),$$

equality being only possible when

$$\vartheta' = \vartheta, \ \xi_1' = \xi_1, \ \xi_2' = \xi_2, \dots.$$

Similarly, $$S''(\vartheta'', \xi_1'', \xi_2'', \dots) \leqslant S''(\vartheta, \xi_1, \xi_2, \dots),$$

equality being only possible when

$$\vartheta'' = \vartheta, \ \xi_1'' = \xi_1, \ \xi_2'' = \xi_2, \dots.$$

We see therefore at once that $S' + S'' \leqslant S$, equality being only possible when

$$\vartheta' = \vartheta'' = \vartheta, \ \xi_1' = \xi_1'' = \xi_1, \ \xi_2' = \xi_2'' = \xi_2, \dots.$$

Since the ϑ, ξ's are intensive parameters (see equations (343), (344), (345), generalized) the necessary and sufficient conditions are

$$\vartheta' = \vartheta'', \ \xi_1' = \xi_1'', \ \xi_2' = \xi_2'', \dots, \qquad \dots\dots(404)$$

which are equivalent to asserting that, if there is no change of entropy on junction, the separate assemblies must have had equal temperatures and concentrations, or rather temperatures and partial potentials (§ 6·5).

§ 6·5. *The physical meaning of the ξ's.* The parameters $\xi_1, \xi_2, \dots$ which we have been led to introduce by the nature of the mathematics play such a natural part in the preceding discussions, that one is led to expect them to possess a natural physical interpretation, just as ϑ may be interpreted as the temperature. This is the case, and we can relate them in a simple way to the *partial potentials* of the various constituents in the assembly, as is in fact already obvious from the form (395). Just as ϑ was identified with the temperature because it helps to define and has the same value for every component fraction of the assembly, so ξ_r must be equivalent to the partial potential of the rth constituent because it helps to define and has the same value for every component fraction of the assembly *in which the rth constituent occurs.*

Thermodynamic partial potentials μ_r may be defined by the equation[†]

$$dE + \Sigma Y dy = dQ = TdS + \Sigma_r \mu_r dM_r{}^*; \qquad \text{......(405)}$$

in forming this variation we are to suppose that the total masses[‡] $M_r{}^*$ of the various constituents in our assembly or in any phase or part of it are varied, as well as the temperature and the ordinary geometrical parameters y. If we form the variations of (388) in this manner we obtain

$$TdS = dQ - \Sigma_r kT \log \xi_r dX_r.$$

Now X_r is the total number of atoms of type r and $M_r{}^*$ is the mass of the rth independent constituent in gram-molecules. Therefore

$$X_r = RM_r{}^*/k,$$

and

$$\mu_r = RT \log \xi_r. \qquad \text{......(406)}$$

This is the relation between ξ_r and the corresponding partial potential. If we evaluate ξ_r by means of the equation

$$\overline{M_r} = \xi_r V_r F_r(\vartheta)$$

for the concentration of free atoms of type r we find, using (97),

$$\log \xi_r = \log \nu_r - \log F_r(\vartheta), \qquad \text{......(407)}$$

$$\mu_r/RT = \log \nu_r - \tfrac{3}{2}\log T + \log \frac{h^3}{(2\pi mk)^{\frac{3}{2}}}, \qquad \text{......(408)}$$

which is consistent with the usual value of μ_r for a perfect gas.[§]

If in a similar manner we imagine an addition to the assembly not of free atoms, but of $dN_s{}^*$ gram-molecules of the molecule s, then

$$dX_r = Rq_s{}^r dN_s{}^*/k,$$

and the partial potential μ_s of the sth molecule is given by

$$\mu_s = RT\Sigma_r q_s{}^r \log \xi_r,$$

$$\mu_s/RT = \log \nu_s - \log G_s(\vartheta), \qquad \text{......(409)}$$

which is also consistent with the usual value. We can thus see that the partial potential of the molecule s in the equilibrium state is equal to the sum of the partial potentials of its constituent atoms. This is the usual relation between partial potentials necessitated by the existence of a chemical reaction.[||] It is another aspect of the usual theorem that the partial potential of any constituent must be the same in all phases in which it occurs.

Let us consider also in conclusion the thermodynamic form in the more general case of § 5·9 in which two components form a crystal in variable

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[†] Bryan, *Thermodynamics*, p. 152.

[‡] The masses are here written $M_r{}^*$ to avoid confusion with the numbers of free atoms M_r.

[§] Bryan, *loc. cit.* p. 120.

[||] Gibbs, *Scientific Papers*, "Equilibrium of Heterogeneous substances," pp. 67–70.

proportions. Applying (391) to (378) we find for the entropy contribution S_K by the crystal

$$S_K = k\,[\log K - P\log \xi - P' \log \xi' - \overline{E} \log \vartheta],$$

or for the contribution to the work function

$$A_K = kT\,[P\log \xi + P' \log \xi' - \log K]. \qquad \text{......(410)}$$

It follows that at constant temperature and volume

$$dA_K = kT\,[\log \xi dP + \log \xi' dP'], \qquad \text{......(411)}$$

for in view of (379)

$$Pd\log \xi + P' d\log \xi' - d\log K = 0.$$

But (411) corresponds exactly to the thermodynamic form

$$dA_K = \mu dM^* + \mu' dM'^*,$$

so that the relation (406) between the μ's and ξ's is repeated. The ξ's therefore, or rather the log ξ's, have all the thermodynamic properties of the μ's. In particular, since the complete A_K is a perfect differential,

$$\frac{\partial \mu}{\partial T} = -\frac{\partial S}{\partial M^*},$$

or

$$-\frac{\partial}{\partial T}(T\log \xi) = \frac{\partial}{\partial T}(T\log K(T)) = \frac{1}{R}\frac{\partial S}{\partial M^*}, \qquad \text{......(412)}$$

a relation which will be useful later.

§ **6·6**. *The invariance of weight.* We can now examine somewhat more closely the postulate of the invariance of weight for slow reversible changes, formulated in § 2·3. The preceding discussion, establishing the existence of S, has proceeded on the assumption that

$$\begin{aligned} Y_1 &= \Sigma_r \Sigma_u \overline{a_u{}^r}\left(\frac{-\partial \epsilon_u{}^r}{\partial y_1}\right) + \Sigma_s \Sigma_v \overline{a_v{}^s}\left(\frac{-\partial \epsilon_v{}^s}{\partial y_1}\right), \\ &= \frac{1}{\log 1/\vartheta}\left\{\Sigma_r \xi_r \frac{\partial f_r}{\partial y_1} + \Sigma_s \xi_1{}^{q_s{}^1} \xi_2{}^{q_s{}^2} \dots \frac{\partial g_s}{\partial y_1}\right\}. \qquad \text{......(413)} \end{aligned}$$

This, however, is only true if the ϖ's do not depend on the y's (are in fact adiabatic invariants). For if they do so depend, we have the additional terms in (413)

$$-\frac{1}{\log 1/\vartheta}\left[\Sigma_r \Sigma_u \xi_r \frac{\partial \varpi_u{}^r}{\partial y_1} \vartheta^{\epsilon_u{}^r} + \Sigma_s \Sigma_v \xi_1{}^{q_s{}^1} \xi_2{}^{q_s{}^2} \dots \frac{\partial \varpi_v{}^s}{\partial y_1} \vartheta^{\epsilon_v{}^s}\right] dy_1 - \dots.$$

Therefore the general form of $\log 1/\vartheta\, dQ$ will be

$$dS(\vartheta, \xi_1, \xi_2, \dots) - \mu_1(\vartheta, \xi_1, \dots, y_1, \dots)\, dy_1 - \qquad \text{......(414)}$$

where

$$\mu_1(\vartheta, \xi_1, \dots, y_1, \dots) = \Sigma_r \Sigma_u \xi_r \frac{\partial \varpi_u{}^r}{\partial y_1} \vartheta^{\epsilon_u{}^r} + \Sigma_s \Sigma_v \xi_1{}^{q_s{}^1} \xi_2{}^{q_s{}^2} \dots \frac{\partial \varpi_v{}^s}{\partial y_1} \vartheta^{\epsilon_v{}^s}.$$

We may suppose that the independent parameters which define the state of the system are $S, y_1, y_2, \ldots$. Then the conditions that (414) should be a perfect differential contain the equations

$$\left(\frac{d\mu_1}{dS}\right)_{(y)} = \left(\frac{d\mu_2}{dS}\right)_{(y)} = \ldots = 0 \qquad \ldots\ldots(415)$$

for all values of S (or ϑ) and the y's. It must also hold for all X's and however many types of molecule or atom may be supposed to be present or not.

Consider first the simplest case in which the assembly contains a single type of atom. The expressions then simplify to

$$\mu_1 = X_r \Sigma_u \frac{\partial \varpi_u{}^r}{\partial y_1} \vartheta^{\epsilon_u{}^r} / f_r(\vartheta),$$

and (415) reduces to $\partial\mu_1/\partial\vartheta = 0$. Now μ_1 is of the form

$$\Sigma a_n \vartheta^n / \Sigma b_n \vartheta^n,$$

and therefore if it is a function of y_1 alone we must have

$$\Sigma\, (b_n \mu_1 - a_n)\, \vartheta^n = 0 \quad (\mathit{all}\ \vartheta),$$

or

$$\mu_1 = \mu_1(y_1 \ldots) = a_n/b_n \quad (\mathit{all}\ n,\ y_1 \ldots).$$

That is to say, we must have

$$\frac{\partial \varpi_u{}^r}{\partial y_1} = \kappa_r \varpi_u{}^r, \;\; \kappa_r = \frac{\partial}{\partial y_1} \log \varpi_u{}^r, \qquad \ldots\ldots(416)$$

where κ_r depends only on the y's. Thus the $\varpi_u{}^r$ may have a common factor $\omega_r(y_1, \ldots)$ and the resulting change in S would be $-X_r \log \omega_r$. This would not affect any argument for such assemblies. Similar arguments hold for assemblies of a single type of molecule.

Returning now to the general gaseous assembly we should have

$$\mu_1 = \Sigma_r \xi_r f_r(\vartheta) \frac{\partial}{\partial y_1} \log \omega_r + \Sigma_s \xi_1{}^{q_s{}^1} \xi_2{}^{q_s{}^2} \ldots g_s(\vartheta) \frac{\partial}{\partial y_1} \log \omega_s,$$

and the extra terms in $\log 1/\vartheta\, dQ$ reduce to

$$-\Sigma_r \xi_r f_r(\vartheta)\, d \log \omega_r - \Sigma_s \xi_1{}^{q_s{}^1} \xi_2{}^{q_s{}^2} \ldots g_s(\vartheta)\, d \log \omega_s,$$

or

$$-\Sigma_r X_r\, d \log \omega_r - \Sigma_s \xi_1{}^{q_s{}^1} \xi_2{}^{q_s{}^2} \ldots g_s(\vartheta)\, d \log \frac{\omega_s}{\Pi_r \omega_r{}^{q_s{}^r}}.$$

The ω_r and ω_s being functions of $y_1, y_2, \ldots$, these extra terms can in general only be a perfect differential if

$$d \log \frac{\omega_s}{\Pi_r \omega_r{}^{q_s{}^r}} = 0 \qquad \ldots\ldots(417)$$

for all s. For the extra terms are of the form

$$\Sigma_s A_s(\vartheta, y_1, y_2, \ldots)\, dB_s(y_1, y_2 \ldots)$$

and can only be a perfect differential if for $y_1, y_2, \ldots$

$$\Sigma_s \frac{\partial A_s}{\partial \vartheta} \frac{\partial B_s}{\partial y_1} \equiv 0.$$

Since $\partial A_s/\partial \vartheta \neq 0$ and the A_s have in general no special relations between them, these relations can only be satisfied if $\partial B_s/\partial y_1 = 0 \ldots$, which are the equations (417). It follows, therefore, that the weights can contain factors dependent on the $y_1, y_2, \ldots$ provided that

$$\omega_s = \alpha_s \Pi_r \omega_r^{q_s^r},$$

where the α's are absolute constants. Thus the non-invariant factors ω_r, if they exist, must persist with the atom through every combination into which the atom can enter. They are therefore without significance in any physical problem and can be omitted without loss of generality, and apart from these trivial factors the adiabatic invariance of the weights is established.* The conclusion holds good for the most general assemblies so far discussed.

§ **6·7**. *The inverse relation between specific heats or average energies and the weights and energies of the states of an individual system.* In the foregoing chapters we have shown how to determine the mean energy and specific heats of any system or set of systems, when the weights and energies of the permitted states of one system are known so that the partition function may be constructed. We have had in fact the relations

$$\overline{E} = M\vartheta \frac{d}{d\vartheta} \log f(\vartheta),$$

$$C_v = Mk (\log 1/\vartheta)^2 \left(\vartheta \frac{d}{d\vartheta}\right)^2 \log f(\vartheta), \qquad \ldots\ldots(418)$$

where $\qquad f(\vartheta) = \Sigma_r \varpi_r \vartheta^{\epsilon_r}.$

It is desirable at some stage to pause and attempt to answer the question whether given $\overline{E}$ or C_v, and so the form of the function $f(\vartheta)$, we can deduce the ϖ_r and ϵ_r, and in particular whether such values, if they can be derived, are unique. It appears that the theoretical answer is "yes". The ϖ_r and ϵ_r can be derived and are unique, with the exception of trivial constant factors, which arise as the constants of integration in determining $f(\vartheta)$ from (418). The practical importance of this answer is (as will be seen) limited, but its theoretical importance is still considerable.

The most convenient variable to work with here is τ where $\vartheta = e^{-\tau}$. Then

$$C_v = Mk\tau^2 \left(\frac{d}{d\tau}\right)^2 \log f(\tau), \quad \overline{E} = -M \frac{d}{d\tau} \log f(\tau),$$

$$f(\tau) = \sum_0^\infty \varpi_r e^{-\epsilon_r \tau}.$$

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* Bohr, *Proc. Camb. Phil. Soc.*, Suppl. p. 17, and previously Ehrenfest, *Phys. Zeit.* vol. xv p. 660 (1914), have considered this question and shown that the weights must be adiabatic invariants. It appears, in the light of the foregoing discussion, that their arguments hardly go deep enough.

A knowledge of C_v determines $f(\tau)$ with trivial exceptions; the problem is to derive from this $f(\tau)$ the ϖ_r and ϵ_r. For this purpose we express $f(\tau)$ as a Stieltjes' integral in the form

$$f(\tau) = \int_0^\infty e^{-\tau\epsilon}\, dw(\epsilon), \qquad \text{......(419)}$$

where $dw(\epsilon)$ represents the weight corresponding to the energy ϵ or the range ϵ, $\epsilon + d\epsilon$, and it is indifferent whether we are concerned with quantized systems or with classical. In all cases $w(\epsilon)$, the integrated weight, is an increasing function in the wider sense, which has simple isolated discontinuities if the system is quantized or contains a quantized part.

Now it has been shown that (419) can be inverted so as to express $w(\epsilon)$ as an integral of $f(\tau)$.* It may be supposed that $w(\epsilon)$ is a monotonic increasing function of ϵ for all values of ϵ considered, which has only a finite number of simple discontinuities or steps ϖ_i in any finite interval. The function $w'(\epsilon)$, derived from $w(\epsilon)$ by the removal of the discontinuities, has a differential coefficient Ω which exists and is continuous, except perhaps at a finite number of points in any finite range, and is bounded in any finite range. These conditions will be referred to as conditions W. Then we have the following

Theorem 6·7. *If* $w(\epsilon)$ *satisfies conditions* W, *and if* $\overset{\infty}{\Sigma}\varpi_i e^{-\tau\epsilon_i}$ *and* $\int^\infty e^{-\tau\epsilon}\,\Omega d\epsilon$ *converge for* $\tau = \gamma_0$, *and if*

$$f(\tau) = \int_{-a}^\infty e^{-\tau\epsilon}\, dw(\epsilon), \qquad \text{......(420)}$$

then $f(\tau)$ *is a holomorphic function of* τ *in the half-plane* $R(\tau) > \gamma_0$, *and*

$$\tfrac{1}{2}\{w(\epsilon+0) + w(\epsilon-0)\} - w(-a) = \frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty} f(\tau)\, e^{\epsilon\tau}\frac{d\tau}{\tau}, \qquad \text{......(421)}$$

where $\gamma > \gamma_0$, $\gamma > 0$, *and the infinite integral in* (421) *is evaluated as*

$$\operatorname*{Lt}_{T\to\infty} \int_{\gamma-iT}^{\gamma+iT}.$$

It is clear that the theorem theoretically must apply to the physical problem in hand, and therefore, given $f(\tau)$, the ϖ_r and ϵ_r (and any classical part) are uniquely determinate. But it is not practically applicable unless our knowledge of $f(\tau)$ is so precise that we know it not merely numerically but formally, as a function of the complex variable τ. This difficulty can be turned by a method due to Schwartzschild†, but as it is still doubtful whether even so the method would give results of practical interest, we shall not pursue it further.

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* For a proof see R. H. Fowler, *Proc. Roy. Soc.* A, vol. xcix, p. 464 (1921). A deeper version of the same theorem has been given by Burkill, *Proc. Camb. Phil. Soc.* vol. xxiii, p. 356 (1926); *Proc. Lond. Math. Soc.* vol. xxv, p. 513 (1926).

† See Fowler, *loc. cit.* p. 470.

In the case, however, of radiation (or the linear harmonic oscillator) we believe that we do know the exact form of $f(\tau)$. It is then of interest to see that the weights must be of the form assigned. For if

$$\overline{E} = M \frac{h\nu}{\vartheta^{-h\nu} - 1},$$

so that
$$f(\tau) = C(1 - e^{-h\nu\tau})^{-1}, \quad (C \textit{ constant}), \qquad \text{......(422)}$$

then
$$\tfrac{1}{2}\{w(\epsilon + 0) + w(\epsilon - 0)\} = \frac{C}{2\pi i}\int_{\gamma - i\infty}^{\gamma + i\infty} \frac{e^{\tau\epsilon}}{1 - \epsilon^{-h\nu\tau}} \frac{d\tau}{\tau}.$$

Now $(1 - e^{-h\nu\tau})^{-1} = 1 + e^{-h\nu\tau} + \ldots + e^{-ph\nu\tau} + e^{-(p+1)h\nu\tau}/(1 - e^{-h\nu\tau})$.

Choose p so that $p < \epsilon/h\nu < p + 1$. Then

$$\begin{aligned}\tfrac{1}{2}\{w(\epsilon + 0) + w(\epsilon - 0)\}& \\ &= C\left\{\sum_0^p \frac{1}{2\pi i}\int_{\gamma - i\infty}^{\gamma + i\infty} e^{(\epsilon - rh\nu)\tau}\frac{d\tau}{\tau} + \frac{1}{2\pi i}\int_{\gamma - i\infty}^{\gamma + i\infty} \frac{e^{(\epsilon - (p+1)h\nu)\tau}}{1 - e^{-h\nu\tau}}\frac{d\tau}{\tau}\right\}, \\ &= C(p + 1 + J). \qquad \text{......(423)}\end{aligned}$$

By an application of Cauchy's theorem it is easily shown that $J = 0$. It follows that the weights must be C for $\epsilon = rh\nu$ and zero for all other ϵ. No other scheme of weights can be admitted.

If alternatively we demand the average energy

$$\overline{E} = M\left\{\frac{h\nu}{e^{h\nu\tau} - 1} + \tfrac{1}{2}h\nu\right\},$$

then by simple integration

$$f(\tau) = \frac{Ce^{\frac{1}{2}h\nu\tau}}{1 - e^{-h\nu\tau}} \quad (C \textit{ constant}). \qquad \text{......(424)}$$

The weight function can be evaluated by the same arguments and we find that the only admissible weights are weights C for $\epsilon = (r + \frac{1}{2})\,h\nu$ and zero for all other ϵ.

If we accept the general basis from which we have developed the equilibrium theory of statistical mechanics in this monograph, then the laws of temperature radiation may be taken as demanding that $f(\tau)$ for a simple linear harmonic oscillator shall be given by (422). It then follows that the weight function must be determined by (423), that is, *must* be that assumed by Planck. It is of course possible to call in question the general basis, but not, accepting this basis, Planck's assumption.*

A direct analysis of the Stefan-Boltzmann law by this method is also not without interest; the value of $f(\tau)$ is

$$f(\tau) = C \exp(\sigma V/\tau^3).$$

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* This discussion contains the whole substance of Poincaré, *J. de Phys.* V, vol. II, p. 5 (1912), but much simplified and rendered more rigorous by the use of the machinery of the present methods. The hypothesis and conclusions are essentially the same.

From this it follows by further applications of Cauchy's theorem that

$$w(-0) = 0,$$

$$w(\epsilon) = C\left[1 + \frac{\sigma V}{1!}\frac{\epsilon^3}{3!} + \frac{(\sigma V)^2}{2!}\frac{\epsilon^6}{6!} + \frac{(\sigma V)^3}{3!}\frac{\epsilon^9}{9!} + \dots\right].$$

The weight function therefore must have a discontinuity C at $\epsilon = 0$. The state of zero energy must have a non-zero weight. For other energies the function is too complicated to give us much information, but the non-classical nature* of the weight function is already evident.

§ 6·8. *Entropy and thermodynamic probability.* It is not in general our purpose in this monograph to attempt critical discussions of alternative presentations of statistical mechanics, but rather to develop the theory on a single consistent plan in a manner as logical as possible. It is not, however, possible at this point to pass by entirely in silence other methods of introducing entropy into statistical mechanics, without giving some indication of why the very strict analogy to classical thermodynamics has been preferred here.

Entropy is usually introduced into statistical mechanics by means of Boltzmann's hypothesis relating it to probability. We cannot do more than abstract the various arguments here; for the best systematic account the reader should refer to Planck†. It will be assumed that he is familiar with Planck's account. Boltzmann's hypothesis is based in general on the fact that on the one hand the assembly tends to get into its most probable state (which is equivalent to the average state with which we work here), while on the other hand its entropy tends to increase so that a functional relation between the entropy and the probability W of a state

$$S = f(W)$$

may be postulated by a legitimate analogy. The analogy is of the same type as that by which we have postulated functional relationships between ϑ and T and the ξ's and the μ's. The argument then proceeds somewhat as follows. Suppose we can assign the numerical value of W for the probability of the state of any assembly. If then we have two such assemblies which are entirely independent, then by a fundamental principle of probability, the joint probability is the product of the two separate probabilities or

$$W_{12} = W_1 W_2. \qquad \text{......(425)}$$

On the other hand, by the second law of Thermodynamics the joint entropy

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* See the classical paper by Ehrenfest, *Ann. der Phys.* IV, vol. XXXVI, p. 103 (1911), where just this point is established by reasoning essentially the same. The present methods again allow of great simplification.

† Planck, *Wärmestrahlung*, 3rd Abschnitt, ed. 5 (or later).

is the sum of the separate entropies (with suitable adjustments of the additive constants) and so

$$S_{12} = S_1 + S_2. \qquad \text{......(426)}$$

The functional relationship must then be

$$S = k \log W, \qquad \text{......(427)}$$

k being a universal constant. We have still to assign a definite way of specifying W for any statistical state of any assembly. For use as W in this connection the quantity "thermodynamic probability" is introduced and defined to be equal to the number of weighted complexions corresponding to the specified state. This number W is then made a maximum subject to the condition of constant energy—the assembly is then in its most probable state—and the maximum value of $k \log W$ so obtained is equated to the entropy S. The entropy S so defined has been shown by (391)* to agree with the entropy of classical thermodynamics, and in general possesses the fundamental increasing property. It should be observed that there are two quite distinct steps in the argument after W has been equated to the thermodynamic probability. In the first the determination of the maximum fixes the most probable state of the assembly *by itself*. In the second the assembly is related *to the outside world* by determining its entropy by (427). Finally, the absolute temperature scale is introduced by the relation $\partial S/\partial E = 1/T$.†

Unfortunately, there is much to be criticized in this argument. In the first place there is some vagueness as to what precisely is happening in the building up of one assembly out of two to yield equations (425) and (426). The addition of entropies can usually only be realized by some form of thermal contact, and is then true in general only when the temperatures are equal. But both these conditions require that the assemblies shall not be independent. So it is only possible to give a meaning to (426) by making (425) invalid or at best not necessarily valid, which destroys the *a priori* nature of the argument. For example, it is argued that $S_{12} = S_1 + S_2$ follows directly from the second law. It is hard to see how this can be derived except from the equation $dQ_{12} = dQ_1 + dQ_2$ which is true neglecting surface interactions. This then leads to $dS_{12} = dS_1 + dS_2$, and so to (426), only if the temperatures are equal.‡ It is not maintained that this criticism could not be turned, but it disposes at least of Planck's example of a com-

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* A slight extension of (391) is required to show that $W_{\max}$ and W_{t_0} are effectively the same. The correctness of S is easily verified directly in simple cases.

† This abstract is intended to do proper justice to the argument described, which is in any case elegant and attractive. The reader should supplement it by reference to Planck (*loc. cit.*) at least.

‡ It is just at this step that an important logical obscurity enters. We have no right to derive $S_{12}=S_1+S_2$ from $dS_{12}=dS_1+dS_2$ without an *explicit* recognition that we have made a special choice of the additive constants in the entropies.

posite assembly consisting of any body on the Earth's surface and an enclosure of temperature radiation on Sirius.

In the second place, the probability W of any statistical state of an assembly requires of course precise and careful definition in such a way that (425) holds *a priori*. The definition of W actually used, thermodynamic probability or number of complexions, makes W a large integer and not a probability at all (which must be a proper fraction); thus (425) cannot be maintained by any appeal to the theory of probability, for, frankly, that theory is irrelevant. On the other hand, genuine probabilities such as the ratio of the number of complexions representing any statistical state to the total number of complexions do not lead (straightforwardly) to the right result.

It is well known that actually the "thermodynamic probability" does lead to the right value of the entropy, and it is perhaps worth while to pause and enquire how the criticism just formulated is to be satisfied. If we take the genuine probability, in so far as we have to calculate the most probable state for given energy the total number of complexions C is constant, we are concerned only with the equation

$$S' - S'' = k \log (W'/W''), \qquad \text{......(428)}$$

i.e. with ratios of W, and so the argument is unaffected. But when in the second step we attempt to determine the value of the entropy itself from (427) with $W_{\max}$ we find in all cases the trivial result $S = 0$. It is a simple consequence of the arguments leading to (391) that $W_{\max}/C$ or

$$W \text{ (average state)}/C$$

is always effectively unity, expressing the fact that the possession of the average or most probable state is a normal property of the assembly.

It is thus clear that the straightforward process is useless, and if we are to retain a relation between entropy and probability we must find a way of justifying the omission of the denominator C. As long as we consider the assembly as a whole this is impossible, for C depends on ϑ and cannot be ignored when variations of temperature are contemplated. In fact the usual arguments are attempting an impossibility, for they attempt to determine the entropy of an assembly, which determines its relation to the outside world, by consideration of the assembly by itself. The difficulty can be overcome, therefore, only by considering the assembly in question as part of a much larger assembly. Consider, for example, a group of M general quantized systems immersed in a bath of a very much larger number N of other systems. The statistical state of the whole is specified as usual by $a_0, a_1, \ldots, b_0, b_1, \ldots$, the numbers of systems in the permitted states or cells. The probability of the statistical state specified by $a_0, a_1, \ldots$ is

$$W(a_0, a_1, \ldots) = \left(\frac{M!\, \varpi_0^{a_0} \varpi_1^{a_1} \ldots}{a_0!\, a_1! \ldots}\right) \left(\Sigma_b \frac{N!\, \rho_0^{b_0} \rho_1^{b_1} \ldots}{b_0!\, b_1! \ldots}\right) \Big/ C,$$

where Σ_b denotes summation over all b's such that $\Sigma_s \eta_s b_s = E - \Sigma_r \epsilon_r a_r$. Comparing C and Σ_b we see at once that

$$C = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}\,(f(z))^M\,(g(z))^N,$$

$$\Sigma_b = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E-E_a+1}}\,(g(z))^N.$$

Since N is very large compared to M, theorem (2·5) shows that approximately

$$\frac{\Sigma_b}{C} = \frac{\vartheta^{E_a}}{(f(\vartheta))^M},$$

where ϑ is fixed by

$$\frac{d}{d\vartheta}\left(\frac{g(\vartheta)}{\vartheta^E}\right) = 0.$$

Thus

$$W(a_0, a_1, \ldots) = \frac{M!\,\varpi_0^{a_0}\varpi_1^{a_1}\ldots}{a_0!\,a_1!\ldots}\,\frac{\vartheta^{E_a}}{(f(\vartheta))^M}. \qquad \ldots\ldots(429)$$

Equation (429) shows that the true probability W is proportional to the thermodynamic probability provided E_a, the total energy of the M systems, is fixed, but even now not otherwise unless the temperature of the large assembly is practically infinite, $\vartheta = 1$. If we wish to maintain the relation between the entropy and probability it seems as if we can only justify the use of "thermodynamic probability" by considering a group of systems as part of a very large assembly at a very great temperature. If we do this, then it is easily verified that $W_{12} = W_1 W_2$ for any two parts of such an assembly (whether or no the temperature is very great) and the first difficulty is also turned. This treatment would be perhaps artificial but not illogical.

We can cast (429) into an alternative, more illuminating form. For the natural contribution of the M systems to the entropy of the assembly in equilibrium is

$$k\{M \log f(\vartheta) - E_a \log \vartheta\},$$

which we may call S_{max}. Therefore

$$W(a_0, a_1, \ldots) = \frac{M!\,\varpi_0^{a_0}\varpi_1^{a_1}\ldots}{a_0!\,a_1!\ldots}\,e^{-S_{\text{max}}/k} \qquad \ldots\ldots(430)$$

which shows at once that $W_{\text{max}} = 1$ as before, and that, defining entropy *via* probability, we arrive at

$$W/W_{\text{max}} = W = e^{(S-S_{\text{max}})/k}. \qquad \ldots\ldots(431)$$

It is only in some such sense as this that a meaning can be assigned to Boltzmann's hypothesis, but then it must be noted that it survives in Boltzmann's own form

$$S - S' = k \log W/W'. \qquad \ldots\ldots(432)$$

The whole development has thus become rather clumsy, for the entropy itself is a function only of the group and its temperature, but has to be derived for the group in relation to an infinite assembly at infinite temperature. It would appear to be much better, if a direct definition of entropy is required in terms of complexions and not *via* the classical form $dQ = TdS$, to abandon all reference to the theory of probability and define the entropy simply as k times the logarithm of the number of weighted complexions. This definition must then of course be justified by direct comparison with classical thermodynamics, not by the *a priori* arguments which we have been criticizing here.

As yet no reason has been given against the introduction of entropy by (432), if such a way is still preferred. It must be observed, however, that there is no hope of a logical definition of *absolute entropy* by such an equation. This is as it should be. Much has been written of absolute entropy in the belief that in this way a basis could be found for Nernst's heat theorem. We shall show in the next chapter that this theorem takes its natural place in the equilibrium theory of pure statistical mechanics, and can be formulated without reference to entropy at all, still less to absolute entropy.*

There is, however, yet a further difficulty in the introduction of entropy in this way, logically founded on its increasing property. The identification of S and $k \log W$ is based on an analogy, correct enough so far as it goes, but insufficiently deep. For it is tacitly assumed that the entropy is the only function of the state of the assembly which has this increasing property. This, however, is untrue, for $\Sigma = S + bE$, where b is any constant, also has the same increasing property, and we have no *a priori* reason for preferring one value of b to any other. If we take the general value Σ for the entropy we find for the relation between T and ϑ

$$\frac{1}{T} = \frac{\partial \Sigma}{\partial E} = k \log 1/\vartheta + b,$$

which does not determine a unique temperature scale. In fact we can only see that $b = 0$ by a direct appeal to the second law $dQ = TdS$, which will only hold with $b = 0$. The use of functions with the increasing property can apparently never lead to precise results without an appeal to dQ. If this appeal has to be made in any case, the method of approach by the

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[*] Even in the 5th edition (p. 119) of his *Wärmestrahlung* Planck says: "As opposed to [Boltzmann's hypothesis (432)] we assign to the entropy S a quite definite absolute value. This is a step of essential import, which can only be justified by the verification of its consequences. It leads, as we shall see later, of necessity to the quantum hypothesis, and thereby on the one hand, for radiant heat, to a definite law of distribution of energy for black radiation and on the other for the heat of solids to Nernst's heat theorem." It should be remembered that Planck is thinking primarily of the fact that in the classical theory the entropy of a solid would not remain finite as $T \to 0$, and the requirement that it should remain finite demands the quantum theory. Even allowing for this, it is impossible to accept his statement fully. It will be maintained in this monograph that whatever the practical convenience of the idea of absolute entropy (often great) it is of no theoretical importance whatever.

increasing property loses any possible advantage over the classical method adopted in this monograph.

The difficulties pointed out above occur for the simplest non-dissociating assemblies, and render unsatisfactory, even for these, the introduction of entropy *via* Boltzmann's hypothesis. When we come to general dissociating assemblies the difficulties become still more pronounced, because the logical determination of the proper dependence of the entropy on the number of systems of any type present is almost impossible by this method. These difficulties have been pointed out by Ehrenfest and Trkal* and we need not stress them here. They again arise in what is virtually an attempt to determine the dependence of S on N or M without reference to any reversible method by which N or M may be supposed to be varied, and as such are doomed to failure.

§ **6·9**. *Position of Boltzmann's hypothesis in the present theory.* The very general form of (431) or (432) makes these equations important instruments of investigation especially in complicated assemblies for which explicit forms for the partition function may be difficult or impossible to construct. It is important, therefore, to fix their position in the theory as here developed, a position of course not that of a fundamental hypothesis but of a general theorem, when our definition of the entropy S is suitably extended. We have shown in equation (391) that for the whole assembly $S = k \log C_0$. We can extend our definition of S, in conformity with the usages of classical thermodynamics, so as to apply to any physically separable part of the assembly by the convention that the entropy of the part may be calculated as in § 6·3 as if the part were a separate assembly with specified energy and configuration. This convention is obviously self-consistent. Special adjustments of S_0 are of course implied to make the entropy additive in equilibrium. We then recover (432) as a general theorem, valid at least for any small part of a large assembly, if ratio of probabilities means simply ratio of representative weighted complexions.

In order to provide *a priori* for a connection between entropy and probability we were logically compelled to discuss a part of a very much larger assembly, and have formulated (432) in this connection. The large assembly, however, is irrelevant to the truth of (432) as a general theorem in statistical mechanics. It is easy to verify that (432) applies at once to any specified configurations of the whole assembly or of the whole of any parts into which we choose to divide it. We can calculate the entropy of each part as specified,† and it follows at once by (391) that for each part $S = k \log C_0$. The total number of weighted complexions representing the specification is therefore $\Pi\ (C_0)$ taken over each part and therefore the

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* Ehrenfest and Trkal, *loc. cit.*; Fowler, *Phil. Mag.* vol. XLV, p. 497 (1923).

† Subject to the conditions specified, each part will be in its own equilibrium state.

probability is proportional to exp $(\Sigma S/k)$. When the specified state is the equilibrium state for the whole assembly ΣS reduces to the usual S and $\Pi\,(C_0)$ effectively to C. For the ratio of the probabilities of two such specifications we have therefore exp $\{(\Sigma S - \Sigma S')/k\}$ which is (432). We summarize this conclusion in the following

Theorem (*Boltzmann's hypothesis*). *If the entropy S of any assembly or its parts is defined as in* § 6·3 (*with suitable additive constants*), *and if as usual the probability W of any specification of the assembly is proportional to the number of representative weighted complexions, then*

$$S - S' = k \log W/W'. \qquad \ldots\ldots(433)$$

The theorem as proved refers only to specifications of the assembly or its parts in which molar variables alone are concerned. If the specifications become so detailed as to be molecular, then our S ceases to have a meaning. We shall not be concerned to use S in such cases, but if an extended definition to cover such cases is required it can obviously be provided by the equation $S = k \log C_0$, which we have already seen to be valid in all cases in which a thermodynamic S exists.

Problems arising in complicated systems such as liquids or far from perfect gases, particularly in connection with fluctuations, can sometimes be handled with the help of (433) and the theorems of classical thermodynamics, when a direct treatment would fail for lack of power to construct or handle the complicated partition function. A well-known example is the theory of density fluctuations and the opalescence of liquids near their critical point.* A formula is required for the relative frequency of volume fluctuations of specified range in a given small element of volume. This frequency is given of course by the W of (433), which can be used in the form

$$W = ae^{\Sigma(\Delta S)/k} \quad (a \text{ constant}). \qquad \ldots\ldots(434)$$

If, however, the volume fluctuations may be thought of as isothermal —legitimate certainly for a small element of volume out of the large assembly—this can be cast in a form which is easier to use. For then, since

$$S = (E - A)/T$$

where A is the work function, and since for the volume element and the rest of the fluid $\Sigma\,(\Delta E) = 0$, we have

$$W = ae^{-\Sigma(\Delta A)/kT}, \qquad \ldots\ldots(435)$$

where $\Sigma\,(\Delta A)$ denotes the maximum work that the assembly can be made to do in returning isothermally and reversibly to its equilibrium state.

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* Einstein, *Ann. der Phys.* vol. XXXIII, p. 1275 (1910). See Chapter XX.

CHAPTER VII

NERNST'S HEAT THEOREM AND THE CHEMICAL CONSTANTS

§ **7·1.** *Vapour pressure equations in thermodynamics and statistical mechanics.* As an introduction to the main subject of this chapter we must compare the formulae of classical thermodynamics and statistical mechanics (§§ 5·7 and 5·3) for the vapour-pressure equation and the reaction-isobar.

The classical thermodynamic formula for the vapour-pressure of a solid or a liquid is deduced from a combination of the Clausius-Clapeyron equation, in the simplified form applicable to perfect vapours of specific volume large compared with that of the condensed phase, and Kirchhoff's equation for the latent heat of vaporization (see also § 7·31). If C_{vap} and C_{sol} denote the specific heats per gram-molecule of the vapour and the solid at constant pressure, the thermodynamic result is

$$\log p = -\frac{\lambda_0}{RT} + \int^T \frac{dT}{RT^2}\int_0^T (C_{\text{vap}} - C_{\text{sol}})\, dT + A. \quad \text{......(436)}$$

In (436) λ_0 is the work required to evaporate one gram-molecule at $T = 0$, and A is a constant of integration about which classical thermodynamics has nothing to say. Now we have seen in Chapter III that the specific heats of perfect gases contain a constant part which we will here call $(C_p)_0$; this may be the whole of C_{vap} over long ranges of temperature. In addition there may be a variable part which we will call $(C_p)_1$. The constant term can be integrated and gives rise to a term $\{(C_p)_0 \log T\}/R$. Classical thermodynamics has nothing to say concerning the convergence of the remaining integrals over the range $(0, T)$, but in fact they do so converge, since the variable energy content of solids is $O(T^4)$ and of the vibrations and rotations of molecules $O(e^{-\epsilon/kT})$. Thus we may write this equation in the precise form

$$\log p = -\frac{\lambda_0}{RT} + \frac{(C_p)_0}{R}\log T + \int_0^T \frac{dT}{RT^2}\int_0^T \{(C_p)_1 - C_{\text{sol}}\}\, dT + i. \quad \text{......(437)}$$

The constant i defined by this equation is called the chemical constant. It can be numerically determined from (437), since all the other quantities are experimentally determinable.* The value of the constant i will differ according to the value assigned to the constant part $(C_p)_0$ of C_{vap}; this may conveniently be varied according to the temperature range. In all statements of i $(C_p)_0$ must be specified.

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* In practice both λ_0 and i must be regarded as constants to be determined by fitting a long series of measurements.

In § 5·7 we determined the analogous formula in terms of partition functions:

$$\log p = -\frac{\chi}{kT} + \tfrac{5}{2}\log T + \log\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3} + \log R(T)\,V(T) - \log K(T), \qquad \text{......(438)}$$

in which $(C_p)_0$ is identified with the contribution of the translational energy to C_{vap}. It is easy to see that (438) and (437) are equivalent, *except that* (438) *makes an explicit determination of* i. For $\lambda_0/R = \chi/k$, and in (437)

$$\int_0^T \{(C_p)_1 - C_{\text{sol}}\}\,dT = [E_1 - E_{\text{sol}}]_0^T,$$

where E_1 is the internal and rotational energy of the molecules, and for a perfect gas is independent of the pressure. In terms of partition functions this is

$$\left[\vartheta\frac{\partial}{\partial\vartheta}\{M\log r(\vartheta)\,v(\vartheta) - M\log k(\vartheta)\}\right]_0^T,$$

or

$$RT^2\frac{\partial}{\partial T}\{\log R(T)\,V(T) - \log K(T)\},$$

when, as in § 5·7, the zeros of energy have been so chosen that the first term in each partition function is a constant. The identity of (438) and (437) is thus obvious, with i given by the equation

$$i = \log\frac{(2\pi m)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3} + \log\frac{R(0)\,V(0)}{K(0)}. \qquad \text{......(439)}$$

In testing the theory here by comparison with experiment, it is immaterial whether or no we can actually construct partition functions which perfectly represent the specific heats. Ideally they are constructable, and in the analysis of these equations we can when necessary use observed values. In view therefore of the general validity of thermodynamical laws it remains only to test the value of i.

With the rules for weights which we have adopted here, we shall have $V(0) = K(0) = 1$, but only if we ignore electronic structure and treat atoms as structureless mass-points. On the same view, for monatomic vapours there is no R-factor at all so that $R(T) \equiv 1$. For other vapours, collecting the results of §§ 2·63, 3·3, and 4·5 we shall expect first of all for diatomic or linear* molecules

$$R(0) = \varpi_1/\sigma, \qquad \text{......(440)}$$

where ϖ_1 is the weight of the lowest rotational state taken from (91) or (92). This formula could, however, only be of value to us at present for H_2 in the region of temperature in which H_2 is effectively rotationless,

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* By a linear molecule we mean one in which the centres of all the atoms lie in equilibrium on a straight line, for example possibly, some states of CO_2.

with $(C_p)_0/R = \frac{5}{2}$. Actually, the partition function for H_2 is complicated by the lack of intercombinations (§ 3·4) and cannot be discussed so simply (see § 7·41). For other diatomic or linear molecules we shall prefer to take $(C_p)_0/R = \frac{7}{2}$ and

$$R(T) = \delta\,\frac{8\pi^2 AkT}{\sigma h^2}, \qquad \text{......(441)}$$

where $\delta = 1, 2$ according as we have to use (91) or (92). For general polyatomic molecules we shall prefer to take $(C_p)_0/R = 4$ and

$$R(T) = \frac{8\pi^2 (8\pi^3 ABC)^{\frac{1}{2}} (kT)^{\frac{3}{2}}}{\sigma h^3}. \qquad \text{......(442)}$$

The logarithms of the factors

$$\delta\,\frac{8\pi^2 Ak}{\sigma h^2},\quad \frac{8\pi^2 (8\pi^3 ABC)^{\frac{1}{2}} k^{\frac{3}{2}}}{\sigma h^3},$$

then appear as extra terms added to i.

Theoretically we should be able to go a stage higher yet and find for a diatomic molecule a temperature range in which the vibrational energy is classical. In such a range, if simple harmonic oscillations were still a good enough approximation we should have

$$\log V(T) = -\log(1 - e^{-v/kT}) \sim \log\frac{kT}{v},$$

so that $(C_p)_0/R = \frac{9}{2}$ and there would be an extra term $\log k/v$ in i. Similar forms should hold at least as rough approximations for polyatomic molecules. If there are f normal modes in the molecule which are effectively both simple harmonic and fully excited, of energy increments $v_1, \ldots, v_f$, then

$$\log V(T) \sim \log\frac{(kT)^f}{v_1 \ldots v_f},$$

and we take $(C_p)_0/R = 4 + f$ and an extra term $\log(k^f/v_1 \ldots v_f)$ in i. The full modification necessary when the electronic structure of the atoms and molecules is considered will appear in Chapter XIV. We may summarize this discussion as follows:

Theoretical values of i and $(C_p)_0$.

A. *Structureless atoms, $K(0) = 1$*

(i) *Monatomic Vapours*

$$(C_p)_0 = \tfrac{5}{2}R,\quad i = \log\frac{(2\pi m)^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3}. \qquad \text{......(443)}$$

(ii) *Diatomic Vapours*

Low temperatures [*the only known example*, H_2, *cannot be discussed in this way*]

$$(C_p)_0 = \tfrac{5}{2}R,\quad i = \log\frac{(2\pi m)^{\frac{3}{2}} k^{\frac{5}{2}} \varpi_1}{\sigma h^3}. \qquad \text{......(444)}$$

Ordinary temperatures; vibrations unexcited

$$(C_p)_0 = \tfrac{7}{2}R,\ i = \log\left\{\frac{(2\pi m)^{\frac{3}{2}}\,k^{\frac{5}{2}}}{h^3}\cdot\frac{4\pi\,(2\pi A)\,k\delta}{\sigma h^2}\right\}. \qquad \ldots\ldots(445)$$

High temperatures; vibrations classical (rough approximation only)

$$(C_p)_0 = \tfrac{9}{2}R,\ i = \log\left\{\frac{(2\pi m)^{\frac{3}{2}}\,k^{\frac{5}{2}}}{h^3}\cdot\frac{4\pi\,(2\pi A)\,k\delta}{\sigma h^2}\cdot\frac{k}{v}\right\}. \qquad \ldots\ldots(446)$$

(iii) *Polyatomic linear molecules*

For low and ordinary temperatures see diatomic.
High temperatures; f vibrations classical (rough approximation only)

$$(C_p)_0 = (\tfrac{7}{2}+f)\,R,\ i = \log\left\{\frac{(2\pi m^{\frac{3}{2}}\,k^{\frac{5}{2}}}{h^3}\cdot\frac{4\pi\,(2\pi A)\,k\delta}{\sigma h^2}\cdot\frac{k^f}{v_1\ldots v_f}\right\}. \ (447)$$

(iv) *Polyatomic (non-linear) molecules*

Low temperatures (no known example)

$$(C_p)_0 = \tfrac{5}{2}R,\ i = \log\frac{(2\pi m)^{\frac{3}{2}}\,k^{\frac{5}{2}}\,\varpi_1}{\sigma h^3}. \qquad \ldots\ldots(447)'$$

Ordinary temperatures; vibrations unexcited

$$(C_p)_0 = 4R,\ i = \log\left\{\frac{(2\pi m)^{\frac{3}{2}}\,k^{\frac{5}{2}}}{h^3}\cdot\frac{8\pi^2\,(8\pi^3 ABC)^{\frac{1}{2}}\,k^{\frac{3}{2}}}{\sigma h^3}\right\}. \ \ldots(447)''$$

High temperatures; f vibrations classical (rough approximation only)

$$(C_p)_0 = (4+f)\,R,\ i = \log\left\{\frac{(2\pi m)^{\frac{3}{2}}\,k^{\frac{5}{2}}}{h^3}\cdot\frac{8\pi^2\,(8\pi^3 ABC)^{\frac{1}{2}}\,k^{\frac{3}{2}}}{\sigma h^3}\cdot\frac{k^f}{v_1\ldots v_f}\right\}. \qquad \ldots\ldots(447)'''$$

B. *Atoms and molecules as electronic structures*

An additional factor

$$\frac{\varpi_a}{\varpi_s}$$

occurs in the argument of every log, where ϖ_s (= $K(0)$) is the weight of the atom or molecule in the solid state, and ϖ_a is the extra weight factor of the free atom or molecule due to its electronic or nuclear structure.

In certain cases ϖ_a may have even to be replaced by $L(T)$, where $L(T)$ is the internal partition function for the electronic energy of the free atom or molecule.

We discuss the numerical values of i in relation to experiment in § 7·4. It is to be emphasized again that all the formulae A above are derived ignoring the electronic structure of atoms and regarding them as structureless mass-points.*

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* Except perhaps the factor δ which only enters when we contemplate the possibility of axial rotation of linear molecules. Such molecules must therefore be something more than a linear distribution of mass-points.

§ **7·11**. *The vapour pressure equation for a partial constituent.* It may sometimes be necessary to suppose that the vapour studied is only one of the constituents of the crystal with which it is in equilibrium. In that case it follows from §§ 5·9, 6·5 that equation (367) still holds, but that $K(T)$ must be replaced by $\kappa(T)$ defined by the equation (380). The strict analogy between the statistical and thermodynamic theories is still maintained. For if we start from (412) and write for the entropy of the solid (C the specific heat)

$$S - S_0 = \int_0^T \frac{C\,dT}{T},$$

then

$$T \log \kappa(T) = \frac{1}{R}\int_0^T dT \frac{\partial}{\partial M^*}\left\{\int_0^T \frac{C\,dT}{T} + S_0\right\},$$

$$= \frac{1}{R}\int_0^T dT \int_0^T \frac{\sigma\,dT}{T} + AT,$$

where $\sigma\ (= \partial C/\partial M^*)$ is the variation of the specific heat with constitution. The notation is suggested by the application to thermoelectric phenomena, where σ reappears as the specific heat of electricity. It follows that

$$\log \frac{\kappa(T)}{\kappa(0)} = \frac{1}{RT}\int_0^T dT \int_0^T \frac{\sigma\,dT}{T},$$

$$= \int_0^T \frac{dT}{RT^2}\int_0^T \sigma\,dT, \qquad \text{......(448)}$$

analogous to the foregoing results.

§ **7·2**. *The reaction-isobar in thermodynamics and statistical mechanics.* The classical formula for the reaction-isobar of a homogeneous gas reaction† is derived from a combination of van't Hoff's equation and Kirchhoff's equation as above. We find, if K_p is the equilibrium constant,

$$\log \mathrm{K}_p = \log \{\Pi_t p_t^{q_t}\},$$

$$= \frac{-(Q_p)_0}{RT} + \frac{\Sigma_t q_t (C_p^{\,t})_0}{R} \log T + \int_0^T \frac{dT}{RT^2}\int_0^T \{\Sigma_t q_t (C_p^{\,t})_1\}\,dT + I. \qquad \text{......(449)}$$

In this equation q_t is the number of gram-molecules of the tth species reacting, with a negative sign for those that disappear when the reaction takes place, and p_t is the partial pressure of the tth species. $(Q_p)_0$ is the work which must be done to make the reaction go in this sense at constant pressure at the absolute zero, and $(C_p^{\,t})_0$ and $(C_p^{\,t})_1$ are the constant and variable part of the specific heat at constant pressure of the tth species. I is a constant of integration, about which classical thermodynamics has nothing to say.

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† Heterogeneous reactions can also be considered, but we omit them here for simplicity of exposition.

The corresponding formula of statistical mechanics is (333), but this needs expressing in the partial pressure form.

By combining examples of (333) to give K_p for the reaction here considered we get

$$\Pi_t\,(\nu_t^{q_t}) = \Pi_t\{F_t\,(\vartheta)\}^{q_t},$$

where F as usual denotes the partition function f from which the V-factor has been extracted. Since $p_t = \nu_t/\log 1/\vartheta$, this becomes

$$\log K_p = \log\{\Pi_t p_t^{q_t}\} = \Sigma_t \log\,(F_t\,(\vartheta)\log 1/\vartheta)^{q_t}. \qquad \text{......(450)}$$

If we convert (449) into partition functions as we converted (437), we find at once that (450) and (449) are equivalent, but that (450) assigns to the undetermined I the precise value

$$I = \Sigma_t q_t i_t, \qquad \text{......(451)}$$

where the i_t are the chemical constants of the various gases taking part in the reaction, as determined in the last section.

Equation (451), due to Nernst, is of great importance and in fact justifies the name chemical constant which is attached to the i. We have here derived it as a theorem in pure statistical mechanics, but, it must be noted, on the hypothesis that, for the crystalline form of any of the gases concerned, $\log K\,(T) \to 0$ as $T \to 0$. This hypothesis will be further analysed in a later section; what is essential is of course that some such hypothesis is a necessary condition for the truth of (451). The logical positions of this equation, and also of the third law of thermodynamics, from which (451) was originally derived by Nernst, are made much clearer by presentation in this way as theorems in statistical mechanics.

If $\log K(0) \neq 0$ in all cases and the i's are still defined by (437) the general form of (451) will be

$$I = \Sigma q_t\,(i + \log K\,(0))_t, \qquad \text{......(452)}$$

$$= \Sigma q_t i_t', \qquad \text{......(453)}$$

say. These i_t' then refer entirely to the gas phase and it is their theoretical values which are given by equations (443)–(447), or, when electronic structures are considered, by these formulae with the inclusion of the factors ϖ_a, and the omission of ϖ_s.

§ **7·3**. *Nernst's heat theorem or the third law of thermodynamics.*[*] This theorem can be enunciated in various ways. The commonest are:

(*a*) *For any condensed system and any reversible isothermal process,*

$$\frac{\partial A}{\partial T} \to 0 \ \textit{as} \ T \to 0,$$

where A is the maximum work that the reaction can be made to do.

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[*] For an account of this theorem see Nernst, *Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes* (1918). For a more recent analysis, Lewis and Randall, *Thermodynamics*, esp. Chap. XXXI (1924).

(*b*) *For any condensed system and any reversible isothermal process*

$$\Delta S \to 0 \text{ as } T \to 0.$$

The equivalence of (*a*) and (*b*) is a consequence of the laws of Thermodynamics.

(*c*) (*Less precisely.*) *At* $T = 0$ *all reactions in condensed systems take place without change of entropy.*

The theorem as thus enunciated is a generalization from experimental data on specific heats, heats of combination, and the electromotive force of reversible cells. The body of evidence in its favour is great, but the generalizations above have probably been rather too hastily made. A very careful rediscussion of the law has been given by Lewis and Randall*. They conclude that its original enunciation, as applying to condensed systems other than solids or even rather other than pure crystals is probably fallacious and that the theorem may be more properly enunciated thus:

(*d*) "*The entropy of each element in some crystalline state can be taken to be zero at the absolute zero of temperature. Every substance then has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero and does so become zero in the case of perfect crystalline substances, including compounds.*"

By this enunciation the behaviour of the entropy of supercooled liquids and solutions is properly left open. It will be observed that Lewis and Randall have been careful so to formulate the theorem that the idea of absolute entropy is not introduced. We can really (if the theorem is true) leave arbitrary the constant S_0 which denotes the entropy of any *element* in a specified crystalline form at $T = 0$ and then the constant S_0' for any compound will be the sum of the S_0's for the elements implicated. The content of the theorem is rendered more striking and practical convenience is furthered by putting $S_0 = 0$ for all elements; so long as this is not taken to imply the existence of an absolute entropy no harm but only good is done.

Equation (451) was derived by Nernst from his theorem by considering the following reversible cycle:

(i) Condense a unit set of reactants to solid form isothermally. The work done and the change of entropy are known in terms of the vapour-pressure equation and involve the i's. [For initial temperatures above a certain limit, a preliminary cooling of the gaseous reactants will be required involving their specific heats. Preliminary expansions will in general also be necessary to adjust pressures to equality with the vapour pressures of the solids.]

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* Lewis and Randall, *loc. cit.*

(ii) Cool the condensed form to the absolute zero. The entropy change is again known in terms of the specific heats of the solids.

(iii) Allow the reaction to proceed completely at the absolute zero. This may be supposed ideally possible, and by the theorem *there is no change of entropy.*

(iv) Heat up the condensed resultants again as in (ii).

(v) Evaporate the resultants to gases again as in (i) and adjust pressures and temperatures.

(vi) Let the reaction go back again isothermally in the gas phase, so that the assembly returns to its initial state. The entropy change here will depend on I.

The change of entropy for the cycle must vanish, and it is easily proved that the condition for this is (451).

Nernst's Heat Theorem thus formulated rests on a purely empirical basis. The theoretical position becomes clearest when it is regarded as a theorem in statistical mechanics. It will be shown to follow at once from the theorems here proved, with the help of a certain extra hypothesis which is itself plausible; namely, that *the weights of the lowest quantum states of all condensed systems* (*or, more probably, all pure crystals*) *are the same.* If this condition is fulfilled then it follows that the entropy changes of reactions in condensed systems (or at least pure crystals) must tend to zero as $T \to 0$, which is the theorem. This extra condition, however, is certainly not more than plausible for doubt is cast on it by the very example, H_2, of which we know most.

Consider first, for simplicity, an ideal case in which the partition function for a single atom in the condensed state, before and after any chemical reaction, has the forms

$$\Sigma_r \varpi_r \vartheta^{\epsilon_r}, \quad \Sigma_r \rho_r \vartheta^{\eta_r}.$$

All the degrees of freedom of the solid are thought of as of one type in this idealization, and the total number cannot be altered by any reaction. The entropy contribution to any assembly is, by (397) and the formula for $\overline{E}$, before the reaction

$$Nk\left[\log f(\vartheta) + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta} \log f(\vartheta)\right].$$

As $\vartheta \to 0$ this tends to

$$Nk\left[\log \varpi_0 \vartheta^{\epsilon_0} + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta} \log \varpi_0 \vartheta^{\epsilon_0}\right],$$
$$= Nk \log \varpi_0.$$

After the reaction the entropy contribution tends to $Nk \log \rho_0$. If $\varpi_0 = \rho_0$, Nernst's theorem follows. This example has the merit of showing just how plausible the hypothesis $\varpi_0 = \rho_0$ is. For structureless atoms nothing else could well be true. For actual atoms when their possible differences of electronic structure in two phases are remembered it is not so convincing *a priori* that $\varpi_0 = \rho_0$, and it may in fact be untrue. If it is untrue, then even the restricted enunciation of Lewis and Randall loses its general validity, though it may still be true of the great majority of examples.

For a more genuine example, say a crystalline solid, we have determined the partition functions in § 4·5 by an analysis of the motion of the solid into its normal modes, each of which behaves like a linear harmonic oscillator of a certain frequency, and obeys, it is presumed, the quantum rules for such a system. Its lowest quantum state has therefore had attached the weight 1. This convention of course is unessential, for only relative weights matter. Taking it as ϖ_0 for generality, it follows at once, from (212) so generalized, that, as $\vartheta \rightarrow 0$,

$$\log K(\vartheta) \sim \frac{-F_0}{kT} + 3Nn \log \varpi_0,$$

$$\log K(\vartheta) + \log 1/\vartheta \,.\, \vartheta \frac{\partial}{\partial \vartheta} \log K(\vartheta) \rightarrow 3Nn \log \varpi_0,$$

where N is the number of crystal unit cells and n the number of atoms in a unit cell. In these considerations we must consistently either ignore or include the degrees of freedom due to the electronic structure of the atoms, and we are at present ignoring them. We find of course the same result by working from the prepared approximate form (218) for $K(\vartheta)$. If now a reaction is supposed to occur near $T = 0$ between crystals, the entropy change, as $T \rightarrow 0$, will tend to

$$\Sigma_t q_t \{3N_t n_t \log (\varpi_0)_t\}.$$

Since the number of atoms of each sort cannot change, $\Sigma_t q_t a_t^p N_t n_t = 0$, where a_t^p is the number of atoms of type p in the tth constituent of the reaction. Therefore the necessary and sufficient conditions that all such reactions should occur with a vanishing entropy change as $T \rightarrow 0$ can easily be shown by the method of undetermined multipliers to be

$$\log (\varpi_0)_t = \Sigma_p \lambda_p a_t^p \quad (\textit{all } t). \qquad \text{......(454)}$$

This means of course that the weight of the atom of type p need not be unity but may have any value (e^{λ_p}) provided every such atom carries this weight with it into every combination.

When we regard matter purely from the atomic standpoint, ignoring electronic structures, it seems very difficult to suppose that (454) can be untrue. We must presumably attach the same weight to the same systems (linear harmonic oscillators) wherever we find them. As before, this is not so clear when electronic and still more nuclear structures are considered, and the evidence of § 7·4 suggests that further researches in this direction may not be without profit. Whether or no Nernst's heat theorem is universally true, it is no doubt true in very many cases, and its exact position as a theorem in statistical mechanics is now clear,* together with the particular hypothesis which may have to be abandoned, if the universality of the theorem proves false.

§ **7·31**. *Basis of comparison between theory and experiment.* (i) *Use of diatomic and polyatomic formulae for i.* We have already mentioned that by use of (437) i can be derived almost directly from experimental determinations alone. If we use (437) with $(C_p)_0 = \frac{5}{2}R$ the only theoretical result which we use is a theoretical extension of the laws of perfect gases down to the absolute zero.† For the remainder of $(C_p)_{\text{vap}}$ and the other quantities experimental values can (at least ideally) be used. For monatomic gases the formula can always be and is always so used, with $(C_p)_1 = 0$. For other gases the monatomic formula can still be used so long as we retain the whole rotational and vibrational energy in $(C_p)_1$ and use observed values for it. We could obtain in this way further direct tests of the monatomic i, unaffected by specific heat *theory*.

This procedure, however, is often impracticable or inconvenient and we use $(C_p)_0 > \frac{5}{2}$ with other corresponding forms for i. It must be remembered, however, in comparing such forms with experiment that they no longer are independent of specific heat theory and errors in that theory will reveal themselves as errors in i. Consider, for example, the rotational term. The formula for $\log p$ strictly contains an expression which we may write

$$\left[\int_0^T \frac{dT}{RT^2}\int_0^T C_{\text{rot}}\, dT\right]_{\text{obs}},$$

which can be reduced as in § 7·1 to

$$[\log R'(T)/R'(0)]_{\text{obs}},$$

where $R'(T)$ is the true partition function exactly reproducing the observed specific heats. But when we take the rotations as classical and use a corresponding formula for i, we replace this by a theoretical expression which of course varies with T in very nearly the correct manner for large enough T. When we then compare theory and experiment for i, we adjust some atomic constant in $[R'(T)]_{\text{theory}}$ so as to make

$$[R'(T)/R'(0)]_{\text{obs}} = [R'(T)/R'(0)]_{\text{theory}}, \qquad \ldots\ldots(455)$$

assuming for simplicity that the value of i given by the monatomic formula is correct. For a diatomic gas for example, in comparing the moments of

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* W. Schottky, *Phys. Zeit.* vol. XXII, p. 1 (1921), vol. XXIII, p. 9 (1922); *Ann. der Phys.* vol. LXVIII, p. 481 (1922), has given independently a similar analysis of the basis of Nernst's theorem as a theorem in statistical mechanics, and pointed out the dependence of chemical constants on the weights of the lowest quantum states.

† For the validity of this see Chapter XXI.

inertia A derived from the chemical constant and band spectra we take that value of A which solves (455). If however $(C_{\text{rot}})_{\text{theory}} > (C_{\text{rot}})_{\text{obs}}$ for the true value of A, then the value of A from (455) will come out too *small*, and conversely. We see that it is now rather specific heat theory than chemical constant theory that we are testing.

(ii) *Changes of phase in the condensed form.* Changes of phase in the condensed form may be regarded as automatically allowed for by equation (437) when we use proper observed values of C_{sol}. The general equations from which (437) arises reduce for perfect gases of large specific volume to

$$\frac{1}{p}\frac{dp}{dT} = \frac{\lambda}{RT^2}, \quad \frac{d\lambda}{dT} = (C_p)_{\text{vap}} - (C_p)_{\text{sol}},$$

which lead at once by integration to (437). When we pass through a transition point, however, at which the solid changes to another crystalline form, or melts, we must refer back to the precise meaning of $(C_p)_{\text{sol}}\, dT$ in this equation. It is of course a quantity of heat supplied to the solid to cause a specified change. At an ideal transition point $(C_p)_{\text{sol}}\, dT$ becomes illusory and we have instead a latent heat of transformation. In (437), where the term $\int_0^T (C_p)_{\text{sol}}\, dT$ occurs, the inclusion of such latent heat terms must be understood. In terms of what are normally called specific heats, this integral can be replaced by

$$\int_0^T (C_p)_{\text{sol}}\, dT \qquad (T < T_t),$$

$$\lambda_t + \int_0^T (C_p)_{\text{sol}}\, dT \qquad (T > T_t),$$

where T_t is a transition temperature and λ_t is the latent heat of transition, which will usually be positive as written above.

Trouble, however, will arise if we have extrapolated back to zero an apparently well-determined curve of specific heats through an unknown transition point. This can of course only happen at low temperatures at which, apart from changes of phase, $\int_0^T (C_p)_{\text{sol}}\, dT$ will be given sufficiently closely by AT^4. If, however, there was really a transition point (λ_t) at T_t, then the correct value of the integral for $T > T_t$ is not AT^4 but

$$AT^4 + \lambda_t + (A' - A)\, T_t^4.$$

In this $A'T^4$ is the form of the integral for $T < T_t$. We may assume that $\lambda_t > 0$ and perhaps that $A' < A$, since the transition is likely to be to a more stable and therefore more rigid form. It seems to be the case, however, that A' and A, or more generally the specific heats on either side of the transition point are very nearly equal, and therefore that the sign of the error, which we will call μ_t, is the same as that of λ_t. Instead of the correct value of

$$\int_0^T \frac{dT}{RT^2}\int_0^T (C_p)_{\mathrm{sol}}\,dT$$

we shall therefore be using

$$\int_0^T \frac{dT}{RT^2}\int_0^T (C_p)_{\mathrm{sol}}\,dT - \int_{T_t}^T \frac{\mu_t\,dT}{RT^2}.$$

The right-hand side of our formula for $\log p$ is therefore too *large* by

$$\frac{\mu_t}{R}\left(\frac{1}{T_t}-\frac{1}{T}\right).$$

The term in $1/T$ does not matter. It is absorbed in λ_0, which is in practice an adjustable constant. The observed value of i will therefore be too *small* by μ_t/RT_t, which may be expected to be positive.*

(iii) *Monatomic chemical constants* via *dissociation equilibria.* In order to obtain as many examples of monatomic chemical constants as possible, it is important to recognize that a knowledge of vapour pressures and dissociation equilibria for diatomic gases such as the halogens provides us at once with a direct determination of the chemical constant of the atom into which theoretical uncertainties as to the structure of the molecule do not enter. Expressed in partition functions we have

$$\frac{\overline{N_1}}{V}=\frac{G_1(T)}{K(T)},\quad \frac{(\overline{M}/V)^2}{\overline{N_1}/V}=\frac{F^2(T)}{G_1(T)},$$

and therefore

$$\frac{\overline{M}}{V}=\frac{F(T)}{\{K(T)\}^{\frac{1}{2}}},$$

an expression into which no reference to the molecular form enters. Since

$$\frac{\overline{M}}{V}=\left\{\frac{(\overline{M}/V)^2}{\overline{N_1}/V}\cdot\overline{N_1}/V\right\}^{\frac{1}{2}}=\left\{\frac{\mathrm{K}_p p}{kT}\right\}^{\frac{1}{2}},$$

where K_p is the equilibrium constant, and p the vapour pressure, $\overline{M}/V$ can be "observed" and the monatomic chemical constant directly determined. In practice vapour pressures and equilibrium constants are not observed for the same temperatures and an extrapolation of one or other is needed by the theoretical formula. This will involve a knowledge of the specific heats of the molecule over the range of extrapolation, but will involve the molecule in no other way. The same result can easily be obtained from the thermodynamical forms. In practice the analysis will be carried out separately to determine $2i(X)-i(X_2)$ from $\log \mathrm{K}_p$ and $i(X_2)$ from $\log p$. These are then added together and halved, to give the entry in the table.

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* For this discussion see Cox, *Proc. Camb. Phil. Soc.* vol. XXI, p. 541 (1923).

§ 7·4. *Experimental values of i, and the comparison with theory. Monatomic gases.* The theoretical formula is (443). It is usual to express it numerically for the case in which p is measured in atmospheres ($= 1{\cdot}013 \times 10^6$ dynes per cm.^{2}) and the log's are $\log_{10}$. Then

$$i = -\ 1{\cdot}587 + \tfrac{3}{2}\log_{10} m^* = i_0 + \tfrac{3}{2}\log_{10} m^*, \qquad \text{......(456)}$$

where m^* is the chemical atomic weight, defined by taking the value of m^* for the oxygen atom 16·000. The following table contains all the reliable determinations of which I am aware.†

TABLE 11.

Monatomic chemical constants.

$$i = i_0 + \tfrac{3}{2}\log_{10} m^*.$$

The theoretical value of $-i_0$ is given by

$$-i_0 = 1{\cdot}587 - \log_{10} \varpi_a/\varpi_s.$$

Gas	i observed (mean value and range)*	$-i_0$	Authorities
Hg	1·82 ± ·03	1·63 [1·62]	1 [2]
Cd	1·65 ± ·3	1·42 [1·63]	1 [2]
Zn	1·23 ± ·26	1·49 [1·62]	1 [2]
Pb	1·3 ± ·2	1·67	2
A	0·75 ± ·02	1·65 [1·61]	3 [2]
H_2	− 1·09 ± ·02	1·55	4
Na	0·63 ± ·2	1·41 [1·11]	5 [6]
K	0·92 ± ·2	1·47 [1·26]	5 [6]
Cl	1·44 ± ·2	0·88	7
Br	2·03 ± ·2	0·82	7
I	2·21 ± ·2	0·94	7

* By range is meant that the evidence indicates that i lies between e.g. 1·79 and 1·85 for Hg apart from concealed errors in the specific heats used. Owing to difficulties of extrapolation the real uncertainty in i may well be greater than the range.

(1) Egerton, *Phil. Mag.* vol. XXXIX, p. 1 (1920).

(2) Egerton, *Proc. Phys. Soc. Lond.* vol. XXXVII, p. 75 (1925). The alternative values in [ ] for Hg, Cd, Zn and A are those given in this later paper by Egerton, corresponding to similar differences in the observed i. They should probably be preferred.

(3) Nernst, *loc. cit.*

(4) Eucken, *Zeit. für Phys.* vol. XXIX, p. 12 (1924); low temperatures only.

(5) Edmonson and Egerton, *Proc. Roy. Soc.* A, vol. CXIII, p. 533 (1927).

(6) Zeidler, *Zeit. für Phys. Chem.* vol. CXXIII, p. 383 (1926). The values of $-i_0$ in [ ] correspond to Zeidler's observations. Egerton (5) gives reasons for thinking that the true value lies between (5) and (6).

(7) These values have been obtained, as explained in the last section, from the best available data as follows:

Cl: $2i\,(\mathrm{Cl}) - i\,(\mathrm{Cl}_2) = 1{\cdot}366$ [Wohl, *Zeit. für Elektroch.* vol. XXX, p. 37 (1924)].
$i\,(\mathrm{Cl}_2) = 1{\cdot}51$ [Eucken, *loc. cit.* (4)].

Br: $2i\,(\mathrm{Br}) - i\,(\mathrm{Br}_2) = 1{\cdot}513$ [Cox, *loc. cit.*].
$i\,(\mathrm{Br}_2) = 2{\cdot}546$ [Suhrmann and v. Lüde, *Zeit. für Phys.* vol. XXIX, p. 71 (1924)].

I: $2i\,(\mathrm{I}) - i\,(\mathrm{I}_2) = 1{\cdot}302$ [Cox, *loc. cit.*].
$i\,(\mathrm{I}_2) = 3{\cdot}124$ [Eucken, *loc. cit.*].

† For the chemical constant of the electron, see Chapter XI.

These values are extremely interesting and suggestive. They indicate, firstly, that the theoretical value is correct for the first group, and no doubt for the other inert gases as well. That is to say, for these vapours the chemical constant is correctly given by (443) and the assumption of equal (unit) weights for the atom in the solid and vapour phase is justified. The value for H_2 will be discussed separately in § 7·41.

The accuracy of the results and the agreement of different observers for Na and K is poor, but they suggest distinctly that $-i_0$ is less than 1·6 for these alkaline vapours, and they are in no way inconsistent with its being less than 1·6 by 0·3 or $\log_{10} 2$. This is in fact the final conclusion of Edmonson and Egerton taking account of Zeidler's work with their own. This, however, is just what we should expect if the weight of the alkaline atom in the condensed form is unity ($K(0) = 1$). It is impossible to retain the conception of structureless mass points for these vapours. We must recognize the electronic structure, which leads, as we shall see in Chapter XIV, to a weight 2 for all free alkaline atoms in their normal state. Only the normal state ^2S will be present at the temperatures in question and the full atomic partition function need not be introduced.

This would by itself be far from convincing. The interpretation offered is at least rendered plausible by the similar state of affairs for the halogens. For these $-i_0$ is smaller than normal by from 0·6 to 0·8, and this again is just what we should expect for halogen atoms (with $K(0) = 1$) when the electronic structure of the free atom is recognized. The deepest term of the free halogen is an inverted doublet ^2P, so that the normal state is a term $^2P_2$, weight 4, the term $^2P_1$, weight 2, being only slightly higher.* The "weight" of the free atom must therefore here be replaced by two terms of the partition function

$$4 + 2e^{-\Delta P/kT}.$$

Over the small temperature ranges in question this will behave like a constant effective weight. We can therefore construct the following Table 12. On adding 0·7 for Cl and 0·6 for Br and I we find for $-i_0$ the values 1·58, 1·42, 1·53 which are in not at all bad agreement with the theoretical value, considering the elaborate and difficult experimental data required.

As a general summary of this discussion we may conclude that the foregoing results, so far as present accuracy goes, are in full accord with the theory, *taking atomic structure into account*, if the proper weights of Chapter XIV are assigned to the states of the free atoms and the weights of the atoms in the solid form near the absolute zero remain unity. The revived electronic theory of metals necessarily requires a weight unity for the atom in the crystal of a halogen.

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* Empirical generalizations from the theory of Heisenberg and Hund. For a convenient summary see McLennan, McLay and Smith, *Proc. Roy. Soc.* A, vol. CXII, p. 76 (1926).

TABLE 12.

Effective weights of free halogen atoms.

Atom	Mean Temp. ° K.	ΔP (volts)*	$\Delta P/kT$	ϖ_1 effective	$\log_{10} \varpi_1$
Cl	1000	0·11	1·28	4·56	0·66
	1700		0·752	4·94	0·69
Br	1350	0·45	3·88	4·04	0·6
I	1200	0·94	9·1	4	0·6

* Electron volts, see § 3·2. Values from Turner, *Phys. Rev.* vol. XXVII, p. 397 (1926).

§ **7·41**. *The chemical constant of H_2 at low temperatures.* We have yet to comment on the observed value for hydrogen at low temperatures which obviously has the value characteristic of a monatomic vapour for which $\varpi_a/\varpi_s = 1$. But we must remember that at these temperatures the specific heat of H_2 (§ 3·4) proves that H_2 must be regarded as a 3 : 1 mixture of two different gases, the antisymmetrical and the symmetrical, with partition functions

$$f_a(\sigma) \sim 9e^{-2\sigma}, \quad f_s(\sigma) \sim 1$$

respectively.* In order that experiments at low temperatures should give consistent results it is necessary to suppose that both these independent types of H_2 are in equilibrium with the liquid and solid form and continually condense on to or evaporate from it in the proper proportions. This again seems only possible if the condensed forms are indifferent to the two types of H_2, that is, if the antisymmetrical or the symmetrical molecules can be substituted for each other without effect on the condensed form, which is thus to be regarded like the vapour as a random 3 : 1 mixture of the two forms. Each form will then have in the condensed state the same rotational partition function as in the vapour, or at least the same lowest terms, and the same heat of evaporation, and may be expected to be present in the same 3 : 1 proportion.

This can be expressed formally as follows. In the language of § 5·9 we have an assembly in which the general crystalline partition function for the mixture, namely

$$\Sigma_{P,P'}\, x^P,\, x'^{P'} \kappa_{P,P'}(z),$$

is of the form

$$\Sigma_{P,P'}\, x^P x'^{P'} \{f_a(z)\}^P \{f_s(z)\}^{P'} \frac{(P+P')!\,[\kappa(z)]^{P+P'}}{P!\,P'!}.$$

There are in a mixed crystal of P, P' elements $(P+P')!/P!\,P'!$ distinct arrangements of the two types of molecule, the resulting crystal having the indistinguishable partition function $[\kappa(z)]^{P+P'}$ for any arrangement.

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* A factor 3 for the rotations of the molecule, and 3 for the orientations of the nuclei.

The orientational factors f_a and f_s must then be added. This sums to the expression

$$\frac{1}{1 - xf_a(z)\,\kappa(z) - x'f_s(z)\,\kappa(z)}. \qquad \text{......(457)}$$

We then form the usual expression for C which is here

$$C = \frac{X\,!\,X'\,!}{(2\pi i)^3}\iiint \frac{dx\,dx'\,dz}{x^{X+1}x'^{X'+1}z^{E+1}}\,\frac{\exp\{xg_a(z) + x'g_s(z)\}}{1 - \{xf_a(z) + x'f_s(z)\}\,\kappa(z)}. \qquad \text{......(458)}$$

The usual evaluations then give

$$X = \overline{N} + \overline{P} = \xi g_a(\vartheta) + \frac{\xi f_a(\vartheta)\,\kappa(\vartheta)}{1 - \{\xi f_a(\vartheta) + \xi' f_s(\vartheta)\}\,\kappa(\vartheta)}, \qquad \text{......(459)}$$

$$X' = \overline{N'} + \overline{P'} = \xi' g_s(\vartheta) + \frac{\xi' f_s(\vartheta)\,\kappa(\vartheta)}{1 - \{\xi f_a(\vartheta) + \xi' f_s(\vartheta)\}\,\kappa(\vartheta)}. \qquad \text{......(460)}$$

To these we must add here $X = 3X'$ and note that the last term in (459) and (460) must be very large, so that effectively

$$\xi f_a(\vartheta)\,\kappa(\vartheta) + \xi' f_s(\vartheta)\,\kappa(\vartheta) = 1. \qquad \text{......(461)}$$

Since $g_a(\vartheta)/g_s(\vartheta)$ is by our hypotheses equal to $f_a(\vartheta)/f_s(\vartheta)$ we must have also

$$\frac{\xi f_a(\vartheta)}{\xi' f_s(\vartheta)} = \frac{3}{1}.$$

Thus $$\xi = \tfrac{3}{4}\frac{1}{f_a(\vartheta)\,\kappa(\vartheta)}, \quad \xi' = \tfrac{1}{4}\frac{1}{f_s(\vartheta)\,\kappa(\vartheta)}. \qquad \text{......(462)}$$

It follows that $$\frac{\overline{N}}{V} = \tfrac{3}{4}\frac{g_a(\vartheta)}{f_a(\vartheta)\,\kappa(\vartheta)} = 3\,\frac{\overline{N'}}{V}. \qquad \text{......(463)}$$

From (463) it follows at once that the chemical constant of H_2 has the normal value observed, for we find

$$\frac{\overline{N} + \overline{N'}}{V} = \frac{g_a(\vartheta)}{f_a(\vartheta)\,\kappa(\vartheta)} = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}\,e^{-\chi/kT}. \qquad \text{......(464)}$$

This analysis of the observations seems satisfactory in itself and there are no obvious alternatives. We must accept the two rotational forms of the H_2 molecule as both present in crystals, liquids and vapours alike, mixed at random in the proportion 3 : 1 and surviving in this ratio over periods of time long compared with ordinary observations. We must then also accept for the mixed H_2 crystal a non-unit weight for the lowest possible state. Due to the orientations $\frac{3}{4}$ of the molecules have weight 9 and the rest 1. This is equivalent to assigning the value $\log \varpi_s = \frac{3}{4}\log 9$ in all formulae, *and at once suggests the likelihood of exceptions to Nernst's heat theorem.*

§ **7·42.** *Diatomic gases (and linear molecules).* The usual formula to use for i is (445), where A is the moment of inertia of the molecule in its normal state. A serious comparison of theory and experiment in this region has only recently been made possible by the work of Eucken and his collaborators,† who have carefully collected all the available material, corrected the observations systematically for deviations from the perfect gas laws, and tabulated the results. We repeat these in a slightly different form with some additions.

TABLE 13.

Chemical constants of diatomic (linear) molecules.

$$i = 36{\cdot}815 + \tfrac{3}{2}\log_{10} m^* + \log_{10}(\delta A/\sigma)$$

if the state of lowest energy of the crystal and the molecule both have the same (unit) weight: otherwise add

$$\log_{10} \varpi_a/\varpi_s.$$

Gas	i observed and range	$-\log A$ from i	$-\log A$ optical	Authorities and remarks
H_2	$-3{\cdot}685 \pm {\cdot}03$	40·29	40·33	(1)
N_2	$-0{\cdot}11 \pm {\cdot}05$	38·80	38·75	(2) Doubtful
O_2	$0{\cdot}54 \pm {\cdot}05$	38·23	38·72	
NO	$0{\cdot}52 \pm {\cdot}06$	38·52	38·78	
CO	$-0{\cdot}05 \pm {\cdot}07$	39·03	38·83	(3)
HCl	$-0{\cdot}26 \pm {\cdot}04$	39·40	39·59	
HBr	$0{\cdot}53 \pm {\cdot}07$	39·14	39·49	
HI	$0{\cdot}90 \pm {\cdot}15$	39·09	[39·40]	Extrapolated
Cl_2	$1{\cdot}51 \pm {\cdot}16$	37·80	—	
Br_2	$2{\cdot}55 \pm {\cdot}10$	37·27	—	
I_2	$3{\cdot}12 \pm {\cdot}15$	37·00	37·09	(4)
CO_2	$0{\cdot}91 \pm {\cdot}06$	38·08	38·30	

The authority is Eucken, *loc. cit.* for the chemical data except where otherwise stated. Optical data later than that given by him is available; the chief collected sources are Mecke, *Zeit. für Phys.* vol. XLII, p. 390 (1927), and "Molecular Spectra in Gases," *Bulletin of the N.R.C.* No. 57 (1926).

(1) Hori, *loc. cit.*

(2) Cox, *loc. cit.* gives the observed value $-0{\cdot}15$ for i.

(3) Infra-red absorption bands, see *Bulletin N.R.C.*

(4) This is Mecke's value for $-(\log A)$ optical. Loomis, *Phys. Rev.* vol. XXIX, p. 112 (1927), gives 37·13.

In determining $\log A$ from i in this table we have taken $\delta = 1$ throughout (no axial spin), $\sigma = 2$ for molecules such as H_2, N_2, O_2, etc., and $\sigma = 1$ for HCl, etc. We have also taken $\log \varpi_a/\varpi_s = 1$ except for H_2 where we know its actual value to be $-\tfrac{3}{4}\log 9$.‡

In Table 13 the general agreement as to order is excellent, but there remain some interesting individual discrepancies. In view of the rather elaborate discussion which our fuller knowledge has shown to be necessary for H_2 it is really premature to attempt a detailed discussion, but some remarks may be made. The outstanding discrepancy is for O_2, which it is natural to associate with the paramagnetic properties of the O_2-molecule.

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† Eucken, Karwat and Fried, *loc. cit.*

‡ This follows from § 7·41, but the corresponding result for i can also be derived easily by following through the argument of § 7·31.

In that case NO must be taken with O_2, being the only other paramagnetic molecule known to occur in ordinary gases at ordinary temperatures. The normal molecule O_2 has a permanent magnetic moment of two Bohr magnetons, and probably weight three due to its orientational possibilities. It corresponds closely to a ^3S atomic state (see Table 41). The theory for NO is not so simple (§§ 12·61, 12·7). Its normal state appears to correspond to a state $^2P_1$ of magnetic moment zero and weight two (?). The other state of the doublet $^2P_2$ is higher by 122 in wave number, of magnetic moment two Bohr magnetons and weight four (?). If this is correct the normal state of NO must be assigned a partition function

$$2 + 4e^{-161/T},$$

instead of a constant weight. It is assumed that the usual rotational partition function can be superposed on this. A factor of two probably arises from similar left- and right-handed spins of the normal molecule (in fact a case of $\delta = 2$ included in this part of the specification). At ordinary temperatures this reduces to about $2 + 2{\cdot}2 = 2 \times 2{\cdot}1$. If the crystalline forms of O_2 and NO are not paramagnetic it is possible for the molecules to have unit weight in the solid state. We might then have unit weight for the O_2 molecule and perhaps two for NO preserving its left- and right-handedness. In that case we should have extra terms $+\log 3$ and $+\log 2{\cdot}1$ in the formula for i in these two cases, and $-\log A$ would be increased to 38·71 for O_2 and 38·84 for NO. These values are in satisfactory agreement with the optical ones. In the present state of the theory of these molecules this explanation can only be regarded at the best as a plausible speculation*.

§ 7·43. *Polyatomic molecules.* The few reliable values of chemical constants for polyatomic gases are given below.

TABLE 14.

Chemical constants of polyatomic molecules.

$$i = 56{\cdot}265 + \tfrac{3}{2}\log m^* + \log\frac{(ABC)^{\frac{1}{2}}}{\sigma}$$

if the state of lowest energy of the crystal and the molecule both have unit (the same) weight.

Gas	i observed and range	σ	$-\log(ABC)^{\frac{1}{2}}$	$\log(ABC)^{\frac{1}{2}}$ optical	Authority†
OH_2	$-1{\cdot}935 \pm {\cdot}025$	2	59·78	59·55	
NH_3	$-1{\cdot}415 \pm {\cdot}06$	6	58·75	—	
CH_4	$-2{\cdot}30 \pm {\cdot}08$	12	59·29	—	

† Eucken, *loc. cit.* except where otherwise stated.

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* It may be worth while to notice here a list of the very few common *permanent* molecules of which the normal electronic state can be described with any confidence. They are H_2, ^1S; O_2, ^3S; NO, $^2P_{1,2}$; CO, ^1S; Halogen hydrides, ^1S. Numbers of other non-permanent molecules (e.g. metal hydrides) and some molecular ions also have completely analysed spectra.

The values of σ are very uncertain for NH_3 and CH_4 and all discussion is premature.

§ 7·5. *Gas reactions. Nernst's equation* $I = \Sigma_t q_t i_t$. Besides his table of values of i, Eucken has determined I for a number of reactions in which gaseous constituents are involved. These are not all homogeneous gas reactions—a number of them are heterogeneous. The theory, however, obviously applies as before, the summation $\Sigma_t q_t i_t$ being taken over all the *gases* concerned in the reaction. Eucken gives the following values. The ranges of $\Sigma_t q_t i_t$ can be derived from the ranges in the preceding tables.

TABLE 15.

Reactions involving gases. Values of I observed compared with $\Sigma_t q_t i_t$.

Condensed forms omitted from Σ_t are indicated thus [ ]. The values of i_t are in all cases the observed values given in Tables 12, 13, 14.

	Reaction	I observed and range	$\Sigma_t q_t i_t$	$\Sigma_t q_t i_t'$
Homogeneous	$3H_2 + N_2 - 2NH_3$	− 7·04 ± ·10	− 8·33	− 7·25
	$2H_2 + O_2 - 2H_2O$	− 2·45 ± ·10	− 2·96	− 2·24
	$H_2 + Cl_2 - 2HCl$	− 1·12 ± ·20	− 1·65	− 1·29
	$H_2 + Br_2 - 2HBr$	− 1·25 ± ·45	− 2·19	− 1·83
	$H_2 + I_2 - 2HI$	− 1·51 ± ·12	− 2·36	− 2·00
	$2NO - N_2 - O_2$	+ 0·95 ± ·30	+ 0·61	+ 0·61
	$2CO + O_2 - 2CO_2$	− 0·80 ± ·25	− 1·38	− 1·38
	$H_2O + CO - H_2 - CO_2$	+ 0·82 ± ·15	+ 0·79	+ 0·43
	$4HCl + O_2 - 2H_2O - 2Cl_2$	− 0·20 ± ·14	+ 0·35	+ 0·35
	$3H_2 + CO - CH_4 - H_2O$	− 6·25 ± ·30	− 6·87	− 5·79
	$4H_2 + CO_2 - CH_4 - 2H_2O$	− 7·00 ± ·25	− 7·66	− 6·22
Heterogeneous	$2CO - [C] - CO_2$	− 0·85 ± ·18	− 1·01	− 1·01
	$[C] + 2H_2 - CH_4$	− 4·47 ± ·25	− 5·07	− 4·35
	$2Hg + O_2 - 2[HgO]$	+ 4·32 ± ·18	+ 4·18	+ 4·18
	$[CaO] + H_2O - [Ca(OH)_2]$	− 2·00 ± ·15	− 1·93	− 1·93
	$[CuSO_4] + H_2O - [CuSO_4.H_2O]$	− 2·11 ± ·12		
	$[CaO] + CO_2 - [CaCO_3]$	+ 0·80 ± ·15	+ 0·91	+ 0·91
	$H_2 + [HgO] - [Hg] - [H_2O]$	− 3·63 ± ·15	− 3·68	− 3·32
	$2[Ag] + Cl_2 - 2[AgCl]$	+ 2·03 ± ·43	+ 1·51	+ 1·51
	$2[Hg] + Cl_2 - 2[HgCl]$	+ 1·60 ± ·40		
	$[Pb] + Cl_2 - [PbCl_2]$	+ 1·95 ± ·43		

Unless Eucken's estimates of his ranges are grossly in error, one sees at once *empirically* that Nernst's theorem cannot possibly be true in all cases. And, in fact, we know already from the foregoing discussions that the lowest state for solid H_2 cannot have unit weight. Long before there was any theoretical justification for this Eucken had constructed Table 15 and observed that the worst offenders against Nernst's theorem are the reactions containing H_2, but that the greater part of the discrepancies could be removed by taking a weight two for H_2 in the crystal, thereby increasing i for gaseous H_2 from $-3{\cdot}68$ to $-3{\cdot}38$. We have seen theoretically that for H_2 $\log \varpi_s = \frac{3}{4}\log 9 = 0{\cdot}72$, so that the proper chemical constant of gaseous H_2 is $-2{\cdot}96$. Owing to the nuclear weights included in this 9 it is of course not possible merely to take this value for H_2 and try it in the equations with unit weights for the other substances with any hope of success. Nuclear weights must pursue H through all its combinations. As an experiment we have retained the one weight factor 3 as possibly peculiar, since it arises from the metastability, and used a constant $-3{\cdot}32$ for gaseous H_2. The values of $\Sigma_t q_t i_t'$ given in column 4 of Table 15 have been derived from $\Sigma_t q_t i_t$ by making this single change. There is now no serious bias in the remaining residuals of the ten reactions involving H_2. If we take the algebraic mean of any nine of these ten residuals, arranging the reaction formula so that H_2 is always on the positive side, we find only a trivial mean deviation instead of $+\ 0{\cdot}68$.

If we could properly correct all the observed i_t as we can for H_2 so as to derive the true gaseous i_t', then of course I and $\Sigma_t q_t i_t'$ must agree. Eucken has made various interesting and possible emendations of this type on the basis of the residuals of Table 15. It is, however, obviously impossible to make such emendations in a satisfactory manner, until we have a much more complete knowledge of the detailed behaviour of molecules other than H_2, and we shall not discuss them further here.

CHAPTER VIII

THE THEORY OF IMPERFECT GASES

§8·1. *General gaseous assemblies with molecules not fully independent.* We have so far only considered assemblies of "isolated" or effectively isolated systems, which almost never interfere with each other. It is only in such assemblies that the energy can be assigned to individual systems rather than to the assembly as a whole, and it is on this partition of the energy among the systems that the foregoing analysis is based. When this independence breaks down between the separate atoms as in a molecule or a crystal, we take the whole complex (molecule or crystal) to be the system. In the worst case the whole assembly must be one system in this sense—the analysis will then apply, but progress is difficult (except by special devices in specially simple cases), unless the dynamical equations for the whole complex (assembly) can be approximately solved. The essential step is, as always, to evaluate the partition function.

The assemblies which we are now contemplating differ essentially from perfect gases only because there is in the energy of the assembly as a whole a general term W which is a function at least of the positional coordinates of all the constituent systems. The justification for regarding the extra energy W as a *potential energy* depending only on positional coordinates merits close scrutiny. Let us suppose that two simple systems (atoms or molecules) of types α and β have energies E_α, E_β when they are very far apart. These energies will then be functions only of the Hamiltonian coordinates of the systems α and β respectively and each will be independent of the coordinates of the other. The internal energies will be specified by quantum conditions. When, however, they approach each other this independence must sooner or later cease. The energy of the pair will no longer be $E_\alpha + E_\beta$ but $E_\alpha + E_\beta + E_{\alpha\beta}$, say, where $E_{\alpha\beta}$ is a correcting term, at first small, depending on the coordinates, and perhaps velocities, of both systems. We assume as a first approximation that the effect of α on any β can be expressed by saying that α is surrounded by a constant field of force. This must of course be derived from the mean fields of the moving electric charges in α. The electric charges in β will then have a mean potential energy in the field of α depending on the relative positions of α and β. This, however, is not the whole of the effect, for the field of α may alter the internal energy of β and β that of α. A simple example is polarization in the field of the other body. Such changes of energy are a proper part of $E_{\alpha\beta}$. If α and β approach each other slowly then all the effects must be adiabatic in Ehrenfest's sense, and will depend only on relative coordinates, being independent of velocities. In this case the complete $E_{\alpha\beta}$, derived from all the sources specified, may legitimately be expected to behave like a potential energy depending only on the relative coordinates, whose derivates give the forces. Moreover in actual applications nearly all molecular encounters are slow compared with the velocities of electrons in atoms and molecules, and will therefore be adiabatic in the required sense. This is the assumption as to the nature of $E_{\alpha\beta}$ tacitly made in all discussions of molecular interactions.

The function $E_{\alpha\beta}$ so specified must in general depend on the quantum states of the systems α and β. It is obvious that for atoms and molecules changes of electronic orbits must affect $E_{\alpha\beta}$, for they must at least affect the polarizability. It is usual, however, and not unreasonable to assume (at least as an approximation) that $E_{\alpha\beta}$ will be independent of molecular states of rotation and perhaps vibration*. As it is almost universal in gas problems for only one electronic state of atom or molecule to be relevant, the usual approximation should apply. If it does not then, as we shall see, it is only necessary to treat different electronic or vibrational states of atom or molecule as different systems.

§ 8·2. *Partition functions for the potential energy of the whole gas.* We can at once proceed to construct a partition function for the potential energy of the whole gas, which in conjunction with previous results will determine all the equilibrium properties.

Let us start by considering a *perfect* gas mixture and examine how to construct a partition function for the whole classical energy of translation of its molecules. The internal energies of the molecules are independent of their translations and will be accounted for as usual by separate partition functions. Let there be $N_\alpha, N_\beta, \ldots$ free atoms and molecules of types $\alpha, \beta, \ldots$, internal partition functions $j_\alpha(\vartheta), j_\beta(\vartheta), \ldots$, and masses $m_\alpha, m_\beta, \ldots$, supposed for the moment not to dissociate or combine. In accordance with the general principles of § 2·2, the phase space of the whole gas must then be cut up into elements of extension

$$(m_\alpha{}^{N_\alpha} m_\beta{}^{N_\beta} \ldots)^3 \prod_{r=1}^{N_\alpha} (dx_\alpha \ldots dw_\alpha)_r \prod_{s=1}^{N_\beta} (dx_\beta \ldots dw_\beta)_s \ldots,$$

and prepared weight

$$\frac{(m_\alpha{}^{N_\alpha} m_\beta{}^{N_\beta} \ldots)^3}{h^{3(N_\alpha+N_\beta+\cdots)}} \prod_{r=1}^{N_\alpha} (dx_\alpha \ldots dw_\alpha)_r \prod_{s=1}^{N_\beta} (dx_\beta \ldots dw_\beta)_s \ldots . \qquad \ldots(465)$$

The classical partition function $H(\vartheta)$ for the translatory motion is therefore given by

$$H(\vartheta) = \frac{(m_\alpha{}^{N_\alpha} m_\beta{}^{N_\beta} \ldots)^3}{h^{3(N_\alpha+N_\beta+\cdots)}} \int \ldots \int \vartheta^{\sum_{r=1}^{N_\alpha} \frac{1}{2} m_\alpha (u_\alpha{}^2+v_\alpha{}^2+w_\alpha{}^2)_r + \sum_{s=1}^{N_\beta} \frac{1}{2} m_\beta (u_\beta{}^2+v_\beta{}^2+w_\beta{}^2)_s + \ldots}$$

$$\times \prod_{r=1}^{N_\alpha} (dx_\alpha \ldots dw_\alpha)_r \prod_{s=1}^{N_\beta} (dx_\beta \ldots dw_\beta)_s \ldots . \qquad \ldots\ldots(466)$$

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* If this is not true then of course $E_{\alpha\beta}$ is a mean value taken in a way not yet specified.

It is assumed that there are no external fields of force except local boundary fields. All the space and velocity integrations in (466) are independent and can be carried out one by one, and we find

$$H(\vartheta) = \left[\frac{(2\pi m_\alpha)^{\frac{3}{2}} V}{h^3 (\log 1/\vartheta)^{\frac{3}{2}}}\right]^{N_\alpha} \left[\frac{(2\pi m_\beta)^{\frac{3}{2}} V}{h^3 (\log 1/\vartheta)^{\frac{3}{2}}}\right]^{N_\beta} \ldots,$$

$$= [h_\alpha(\vartheta)]^{N_\alpha}[h_\beta(\vartheta)]^{N_\beta} \ldots . \qquad \ldots\ldots(467)$$

In equation (467) $h_\alpha(\vartheta)$, $h_\beta(\vartheta)$, ... are the ordinary partition functions for the translatory motion of single molecules of types α, β, ..., and we recover, as we must, the ordinary result. For the complete partition function we have of course to add to $H(\vartheta)$ the factor

$$[j_\alpha(\vartheta)]^{N_\alpha}[j_\beta(\vartheta)]^{N_\beta} \ldots . \qquad \ldots\ldots(468)$$

The extension to an imperfect gas is immediate. Under the specified conditions $j_\alpha(\vartheta)$, $j_\beta(\vartheta)$, ... are still separable factors. The function $H(\vartheta)$ is altered only by the addition of a term W to the index of ϑ, where W is the potential energy of the whole assembly, a function of all the positional coordinates $(x_\alpha, y_\alpha, z_\alpha)_r$, $(x_\beta, y_\beta, z_\beta)_s$, ..., built up to a first approximation out of the functions $E_{\alpha\beta}$ which we have already specified. The addition of W will not affect the velocity integrations, which can be carried out as before. We therefore find in general

$$H(\vartheta) = \left[\frac{(2\pi m_\alpha)^{\frac{3}{2}}}{h^3 (\log 1/\vartheta)^{\frac{3}{2}}}\right]^{N_\alpha} \left[\frac{(2\pi m_\beta)^{\frac{3}{2}}}{h^3 (\log 1/\vartheta)^{\frac{3}{2}}}\right]^{N_\beta} \ldots \times B(\vartheta), \qquad \ldots(469)$$

where $$B(\vartheta) = \int \ldots \int \vartheta^W \prod_{r=1}^{N_\alpha} (dx_\alpha \ldots dz_\alpha)_r \prod_{s=1}^{N_\beta} (dx_\beta \ldots dz_\beta)_s \ldots . \qquad \ldots\ldots(470)$$

The integrals in $B(\vartheta)$ are extended over the whole positional phase space accessible to the gas. It is therefore assumed that in no case can $W \to -\infty$, but that ultimately there must be repulsive fields between any two particles for which $W \to +\infty$ when they approach sufficiently closely. No other assumption would be physically consistent with the continued existence of ordinary matter*. When $W \equiv 0$, $B(\vartheta) = V^{N_\alpha + N_\beta + \cdots}$, and $H(\vartheta)$ reduces to (467).

From the form of (469) it is clear that classical potential and kinetic energies in a gas can always be handled with separate partition functions. The kinetic energy can be dealt with in the ordinary way, as if the gas were perfect, by ordinary partition functions without the V-factor. The potential energy is accounted for by $B(\vartheta)$. It should be observed also that (469) and (470) are perfectly general, so long as all the particles are free to move

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* But always only so long as degeneracy effects can be neglected. See Chapter XXI.

individually, and apply to assemblies in which the imperfections are of any degree and the intermolecular forces of any range, and whether or no there are external fields of force*. It is not, of course, true for higher degrees of imperfection that W can be regarded as built up entirely of terms such as $E_{\alpha\beta}$, that is, terms arising from binary encounters. Ternary encounters must next be considered in which three molecules are concerned with a total energy $(E_\alpha + E_\beta + E_\gamma + E_{\beta\gamma} + E_{\gamma\alpha} + E_{\alpha\beta}) + E_{\alpha\beta\gamma}$, where $E_{\alpha\beta\gamma}$ depends essentially on the coordinates of all three systems. At higher concentrations encounters of all orders must be successively taken into account. But, assuming W can be constructed, equation (470) continues to give $B(\vartheta)$. If there are no external fields of force, W will be a function only of the relative coordinates of the molecules. If there are local boundary fields representing walls of the enclosure, this will still be true in the limit when the whole volume is very large compared with the volume affected by the local fields.

The partition function $B(\vartheta)$ refers to what is strictly a single system, the whole gas. It therefore appears by itself, not raised to a high power, in the complex integrals which give the properties of the equilibrium state, resembling thereby the partition functions for radiation and for crystals. Some average values derived in the usual way from $B(\vartheta)$ may be small; they will none the less be true averages, but will merely be subject to relatively large fluctuations. But any derived average number of molecules which is itself large, like the average values of the theory of the perfect gas, will have its usual validity and its usual insignificant fluctuation which guarantees normality.

In specifying, for example, a statistical state of the assembly in order to derive average values from $B(\vartheta)$ it is necessary strictly to specify the positions of *all* molecules. There is also only *one* system, the whole gas. In Chapter II, for example, we proved with the help of a partition function $f(\vartheta)$ that the average number $\overline{a}$ of systems satisfying certain conditions represented by part of $f(\vartheta)$, $\delta f(\vartheta)$ say, was given by

$$\overline{a} = N\delta f(\vartheta)/f(\vartheta). \qquad \text{......(471)}$$

Here, however, $N = 1$; the meaning of (471) is unaltered, but is better appreciated if we say that $\delta f(\vartheta)/f(\vartheta)$ is the fraction of time during which the gas is in the specified state, or if we like the *frequency ratio* or *probability* of that state. Equation (471) still describes a genuine equilibrium property of the assembly, but only those mean values derived from (471), which have insignificant fluctuations, are physically significant.

The potential energy W will contain terms which depend on the values of the parameters which fix the positions of bodies producing external

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* But always only so long as degeneracy effects can be neglected. See Chapter XXI.

fields. The generalized reaction Y_W of the whole gas arising from W in any configuration is therefore $-\partial W/\partial y$, and

$$\overline{Y_W} = \frac{1}{B(\vartheta)} \int \cdots \int \left(-\frac{\partial W}{\partial y}\right) \vartheta^W \prod_{r=1}^{N_\alpha} (dx_\alpha \ldots dz_\alpha)_r \prod_{s=1}^{N_\beta} (dx_\beta \ldots dz_\beta)_s \ldots, \qquad \ldots\ldots(472)$$

$$= \frac{\partial}{\partial y} \log B(\vartheta) \Big/ \log 1/\vartheta. \qquad \ldots\ldots(473)$$

The average value of the potential energy is

$$\overline{W} = \vartheta \frac{\partial}{\partial \vartheta} \log B(\vartheta). \qquad \ldots\ldots(474)$$

The former result is, of course, the exact analogue of § 2·74. From it, it follows at once, as in Chapter VI, that the more general assemblies here contemplated obey the laws of Thermodynamics, and that $B(\vartheta)$ contributes

$$k \log B(\vartheta)$$

to the characteristic function Ψ, and

$$k(\log B(\vartheta) - \overline{W} \log \vartheta)$$

to the entropy.

It is, of course, necessarily true, and becomes particularly obvious in this section, that the partition functions of our theory are identical with the separable factors in the phase integrals of Gibbs. The further developments will therefore hardly differ at all, whether one starts from the canonical ensemble of Gibbs or the conservative dynamical system of Boltzmann. We shall continue for consistency and practical convenience to use the terminology of partition functions.

In applications it is convenient to use an abbreviated notation. We write $d\omega_{\alpha r}$ for $(dx_\alpha dy_\alpha dz_\alpha)_r$ and contract

$$\prod_{r=1}^{N_\alpha} d\omega_{\alpha r} \prod_{s=1}^{N_\beta} d\omega_{\beta s} \ldots$$

into

$$\Pi_\alpha (d\omega_\alpha)^{N_\alpha}.$$

Thus

$$B(\vartheta) = \int \cdots \int \vartheta^W \, \Pi_\alpha (d\omega_\alpha)^{N_\alpha} = \int \cdots \int e^{-W/kT} \, \Pi_\alpha (d\omega_\alpha)^{N_\alpha}. \qquad \ldots\ldots(475)$$

We shall similarly write $\Sigma_\alpha N_\alpha$ for $N_\alpha + N_\beta + \ldots$.

§ 8·3. *A first approximation for imperfect gases. Short range forces.* We shall now suppose that the field of an α or β, in which $E_{\alpha\beta}$ is sensible, is of strictly limited range, so that there is a certain small volume $v_{\alpha\beta}$ round α in which β (or round β in which α) must lie so that $E_{\alpha\beta} \neq 0$. Otherwise $E_{\alpha\beta} = 0$. For the present we neglect external fields of force. We suppose also that ternary and higher complexes may be neglected, so that W consists only of terms such as $E_{\alpha\beta}$. It can be shown that in so doing we neglect terms in log $B(\vartheta)$ of order at most $N_\alpha(\Sigma_\beta N_\beta v_{\alpha\beta}/V)^2$. We therefore suppose that $\Sigma_\beta N_\beta v_{\alpha\beta}/V$ is small and that terms of higher order than the first in this ratio are to be neglected compared with unity. The terms to be neglected in any step require, however, the most careful scrutiny*.

To evaluate $B(\vartheta)$ retaining only binary complexes we consider first an assembly with only one type of molecule. The argument extends at once to any number of types, but the algebra is complicated enough to postpone for the moment. If one α, α pair lies in $v_{\alpha\alpha}$ (shortly v) then $W = E_{\alpha\alpha}$ (more shortly E) and is otherwise zero. Let us first take $W = 0$ everywhere. We obtain the contribution V^N. The rest of $B(\vartheta)$ comes from integrating $\vartheta^W - 1$ over the whole phase space. This is zero unless at least one v is occupied. Let us put $W = E$ and integrate for the relative coordinates of one pair over v and for the other coordinates over V. We obtain

$$\Sigma \int_v (\vartheta^E - 1)\, d\omega \int_{(V)} \dots \int (d\omega)^{N-1},$$

where Σ is the sum over all pairs. This reduces to

$$V^{N-1}.\ \tfrac{1}{2}N(N-1)\int_v (\vartheta^E - 1)\, d\omega.$$

This contribution is exact so long as only one v is occupied. If two are occupied simultaneously the proper contribution to $B(\vartheta) - V^N$ comes from integrating $\vartheta^{E+E'} - 1$ over vv' for two sets of relative coordinates, and the others over V. The integrand we have actually used above is, however, $(\vartheta^E - 1) + (\vartheta^{E'} - 1)$. It remains, therefore, to integrate in this manner

$$\vartheta^{E+E'} - 1 - (\vartheta^E - 1) - (\vartheta^{E'} - 1) = (\vartheta^E - 1)(\vartheta^{E'} - 1).$$

Using this integrand the next contribution is

$$V^{N-2}.\ (\tfrac{1}{2})^2 \frac{N(N-1)(N-2)(N-3)}{2\,!}\left\{\int_v (\vartheta^E - 1)\, d\omega\right\}^2.$$

The numerical coefficient is the number of sets of two pairs. This contribution is again exact so long as there are no sets of three pairs. The correct integrand is then $\vartheta^{E+E'+E''} - 1$ taken over $vv'v''$ for three sets of relative coordinates and the others over V. The complete integrand we have used so far is

$$\Sigma(\vartheta^E - 1)(\vartheta^{E'} - 1) + \Sigma(\vartheta^E - 1),$$

and there remains

$$(\vartheta^{E+E'+E''} - 1) - \Sigma(\vartheta^E - 1)(\vartheta^{E'} - 1) - \Sigma(\vartheta^E - 1) = \Pi(\vartheta^E - 1).$$

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* The following presentation is due to Ursell, *Proc. Camb. Phil. Soc.* vol. XXIII, p. 685 (1927). Many current analyses of this type are completely fallacious, e.g. Jeans, *Dynamical Theory of Gases*, ed. 2, § 218; Fowler, *Proc. Camb. Phil. Soc.* vol. XXII, p. 861 (1925).

Using this integrand the contribution is

$$V^{N-3}.\ (\tfrac{1}{2})^3 \frac{N\,!}{3\,!\,(N-6)\,!}\left\{\int_v (\vartheta^E - 1)\,d\omega\right\}^3.$$

The generality of the method may be established by a simple induction, and the full form of $B(\vartheta)$ is therefore

$$B(\vartheta) = V^N \sum_{r=0}^{\frac{1}{2}N} \frac{N\,!}{r\,!\,(N-2r)\,!\,N^r} x^r, \qquad \text{......(476)}$$

where

$$x = \frac{N}{2V}\int_v (\vartheta^E - 1)\,d\omega, \qquad \text{......(477)}$$

and is therefore small.

It is obvious that the form of $B(\vartheta)$, at least for the earlier terms, is approximately given by

$$V^N (1+x)^N = V^N \sum_{r=0}^{N} \frac{N\,!}{r\,!\,(N-r)\,!} x^r,$$

and one is led to expect (as is in fact true) that

$$B(\vartheta) = V^N \{1 + x + O(x^2)\}^N, \qquad \text{......(478)}$$

which is an approximation of the desired order. It is *not* sufficient, in order to derive (478), to retain only the first two terms in (476), as is commonly done, and assume that the second is small compared with the first and so on. For the ratio of the first two terms is $(N-1)\,x$, and it is only x which we are entitled to assume small! We proceed, therefore, as follows, using an argument adapted to the generalizations required in § 8·31.

Consider the function $F(x, y)$ defined by the equation

$$F(x, y) = \sum_{r=0}^{\frac{1}{2}N} \frac{N\,!}{r\,!\,(N-2r)\,!\,N^r} x^r y^{N-2r}. \qquad \text{......(479)}$$

By partial differentiation this function obviously satisfies the equation

$$\frac{1}{N}\frac{\partial F}{\partial x} = \left(\frac{1}{N}\frac{\partial}{\partial y}\right)^2 F. \qquad \text{......(480)}$$

Put

$$F = e^{Ng}.$$

Then this equation reduces to

$$\frac{\partial g}{\partial x} = \left(\frac{\partial g}{\partial y}\right)^2 + \frac{1}{N}\frac{\partial^2 g}{\partial y^2}, \qquad \text{......(481)}$$

and g is uniquely defined as that solution of (481) which is equal to $\log y$ for $x = 0$. Since N is very large the last term can be neglected. Since also $F = y^N f(x/y^2)$,

$$x\frac{\partial F}{\partial x} + \tfrac{1}{2}y\frac{\partial F}{\partial y} = \tfrac{1}{2}NF,$$

or

$$y\frac{\partial g}{\partial y} = 1 - 2x\frac{\partial g}{\partial x}.$$

Substituting this in (481) we find the approximate equation for g

$$\frac{\partial g}{\partial x} = \frac{1}{y^2}\left(1 - 2x\frac{\partial g}{\partial x}\right)^2.$$

The actual value of g required is $g(x, 1)$; which is that solution of

$$\frac{\partial g}{\partial x} = \left(1 - 2x\frac{\partial g}{\partial x}\right)^2, \qquad \text{......(482)}$$

which is 0 for $x = 0$, terms of order $1/N$ being neglected. This is easily verified directly without the introduction of the auxiliary variable y.

Equation (482) can be solved in finite terms, but of course no physical importance attaches to any terms other than the lowest in x since we have only hitherto included binary complexes. We find formally

$$\frac{dg}{dx} = \frac{1 + 4x - \sqrt{(1 + 8x)}}{8x^2},$$

$$g = \log\frac{1 - \sqrt{(1 + 8x)}}{4x} - \frac{1 + 4x - \sqrt{(1 + 8x)}}{8x},$$

and the significant terms

$$g = x + O(x^2).$$

Thus
$$\log B(\vartheta) = N\{\log V + x + O(x^2)\}, \qquad \text{......(483)}$$

which is equivalent to (478) and contains all the relevant information.

Our result therefore is for a simple gas

$$\log B(\vartheta) = N\log\{V + \tfrac{1}{2}N\int_v (\vartheta^E - 1)\,d\omega\}, \qquad \text{......(484)}$$

and for the general mixture, to which we devote part of § 8·31,

$$\log B(\vartheta) = \Sigma_\alpha N_\alpha \log\{V + \tfrac{1}{2}\Sigma_\beta N_\beta \int_{v_{\alpha\beta}} (\vartheta^{E_{\alpha\beta}} - 1)\,d\omega_\beta\}, \text{......(485)}$$

$$= \Sigma_\alpha N_\alpha \log V + \Sigma_{\alpha\beta}\frac{N_\alpha N_\beta}{\sigma_{\alpha\beta} V}\int_{v_{\alpha\beta}} (\vartheta^{E_{\alpha\beta}} - 1)\,d\omega_\beta. \text{...(486)}$$

In this equation $\sigma_{\alpha\beta} = 1\ (\alpha \mp \beta)$, $\sigma_{\alpha\alpha} = 2$, and $\Sigma_{\alpha\beta}$ means summation over every pair of types α and β. In every case the terms omitted are of order smaller by the factor $\Sigma N_\beta v_{\alpha\beta}/V$ than those retained.

The other partition functions for our assembly are normal, those for the translatory motion being without their V-factors. When therefore we add $\log B(\vartheta)$ to Ψ/k we restore the V-factors to the translatory partition functions and add to Ψ/k the new term

$$\Sigma_{\alpha\beta}\frac{N_\alpha N_\beta}{\sigma_{\alpha\beta} V}\int_{v_{\alpha\beta}} \{e^{-E_{\alpha\beta}/kT} - 1\}\,d\omega_\beta. \qquad \text{......(487)}$$

The integral in (487) is more commonly expressed in polar coordinates, for by ignoring coordinates defining the orientation of molecules we have tacitly assumed that $E_{\alpha\beta}$ is a function of r alone, or may be replaced by a mean value for all orientations. Expressed thus (487) becomes

$$\Sigma_{\alpha\beta}\frac{N_\alpha N_\beta}{\sigma_{\alpha\beta}V}\,4\pi\int_{v_{\alpha\beta}}\{e^{-E_{\alpha\beta}/kT}-1\}\,r^2dr. \qquad \text{......(488)}$$

The method can easily be extended to systems for which orientations are relevant, and the potential a general function of relative position, but we shall not take up such extensions here.

We have hitherto assumed that $E_{\alpha\beta}$ is due to forces of finite range. It is more usual and convenient in practice to represent molecular forces by forces which fall off like some inverse sth power of the distance. If $s > 4$ the integral in (477) will converge when extended over all space. Any such integral, if sufficiently rapidly convergent, can be substituted for the finite integral in (477) and elsewhere, without modification of the argument, for the integral over all space differs negligibly from the integral over a $v_{\alpha\beta}$ of atomic dimensions. We thus find for the extra terms

$$\Sigma_{\alpha\beta}\frac{N_\alpha N_\beta}{\sigma_{\alpha\beta}V}\,4\pi\int_0^\infty\{e^{-E_{\alpha\beta}/kT}-1\}\,r^2dr. \qquad \text{......(489)}$$

By (474) the average potential energy of the assembly is

$$\overline{W}=\Sigma_{\alpha\beta}\frac{N_\alpha N_\beta}{\sigma_{\alpha\beta}V}\,4\pi\int_0^\infty E_{\alpha\beta}\,e^{-E_{\alpha\beta}/kT}\,r^2dr. \qquad \text{......(490)}$$

If F_α is the complete partition function for the system of type α without its V-factor, then the complete Ψ/k is given by

$$\Psi/k=\Sigma_\alpha N_\alpha\left\{\log\frac{VF_\alpha}{N_\alpha}+1\right\}+\Sigma_{\alpha\beta}\frac{N_\alpha N_\beta}{\sigma_{\alpha\beta}V}\,4\pi\int_0^\infty\{e^{-E_{\alpha\beta}/kT}-1\}\,r^2dr. \quad \text{...(491)}$$

Since $p = T\dfrac{\partial\Psi}{\partial V}$, we find at once

$$p=kT\left[\frac{\Sigma_\alpha N_\alpha}{V}-\frac{1}{V^2}\Sigma_{\alpha\beta}\frac{N_\alpha N_\beta}{\sigma_{\alpha\beta}}\,4\pi\int_0^\infty\{e^{-E_{\alpha\beta}/kT}-1\}\,r^2dr\right]. \qquad \text{......(492)}$$

This is the well-known formula of van der Waals, correct to terms in $1/V^2$, for a mixture of imperfect gases.

In concluding this section let us include an external field of force in which the potential energy of the molecule of type α is Ω_α. This must not be so large that the approximations we have made become invalid in any part of the assembly. At the densest point ternary encounters must still be negligible. The condition for this is, of course, that if the densest element of the gas in its average state is treated as a separate assembly then $\Sigma_\beta N_\beta v_{\alpha\beta}/V$ must still be small there.

The extended form of log B (ϑ) is easily written down. Wherever before we obtained a factor V by integrating $d\omega_\alpha$ over the whole volume, we now obtain instead the factor

$$A_\alpha(\vartheta) = \int_V \vartheta^{\Omega_\alpha}\, d\omega. \qquad \text{......(493)}$$

Wherever before we had to deal with an α, β pair we integrated their relative coordinates over $v_{\alpha\beta}$ and the coordinates of their centre of mass over V, obtaining the factors $V\int_{v_{\alpha\beta}} (\vartheta^{E_{\alpha\beta}} - 1)\, d\omega_\beta$. Now, however, we have instead

$$\int_V \vartheta^{\Omega_\alpha + \Omega_\beta}\, d\omega \,.\int_{v_{\alpha\beta}} (\vartheta^{E_{\alpha\beta}} - 1)\, d\omega_\beta.$$

In place of the old V in this connection we obtain now the factor

$$A_{\alpha\beta}(\vartheta) = \int_V \vartheta^{\Omega_\alpha + \Omega_\beta}\, d\omega. \qquad \text{......(494)}$$

There are no other alterations and the argument is unaffected. Therefore

$$\log B(\vartheta) = \Sigma_\alpha N_\alpha \log \left\{ A_\alpha(\vartheta) + \tfrac{1}{2}\Sigma_\beta N_\beta \frac{A_{\alpha\beta}(\vartheta)}{A_\beta(\vartheta)} \int_{v_{\alpha\beta}} (\vartheta^{E_{\alpha\beta}} - 1)\, d\omega_\beta \right\}, \qquad \text{......(495)}$$

$$= \Sigma_\alpha N_\alpha \log A_\alpha(\vartheta) + \Sigma_{\alpha\beta} \frac{N_\alpha N_\beta}{\sigma_{\alpha\beta}} \frac{A_{\alpha\beta}(\vartheta)}{A_\alpha(\vartheta) A_\beta(\vartheta)} \int_{v_{\alpha\beta}} (\vartheta^{E_{\alpha\beta}} - 1)\, d\omega_\beta. \qquad \text{......(496)}$$

§ **8·31**. *The general theory of* $B(\vartheta)$*. In attempting a more general theory than that expounded in § 8·3, it is best to make a fresh start with assemblies of N molecules represented by rigid elastic spheres of one type. For such assemblies $B(\vartheta)$ is independent of ϑ and is the volume of $3N$-dimensional space, contained in V^N for which no one of a set of conditions in number $\frac{1}{2}N(N-1)$, of the form

$$(x_r - x_s)^2 + (y_r - y_s)^2 + (z_r - z_s)^2 \geqslant D^2, \qquad \text{......(497)}$$

is violated. Suppose we choose a set of these conditions in number k and calculate the volume of that part of V^N in which they are all violated, and then let B_k denote the sum of these volumes for all possible sets of k conditions. Then

$$B(\vartheta) = B_0 - B_1 + B_2 - \dots + (-)^k B_k + \dots. \qquad \text{......(498)}$$

This identity follows from the fact that an element of $3N$-space in which s conditions are violated is counted ${}_sC_k$ times in B_k if $0 \leqslant k \leqslant s$ and otherwise not counted; and

$$\sum_{k=0}^{s} (-)^k\, {}_sC_k = (1-1)^s = 0 \quad (s > 0),$$
$$= 1 \quad (s = 0).$$

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* Ursell, *loc. cit.*

Thus the sum on the right of (498) is precisely that part of $3N$-space in which no conditions are violated, that is, $B(\vartheta)$. The approximation of § 8·3 follows immediately.

To evaluate $B(\vartheta)$ in general we must expand each B_k. Consider a group of t molecules whose positions can be represented in $3t$-space. At any particular point of this space a certain set of conditions (497) are violated, and there is a surrounding region in which the same conditions are all broken. We can enumerate all the sets of broken conditions (497) in such a way that each set binds the molecules it involves into a single connected group, the connecting links being the broken conditions (497). For any such group there is a symmetry number σ which is defined as the number of permutations of the molecules among themselves which leave the set of defining conditions unaltered. In $3t$-space there is a definite region in which these conditions (and possibly others as well) are violated; by permuting the molecules among themselves we get $t!/\sigma$ such regions, which may of course overlap. We now enumerate the *types* of such sets of conditions in any convenient order, and specify the rth type as follows: the number of molecules involved is t_r with a symmetry number σ_r, and the number of conditions violated is p_r; the extension of $3t_r$-space corresponding to these conditions is η_r. We find it convenient later on to use a symbol ξ_r defined by the equation

$$\xi_r = (-)^{p_r} N^{t_r - 1} \eta_r / (V^{t_r} \sigma_r).$$

Following the definition of B_k we now choose any conditions (497) and calculate the volume of $3N$-space in which they at least are violated. Any such set resolves into a number of sets of the types defined above, the corresponding groups of molecules being disconnected and mutually exclusive. Let there be ν_r sets of the rth type so that

$$k = \Sigma_r \nu_r p_r. \qquad \ldots\ldots(499)$$

The number of sets of conditions for which the ν_r have assigned values is

$$\frac{N!}{(N - \Sigma_r t_r \nu_r)!\, \Pi_r (\nu_r!\, \sigma_r^{\nu_r})}.$$

Hence
$$B_k = \Sigma \frac{N!\, V^{N - \Sigma_r t_r \nu_r}}{(N - \Sigma_r t_r \nu_r)!\, \Pi_r (\nu_r!\, \sigma_r^{\nu_r})} \Pi_r \eta_r^{\nu_r},$$

the summation being over all positive integral values of the ν_r satisfying (499). Thus on introducing the ξ_r

$$B(\vartheta) = \Sigma_k (-)^k B_k = V^N \Sigma \frac{N!\, \Pi_r \xi_r^{\nu_r} N^{-\Sigma_r \nu_r (t_r - 1)}}{(N - \Sigma_r \nu_r t_r)!\, \Pi_r \nu_r!}, \qquad \ldots\ldots(500)$$

the summation being over all positive integral ν_r. It is obvious that if b is four times the volume of all the molecules (van der Waals' b),

$$\xi_r = O\left\{\left(\frac{b}{V}\right)^{t_r - 1}\right\}.$$

We have now to find a means of summing (500). Write

$$F \equiv F(\xi_r, y) = \Sigma \frac{(yN)^{N-\Sigma_r t_r \nu_r}\,\Pi_r\,(\xi_r N)^{\nu_r}\,N\,!\,N^{-N}}{(N-\Sigma_r t_r \nu_r)\,!\,\Pi_r \nu_r\,!}.$$

Then
$$\frac{1}{N}\frac{\partial F}{\partial \xi_r} = \left(\frac{1}{N}\frac{\partial}{\partial y}\right)^{t_r} F,$$

and F is defined completely by these equations together with the condition that it is regular in the ξ_r at the origin and takes the value y^N there. Further, if $t_r = t_s$, that is, if the number of molecules concerned in the rth and sth type of connected group is the same, then

$$\frac{\partial F}{\partial \xi_r} = \frac{\partial F}{\partial \xi_s},$$

and F is therefore a function of the sums

$$x_s = (\Sigma_r \xi_r)_{t_r = s}$$

only. We therefore have

$$F = \Sigma \frac{(yN)^{N-\Sigma_s s\nu_s}\,\Pi_s\,(x_s N)^{\nu_s}\,N\,!\,N^{-N}}{(N-\Sigma_s s\nu_s)\,!\,\Pi_s \nu_s\,!}, \qquad \text{......(501)}$$

together with
$$\frac{1}{N}\frac{\partial F}{\partial x_s} = \left(\frac{1}{N}\frac{\partial}{\partial y}\right)^{s} F. \qquad \text{......(502)}$$

Let us now write
$$y = e^z,\ \delta = \Sigma_s s x_s \frac{\partial}{\partial x_s}.$$

Then from (501)
$$\left(\frac{\partial}{\partial z} + \delta\right)^k F = N^k F, \qquad \text{......(503)}$$

and from (502)

$$\frac{1}{N}\frac{\partial F}{\partial x_s} = e^{-sz}\left(\frac{1}{N}\frac{\partial}{\partial z} - \frac{s-1}{N}\right)\cdots\left(\frac{1}{N}\frac{\partial}{\partial z} - \frac{1}{N}\right)\frac{1}{N}\frac{\partial}{\partial z}F.$$

On substituting from (503) we find

$$\frac{1}{N}\frac{\partial F}{\partial x_s} = e^{-sz}\left(1 - \frac{s-1}{N} - \frac{\delta}{N}\right)\cdots\left(1 - \frac{1}{N} - \frac{\delta}{N}\right)\left(1 - \frac{\delta}{N}\right)F.$$

Let us now write, as before,

$$F = e^{Ng}$$

and put $y = 1$ or $z = 0$. Then after reduction

$$\frac{\partial g}{\partial x_s} = \left(1 - \frac{s-1}{N} - \delta g - \frac{\delta}{N}\right)\cdots\left(1 - \frac{1}{N} - \delta g - \frac{\delta}{N}\right)\left(1 - \delta g\right),$$

in which the free δ's are to operate on everything to the right of them This is exact. Making $N \to \infty$ we get

$$\frac{\partial g}{\partial x_s} = (1 - \delta g)^s. \qquad \text{......(504)}$$

If we write h for $1 - \delta g$, then in virtue of the definition of δ

$$h = 1 - \Sigma_s s x_s h^s. \qquad \text{......(505)}$$

The summation begins for $s = 2$. It is easily verified that subject to (505) the partial differential equations

$$\frac{\partial g}{\partial x_s} = h^s \qquad \ldots\ldots(506)$$

are integrable. The method of evaluating g in series is now clear. We solve (505) for h in series and so form g from (506), putting $g = 0$ for $x_s = 0$. We then have

$$B(\vartheta) = V^N e^{Ng}.$$

The method extends at once to a gas of any number of kinds of molecules; it is sufficient to discuss a mixture of two kinds only, in number N_α and N_β. We must now define the ξ_r so that the volume of $3(t_r + t_r')$-space corresponding to the rth type of group, composed of t_r molecules of the first kind and t_r' of the second, is

$$(-)^{p_r}\, \xi_r V^{t_r+t_r'}\, \sigma_r / N_0^{\,t_r+t_r'-1}.$$

Here N_0 is supposed to be a number of the order of magnitude of N_α and N_β; it may with advantage be taken to be an absolute constant such as Loschmidt's number, or else proportional to V. We now find

$$B(\vartheta) = V^{N_\alpha + N_\beta}\, F(\xi_r, 1, 1), \qquad \ldots\ldots(507)$$

where

$$F(\xi_r, y, z) = \Sigma \frac{y^{N_\alpha - \Sigma_r t_r \nu_r}\, z^{N_\beta - \Sigma_r t_r' \nu_r}\, \Pi_r \xi_r^{\nu_r}}{(N_\alpha - \Sigma_r t_r \nu_r)!\, (N_\beta - \Sigma_r t_r' \nu_r)!\, \Pi_r \nu_r!}\, N_0^{-\Sigma_r (t_r + t_r' - 1)\nu_r}\, N_\alpha!\, N_\beta!.$$

From this it follows that

$$\frac{1}{N_0}\frac{\partial F}{\partial \xi_r} = \left(\frac{1}{N_0}\frac{\partial}{\partial y}\right)^{t_r} \left(\frac{1}{N_0}\frac{\partial}{\partial z}\right)^{t_r'} F. \qquad \ldots\ldots(508)$$

We therefore put $\qquad x_{r,s} = (\Sigma_q \xi_q)_{t_q = r,\, t_q' = s},$

so that F is a function of the $x_{r,s}$ only, and $F = e^{N_0 g}$. We find eventually, by the same reduction and approximation as before,

$$\frac{\partial g}{\partial x_{r,s}} = \left(\frac{N_\alpha}{N_0} - \delta_\alpha g\right)^r \left(\frac{N_\beta}{N_0} - \delta_\beta g\right)^s = h_\alpha{}^r h_\beta{}^s, \qquad \ldots\ldots(509)$$

where

$$h_\alpha = \nu_\alpha - \delta_\alpha g = \nu_\alpha - \Sigma_{r,s}\, r x_{r,s} h_\alpha{}^r h_\beta{}^s, \qquad \ldots\ldots(510)$$

$$h_\beta = \nu_\beta - \delta_\beta g = \nu_\beta - \Sigma_{r,s}\, s x_{r,s} h_\alpha{}^r h_\beta{}^s. \qquad \ldots\ldots(511)$$

We have written ν_α and ν_β here for N_α/N_0 and N_β/N_0, and have to solve these equations for g with the boundary condition $g = 0$ for $x_{r,s} = 0$. It should be noted that the summations lack the terms $r = 1$, $s = 0$ and $r = 0$, $s = 1$. These terms are precisely the h_α and h_β on the left of the equations, which take a fully symmetrical form if transposed. But they must be used in the form in which they are written.

We shall now calculate the terms of the first three orders in h and g, remembering that x_r is $O\,(b/V)^{r-1}$. For a pure gas we obtain successively from (505) and (506)

$$\begin{aligned} h &= 1, \\ &= 1 - 2x_2, \\ &= 1 - 2x_2\,(\,1 - 4x_2) - 3x_3, \end{aligned}$$

giving

$$\left.\begin{aligned} g &= x_2, \\ &= x_2 - 2x_2^2 + x_3, \\ &= x_2 + (x_3 - 2x_2^2) + (x_4 - 6x_2x_3 + \tfrac{20}{3}x_2^3). \end{aligned}\right\} \qquad \text{......(512)}$$

For a mixture

$$\begin{aligned} h_\alpha &= \nu_\alpha, & h_\beta &= \nu_\beta, \\ &= \nu_\alpha\,(1 - 2x_{2,0}\,\nu_\alpha - x_{1,1}\,\nu_\beta), & &= \nu_\beta\,(1 - 2x_{0,2}\,\nu_\beta - x_{1,1}\,\nu_\alpha), \end{aligned}$$

$$h_\alpha = \nu_\alpha - 2x_{2,0}\,\nu_\alpha^2\,(1 - 4x_{2,0}\,\nu_\alpha - 2x_{1,1}\,\nu_\beta)$$

$$- x_{1,1}\,\nu_\alpha\nu_\beta\,(1 - 2x_{2,0}\nu_\alpha - x_{1,1}\,[\nu_\alpha + \nu_\beta] - 2x_{0,2}\nu_\beta) - 3x_{3,0}\nu_\alpha^3 - 2x_{2,1}\nu_\alpha^2\,\nu_\beta - x_{1,2}\,\nu_\alpha\nu_\beta^2,$$

with a corresponding last formula for h_β. The terms in g of the first two orders are therefore

$$\begin{aligned} g = \{\nu_\alpha^2 x_{2,0} + \nu_\alpha\nu_\beta x_{1,1} + \nu_\beta^2 x_{0,2}\} + \nu_\alpha^3\,\{x_{3,0} - 2x_{2,0}^2\} + \nu_\beta^3\,\{x_{0,3} - 2x_{0,2}^2\} \\ + \nu_\alpha^2\nu_\beta\,\{x_{2,1} - 2x_{2,0}x_{1,1} - \tfrac{1}{2}x_{1,1}^2\} + \nu_\alpha\nu_\beta^2\,\{x_{1,2} - 2x_{0,2}x_{1,1} - \tfrac{1}{2}x_{1,1}^2\}. \end{aligned} \qquad \text{......(513)}$$

For the terms of the next higher order the coefficients of ν_α^4 and ν_β^4 can be written down from those for a pure gas. The coefficient of $\nu_\alpha^3\nu_\beta$ is

$$x_{3,1} - (4x_{2,0} + x_{1,1})\,x_{2,1} + \tfrac{1}{3}x_{1,1}^3 + 2x_{2.0}x_{1,1}^2 + 8x_{2,0}^2x_{1,1}. \qquad \text{......(514)}$$

The coefficient of $\nu_\alpha\nu_\beta^3$ can be written down from this by symmetry. The coefficient of $\nu_\alpha^2\nu_\beta^2$ is

$$\begin{aligned} x_{2,2} - 2x_{2,1}\,(x_{0,2} + x_{1,1}) - 2x_{1,2}\,(x_{2,0} + x_{1,1}) + (3x_{2,0} + x_{1,1} + 3x_{0,2})\,x_{1,1}^2 \\ + 4x_{2,0}x_{1,1}x_{0,2}. \end{aligned} \qquad \text{......(515)}$$

We shall now calculate the $x_{r,s}$ required for the terms of the first two orders, for hard spherical molecules. For x_2 or $x_{2,0}$ we have a single ξ and $p = 1$, $\sigma = 2$. Hence

$$x_2 = -\frac{N}{2V^2}\,.\,V\,.\,\tfrac{4}{3}\pi D^3 = -\,\tfrac{2}{3}\,N\pi D^3/V, \qquad \text{......(516)}$$

D being the diameter of the molecule. Similarly,

$$x_{2,0} = -\,\tfrac{2}{3}N_0\pi D_\alpha^3/V,\ \ x_{0,2} = -\,\tfrac{2}{3}N_0\pi D_\beta^3/V,\ \ x_{1,1} = -\,\tfrac{4}{3}N_0\pi D_{\alpha\beta}^3/V, \ \text{...(517)}$$

D_α, D_β being the respective diameters, and $D_{\alpha\beta}$ the sum of the radii.

Again, x_3 is the sum of two different ξ's. For one ξ one molecule overlaps two others, but these do not necessarily overlap. Hence $p = 2$, $\sigma = 2$, and

$$\frac{2\xi V^3}{N^2} = V\,(\tfrac{4}{3}\pi D^3)^2,\ \ \xi = 2x_2^2.$$

For the other ξ each pair of molecules must overlap and $p = 3$, $\sigma = 6$. When the first two have their centres at a distance r less than D, the volume in which the centre of the third molecule must lie is

$$K(r) = 2\int_{\frac{1}{2}r}^{D} \pi (D^2 - x^2)\,dx = 2\pi \left(\tfrac{2}{3}D^3 - \tfrac{1}{2}D^2 r + \tfrac{1}{24}r^3\right).$$

Hence

$$\frac{-6\,\xi V^3}{N^2} = V\int_0^D 4\pi r^2 K(r)\,dr,$$

$$\xi = \frac{-N^2}{6V^2}\, 8\pi^2 \int_0^D r^2 \left(\tfrac{2}{3}D^3 - \tfrac{1}{2}D^2 r + \tfrac{1}{24}r^3\right) dr,$$

$$= -\tfrac{5}{16}x_2^2.$$

Thus $$x_3 = (2 - \tfrac{5}{16})\,x_2^2, \qquad \text{......(518)}$$

and for a mixture $$x_{3,0} = (2 - \tfrac{5}{16})\,x_{2,0}^2. \qquad \text{......(519)}$$

The next x, $x_{2,1}$, is the sum of three terms. For the first one the β-molecule overlaps each of the α-molecules which do not themselves necessarily overlap. We have $p = 2$, $\sigma = 2$, and therefore

$$\xi = \tfrac{1}{2}x_{1,1}^2.$$

For the second, one of the α-molecules overlaps each of the others and $p = 2$, $\sigma = 1$,

$$\xi = 2x_{2,0}x_{1,1}.$$

For the third each pair of molecules must overlap and $p = 3$, $\sigma = 2$. When the α-centres are at a distance r, less than D_α, the centre of the β-molecule must lie in a volume

$$K(r) = 2\int_{\frac{1}{2}r}^{D_{\alpha\beta}} \pi (D_{\alpha\beta}^2 - x^2)\,dx.$$

Hence $$\xi = \frac{-N_0^2}{2V^2}\int_0^{D_\alpha} 4\pi r^2 K(r)\,dr,$$

$$= \frac{-4\pi^2 N_0^2 D_\alpha^3}{V^2}\left[\tfrac{2}{9}D_{\alpha\beta}^3 - \tfrac{1}{8}D_\alpha D_{\alpha\beta}^2 + \tfrac{1}{144}D_\alpha^3\right].$$

On substituting in g the second order terms simplify very greatly and we find

$$\begin{aligned} g = &-\left\{\nu_\alpha^2 \frac{\frac{2}{3}\pi N_0 D_\alpha^3}{V} + \nu_\alpha\nu_\beta \frac{\frac{4}{3}\pi N_0 D_{\alpha\beta}^3}{V} + \nu_\beta^2 \frac{\frac{2}{3}\pi N_0 D_\beta^3}{V}\right\} \\ &- \tfrac{5}{16}\nu_\alpha^3 \left(\frac{\frac{2}{3}\pi N_0 D_\alpha^3}{V}\right)^2 - 4\pi^2 \nu_\alpha^2 \nu_\beta \frac{N_0^2 D_\alpha^3}{V^2}\left\{\tfrac{2}{9}D_{\alpha\beta}^3 - \tfrac{1}{8}D_{\alpha\beta}^2 D_\alpha + \tfrac{1}{144}D_\alpha^3\right\} \\ &- \tfrac{5}{16}\nu_\beta^3 \left(\frac{\frac{2}{3}\pi N_0 D_\beta^3}{V}\right)^2 - 4\pi^2 \nu_\alpha \nu_\beta^2 \frac{N_0^2 D_\beta^3}{V^2}\left\{\tfrac{2}{9}D_{\alpha\beta}^3 - \tfrac{1}{8}D_{\alpha\beta}^2 D_\beta + \tfrac{1}{144}D_\beta^3\right\}. \end{aligned}$$

......(520)

The value of $\log B(\vartheta)$ is then, with this g,

$$(N_\alpha + N_\beta)\log V + N_0 g.$$

In terms of N_α and N_β only we therefore have

$$\begin{aligned}\log B(\vartheta) = (N_\alpha + N_\beta)\log V - \frac{1}{V}\{N_\alpha{}^2(\tfrac{2}{3}\pi D_\alpha{}^3) + N_\alpha N_\beta(\tfrac{4}{3}\pi D_{\alpha\beta}{}^3) + N_\beta{}^2(\tfrac{2}{3}\pi D_\beta{}^3)\}\\ - \frac{1}{V^2}[\tfrac{5}{16}N_\alpha{}^3(\tfrac{2}{3}\pi D_\alpha{}^3)^2 + 4\pi^2 N_\alpha{}^2 N_\beta D_\alpha{}^3\{\tfrac{2}{9}D_{\alpha\beta}{}^3 - \tfrac{1}{8}D_{\alpha\beta}{}^2 D_\alpha + \tfrac{1}{144}D_\alpha{}^3\}\\ + \tfrac{5}{16}N_\beta{}^3(\tfrac{2}{3}\pi D_\beta{}^3)^2 + 4\pi^2 N_\alpha N_\beta{}^2 D_\beta{}^3\{\tfrac{2}{9}D_{\alpha\beta}{}^3 - \tfrac{1}{8}D_{\alpha\beta}{}^2 D_\beta + \tfrac{1}{144}D_\beta{}^3\}].\end{aligned} \quad\text{......(521)}$$

The method of calculating $B(\vartheta)$ for a gas of rigid spheres extends at once to any gas, $B(\vartheta)$ being given formally by (475). In the integrand ϑ^W, W is of course the complete potential energy of the gaseous assembly, which will, speaking roughly, be a sum of terms corresponding to the various groups of molecules engaged in the various elements of $3N$-space in a close encounter. We can make successive approximations to W in any element of $3N$-space by making the groups of molecules which we regard as independent more and more all-inclusive. We shall still obtain for a pure gas in the absence of an external field of force

$$B(\vartheta) = V^N e^{Ng}, \quad\text{......(522)}$$

where g is the same function of the x_r as before, but the x_r are now defined so that $x_r V^r r!/N^{r-1}$ is the integral taken over $3r$-space of a certain quantity which we shall denote by u_r. These quantities u_r must be such that $u_1 = 1$ and that u_r, together with all the contributions from preceding $u_{r'}$ $(r' < r)$, builds up the correct integrand $\vartheta^{E_{12\ldots r}}$, or ϑ_r for short, for the group of r molecules considered by themselves. This u_r is then to be integrated over $3r$-space. It is obvious that

$$\vartheta_2 = u_2 + u_1 u_1, \quad u_2 = \vartheta_2 - 1,$$

$$\vartheta_3 = u_3 + \Sigma u_2 u_1 + u_1 u_1 u_1,$$

in which Σ is the sum over all pairs selected from the three molecules. Thus

$$u_3 = \vartheta_3 - \Sigma\vartheta_2 + 2.$$

In general we must have

$$\vartheta_n = \Sigma\Pi u_{(i_r)}, \quad\text{......(523)}$$

where the suffixes (i_r) denote any partition of the group of n molecules into (say) s subgroups containing $i_1, i_2, \ldots, i_s$ molecules respectively, and the summation is taken over all possible distinct partitions into any number s of subgroups. If we fix attention on a particular molecule, the nth, we can sum first in (523) all the terms in which the group containing this molecule is the same. This leads to

$$\vartheta_n = u_n + \Sigma u_{n-1}\vartheta_1 + \Sigma u_{n-2}\vartheta_2 + \ldots, \quad\text{......(524)}$$

where the u's refer to the various possible subgroups which include the nth molecule and the ϑ's to the complementary subgroups, with $\vartheta_1 = 1$. If, then, we denote by

$$(i_1, i_2, \ldots, i_s)$$

the coefficient of $\vartheta_{i_1}\vartheta_{i_2}\ldots\vartheta_{i_s}$ in u_n we find by equating coefficients in (524), when the nth molecule is in the sth group,

$$0 = (i_1, i_2, \ldots, i_s) + (i_2, i_3, \ldots, i_s) + (i_1, i_3, \ldots, i_s) + \ldots + (i_1, \ldots, i_{s-2}, i_s).$$

In the special case of one group this fails and is replaced by

$$1 = (n).$$

By varying the group in which the nth molecule lies we show at once that, for example,

$$(i_1, i_2, \ldots, i_{s-1}) = (i_2, i_3, \ldots, i_s),$$

so that all the $(s-1)$ group coefficients must be equal. Thence by induction

$$(i_1, i_2, \ldots, i_s) = (-)^{s-1}(s-1)\,!.$$

Therefore, finally,

$$u_n = \Sigma\,(-)^{s-1}(s-1)\,!\,\vartheta_{i_1}\vartheta_{i_2}\ldots\vartheta_{i_s}, \qquad \ldots\ldots(525)$$

the summation being taken over every distinct partition of the n molecules into subgroups. For example,

$$u_4 = \vartheta_4 - (\Sigma\vartheta_3 - \Sigma\vartheta_2\vartheta_{2'}) + 2\Sigma\vartheta_2 - 6, \qquad \ldots\ldots(526)$$

in which

$$\Sigma\vartheta_3 = \vartheta^{E_{123}} + \vartheta^{E_{234}} + \vartheta^{E_{341}} + \vartheta^{E_{412}},$$

$$\Sigma\vartheta_2\vartheta_{2'} = \vartheta^{E_{12}+E_{34}} + \vartheta^{E_{13}+E_{24}} + \vartheta^{E_{14}+E_{23}},$$

$$\Sigma\vartheta_2 = \vartheta^{E_{12}} + \vartheta^{E_{23}} + \vartheta^{E_{31}} + \vartheta^{E_{14}} + \vartheta^{E_{24}} + \vartheta^{E_{34}}.$$

When the gas is in a field of force, (525) remains true, but ϑ_1 is no longer 1, and the first term of the series is no longer V^N but $[A\,(\vartheta)]^N$, where

$$A\,(\vartheta) = \iiint \vartheta^{\Omega}\,d\omega,$$

Ω being the potential energy of a single molecule in the external field. It is necessary to redefine x_r using $A\,(\vartheta)$ in place of V. For a mixture we have a V_α and V_β in general different and

$$B\,(\vartheta) = V_\alpha{}^{N_\alpha}\,V_\beta{}^{N_\beta}e^{N_0 g},$$

where, in g, $x_{r,s}$ is such that

$$\frac{x_{r,s}V_\alpha{}^r V_\beta{}^s r\,!\,s\,!}{N_0{}^{s+r-1}} = \int u_{(r+s)}\,d\omega_{r,s}.$$

The formal connection of the u's with the ϑ's is unchanged by distinctions between molecules of different types, but the ϑ's themselves are changed.

In this extended theory we no longer can say positively *a priori* what the relative orders of x_r and $x_{r,s}$ must be; we can only say that x_r varies as the rth power of the molecular density and that in the general case $x_{r,s}$ occurs in g with a coefficient $(N_\alpha/V_\alpha)^r\,(N_\beta/V_\beta)^s$.

§ **8·4**. *Molecular distribution laws.* The ordinary uniform space distribution law may be derived at once for a gas of any degree of imperfection when there are no external fields, and no long range forces. The frequency ratio for the presence of a selected α molecule in a given element δV is $\delta B(\vartheta)/B(\vartheta)$, where

$$\delta B(\vartheta) = \int_{\delta V} d\omega_a \int_{(V)} \cdots \int \vartheta^{W} \Pi_\kappa' (d\omega_\kappa)^{N_\kappa}, \qquad \ldots\ldots(527)$$

just one $d\omega_a$ integration over V being omitted. If there are no long range forces or external fields, then W depends only on the relative coordinates of the molecules, and

$$\int_{(V)} \cdots \int \vartheta^{W} \Pi_\kappa' (d\omega_\kappa)^{N_\kappa}$$

must be a constant Q independent of the coordinates of the selected α. Therefore $\delta B(\vartheta) = Q\delta V$, and obviously $B(\vartheta) = QV$. Hence the frequency ratio is $\delta V/V$, and since there are N_a such α's

$$\overline{a_a} = N_a \delta V/V, \qquad \ldots\ldots(528)$$

which is the usual formula. If there are long range forces these *may*, as we shall see, build up the equivalent of external fields from the point of view of any specified element of the assembly. If there are any external fields Ω, then of course (528) is no longer true of the whole assembly but only of an elementary part of it over which the variation of Ω is negligible. In accordance with Gibbs' analysis showing that the laws of thermodynamics include the laws of mechanical equilibrium it is possible to deduce from (495) the distribution law in the field of force and the existence of mechanical equilibrium—the equation $dp = -v d\Omega$ being satisfied to the accuracy of the formulae. The investigation, however, is not elegant, and it is better in handling imperfect gases in external fields to apply the laws of statistical mechanics only to *elements* of the gas, and supplement these by the laws of mechanical equilibrium, or general thermodynamic theorems. Since these mechanical laws can be derived from the characteristic function for the whole assembly and lead by themselves to a unique equilibrium state for an assembly at uniform temperature, they must, together with the characteristic functions for the volume elements, be equivalent to the characteristic functions for the complete assembly.

By a similar argument we see that the average number $\overline{a_{\alpha\beta}}$ of α, β pairs simultaneously present in selected $d\omega_a$, $d\omega_\beta$ must be given by the formula

$$\overline{a_{a\beta}} = \frac{N_a N_\beta d\omega_a d\omega_\beta}{B(\vartheta)} \int_{(V)} \cdots \int \vartheta^{W} \Pi_\kappa'' (d\omega_\kappa)^{N_\kappa}. \qquad \ldots\ldots(529)$$

When no effective long range* or external forces are present the integral in (529) must be a function only of the relative coordinates of the selected $d\omega_a$ and $d\omega_\beta$. We may then write it in the form

$$Q\vartheta^{W_{a\beta}}, \qquad \ldots\ldots(530)$$

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* We shall see that this allows of the consideration of electrostatic forces in ionic media of zero space charge.

where $W_{\alpha\beta}$ is defined so that $W_{\alpha\beta} \rightarrow 0$ at infinite separation and Q is a constant. *So defined, $W_{\alpha\beta}$ may be called the average potential energy of β in the specified position in the field of α.* It may depend on the average positions of a large number of other molecules and may therefore itself be a function of ϑ. Again,

$$B(\vartheta) = \iint Q\vartheta^{W_{\alpha\beta}} d\omega_\alpha d\omega_\beta = QV^2,$$

provided only that $W_{\alpha\beta} \rightarrow 0$ rapidly for large separations, as in practice it always does. Thus the average number of pairs is

$$\overline{a_{\alpha\beta}} = N_\alpha N_\beta e^{-W_{\alpha\beta}/kT} \, d\omega_\alpha d\omega_\beta / V^2. \qquad \text{......(531)}$$

After integration with respect to $d\omega_\alpha$ the average number of β's in a selected region near any α anywhere in the assembly is

$$N_\beta e^{-W_{\alpha\beta}/kT} d\omega_\beta / V. \qquad \text{......(532)}$$

The factor $1/\sigma_{\alpha\beta}$ is not required in the formulae until we integrate $d\omega_\beta$ over the whole of $v_{\alpha\beta}$ round α. It is not until we do this that we count twice over each α, α pair.

Formulae (531) and (532) are forms of Boltzmann's theorem. It is important to realize, however, the precise meaning of $W_{\alpha\beta}$ for which the theorem is true. In accordance with the discussion in § 6·9 $W_{\alpha\beta}$ may be loosely called the free energy of a β in the field of an α, and it may be that $W_{\alpha\beta} \neq E_{\alpha\beta}$. In the case of short range forces with ternary and higher complexes neglected it is, however, true that $W_{\alpha\beta} = E_{\alpha\beta}$ to the first approximation. For

$$\vartheta^{W_{\alpha\beta}} = \frac{\vartheta^{E_{\alpha\beta}} V^2}{B(\vartheta)} \int_{(V)} \cdots \int \vartheta^{W - E_{\alpha\beta}} \prod\nolimits_\kappa{}'' \, (d\omega_\kappa)^{N_\kappa},$$

and it is obvious that the first approximation to the coefficient of $\vartheta^{E_{\alpha\beta}}$ is unity. Thus for short range forces in assemblies of not too high concentration (531) and (532) take the more familiar forms

$$\overline{a_{\alpha\beta}} = N_\alpha N_\beta e^{-E_{\alpha\beta}/kT} \, d\omega_\alpha d\omega_\beta / V^2, \qquad \text{......(533)}$$

and

$$N_\beta e^{-E_{\alpha\beta}/kT} \, d\omega_\beta / V. \qquad \text{......(534)}$$

It is clear, however, that $W_{\alpha\beta} \neq E_{\alpha\beta}$ even for short range forces at higher concentrations as in a liquid, and that the distribution may then be more uniform than is indicated by Boltzmann's law (534).

§ 8·5. *Generalities on dissociative equilibria in imperfect gases, and the use of the thermodynamic function* Ψ. We can construct a general theory of dissociating imperfect gases as a direct extension of the theory of Chapter v. We will consider for simplicity the theory of § 5·3 which we will here extend to imperfect gases. We there started (for perfect gases) by constructing the generating function (303)

$$X_1 ! \, X_2 ! \, \Sigma_{a,b} \frac{(\varpi_1{}^1 x_1 z^{\epsilon_1{}^1})^{a_1{}^1} \ldots (\varpi_1{}^2 x_2 z^{\epsilon_1{}^2})^{a_1{}^2} \ldots (\rho_1 x_1 x_2 z^{\eta_1})^{b_1} \ldots}{a_1{}^1 ! \ldots a_1{}^2 ! \ldots b_1 ! \ldots}.$$

This can be partially summed to the form

$$X_1 !\, X_2 !\, \Sigma_{a,b} \frac{(x_1 V F_1 (z))^{a_1}}{a_1 !} \frac{(x_2 V F_2 (z))^{a_2}}{a_2 !} \frac{(x_1 x_2 V G (z))^b}{b !}, \qquad \ldots(535)$$

a summation which will still be valid here. When the gases are perfect, (535) sums again, of course, to the familiar form (304)

$$X_1 !\, X_2 ! \exp [x_1 V F_1 (z) + x_2 V F_2 (z) + x_1 x_2 V G (z)].$$

When, however, the gases are imperfect the factor $V^{a_1+a_2+b}$ in the terms of (535) must be replaced by $B(z)$ which of course can be put in the approximate form

$$V^{a_1+a_2+b} \{1 + \alpha_1 (a_1, a_2, b)\}^{a_1} \{1 + \alpha_2 (a_1, a_2, b)\}^{a_2} \{1 + \beta (a_1, a_2, b)\}^b. \qquad \ldots\ldots(536)$$

The correcting terms α_1, α_2, β are also functions of z and are, of course, the extra terms of (485). They are supposed small, and only their first powers retained. We therefore replace the generating function (304) by Z say, whose approximate form is

$$X_1 !\, X_2 !\, \Sigma_{a,b} \frac{\{x_1 V F_1 (z) (1 + \alpha_1)\}^{a_1}}{a_1 !} \frac{\{x_2 V F_2 (z) (1 + \alpha_2)\}^{a_2}}{a_2 !} \frac{\{x_1 x_2 V G (z) (1 + \beta)\}^b}{b !}, \qquad \ldots\ldots(537)$$

and operate with Z throughout. Thus, nearly enough,

$$C = \frac{X_1 !\, X_2 !}{(2\pi i)^3} \iiint \frac{dx_1 dx_2 dz}{x_1^{X_1+1} x_2^{X_2+1} z^{E+1}} Z. \qquad \ldots\ldots(538)$$

The critical point of the integrand is determined as usual by the equations

$$X_1 = x_1 \partial \log Z / \partial x_1, \quad X_2 = x_2 \partial \log Z / \partial x_2, \quad E = z \partial \log Z / \partial z, \quad \ldots(539)$$

which will have a unique root μ_1, μ_2, ϑ. The equilibrium state is specified by equations like

$$\overline{N_1} = [F_1 \partial \log Z / \partial F_1]_{\mu_1, \mu_2, \vartheta}, \qquad \ldots\ldots(540)$$

and similar equations. The proof that the assembly obeys the laws of thermodynamics remains valid.

By comparison with the case of a perfect gas the root μ_1, μ_2, ϑ is such that the arguments, $\mu_1 V F_1 (\vartheta)$, etc., of Z are all large. We therefore study the asymptotic forms of the function

$$\Sigma_{a,b} \frac{\{A_1 (1 + \alpha_1)\}^{a_1}}{a_1 !} \frac{\{A_2 (1 + \alpha_2)\}^{a_2}}{a_2 !} \frac{\{B (1 + \beta)\}^b}{b !}$$

for large A, B, the α, β being functions of the a, b which are small compared with unity. To this end we pick out the maximum term of the multiple series by making the first order partial differential coefficients of

$$a_1 \left\{\log \frac{A_1 (1 + \alpha_1)}{a_1} + 1\right\} + a_2 \left\{\log \frac{A_2 (1 + \alpha_2)}{a_2} + 1\right\} + b \left\{\log \frac{B (1 + \beta)}{b} + 1\right\}$$

with respect to a_1, a_2, b vanish. It can easily be shown by the argument used in Theorem 2·5 that the value of the complete multiple series is practically determined by the maximum term, and that the summations may be replaced by integrations formally from $-\infty$ to $+\infty$ on either side of the maximum term. We find after simple reductions that, to the first order in α, β,

$$\log Z \sim A_1\{1+\alpha_1(A_1, A_2, B)\} + A_2\{1+\alpha_2(A_1, A_2, B)\} \\ + B\{1+\beta(A_1, A_2, B)\}. \qquad \ldots\ldots(541)$$

We find also that this asymptotic relation can be differentiated. The equilibrium conditions such as (540) are therefore

$$\overline{N_1} = A_1 \partial \log Z/\partial A_1,$$

etc., in which $A_1, \ldots$ are to be replaced by $\mu_1 V F_1, \ldots$ after differentiation. Thus

$$\overline{N_1} = A_1(1+\alpha_1) + A_1\left(A_1\frac{\partial\alpha_1}{\partial A_1} + A_2\frac{\partial\alpha_2}{\partial A_1} + B\frac{\partial\beta}{\partial A_1}\right), \qquad \ldots\ldots(542)$$

$$= \mu_1 V F_1[1+\alpha_1(\overline{N_1}, \overline{N_2}, \overline{M})]\left[1 + \overline{N_1}\frac{\partial\alpha_1}{\partial\overline{N_1}} + \overline{N_2}\frac{\partial\alpha_2}{\partial\overline{N_1}} + \overline{M}\frac{\partial\beta}{\partial\overline{N_1}}\right] \qquad \ldots\ldots(543)$$

to the approximation to which we are working. The law of mass-action is obtained, by eliminating μ_1, μ_2, in the form

$$\log\frac{\overline{N_1}\,\overline{N_2}}{V\overline{M}} = \log\frac{F_1F_2}{G} + \left[\frac{\partial}{\partial\overline{N_1}} + \frac{\partial}{\partial\overline{N_2}} - \frac{\partial}{\partial\overline{M}}\right]\{\overline{N_1}\alpha_1 + \overline{N_2}\alpha_2 + \overline{M}\beta\}. \qquad \ldots\ldots(544)$$

A similar formula can be given correcting the vapour-pressure equation for imperfection of the vapour phase. We obtain obviously in place of (544)

$$\log\frac{\overline{N}}{V} = \log\frac{F}{K} + \frac{\partial}{\partial\overline{N}}\{\overline{N}\alpha(\overline{N})\}, \qquad \ldots\ldots(545)$$

where K or $K(T)$ is the partition function for the crystal. At the same time

$$\frac{p}{kT} = \frac{\overline{N}}{V} + \frac{\partial}{\partial V}\{\overline{N}\alpha(\overline{N})\},$$

so that the equilibrium vapour-pressure is given by

$$\log p = \log\frac{kTF}{K} + \left[\frac{\partial}{\partial\overline{N}} + \frac{V}{\overline{N}}\frac{\partial}{\partial V}\right]\{\overline{N}\alpha(\overline{N})\}. \qquad \ldots\ldots(546)$$

In the usual first approximation

$$\overline{N}\alpha(\overline{N}) = \frac{(\overline{N})^2}{V}\,2\pi\int_0^\infty\{e^{-E_{\alpha\beta}/kT} - 1\}\,r^2dr,$$

so that

$$\log p = \log\frac{kTF}{K} + \frac{\overline{N}}{V}\,2\pi\int_0^\infty\{e^{-E_{\alpha\beta}/kT} - 1\}\,r^2dr. \qquad \ldots\ldots(547)$$

The foregoing arguments could easily be generalized, but the general method for imperfect gases in problems of dissociation or of external fields is not particularly convenient. It is of interest to have shown that the complete laws are given as they should be by the properties of C. In practice a more convenient working method can be developed based on the fact that our assemblies are thermodynamic systems, so that thermodynamic theorems may be applied.

Consider an assembly in which the dissociation is fixed, so that it contains N_1, N_2 and M free atoms and molecules. For such an assembly we can at once construct Ψ. By (491) it has the form

$$\Psi/k = N_1\left(\log\frac{VF_1}{N_1}+1\right)+N_2\left(\log\frac{VF_2}{N_2}+1\right)+M\left(\log\frac{VG}{M}+1\right)$$
$$+N_1\alpha_1+N_2\alpha_2+M\beta, \qquad \text{......(548)}$$

the α, β being the same functions of the N, M as in the foregoing argument. This must hold for any fixed values of N_1, N_2, M, whether or not they happen to agree with the true equilibrium values when dissociation is able to occur. Now suppose that the dissociation, temporarily fixed, is again allowed to proceed in either direction. It is a general thermodynamical principle* that in the final equilibrium state $\Delta\Psi = 0$ for any variation of the dissociation (or any other variation consistent with the given temperature and volume). Thus the condition of dissociative equilibrium can be at once obtained from the equation

$$\left[\frac{\partial}{\partial N_1}+\frac{\partial}{\partial N_2}-\frac{\partial}{\partial M}\right]\Psi = 0, \qquad \text{......(549)}$$

or

$$\log\frac{VF_1}{N_1}+\log\frac{VF_2}{N_2}-\log\frac{VG}{M}+\left[\frac{\partial}{\partial N_1}+\frac{\partial}{\partial N_2}-\frac{\partial}{\partial M}\right]\{N_1\alpha_1+N_2\alpha_2+M\beta\}=0,$$

which is equation (544) as obtained before.

The foregoing paragraph shows clearly the advantage to be gained in brevity by using thermodynamic arguments at suitable places for these more complicated assemblies. There is the same advantage in discussing imperfect gases in a field of force in this way, as compared with the general statistical method. We apply the general statistical arguments only to construct $\delta\Psi$ for each volume element δV and determine the complete equilibrium by making

$$\Delta\,(\Sigma\delta\Psi) = 0$$

for all relevant variations of numbers of particles between the different volume elements.

§ 8·6. *Dissociative equilibria for molecules of finite extension.* The formulae of this chapter take a specially simple form when the constituent

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* See, for example, Planck, *Thermodynamik*, ed. 6, § 151.

systems are of a definite size, without further fields of force. In such a case $E_{\alpha\beta} \rightarrow +\infty$ inside $v_{\alpha\beta}$ and is zero elsewhere, and

$$\Psi/k = \Sigma_\alpha N_\alpha \left\{\log \frac{VF_\alpha}{N_\alpha} + 1\right\} - \frac{1}{V} \Sigma_{\alpha\beta} \frac{N_\alpha N_\beta v_{\alpha\beta}}{\sigma_{\alpha\beta}}. \qquad \ldots\ldots(550)$$

Equation (550) forms the best starting point for discussing the equilibrium state of an assembly in which one of the systems has a sequence of possible states of definite sizes which differ from state to state.

Suppose there are present in the assembly systems of a certain type in a number of different stationary states of different sizes; these will be initially regarded as distinct systems, specified by different α's. Systems not belonging to this set will be specified by yet other α's. To determine the complete equilibrium state, we construct Ψ as above and vary the N_α among the states of the special systems until $d\Psi = 0$ for all such possible variations. A typical variation is to increase N_0 and decrease N_γ by equal amounts. We must therefore have

$$\left[\frac{\partial}{\partial N_0} - \frac{\partial}{\partial N_\gamma}\right]\Psi = 0,$$

or, in equilibrium,

$$\frac{\overline{N_\gamma}}{\overline{N_0}} = \frac{F_\gamma \, e^{-\Sigma_\beta \overline{N_\beta} v_{\gamma\beta}/V}}{F_0 \, e^{-\Sigma_\beta \overline{N_\beta} v_{0\beta}/V}}. \qquad \ldots\ldots(551)$$

The necessary and sufficient conditions for $d\Psi = 0$ for all possible variations of this kind is that (551) should hold for all γ's which specify the different states of the special systems. Now if we were to ignore the differences in size of the various states of the special systems we should treat them all together and construct a partition function

$$b(\vartheta) = \Sigma_\gamma \varpi_\gamma \vartheta^{\epsilon_\gamma}$$

to take account of the distribution of their *internal* energy. Here we temporarily treat each state separately and their separate partition functions are connected by the equations

$$F_\gamma/F_0 = \varpi_\gamma \vartheta^{\epsilon_\gamma}/\varpi_0 \vartheta^{\epsilon_0}. \qquad \ldots\ldots(552)$$

Inserting this ratio in (551) and putting $N = \Sigma_\gamma N_\gamma$ for the total number of special systems we have*

$$\overline{N_\gamma} = N \varpi_\gamma \vartheta^{\epsilon_\gamma} e^{-\Sigma_\beta \overline{N_\beta} v_{\gamma\beta}/V} / u(\vartheta), \qquad \ldots\ldots(553)$$

where

$$u(\vartheta) = \Sigma_\gamma \varpi_\gamma \vartheta^{\epsilon_\gamma} e^{-\Sigma_\beta \overline{N_\beta} v_{\gamma\beta}/V}. \qquad \ldots\ldots(554)$$

The γ-summation is of course only over all states of the special systems.

In all calculations we have therefore only to replace $b(\vartheta)$ and its terms by $u(\vartheta)$ and its terms in order to take full account of the excluded volumes.

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* Special cases of (553) and (554) were first given in discussions of high temperature atmospheres by Urey, *Astroph. Jour.* vol. LIX, p. 1 (1924), and independently by Fermi, *Zeit. für Phys.* vol. XXVI, p. 54 (1924).

If we use $u(\vartheta)$ so, we may group all the separate states of the special systems together as before. To reconstruct Ψ/k in terms of $u(\vartheta)$ we have

$$\frac{VF_\gamma e^{-\Sigma_\beta \overline{N_\beta} v_{\gamma\beta}/V}}{\overline{N_\gamma}} = \frac{Vu(\vartheta)\, h(\vartheta)}{N} = \frac{VF(\vartheta)}{N},$$

where $VF(\vartheta)$ is the complete modified partition function. The terms under Σ_α in (550) which belong to the special systems become

$$N\left\{\log\frac{VF(\vartheta)}{N} + 1\right\} + \frac{1}{V}\Sigma_\gamma \overline{N_\gamma}\,(\Sigma_\beta \overline{N_\beta}\, v_{\gamma\beta}).$$

When every system has been treated in this way we find

$$\Psi/k = \Sigma_r N_r\left\{\log\frac{VF_r(\vartheta)}{N_r} + 1\right\} + \frac{1}{V}\Sigma_{\alpha\beta}\frac{\overline{N_\alpha}\,\overline{N_\beta}\, v_{\alpha\beta}}{\sigma_{\alpha\beta}}, \quad \ldots\ldots(555)$$

where Σ_r is a summation over the separate systems and $\Sigma_{\alpha\beta}$ as before a summation over every pair of states of all the separate systems. It can be verified at once that in the equilibrium state

$$\frac{\partial\Psi}{\partial\overline{N_\gamma}} = 0 \quad (\mathit{all}\ \gamma). \qquad \ldots\ldots(556)$$

Thus the N_γ of the separate states are only apparent variables in Ψ/k. They do not affect the determination of dissociative equilibrium, which is to be carried out by varying the N_r in (555), without explicit notice of the $\overline{N_\gamma}$. The usual equilibrium laws will be at once obtained in terms of $F_r(\vartheta)$ or $(u(\vartheta)\, h(\vartheta))_r$.

It must be remembered that all the foregoing formulae are necessarily only correct to the first power of $1/V$, so that the exponential correcting factors are largely illusory. At the same time the use of the formulae seems to be justifiable for rough quantitative work, right outside the range in which the corrections are small, in fact for all orders. It will be remembered that states for which the correcting factors are large will *ipso facto* be scarce and therefore affect but little the equilibrium state. A closer examination of this point will, moreover, explain a numerical discrepancy from Urey's work*. Equation (550) may equally well be written in the form

$$\Psi/k = \Sigma_\alpha N_\alpha\left\{\log\frac{(V - \frac{1}{2}\Sigma_\beta N_\beta v_{\alpha\beta})\, F_\alpha}{N_\alpha} + 1\right\}, \qquad \ldots\ldots(557)$$

which has exactly the same validity so far as terms to the order $1/V$ are concerned. Equation (557), however, is the exact form of Ψ/k for a mixture of gases which obeys exactly van der Waals' equation in the form†

$$p = kT\Sigma_\alpha \frac{N_\alpha}{V - b_\alpha} \quad (b_\alpha = \tfrac{1}{2}\Sigma_\beta N_\beta v_{\alpha\beta}). \qquad \ldots\ldots(558)$$

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* Urey, *loc. cit.*

† See equation (631) of Chapter IX, of which this is an obvious generalization.

If now we work out the equilibrium state by varying the Ψ/k of (557) we find

$$\frac{(V-b_0)\,F_0}{N_0}\,e^{-\frac{1}{2}\Sigma_\beta N_\beta \frac{v_{0\beta}}{V-b_\beta}} = \frac{(V-b_\gamma)\,F_\gamma}{N_\gamma}\,e^{-\frac{1}{2}\Sigma_\beta N_\beta \frac{v_{\gamma\beta}}{V-b_\beta}}, \qquad \text{......(559)}$$

which to the first order in b/V reduces to (551). If the differences between $V - b_0$ and the $V - b_\gamma$ are ignored we can cast (559) into Urey's form

$$\frac{F_0}{N_0}\,e^{-\frac{1}{2}\frac{p}{kT}v_0{}^*} = \frac{F_\gamma}{N_\gamma}\,e^{-\frac{1}{2}\frac{p}{kT}v_\gamma{}^*}, \qquad \text{......(560)}$$

where $v_0{}^*$ and $v_\gamma{}^*$ are mean excluded volumes for the states 0 and γ, and p is the total pressure. This form, as we have seen, is incorrect (by the factor $\frac{1}{2}$ in the exponential) for small values of b/V. This difference is of no importance as the formulae cannot anyhow be exact. What is important is that the approximate agreement of (560) and (551) justifies to some extent the use of the latter for all values of b/V in rough numerical calculations.

It may be noted in conclusion that formulae of exactly the same validity can be obtained for the general assembly in which Ψ is given by (491), so that the excluded volumes are functions of the temperature and may in fact be negative.

§ **8·7**. *Inverse square law forces. Large scale effects.* The only important long range forces ($s \leqslant 4$) which appear to act between actual atoms and molecules are gravitational and electrostatic forces, following the inverse square law ($s = 2$). When such forces or external fields are acting the analysis of § 8·4 must be revised. In equation (527) W must be held to include the long range forces and external fields, and is no longer a function only of the relative coordinates of the systems. Thus

$$\int_{(V)} \cdots \int \vartheta^W \Pi_\kappa{}' \, (d\omega_\kappa)^{N_\kappa}$$

is no longer necessarily a constant Q independent of the coordinates of the selected α. Instead, we must define a function w by the equation

$$Q\vartheta^w = \int_{(V)} \cdots \int \vartheta^W \, \Pi_\kappa{}' \, (d\omega_\kappa)^{N_\kappa}, \qquad \text{......(561)}$$

where Q is a constant adjusted so that w takes any convenient value at an assigned point. We then have

$$\bar{a}_\alpha = N_\alpha Q \vartheta^w \delta V / B\,(\vartheta), \qquad \text{......(562)}$$

where
$$Q \int_V \vartheta^w dV = B\,(\vartheta).$$

Thus (562) reduces at once to

$$\bar{\nu}_t = \bar{\nu}_0\, e^{-(w_t - w_0)/kT}, \qquad \text{......(563)}$$

where $\bar{\nu}_t$ and $\bar{\nu}_0$ are the average concentrations of the α-molecules in different volume elements δV_t and δV_0. The average potential energy defined by (561) is the potential energy for which alone Boltzmann's theorem (563) is strictly true. The boundary field of an imperfect gas, which is investigated by a special method in § 9·8, is an example of a field such as is considered here—effectively equivalent to an external field though built up from short range forces.

It is desirable to investigate more closely the average potential energy w of this section and the $W_{\alpha\beta}$ of § 8·4, for it does not follow without further investigation that they agree with their values calculated when the rest of the assembly is in its average state. For most purposes of calculation it is almost essential to make this identification owing to the extreme complication of (561). It can easily be seen that the method of § 9·8 for boundary fields is based on this identification.

If we differentiate (561) with respect to the coordinates x, y, z of δV we find

$$\frac{\partial w}{\partial x}\int_{(V)}\dots\int \vartheta^W \Pi_\kappa{}' \,(d\omega_\kappa)^{N_\kappa} = \int_{(V)}\dots\int \frac{\partial W}{\partial x}\,\vartheta^W \Pi_\kappa{}' \,(d\omega_\kappa)^{N_\kappa}, \quad \dots\dots(564)$$

and two similar equations. In (564) W is of course the total potential energy of the gas phase in any configuration, and therefore $-\partial W/\partial x$, etc., are the force components acting on the selected α-molecule in δV. The function w has therefore been so defined that its partial derivatives are the average values with α fixed of the partial derivatives of W, or

$$\frac{\partial w}{\partial x} = \overline{\frac{\partial W}{\partial x}}, \quad \dots\dots(565)$$

and two similar equations. Thus if w is derived by calculating $\partial w/\partial x$ as the average value of the forces acting on the α-molecule—that is, as the force acting on the α-molecule when the rest of the assembly is in its average distribution—such a w is identical with the w of (561). This is the method to be used in § 9·8, which is hereby justified.

In (564) or (565) it is sometimes convenient to distinguish between the parts of $\partial W/\partial x$ which arise from forces of long and short range. If these are distinguished by suffixes l and s so that $W = W_l + W_s$ it may happen that

$$\frac{\partial w_s}{\partial x} = \overline{\frac{\partial W_s}{\partial x}} = 0. \quad \dots\dots(566)$$

This will always hold except near a boundary when $W_l = 0$, and will continue to hold with the same exception when $W_l \neq 0$ so long as the alterations in $\bar{\nu}_t$ introduced by W_l are insufficient to affect the perfection of the gas laws. When these imperfections begin to matter, W_s must make just such a contribution as to account for the difference between (563), which may be written

$$kT\frac{\partial\bar{\nu}}{\partial s} = -\bar{\nu}\frac{\partial w}{\partial s}, \qquad \text{......(567)}$$

and the laws of hydrostatic equilibrium,

$$\frac{\partial p}{\partial s} = -\bar{\nu}\frac{\partial w_l}{\partial s}. \qquad \text{......(568)}$$

It is an interesting and easy exercise to check the equivalence of (567) and (568) for first order deviations from the perfect gas laws.

Returning to conditions in which (566) is true, we find that

$$\frac{\partial w}{\partial x}\int_{(V)}\cdots\int \vartheta^{W}\Pi_\kappa{}'\,(d\omega_\kappa)^{N_\kappa} = \int_{(V)}\cdots\int\frac{\partial W_l}{\partial x}\,\vartheta^{W}\,\Pi_\kappa{}'\,(d\omega_\kappa)^{N_\kappa}. \qquad \text{......(569)}$$

If we differentiate (569) we find

$$\left[\frac{\partial^2 w}{\partial x^2} + \log\vartheta\left(\frac{\partial w}{\partial x}\right)^2\right]\int_{(V)}\cdots\int\vartheta^{W}\Pi_\kappa{}'\,(d\omega_\kappa)^{N_\kappa}$$

$$= \int_{(V)}\cdots\int\left[\frac{\partial^2 W_l}{\partial x^2} + \log\vartheta\left(\frac{\partial W_l}{\partial x}\right)^2\right]\vartheta^{W}\Pi_\kappa{}'\,(d\omega_\kappa)^{N_\kappa}, \qquad \text{......(570)}$$

and two similar expressions*. By addition

$$\left[\nabla^2 w + \log\vartheta\Sigma\left(\frac{\partial w}{\partial x}\right)^2\right]\int_{(V)}\cdots\int\vartheta^{W}\Pi_\kappa{}'\,(d\omega_\kappa)^{N_\kappa}$$

$$= \int_{(V)}\cdots\int\left[\nabla^2 W_l + \log\vartheta\Sigma\left(\frac{\partial W_l}{\partial x}\right)^2\right]\vartheta^{W}\Pi_\kappa{}'\,(d\omega_\kappa)^{N_\kappa}. \qquad \text{......(571)}$$

In (571) we shall take W_l to be a potential energy due to inverse square law forces, and obeying Poisson's equation

$$\nabla^2 W_l = \mu\nu, \qquad \text{......(572)}$$

where ν is the smoothed local concentration of systems in δV in any configuration. The value of μ will depend on the precise mixture of gravitational and electrostatic forces concerned. We find therefore that w satisfies the equation

$$\nabla^2 w - \mu\,\bar{\nu}_a = \log\vartheta\Sigma\left\{\overline{\left(\frac{\partial W_l}{\partial x}\right)^2} - \left(\frac{\partial w}{\partial x}\right)^2\right\}. \qquad \text{......(573)}$$

The right-hand side is the mean square fluctuation of the resultant force on the system in δV, divided by $(-kT)$. The mean density $\bar{\nu}_a$ is an average of ν for all configurations in which the a-molecule is fixed at the point concerned (but not counted in ν). The suffix is inserted to distinguish $\bar{\nu}_a$ from $\bar{\nu}$ of equation (563), which is an average for all positions of the

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* It is assumed that not only is $\overline{\partial W_s/\partial x}=0$ but also $\overline{\partial W_s/\partial x\,.\,\partial W_l/\partial x}=0$.

α-molecule as well as of the others. In practice, we replace $\bar{\nu}_a$ by $\bar{\nu}$ and omit the fluctuation terms, so that (573) reduces to

$$\nabla^2 w - \mu\bar{\nu} = 0. \qquad \text{......(574)}$$

The equilibrium state of the assembly may then be calculated by the combined use of Boltzmann's and Poisson's equations, (563) and (574), a fertile procedure in frequent use.

There are, however, three points which require critical examination: the smoothing employed in (572), the replacement of $\bar{\nu}_a$ by $\bar{\nu}$, and the neglect of the fluctuation terms on the right-hand side of (573).

In dealing with point charges† smoothing of some sort is essential to mathematical simplicity; if the charges are spread over finite volumes, each defined in position by the coordinates of its centre, the "smoothing" is automatic and inevitable. Thus for point charges we define the smoothed density at any point by some such formula as

$$\nu(x) = \sum_a \epsilon_a f(x - x_a), \qquad \text{......(575)}$$

where x is short for x, y, z, ϵ_a is the charge on an α-molecule, $f(x)$ diminishes rapidly with increasing distance from the origin, and

$$\int_{(V)} f(x)\, d\omega = 1. \qquad \text{......(576)}$$

In the case of charges spread over finite volumes, (575) necessarily holds good, and $\epsilon_a f(x)$ is the actual density in a single particle with its centre at the origin. The possibility of interpenetration is not excluded. The corresponding smoothed function $F^*(x)$, derived from any function of position $F(x)$, is

$$F^*(x) = \int_{(V)} F(x') f(x - x')\, d\omega'. \qquad \text{......(577)}$$

If $F(x_1, x_2, \ldots)$ is a function of many points, the smoothing is to be carried out for all of them, so that

$$F^*(x_1, x_2, \ldots) = \int_{(V)} \cdots \int F(x_1', x_2', \ldots) f(x_1 - x_1') f(x_2 - x_2') \ldots d\omega_1' d\omega_2' \ldots. \qquad \text{......(578)}$$

In the case of charged particles of finite size, this smoothing is again automatic, provided that F is linear in each of the charges concerned—e.g. a potential, or a mutual potential energy.

Equation (572) requires that W_l shall be equal to W^*, the smoothed electrostatic potential energy. It appears to be simplest to replace W by W^* throughout the argument. Thus w would be defined by

$$Q\vartheta^w = \int_{(V)} \cdots \int \vartheta^{W^*} \Pi_\kappa' (d\omega_\kappa)^{N_\kappa} \qquad \text{......(579)}$$

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† It is convenient to write in the language of electrostatics, but other fields of force are not excluded.

(compare (561)); and in (563)

$$\bar{\nu}(x) = \sum_{a} N_a \left[\int_{(V)} \cdots \int \vartheta^{W^*} \Pi_\kappa' \ (d\omega_\kappa)^{N_\kappa} \right]_{x_a = x} \Big/ \int_{(V)} \cdots \int \vartheta^{W^*} \Pi_\kappa \ (d\omega_\kappa)^{N_\kappa}. \qquad \text{......(580)}$$

This is not our ordinary equation for the average density; nor is it precisely the smoothed average density, nor even the average smoothed density. In all probability, however, it does not differ considerably from any of these. The difficulties introduced by smoothing are mostly of this kind, and are not likely to be important.

On the other hand, thorough smoothing, when it can be employed, gives the greatest assistance in answering the other two points of criticism. Consider first the relation between $\bar{\nu}_a$ and $\bar{\nu}$. Their difference depends on the difference between the value of ν at the position of the a-molecule and its more normal values. Now the a-molecule induces a considerable excess or deficiency of charge in its immediate neighbourhood; but its effect at some little distance is negligible. If the smoothing function $f(x)$ is appreciable only at very small distances, the effect of the a-molecule's field is an important feature in ν. If, however, $f(x)$ is appreciable also in a considerable volume in which the field of the a-molecule is negligible, the local excess or deficiency has comparatively little effect upon ν. In other words, slight smoothing retains a large part of the difference between $\bar{\nu}_a$ and $\bar{\nu}$, but a more thorough smoothing decreases the divergence.

So long, then, as we are concerned only with smoothed space charges (as in the problem, mentioned below, of a gravitating gas and in the theory of an electron atmosphere, developed in § 11·4), it is permissible and advantageous to smooth thoroughly, with a function which is effective over a volume large compared with molecular dimensions. $\bar{\nu}_a$ may then be replaced by $\bar{\nu}$. When, however, our whole concern is with concentrations on a molecular scale, as in formula (530) and the Debye-Hückel theory described below, any but the slightest smoothing is impossible, and $\bar{\nu}_a$ and $\bar{\nu}$ may be widely different.

For the validity of the neglect of the fluctuation terms no general conditions have yet been obtained. At present it seems possible to proceed only by verification *a posteriori*.

As an example, consider the equilibrium state of an isothermal gravitating gas of which each small element is effectively perfect*. This is of course a special case of the equilibria of such gaseous masses handled by

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* In order to discuss such an assembly completely from the point of view of statistical mechanics it is necessary to idealize the problem so that the mass of gas is contained in a reflecting enclosure so large that molecular impacts on the walls do not effectively alter the position of the centre of gravity of the mass of gas or its total momentum which must be fixed by the conditions of the problem. This is not strictly realizable. Such conditions can be formally accounted for by additional selector variables both for momenta and positional coordinates.

Emden*. There is no explicit solution for w or for ρ, the mass density at any point, but it is found that if r is the distance from the centre of the gravitating mass

$$\rho \sim \frac{2}{r^2}\left(\frac{kT}{m}\right)\frac{1}{4\pi G},$$

where G is the constant of gravitation. It follows that to the same approximation

$$w = 2kT \log r + const.$$

If we then compare one of the ignored terms $(\partial w/\partial r)^2/kT$ with a term retained such as $\partial^2 w/\partial r^2$ we find that the numerical ratio is 2. If therefore the fluctuation in the resultant force at any point is small compared with the force itself the neglect of all the terms on the right in (573) is at once justified.

A similar example is the electron atmosphere in equilibrium with a metal at high temperature. If the form of the atmosphere is effectively that of the gap between the parallel plates of an infinite condenser the problem admits of the exact solution (see (808)),

$$e^{w/2kT} = A \cos \frac{Bx}{\sqrt{(2kT)}},$$

where A and B are constants of which B depends on the electron density at a standard potential. Here again the numerical ratio of the ignored term $(\partial w/\partial r)^2/kT$ to the term retained $\partial^2 w/\partial r^2$ is less than 2, and the same conclusions can be drawn if the same hypothesis is admitted.

The problem of the ignorability of the fluctuation term can be formulated as follows: Let $-\partial\Omega_r/\partial x$ be the x-component of the force at x due to a single molecule in the rth cell of the assembly. Then

$$\frac{\partial W_l}{\partial x} = \Sigma_r a_r \frac{\partial \Omega_r}{\partial x}, \quad \frac{\partial w}{\partial x} = \overline{\frac{\partial W_l}{\partial x}} = \Sigma_r \bar{a}_r \frac{\partial \Omega_r}{\partial x},$$

$$\overline{\left(\frac{\partial W_l}{\partial x}\right)^2} = \Sigma_r \overline{a_r^2}\left(\frac{\partial \Omega_r}{\partial x}\right)^2 + 2\Sigma_{r,s}\overline{a_r a_s}\frac{\partial \Omega_r}{\partial x}\frac{\partial \Omega_s}{\partial x},$$

$$\overline{\left(\frac{\partial W_l}{\partial x}\right)^2} - \left(\frac{\partial w}{\partial x}\right)^2 = \Sigma_r\{\overline{a_r^2} - (\bar{a}_r)^2\}\left(\frac{\partial \Omega_r}{\partial x}\right)^2 + 2\Sigma_{r,s}\{\overline{a_r a_s} - \bar{a}_r\bar{a}_s\}\frac{\partial \Omega_r}{\partial x}\frac{\partial \Omega_s}{\partial x}.$$

A complete solution requires a knowledge of $\overline{a_r^2} - (\bar{a}_r)^2$ and $\overline{a_r a_s} - \bar{a}_r\bar{a}_s$ for these complicated assemblies. On general grounds, however, it is quite certain that these quantities will be all positive and very small compared with $(\bar{a}_r)^2$ and $\bar{a}_r\bar{a}_s$ *provided that the cells need not be taken too small*, that is, provided the smoothing is sufficiently macroscopic. It must be remembered that we are dealing with smoothed functions. The appropriate cell is that volume in which the smoothing function is effective. A thorough smoothing is again what we require, in order to make the cells conveniently

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* Emden, *Gaskugeln*; see also for this, Milne, *Trans. Camb. Phil. Soc.* vol. XXII, p. 483 (1923).

large. In evaluating long range large scale effects this is possible, and the above condition can be satisfied. It is not possible to conclude at once that

$$\overline{\left(\frac{\partial W_l}{\partial x}\right)^2} - \left(\frac{\partial w}{\partial x}\right)^2 \leqslant \left(\frac{\partial w}{\partial x}\right)^2,$$

for the terms $\partial\Omega_r/\partial x$ are not all positive. Their signs depend on the sign of $x - x'$. We can, however, conclude that

$$\overline{\left(\frac{\partial W_l}{\partial x}\right)^2} - \left(\frac{\partial w}{\partial x}\right)^2 \leqslant \left(\frac{\partial w'}{\partial x}\right)^2,$$

where $\partial w'/\partial x$ is the force component at x, y, z due to all the matter in the assembly on that side of the plane $\xi = x$ which gives the greater value of $\partial w'/\partial x$. It is therefore sufficient to verify *a posteriori* that $\partial^2 w/\partial x^2$ and similar terms are of the same order as $(\partial w'/\partial x)^2/kT$ and similar terms. The neglect of the fluctuation terms is then in general justified.

§ 8·8. *Inverse square law forces. Effect on molecular distribution laws.* A similar investigation can be made for the local field $W_{\alpha\beta}$ of formula (530) so far as it depends effectively on inverse square law forces. In this problem gravitational forces are so minute from the atomic standpoint that their local effect in clustering the molecules can be ignored. Electrical forces, however, are large from the atomic standpoint, and, even when their long range effects are zero owing to zero or negligible space charges, may exercise a decisive control over local conditions by establishing a state of polarization near a selected ion or near the surface of a conducting solid. We conclude that $W_{\alpha\beta}$, like w, satisfies Poisson's equation, at least on the average in the neighbourhood of a number of ions if not near a single ion, provided we may ignore the fluctuations. The volume elements near any one ion to which this process must be applied are, however, now small on the molecular scale and it is impossible to conclude with certainty by the argument used above that the fluctuations are negligible when $(\partial W_{\alpha\beta}/\partial x)^2/kT$ is of the same order as terms retained. This may be true, but the utmost that it is safe to conclude is that Poisson's equation may be used so long as

$$\frac{1}{kT}\left(\frac{\partial W_{\alpha\beta}}{\partial x}\right)^2$$

is itself *small* compared with terms retained. This conclusion may be made slightly less restrictive by remembering that any non-fluctuating part of $W_{\alpha\beta}$ may be removed before applying this argument.

In illustration of this argument we study here in detail the application of these equations to ions of negligible size in dilute solution according to the empirically successful theory of Debye and Hückel*. This investigation and others similar will be essential to us in Chapters XI, XIII, and XIV.

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* Debye and Hückel, *Phys. Zeit.* vol. XXIV, pp. 185, 305 (1923). For later references, see Chapter XIII.

Let $\psi_\alpha(x)$ be the average electrostatic potential near an ion of type α. That is,

$$\psi_\alpha(x)\int_{(V)}\cdots\int \vartheta^W \Pi_\kappa{}'(d\omega_\kappa)^{N_\kappa} = \int_{(V)}\cdots\int \psi(x)\,\vartheta^W \Pi_\kappa{}'(d\omega_\kappa)^{N_\kappa}. \quad \ldots\ldots(581)$$

Then evidently, since W is independent of x,

$$\nabla^2\psi_\alpha(x)\int_{(V)}\cdots\int \vartheta^W \Pi_\kappa{}'(d\omega_\kappa)^{N_\kappa} = \int_{(V)}\cdots\int \nabla^2\psi(x)\,\vartheta^W \Pi_\kappa{}'(d\omega_\kappa)^{N_\kappa},$$

$$= \frac{-4\pi}{D}\int_{(V)}\cdots\int \rho(x)\,\vartheta^W \Pi_\kappa{}'(d\omega_\kappa)^{N_\kappa}, \quad \ldots\ldots(582)$$

where $\rho(x)$ is the density of charge at x. Thus

$$\nabla^2\psi_\alpha = -4\pi\rho_\alpha/D, \quad \ldots\ldots(583)$$

where $\rho_\alpha(x) = \int_{(V)}\cdots\int \rho(x)\,\vartheta^W \Pi_\kappa{}'(d\omega_\kappa)^{N_\kappa}\Big/\int_{(V)}\cdots\int \vartheta^W \Pi_\kappa{}'(d\omega_\kappa)^{N_\kappa}$,

$$= \sum_\gamma z_\gamma \epsilon \frac{N_\gamma}{V}\vartheta^{W_{\alpha\gamma}}, \quad \ldots\ldots(584)$$

by the argument of § 8·4. Here ϵ is the electronic charge, z_γ the valency of the γ-ion—a small positive or negative integer—and N_γ/V is the concentration of these ions in the whole volume.

The equation for $W_{\alpha\beta}$, corresponding to (573), is

$$\nabla^2 W_{\alpha\beta}(x) + \frac{4\pi}{D} z_\beta \epsilon \rho_{\alpha\beta}(x) = \log\vartheta\,\Sigma\left\{\left(\frac{\partial W}{\partial x}\right)^2 - \left(\frac{\partial W_{\alpha\beta}}{\partial x}\right)^2\right\}, \quad \ldots\ldots(585)$$

where

$$\rho_{\alpha\beta}(x) = \left[\int_{(V)}\cdots\int \rho(x)\,\vartheta^W \Pi_\kappa{}''(d\omega_\kappa)^{N_\kappa}\Big/\int_{(V)}\cdots\int \vartheta^W \Pi_\kappa{}''(d\omega_\kappa)^{N_\kappa}\right]_{x_\beta = x}. \quad \ldots\ldots(586)$$

The ρ's of (585) and (583) are essentially different! Thus $\rho_{\alpha\beta}(x)$ is the mean density with the β-molecule fixed at the point considered. In fact, $\rho_{\alpha\beta}$ is likely to be determined by β rather than α; and its difference from ρ_α, as is explained above, cannot be removed by smoothing in this theory. Our only hope is that this difference may be compensated for by the fluctuation terms. For $\log\vartheta$ is negative, and the expression under the Σ is positive making the right-hand side of (585) negative; and since β repels charges of its own sign, $z_\beta\epsilon$ and $\rho_{\alpha\beta} - \rho_\alpha$ have opposite signs, and so a negative product. Thus in passing from (585) to the equation assumed by Debye and Hückel,

$$\nabla^2 W_{\alpha\beta} + 4\pi z_\beta \epsilon \rho_\alpha/D = 0, \quad \ldots\ldots(587)$$

we subtract a negative quantity from each side, and these may chance to be nearly equal.

Supposing that for some reason (587) is justifiable, we have

$$W_{\alpha\beta} = z_\beta \epsilon \psi_\alpha. \quad \ldots\ldots(588)$$

Since ψ_α has spherical symmetry, equations (583), (584) and (588) reduce to

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_\alpha}{dr}\right) = -\frac{4\pi\epsilon}{D}\sum_\gamma z_\gamma \frac{N_\gamma}{V} e^{-z_\gamma\epsilon\psi_\alpha/kT}. \qquad \text{......(589)}$$

The *equation* satisfied by ψ_α does not depend on the choice of α but the boundary conditions do. They must be $\psi_\alpha \to 0$ as $r \to \infty$, $\psi_\alpha \sim z_\alpha\epsilon/Dr$, $r \to 0$, where D is the dielectric constant of the medium. The difficulties connected with the idea of D in a molecular problem will be postponed for consideration in Chapter XIII.

The first attack on the theory of electrostatic effects in gases or solutions is due to Milner*. The various difficulties in the way of a successful calculation were clearly presented by him, though of course as he did not attempt to use Poisson's equation he was not troubled with fluctuations. His method is unexceptionable but prohibitively laborious. More recently a method of some promise has been proposed by Kramers†, avoiding the pitfalls of Debye and Hückel's method, and the tedium of Milner's. It remains to be seen if this can be developed further. Both Milner and Kramers seem to confirm the limiting form of Debye's result at great dilutions. But the interest of Debye's result lies in regions where theoretical basis is lacking, and we shall develop the theory and make tentative use of it here in default of anything better.

Equation (589) is soluble in principle as it stands, but requires elaborate treatment, and an explicit recognition of the fact that ions have sizes so that ions of opposite sign cannot really approach indefinitely close‡. The approximation made by Debye and Hückel which renders (589) soluble in finite terms is to assume that for all important values of r $z_\gamma\epsilon\psi_\alpha/kT$ is small. The equation then becomes

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi_\alpha}{\partial r}\right) = \kappa^2\psi_\alpha, \quad \kappa^2 = \frac{4\pi\epsilon^2}{DkT}\Sigma_\gamma z_\gamma{}^2\frac{N_\gamma}{V}. \qquad \text{......(590)}$$

The leading term, $$-\frac{4\pi\epsilon}{D}\Sigma_\gamma z_\gamma\frac{N_\gamma}{V},$$

vanishes when the average space charge is zero, a condition which may usually be assumed to be satisfied in applications. If the condition of zero space charge is not fulfilled, the proper solution of $(\nabla^2 - \kappa^2)\,\psi_\alpha = \mathit{const.}$ must be added to ψ_α so as to satisfy the boundary conditions. The solution of (590) which satisfies the conditions at $r = 0$ and $r = \infty$ is

$$\psi_\alpha = \frac{z_\alpha\epsilon}{D}\frac{1}{r}e^{-\kappa r}, \qquad \text{......(591)}$$

or

$$W_{\alpha\beta} = \frac{z_\alpha z_\beta\epsilon^2}{D}\frac{1}{r}e^{-\kappa r}. \qquad \text{......(592)}$$

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* Milner, *Phil. Mag.* vol. XXIII, p. 551 (1912); vol. XXV, p. 743 (1913).

† Kramers, *Proc. Sect. Sci. Amsterdam*, vol. XXX, p. 145 (1927).

‡ For this more exact treatment see § 13·72.

In considering the legitimacy of ignoring the fluctuation term, we remember that the portion $z_\alpha z_\beta \epsilon^2/Dr$ of $W_{\alpha\beta}$ is non-fluctuating, being the energy in the field of the selected α-ion itself. We may be content, therefore, to consider

$$W_{\alpha\beta}' = \frac{z_\alpha z_\beta \epsilon^2}{D}\frac{1}{r}(e^{-\kappa r} - 1), \qquad \text{......(593)}$$

and to examine whether $(\partial W_{\alpha\beta}'/\partial r)^2/kT$ is or is not small compared with a term retained such as $2\,(\partial W_{\alpha\beta}'/\partial r)/r$ or $\partial^2 W_{\alpha\beta}'/\partial r^2$ or $\kappa^2 W_{\alpha\beta}'$. The comparison with the first of these is simplest. We find a ratio

$$\frac{z_\alpha z_\beta \epsilon^2 \kappa}{2DkT}\left[\frac{1-(1+\kappa r)\,e^{-\kappa r}}{\kappa r}\right].$$

Since for all positive x $\qquad e^x \leqslant 1 + x + xe^x,$

it follows that the term in [ ] never exceeds unity, and the omission of the fluctuation term is legitimate if

$$\frac{z_\alpha z_\beta \epsilon^2 \kappa}{2DkT} \quad \textit{is small.}$$

This condition is equivalent to $W_{\alpha\beta}'/kT$ small.

§ **8·91**. *Contributions to the work function or characteristic function.* We have been studying at some length in the last sections methods of evaluating the distribution laws in various more complicated cases in which a direct attack on $B(\vartheta)$ seems almost hopeless. It is of the first importance to be able to combine these calculations with calculations of the corresponding terms in the work function or characteristic function of the assembly. This is of course equivalent to the calculation of $B(\vartheta)$, for which direct methods fail.

We have seen that our definition of w or $W_{\alpha\beta}$ is such that their gradients give the average value of the force at any point when the assembly is in equilibrium. Let us suppose, therefore, that the fields of force which give rise to w or $W_{\alpha\beta}$ are gradually built up from zero by differential additions to the various force centres, *the assembly being at a constant temperature during each successive stage and in the equilibrium state appropriate to the force centres already present.* No external work is done in rearrangement of the assembly into its equilibrium state at the given temperature in between the "stages". This is, of course, an ideal process requiring the treatment of individual molecules, but it is a conceivable isothermal reversible thermodynamic process, and the work done on the assembly in the process must on general thermodynamical principles be the increase in A, the work function, due to the establishment of the intermolecular fields. This is an extremely important result. It is analogous to the familiar method of calculating the contribution of such forces to the energy, when we suppose the fields of force gradually built up from zero, *the various* *systems of the assembly being fixed in their average final positions.* This is the origin of the familiar $\frac{1}{2}\int \rho W dV$ in the theory of attractions. A direct statistical proof may be given as follows.

Suppose that every intermolecular energy term is at a fraction σ of its final value. Then the partition function is $B_\sigma(\vartheta)$, say, given by

$$B_\sigma(\vartheta) = \int_{(V)} \dots \int \vartheta^{\sigma W} \Pi_\kappa (d\omega_\kappa)^{N_\kappa},$$

and the energy of the force system in equilibrium

$$\vartheta \frac{\partial}{\partial \vartheta} \log B_\sigma(\vartheta) = \frac{\sigma \int_{(V)} \dots \int W \vartheta^{\sigma W} \Pi_\kappa (d\omega_\kappa)^{N_\kappa}}{\int_{(V)} \dots \int \vartheta^{\sigma W} \Pi_\kappa (d\omega_\kappa)^{N_\kappa}}.$$

Keeping the distribution laws unaltered and increasing each energy term from σ to $\sigma + d\sigma$ requires an increase in the energy of the force system of

$$\frac{d\sigma \int_{(V)} \dots \int W \vartheta^{\sigma W} \Pi_\kappa (d\omega_\kappa)^{N_\kappa}}{\int_{(V)} \dots \int \vartheta^{\sigma W} \Pi_\kappa (d\omega_\kappa)^{N_\kappa}}.$$

This increase of energy must therefore be the work necessary to strengthen the force centres from a fraction σ to $\sigma + d\sigma$ of their final values. The total work required to build up the final force system by a reversible isothermal process is therefore

$$\frac{1}{\log \vartheta} \int_0^1 \frac{d}{d\sigma} \{\log B_\sigma(\vartheta)\}\, d\sigma = \log\{B(\vartheta)/V^{\Sigma_\kappa N_\kappa}\}/\log \vartheta. \quad \text{......(594)}$$

But this expression is just exactly

$$-kT \log\{B(T)/V^{\Sigma_\kappa N_\kappa}\},$$

or $-kT$ times the increase in Ψ/k due to the establishment of the intermolecular fields, and $-T\Psi = A$.

An obvious extension of this theorem leads to the same result when only the forces of one type, e.g. electrostatic forces, are considered, other forces such as those which give molecules their sizes being left unaltered throughout.

The most important application of this theorem is that it enables us to calculate the change in Ψ/k due to the establishment of the electrostatic charges of the ions in the theory of Debye and Hückel. This change we will call Ψ_ϵ/k. By (593) the final potential of the electrostatic field at the centre of an α-ion is

$$-\kappa z_\alpha \epsilon/D.$$

If all charges are reduced to the fraction σ then this potential is reduced to the fraction σ^2 since κ varies as ϵ. The work done on the assembly in bringing up a charge $z_\alpha \epsilon d\sigma$ is

$$(-\kappa z_\alpha{}^2 \epsilon^2/D)\,\sigma^2 d\sigma.$$

Summed over all ions this gives a work term

$$\left(-\frac{\kappa\epsilon^2}{D}\Sigma_\alpha N_\alpha z_\alpha{}^2\right)\sigma^2 d\sigma.$$

Therefore $$\Psi_\epsilon/k = \frac{\kappa\epsilon^2}{3DkT}(\Sigma_\alpha N_\alpha z_\alpha{}^2), \qquad \text{......(595)}$$

which is the standard result. It can, however, hardly be logically reached by any argument less deep than the foregoing. It will be observed that all questions of temperature variation of D and so on are irrelevant in forming the contribution to Ψ_ϵ/k. But to deduce U_ϵ the extra internal energy from Ψ_ϵ/k the temperature variation of D is relevant and important, and the value of U_ϵ was wrongly given in the earlier work on this theory.

CHAPTER IX

THE THEORY OF IMPERFECT GASES (*continued*)

§ 9·1. *Applications of the theory to simple imperfect gases and binary mixtures.* The number of empirical or semi-empirical equations of state in common use as interpolation formulae or as working digests of tabulated data is very large*. It is only possible here to discuss three of the simplest in relation to the theoretical results of the last chapter. For the purposes of this chapter readers who do not wish to follow the general theory of Chapter VIII in detail can be content with any one of the three elementary discussions given in §§ 9·6, 9·7, 9·8. Any one of these methods gives for a simple gas, correct to terms in $1/V$,

$$pV = NkT - f(T)/V,\ f(T) = 2\pi N^2 kT \int_0^\infty r^2 (e^{-E/kT} - 1)\, dr. \qquad \text{......(596)}$$

The best known practical equation of state is that of van der Waals, namely,

$$\left(p + \frac{a}{V^2}\right)(V - b) = NkT, \qquad \text{......(597)}$$

where a and b are constants. To the first power of $1/V$ this is equivalent to

$$pV = NkT + \frac{NkTb - a}{V}. \qquad \text{......(598)}$$

It is therefore equivalent, as a first order equation, to the approximation

$$f(T) = 2\pi N^2 kT \int_0^\infty r^2 (e^{-E/kT} - 1)\, dr = -NkTb + a. \qquad \text{......(599)}$$

Though obviously incomplete this is useful from its simplicity and a sufficient analogy to the true form. For if the molecules are almost rigid volumes without external fields, then $E = +\infty$ $(r < \sigma)$, and $E = 0$ $(r > \sigma)$, so that

$$f(T) = -\tfrac{2}{3}\pi N^2 kT\sigma^3.$$

Thus for such a model $b = \frac{2}{3}\pi N\sigma^3$ (four times the volume of all the molecules) and $a = 0$. Historically, van der Waals' formula was derived by superposing on this volume effect b the independent effect of weak attractive fields in creating a boundary field (see § 9·8) and thereby diminishing the pressure. In asserting that the effect of this boundary field could be represented by a constant a added as in (598) to the unaltered volume effect, two mistakes are made. One is that the boundary field is calculated

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* See, for example, Partington and Shilling, *The specific heats of gases* (1924); Kamerlingh-Onnes and Keeson, "Die Zustandsgleichungen", *Encyk. Math. Wiss.* Bd. V, No. 10; Jeans, *loc. cit.* chaps. VI, VII.

ignoring the effects of the intermolecular attractions on the distribution of molecular pairs, which is equivalent to replacing $(e^{-E/kT}-1)$ by $-E/kT$ in (599). The other is that the effect of the attractions on the volume effect itself is forgotten. When these mistakes are corrected, formulae (596) and (599) are recovered*. The value of (597) as a substitute for (598) rests entirely on its simplicity in applications, but its success is strictly limited.

The equation of state of D. Berthelot has an appreciably greater range of validity since it gives a closer representation of the theoretical first order terms. It is used empirically in either of the forms

$$pV = NkT\left\{1 - \frac{p}{NkT}\left(\frac{a'}{NkT^2} - b\right)\right\}, \qquad \ldots\ldots(600)$$

$$\left(p + \frac{a'}{TV^2}\right)(V-b) = NkT, \qquad \ldots\ldots(601)$$

where a' and b are constants. Either of these is equivalent to the first order form

$$pV = NkT + \frac{NkTb - a'/T}{V}, \qquad \ldots\ldots(602)$$

so that they are based on the approximation

$$f(T) = -NkTb + a'/T. \qquad \ldots\ldots(603)$$

If we contemplate a molecular model of an elastic sphere surrounded by an attractive field of force, of potential energy $-P$, we have

$$f(T) = 2\pi N^2 kT\left[-\tfrac{1}{3}\sigma^3 + \int_\sigma^\infty r^2\{e^{P/kT}-1\}\,dr\right]. \qquad \ldots\ldots(604)$$

Thus as before $b = \frac{2}{3}\pi N\sigma^3$, and

$$a' = 2\pi N^2 kT^2 \int_\sigma^\infty r^2\,(e^{P/kT}-1)\,dr. \qquad \ldots\ldots(605)$$

The assumption that a' is independent of T may be expected to be fairly near the truth in suitable regions of temperature. For the extra T-factor makes it possible for $da'/dT = 0$ for some T, whereas for a we have always $da/dT < 0$. It would perhaps be better still to use a'/T^s instead of a'/T in (600) with the corresponding changes elsewhere, and adjust s to bring the zero of da'/dT into the most important temperature range.

Another equation of state of considerable importance is that of Dieterici. It is used empirically in the forms

$$p(V-b) = NkT\,e^{-a/NkTV}, \qquad \ldots\ldots(606)$$

$$p(V-b) = NkT\,e^{-a'/NkT^sV}, \qquad \ldots\ldots(607)$$

in which a, a', b and s are constants. The value of s (other than 1) most often used is $\frac{3}{2}$. To the first order in $1/V$ these equations have still the same form

$$pV = NkT + \frac{NkTb - a'/T^{s-1}}{V}, \qquad \ldots\ldots(608)$$

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* Fowler, *Phil. Mag.* vol. XLIII, p. 785 (1922).

and the same first order validity. They are, however, empirically very much more successful at reproducing observed facts, and this is undoubtedly due to the exponential instead of the additive form of the *a*-correction. Though we have really only studied first order corrections here, it is not difficult to see that Dieterici's form ought theoretically to be successful over a wider range than van der Waals' or Berthelot's. For we shall show in § 9·8, by a discussion of the boundary field, that approximately

$$pV = NkT \exp\left[\frac{-2\pi N}{V}\int_0^\infty r^2\{e^{-E/kT} - 1\}\,dr\right]. \qquad \text{......(609)}$$

The discussion on which this is based is admittedly inadequate, since only first order accuracy was aimed at in the intermolecular distribution law, and there are other approximations. But we may expect qualitative accuracy in the form of these approximations, and the rest of the argument inevitably leads to an equation of the form (609). Dieterici's form is derived by approximating to

$$\frac{2\pi N}{V}\int_0^\infty r^2\,\{e^{-E/kT} - 1\}\,dr$$

with the usual $-\,b/V + a/NkT^s V$, and replacing $Ve^{-b/V}$ by $V - b$.

For practical use the a, a' and b of these and similar equations are adjusted to give the best fit with the facts over some particular temperature and pressure range, or to reproduce exactly some particular phenomenon such as the critical conditions (see below). It must be remembered that the constants so determined have no direct connection with the interatomic fields of force and cannot be used for anything more than a rough qualitative estimate of these fields or of the sizes of molecules. The mistake of using data from the critical point, for example, for quantitative estimates of molecular diameters has frequently been made. The only correct course is to reduce the observed equation of state to the form*

$$pV = NkT - f(T)/V + O(1/V^2), \qquad \text{......(610)}$$

and thus determine the observational value of $f(T)$, often called the second virial coefficient. Thus determined, $f(T)$ can be directly equated to its theoretical value. We give an account in the next chapter of the latest work of this nature which has succeeded in coordinating into one consistent scheme the requirements of interatomic fields both in gases and in crystals.

§ **9·2**. *Critical points and reduced equations of state.* The semi-empirical equations of this section agree in predicting the existence of two types of isothermal separated by a *critical isothermal* for which $T = T_c$. When $T > T_c$, $\partial p/\partial V < 0$ for all V. When $T < T_c$, $\partial p/\partial V$ vanishes twice and is

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* This is the method followed by Kamerlingh-Onnes and Keesom and their collaborators at Leiden, and first correctly applied to the study of atomic fields by Keesom.

positive between these roots. This behaviour can be regarded as a satisfactory description of the observed facts that for any substance there exists a critical temperature above which the substance can exist only in a single phase—the gaseous state, while below there are two possible phases, the gaseous or vapour state and the liquid state, which can co-exist in equilibrium together. Mathematically, the critical isothermal must be determined by the condition that on it the two roots of $\partial p/\partial V = 0$ which are real for $T < T_c$ coalesce to form a single double root. This condition is obviously that the critical isothermal is that on which there exists a point, called the *critical point*, at which

$$\partial p/\partial V = \partial^2 p/\partial V^2 = 0. \qquad \text{......(611)}$$

Combined with the equation of state these equations suffice in general to fix the values of p, V and T for the critical point. These values are usually denoted by p_c, V_c and T_c. At this point the properties of the liquid and vapour phase finally become identical and the two phases fuse into one. The position of the critical point predicted by some of the equations is as follows:

van der Waals— $V_c = 3b,\ p_c = a/27b^2,\ T_c = 8a/27Nkb.$ ......(612)

Dieterici— $V_c = 2b,\ p_c = a/4e^2b^2,\ T_c = a/4Nkb.$ ......(613)

Dieterici's equation reproduces the position of the critical point with considerable success for many gases. The predicted relation

$$NkT_c/p_cV_c = \tfrac{1}{2}e^2 = 3{\cdot}695$$

is particularly successful. The reader should refer to Jeans* for a further discussion. Some typical isothermals for carbon dioxide are shown in Fig. 10, reproduced from Partington and Shilling†.

The equations of state discussed here are alike in possessing only two adjustable constants. In each case, and in all similar cases, these two constants and Nk can be eliminated by introducing instead p_c, V_c and T_c. The equation of state then takes the form

$$\frac{p}{p_c} = f\left(\frac{V}{V_c}, \frac{T}{T_c}\right), \qquad \text{......(614)}$$

where f is a function which is the same for all a and b, that is, to this approximation the same for all gases. This can easily be verified directly, or alternatively deduced by a dimensional argument. It is usual to introduce new variables π, v, ϑ, called *reduced variables,* defined by the relations

$$p = \pi p_c,\ V = vV_c,\ T = \vartheta T_c.$$

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* Jeans, *loc. cit.*

† Partington and Shilling, *loc. cit.* p. 37.

The equation of state then takes an absolute form called the *reduced equation of state.* As examples:

van der Waals— $$(\pi + 3/v^2)(3v - 1) = 8\vartheta. \qquad \text{......(615)}$$

Berthelot— $$(\pi + 3/v^2\vartheta)(3v - 1) = 8\vartheta. \qquad \text{......(616)}$$

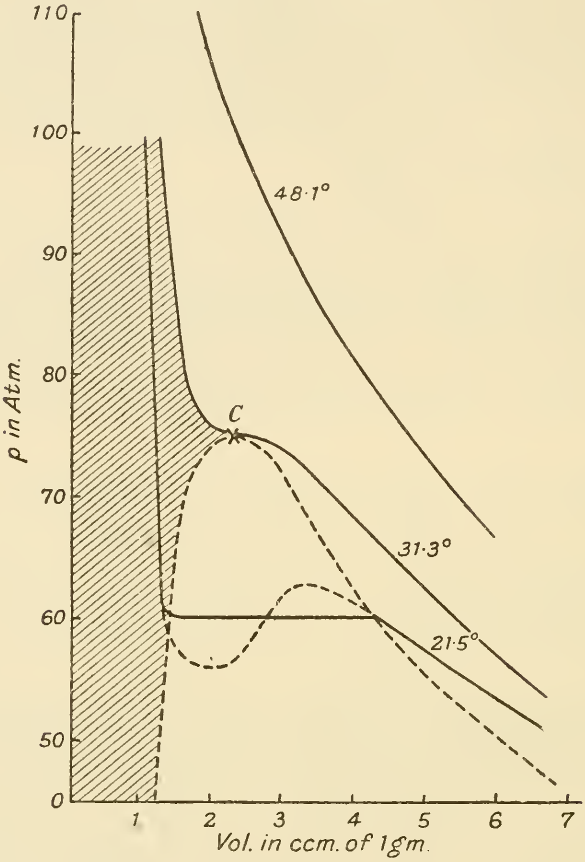

Fig. 10. Isothermals of CO_2. The critical point is at C. The shaded portion represents liquid states and the part within the dotted curve liquid-vapour mixtures.

Berthelot modified—An empirical equation used in the reduced forms

$$(\pi + 16/3v^2\vartheta)(v - \tfrac{1}{4}) = \frac{32}{9}\vartheta, \qquad \text{......(617)}$$

$$\pi v = \frac{32}{9}\vartheta\left\{1 + \frac{9\pi}{128\vartheta}\left(1 - \frac{6}{\vartheta^2}\right)\right\}. \qquad \text{......(618)}$$

These of course do not give the critical point 1, 1, 1 as a reduced equation should, but are more successful in the region of moderate deviations from the perfect gas laws*.

Dieterici— $$\pi(2v - 1) = \vartheta e^{2-2/(v\vartheta^s)}. \qquad \text{......(619)}$$

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* See also Henning, *Temperaturmessung*, Braunschweig (1915); Eucken, *Zeit. für Phys.* vol. XXIX, p. 1 (1924).

Equal values of the reduced variables are said to be *corresponding* values of the ordinary variables for different gases. The suggestion of these equations that for corresponding temperatures and volumes the pressures have corresponding values for all substances is called *the law of corresponding states*. This law is approximately true over wide ranges of the variables for not too dissimilar molecules, but is by no means true in general.

§ 9·3. *Inversion points in the Thomson-Joule effect.* The thermodynamic theory of the Thomson-Joule effect is well known* and need not be repeated here. Gas is allowed to stream through a valve, porous plug or other throttling device under a steady pressure difference which maintains the flow against frictional resistances. In the steady state there is a temperature difference on the two sides of the plug or valve for an imperfect gas. For a differential pressure drop Δp this temperature difference ΔT is given by

$$\Delta T = \left\{T\left(\frac{\partial V}{\partial T}\right)_p - V\right\}\frac{\Delta p}{C_p}. \qquad \text{......(620)}$$

Since necessarily $\Delta p < 0$, ΔT has the sign of $V - T\,(\partial V/\partial T)_p$. The effect may therefore be either a heating or cooling of the gas. The heating and cooling regions in the p, V or p, T planes are divided from one another by *the curve of inversion points*, whose equation is obtained by eliminating one variable from the equation of state by means of the equation

$$T\left(\frac{\partial V}{\partial T}\right)_p - V = 0. \qquad \text{......(621)}$$

In reduced variables the curve of inversion points has the following forms:

van der Waals— $(12\vartheta + \pi - 81)^2 + 216\,(4\vartheta + \pi - 27) = 0.$ ......(622)

Dieterici— $\pi\vartheta^{s-1} = \{4\,(s+1) - \vartheta^s\}\, e^{\frac{2s+3}{s+1} - \frac{4}{\vartheta^s}}.$ ......(623)

A diagrammatic presentation of these curves and observed inversion points is shown in Fig. 11 taken from Lewis†. It will be seen at once that Dieterici's equation with $s = \frac{3}{2}$ gives a very faithful representation of the properties of these gases in the neighbourhood of the curve of inversion points. This is a somewhat severe test of any practicable equation of state.

It will be seen on inspection of Fig. 11 that the cooling region is limited in area, the main portion of the p, T plane being the heating region. At the same time for the commoner gases the cooling region practically covers the range of ordinary temperatures and pressures. Hydrogen, helium and neon are exceptions. The limitation of the cooling region is

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* W. C. McC. Lewis, *A System of Physical Chemistry*, vol. II, *Thermodynamics*, ed. 2, p. 67; Planck, *Thermodynamik*, ed. 6, § 70; Birtwistle, *Thermodynamics*, chap. VIII.

† W. C. McC. Lewis, *loc. cit.* p. 71.

of great importance in liquefaction practice by Linde's process, which is based on the Thomson-Joule effect to obtain the reduction of temperature in each cycle. Unless the temperature is low enough for the greater part of the designed pressure drop to lie in the cooling region, the gas will not cool but heat and the liquefaction process cannot be carried out. In the manufacture of liquid hydrogen and helium by Linde's process efficient cooling will not occur unless the hydrogen used has been already cooled with liquid air, and the helium used with liquid hydrogen.

All these aspects of the theory of simple gases have long been fully appreciated, except the precise determination of intermolecular forces to which we devote the following chapter. It therefore seems unnecessary to give further space to them here.

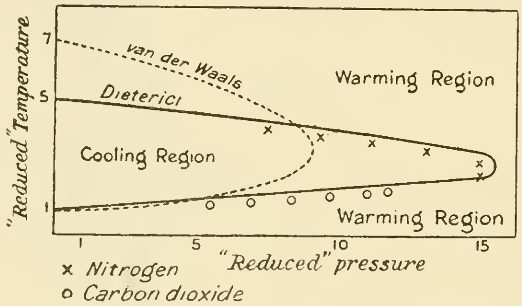

Fig. 11. The curves of inversion points in the Thomson-Joule effect.

§ 9·4. *Binary mixtures.* Except for the variation of their properties with composition binary (and higher) mixtures of gases which do not react chemically behave like simple gases and no further discussion is required. It does, however, appear desirable to examine the theory of the variation with composition, as curiously erroneous statements appear to be current.

For a binary mixture equation (492) gives us

$$p = kT\left[\frac{N_1+N_2}{V} - \frac{1}{V^2}\{\tfrac{1}{2}\rho_{11}N_1{}^2 + \rho_{12}N_1N_2 + \tfrac{1}{2}\rho_{22}N_2{}^2\}\right], \quad \text{......(624)}$$

where

$$\rho_{\alpha\beta} = 4\pi\int_0^\infty \{e^{-E_{\alpha\beta}/kT} - 1\}r^2dr. \quad \text{......(625)}$$

If we write

$$N_1 = xN,\ N_2 = (1-x)N,$$

so that x is the fraction of the first constituent in numbers of molecules, and so approximately the volume fraction at standard temperature and pressure, we have

$$p = kT\left[\frac{N}{V} - \tfrac{1}{2}\frac{N^2}{V^2}\{\rho_{11}x^2 + 2\rho_{12}x\,(1-x) + \rho_{22}\,(1-x)^2\}\right]. \quad \text{......(626)}$$

It is at once obvious that a linear dependence on x must be the exception rather than the rule. The second virial coefficient must in general be a quadratic function of x, and it is obvious without explicit calculation that the nth virial coefficient must in general be a polynomial of the nth degree in x. The condition for linearity of the second virial coefficient in x is

$$\rho_{11} + \rho_{22} = 2\rho_{12}. \qquad \text{......(627)}$$

There is obviously no reason why this should be satisfied in general, but it is clear that it is likely to be true or nearly true when the molecular fields are very closely similar, for the condition states in a sense that the intermolecular forces between molecules 1 and 2 are the mean of those between 1 and 1 and between 2 and 2. This appears to hold for oxygen-nitrogen mixtures with very considerable accuracy*, and was once assumed to hold for helium-neon mixtures for the purpose of deducing the isotherms of pure neon, an assumption shown to be invalid by later work on pure neon.

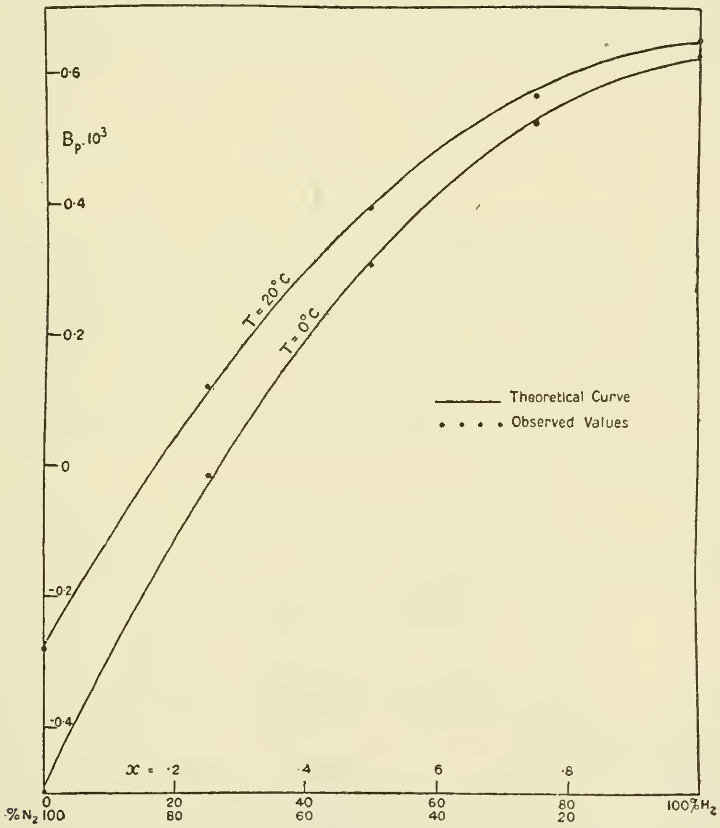

Fig. 12. Variation of the second virial coefficient with composition in hydrogen-nitrogen mixtures.

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* Holborn and Otto, *Zeit. für Phys.* vol. x, p. 367 (1922); vol. xxiii, p. 77 (1924).

In an interesting paper, Verschoyle* has established a case of marked failure of (627) by the study of hydrogen-nitrogen mixtures, which has been discussed theoretically by Lennard-Jones and Cook†. Fig. 12 is taken from their paper and shows the variation with composition of the second virial coefficient, proportional to their B_p. The observed points can be fitted reasonably well by a parabola of the theoretical form, though the fit is hardly as good as might have been expected. These mixture curves may be taken as determining ρ_{12} when ρ_{11} and ρ_{22} are already known, and therefore as determining E_{12}, that is, the law of force between unlike molecules. A detailed experimental study of inert gas mixtures in various proportions would provide information of great value in the further development of the theories of Chapter x.

§ **9·5**. *The construction of* Ψ/k. For the logical completion of the elementary methods of §§ 9·7 and 9·8 for the study of imperfect gases it is necessary to have a means of deriving the correction to Ψ/k corresponding to the directly calculated correction to the pressure. Such a method is also applicable to the semi-empirical pressure corrections of the preceding sections.

We start from the thermodynamic relation

$$p = T\partial\Psi/\partial V. \qquad \text{......(628)}$$

In general a knowledge of the equation of state, p, does not suffice to determine Ψ by integration, for the integration constant, which is unfixed, is an unknown function of N and T. But if we already know completely the exact form Ψ_∞ of Ψ in the limit $V \to \infty$, then (628) is sufficient; and in fact Ψ_∞ is known, for the assembly becomes a perfect gas. Owing to the linear form of (628) the corresponding corrections to p and Ψ must be additive. If we denote the imperfect gas correction to p by p_w and to Ψ by Ψ_w we obtain from (628)

$$\Psi_w = \Psi - \Psi_\infty = -\int_V^\infty \frac{p_w}{T}\,dV. \qquad \text{......(629)}$$

By (596) the general correction is

$$\frac{p_w}{T} = -\tfrac{1}{2}\frac{N^2k}{V^2}4\pi\int_0^\infty r^2\,(e^{-E/kT}-1)\,dr.$$

Therefore

$$\frac{\Psi_w}{k} = \tfrac{1}{2}\frac{N^2}{V}4\pi\int_0^\infty r^2\,(e^{-E/kT}-1)\,dr, \qquad \text{......(630)}$$

which agrees with (491).

In connection with any semi-empirical equation of state we use this method to determine Ψ_w and so Ψ, and to deduce from Ψ by the usual thermodynamic equations the corrections to C_v and C_p. In this way observed values of p, C_v and C_p can be corrected for deviations from the

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* Verschoyle, *Proc. Roy. Soc.* A, vol. cxi, p. 552 (1926).

† Lennard-Jones and Cook, *Proc. Roy. Soc.* A, vol. cxv, p. 334 (1927).

perfect gas laws, and the corresponding p_∞, $(C_v)_\infty$, and $(C_p)_\infty$ determined. For the foregoing empirical equations we have

van der Waals— $$\Psi = Nk\left\{\log\frac{(V-b)\,F}{N}+1\right\}+\frac{a}{TV}. \qquad \text{......(631)}$$

Berthelot (V-form)— $$\Psi = Nk\left\{\log\frac{(V-b)\,F}{N}+1\right\}+\frac{a'}{T^2V}. \qquad \text{......(632)}$$

Berthelot (p-form)— $$\Psi = Nk\left\{\log\frac{(V-b+a'/NkT^2)\,F}{N}+1\right\}. \qquad \text{......(633)}$$

Dieterici— $$\Psi = \Psi_\infty - Nk\int_{NkT^sV/a'}^{\infty}\left(\frac{e^{-x}}{x-b'}-\frac{1}{x}\right)dx \quad (b' = NkT^sb/a'). \qquad \text{......(634)}$$

The last formula cannot be given in finite terms. Equation (633) is of greater value when we form the other characteristic function Φ in terms of p and T,* based on the free energy instead of the work function. The relation is

$$\Phi = \Psi - pV/T, \qquad \text{......(635)}$$

and we find

Berthelot (p-form)—

$$\Phi = Nk\left\{\log\frac{kTF}{p}+\frac{p}{NkT}\left(\frac{a'}{NkT^2}-b\right)\right\}. \qquad \text{......(636)}$$

From Ψ we can at once deduce C_v and so the correction to $(C_v)_\infty$ by the equation

$$C_v = \frac{\partial}{\partial T}\left(T^2\frac{\partial\Psi}{\partial T}\right)_V, \qquad \text{......(637)}$$

and, similarly, from Φ $$C_p = \frac{\partial}{\partial T}\left(T^2\frac{\partial\Phi}{\partial T}\right)_p. \qquad \text{......(638)}$$

§ **9·6**. *Alternative methods of calculation. Method* (i). *As a problem in dissociation.* The results of this chapter can be reached in a variety of other ways, some of which will be considered in the following sections. Since we need no longer attempt maximum generality we shall be content to consider the case of a simple imperfect gas of N molecules.

The results for a perfect gas can be extended at once to an imperfect gas (short range forces) by the device† of regarding any pair of molecules within each other's field of force as a *system* to be discussed as a whole. Any single molecule outside the fields of force remains a system as before.

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* Planck, *Thermodynamik*, ed. 6, § 283 (1922).

† Jeans, *loc. cit.* p. 91. The discussion of dissociation and aggregation there given on a classical basis is inadmissible *in general*. The phenomena are essentially phenomena of the quantum theory. The device is, however, admirably adapted to the discussion of classical systems required here. It is essentially equivalent to Boltzmann's discussion of dissociation, *Vorlesungen über Gastheorie*, II, Abschnitt VI.

The equilibrium state of the assembly can then at once be studied as a problem in the dissociation of perfect gases. We consider only interactions in pairs. Let $f(\vartheta)$, equal to $h(\vartheta)\, j(\vartheta)$, as before be the partition function for the free systems of average number $\overline{N_1}$. Let $g(\vartheta)$ be the partition function for systems which are pairs of molecules in interaction, of average number $\overline{N_2}$. The function $g(\vartheta)$ will contain the factor $j^2(\vartheta)$ dealing with the internal energies. It remains to construct the classical part. The element of phase space for the pair is

$$m^6 dx_1 \ldots dw_1 dx_2 \ldots dw_2$$

in rectangular Cartesian coordinates and velocities. This can be transformed to coordinates and velocities of the centre of gravity of the pair $x^*, \ldots, w^*$ and coordinates and velocities of 1 relative to 2, $\xi, \ldots, w$. The Jacobian of the transformation is 1 and the element of phase space is

$$m^6 dx^* \ldots dw^* d\xi \ldots dw,$$

of prepared weight

$$\delta_t = m^6 \frac{dx^* \ldots dw^*\, d\xi \ldots dw}{2h^6}, \qquad \ldots\ldots(639)$$

the symmetry number being 2. The corresponding energy is

$$\epsilon_t = \tfrac{1}{2}(2m)(\Sigma u^{*2}) + \tfrac{1}{2}(\tfrac{1}{2}m)(\Sigma u^2) + E(\xi, \eta, \zeta). \qquad \ldots\ldots(640)$$

Thus in the classical limit this factor of the partition function is

$$\frac{m^6}{2h^6}\int \ldots \int \vartheta^{\epsilon}\, dx^* \ldots dw^*\, d\xi \ldots dw, \qquad \ldots\ldots(641)$$

where ϵ is given by (640). This reduces at once to

$$h_2(\vartheta)\, \frac{(2\pi\tfrac{1}{2}m)^{\frac{3}{2}} A(\vartheta)}{h^3 (\log 1/\vartheta)^{\frac{3}{2}}}, \qquad \ldots\ldots(642)$$

where $h_2(\vartheta)$ is the ordinary partition function for the motion of the aggregate as a whole of mass $2m$, and

$$A(\vartheta) = \tfrac{1}{2}\int_v \vartheta^{E(\xi,\eta,\zeta)}\, d\xi\, d\eta\, d\zeta. \qquad \ldots\ldots(643)$$

$A(\vartheta)$ is obviously the partition function for the potential energy of the pair, and v is the volume in which E is sensible.

The gas here considered of "free" molecules and aggregates obeys the dissociation theory and in particular equation (333). We therefore find

$$\frac{\overline{N_2}}{(\overline{N_1})^2} = \frac{j^2(\vartheta)\, h_2(\vartheta)\, (2\pi\tfrac{1}{2}m)^{\frac{3}{2}} A(\vartheta)/\{h^3 (\log 1/\vartheta)^{\frac{3}{2}}\}}{\{j(\vartheta)\, h(\vartheta)\}^2}.$$

To the first approximation the V-factors are just V in both $h(\vartheta)$ and $h_2(\vartheta)$, so that approximately

$$\overline{N_2}/(\overline{N_1})^2 = A(\vartheta)/V. \qquad \ldots\ldots(644)$$

In calculating first order corrections v/V and therefore $A(\vartheta)/V$ will be small, so that $\overline{N_2}/(\overline{N_1})^2$ will be small and (644) is correct to the order required. $\overline{N_1}$ will differ from N only by first order terms. If we ask for $\overline{(a_2)_t}$, the average number of aggregates with given ranges of relative positional coordinates, we find at once by (332)

$$\overline{(a_2)_t} = \tfrac{1}{2}\,\overline{N_2}\,\vartheta^E\,(d\xi\,d\eta\,d\zeta)_t/A(\vartheta),$$

and therefore to a sufficient approximation

$$\overline{(a_2)_t} = \tfrac{1}{2}\,(\overline{N_1})^2\,e^{-E/kT}\,(d\xi\,d\eta\,d\zeta)_t/V. \qquad \ldots\ldots(645)$$

The velocity distribution laws can similarly be shown to be unaltered by the forces.

We can derive at once any of the laws previously established, but it will suffice as an example to calculate the form of Ψ/k. By Theorem 6·31

$$\Psi/k = \overline{N_1}\left(\log\frac{f(\vartheta)}{\overline{N_1}} + 1\right) + \overline{N_2}\left(\log\frac{g(\vartheta)}{\overline{N_2}} + 1\right). \qquad \ldots\ldots(646)$$

We require here a more exact evaluation of the V-factor in $f(\vartheta)$. It is no longer V exactly, because if any one molecule is in the field of another the pair rank as a system and not as free molecules. Thus in $f(\vartheta)$ the V-factor is approximately apparently

$$V - Nv. \qquad \ldots\ldots(647)$$

This, however, would not be correct, as it would lead to counting the whole of each excluded volume twice over, once for each member of the pair. Thus in $f(\vartheta)$ the V-factor should be taken to be $V - \tfrac{1}{2}Nv$, and to a sufficient approximation

$$\Psi/k = \overline{N_1}\left\{\log\frac{(V - \tfrac{1}{2}Nv)\,F(\vartheta)}{\overline{N_1}} + 1\right\} + \overline{N_2}\left\{\log\frac{g(\vartheta)}{\overline{N_2}} + 1\right\}.$$

This is most satisfactorily expressed as perfect gas terms plus corrections. Remembering that $\overline{N_1} = N - 2\overline{N_2}$ we find after an easy reduction that

$$\Psi/k = N\left(\log\frac{VF}{N} + 1\right) + \frac{N^2}{V}\{A(\vartheta) - \tfrac{1}{2}v\}, \qquad \ldots\ldots(648)$$

which agrees exactly with (491).

This method is really much simpler to handle than the general method and easily extended to mixtures. It might extend conveniently to the calculation of higher order corrections, though hardly so effectively as the general method of § 8·31.

§ **9·7**. *Method* (ii). *The use of the virial of Clausius.* The general method and the method of aggregations evaluate the complete equilibrium laws without the aid of additional theorems. Two other methods of some importance can be used to obtain the equation of state with the aid of the distribution law (534). The first of these to be considered is the use o the virial of Clausius. We give the underlying theorem in a general form due to Milne*.

The equations of motion of a particle of mass m at x, y, z, moving under a force whose components are X, Y, Z and subject to frictional resistances of the form $-\kappa(\dot{x}, \dot{y}, \dot{z})$, are

$$m\ddot{x} = X - \kappa\dot{x} \qquad \text{......(649)}$$

and two similar equations. When this is multiplied by $\frac{1}{2}x$ it may be written

$$\tfrac{1}{4}\frac{d^2}{dt^2}(mx^2) + \tfrac{1}{4}\frac{d}{dt}(\kappa x^2) - \tfrac{1}{2}m\dot{x}^2 = \tfrac{1}{2}Xx. \qquad \text{......(650)}$$

Hence, adding three similar equations,

$$\tfrac{1}{4}\frac{d^2}{dt^2}(mr^2) + \tfrac{1}{4}\frac{d}{dt}(\kappa r^2) = \tfrac{1}{2}mv^2 + \tfrac{1}{2}(Xx + Yy + Zz). \qquad \text{......(651)}$$

Now sum this expression over all the systems in an assembly, and integrate over a long time τ. We find

$$\frac{1}{\tau}\left[\tfrac{1}{4}\frac{d}{dt}(\Sigma mr^2) + \tfrac{1}{4}\Sigma\kappa r^2\right]_0^\tau = \tfrac{1}{2}\overline{\Sigma mv^2} + \tfrac{1}{2}\,\Sigma\overline{Xx + Yy + Zz}. \qquad \text{......(652)}$$

The bars denote time averages from 0 to τ. Now if the state of the assembly is steady, the values of the expression in [ ] must be of the same order at 0 and τ, and will at least display no secular change with τ. Hence the left-hand side of (652) is effectively zero, and we have

$$\tfrac{1}{2}\overline{\Sigma mv^2} = -\tfrac{1}{2}\Sigma\overline{Xx + Yy + Zz}. \qquad \text{......(653)}$$

This is the theorem of Clausius, who named the expression on the right *the virial*. Provided frictional forces permit of an effectively steady state they do not alter the form of the theorem. We may note also that, provided the forces in the virial include all stresses due to bodies other than the systems to which Σ refers, the theorem is true for any collection of systems not necessarily the whole assembly.

Let us now apply (653) to an assembly consisting of an imperfect gas or to any portion of such assembly enclosed by an imaginary geometrical boundary. In either case the virial is made up of the forces between the molecules and the stresses across the physical or geometrical boundary. This stress per unit area is of course the pressure, and we may insist once again that the pressures on any boundary or across any internal surface are always equal in the absence of surface tension and external fields of force. If dS is a surface element of the boundary and l, m, n the direction cosines of its outward normal, the stress components are $-lp\,dS$, $-mp\,dS$, $-np\,dS$, which contribute to the virial

$$\tfrac{1}{2}p\iint(lx + my + nz)\,dS.$$

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* Milne, *Phil. Mag.* vol. L, p. 409 (1925).

By Green's theorem this is equal to

$$\tfrac{1}{2}p\iiint\left(\frac{\partial x}{\partial x}+\frac{\partial y}{\partial y}+\frac{\partial z}{\partial z}\right)dV=\tfrac{3}{2}pV. \qquad \text{......(654)}$$

We have supposed above that the force between two molecules is radial and equal to $-\partial E/\partial r$. Continuing on this basis, if the centres of a pair of molecules are at x, y, z, x', y', z' and the force components are X, Y, Z, X', Y', Z', then

$$X=-\frac{\partial E}{\partial r}\frac{x-x'}{r},\quad X'=-\frac{\partial E}{\partial r}\frac{x'-x}{r}.$$

$$xX+x'X'=-\frac{\partial E}{\partial r}\frac{(x-x')^2}{r}.$$

Thus the contribution of the force between this pair of molecules to the virial is

$$\tfrac{1}{2}r\frac{\partial E}{\partial r},$$

and the total contributions of all intermolecular forces

$$\tfrac{1}{2}\Sigma r\frac{\partial E}{\partial r}, \qquad \text{......(655)}$$

summed over all pairs of molecules. Combining (654) and (655) with (653) we obtain finally

$$pV=\overset{\swarrow 2/3}{\tfrac{1}{3}}\,\overline{\Sigma mv^2}-\tfrac{1}{3}\Sigma r\frac{\partial E}{\partial r}. \qquad \text{......(656)}$$

This is the general form of the equation of state derived from the virial. To interpret it further we need to use distribution laws. For the mean kinetic energy of translation we have

$$\tfrac{1}{3}\overline{\Sigma mv^2}=NkT. \qquad \text{......(657)}$$

For the average number of pairs of molecules at a distance apart between r and $r+dr$ we find by (534)

$$\tfrac{1}{2}N^2e^{-E/kT}\frac{4\pi r^2dr}{V}. \qquad \text{......(658)}$$

The factor $\tfrac{1}{2}$ must be introduced when (534) is integrated over all relative directions. Using (657) and (658) we find

$$pV=NkT-\tfrac{1}{6}\frac{N^2}{V}4\pi\int_0^\infty r^3\frac{\partial E}{\partial r}e^{-E/kT}\,dr.$$

On integrating this by parts in such a way that the conditions of convergence at infinity are satisfied we find

$$pV=NkT\left[1-\tfrac{1}{2}\frac{N}{V}4\pi\int_0^\infty r^2\left(e^{-E/kT}-1\right)dr\right], \qquad \text{......(659)}$$

which agrees with (492).

The argument must be completed by an appeal to (629) to derive Ψ.

§ 9·8. *Method* (iii). *A direct calculation of the stress per unit area.* It is easily seen that the main conclusions of the calculation of stress in § 5·71 are unaffected by intermolecular forces. The internal stress is necessarily an isotropic pressure, everywhere equal in the absence of external fields to the boundary pressure. It consists of a term arising from the rate of transfer of momentum, which is absolutely unaltered by the forces, together with a new term the average stress per unit area due to the intermolecular forces themselves. To calculate this extra term we have merely to calculate the average force per unit area exerted by all the molecules on one side of a geometrical interface on those on the other. This requires a use of the distribution law (534).

Let us consider an infinite plane slab of thickness df and calculate the average force dF exerted by all the molecules in this slab on a molecule at P, distant z from the slab. Our molecules are of course regarded here as point centres of force. The calculation is a generalization of the classical calculation in Laplace's theory of surface tension, generalized so as to apply directly to a molecular structure[*]. The average number of molecules in the slab per unit area at a distance r from P is[†]

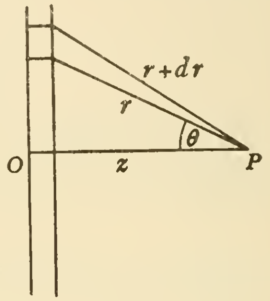

Fig. 13.

$$\frac{N}{V}\,df\,e^{-E(r)/kT}.$$

It is safer in this section to show explicitly the argument of E. The average number in the annulus at distances between r and $r+dr$ from P is

$$2\pi r\sin\theta.\frac{dr}{\sin\theta}\cdot\frac{N}{V}\,df\,e^{-E(r)/kT},$$

and their resultant repulsion along PO is

$$2\pi\frac{N}{V}\,z\,df\left(-\frac{\partial E}{\partial r}\right)e^{-E(r)/kT}\,dr. \qquad \text{......(660)}$$

To obtain the average repulsion of the whole slab we must integrate (660) for all values of r from z to infinity. This gives

$$dF=-\frac{2\pi NkT}{V}\,z\,df\{e^{-E(z)/kT}-1\}. \qquad \text{......(661)}$$

The average repulsion per unit area on the molecules in a slab of thickness dz is therefore, since there are Ndz/V such molecules,

$$-\frac{2\pi N^2kT}{V^2}\,z\,dz\,df\{e^{-E(z)/kT}-1\}. \qquad \text{......(662)}$$

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[*] See Rayleigh, *Scientific Papers*, vol. III, pp. 397, 513 (1890, 1892).

[†] More generally $E(r)$ must of course be replaced by the mean $W_{\alpha\beta}(r)$ of formula (530).

We now replace z by $z + f$, the distance apart of any two slabs, and integrate with respect to both z and f from zero to infinity. We thus obtain the total stress per unit area due to the molecular forces, that is,

$$-\frac{2\pi N^2 kT}{V^2}\int_0^\infty\int_0^\infty (z+f)\{e^{-E(z+f)/kT}-1\}\,dz\,df, \qquad \text{......(663)}$$

or

$$-\frac{2\pi N^2 kT}{V^2}\int_0^\infty x\{e^{-E(x)/kT}-1\}\,dx\int_0^x dy,$$

or

$$-\frac{2\pi N^2 kT}{V^2}\int_0^\infty x^2\{e^{-E(x)/kT}-1\}\,dx, \qquad \text{......(664)}$$

which agrees with (659).

The differential formulae (661) and (662) can also be used in a number of other ways. To obtain the work $dw\,(f)$ done by the repulsions when a molecule is removed from a distance f from the slab to infinity we have to integrate (661) with respect to z. Thus

$$dw\,(f) = -\frac{2\pi NkT}{V}\,df\int_f^\infty z\{e^{-E(z)/kT}-1\}\,dz. \qquad \text{......(665)}$$

The work $w\,(f)$ done when the molecule is removed from a distance f from the plane boundary of a large mass of gas to infinity is

$$-\frac{2\pi NkT}{V}\int_f^\infty df'\int_{f'}^\infty z\{e^{-E(z)/kT}-1\}\,dz,$$

or

$$w\,(f) = -\frac{2\pi NkT}{V}\left[\int_f^\infty z^2\{e^{-E(z)/kT}-1\}\,dz - f\int_f^\infty z\{e^{-E(z)/kT}-1\}\,dz\right]. \qquad \text{......(666)}$$

The average work done when one molecule is taken from the plane boundary to infinity is $w\,(0)$.

Again, it is obvious that $dw\,(-f) = dw\,(f)$, for the work done in taking the molecule from a distance f on one side of the slab to a distance f on the other is zero. Hence the work $w\,(-f)$ done by the repulsions when a molecule is removed to infinity from a depth f inside the plane boundary is equal to $w\,(0)$ together with the work done by the repulsions when the molecule leaves the surface of a finite slab of thickness f. This latter part is of course $w\,(0) - w\,(f)$. Thus

$$w\,(-f) = 2w\,(0) - w\,(f), \qquad \text{......(667)}$$

$$w\,(-\infty) = 2w\,(0). \qquad \text{......(668)}$$

The work done when the molecule comes from right inside to the surface is therefore equal to $w\,(-\infty) - w\,(0)$ or $w\,(0)$, which is also the work done when the molecule goes from the surface to infinity. These calculations of work terms are of course all *work done in reversible isothermal processes in which equilibrium conditions are maintained throughout.*

The foregoing formulae take no account of changes of the average density of the molecules near the boundary of the gas. There must in fact be such changes, as a consequence of Boltzmann's theorem. The reversible isothermal work done by the forces on a molecule when it is brought from deep in the gas to a depth f is by the preceding argument $w(-\infty) - w(-f)$, or $w(f)$ as given in (666). Hence by (529) and the following paragraphs $-w(f)$ is just exactly the energy term to be inserted in Boltzmann's theorem, and

$$\nu(f) = \frac{N}{V} e^{w(f)/kT}, \qquad \text{......(669)}$$

where $\nu(f)$ is the equilibrium density at a depth f inside the boundary. A more accurate investigation must proceed by constructing an integral equation for $w(f)$ instead of using (666)*.

This calculation of the boundary density and the boundary field can be made to give at once the value of the boundary pressure, and is in fact the correct form of the classical calculations by which van der Waals derived his famous equation. For by (669) the density at the boundary itself is

$$\begin{aligned}\nu(0) &= \frac{N}{V} e^{w(0)/kT},\\ &= \frac{N}{V} \exp\left[-\frac{2\pi N}{V}\int_0^\infty z^2\{e^{-E(z)/kT} - 1\}\,dz\right], \qquad \text{......(670)}\end{aligned}$$

and by the usual bombardment argument the pressure is $kT\nu(0)$. Therefore

$$pV = NkT \exp\left[-\frac{2\pi N}{V}\int_0^\infty z^2\{e^{-E(z)/kT} - 1\}\,dz\right], \qquad \text{......(671)}$$

which to the order of accuracy agrees with (659).

Further developments of these ideas belong more properly to the theory of surface tension.

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* Fowler, *Phil. Mag.* vol. XLIII, p. 785 (1922).

CHAPTER X

INTERATOMIC FORCES*

§ **10·1.** *Classification of forces.* The work of the two previous chapters proceeds on the assumption that the forces between molecules and therefore such functions as $E_{\alpha\beta}$ are known, but little is as yet known theoretically about the magnitude of these forces, though their nature is already fairly clear. It will no doubt be possible one day, probably soon, to calculate the forces between atoms in terms of their electronic structure, and thus to bridge one of the gaps which still separate molar physics from atomic physics†. At present we have to rely entirely on indirect methods for such knowledge as we have of intermolecular fields.

The tendency of all molecules to aggregate at low temperatures is sufficient indication of the existence of forces of cohesion between molecules, and the very existence of matter leads of necessity to the conclusion that the forces between molecules become repulsive at short distances. Any adequate representation of intermolecular fields must therefore satisfy these two elementary requirements, that it gives an attractive field at large distances and a repulsive at small. The simplest picture of this kind is that molecules consist of hard, impenetrable surfaces surrounded by an attractive field. This picture we owe to van der Waals. It leads to the equation of state discussed in Chapter IX and has also had other successes. It is, however, inadequate to explain the observed compressibility of matter, and for this and other reasons must be discarded. It is convenient, if somewhat artificial, to represent atomic fields by the superposition of two fields, one attractive and the other repulsive, such that the former predominates at large distances. The former of these we shall refer to as the *van der Waals attractive field*, and the latter as the *intrinsic repulsive field*. It is convenient to label the fields in this way as they are thus more easily differentiated from the attractive and repulsive *electrostatic forces* of the Coulomb type between ions with net charges. All interatomic forces are ultimately of electrostatic or electromagnetic origin, but it is best to reserve the name electrostatic for the familiar forces between charged bodies.

Where atoms in matter exist permanently in an ionized state, and the work of Arrhenius, of Kossel and others has shown that they often do, the electrostatic forces play an important part in determining the physical properties of the matter in bulk. Such fields are to be regarded as super-

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* This chapter has been contributed by J. E. Lennard-Jones.

† The work of Heitler and London, *Zeit. für Phys.* vol. XLIV, p. 455 (1927), makes perhaps the first secure step in this direction, but even this has oversimplified the discussion so that the atoms do not exhibit as they should the van der Waals attractions.

imposed on the other attractive and repulsive fields already discussed, though not without modification. Owing to the deformation of the electronic systems of the atoms and ions in the presence of charged ions or in any other electric field, certain other forces are introduced which may be termed *primary polarization forces*. We use this description because it is becoming clear that the van der Waals attractive forces are really due to the polarization of one (neutral) atom by the electric field of the other (neutral), so that these may be called *secondary polarization forces*. Finally, some molecules are known to possess a permanent electric moment, even in the absence of an electric field. The magnitudes of these can often be deduced from a study of the dielectric properties of gases and perhaps liquids (see Chapter XII), and the corresponding forces between the two molecules are then known.

We may thus summarize our classification of interatomic forces under the following headings, arranged in order of simplicity and probably of range:

(1) Electrostatic forces between atoms (or ions) with net charges.
(2) Electrostatic forces between permanent dipoles.
(3) Forces due to primary polarization.
(4) Forces due to secondary polarization (or van der Waals' attractive forces).
(5) Intrinsic repulsive forces.

We shall not, however, discuss the forces in this (the natural) order, as it is more convenient to deal first with the forces of more complex origin but shorter range.

§ **10·2**. *Intrinsic repulsive and van der Waals' attractive fields.* In general, the forces between molecules depend on their relative orientation as well as on their distance apart, but the mathematical difficulties of dealing with such laws of force in theories of the properties of matter are considerable. Keesom has given a method of deriving the equation of state of a gas of unsymmetrical molecules, though he has only applied it to solid ellipsoids of revolution*, and the expression obtained is not in very good agreement with observation. He has made no attempt to deduce any information of a quantitative character from a comparison of theoretical and observed results. The general method given by Ursell† (see Chapter VIII) is applicable, but has never yet been applied to an unsymmetrical model. Rankine‡ has tried to represent the fields of polyatomic gases by aggregates of over-

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* Keesom, *Proc. Sect. Sci. Amsterdam*, vol. XV (1), p. 240 (1912).

† Ursell, *loc. cit.*

‡ Rankine, *Phil. Mag.* vol. XL, p. 516 (1920); *Roy. Soc. Proc.* A, vol. XCVIII, pp. 360, 369 (1921); *Proc. Lond. Phys. Soc.* vol. XXXIII, p. 362 (1921); *Phil. Mag.* vol. XLII, pp. 601, 615 (1921); *Trans. Far. Soc.* vol. XVII, p. 1 (1922).

lapping spheres, the sizes of which are fixed by observations of the viscosity of simple gases, but it is difficult to verify these proposed structures from observations of the viscosity of the polyatomic gas, as Rankine has tried to do, seeing that no theoretical formula has yet been produced for the viscosity of an assembly of unsymmetrical molecules.

We shall, therefore, confine our attention to those structures which may with reason be regarded as spherically symmetrical, that is, the inert gas atoms, and ions of similar structure. It is natural that such structures should at first have been represented by rigid spheres, for the field (apart from the attractive field) is completely determined so soon as one parameter, the diameter, is known, and this simplicity undoubtedly accounts for its popularity as a molecular model*. But a conglomeration of closely packed, rigid spheres would be incompressible and would not therefore possess the observed properties of ordinary solids.

This objection can be met by supposing the intrinsic repulsive field to be of the type λr^{-n}. This is a more general representation than the elastic sphere, as its complete determination requires two parameters, λ and n, instead of one. Probably it is the simplest type of force which possesses this characteristic. It includes also the simpler model as a special case, since a rigid sphere is the limit of λr^{-n} as n tends to infinity, with a suitable corresponding variation in λ.

It is convenient to represent attractive fields by a similar function μr^{-m}, as Keesom was the first to do, though he superimposed it on the rigid sphere model. If we represent both repulsive and attractive fields by inverse power laws as $\lambda r^{-n} - \mu r^{-m}$, then the complete specification of the field requires a knowledge of four parameters. In order that the field may be effectively attractive at large distances, it is necessary that $n > m$. It is unlikely that such a simple function of the distance adequately represents actual interatomic forces over all distances, but it is the most general that has as yet yielded to mathematical treatment. The methods of determining the constants which have proved most successful are based on the physical properties of matter in the gaseous state, and these we shall now proceed to consider. We shall deal first with the equation of state of a gas and then with its viscosity.

§ **10·31**. *The equation of state of gases. The empirical representation of observed isothermals.* In Chapter IX it has been shown that for gases of moderately large dilution

$$pV = NkT\left\{1 + \frac{B}{V} + O\left(\frac{1}{V^2}\right)\right\}, \qquad \ldots\ldots(672)$$

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* For a discussion of the diameters of such model molecules, determined by a variety of methods, see Jeans, *loc. cit.*; Herzfeld, *Kinetische Theorie der Wärme* (Braunschweig, 1925); "Grösse u. Bau der Moleküle", *Handbuch der Physik*, vol. XXII (Berlin, 1926).

where B is a function of the temperature and of the interatomic forces. Kamerlingh-Onnes* has shown that the observations require in general a similar expansion, and he has expressed the results in the form of an empirical equation of state of the type

$$pV = A_v + \frac{B_v}{V} + \frac{C_v}{V^2} + \frac{D_v}{V^4} + \frac{E_v}{V^6} + \frac{F_v}{V^8}, \qquad \text{......(673)}$$

where the coefficients $A, B, \ldots$ are functions of the temperature, usually called *first, second, ... virial coefficients.*

There is some divergence in the units used in the observational equation (673). Kamerlingh-Onnes and other workers at Leiden have adopted the international atmosphere as the unit of pressure, the volume being regarded as unity under this unit pressure at 0° C. When this system of units is employed, we shall distinguish the coefficients of (673) by writing them $A_v, B_v, \ldots$. Workers at Berlin†, on the other hand, have taken the unit of pressure to be equivalent to a column of mercury 1 metre long (under standard conditions) with a corresponding change in the unit of volume. In this case we shall write $\mathfrak{A}_v, \mathfrak{B}_v, \ldots$.‡

Again, it has proved convenient both at Leiden and at Berlin to express the value of pV, not in powers of $1/V$, but in powers of p, so that then we have

$$pV = A_p + B_p p + C_p p^2 + \ldots, \qquad \text{......(674)}$$

and

$$pV = \mathfrak{A}_p + \mathfrak{B}_p p + \mathfrak{C}_p p^2 + \ldots, \qquad \text{......(675)}$$

respectively. The various coefficients are easily related to each other. Thus we have

$$A_p = A_v = \frac{\mathfrak{A}_p}{(\mathfrak{A}_p)_0 + (\mathfrak{B}_p)_0\, l + (\mathfrak{C}_p)_0\, l^2}, \qquad \text{......(676)}$$

$$B_p = \frac{B_v}{A_v} = \frac{l\,\mathfrak{B}_p}{(\mathfrak{A}_p)_0 + (\mathfrak{B}_p)_0\, l + (\mathfrak{C}_p)_0\, l^2}, \qquad \text{......(677)}$$

where l is the pressure of one atmosphere in the Berlin units, and the suffix 0 refers to the isothermal 0° C. It is thus possible without difficulty to pass from one system of units to another.

For comparison with the theoretical work, the Leiden method of presenting the results is preferable, as the units refer to the normal conditions under which Avogadro's number for the molecular concentration is applicable. We shall regard the Leiden equations, therefore, as the standard experimental equations to which all others are convertible.

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* Kamerlingh-Onnes, *Comm. Phys. Lab. Leiden*, No. 71, or *Proc. Sect. Sci. Amsterdam*, vol. IV, p. 125 (1902).

† Holborn and Otto, *Zeit. für Phys.* vol. XXIII, p. 77, vol. XXX, p. 320 (1924), vol. XXXIII, p. 1 (1925), vol. XXXVIII, p. 359 (1926).

‡ Another method of presenting the results has been given by Smith and Taylor, *Journ. Amer. Chem. Soc.* vol. XLV, p. 2107 (1923), though not in a form suitable for comparison with theory.

§ **10·32**. *Theoretical expressions for the second virial coefficient.* If we write equation (672) in terms of molecular concentration, thus

$$p = \nu kT\,(1 + B'\nu), \qquad \text{......(678)}$$

we have*

$$\nu_0 kT = A_v, \;\; \nu_0 B' = B_v/A_v, \qquad \text{......(679)}$$

where, for a spherically symmetrical field, by (659)

$$B' = 2\pi \int_0^\infty r^2 \{1 - e^{-E(r)/kT}\}\, dr, \qquad \text{......(680)}$$

or

$$B' = \frac{2\pi}{3kT}\int_0^\infty r^3 \left(-\frac{dE}{dr}\right) e^{-E(r)/kT}\, dr. \qquad \text{......(681)}$$

The condition that B' shall remain finite places a restriction on the molecular models which are possible. For instance, if

$$-\frac{dE}{dr} = f\,(r) = \lambda r^{-n} - \mu r^{-m},$$

the condition requires that $n > 4$, $m > 4$. Equation (679) provides a criterion for any assumed law of atomic interaction.

Although equation (680) gives a formal solution for B' for any field of a spherically symmetrical type, the actual evaluation of the integral has been effected in only three cases, viz. (1) molecules which repel according to the law λr^{-n}; (2) molecules which behave as rigid spheres of diameter σ, surrounded by an attractive field μr^{-m}; (3) molecules whose fields can be represented by $\lambda r^{-n} - \mu r^{-m}$. The first of these has been given by Jeans†, the second by Keesom‡. For the third it is found that§

$$B' = \tfrac{2}{3}\pi \left(\frac{\lambda}{n-1}\,\frac{m-1}{\mu}\right)^{3/(n-m)} F\,(y), \qquad \text{......(682)}$$

where

$$F\,(y) = y^{3/(n-m)} \left\{\Gamma\left(\frac{n-4}{n-1}\right) - \sum_{r=1}^{\infty} c_r y^r\right\}, \qquad \text{......(683)}$$

and y is a function of temperature given by

$$y = \frac{\mu}{(m-1)\,kT}\left(\frac{\{n-1\}\,kT}{\lambda}\right)^{(m-1)/(n-1)}. \qquad \text{......(684)}$$

The coefficients c_r are written for

$$c_r = \frac{3\Gamma\left(\dfrac{r\{m-1\}+n-4}{n-1}\right)}{r\,!\,(r\{m-1\}-3)} = \frac{3\Gamma\left(\dfrac{r\{m-1\}-3}{n-1}\right)}{r\,!\,(n-1)}. \qquad \text{......(685)}$$

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* On the Leiden conventions ν_0 is a standard concentration equal to Avogadro's number, $2{\cdot}70 \times 10^{19}$.

† Jeans, *loc. cit.* p. 134.

‡ Keesom, *Comm. Phys. Lab. Leiden*, Suppl. 24 B, p. 32 (1912).

§ Lennard-Jones, *Proc. Roy. Soc.* A, vol. CVI, p. 463 (1924). For the case $n=10$, $m=9$, see Zwicky, *Phys. Zeit.* vol. XXII, p. 449 (1921), but the integrals were evaluated only by quadrature.

The formulae for the first two models can be deduced as special cases. Thus for λr^{-n} and no attractive field,

$$B' = \tfrac{2}{3}\pi \left(\frac{\lambda}{\{n-1\}\, kT}\right)^{3/(n-1)} \Gamma\left(\frac{n-4}{n-1}\right). \qquad \text{......(686)}$$

For the sphere with an attracting field μr^{-m},

$$B' = \tfrac{2}{3}\pi\sigma^3 \left\{1 - \sum_{r=1}^{\infty} \frac{3}{r\,!\,(r\{m-1\}-3)} \left(\frac{u}{kT}\right)^r\right\}, \qquad \text{......(687)}$$

where

$$u = \frac{\mu}{(m-1)\,\sigma^{m-1}}, \qquad \text{......(688)}$$

so that u is the potential energy of two molecules in contact.

Keesom* has also evaluated B' for molecules which can be represented as rigid spheres with a permanent electric dipole at their centre. For this model, he finds

$$B' = \tfrac{2}{3}\pi\sigma^3 \left\{1 - \frac{1}{3}\left(\frac{u}{kT}\right)^2 - \frac{1}{75}\left(\frac{u}{kT}\right)^4 - \frac{29}{55125}\left(\frac{u}{kT}\right)^6 - \dots\right\}, \qquad \text{......(689)}$$

where

$$u = \frac{m_e^{\,2}}{\sigma^3}, \qquad \text{......(690)}$$

so that u is thus the potential energy of two molecules in contact with the axes of their doublets parallel and at the same time perpendicular to the line joining their centres.

Another model which has been worked out consists of rigid spheres with permanent quadrupoles† at their centres‡. The appropriate formula for B' proves to be

$$B' = \tfrac{2}{3}\pi\sigma^3 \left\{1 - (1{\cdot}0667)\left(\frac{u}{kT}\right)^2 + (0{\cdot}1741)\left(\frac{u}{kT}\right)^3 - \dots\right\}, \qquad \text{......(691)}$$

where

$$u = \tfrac{3}{4}\,\frac{\mu^2}{\sigma^5},$$

so that u is the potential energy of two molecules in contact with the axes of the quadrupoles perpendicular to one another and to the line of centres. Keesom § has also generalized this case somewhat by supposing that the atoms are in addition polarized in the presence of each other in a manner suggested by Debye ||.

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* Keesom, *Proc. Sect. Sci. Amsterdam*, vol. xv (1), p. 256 (1912); *Comm. Phys. Lab. Leiden*, Suppl. No. 24 B; *Phys. Zeit.* vol. XXII, pp. 129, 643 (1921).

† A quadrupole consists of two equal and parallel doublets at a small distance apart pointing in opposite directions. (The strength of a quadrupole has therefore the dimensions of a charge multiplied by the square of a length.)

‡ Keesom, *Phys. Zeit., loc. cit.*

§ Keesom, *Phys. Zeit.* vol. XXII, p. 129 (1921).

|| Debye, *Phys. Zeit.* vol. XXI, p. 178 (1920).

§ **10·33**. *Comparison of theory and observation.* Equations (682), (686), (687), (689) and (691) express B' in various ways as a function of the temperature, ready for comparison with the observed variation of B_v/A_v, equation (679). The comparison may be carried out as follows*: Plot on transparent paper $\log (B_v/A_v)$ as a function of $\log T$, and on squared paper plot $\log | F(y) |$ as a function of $\log y$, the scale of $\log | F(y) |$ being the same as that of $\log (B_v/A_v)$, while the scale of $\log y$ is taken to be $(n-1)/(n-m)$ times that of $\log T$, and to increase in the opposite direction. This has the effect of making $\log y + \{(n-m)/(n-1)\} \log T$ invariant for any corresponding values of y and T. The experimental curve is moved over the theoretical curve (keeping always the two sets of axes parallel) until the best agreement is obtained between the two. The degree of closeness between the two curves is a measure of the suitability of the molecular model chosen. If, for instance, values of n and m can be found for which the $\log | F(y) |$ curve is a sufficiently close representation of the observed curve, then the law $\lambda r^{-n} - \mu r^{-m}$ may be regarded as a suitable representation of the molecular fields in the gas, at least at those distances apart for which the intermolecular forces are then important. It is then only necessary to determine the numerical values of λ and μ to complete the determination of the field. This can be done by noting the parallel transformation (X, Y) necessary to effect coincidence between the two curves, so that

$$\log y + \frac{n-m}{n-1} \log T = X, \qquad \text{......(692)}$$

$$\log B_v/A_v - \log F(y) = Y, \qquad \text{......(693)}$$

from which we have, on substituting the theoretical expressions for y and $F(y)$ from equations (682) and (684) and using (679),

$$\log \frac{\lambda}{n-1} = \frac{n-1}{n-m} X + \frac{n-1}{3} Y - \frac{n-1}{3} \log \frac{2\pi\nu_0}{3} + \log k, \qquad \text{......(694)}$$

$$\log \frac{\mu}{m-1} = \frac{n-1}{n-m} X + \frac{m-1}{3} Y - \frac{m-1}{3} \log \frac{2\pi\nu_0}{3} + \log k. \qquad \text{......(695)}$$

In order to illustrate the difference in the theoretical curves for various values of n and m, four curves are given in Fig. 14† for the same m and different values of n, and in Fig. 15 for the same n and different values of m. The curves have been superimposed (with their axes parallel) so that the left-hand portions of the curves, corresponding to negative values of $F(y)$, are as nearly as possible in coincidence. These portions are clustered

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* We consider only equation (682). The method can easily be adapted to the other simpler cases. It is a modification of the one first used by Keesom, *loc. cit.*

† In this and other figures, the left-hand portion of the curve corresponds to negative values of $F(y)$; $\log | F(y) |$ is plotted.

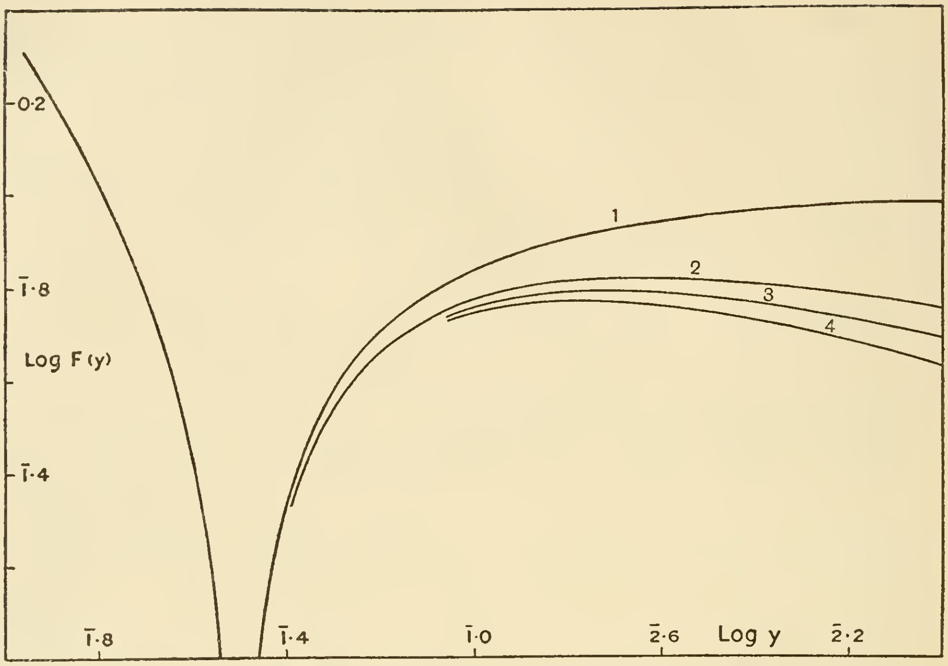

Fig. 14. Theoretical forms of the second virial coefficient for $m=5$ and (1) $n=\infty$, (2) $n=14\frac{1}{3}$, (3) $n=11$, (4) $n=9$.

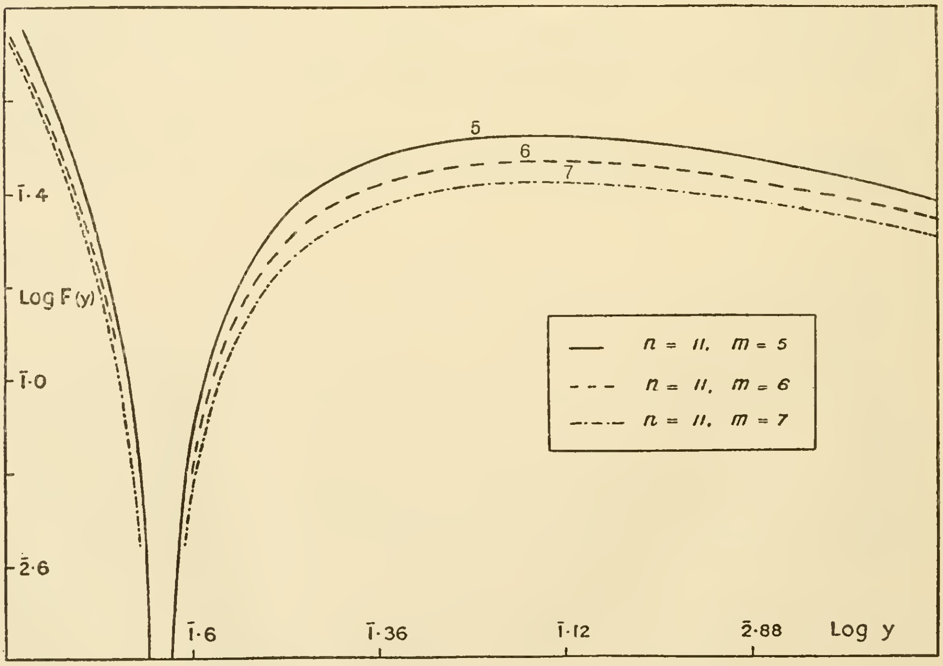

Fig. 15. Theoretical forms of the second virial coefficient.

about the line shown in the figure, and are too near together to be distinguished in a diagram. (This method of superposition is virtually the same as making the "Boyle points" coincide, that is, the points for which $B' = F(y) = 0$.)

It is to be noted that all the curves show a maximum except that for $n = \infty$, which corresponds to the rigid sphere, and this curve tends to an asymptote for infinite y. The physical interpretation of this is that for hard impenetrable molecules, there is always an "excluded volume" however high the temperature, whereas for "compressible" molecules (λr^{-n}) there is an ever-growing interpenetration of the molecular fields as the temperature increases, and since the forces at any given stage are finite, the gas tends to become more and more like an ideal gas. Again all the curves shown cross the log y axis and also have a Boyle point. This is not true, however, of the curve corresponding to equation (686) (for a repulsive field alone). For this reason, the latter curve need not be further considered, as all gases show a reversal in sign of B_v/A_v at low temperatures. The curve for the rigid sphere plus permanent electric dipole, like the curves for all models which comprise hard impenetrable shells, does not possess a maximum. As will be shown presently, the observations of B_v/A_v for helium and neon do exhibit a maximum and thus discount any rigid molecular model. It may be regarded as certain that all other gases would show the same maximum property if the observations could be carried to a high enough temperature.

§ **10·34**. *The observed values of the second virial coefficient: forces between molecules.* Although observations on the isothermals of gases have been accumulating since the classical experiments of Andrews on carbon dioxide*, a strict comparison of theory and experiment has only been possible since the elaborate analysis of the observational material made by Kamerlingh-Onnes†. His method, or slight modifications of it, has fortunately been adopted by many subsequent workers, and especially by Holborn and Otto‡, who have recently carried out a series of accurate observations on the inert gases and have presented their results in a form comparable with theory. Their experiments cover a wide range of temperature, as is shown in the following table where their results for several gases are summarized. The values of B_v/A_v, or rather of $\log (B_v/A_v)$, are given after the conversion of the results to the standard form (673) in the usual units. Three sets of results for helium are given in adjacent columns, one set due

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* For a full account of the earlier literature on equations of state, see Kamerlingh-Onnes and Keesom, "Die Zustandsgleichung," *Encyk. der math. Wiss.* vol. v, p. 615 (1912).

† Kamerlingh-Onnes, *Comm. Phys. Lab. Leiden*, No. 71, or *Proc. Sect. Sci. Amsterdam*, vol. IV, p. 125 (1902).

‡ Holborn and Otto, *Zeit. für Phys.* vol. XXIII, p. 77 (1924); vol. XXX, p. 320 (1924); vol. XXXIII, p. 1 (1925); vol. XXXVIII, p. 359 (1926).

to Kamerlingh-Onnes and the other two to Holborn and Otto, deduced from their observations by different methods. The results of Kamerlingh-Onnes are inconsistent with those of Holborn and Otto at low temperatures. The latter are, however, consistent among themselves and, being the more recent observations, have been chosen for comparison with theory. The theoretical curve for $n = 14\frac{1}{3}$ and $m = 5$ fits the observed points with one exception over the whole range of 658°. Other curves can be superimposed on the observed points, though not with the same agreement as that shown. The maximum property exhibited by the observed points provides a stringent test for the theoretical curves and some, like that of the attracting rigid sphere (Fig. 15), are definitely unsuitable. The only curves which can be regarded as possible ones are: $(n, m) = (9, 5)$, $(11, 5)$, $(11, 6)$ and $(14\frac{1}{3}, 5)$. Of these, the first cannot be regarded as quite satisfactory, the second is better, the third and last best of all; the last, in fact,

TABLE 16.

The observed values of log (B_v/A_v).

Temp. °C	Helium			Neon	Argon	Hydrogen (H_2)	Nitrogen (N_2)
	(1)	(2)	(3)	(2)	(2)	(2)	(2)
– 258·0	—	$\bar{4}\cdot7823$ (*n*)	—	—	—	—	—
– 252·8	—	$\bar{4}\cdot0961$ (*n*)	—	—	—	—	—
– 216·56	$\bar{4}\cdot6664$	—	—	—	—	—	—
– 208·0	—	$\bar{4}\cdot6216$	—	—	—	—	—
– 207·9	—	—	—	$\bar{4}\cdot9707$ (*n*)	—	$\bar{4}\cdot9129$ (*n*)	—
– 183·0	—	$\bar{4}\cdot6750$	—	—	—	$\bar{4}\cdot3925$ (*n*)	—
– 182·75	$\bar{4}\cdot7261$	—	—	—	—	—	—
– 182·5	—	—	—	$\bar{4}\cdot5618$ (*n*)	—	—	—
– 150·0	—	—	—	$\bar{6}\cdot6440$	—	$\bar{4}\cdot1187$	—
– 130·0	—	—	—	—	—	—	$\bar{3}\cdot5513$ (*n*)
– 103·57	$\bar{4}\cdot7350$	—	—	—	—	—	—
– 100	—	—	—	$\bar{4}\cdot4588$	$\bar{3}\cdot458$ (*n*)	$\bar{4}\cdot6106$	$\bar{3}\cdot3642$ (*n*)
– 50	—	—	—	$\bar{4}\cdot6089$	$\bar{3}\cdot227$ (*n*)	$\bar{4}\cdot7319$	$\bar{3}\cdot0706$ (*n*)
0	$\bar{4}\cdot7094$	$\bar{4}\cdot7231$	$\bar{4}\cdot7233$	$\bar{4}\cdot6770$	$\bar{4}\cdot9939$ (*n*)	$\bar{4}\cdot7949$	$\bar{4}\cdot6638$ (*n*)
20	$\bar{4}\cdot6970$	—	—	—	—	—	—
50	—	$\bar{4}\cdot7190$	$\bar{4}\cdot7185$	—	$\bar{4}\cdot6920$ (*n*)	$\bar{4}\cdot8300$	$\bar{5}\cdot0606$ (*n*)
100	—	$\bar{4}\cdot7057$	$\bar{4}\cdot7099$	$\bar{4}\cdot7232$	$\bar{4}\cdot2826$ (*n*)	$\bar{4}\cdot8416$	$\bar{4}\cdot4374$
100·35	$\bar{4}\cdot6923$	—	—	—	—	—	—
150	—	—	—	—	$\bar{5}\cdot7159$	—	4·7112
200	—	4·6934	$\bar{4}\cdot6931$	4·7648	4·3191	4·8452	4·8353
300	—	4·6704	4·6719	$\bar{4}\cdot7880$	$\bar{4}\cdot6997$	—	4·9642
400	—	$\bar{4}\cdot6550$	$\bar{4}\cdot6599$	$\bar{4}\cdot7869$	$\bar{4}\cdot8344$	—	$\bar{3}\cdot0206$

For entries marked (*n*) B' or $F(y)$ is negative.

(1) Kamerlingh-Onnes, *Comm. Phys. Lab. Leiden*, No. 102 A (1908).

(2) and (3) Holborn and Otto (*loc. cit.*).

is as nearly perfect as can be hoped for (see Fig. 16). The appropriate values for the force constants for the first two and the last of these models are given in Table 17 below. Here, too, are collected the results for other gases obtained by the same method.

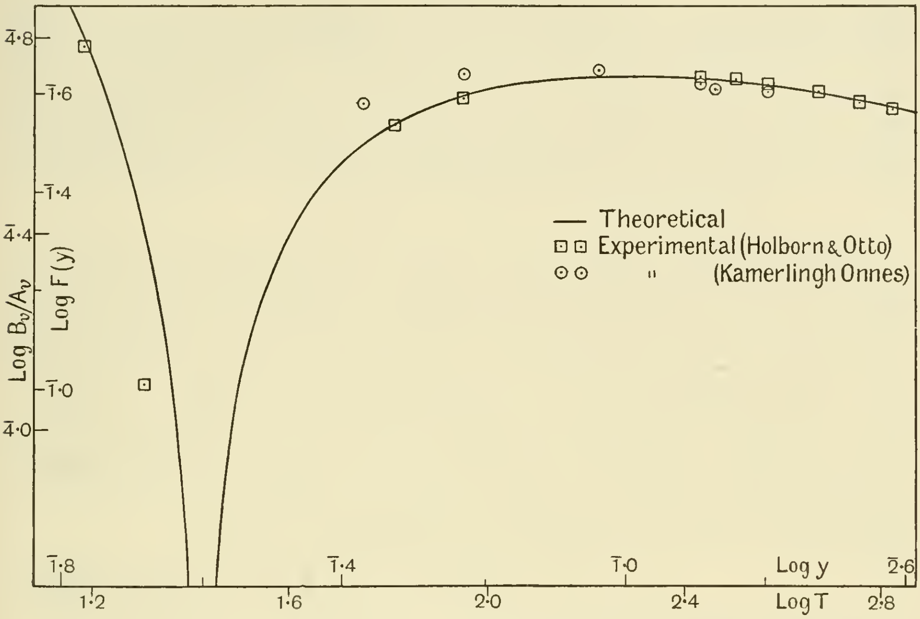

Fig. 16. Observed and theoretical values of the second virial coefficient for helium.

TABLE 17.

The force constants of gases (λ and μ) from the equation of state.

(The figures in brackets are the "diameters" in Ångström units as defined below.)

	$n = 9$, $m = 5$		$n = 11$, $m = 5$		$n = 14\frac{1}{3}$*, $m = 5$		$n = \infty$, $m = 5$	
	$\lambda \,.\, 10^{74}$	$\mu \,.\, 10^{45}$	$\lambda \,.\, 10^{90}$	$\mu \,.\, 10^{45}$	$\lambda \,.\, 10^{115}$	$\mu \,.\, 10^{45}$	σ	$\mu \,.\, 10^{45}$
Helium	1·31 (4·10)	5·25	6·97 (3·57)	3·56	2·35 (3·12)	2·33	—	—
Neon	6·32 (4·99)	22·3	43·8 (4·29)	17·2	22·2 (3·70)	13·3	— (2·42)	7·3
Argon	101·0 (7·05)	162·0	1310·0 (6·03)	138·0	1640·0 (5·11)	113·0	— (3·13)	70·4
Hydrogen	9·19 (5·23)	25·4	73·8 (4·52)	19·8	48·9 (3·92)	15·6	— (2·59)	8·5
Nitrogen	158·2 (7·46)	182·0	2245·0 (6·36)	151·0	3610·0 (5·42)	123·0	— (3·38)	77·0

* This fractional number has advantages in the numerical work.

For details, the reader is referred to the original papers*. As a convenient method of comparing the λ's which are of different orders of magnitude (10^{-8n} about), a quantity σ_n is calculated from the formula

$$\sigma_n = \left(\frac{\lambda}{\{n-1\}W}\right)^{1/(n-1)}. \qquad \text{......(696)}$$

This is the distance at which the potential energy of two atoms is equal to an arbitrary amount W. It is easy to see that this quantity becomes the diameter of the atom when $n \rightarrow \infty$.† For purposes of comparison, any value of W may be chosen. Here it is taken to be $\frac{3}{2}k$, the average kinetic energy of an atom at 1° K. The numbers thus calculated are included in Table 17 in brackets, the unit being the Ångström.

§ **10·35**. *Gaseous mixtures.* The force constants just given apply to the field between two atoms of the same kind. To extend the work to atoms of different kinds, it is necessary to consider gaseous mixtures. With the same validity as the equation of state of a single gas, we have for a mixture

$$p = kT\{(\nu_1+\nu_2) + \nu_1^2 B_{11}' + 2\nu_1\nu_2 B_{12}' + \nu_2^2 B_{22}'\}, \qquad \text{......(697)}$$

where
$$B_{rs}' = 2\pi\int_0^\infty r^2\{1 - e^{-E_{rs}(r)/kT}\}\,dr. \qquad \text{......(698)}$$

The observed isothermals are to be expressed as before by

$$pV = A_v + \frac{B_v}{V},\ pV = A_p + B_p p, \qquad \text{......(699)}$$

and then by comparison we have

$$A_v = \nu_0 kT, \qquad \text{......(700)}$$

$$\frac{B_v}{A_v} = B_p = \nu_0\,(B_{11}'x_1^2 + 2B_{12}'x_1x_2 + B_{22}'x_2^2), \qquad \text{......(701)}$$

or
$$B_{11}x_1^2 + 2B_{12}x_1x_2 + B_{22}x_2^2 = B_v/A_v. \qquad \text{......(702)}$$

In (701) ν_0 refers to the concentration of the mixture under standard conditions and

$$B_{rs} = \nu_0 B_{rs}',\ x_1 = \nu_1/\nu,\ x_2 = \nu_2/\nu,\ x_1 + x_2 = 1. \qquad \text{......(703)}$$

The dependence of B_v/A_v on the relative concentrations has been studied experimentally by Verschoyle‡ at temperatures of 0° and 20° C. for mixtures of hydrogen and nitrogen, and his values are plotted in Fig. 12. That figure shows two curves, quadratic in ν_1/ν_2, which are drawn so that the mean square of the distances of the observed points from them is a minimum. It is clear that a quadratic function of this kind

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* Lennard-Jones, *Proc. Roy. Soc.* A, vol. cvi, p. 463 (1924); vol. cvii, p. 157 (1925); vol. cxii, p. 214 (1926).

† Cf. *ibid.* vol. cix, p. 481 (1925).

‡ Verschoyle, *Proc. Roy. Soc.* A, vol. cxi, p. 552 (1926).

satisfactorily accounts for the facts, and hence we may deduce from the observations the numerical values of each of the coefficients B_{11}, B_{12} and B_{22} in equation (702).

This process, if continued for a number of temperatures, would determine the variation of B_{11}, B_{12} and B_{22} with temperature. Each of these functions could then be dealt with separately, just as the B_v/A_v for a single gas, leading to the evaluation of the four constants of the fields between like and unlike atoms. Unfortunately, there does not appear to be any experimental data so extensive as this for any pair of gases. The work of Verschoyle refers only to two temperatures 0° and 20° C. and is thus scarcely adequate. Tentative calculations have been carried out on the basis of this work, but the results cannot be regarded as final*.

A series of experiments has been carried out by Holborn and Otto† on a mixture of helium and neon of fixed concentration (72·39 per cent. neon and 27·61 per cent. helium) as well as on the single gases, over a temperature range 0° to 400° C. This provides just the minimum information necessary for the determination of B_{11}, B_{12} and B_{22} as functions of temperature and so of the interatomic fields*. An extension of this work to lower temperatures and to mixtures of other concentrations is desirable. The numerical results suggest a simple relation between the repulsive force constants of the fields between like and unlike atoms. It appears that

$$\sigma_{12}{}^{(n)} = \tfrac{1}{2}\left(\sigma_{11}{}^{(n)} + \sigma_{22}{}^{(n)}\right), \qquad \text{......(704)}$$

approximately, so that

$$\lambda_{12}{}^{\frac{1}{n-1}} = \tfrac{1}{2}\left(\lambda_{11}{}^{\frac{1}{n-1}} + \lambda_{22}{}^{\frac{1}{n-1}}\right). \qquad \text{......(705)}$$

This means physically that the closest distance of approach of two unlike atoms in a direct encounter with a given energy is equal to the mean of the corresponding distances in the encounter of two pairs of like atoms with the same energy.

§ **10·41**. *The viscosity of a gas. Theoretical formulae.* Another method of determining interatomic fields is by a comparison of the observed and calculated variation of the viscosity of a gas with temperature. The theory of viscosity lies outside the range of this monograph, but mention must be made of the results in so far as they provide information on interatomic forces. Unfortunately, the calculations involved in the theoretical work are so complicated that progress has been made only in the case of spherically symmetrical fields, and then only in certain special cases. The original investigation by Maxwell‡ applied only to atoms repelling as an inverse

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* Lennard-Jones and Cook, *Proc. Roy. Soc.* A, vol. cxv, p. 334 (1927).

† Holborn and Otto, *Zeit. für Phys.* vol. xxiii, p. 77 (1924).

‡ Maxwell, *Scientific Papers*, vol. ii, p. 26.

fifth power of the distance. This has since been generalized by Chapman* and Enskog† to any inverse power law. These authors have also given rigorous calculations for atoms behaving on collision like rigid elastic spheres with a weak attractive field surrounding them. They have confirmed the general form of the formula first given by Sutherland on this assumption.

Another law of force for which calculations can be made is a repulsion according to an inverse nth power law to which is added an attraction according to an inverse third power‡. This special attractive law does not possess any physical significance and cannot continue to represent the forces at great distances. Its advantage is purely mathematical. For this case, the coefficient of viscosity varies with temperature according to the law

$$\mu = \mu_0 \left(\frac{T}{T_0}\right)^{\frac{n+3}{2(n-1)}} \frac{1+\sum\limits_{r=1}^{\infty} S_r T_0^{-r\frac{n-3}{n-1}}}{1+\sum\limits_{r=1}^{\infty} S_r T^{-r\frac{n-3}{n-1}}}, \qquad \text{......(706)}$$

where T_0 is a standard temperature and S_r is a function of $\lambda_3/\lambda_n^{2/(n-1)}$ but independent of temperature§. If the attractive field is assumed weak (that is, $\lambda_3/\lambda_n^{2/(n-1)}$ assumed small), the formula reduces to

$$\mu = \mu_0 \left(\frac{T}{T_0}\right)^{\frac{3}{2}} \frac{T_0^{\frac{n-3}{n-1}}+S}{T^{\frac{n-3}{n-1}}+S}. \qquad \text{......(707)}$$

When there is no attractive field, S vanishes and the formula reduces to that given by Chapman|| and Enskog¶ for a gas in which the atoms repel according to the inverse nth power law. This formula in full is

$$\mu = \epsilon_c \frac{B_n m^{\frac{1}{2}}}{\lambda_n^{2/(n-1)}} T^{\frac{n+3}{2(n-1)}}, \qquad \text{......(708)}$$

where m is the mass of the molecule, and ϵ_c and B_n are numbers, depending

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* Chapman, *Phil. Trans.* A, vol. CCXVI, p. 279 (1915).

† Enskog, *Kinetische Theorie der Vorgänge in massig verdünnten Gasen*, Inaug. Diss. (Uppsala, 1917).

‡ Lennard-Jones, *Proc. Roy. Soc.* A, vol. CVI, p. 441 (1924).

§ *Ibid.* p. 450, equation (4·21).

|| Chapman, *loc. cit.*, equations (183) and (251); cf. also *Phil. Trans.* A, vol. CCXI, p. 433 (1912); Jeans, *loc. cit.* p. 287; and again Chapman, *Memoirs Manchester Lit. and Phil. Soc.* vol. LXVI, p. 7 (Appendix), 1922. In the first paper cited it should be noted that $\lambda_n m^2$ is used as the force constant instead of λ_n (although the contrary is stated, p. 321), and in the other papers the formulae should all be multiplied by a factor $(2/\{n-1\})^{2/(n-1)}$.

¶ Enskog, *loc. cit.*

only on n, the former lying between the narrow limits 1·000 and 1·016*, and the latter being given by

$$B_n = \frac{5\pi^{\frac{1}{2}} k^{(n+3)/2(n-1)}}{4 I_2(n)\, \Gamma\left(4 - \dfrac{2}{n-1}\right) 2^{(n-3)/(n-1)}}. \qquad \text{......(709)}$$

In this expression, k is the usual gas constant, and $I_2(n)$ is a function of n which has been tabulated†.

In the same notation the more general formula is

$$\mu = \frac{B_n m^{\frac{1}{2}}}{\lambda_n^{2/(n-1)}} \frac{T^{\frac{3}{2}}}{T^{\frac{n-3}{n-1}} + S}. \qquad \text{......(710)}$$

The well-known Sutherland formula is obtained from this by letting n tend to infinity, while $\lambda_n^{1/(n-1)}$ tends to σ, the molecular diameter. We then find

$$\mu = \frac{B_\infty m^{\frac{1}{2}}}{\sigma^2} \frac{T^{\frac{3}{2}}}{T + S}, \qquad \text{......(711)}$$

where

$$B_\infty = \frac{5\pi^{\frac{1}{2}} k^{\frac{1}{2}}}{48 I_2(\infty)}. \qquad \text{......(712)}$$

All the above formulae are, however, restricted to weak attractive fields. This restriction has recently been removed in one special case‡, where the repulsive field is represented by a rigid sphere and the attractive field varies as the inverse fifth power of the distance. The analysis is similar to the theory of diffusion given by Langevin § to account for the mobilities of ions in gases. In this case it is not possible to give the viscosity as an explicit function of temperature. It is found that

$$\mu = \frac{5}{64}\left(\frac{kmT}{\pi}\right)^{\frac{1}{2}} \frac{f(x)}{\sigma^2}, \qquad \text{......(713)}$$

where

$$x = 2\sigma^2 \left(\frac{kT}{\mu}\right)^{\frac{1}{2}} \qquad \text{......(714)}$$

and $f(x)$ is computed for x at small intervals from 0 to 4·0‖.

§ **10·42**. *Viscosity of a gas. Experimental.* The possibility of obtaining information of intermolecular fields from a knowledge of the variation of the viscosity of gases with temperature has long been recognized, and much experimental data has been accumulated with this object in view. A review of the important work of Dorn and his school at Halle has been given by K. Schmidt¶, who has also compared the results with those

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* Chapman, *loc. cit.* (1915), p. 273, Table V.

† Chapman, *loc. cit.* (1922) and Lennard-Jones, *Proc. Roy. Soc.* A, vol. CVI, p. 456 (1924).

‡ Hassé and Cook, *Phil. Mag.* vol. III, p. 977 (1927).

§ Langevin, *Ann. de Chim. et de Phys.* (8), vol. V, p. 245 (1905).

‖ In the notation of the paper $f(\lambda) = \lambda/X$, where X is computed in terms of λ (Table IV, p. 982)

¶ Schmidt, *Ann. der Phys.* vol. XXX, p. 399 (1909).

calculated by means of the Sutherland formula (711). In the cases where the viscosity was measured over only a small range of temperature, the agreement was fairly good, but in other cases, e.g. argon, where the viscosity was measured at very low temperatures, the agreement is good only at high temperatures. Later researches by Kamerlingh-Onnes and Weber* on the viscosity of hydrogen and helium at low temperatures showed conclusively that the Sutherland model was inadequate. This conclusion was confirmed by Vogel†, who carried out much work on viscosity at low temperatures. The more extensive observations on gases are summarized in the following table.

TABLE 18.

The viscosity of gases.

	Observers	Temperature range ° K.	μ at 0° C.
He	Kamerlingh-Onnes and Weber[1]	15·0 to 456·8	$1{\cdot}887 \times 10^{-4}$
Ne	Rankine[2]	286·9 and 373·1	$2{\cdot}946 \times 10^{-4}$
	Weber[3]	91·66 to 378·90	—
Ar	Schmidt[4]	89·9 to 456·4	$2{\cdot}118 \times 10^{-4}$
H_2	Markowski[5]	20 to 457·3	$0{\cdot}844 \times 10^{-4}$
	Kamerlingh-Onnes and Weber[6]		
N_2	Schmidt[4]	81·6 to 455·8	$1{\cdot}678 \times 10^{-4}$
	Vogel[7]		
	Kia Lok Yen[8]		

[1] Kamerlingh-Onnes and Weber, *Comm. Phys. Lab. Leiden*, No. 134 B, p. 18 (1913).
[2] Rankine, *Proc. Roy. Soc.* A, vol. LXXXIV, p. 191 (1911).
[3] Weber, *Comm. Phys. Lab. Leiden*, Suppl. No. 42 B (1918).
[4] Schmidt, *Ann. der Phys.* vol. XXX, p. 399 (1909).
[5] Markowski, *Ann. der Phys.* vol. XIV, p. 742 (1904).
[6] Kamerlingh-Onnes and Weber, *Comm. Phys. Lab. Leiden*, No. 134 A (1913).
[7] Vogel, *Ann. der Phys.* vol. XLIII, p. 1258 (1914).
[8] Kia Lok Yen, *Phil. Mag.* vol. XXXVIII, p. 582 (1919).

The theoretical formula (707) (repulsive field $\lambda_n r^{-n}$, attractive field $\lambda_3 r^{-3}$) has been compared with these experimental results and has been shown to give a satisfactory representation of the facts when suitable values are chosen for S.‡ The magnitudes of the force constants can then be determined from equation (710).

The viscosity of helium is represented with remarkable accuracy over the whole range of temperature when $S = 0$, and $n = 14{\cdot}6$. The appropriate value of λ_n thus deduced is in close agreement with that obtained from the equation of state for $n = 14\frac{1}{3}$ and given in Table 17 above. The viscosity results for this gas allow little flexibility in n, and so the combined results of viscosity and equation of state may be regarded as definitely deter-

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* Kamerlingh-Onnes and Weber, *Comm. Phys. Lab. Leiden*, Nos. 134 A, B and C (1913).

† Vogel, *Inaug. Diss., Berlin* (1914).

‡ Lennard-Jones, *Proc. Roy. Soc.* A, vol. CVI, p. 441 (1924); vol. CVII, p. 157 (1925); vol. CXII, p. 214 (1926).

mining the atomic field of helium. It is satisfactory that methods so different experimentally, as well as theoretically, should lead to such consistent results.

Equally consistent results are obtained by the two methods for hydrogen and neon. In the former case, $S = 0$ again and the only value of n permitted by viscosity is $n = 11$. In no case does the viscosity method determine the attractive field, and for this reason the alternative method is to be preferred. It is to be noted from Table 17 that the attractive fields of helium, neon and molecular hydrogen are all weak and probably satisfy the conditions for which the formula (710) is valid. This cannot be said of argon and nitrogen, and it is significant that the values of the repulsive force constants found from viscosity for these two gases do not show the same consistency with those obtained from the equation of state, as is shown by the other gases. It suggests that the theoretical formula (710) is not strictly applicable to these gases. A rigorous theoretical formula for viscosity, true for attractive fields of any magnitude, might lead to force constants different from those now found and nearer to the values obtained from the equation of state.

This conclusion is supported by the work of Cook and Hassé already referred to. They compare the formula (713) with the experimental results by graphical methods similar to those used in the equation of state described above. The main results are given in Table 19, in which are also included the corresponding values obtained by the use of the Sutherland formula, and the results found from the equation of state (rigid sphere model).

TABLE 19.

Diameters and attractive fields (μr^{-5}) *of certain gases.*
(*Rigid sphere model.*)

Gas	Viscosity (Sutherland) formula		Viscosity (Hassé and Cook)		Equation of state	
	$\sigma . 10^{8}$	$\mu . 10^{43}$	$\sigma . 10^{8}$	$\mu . 10^{43}$	$\sigma . 10^{8}$	$\mu . 10^{43}$
Argon	2·90	2·94	2·98	1·29	3·13	0·704
Nitrogen	3·15	2·96	3·28	1·27	3·38	0·774
Carbon dioxide	3·36	8·17	3·55	3·40	—	—
Air	3·10	2·88	3·22	1·27	—	—

The accurate formula of Hassé and Cook has resulted in an increase in the diameter and a decrease in the attractive force constant from that obtained by the Sutherland formula, and each is in the direction of the equation of state results. Seeing that a rigid sphere representation of molecules is inadequate, the results are in as good agreement as can be expected.

The combined results for the repulsive force constants of the inert gases together with those of hydrogen and nitrogen are given in Table 20. The method of arriving at the results for krypton and xenon will be described below.

TABLE 20.

Repulsive force constants and "diameters" of gases (in Ångströms).

	Method	$n = 9$	11	14	$14\frac{1}{3}$	15	21	∞
He	(1)	$1{\cdot}31 \times 10^{-74}$ 4·10	$6{\cdot}97 \times 10^{-90}$ 3·57		$2{\cdot}35 \times 10^{-115}$ 3·12			
	(2)			$5{\cdot}74 \times 10^{-113}$ 3·12				
Ne	(1)	$6{\cdot}32 \times 10^{-74}$ 4·99	$4{\cdot}38 \times 10^{-89}$ 4·29		$2{\cdot}22 \times 10^{-114}$ 3·70			— 2·42
	(2)	$6{\cdot}66 \times 10^{-74}$ 5·02	$4{\cdot}45 \times 10^{-89}$ 4·30			$1{\cdot}76 \times 10^{-119}$ 3·60	$3{\cdot}89 \times 10^{-165}$ 3·153	— 2·35
Ar	(1)	$1{\cdot}01 \times 10^{-72}$ 7·05	$1{\cdot}31 \times 10^{-87}$ 6·03		$1{\cdot}64 \times 10^{-112}$ 5·11		$2{\cdot}34 \times 10^{-162}$ 4·34	— 3·13
	(2)		$3{\cdot}92 \times 10^{-88}$ 5·35		$3{\cdot}57 \times 10^{-113}$ 4·70		$2{\cdot}82 \times 10^{-163}$ 3·99	— 2·84
Kr	(3)	($n = 10$) $7{\cdot}34 \times 10^{-80}$ 6·98						
Xe	(3)		$6{\cdot}21 \times 10^{-87}$ 7·05					
H_2	(1)	$9{\cdot}19 \times 10^{-74}$ 5·23	$7{\cdot}38 \times 10^{-89}$ 4·52		$4{\cdot}89 \times 10^{-114}$ 3·92			— 2·59
	(2)		$7{\cdot}19 \times 10^{-89}$ 4·51					
N_2	(1)	$15{\cdot}82 \times 10^{-73}$ 7·46	$22{\cdot}45 \times 10^{-88}$ 6·36		$3{\cdot}61 \times 10^{-112}$ 5·42			— 3·38
	(2)	$7{\cdot}59 \times 10^{-73}$ 6·81	$9{\cdot}08 \times 10^{-88}$ 5·81			$1{\cdot}17 \times 10^{-117}$ 4·84		— 3·15

(1) From equation of state. (2) From viscosity. (3) From crystal data.

Except in the cases of helium and hydrogen, neither the equation of state nor the viscosity determines the molecular fields uniquely. Other methods have to be employed to single out the right model from the array of possible ones thus determined. One method by which this has been done is described in the next paragraph. The numbers underlined in this table indicate the molecular models which have been selected.

Fig. 17 shows the results embodied in Table 20. The diameter $\sigma^{(n)}$, defined in (696), is plotted against n in the various cases. It will be observed how consistent are the results for helium, hydrogen and neon.

§ **10·5**. *The forces between ions.* The physical properties of certain solids indicate that the main forces of attraction between the constituents are of an entirely different order from those considered in the preceding paragraph. The difference in the melting points of rock-salt and crystalline argon may be quoted as an example. It may now be regarded as certain that a solid, such as rock-salt, consists of an array of closed electronic systems of the inert gas type, formed by the transfer of the valency electrons of the metal to the halogen, but differing therefore from inert gas atoms by the possession of a resultant charge. The forces between these electrostatic charges provide the main cohesion of the crystal. For a full account of the electron theory of valency, the reader is referred to the treatises of Kossel*, Lewis† and Sidgwick‡. X-ray analysis reveals to us the design on which large numbers of crystals are built up, and this information, together with the postulate of electrostatic forces of cohesion, permits of theoretical calculation of their physical properties which, when compared with observation, serves to support or discredit the assumption as to the nature of the cohesion.

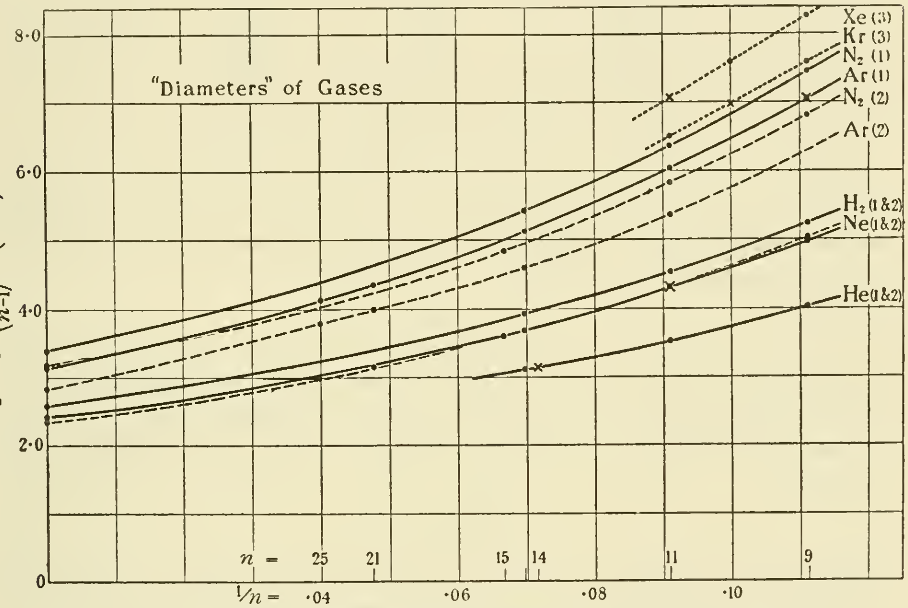

Fig. 17. The "diameters" of gases in Ångström units, (1) from equation of state, (2) from viscosity, (3) from crystal data.

The first attempt to interpret the properties of crystals in terms of electrostatic forces is due to Haber§. Following him, Lindemann|| tried

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* Kossel, *Ann. der Phys.* vol. XLIX, p. 229 (1916); *Valenzkräfte und Röntgenspektrum*, 2nd ed. (Berlin, 1924).

† G. N. Lewis, *Valence* (1916).

‡ Sidgwick, *The Electronic Theory of Valency* (1927).

§ Haber, *Verh. der Deutsch. Phys. Ges.* vol. XIII, p. 1117 (1911).

|| Lindemann, *Verh. der Deutsch. Phys. Ges.* vol. XIII, p. 1107 (1911).

to deduce relations between the interatomic distances, heats of sublimation, melting points and infra-red frequencies. The analysis did not lay claim to rigour, but sufficed to produce formulae dimensionally correct. To improve the theory it was necessary to find out something about the intrinsic repulsive fields which keep atoms apart in solids. Born and Landé* first tried to do this by building up certain simple static atomic models consistent with Bohr's conception of the atom, and in terms of these tried to explain interatomic distances and compressibilities of crystals. This and other subsequent attempts by Born†, Landé‡, Haber§, Smekal|| and others¶ naturally met with only a partial success, and the repulsive forces still await calculation in terms of electronic structure.

Born was therefore led to represent the repulsive field empirically by a spherically symmetrical force of the type λr^{-n}. The interatomic distance of a crystal is then regarded as the equilibrium position of ions under the joint influence of electrostatic and intrinsic repulsive fields. The crystals discussed are simplified by being regarded as devoid of heat motion.

As we saw in § 4·9, the mathematical function which is of paramount importance is the potential energy of a unit cell ϕ, which we may here regard as made up of two parts $\phi^{(e)}$ and $\phi^{(n)}$, the respective contributions of the electrostatic and intrinsic repulsive fields,

$$\phi = \phi^{(e)} + \phi^{(n)}. \qquad \text{......(715)}$$

For a crystal like rock-salt, which consists of two interpenetrating face-centred lattices, only one parameter a (the closest distance between atoms) appears in $\phi^{(e)}$ and $\phi^{(n)}$ and the equilibrium value is determined by the equation

$$\left(\frac{\partial \phi}{\partial r}\right)_{r=a} = 0. \qquad \text{......(716)}$$

Assuming the value of a to be known, either from density measurements or X-ray measurements, this equation can be used to determine λ (the repulsive force constant) in terms of known quantities. There remains then only one unknown n. This Born determined from measurements of the compressibility κ, equations (244), (245), or

$$\frac{1}{\kappa} = -V\frac{dp}{dV} = V\frac{d^2\phi}{dV^2}. \qquad \text{......(717)}$$

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* Born and Landé, *Berl. Ber.* p. 1048 (1918).

† Born, *Verh. der Deutsch. Phys. Ges.* vol. xx, p. 230 (1918).

‡ Landé, *Verh. der Deutsch. Phys. Ges.* vol. xxi, pp. 2, 644, 653 (1919); *Zeit. für Phys.* vol. i, p. 191 (1920); vol. ii, pp. 83, 87, 380 (1920).

§ Haber, *Verh. der Deutsch. Phys. Ges.* vol. xxi, p. 750 (1919).

|| Smekal, *Zeit. für Phys.* vol. i, p. 309 (1920).

¶ Rella, *Zeit. für Phys.* vol. iii, p. 157 (1920); Schwendenwein, *Zeit. für Phys.* vol. iv, p. 73 (1921).

Writing V in terms of the interatomic distance a, we thus find (for the rock-salt type)

$$\frac{1}{\kappa}=\frac{1}{36a}\left(\frac{d^2\phi}{dr^2}\right)_{r=a}. \qquad \text{......(718)}$$

This equation suffices to determine n. In this way Born* obtained the numerical values given in Table 21.

TABLE 21.

Index of repulsive field (*Born*).

	κ (obs.) × 10^{12}	n
NaCl	4·13	8·84
NaBr	5·1	9·61
NaI	6·9	9·45
KCl	5·62	9·86
KBr	6·2	10·78
KI	8·6	10·31

Assuming an average value 10 for n for all crystals, Born then proceeded to calculate other crystal properties such as elastic constants, crystal energy, etc. This was followed by more accurate calculations in which the actual values of n given above were used†. These will be referred to below.

The disadvantage of Born's method is that it uses two principal properties of crystals to calculate the rest. This was inevitable in view of the lack of information about repulsive fields, but now that this has been supplied by other methods (as described in the preceding paragraphs) the way is open for a new attack on crystal problems and incidentally for the correlation of the properties of gases with the properties of crystals. A further assumption in the earlier work is that all the ions in one crystal, whether alike or unlike, repel according to the same law, so that for instance the Cl ions in NaCl interact with each other according to a different law from those in KCl. It seems more reasonable to assume that a Cl^- ion, being of the same electronic structure as argon, repels according to the same law (λr^{-n}) as argon, but to a different degree, that is, with the same n but with a different λ. The problem then remains of determining the λ for an ion when λ for the inert gas of the same structure is known.

If atoms and ions *could* be faithfully represented by spherical shells, the method of passing from the size of an inert gas atom to that of neighbouring ions would be easy. From the refractive indices of crystals and salts it is possible, as Wasastjerna has shown, to deduce the refractivities of atoms and ions, and from them the relative sizes of atoms and ions of similar electronic structure‡. Presumably the ratios obtained in this way

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* Born, *Ann. der Phys.* vol. LXI, p. 87 (1919); *Verh. der D. Phys. Ges.* vol. XXI, pp. 199, 533 (1919).

† Born and Brody, *Zeit. für Phys.* vol. XI, p. 327 (1922).

‡ Wasastjerna, *Soc. Scient. Fenn. Comm. Phys. Math.* vol. I, No. 38 (1923).

refer to the average distance of the outer electronic orbits from the nucleus, these distances depending on the effective nuclear charge. Now the forces between these electronic systems will clearly depend on the size of the outer orbits; and so, when the forces are represented by hard impenetrable shells, as they often are in applications of the kinetic theory, the dimensions of the shell may be taken to be directly proportional to the scale of the outer orbits. When the repulsive field is represented by the law $\lambda_n r^{-n}$, the function

$$\sigma^{(n)} = \left[\frac{\lambda_n}{(n-1)\,W}\right]^{\frac{1}{n-1}} \qquad \text{......(719)}$$

replaces the kinetic theory diameter of the atom (W being any convenient energy value). It therefore seems natural to suppose that this function is proportional to the size of the outer orbits.

TABLE 22.

The relative sizes of ions and atoms (*Wasastjerna*)*.

$\frac{\rho^{--}}{\rho}$	$\frac{\rho^{-}}{\rho}$	$\frac{\rho}{\rho}$	$\frac{\rho^{+}}{\rho}$	$\frac{\rho^{++}}{\rho}$
O^{--} 1·445	F^{-} 1·240	Ne 1·00	Na^{+} 0·938	Mg^{++} 0·817
S^{--} 1·386	Cl^{-} 1·205	Ar 1·00	K^{+} 0·912	Ca^{++} 0·838
Se^{--} 1·264	Br^{-} 1·173	Kr 1·00	Rb^{+} 0·919	Sr^{++} 0·856
Te^{--} 1·169	I^{-} 1·152	Xe 1·00	Cs^{+} 0·922	Ba^{++} 0·853

Thus we write

$$\sigma_+^{(n)} = \frac{\rho_+}{\rho}\,\sigma^{(n)}, \qquad \text{......(720)}$$

and so

$$\left[\frac{\lambda_n^{+}}{(n-1)\,W}\right]^{\frac{1}{n-1}} = \frac{\rho_+}{\rho}\left[\frac{\lambda_n}{(n-1)\,W}\right]^{\frac{1}{n-1}}, \qquad \text{......(721)}$$

that is,

$$\lambda_n^{+} = \left(\frac{\rho_+}{\rho}\right)^{n-1}\lambda_n, \qquad \text{......(722)}$$

a result independent of W.

Using Tables 20 and 22, we can now deduce a series of possible repulsive fields for ions just as we have already done for the inert gases. But this still leaves us in ignorance of the forces between the kations and anions. Whatever be the correct relation between λ_{12}, λ_{11} and λ_{22}, it must, in the limit for infinite values of n, reduce to the law

$$\sigma_{12} = \tfrac{1}{2}\,(\sigma_{11} + \sigma_{22}). \qquad \text{......(723)}$$

This condition is satisfied by the relation

$$\sigma_{12}^{(n)} = \tfrac{1}{2}\,(\sigma_{11}^{(n)} + \sigma_{22}^{(n)}), \qquad \text{......(724)}$$

where $\sigma^{(n)}$ has been defined above, equation (719), and this seems the

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* Wasastjerna, *Soc. Scient. Fenn. Comm. Phys. Math.* vol. II, p. 7 (1924).

natural generalization to take, especially as evidence in favour of it has already been noted. With this assumption we have

$$\lambda_{12}^{\frac{1}{n-1}} = \tfrac{1}{2}\left(\lambda_{11}^{\frac{1}{n-1}} + \lambda_{22}^{\frac{1}{n-1}}\right), \qquad \ldots\ldots(725)$$

a result which is again independent of W.

A typical set of force constants calculated in this way is given in the next table.

TABLE 23.

The repulsive force constants of ions (forces in dynes).

n	$F^- \leftrightarrow F^-$	$F^- \leftrightarrow Na^+$	$Na^+ \leftrightarrow Na^+$
15	$3{\cdot}582\times10^{-118}$	$5{\cdot}837\times10^{-119}$	$7{\cdot}199\times10^{-120}$
11	$3{\cdot}819\times10^{-88}$	$1{\cdot}047\times10^{-88}$	$2{\cdot}344\times10^{-89}$
9	$3{\cdot}723\times10^{-73}$	$1{\cdot}321\times10^{-73}$	$3{\cdot}993\times10^{-74}$

Before we can apply this information to crystals we must examine how the potential energy of a crystal can be evaluated in terms of known interatomic forces.

§ **10·61**. *The electrostatic potential energy of a crystal* $\phi^{(e)}$. In the notation of §§ 4·9, 4·91 the electrostatic potential at any point in space $\mathbf{r}$ other than those occupied by charges is

$$\phi(\mathbf{r}) = \underset{l}{S}\sum_{k} \frac{\epsilon_k}{|\mathbf{r}_k^l - \mathbf{r}|}, \qquad \ldots\ldots(726)$$

where ϵ_k is the charge on the kth ion in the basic cell. One summation is over all the charges in a selected cell, and the other over all the cells of the crystal. It follows that the electrostatic potential energy of all the charges in a cell is given by

$$\phi_0^{(e)} = \underset{l}{S} \sum_{kk'}{}' \frac{\epsilon_k \epsilon_{k'}}{|\mathbf{r}_k^l - \mathbf{r}_{k'}|}, \qquad \ldots\ldots(727)$$

where the accented summation denotes as usual that those terms are omitted for which $k = k'$, $l = 0$. The potential energy of N cells is of course

$$\Phi_0^{(e)} = \tfrac{1}{2} N \phi_0^{(e)}. \qquad \ldots\ldots(728)$$

The evaluation of $\phi_0^{(e)}$ with special reference to a crystal was first made by Madelung*, though, unknown to him, a method of solution had previously been given by Riemann† and Appell‡. Madelung first considered a unidimensional crystal (that is, a *row* of charges with a periodic repetition

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* Madelung, *Phys. Zeit.* vol. XIX, p. 524 (1918).

† Riemann, *Schwere, Electrizität und Magnetismus*, edited by Hattendorf, 2nd ed., para. 23 (Hanover, 1880).

‡ Appell, *Acta Math.* vol. IV, p. 313 (1884); vol. VIII, p. 265 (1886); *Jour. de math.* (4) vol. III p. 5 (1887).

of pattern after a length a). The method consists in replacing the electric density by a Fourier expansion, and deducing a corresponding Fourier expansion for the potential at a point outside it. (The potential must have the same periodicity as the electric density.) This potential expansion must satisfy Laplace's equation at any point and Gauss' theorem near the line charge. These conditions, together with the fact that the potential must vanish at infinity, determine all the constants in the expression for the potential. For a series of discrete charges ϵ_k ($k = 1, 2, \ldots s$) on the unit strip at points x_k, which on the whole are electrically neutral, the potential at a point in space distant ρ from the line proves to be

$$\phi(x, \rho) = \frac{2}{a} \sum_{-\infty}^{+\infty} \sum_k \epsilon_k K_0 \left(\frac{2\pi n \rho}{a}\right) e^{\frac{2\pi i n}{a}(x - x_k)}, \qquad \ldots\ldots(729)$$

where K_0 is the function tabulated by Jahnke and Emde* as $\frac{1}{2} i \pi H_0^{(1)}(iz)$. From the potential of a line charge, that of a plane array of charges and finally that of a space lattice can be deduced.

Improved methods have, however, been given by Ewald† for dealing with three-dimensional lattices. In this case the electric density has a threefold periodicity with respect to the vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$. If p_1, p_2 and p_3 be the perpendiculars between consecutive planes containing the pairs of vectors ($\mathbf{a}_2$, $\mathbf{a}_3$), ($\mathbf{a}_3$, $\mathbf{a}_1$) and ($\mathbf{a}_1$, $\mathbf{a}_2$), then the density can be expressed in terms of a threefold Fourier expansion

$$\rho = \underset{l}{S} \rho_l e^{i(\mathbf{q}^l \cdot \mathbf{r})}, \qquad \ldots\ldots(730)$$

where $\mathbf{r}$, as usual, is the vector (x, y, z) and

$$\mathbf{q}^l = 2\pi \left(\frac{l_1 \mathbf{i}}{p_1} + \frac{l_2 \mathbf{j}}{p_2} + \frac{l_3 \mathbf{k}}{p_3}\right), \qquad \ldots\ldots(731)$$

$$= 2\pi (l_1 \mathbf{b}_1 + l_2 \mathbf{b}_2 + l_3 \mathbf{b}_3). \qquad \ldots\ldots(732)$$

In this equation, $\mathbf{i}$, $\mathbf{j}$ and $\mathbf{k}$ are unit vectors in the directions of p_1, p_2 and p_3, and $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ are vectors in the same directions with magnitudes $1/p_1$, $1/p_2$ and $1/p_3$.

The potential ϕ must have the same periodicity and must be expressible in a series similar to ρ, that is,

$$\phi = \underset{l}{S} c_l e^{i(\mathbf{q}^l \cdot \mathbf{r})}. \qquad \ldots\ldots(733)$$

Poisson's equation determines c_l in terms of ρ_l, giving

$$c_l = \frac{4\pi\rho_l}{|\mathbf{q}^l|^2}. \qquad \ldots\ldots(734)$$

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* Jahnke and Emde, *Funktionentafeln*, p. 135 (Leipzig, 1909). See also Watson, *Bessel's Functions*, p. 78, and Table II, p. 698.

† Ewald, *Ann. der Phys.* vol. LXIV, p. 253 (1921); see also Born, *Atomtheorie des festen Zustandes*, 2nd ed. p. 723 (1923).

If the system is electrically neutral and consists of discrete charges ϵ_k $(k = 1, 2, \dots s)$ and positions $\mathbf{r}_k$, then

$$\int_\Delta \rho e^{-i(\mathbf{q}^l \cdot \mathbf{r})}\, dv = \int_\Delta \underset{l'}{S'} \rho_{l'} e^{i(\mathbf{q}^{l'} - \mathbf{q}^l \cdot \mathbf{r})}\, dv = \rho_l \Delta, \qquad \dots\dots(735)$$

where the integral is taken over a basic cell of volume Δ. We then get

$$\rho_l = \frac{1}{\Delta} \int_\Delta \rho e^{-i(\mathbf{q}^l \cdot \mathbf{r})}\, dv = \frac{1}{\Delta} \sum_k \epsilon_k e^{-i(\mathbf{q}^l \cdot \mathbf{r}_k)}. \qquad \dots\dots(736)$$

We thus find

$$\phi = \frac{4\pi}{\Delta} \underset{l}{S'} \sum_k \frac{\epsilon_k}{|\mathbf{q}^l|^2} e^{i(\mathbf{q}^l \cdot \mathbf{r} - \mathbf{r}_k)}, \qquad \dots\dots(737)$$

$$= \sum_k \epsilon_k \psi(\mathbf{r} - \mathbf{r}_k),$$

where

$$\psi(\mathbf{r}) = \frac{4\pi}{\Delta} \underset{l}{S'} \frac{e^{i(\mathbf{q}^l \cdot \mathbf{r})}}{|\mathbf{q}^l|^2}. \qquad \dots\dots(738)$$

The solution of the problem depends on the evaluation of this summation and therefore of its transformation into a more rapidly converging form. Since

$$\frac{1}{a} = \frac{1}{a} e^{-a\eta} + \int_0^\eta e^{-a\xi}\, d\xi, \qquad \dots\dots(739)$$

we can write

$$\frac{\Delta}{4\pi} \psi = \underset{l}{S'} \frac{e^{i(\mathbf{q}^l \cdot \mathbf{r}) - \eta |\mathbf{q}^l|^2}}{|\mathbf{q}^l|^2} + \int_0^\eta \underset{l}{S'} e^{i(\mathbf{q}^l \cdot \mathbf{r}) - \xi |\mathbf{q}^l|^2}\, d\xi. \qquad \dots\dots(740)$$

The second integral can be transformed in terms of Gauss' error function

$$G(x) = 1 - F(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-a^2}\, da, \qquad \dots\dots(741)$$

which is a known tabulated function; in fact, it can be shown that

$$\psi = \frac{4\pi}{\Delta} \underset{l}{S'} \frac{e^{i(\mathbf{q}^l \cdot \mathbf{r}) - \eta |\mathbf{q}^l|^2}}{|\mathbf{q}^l|^2} + \underset{l}{S} \frac{G\left(\dfrac{|\mathbf{r}^l - \mathbf{r}|}{2\eta^{\frac{1}{2}}}\right)}{|\mathbf{r}^l - \mathbf{r}|} - \frac{4\pi\eta}{\Delta}. \qquad \dots\dots(742)$$

By a suitable choice of η the function ψ is thus divided into two parts, each of which is readily calculable. In practice one or two different values of η are chosen, and from the resulting values of ψ the actual value can be inferred to a high degree of accuracy.

In calculating the potential at a lattice point k, the term $\epsilon_k/(\mathbf{r} - \mathbf{r}_k)$ must be omitted from the summation, and so we have

$$\phi_k = \sum_{k'}{}' \epsilon_{k'} \psi(\mathbf{r}_k - \mathbf{r}_{k'}) + \epsilon_k \psi^*(0), \qquad \dots\dots(743)$$

where

$$\psi^*(0) = \underset{r=0}{\mathrm{Lt}} \left\{ \psi(\mathbf{r}) - \frac{1}{r} \right\}, \qquad \dots\dots(744)$$

and this can be shown to be

$$\psi^* (0) = \frac{4\pi}{\Delta} \underset{l}{S'} \frac{e^{-\eta |\mathbf{q}^l|^2}}{|\mathbf{q}^l|^2} + \underset{l}{S'} \frac{G\left(\frac{|\mathbf{r}^l|}{2\eta^{\frac{1}{2}}}\right)}{|\mathbf{r}^l|} - \frac{1}{\sqrt{(\pi\eta)}} - \frac{4\pi\eta}{\Delta}. \quad \text{......(745)}$$

In this way Ewald has calculated the potential energy of cubic crystals like NaCl and CaF_2.

Modifications of the method have since been made by Born† and Emersleben‡ which considerably simplify the calculation of the potential energy of any crystal of the cubic type. The unit cell of the crystal is divided by three systems of equidistant planes parallel to the sides of the cell so that every charge ϵ_k is at one of these sub-lattice points. For simplicity we suppose the sub-cell to be of unit volume ($\Delta = n^3$), and we suppose the vectors of each sub-cell to be $\frac{1}{n}\mathbf{a}_1, \frac{1}{n}\mathbf{a}_2, \frac{1}{n}\mathbf{a}_3$. The periodicity of the charges throughout space is then expressed by

$$\epsilon_{k+ln} = \epsilon_k,$$

where ϵ_k denotes the charge at the point $k_1\mathbf{a}_1/n,\ k_2\mathbf{a}_2/n,\ k_3\mathbf{a}_3/n$. The charge density ρ, consisting as it does of discrete charges arranged at the sub-lattice points, is expressible as a finite Fourier expansion

$$\rho = \underset{l}{S^*} \rho_l \, e^{i(\mathbf{q}^l \cdot \mathbf{r})}, \quad \text{......(746)}$$

where S^* denotes a finite summation over all integral values of l from 0 to $n - 1$ (or 1 to n), and

$$\mathbf{q}^l = 2\pi\left(\frac{l_1\mathbf{i}}{a_1} + \frac{l_2\mathbf{j}}{a_2} + \frac{l_3\mathbf{k}}{a_3}\right).$$

There are n^3 constants ρ_l to determine, but since ρ is known at n^3 points, there are just enough conditions to determine them. We have, in fact,

$$\rho_l = \frac{1}{n^3} \sum_k \epsilon_k e^{-i(\mathbf{q}^l \cdot \mathbf{r}_k)},$$

$$= \frac{1}{n^3} \sum_k \epsilon_k e^{-\frac{2\pi i}{n}(lk)}, \quad \text{......(747)}$$

where k, like l, is an integer and

$$(lk) = l_1k_1 + l_2k_2 + l_3k_3. \quad \text{......(748)}$$

We can therefore write

$$\epsilon_k = \underset{l}{S^*} \rho_l \, e^{\frac{2\pi i}{n}(lk)},$$

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† Born, *Zeit. für Phys.* vol. VII, p. 124 (1921).

‡ Emersleben, *Phys. Zeit.* vol. XXIV, pp. 73 and 97 (1923).

and substituting this expansion for ϵ_k in (743), we find

$$\phi_k = \underset{l}{S^*} \rho_l \, e^{\frac{2\pi i}{n}(lk)} \, \Pi\left(\frac{l}{n}\right), \qquad \text{......(749)}$$

where

$$\Pi\left(\frac{l}{n}\right) = \psi^*(0) + \underset{k}{\Sigma'} e^{\frac{2\pi i}{n}(lk)} \, \psi(\mathbf{r}_k). \qquad \text{......(750)}$$

The function $\Pi(l/n)$, thus defined in terms of Ewald's functions, determines the potential at any sub-lattice point k. It is clear that

$$\Pi(z+1) = \Pi(z), \quad \Pi(-z) = \Pi(z), \qquad \text{......(751)}$$

and so when $\Pi(l/n)$ is plotted for values of l between the limits 0 and $n-1$ $(0 \leqslant l_1, l_2, l_3 \leqslant n-1)$, the main problem in the evaluation of ϕ_k is solved. Emersleben has given a table of values for $\Pi(l/n)$ for all the sub-lattice points of a cubic cell for which $n = 12$.

The potential energy of a whole cell is easily deduced, since

$$\phi_0^{(e)} = \sum_{k=0}^{n-1} \epsilon_k \phi_k. \qquad \text{......(752)}$$

When the smallest coordinate distance between the ions is a, the potential energy can be calculated in the following way: the potential energy is

$$\phi_0^{(e)} = \frac{\epsilon^2}{a} \underset{l}{S^*} \xi_l \Pi\left(\frac{l}{n}\right), \qquad \text{......(753)}$$

a summation over a cube of side na, l being a vector $(l_1 a, \; l_2 a, \; l_3 a)$, ξ_l being connected with the distribution of charges (ϵ_k) in the cell by the relations

$$n^3 \epsilon^2 \xi_l = A^2 + B^2,$$

$$A\left(\frac{l}{n}\right) = \sum_k \epsilon_k \cos 2\pi \left(\frac{lk}{n}\right),$$

$$B\left(\frac{l}{n}\right) = \sum_k \epsilon_k \sin 2\pi \left(\frac{lk}{n}\right). \qquad \text{......(754)}$$

Emersleben has applied his work to the calculation of ϕ_0 for several types of crystals. The main results are summarized in the annexed table. We propose to write, for brevity,

$$\mathfrak{s} = \underset{l}{S^*} \xi_l \, \Pi\left(\frac{l}{n}\right), \qquad \text{......(755)}$$

so that

$$\phi_0^{(e)} = \frac{\epsilon^2}{a} \mathfrak{s}, \qquad \text{......(756)}$$

with a equal to the smallest *coordinate* distance between two ions. The mutual potential energy of N cells is then

$$\Phi^{(e)} = \tfrac{1}{2} N \phi_0^{(e)} = \tfrac{1}{2} \frac{N\epsilon^2}{a} \mathfrak{s}. \qquad \text{......(757)}$$

TABLE 24.

Values of $\mathfrak{S}$ for various types of crystal.

NaCl	MgO	ZnS	CaF_2	CsCl	Cu_2O
$-\ 3{\cdot}495{,}11^{7}_{3}$	$-\ 13{\cdot}980{,}4^{66}_{56}$	$-\ 7{\cdot}565{,}8^{7}_{1}$	$-\ 5{\cdot}818{,}^{31}_{25}$	$-\ 2{\cdot}035{,}3^{66}_{46}$	$-\ 4{\cdot}752{,}^{22}_{16}$

§ **10·62**. *The potential energy $\phi^{(n)}$ due to the intrinsic repulsive fields.* If we suppose that an ion situated at $\mathbf{r}_k{}^l$ repels an ion at $\mathbf{r}_{k'}$ in the basic cell according to the law

$$f(\mathbf{r}_k{}^l - \mathbf{r}_{k'}) = \frac{\lambda_{k,k'}}{(r_{k,k'}{}^l)^{n_{k,k'}}}, \qquad \text{......(758)}$$

then the contribution to the potential energy $\phi^{(n)}$ of a cell due to these pairs of ions throughout the crystal is given by

$$\phi_{k,k'}{}^{(n)} = \underset{l}{S} \frac{\lambda_{k,k'}}{(n_{k,k'} - 1)\,(r_{k,k'}{}^l)^{n_{k,k'}-1}}, \qquad \phi_{k,k'}{}^{(n)} = \phi_{k',k}{}^{(n)}, \quad \text{......(759)}$$

the summation being a triple one over all values of l. For large values of n, these summations can be calculated with reasonable accuracy by direct summation, since the series rapidly converge. The method is not elegant and leaves undetermined the error involved in neglecting the remainder. More powerful methods have been devised of dealing with these functions for values of $n > 4$ by showing that they can be expressed in terms of Epstein's* generalized zeta-functions†. Emersleben has transformed these zeta-functions in a way analogous to Ewald's transformation of the electrostatic function, considered above, but has not actually made any numerical applications of his method. Recently, the problem has been reconsidered‡, and a method developed analogous in principle to the use of the Euler-Maclaurin sum formula for the Riemann zeta-function. The method has been used to make numerical evaluations of the functions, appropriate to the three cubic structures, *simple*, *body-centred* and *face-centred*.

For the simple cubic, we have $k = 1$ and

$$\phi^{(n)} = \frac{\lambda A_{n-1}}{(n-1)\,a^{n-1}}, \qquad \text{......(760)}$$

where a is the closest distance between two atoms and

$$A_s = \underset{l}{S'}\,(l_1{}^2 + l_2{}^2 + l_3{}^2)^{-\frac{1}{2}s}. \qquad \text{......(761)}$$

Obviously A_s is a function of s only, and so is a constant for a given law of force and may conveniently be called a *crystal potential constant.*

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[*] Epstein, *Math. Ann.* vol. LVI, pp. 615–644 (1903); vol. LXIII, pp. 205–216 (1907).

[†] Emersleben, *Phys. Zeit.* vol. XXIV, p. 73 (1923).

[‡] Lennard-Jones and Ingham, *Proc. Roy. Soc.* A, vol. CVII, p. 636 (1925).

For a body-centred cubic ($k = 1, 2$),

$$\phi^{(n)} = \phi_{11}{}^{(n)} + \phi_{12}{}^{(n)},$$

$$= \mathop{S'}_{l} \frac{\lambda_{11}}{(n_{11} - 1)\,(r_{11}{}^{l})^{n_{11}-1}} + \mathop{S}_{l} \frac{\lambda_{12}}{(n_{12} - 1)\,(r_{12}{}^{l})^{n_{12}-1}},$$

$$= \frac{\lambda_{11} A_{n_{11}-1}}{(n_{11} - 1)\, r_0{}^{n_{11}-1}} + \frac{\lambda_{12} B'_{n_{12}-1}}{(n_{12} - 1)\, r_0{}^{n_{12}-1}}, \qquad \text{......(762)}$$

where r_0 is the length of the edge of the unit cube and

$$B_s' = \mathop{S}_{l} \{(l_1 + \tfrac{1}{2})^2 + (l_2 + \tfrac{1}{2})^2 + (l_3 + \tfrac{1}{2})^2\}^{-\frac{1}{2}s}. \qquad \text{......(763)}$$

For a body-centred cubic crystal consisting of ions of only one kind so that $\lambda_{11} = \lambda_{12}$, $n_{11} = n_{12}$, we have

$$\phi^{(n)} = \frac{\lambda B_{n-1}}{(n - 1)\, a^{n-1}}, \qquad \text{......(764)}$$

with

$$B_s = \left(\frac{a}{r_0}\right)^s A_s + \left(\frac{a}{r_0}\right)^s B_s' = \left(\frac{\sqrt{3}}{2}\right)^s (A_s + B_s'), \qquad \text{......(765)}$$

where we have used a to denote the closest distance between atoms.

For a face-centred cubic,

$$\phi^{(n)} = \frac{\lambda C_{n-1}}{(n - 1)\, a^{n-1}}, \qquad \text{......(766)}$$

where

$$C_s = \left(\frac{a}{r_0}\right)^s \mathop{S'}_{l} \{(l_2 + l_3)^2 + (l_3 + l_1)^2 + (l_1 + l_2)^2\}^{-\frac{1}{2}s}, \qquad \text{......(767)}$$

and r_0 is the smallest coordinate distance between atoms, and a the closest distance between atoms. For two interpenetrating face-centred cubics, as in NaCl, we have

$$\phi^{(n)} = \frac{\lambda_{11} A''_{n_{11}-1}}{(n_{11} - 1)\, a^{n_{11}-1}} + \frac{2\lambda_{12} A'_{n_{12}-1}}{(n_{12} - 1)\, a^{n_{12}-1}} + \frac{\lambda_{22} A''_{n_{22}-1}}{(n_{22} - 1)\, a^{n_{22}-1}}, \qquad \text{......(768)}$$

with

$$A_s' = \mathop{S}_{\substack{l_1 + l_2 + l_3 \\ \text{odd}}} (l_1{}^2 + l_2{}^2 + l_3{}^2)^{-\frac{1}{2}s}, \qquad \text{......(769)}$$

$$A_s'' = \mathop{S'}_{\substack{l_1 + l_2 + l_3 \\ \text{even}}} (l_1{}^2 + l_2{}^2 + l_3{}^2)^{-\frac{1}{2}s}, \qquad \text{......(770)}$$

the summations being over all values of l_1, l_2 and l_3, for which $l_1 + l_2 + l_3$ are respectively odd and even. Clearly $A_s = A_s' + A_s''$.

The functions A_s', A_s'', B_s and C_s have been evaluated for integral values from $s = 4$ to $s = 30$. A few values are given in Table 25.

With the help of this table it has been shown that atoms, whose field can be represented by the law $\lambda r^{-n} - \mu r^{-m}$, will set in the form of a face-centred cubic lattice in preference to a body-centred, and in a body-centred in preference to a simple cubic*.

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* Lennard-Jones and Ingham, *loc. cit.* p. 641.

TABLE 25.

Potential constants for cubic crystals.

s	A_s	A'_s	A''_s	B_s	C_s
4	$16{\cdot}5323^{28}_{14}$	$10{\cdot}1977^{53}_{36}$	$6{\cdot}33457^{8}_{5}$	$22{\cdot}638723^{3}_{0}$	$25{\cdot}338309^{9}_{2}$
5	$10{\cdot}3775^{32}_{23}$	$7{\cdot}3780^{71}_{60}$	$2{\cdot}99946^{3}_{1}$	$14{\cdot}7585^{13}_{07}$	$16{\cdot}9675^{23}_{16}$
6	$8{\cdot}40192^{7}_{3}$	$6{\cdot}59518^{7}_{2}$	$1{\cdot}806740$	$12{\cdot}2533^{70}_{66}$	$14{\cdot}4539^{23}_{19}$
7	$7{\cdot}4670^{61}_{56}$	$6{\cdot}28624^{7}_{1}$	$1{\cdot}18081^{5}_{3}$	$11{\cdot}05424^{6}_{1}$	$13{\cdot}3593^{90}_{86}$
8	$6{\cdot}94580^{9}_{7}$	$6{\cdot}14568^{9}_{6}$	$0{\cdot}800121$	$10{\cdot}355^{200}_{196}$	$12{\cdot}80193^{9}_{6}$
9	$6{\cdot}6288^{61}_{57}$	$6{\cdot}0767^{64}_{59}$	$0{\cdot}55209^{9}_{7}$	$9{\cdot}8945^{92}_{88}$	$12{\cdot}49254^{9}_{5}$
10	$6{\cdot}4261^{20}_{18}$	$6{\cdot}04139^{4}_{2}$	$0{\cdot}38472^{7}_{6}$	$9{\cdot}564^{403}_{399}$	$12{\cdot}31124^{8}_{4}$
11	$6{\cdot}29229^{7}_{2}$	$6{\cdot}0226^{93}_{87}$	$0{\cdot}26960^{6}_{4}$	$9{\cdot}31326^{5}_{1}$	$12{\cdot}2009^{23}_{18}$
12	$6{\cdot}2021^{50}_{48}$	$6{\cdot}0125^{90}_{87}$	$0{\cdot}18956^{1}_{0}$	$9{\cdot}11418^{5}_{1}$	$12{\cdot}1318^{82}_{78}$

§ **10·7**. *Theoretical calculation of interatomic distances in crystals and the determination of ionic models.* In § 10·5 we obtained a series of possible intrinsic repulsive fields for neon-like and argon-like ions. Each of these possible fields leads to a different function for the potential energy of a cell (ϕ_0) of a crystal such as NaF. As we have just shown*,

$$\phi_0 = \phi^{(e)} + \phi^{(n)},$$

and for a crystal of the NaF type

$$\phi^{(e)} = -\frac{\epsilon^2\,(3{\cdot}495)\,z^2}{a},$$

$$\phi^{(n)} = \frac{\lambda_{11} A''_{n_{11}-1}}{(n_{11}-1)\,a^{n_{11}-1}} + \frac{2\lambda_{12} A'_{n_{12}-1}}{(n_{12}-1)\,a^{n_{12}-1}} + \frac{\lambda_{22} A''_{n_{22}-1}}{(n_{22}-1)\,a^{n_{22}-1}},$$

where z is the valency of the ions.

In NaF and KCl, where the ions are of the same type, that is, both neon-like and both argon-like respectively, $n_{11} = n_{12} = n_{22} = n$. The condition that the potential energy shall be a minimum is then

$$a^{n-2} = \frac{(\lambda_{11} + \lambda_{22})\,A''_{n-1} + 2\lambda_{12} A'_{n-1}}{(3{\cdot}495)\,\epsilon^2 z^2}, \qquad \ldots\ldots(771)$$

and so, for a series of force constants, as given in Table 23, we get a series of values of a. Some of the values so calculated for four crystals are given in the next table, with the observed values.

The two sets of results in each case point to the conclusion that neon-like ions repel according to the inverse 11th power and argon-like ions according to the inverse 9th power law. Moreover, these values of n are approximately the same as those obtained by Born from compressibility (Table 21, above).

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* We here neglect the potential energy due to the van der Waals attractive fields, which must exist even between the electronic systems of ions, since it has been shown that these latter forces in a crystal are small compared with the electrostatic forces (*Proc. Roy. Soc.* A, vol. CVI, p. 716 (1924)).

TABLE 26.

Calculated and observed interatomic distances in certain crystals.

n	∞	15	11	9	Obs.
NaF	2·56	2·41	**2·30**	2·20	2·310[*]
MgO	2·66	2·29	**2·10**	1·93	2·09[†]
KCl	3·32	3·32	3·24	**3·13**	3·138[*]
CaS	3·48	3·18	2·98	**2·77**	2·77[‡]

[*] Davey, *Phys. Rev.* vol. XXI, p. 143 (1923); W. H. Bragg and W. L. Bragg, *X-rays and Crystal Structure*, 4th ed. p. 306 (1924).

[†] Wyckoff, *Amer. J. Sci.* ser. 5, vol. CCI, p. 138 (1921); W. H. Bragg and W. L. Bragg, *loc. cit.* p. 300.

[‡] W. L. Bragg, *Phil. Mag.* vol. XL, p. 181 (1920); W. H. Bragg and W. L. Bragg (*loc. cit.* p. 166) give a value 2·82.

The success of this method encourages us to adopt a similar procedure in the cases of krypton-like and xenon-like ions, though modifications are necessary owing to the lack of information about the properties of gaseous krypton and xenon. The index of their repulsive fields can be determined from the compressibilities of the crystals RbBr and CsI, each of which consists of ions of only one type so that $n_{11} = n_{12} = n_{22} = n$. Taking, for instance, the experimental value of $8{\cdot}2 \times 10^{-12}$ for the compressibility of RbBr, as given by Richards and Saerens[§], and the value 3·43 Å. as its crystal constant[||], the resulting value of n is 9·6, or if only integral values of n be considered, $n = 10$. The corresponding result for CsI is $n = 11{\cdot}005$, thus suggesting $n = 11$ as the repulsive index for the whole xenon group[¶].

If the repulsive force constant of the inert gas be denoted by $\lambda_n^{(0)}$, that of an ion of the same type is given by the relation (722) above,

$$\lambda_n^{+} = \left(\frac{\rho_+}{\rho_0}\right)^{n-1} \lambda_n^{(0)}.$$

Wasastjerna's ratios (ρ_+/ρ_0, etc.) are known for both the krypton and the xenon group, and the equation (771) for the interatomic distance involves one unknown only, viz. $\lambda_n^{(0)}$. Conversely, regarding the interatomic distance as known, this equation determines $\lambda_n^{(0)}$, and so that of all the related ions. The force constants for the inert gases prove to be

$$\text{Krypton} \quad \lambda_n = 7{\cdot}340 \times 10^{-80}, \quad n = 10,$$

$$\text{Xenon} \quad \lambda_n = 6{\cdot}214 \times 10^{-87}, \quad n = 11,$$

or, collecting the results for all the inert gases,

	Neon	Argon	Krypton	Xenon
$n =$	11	9	10	11

[§] Richards and Saerens, *Jour. Amer. Chem. Soc.* vol. XLVI, p. 934 (1924).

[||] Davey, *Phys. Rev.* (2) vol. XXI, p. 143 (1923), gives 3·418 Å. and Spangenberg, *Zeit. für Kryst.* vol. LVII, sect. 5 (1923), gives 3·440 Å.

[¶] Lennard-Jones *Proc. Roy. Soc.* A, vol. CIX, p. 584 (1925).

These laws of force are held to be true also of ions of the same electronic structure. Those of ions of different structure are obtained from the above by interpolation, leading to the following scheme.

TABLE 27.

The laws of force of atoms and ions (the values of n in λr^{-n}).

	Neon group	Argon group	Krypton group	Xenon group
Neon group	11	10	10	11
Argon group	10	9	9	10
Krypton group	10	9	10	10
Xenon group	11	10	10	11

Moreover, methods have been devised of evaluating the force constants in the interaction of *unlike* ions*, leading to a complete table of forces between the monovalent and divalent ions of the inert gas type as well as between the inert gases themselves (Table 28).

The force constants are given in units that give the force in dynes when the unit of length is the Ångström. The table is to be used in conjunction with Table 27. For example, to find the force between Na^+ and Cl^-, we note that $\lambda = 2{\cdot}12$ and $n = 10$, so that when they are at a distance of 2 Å. apart, the force is $2{\cdot}12 \times 2^{-10}$ dynes, that is, 0·002 dynes.

§ **10·81**. *Applications of the force constants.* (1) *Calculation of interatomic distances.* The force constants just derived can be applied to the calculation of a number of crystal properties, and a comparison of the results with observation forms an immediate check. Thus the whole set of 16 alkali halogen crystals as well as the corresponding 16 divalent crystals can be considered. The appropriate formula for the interatomic distance is an obvious generalization of equation (771). It is solved for a by writing it in the form

$$(3{\cdot}495)\quad \epsilon^2 z^2 a^{n_{12}-2} = 2A'_{n_{12}-1}\lambda_{12} + A''_{n_{11}-1}\lambda_{11}\, a^{n_{12}-n_{11}} + A''_{n_{22}-1}\lambda_{22} a^{n_{12}-n_{22}},$$

and calculating a first approximation by neglecting the second and third terms on the right-hand side. This result is then used to make further approximations. These converge very rapidly, the difference between the second and third being only in the third decimal place.

Four of the alkaline halogens RbF, CsCl, CsBr and CsI, however, set at room temperature in the form of body-centred cubics (the β form) for a reason not perfectly understood. (This has, in fact, been the subject of independent investigations†.) The form of the crystals is here asumed to

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* Lennard-Jones and Dent, *Proc. Roy. Soc.* A, vol. CXII, p. 230 (1926).

† Emersleben, *Diss. Göttingen* (1922); Brody, *Verh. der Deutsch. Phys. Ges.* vol. XXIV, p. 96 (1922).

Table 28.

The force constants of atoms and ions.

	O^{--}	F^-	Ne	Na^+	Mg^{++}	S^{--}	Cl^-	Ar	K^+	Ca^{++}	Se^{--}	Br^-	Kr	Rb^+	Sr^{++}	Te^{--}	I^-	X	Cs^+	Ba^{++}
O^{--}	17·6	8·42	3·30	2·55	1·51	21·0	10·4	4·37	2·94	2·07	18·9	12·9	6·03	4·11	3·04	79·8	73·4	33·8	22·1	14·9
F^-	8·42	3·81	1·38	1·04	0·58$_6$	11·9	5·64	2·23	1·45	1·00	10·7	7·14	3·15	2·09	1·51	42·5	38·9	17·0	10·8	7·07
Ne	3·30	1·38	0·44$_5$	0·32$_3$	0·17	5·91	2·62	0·95	0·59$_1$	0·38$_9$	5·25	3·38	1·39	0·88$_1$	0·61$_6$	19·3	17·5	7·13	4·34	2·73
Na^+	2·55	1·04	0·32$_3$	0·23$_2$	0·12	4·87	2·12	0·74$_8$	0·46	0·29$_9$	4·31	2·75	1·10	0·69$_4$	0·48	15·5	14·1	5·60	3·37	2·09
Mg^{++}	1·51	0·58$_6$	0·17	0·12	0·05$_8$	3·31	1·39	0·46$_4$	0·27$_8$	0·17$_6$	2·92	1·82	0·70	0·42$_8$	0·29$_1$	10·1	9·10	3·46	2·03	1·23
S^{--}	21·0	11·9	5·91	4·87	3·31	13·7	8·00	4·13	3·06	2·36	12·7	9·47	5·29	3·96	3·15	67·9	63·8	34·8	25·1	18·6
Cl^-	10·4	5·64	2·62	2·12	1·39	8·00	4·49	2·20	1·59	1·19	7·34	5·38	2·87	2·10	1·64	36·7	34·3	17·9	12·6	9·10
Ar	4·37	2·23	0·95	0·74$_8$	0·46$_4$	4·13	2·20	1·00	0·70$_1$	0·51$_2$	3·76	2·68	1·35	0·95$_5$	0·72$_6$	17·4	16·2	7·97	5·42	3·78
K^+	2·94	1·45	0·59$_1$	0·46	0·27$_8$	3·06	1·59	0·70$_1$	0·48$_1$	0·34$_6$	2·78	1·95	0·95$_5$	0·66$_4$	0·50	12·4	11·5	5·50	3·68	2·53
Ca^{++}	2·07	1·00	0·38$_9$	0·29$_9$	0·17$_6$	2·36	1·19	0·51$_2$	0·34$_6$	0·24$_5$	2·13	1·48	0·70$_5$	0·48$_4$	0·35$_9$	9·22	8·52	3·97	2·62	1·77
Se^{--}	18·9	10·7	5·25	4·31	2·92	12·7	7·34	3·76	2·78	2·13	60·4	43·4	22·3	16·0	12·4	62·0	58·2	31·6	22·7	16·7
Br^-	12·9	7·14	3·38	2·75	1·82	9·47	5·38	2·68	1·95	1·48	43·4	30·7	15·4	10·9	8·33	44·5	41·7	22·1	15·7	11·4
Kr	6·03	3·15	1·39	1·10	0·70	5·29	2·87	1·35	0·95$_5$	0·70$_5$	22·3	15·4	7·28	5·01	3·73	23·0	21·4	10·8	7·43	5·25
Rb^+	4·11	2·09	0·88$_1$	0·69$_4$	0·42$_8$	3·96	2·10	0·95$_5$	0·66$_4$	0·48$_4$	16·0	10·9	5·01	3·38	2·49	16·5	15·3	7·52	5·11	3·55
Sr^{++}	3·04	1·51	0·61$_6$	0·48	0·29$_1$	3·15	1·64	0·72$_6$	0·50	0·35$_9$	12·4	8·33	3·73	2·49	1·81	12·8	11·8	5·68	3·81	2·62
Te^{--}	79·8	42·5	19·3	15·5	10·1	67·9	36·7	17·4	12·4	9·22	62·0	44·5	23·0	16·5	12·8	297·0	276·0	140·3	97·3	69·4
I^-	73·4	38·9	17·5	14·1	9·10	63·8	34·3	16·2	11·5	8·52	58·2	41·7	21·4	15·3	11·8	276·0	256·5	129·7	89·7	63·7
X	33·8	17·0	7·13	5·60	3·46	34·8	17·9	7·97	5·50	3·97	31·6	22·1	10·8	7·52	5·68	140·3	129·7	62·4	41·9	29·0
Cs^+	22·1	10·8	4·34	3·37	2·03	25·1	12·6	5·42	3·68	2·62	22·7	15·7	7·43	5·11	3·81	97·3	89·7	41·9	27·7	18·9
Ba^{++}	14·9	7·07	2·73	2·09	1·23	18·6	9·10	3·78	2·53	1·77	16·7	11·4	5·25	3·55	2·62	69·4	63·7	29·0	18·9	12·6

be that determined by observation. The formula corresponding to (771) is deduced from equations (756) and (762) to be

$$(4{\cdot}070)\ \epsilon^2 a^{n_{12}-2} = 2\lambda_{12}\left[\frac{2^{n-1}}{3^{(n-1)/2}}B_{n-1} - A_{n-1}\right] + \lambda_{11}A_{n_{11}-1}a^{n_{12}-n_{11}} + \lambda_{22}A_{n_{22}-1}\,a^{n_{12}-n_{22}}, \quad \ldots\ldots(772)$$

the appropriate value of $\mathfrak{s}$ being 2·035 (Table 24).

Using the force constants and indices given in Tables 27 and 28, we find the following values for the crystal constants:

TABLE 29.

Calculated and observed interatomic distances in crystals.*

$a \,.\, 10^8$	F		Cl		Br		I	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
Na	2·30	2·31	2·85	2·81	2·99	2·97	3·19	3·23
K	2·63	$2{\cdot}66_5$	3·13	3·14	3·24	$3{\cdot}28_5$	3·47	$3{\cdot}52_5$
Rb	3·37†	3·66	3·24	3·27	3·43	3·42	3·58	$3{\cdot}65_5$
Cs	2·97	3·00	4·21†	$\begin{Bmatrix}4{\cdot}12\\4{\cdot}30\end{Bmatrix}$	4·34†	4·29	4·56†	$4{\cdot}55_8$

† Crystals of the β form.

§ **10·82**. (2) *Calculation of compressibilities.* The compressibilities of the same crystals can also be calculated. By (718), for face-centred cubic crystals

$$\frac{1}{\kappa} = \frac{1}{36}\left\{\frac{(n_{11}-n_{12})\,\lambda_{11}A''_{n_{11}-1}}{a^{n_{11}+2}} + \frac{(n_{22}-n_{12})\,\lambda_{22}A''_{n_{22}-1}}{a^{n_{22}+2}} + \frac{(n_{12}-2)\,(3{\cdot}495)\,\epsilon^2 z^2}{a^4}\right\}, \quad \ldots\ldots(773)$$

while for body-centred cubics, using (756) and (762),

$$\frac{1}{\kappa} = \frac{1}{18}\left\{\frac{(n_{11}-n_{12})\,\lambda_{11}A_{n_{11}-1}}{a^{n_{11}+2}} + \frac{(n_{22}-n_{12})\,\lambda_{22}A_{n_{22}-1}}{a^{n_{22}+2}} + \frac{(n_{12}-2)\,(2{\cdot}035)\,2\epsilon^2 z^2}{a^4}\right\}. \quad \ldots\ldots(774)$$

The values of a to be used in the formulae are the calculated ones given in the above table, for, in obtaining the expression for the compressibility κ, the relation $\frac{\partial\phi}{\partial a} = 0$ is used, and this is the equation to determine a. This procedure is therefore the logical one to take, and the values of the

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* The observed values are taken from W. H. and W. L. Bragg, *loc. cit.* p. 306 (1924); cf. also Mauguin, *La Structure des Cristaux*, p. 224 (1924). The unusual difference between calculated and measured values for RbF is surprising. The experimental value is that of Davey (*Phys. Rev.* (2) vol. XXI, p. 149 (1923)). It is to be noted that Spangenberg (*Zeit. für Kryst.* vol. LVII, Heft 5 (1923)) estimates the density of RbF to be 3·740, from which it follows that the edge of the unit cube is 3·49 Å.; by another method he estimates the distance between Rb and F ions to be 2·846 Å., leading to a value of 3·28 Å. for the edge of the unit cube.

compressibility so obtained are a direct consequence of the force constants given in Table 28.

TABLE 30.

Calculated and observed compressibilities of crystals.

$\kappa . 10^{12}$	F			Cl			Br			I		
	Calc.	Obs.*	Obs.†	Calc.	Obs.*	Obs.†	Calc.	Obs.*	Obs.†	Calc.	Obs.*	Obs.†
Na	1·40	—	—	3·88	4·20	4·3	4·51	5·08	5·3	5·18	—	7·1
K	2·73	—	—	6·23	5·63	5·2	7·92	6·70	6·4	8·17	8·54	8·8
Rb	3·10	—	—	8·10	—	7·3	7·72	7·94	8·2	9·26	9·58	9·3
Cs	4·90	—	—	7·71	—	5·9	8·58	—	7·0	9·31	—	9·3

* Slater, *Phys. Rev.* (2) vol. XXIII, p. 488 (1924).

† Richard and Saerens, *Jour. Amer. Chem. Soc.* vol. XLVI, p. 934 (1924).

A high degree of accuracy in the calculated values cannot be expected, as the value of κ depends very closely on that of n_{12}; in fact, $\kappa\ (n_{12} - 2)$ is very nearly constant, and so integral values of n_{12} cannot give κ exactly. A change in n_{12} from 9 to 10 decreases κ by about 12 per cent. The agreement between theory and experiment may therefore be regarded as satisfactory.

§ **10·83**. (3) *Elastic constants*. Born‡ has given general formulae for the elastic constants, as for other properties of a crystal, in terms of the forces between the various constituent particles. He has used them to make numerical calculations of the elastic constants of NaCl crystals on the assumption that $n_{11} = n_{22} = n_{12} = 10$, and that $\lambda_{11} = \lambda_{22} = \lambda_{12}$.§ In a later paper‖ his work has been generalized slightly, but the assumption is still made that $n_{11} = n_{22} = n_{12}$.

The number of independent elastic constants in a crystal of the rock-salt type reduces to two, so that the compressibility having been calculated, only one other need be considered, say Young's modulus, the ratio of stress to strain in the direction of a cubic axis. In the notation of §§ 4·9, 4·91 this can be shown to be

$$c_{11} = \frac{1}{2\Delta} \sum_{k,k'} \underset{l}{S} \left[\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{d\phi_{k,k'}}{dr}\right)\right]_{r^l_{k,k'}} (x^l_{k,k'})^4 \ (k, k' = 1, 2) \ldots\ldots (775)$$

It is thus easy to obtain c_{11} in terms of the force constants¶. The formula is, however, found to be very sensitive to changes in λ, n and a, and great accuracy cannot be expected with integral values of n. A change in n by one integer may change c_{11} by 20 or 30 per cent.

‡ Born, *Atomtheorie des festen Zustandes* (1923).

§ Born, *Ann. der Phys.* vol. LXI, p. 87 (1919).

‖ Born and Brody, *Zeit. für Phys.* vol. XI, p. 327 (1922).

¶ Lennard-Jones and Taylor, *Proc. Roy. Soc.* A, vol. CIX, p. 492 (1925).

The following values have been calculated:

	NaF	NaCl	KF	KCl	MgO	MgS	CaO	CaS
$c_{11} \cdot 10^{-11}$	13·60	3·60	6·71	2·37	64·8	16·11	42·70	13·02

The only two observations with which they can be compared are those of NaCl and KCl by Voigt*, who finds

$$\text{NaCl} \quad c_{11} = 4{\cdot}68 \times 10^{11},$$

$$\text{KCl} \quad c_{11} = 3{\cdot}68 \times 10^{11}.$$

The reverse process of obtaining information about interatomic forces from the elastic constants seems promising if the latter could be measured with sufficient accuracy for a number of crystals, particularly at low temperatures.

§ **10·84**. *Crystal energies.* A further application of the force constants can be made to calculate the work required to separate to infinite dispersion all the ions contained in one gram molecule of the salt. In terms of ϕ, it is given by

$$U = -\tfrac{1}{2} N \phi \text{ in mechanical units,}$$

$$= -\frac{N}{2J} \phi \text{ in thermal units.}$$

For the face-centred cubic, we thus find

$$U = \frac{N}{2J} \left\{ \frac{(3{\cdot}495)\, \epsilon^2 z^2}{a} - \frac{\lambda_{11} A''_{n_{11}-1}}{(n_{11}-1)\, a^{n_{11}-1}} - \frac{\lambda_{22} A''_{n_{22}-1}}{(n_{22}-1)\, a^{n_{22}-1}} - \frac{2\lambda_{12} A'_{n_{12}-1}}{(n_{12}-1)\, a^{n_{12}-1}} \right\}, \quad \ldots\ldots(776)$$

and for the body-centred cubic

$$U = \frac{N}{J} \left\{ \frac{(2{\cdot}035)\, \epsilon^2 z^2}{a} - \frac{\lambda_{11} A_{n_{11}-1}}{2\,(n_{11}-1)\, a^{n_{11}-1}} - \frac{\lambda_{22} A_{n_{22}-1}}{2\,(n_{22}-1)\, a^{n_{22}-1}} \right.$$
$$\left. - \frac{\lambda_{12}}{(n_{12}-1)\, a^{n_{12}-1}} \left(\frac{2^{n-1}}{3^{(n-1)/2}} B_{n-1} - A_{n-1} \right) \right\}. \quad \ldots\ldots(777)$$

The calculated values, given in Table 31, may be compared with the values deduced from observed heats of formation and other chemical quantities by a method due to Born† described in § 10·9.

The values of the surface energy and edge energy of several crystals have also been calculated‡, thus providing quantitative information of crystal properties which have not been observed. The surface energy is defined as being the mutual potential energy of the parts of a crystal

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[*] Voigt, *Lehrbuch der Kristallphysik*, § 373, p. 744; Born, *Atomtheorie des festen Zustandes*, p. 739.

[†] Born, *Verh. des Deutsch. Phys. Ges.* vol. XXI, p. 679 (1919).

[‡] Lennard-Jones and Taylor, *Proc. Roy. Soc.* A, vol. CIX, p. 495 (1925).

separated by a plane, divided by twice the area of the bounding plane. Thus

$$\sigma = -\frac{\Phi_{12}}{2F}.$$

A few results for the (100) plane are appended.

TABLE 31.

Calculated and observed crystal energies in 1000 *calories* (*kilo-calories*) *per gram molecule.*

	F		Cl		Br		I	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
Na	226	—	179	181	172	176	163	166
K	195	—	161	163	156	160	148	151
Rb	177	—	156	159	150	157	143	148
Cs	175	—	142	—	138	—	132	—

TABLE 32.

Surface energies of certain salts (100 *plane, in ergs*).

σ_{100}	F	Cl
Na	304	96
K	180	76·6

The values of σ_{110} corresponding to the (110) plane have also been worked out, and it has been shown that $\sigma_{110}/\sigma_{100} > \sqrt{2}$, from which it follows that the net plane (110) does not form a natural face of the crystal. This is in accordance with observation.

§ **10·85**. *Crystals not of the rock-salt type.* The application of the force constants is not confined to crystals like NaCl. Another cubic ionic crystal of simple structure is CaF_2, in which the Ca^{++} ions are built up in the form of a face-centred cubic and the F^- ions interpenetrate on a simple cubic lattice. In this case a unit cell contains one metal ion and two halogen ions, so that

$$\phi = \phi^{(e)} + \phi^{(n)}_{\text{CaCa}} + 2\phi^{(n)}_{\text{FF}} + 2\phi^{(n)}_{\text{CaF}},$$

with an obvious notation. An explicit form for these functions can easily be found, using the crystal potential constants A, B and C. The condition that ϕ shall be a minimum leads to a value for the edge of the unit cube equal to 5·4 Å.* The observed value is 5·5 Å.† In the same way, the

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* Lennard-Jones and Taylor, *Proc. Roy. Soc.* A, vol. CIX, p. 489 (1925).

† W. H. and W. L. Bragg, *X-rays and Crystal Structure*, p. 168. Other observations range from 5·4 Å. to 5·5 Å.; cf. Mauguin, *La Structure des Cristaux*, p. 231 (1924).

crystal constant for $CaCl_2$ can be calculated, but this has not yet been observed.

Another class of crystals which has been considered is the series of carbonate crystals of the calcite type. These crystals have an interesting feature in that they all possess a rhombohedral angle of approximately the same magnitude. That of calcite is 101° 55′, while the rest range between this value and 103° 28′, the value for $ZnCO_3$. Bragg and Chapman* first proposed a theoretical explanation of this feature in terms of electrostatic forces, a special device being adopted to eliminate the intrinsic repulsive forces. This amounted to a neglect of the repulsive fields between the O^{--} ions of neighbouring CO_3 groups, an assumption which proves on further examination to be unjustified. If, however, the information about repulsive fields given earlier in this chapter is used, the special assumption mentioned above is unnecessary. The potential energy of the crystal can be calculated for all possible configurations (subject to the necessary conditions of symmetry), and its minimum determines the most stable arrangement. Considerations such as these lead to values for the size and shape of the rhombohedral cells of $MgCO_3$ and $CaCO_3$ in close agreement with observation, provided the size of the CO_3 group is regarded as an adjustable parameter. The indication is that the force centres of the O and C ions in CO_3 are 1·08 Å. apart†.

Topping and Chapman‡ have discussed $NaNO_3$, a crystal of the same structure as calcite, in the same way, and have shown that the size and shape of the unit cell are accounted for, provided the force centres of the O and N ions in NO_3^- are 0·96 Å. apart.

The results of these investigations are given in the following table, which also includes a theoretical estimate of the energy required to separate to infinite dispersion the metal ions and the CO_3 or NO_3 groups, a quantity not yet determined by any other method.

TABLE 33.

Calculated and observed values of crystal parameters.

(Distance C to O in CO_3 = 1·08 Å.; and N to O in NO_3 = 0·96 Å.)

	$MgCO_3$		$CaCO_3$		$NaNO_3$	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
Rhombohedral angle	102° 24′	103° 21·5′	102° 18′	101° 55′	102° 15′	102° 42·5′
Dist. between C or N ions	4·66	4·61	4·96	4·96	5·19	5·15
Crystal energy per gram-molecule (in kilo-cals.)	771	—	701	—	176	—

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* Bragg and Chapman, *Proc. Roy. Soc.* A, vol. CVI, p. 369 (1924); cf. also Chapman, Topping and Morrall, *Proc. Roy. Soc.* A, vol. CXI, p. 25 (1926).

† Lennard-Jones and Dent, *Proc. Roy. Soc.* A, vol. CXIII, p. 673 (1927).

‡ Topping and Chapman, *Proc. Roy. Soc.* A, vol. CXIII, p. 658 (1927).

In a later investigation of the other carbonates, $ZnCO_3$, $FeCO_3$, $MnCO_3$ and $CdCO_3$, methods have been given of determining the forces between the divalent positive ions of Zn, Fe, Mn and Cd and the divalent negative ion of O*.

A crystal of a different type which can be considered theoretically is crystalline argon, in which the forces of attraction are not of the Coulomb type but are of the van der Waals type. Recent observations† have shown that this is a face-centred cubic lattice, in which the shortest distance between atomic centres is 3·84 Å. For a law of force $\lambda r^{-n} - \mu r^{-m}$, the potential of one atom of a face-centred cubic lattice due to the rest is

$$\phi = \frac{\lambda C_{n-1}}{(n-1)\,a^{n-1}} - \frac{\mu C_{m-1}}{(m-1)\,a^{m-1}},$$

where a is the closest distance between atoms and C_s has been given above. The theoretical value of a is therefore

$$a = \left(\frac{\lambda C_{n-1}}{\mu C_{m-1}}\right)^{1/(n-m)}.$$

The work described above has suggested that argon atoms repel according to an inverse 9th power law. Corresponding to a repulsion of this type, we found (§ 10·3 above) an attraction μr^{-5} with $\mu = 1{\cdot}625 \,.\, 10^{-43}$. For this model the value $a = 4{\cdot}21$ Å. is obtained, a result which is 10 per cent. greater than the observed value. Various suggestions can be made to account for this discrepancy‡. It is likely that a repulsive force of the type considered can only represent actual fields over a small range, so that while λr^{-9} is a sufficiently good representation of the repulsive field of an argon-like core at distances of about 3 Å.(as in KCl, CaS), at greater distances (such as 3·84 Å. in crystalline argon) a different law of force is necessary. It appears that if n is taken to be 15 (and $m = 5$) the calculated value of a is 3·86 Å., in excellent agreement with observation. Moreover, the calculated heat of evaporation for the same law of force is 1772 cals., while the value deduced from observation is about 1835 cals.§, which is as good an agreement as can be hoped for from integral values of n and m.

§ **10·9**. *Crystal energies. The Born cycle.* There is no direct method of measuring the crystal energies calculated in the previous paragraph, but Born‖ has shown how they can be related to observable thermo-chemical

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* Lennard-Jones and Dent, *Proc. Roy. Soc.* A, vol. CXIII, p. 690 (1927). Cf. also Born and Bollnow, *Naturwiss.* vol. XIII, p. 559 (1925), Bollnow, *Zeit. für Phys.* vol. XXXIII, p. 741 (1925), Lennard-Jones and Dent, *Phil. Mag.* vol. III, p. 1204 (1927), where another group of crystals of the same type (the rutile group) has been considered.

† Simon und Simson, *Zeit. für Phys.* vol. XXI, p. 168 (1924); vol. XXV, p. 160 (1924).

‡ Lennard-Jones and Taylor, *Proc. Roy. Soc.* A, vol. CIX, p. 506 (1925).

§ F. Born, *Ann. der Phys.* vol. LXIX, p. 473 (1922).

‖ Born, *Verh. der Deutsch. Phys. Ges.* vol. XXI, pp. 13, 679 (1919).

quantities. The relations between these quantities are best expressed by a diagram such as that of Fig. 18, first given by Haber*.

In this figure $[M]$ denotes one gram atom of solid metal, (X_2) one gram molecule of gaseous halogen. Beginning with a state 1 in which there is $[M] + \frac{1}{2}(X_2)$, we pass successively to states 2, 3 and 4, in which there is 1 gram molecule of the salt, 1 gram atom each of the ionized metallic vapour and the ionic halogen X^-, and then 1 gram atom each of metallic vapour and atomic halogen respectively. From this state we pass back to the original state, so that on the whole the change of energy is zero. To this simple cycle (the Born cycle) two other subsidiary cycles have been added, that indicated by 5 by Haber† and that indicated by 6 by Fajans‡.

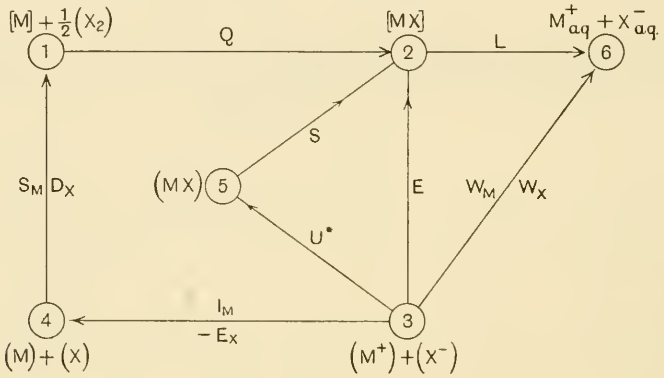

Fig. 18. The Born cycle.

Heat is given out in the processes indicated by the direction of the arrow in the figure and is then regarded (conventionally) as positive. In the first transformation Q denotes the heat of formation of the salt, in the second E denotes the crystal energy as already considered above. I_M is the work of ionization of 1 gram atom of metal, and E_X is the heat of formation of an halogen ion from the atom and electron (otherwise, the electron affinity). S_M is the heat of evaporation of 1 gram atom of metal and D_X the heat of dissociation of the diatomic halogen. We have then the relation

$$E = Q + (I_M + S_M) + (D_X - E_X), \qquad \text{......(778)}$$

and all the quantities on the right have been measured. These are summarized in the annexed table. The values of Q are given by Landolt-Börnstein, those of I are known from the atomic spectra. S_M is determined by direct measurement or by observing the vapour-pressure as a function of temperature and using (437) or (438). The heats of dissociation are determined by the use of (449) or (450) and observed equilibria§. Finally,

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[*] Haber, *Verh. der Deutsch. Phys. Ges.* vol. XXI, p. 750 (1919); cf. also Fajans, *ibid.* pp. 539, 549, 709, 714 (1919).

[†] Haber, *loc. cit.*

[‡] Fajans, *loc. cit.*

[§] See Table 11 for sources for this information.

Angerer and Müller†, following an idea of Franck's‡, have observed in the halogen gases at high temperature a continuous spectrum with a sharp limit on the long-wave side, which they attribute to X^-, and have thus determined E_X. The values of E determined by this indirect process are to be compared with the calculated values given in Table 31 above. The agreement is surprisingly good.

TABLE 34.

Crystal energies in kilo-cals. per gram molecule (observed).

	NaCl	NaBr	NaI	KCl	KBr	KI	RbCl	RbBr	RbI
Q	99	90	77	104	97	85	105	99	87
$I_M + S_M$	117 + 26	117 + 26	117 + 26	99 + 21	99 + 21	99 + 21	95 + 20	95 + 20	95 + 20
$D_X - E_X$	27 − 88	23 − 80	17 − 71	27 − 88	23 − 80	17 − 71	27 − 88	23 − 80	17 − 71
E	181	176	166	163	160	151	159	157	148

Before the values of E_X were determined directly, it was usual to eliminate them from equation (776) above, by considering the halogen acids, for which Q_{HX}, E_{HX}, I_H and D_H were known. The values of E so determined differ by 2 or 3 per cent. from those given above§.

From the subsidiary cycle 2, 3, 5 in the figure we deduce

$$E = U^* + S,$$

where U^* is the heat of formation of the salt vapour from the ions of the metal and the halogen, and S is the heat of evaporation from salt crystal to crystal salt vapour. No measurements of either U^* or S have so far been given, so that the relation cannot yet be used to find E. We may, however, invert the procedure, regard E as known, calculate U^* (as has been done by Born and Heisenberg||) and thus deduce the value of S.

Fajans¶ has used the cycle 2, 6, 3 to investigate the magnitude of the heats of hydration W_M and W_X of metallic and halogen ions, taking E as known and adding the observed value of L, the heat of solution of the salt in water. He has not been able to determine W_M or W_X uniquely by this cycle alone, but has obtained a series of differences $W_{M_1} - W_{M_2}$, $W_{X_1} - W_{X_2}$, by several methods, the results being consistent among themselves. Thus $W_{\mathrm{Na}} - W_{\mathrm{K}}$ is found to be 21,000 calories per gram molecule. By other methods he is, however, able to deduce the absolute value of the heat of

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† Angerer and Müller, *Phys. Zeit.* vol. XXVI, p. 643 (1925).

‡ Franck, *Zeit. für Phys.* vol. V, p. 428 (1921).

§ Born, *Atomtheorie des festen Zustandes*, p. 751 (1923).

|| Born and Heisenberg, *Zeit. für Phys.* vol. XXIII, p. 388 (1924).

¶ Fajans, *Verh. der Deutsch. Phys. Ges.* vol. XXI, p. 549 (1919).

hydration of one ion, K^+, and so is able to infer the absolute values of the rest of the series. A few such values are given in Table 35, though they are only to be regarded as approximate. The values for the kations are uncertain to an extent of 3 or 4 per cent.; those for the anions give the order of magnitude only, as they may be in error by as much as 10,000 calories.

TABLE 35.

Heats of hydration of ions (Fajans).

(1000 calories per gram atom.)

Na^+	K^+	Rb^+	Cs^+	Ca^{++}	Cl^-	Br^-	I^-
203	182	173	174	475	− 23	− 32	− 43

§ **10·91**. *The polarizabilities of atoms and ions.* We now pass on to the forces due to *primary polarization.* Under the influence of an electric field, the positive and negative parts of an atom or ion suffer a relative displacement. This is usually represented (in the theory of dielectrics and elsewhere, see Chapter XII) by an electric doublet at the centre of the atom, whose moment is proportional to the strength of the exciting field, $p = aF$. The coefficient of proportionality a is called the *coefficient of polarizability or deformability.* With this assumption, the forces due to primary polarization may be regarded as determined when a is determined. One method by which this can be done depends on the refractive properties of solutions and of crystals. The usual Lorentz-Lorenz formula for the refractive index n for infinitely long waves is

$$R = \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho} = \frac{4\pi}{3} N_0 a, \qquad \text{......(779)}$$

where M is the molecular weight, ρ the density at which n is measured and N_0 the number of atoms in a gram-atom. The term on the left is called the atomic refractivity R. The theory suggests that the refractivity of a molecule may be equal to the sum of the atomic or ionic refractivities of its various constituents, thus

$$R = a_1 R_1 + a_2 R_2 + \dots,$$

if the molecule contains a_1 atoms of one kind, a_2 of another, and so on.

This law has been tested experimentally by Wiener*, Heydweiler†, Wasastjerna‡ and others, and it has been found to be reasonably accurate for salts in dilute solution, especially when the dissolved ions are of spherical symmetry*. Wasastjerna has calculated the individual refractivities of a

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[*] Wiener, *Leipz. Ber.* vol. LXII, p. 256 (1910).

[†] Heydweiler, *Ann. der Phys.* vol. XLI, p. 499 (1913); vol. XLVIII, p. 681 (1915); vol. XLIX, p. 653 (1916). *Verh. der Deutsch. Phys. Ges.* vol. XVI, p. 722 (1914).

[‡] Wasastjerna, *Soc. Sci. Fenn. Comm. Phys. Math.* vol. I, No. 37 (1923).

series of ions on the basis of the experimental data and the assumption that the ionic refractivity of the hydrogen ion, even in aqueous solution, is zero. Fajans and Joos* have cast doubts on this assumption, as they believe that the hydrogen ion in an aqueous solution exists in the form of H_3O^+. They have therefore proposed another method of estimating the ionic refractivities from the experimental results of Heydweiler, that of Na^+ being fixed as 0·50 for the determination of the rest from the molecular refractivities. The method by which this figure is derived, however, leaves much to be desired and it is doubtful whether the results can be regarded as more reliable than those of Wasastjerna. The two sets of results are reproduced in Table 36.

TABLE 36.

Ionic refractivities.

	(1)	(2)		(1)	(2)		(1)	(2)		(1)	(2)
F^-	2·20	—	Ne	1·01	1·00	Na^+	0·74	0·50	Mg^{++}	0·44	—
Cl^-	8·45	9·00	A	4·23	4·20	K^+	2·85	2·23	Ca^{++}	1·99	—
Br^-	11·84	12·67	Kr	6·42	6·37	Rb^+	4·41	3·58	Sr^{++}	3·22	—
I^-	18·47	19·24	X	10·56	10·42	Cs^+	7·36	6·24	Ba^{++}	5·24	4·28

(1) Wasastjerna, *loc. cit.* (2) Fajans and Joos, *loc. cit.*

Havelock† has obtained formulae for the refractivities of a number of diatomic, triatomic and even more complicated molecules in terms of the refractivities of the constituents, taking into account their interaction on each other. At the same time he has worked out a formula for the ratio of the two components of light scattered by the gas at right angles to the incident beam. By applying this formula to the halogen hydrides, he obtains the following values for the ionic refractivities:—$H^+ = 0·131$, $Cl^- = 6·136$, $Br^- = 8·62$. Similar considerations applied to CO_2, CS_2, H_2S and H_2O lead to $O^{--} = 2·58$, $S^{--} = 8·19$. These values are not, however, strictly comparable with those given above, as the known molecular structures of HCl and HBr place them in a different category from combinations such as NaCl or KCl‡.

Born and Heisenberg§ have attempted to determine the polarizabilities by another method. Assuming the valency electron of the metal atoms to polarize the rest of the atom according to the law $p = \alpha F$, they show that this results in an added force of attraction on the electron by the core proportional to αr^{-5}. The constants of the Rydberg-Ritz formula for the series spectra are then obtained in terms of α so that by a comparison of

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* Fajans and Joos, *Zeit. für Phys.* vol. XXIII, p. 1 (1924).

† Havelock, *Phil. Mag.* vol. III, pp. 158 and 433 (1927).

‡ The indication of band spectra is that the H^+ is embedded in the electronic system of the halogen.

§ Born and Heisenberg, *Zeit. für Phys.* vol. XXIII, p. 388 (1924).

the theoretical values with the constants computed by A. Fowler or by Paschen and Götze, an evaluation of α is possible. The corresponding values of α for the halogen ions are then obtained from the molecular refractivities of the alkali halogen salts. The values of α for the inert gases are calculated from the Lorentz-Lorenz formula already given, but the limiting value of the refractive index for infinitely long wave lengths is calculated by extrapolation from the dispersion formula

$$n_\lambda = n + \frac{a}{\lambda^2}.$$

The final results are given in Table 37.

TABLE 37.

The polarizabilities of atoms and ions (Born and Heisenberg).

$\alpha\ 10^{24}$	He 0·202	Li^+ 0·075	
F^- 0·99	Ne 0·392	Na^+ 0·21	Mg^{++} 0·12
Cl^- 3·05	A 1·629	K^+ 0·87	—
Br^- 4·17	Kr 2·46	Rb^+ 1·81	Sr^{++} 1·42
I^- 6·28	X 4·00	Cs^+ 2·79	—

It is doubtful, however, whether it is legitimate to use the simple assumption that deformability is proportional to field strength in such close interaction between electron and atomic core. It is probably legitimate in the case of refractivity where the field strength is of the order of 0·02 electrostatic unit, but atomic field strengths may be of the order of 10^6 electrostatic units. The numbers obtained by Born and Heisenberg must therefore only be regarded as rough approximations. A proper theory of α will depend on a direct calculation by the new mechanics of the effect of an external field on the electronic structure of the atom.

The inadequacy of this linear law is probably responsible too for the failure of the law of addition of ionic refractivities in crystals. Spangenberg* has determined the refractivities and densities of the alkaline halogen crystals with great accuracy and has shown that the additive law certainly breaks down in these crystals. Fajans and Joos, in the work already quoted, and Bragg†, in an investigation of the effect of atomic arrangement on refractive index, also discuss the alteration in the refractivity of an ion in the presence of other neighbouring ions, from which it is evident that the parameter α cannot be regarded as an absolute ionic constant. It tends to an upper limit when ions are dispersed, and tends to a lower limit when the ion is in the presence of other ions of high refractivity.

The polarizability can also be determined from the dielectric properties of matter. The theory is discussed in a later chapter, where it is shown that

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* Spangenberg, *Zeit. für Kryst.* vol. LVII, p. 494 (1923).

† W. L. Bragg, *Proc. Roy. Soc.* A, vol. CVI, p. 346 (1924).

the observations can in many cases be explained on the supposition that a molecule possesses a permanent electric moment, which tends to set in the direction of an applied field, and that in addition an induced dipole is set up by the presence of the field. The theoretical formula for the dielectric constant ϵ is then

$$\frac{\epsilon - 1}{\epsilon + 2}\frac{M}{\rho} = \frac{4\pi}{3} N_0 \left\{\alpha + \frac{\beta}{T}\right\}, \qquad \text{......(780)}$$

where α is the polarizability as defined above and β is proportional to the square of the electric moment μ. Both α and β (and therefore μ) can be deduced from the observations. For instance, for ammonia*

$$\frac{4\pi}{3} N_0 \alpha = 5{\cdot}45, \quad \frac{4\pi}{3} N_0 \beta = 15250,$$

whence $\alpha = 2{\cdot}24 \,.\, 10^{-24}$ and $\mu = 1{\cdot}56 \,.\, 10^{-18}$. The values of μ are given in Chapter XII, so that all that need be pointed out here is that the values of α are available by the same method.

§ **10·92.** *Surface forces.* In earlier paragraphs applications of interatomic forces have been made to the calculation of the internal properties of solids. It is equally important that the conditions at a surface should be considered, especially as the action of surfaces is now known to be of great importance in many chemical phenomena. One point of interest is the order of magnitude and extent of the forces outside a crystal, as this has a bearing on theories of adsorption and adhesion. For this purpose the forces outside the (100) plane of a crystal of the rock-salt type have been considered† with the hope that the results might indicate the surface forces in other more complicated cases. This problem is interesting in that it provides an illustration of the forces due to primary polarization as well as of the other forces already considered.

The electrostatic potential of the semi-infinite array of the net positive and negative charges of the ions of valency v in a crystal at a point outside a (100) plane and at a distance of z from it may be shown to be

$$\phi = \frac{2v\epsilon}{a} \sum_{l,m}{}' \frac{(-1)^{\frac{1}{2}(l+m)}}{\sqrt{(l^2+m^2)}} \cos\pi\left(\frac{lx}{a} + \frac{my}{a} - \frac{l+m}{2}\right) \frac{e^{-\frac{\pi z}{a}(l^2+m^2)^{\frac{1}{2}}}}{1 + e^{-\pi(l^2+m^2)^{\frac{1}{2}}}},$$

summed over all odd values of l and m positive and negative; a is the distance between consecutive planes. The axes of x and y are taken to coincide with

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* Debye, *Handbuch der Radiologie*, vol. VI, p. 619 (1925). The more recent experiments quoted in Chap. XII, Table 40, give somewhat smaller values of μ.

† Lennard-Jones and Dent, *Trans. Faraday Soc.* vol. XXIV, p. 92 (1928). The electrostatic forces have also been considered independently by Blüh and Stark (*Zeit. für Phys.* vol. XLIII, p. 575 (1927)), though not in the same detail.

the cubic axes. The electrostatic force on a unit charge in a direction normal to the surface is easily deduced to be

$$F_z = -\frac{\partial \phi}{\partial z} = \frac{2\pi v \epsilon}{a^2} \sum_{l,m}{}' \frac{(-1)^{\frac{1}{2}(l+m)}}{1+e^{-\pi\surd(l^2+m^2)}} e^{-\frac{\pi z}{a}(l^2+m^2)^{\frac{1}{2}}} \cos \pi \left(\frac{lx}{a} + \frac{my}{a} - \frac{l+m}{2}\right). \quad \text{......(781)}$$

For a fixed value of z, this is a maximum above the lattice points of the crystal (being alternately positive and negative) and is zero at all points midway between them.

Numerical calculations of the value of this force outside KCl are given in Table 37 A below. It will be observed that the force is reduced by 1/100 by increasing z/a from 1 to 2, that is, increasing z from 3·14 to 6·28 Å.

These forces apply, of course, only to a charged ion in the neighbourhood of the crystal surface. In the case of a neutral atom, forces of attraction arise from primary and secondary polarization. The former may be calculated in terms of the coefficient of polarizability α. The potential energy of the induced dipole at the centre of the atom in an electric field F is $\frac{1}{2}\alpha F^2$, or, using the potential function ϕ already given above,

$$\Phi = \tfrac{1}{2}\alpha \left\{ \left(\frac{\partial \phi}{\partial x}\right)^2 + \left(\frac{\partial \phi}{\partial y}\right)^2 + \left(\frac{\partial \phi}{\partial z}\right)^2 \right\}.$$

The force on the dipole perpendicular to the crystal face is then given by

$$F_z = -\frac{\partial \Phi}{\partial z} = -\alpha \left\{ \frac{\partial \phi}{\partial x}\frac{\partial^2 \phi}{\partial x \partial z} + \frac{\partial \phi}{\partial y}\frac{\partial^2 \phi}{\partial y \partial z} + \frac{\partial \phi}{\partial z}\frac{\partial^2 \phi}{\partial z^2} \right\},$$

$$= \frac{64\sqrt{2}\pi^3 \epsilon^2 v^2 \alpha}{a^5} \frac{e^{-2\surd 2\pi z/a}}{(1+e^{-\surd 2\pi})^2} f(x, y)$$

(very nearly), where $f(x, y)$ represents the variation with respect to x and y. The function $f(x, y)$ is equal to unity over the lattice points and is equal to zero at such points as $x = \frac{1}{2}a$, $y = \frac{1}{2}a$. The variation above a lattice point is seen from Table 37 A, where the example of argon near the surface of KCl is considered.

The van der Waals attraction between the electronic systems of the ions in the crystal and an atom outside it cannot be calculated exactly, because such attractive forces are not yet known for ions. We can, however, estimate the order of magnitude by supposing the neon-like ions to attract like neon, and the argon-like ions to attract like argon. For argon outside KCl we then have a force normal to the surface which can be put in the form

$$H_z = \frac{\mu h^{(s)}(z)}{a^s}, \quad \text{......(782)}$$

if μr^{-s} is the attractive force between the argon atom and any ion in the crystal. In this expression, $h^{(s)}(z)$ is a certain summation over all the ions of the crystal, viz.

$$h^{(s)}(z)=\sum_{l,m,n}\left(\frac{z}{a}+n\right)\left\{l^2+m^2+\left(\frac{z}{a}+n\right)^2\right\}^{-\frac{1}{2}(s+1)},$$

the summation extending over all values of l and m, and all positive values of n. These functions have been evaluated for $s=5$, $s=6$ and a series of values of z. The numerical values of $H(z)$ for argon and KCl are given in Table 37 A.

TABLE 37 A.

Cohesive forces outside KCl.

($a_{\text{KCl}} = 3{\cdot}14$ Å.)

z/a	1·0	1·4	2·0	3·0
Force on charge ϵ	$6{\cdot}80\times10^{-5}$	$1{\cdot}14\times10^{-5}$	$7{\cdot}94\times10^{-7}$	$9{\cdot}30\times10^{-9}$
Primary polarization (Argon)	$4{\cdot}74\times10^{-6}$	$1{\cdot}33\times10^{-7}$	$6{\cdot}36\times10^{-10}$	$8{\cdot}85\times10^{-14}$
Secondary polarization (van der Waals' attraction) (Argon) ($s=5$)	$1{\cdot}11\times10^{-5}$	$4{\cdot}28\times10^{-6}$	$1{\cdot}75\times10^{-6}$	$6{\cdot}70\times10^{-7}$

It will be observed that $H(z)$ falls off very slowly with distance, so much so, in fact, that it becomes the important term at values of $z > 2{\cdot}5a$. It is not difficult to show that $h^{(5)}(z)$ tends asymptotically to z^{-2}, so that at large distances $H(z)$ falls off as the inverse square of the distance. The van der Waals field, usually regarded as a short range force, here becomes one of long range. The reason for this difference in behaviour is that it is assumed in the calculation that the van der Waals attractions are additive for all ions in the crystal, whereas the forces arising from the charges on the ions of the lattice are alternately of opposite signs and so rapidly neutralize each other. This assumption is of course still questionable, but if it is right we certainly have the striking result shown in Table 37 A.

The results can be applied to estimate the concentration of argon in the neighbourhood of KCl by Boltzmann's formula. We find that, at a distance of 10 Å., the concentration is about two to three times the normal at room temperature.

CHAPTER XI

APPLICATIONS OF THE EQUILIBRIUM THEORY TO THERMIONICS

§ **11·1.** *Thermionic phenomena.* The phenomena of the emission of electricity from hot bodies are well known*. We cannot enter here into experimental details. It will be sufficient to record that a great range of phenomena lend practical certainty to the view that an incandescent body of metal emits electrons and to a less extent positive ions at a rate depending primarily on its temperature. The phenomena actually observed depend in general on these rates of emission, for the system studied is not in an equilibrium state. But since there must be an equilibrium state for a similar isolated system, we are led by these phenomena to believe that, when equilibrium is set up between the metal and its surroundings (gas or vacuum), the metal is in equilibrium with a vapour of electrons and perhaps positive ions as well. This is exactly analogous to the equilibrium between a crystal and its own vapour, or rather between a crystal and a vapour of *one* of its own constituents, and can at once be treated by the formulae of § 5·9 if the long-range effects of the electrical charges are neglected. These will be included later with the help of the methods of § 8·7.

We propose therefore to develop in some detail the theory of electron atmospheres in equilibrium with bodies which can emit (and absorb) electrons. We shall be unable in general to make direct comparisons of the equilibrium theory with experiments on the equilibrium state. But the simplest additional considerations of reversible mechanisms of interaction between the vapour and the crystal will enable us to draw some conclusions as to rates of emission and so to compare the theory with experiment, without exceeding the proposed field of this monograph.

§ **11·2.** *The elementary theory of electron atmospheres.* We will suppose for simplicity in this section that the long-range effects of the electronic charges in the vapour and the solid (space charge effects) can be neglected, so that the solid and the evaporated electrons can be treated as independent systems. Then by (382)

$$\overline{N} = g(\vartheta)/\kappa(\vartheta), \qquad \text{......(783)}$$

where $\overline{N}$ is the average number of electrons in the vapour. We have now to examine the structure of these partition functions for the electron in the vapour and in the solid.

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* For a general account see O. W. Richardson, *The Emission of Electricity from Hot Bodies*, 2nd ed. (1921). The reader should also refer to the work of Langmuir, some of whose more important papers on Thermionics are:—*Phys. Rev.* vol. II, p. 450 (1913), vol. XXI, p. 419 (1923), vol. XXII, p. 347 (1923) (with Miss Blodgett), vol. XXVIII, p. 727 (1926) (with Mott-Smith).

If the electron in the vapour were a structureless mass-point we should have

$$g_0(\vartheta) = \frac{(2\pi mkT)^{\frac{3}{2}}\,V}{h^3}.$$

It is, however, now abundantly clear* that this assumption of absence of structure would be wrong. The electron has an axis of spin, which makes it an elementary magnet with two possible orientations in a magnetic field. In accordance with our general principles it therefore has a weight 2, so that actually

$$g_0(\vartheta) = 2\,\frac{(2\pi mkT)^{\frac{3}{2}}\,V}{h^3}. \qquad \text{......(784)}$$

This form, however, is based on an energy zero which is the energy of an electron at rest in field-free space at an infinite distance from all other matter. It is often more convenient, however, as in § 5·7, to define the zero of energy relative to the interior of the solid at the absolute zero of temperature, for it is only if $\kappa(\vartheta)$ tends to a definite limit $\kappa(0)$ as $\vartheta \to 0$ that $\kappa(\vartheta)$ has its simplest thermodynamic form. Relative to the zero used for (784) the most tightly bound electrons in the metal will have an energy $-\chi$. Thus χ *is by definition the heat of evaporation per electron at the absolute zero of temperature*, and

$$g(\vartheta) = g_0(\vartheta)\,\vartheta^{\chi} = 2e^{-\chi/kT}\,\frac{(2\pi mkT)^{\frac{3}{2}}\,V}{h^3}. \qquad \text{......(785)}$$

With the same conventional energy zero, by (448),

$$\log\frac{\kappa(\vartheta)}{\kappa(0)} = \int_0^T \frac{dT'}{kT'^2}\int_0^{T'} \sigma\, dT'', \qquad \text{......(786)}$$

where $\sigma\,(=\partial C/\partial n)$ is the increase of specific heat of the metal for the addition of one electron. It follows that

$$\bar{\nu} = \frac{\bar{N}}{V} = \frac{2}{\kappa(0)}\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}\exp\left\{-\frac{\chi}{kT} - \int_0^T \frac{dT'}{kT'^2}\int_0^{T'} \sigma\, dT''\right\}. \quad (787)$$

By definition, σ is here the increase of specific heat of the metal for the addition of one electron. Kelvin's definition of *the specific heat of electricity*, which we will write σ_t, is such that the heat absorbed reversibly when unit charge of electricity flows in a conductor of uniform material from a point of temperature T to temperature $T + \delta T$ is $\sigma_t \delta T$. This is not necessarily strictly comparable to our σ, for the internal electronic state of a metal conductor carrying a steady current is not *necessarily* exactly the same as that of the same metal at the same temperature in thermodynamic equilibrium, the conditions postulated in the definition of σ†. At the same time,

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* The evidence for this arising from properties of atomic spectra will be summarized in Chapter XIV.

† This possibility is mentioned by Richardson, *loc. cit.*, and analysed in detail by Schottky, *Zeit. für Phys.* vol. XXXIV, p. 645 (1925).

admitting the possibility, there is no *a priori* reason to expect that any such change of electronic state between small currents and zero current will exist, or, if it exists, have any appreciable effect on the thermodynamic properties of the metal. We shall ignore the possibility of this distinction in the rest of this discussion. We then have

$$\sigma = -\epsilon\sigma_t, \qquad \text{......(788)}$$

where $-\epsilon$ is the charge on the electron and ϵ its numerical value*.

It is customary to a first approximation to neglect σ altogether. This is thermodynamically equivalent to assuming that the change of *entropy* on addition of an electron to the metal may be neglected. If (788) is correct we can justify this omission by using observed values of σ_t. The usual values are 10^3 ergs per electromagnetic unit of charge†. Therefore σ/k is about $\frac{1}{10}$. At lower temperatures we may be certain on general grounds that the relative importance of σ will diminish. This is confirmed by the new theory expounded in Chapter XXI. Since σ/k is fairly small compared with $\frac{3}{2}$ it is legitimate to neglect σ in (787) while retaining the $T^{\frac{3}{2}}$ factor. The formula then takes the form‡

$$\bar{\nu} = \frac{2}{\kappa(0)} \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} e^{-\chi/kT}. \qquad \text{......(789)}$$

Inserting numerical values

$$\bar{\nu} = 2{\cdot}43 \times 10^{15} \frac{2}{\kappa(0)} T^{\frac{3}{2}} e^{-\chi/kT}. \qquad \text{......(790)}$$

The only novel feature in these formulae is the extra factor $2/\kappa(0)$, the 2 being the orientational weight of the free electron.

We have so far proceeded quite formally and made no attempt to evaluate $\kappa(\vartheta)$ or even $\kappa(0)$. It has only recently become possible, thanks to the work of Sommerfeld§, to make such a calculation of $\kappa(\vartheta)$, or ξ (see (380)), on a satisfactory basis. The calculations involve the so-called new statistics of Fermi-Dirac and will therefore be given in Chapter XXI. It appears to be quite certain that $\kappa(0) = 1$. We shall use this result here and postpone discussion of other details, contenting ourselves otherwise with formal developments.

It is not possible to observe such densities or the corresponding pressures, p_ϵ $(= \bar{\nu}kT)$. The quantity observed is always a current—the maximum

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[*] In comparing these formulae with Richardson, *loc. cit.*, note that he uses ϵ for the electron's charge, so that his ϵ is negative. It should also be recorded that the new theory of Sommerfeld makes and evaluates a distinction such as that mentioned in the text.

[†] A table is given by Richardson, *Electron theory of matter*, p. 452 (1916 ed.). See also Chapter XXI.

[‡] These formulae have been given substantially in this form (or with σ included) by a number of authors: e.g. O. W. Richardson, *loc. cit.*, and *Phys. Rev.* vol. XXIII, p. 153 (1924); Dushman, *ibid.* vol. XXI, p. 623 (1923); H. A. Wilson, *ibid.* vol. XXIV, p. 38 (1924); Schottky, *loc. cit.*, with other references.

[§] Sommerfeld, *Naturwiss.* p. 825 (1927).

current that can be drawn from an incandescent wire per square centimetre per second, by an external voltage sufficiently large to sweep away the electrons as fast as they are emitted, but not large enough to produce marked potential gradients at the surface. Such a *saturation* current measures the rate of emission of electrons by the hot solid. About such rates of emission neither thermodynamics nor the equilibrium theory of statistical mechanics have anything to say. We must appeal to *some* mechanism, which, however, and here the equilibrium theory comes in, must be such as to be consistent with the equilibrium state, when allowed to act in a normal manner. It must be true, for example, for the equilibrium state that the rates of emission and return of electrons are equal. The assumption is then made that, when the external voltage is applied and the saturation current measured, the rate of emission of electrons is unaltered. Since this is determined by the internal state of a conductor and the applied voltages are not large this assumption may be accepted*.

Now, though we cannot calculate the rate of emission in any elementary way, we can calculate very simply the rate of return of electrons in the equilibrium state in terms of known quantities and a reflection coefficient r. For the electrons will have the usual equilibrium (Maxwellian) distribution in velocity and space, and therefore by (99) the number of electrons in a volume dV with velocity between c and $c + dc$, directed within a solid angle $d\omega$, is

$$\bar{\nu}\, dV \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} c^2 e^{-mc^2/2kT}\, dc\, d\omega.$$

The number of electrons which strike unit area in unit time is therefore obtained by taking

$$d\omega = \sin\theta\, d\theta\, d\phi, \quad dV = c\cos\theta \,.\, 1,$$

and integrating over all c and over a hemisphere. We find

$$\bar{\nu}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_0^{2\pi} d\phi \int_0^{\frac{1}{2}\pi} \sin\theta\cos\theta\, d\theta \int_0^{\infty} c^3 e^{-mc^2/2kT}\, dc,$$

or

$$\tfrac{1}{4}\bar{\nu}\,\frac{2\,(2kT)^{\frac{1}{2}}}{(\pi m)^{\frac{1}{2}}} = \tfrac{1}{4}\bar{\nu}\bar{c}. \qquad \text{......(791)}$$

If in the equilibrium state a fraction r of these is reflected again, the number of electrons which return to unit surface of the metal in unit time is (using (789) with $\kappa(0) = 1$)

$$(1 - r)\, 2\,\frac{2\pi m k^2 T^2}{h^3}\, e^{-\chi/kT}. \qquad \text{......(792)}$$

On the assumptions made, it follows that the saturation current $-I$ flowing

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* If the field at the surface of the metal is great enough the rate of emission *is* affected. Electrons can be drawn thus from comparatively cold bodies. But the fields necessary are of a different order from those used to obtain thermionic saturation currents.

from unit area of the hot body to the collector is given in electrostatic units by the formula

$$I = \tfrac{1}{4}\epsilon\bar{\nu}\bar{c}\,(1-r) = (1-r)\,\frac{4\pi m k^2 \epsilon}{h^3}\,T^2 e^{-\chi/kT}. \qquad \text{......(793)}$$

The numerical value of the absolute constant $4\pi m k^2 \epsilon/h^3$ is $3{\cdot}60 \times 10^{11}$ E.S.U., or 120 amperes per square centimetre.

Previous formulae for I have contained a numerical constant of 60 amperes, since the weight 2 of the free electron has been omitted. The best observations for very pure metals, to which we shall refer further in a moment, have indicated that if I is expressed in the form

$$AT^2 e^{-\chi/kT} = AT^2 e^{-b_0/T}, \qquad \text{......(794)}$$

with A and χ (or b_0) constants, then A has a value close to 60. It was previously argued that this was in satisfactory agreement with the theory, the factor $(1 - r)$ being tacitly ignored. Now all the direct evidence points to a value of r not nearly zero, but rather about $\frac{1}{2}$ for slow electrons*, which is in excellent agreement with the new value but not with the old. In simple cases we should now expect an upper limit for I of

$$120T^2 e^{-\chi/kT} \quad \text{amp./cm.}^2,$$

the greatest values observed being half this. The best recent observations have been analysed by determining A and χ in (794) to give the best fit with the observations; a selection of the more reliable values are given in Table 38. Sometimes, however, in fixing b_0 the value 60 has been *assumed* for A, but in view of the newer theory which gives A in the form $120\,(1 - r)$, this should no longer be done.

TABLE 38.

Thermionic data†.

Metal	b_0	χ volts	A
C	46,500	4·00	—
Ca	26,000	2·24	—
Mb	51,300	4·43	55
Ta	47,200	4·07	60
W	52,400	4·52	60
Pt	59,000	5·08	nearly 60
Th	38,900	3·35	—
Ur on W	35,500	3·06	12
Zr on W	36,500	3·14	5·0
Th on W	30,500	2·63	3·0

While it appears that A is at any rate near 60 for very pure metals, it is clearly certain experimentally that for surface films on tungsten (and

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* Richardson, *The Emission of Electricity from Hot Bodies*, p. 55 (1921).

† I owe my knowledge of thermionic data, particularly as to what values may be trusted, to a letter from Dr S. Dushman, Dec. 1926, containing material and references which will appear in the *International Critical Tables* (Washington).

other metals) it may be very much less, even if the films are monomolecular. The only really reliable quantitative values are given in Table 38 for layers of thorium, zirconium and uranium on tungsten. This drop in A is associated with a corresponding drop in b_0 and can be explained at once as due to a change in the value of r, the reflection coefficient of electrons, at the more complicated potential step produced by such a surface layer. We shall refer in Chapter XXI to the way in which such reflection coefficients can now be roughly computed and their dependence on the nature of the surface studied with the help of the new mechanics.

Owing to the dominance of the exponential term, the observations are not capable of fixing A with high accuracy. In fact it is not observationally possible to distinguish between (794) and a formula

$$I = A'T^{\frac{1}{2}}e^{-b_1/T}, \qquad \text{......(795)}$$

used by Richardson in his earlier work.

As an example of the excellent fit obtainable with good data and (794), we quote from Dushman the following observations for tungsten. In the analyses it is assumed that $A = 60{\cdot}2$ and b_0 is then calculated from the observed I. The values so obtained should be identical and the actual *extreme* variation in Table 39 is 11 parts in 5000.

TABLE 39.

Emission data for tungsten.

The entries i in the second column are the observed currents from 0·1825 cm.^{2} hot surface.

Temp. ° K.	i mille-amperes	$\log_{10}(I/T^2)+10$	b_0
1935·5	0·0934	0·1355	51,890
1986·5	0·1973	0·4378	51,880
2036·0	0·3967	0·7197	51,860
2077·5	0·6784	0·9351	51,880
2086·5	0·7656	0·9838	51,900
2102·0	0·9363	1·0650	51,840
2131·5	1·362	1·2155	51,840
2134·5	1·419	1·2321	51,870
2158·0	1·902	1·3500	51,820
2182·0	2·538	1·4655	51,810
2204·0	3·269	1·5668	51,820
2231·0	4·405	1·6858	51,820
2235·0	4·606	1·7036	51,870
2271·5	6·875	1·8635	51,880
2280·0	7·394	1·8918	51,920
2306·0	9·792	2·0041	51,900
		Mean	51,860

§ **11·21**. *The cooling effect of the evaporation of electrons* has also been investigated experimentally and examined theoretically by Richardson* and others. We are again concerned with a *rate* of working, but we may

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* Richardson, *loc. cit.*, especially chap. v.

perhaps be allowed to record the result for the sake of completeness. If we evaporate N average electrons then their extra energy in the vapour phase will be

$$N\phi = N\left\{\chi + \tfrac{3}{2}kT - \int_0^T \sigma dT\right\}.$$

This, however, is *not* exactly the cooling effect on the metal, for the electrons evaporated are not an average equilibrium group distributed according to Maxwell's law. This can be seen at once if we consider the rates of emission and return *for electrons of given velocity*. The number of electrons of velocity between c and $c + dc$ which strike unit area per second in the equilibrium state is

$$\pi\bar{\nu}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} c^3 e^{-mc^2/2kT}\, dc.$$

If a fraction $r(c)$ of these is reflected, the number which are re-absorbed per unit area per second is

$$\{1 - r(c)\}\,\pi\bar{\nu}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} c^3 e^{-mc^2/2kT}\, dc,$$

which is therefore also the rate of emission. Owing to the extra factor c the rates of emission and return are, as it were, higher for the higher velocities compared with the equilibrium numbers of such electrons present in the gas. The average kinetic energy of the electrons emitted is

$$\tfrac{1}{2}m\int_0^\infty \{1 - r(c)\}\, c^5 e^{-mc^2/2kT}\, dc \Big/ \int_0^\infty \{1 - r(c)\}\, c^3 e^{-mc^2/2kT}\, dc.$$

If we may, to a first approximation, ignore the variation of $r(c)$ with c we have a mean energy

$$\tfrac{1}{2}m\int_0^\infty x^2 e^{-mx/2kT}\, dx \Big/ \int_0^\infty x e^{-mx/2kT}\, dx,$$

or

$$2kT.$$

Thus on these assumptions the cooling effect for the evaporation of N electrons is

$$N(\phi + \tfrac{1}{2}kT) = N\left\{\chi + 2kT - \int_0^T \sigma dT\right\}.$$

This is in good agreement with direct experiment. Experiments, however, could hardly fix the coefficient of kT.

§ **11·3**. *Space variations of the electrostatic potential.* We proceed next to include the effects of electrostatic fields due to the charges on the electrons themselves. The inclusion of these effects does not alter the form of (787) or (789) but only the physical interpretation of $\bar{\nu}$. These formulae remain true in the general case *if $\bar{\nu}$ means the average electron density in the free electron gas immediately outside the surface of the metal.*

The unaffected validity of (787) and (789) is almost obvious. The metal is a conductor at constant potential, and the potential of the electron gas in contact with it will be equal to the potential of the metal, since the potential is a continuous function. Whether electrostatic fields are included or not there will be no question of potential differences between the metal and a thin sheet-like volume element of electron gas in contact with it. The foregoing arguments then apply, with an unaltered interpretation of χ and the interpretation of $\bar{\nu}$ stated above, and yield the old result*.

In addition to this result, we find, of course, that the electron densities of different parts of the gas are connected by Boltzmann's equation

$$\frac{\bar{\nu}}{\bar{\nu}_0} = e^{\epsilon(V-V_0)/kT}. \qquad \text{......(796)}$$

This is the simplest example of the theorems of § 8·7. The details of the distribution of electrons must be studied by the help of the combined use of (796) and Poisson's equation, as there examined. To this we return in § 11·4.

We can draw at once some interesting conclusions. Suppose we have an assembly in equilibrium containing two different metals. Then the density of the electron gas in equilibrium with them will not be equal and therefore the immediate neighbourhoods of the two metals cannot be at the same potential. The metals themselves must therefore differ in potential—this is their *contact potential difference*, for it is obviously immaterial to the foregoing argument whether the metals in question are in so-called metallic contact or not. The contact potential difference V_{12} between metals 1 and 2 can now be related at once to quantities already defined. By considering elements of electron gas near the two metals we have by (787)

$$\log\frac{\bar{\nu}_1}{\bar{\nu}_2} = -\frac{\chi_1-\chi_2}{kT} - \int_0^T \frac{dT'}{kT'^2}\int_0^{T'} (\sigma_1-\sigma_2)\,dT'' - \log\frac{\kappa_1(0)}{\kappa_2(0)}, \qquad \text{......(797)}$$

and by (796)

$$\log\frac{\bar{\nu}_1}{\bar{\nu}_2} = \frac{\epsilon V_{12}}{kT}. \qquad \text{......(798)}$$

[Here V_{12} is the excess of the potential of metal 1 over that of metal 2 in isothermal equilibrium.] We find, therefore,

$$\epsilon V_{12} = \chi_2 - \chi_1 + T\int_0^T \frac{dT'}{T'^2}\int_0^{T'} (\sigma_2-\sigma_1)\,dT'' - kT\log\frac{\kappa_1(0)}{\kappa_2(0)}. \qquad \text{......(799)}$$

According to the new theory the last term is always zero.

This equation is complete. It shows that as $T \to 0$ the contact potential difference must tend to the difference of the χ's (reckoned in volts), and over a wide range of temperature these quantities will be approximately

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* This result still holds, but the argument needs a complete restatement when surface effects are explicitly allowed for. See § 11·8.

equal. An equation almost equivalent to (799) can be derived thermodynamically and is commonly given in the form

$$\epsilon\left(V_{12} - T\frac{\partial V_{12}}{\partial T}\right) = \chi_2 - \chi_1 + \int_0^T (\sigma_1 - \sigma_2)\,dT. \qquad \text{......(800)}$$

This can be obtained by differentiating (799). The quantity on the right is also given as $\phi_2 - \phi_1$, the difference of the average work required *at temperature* T to evaporate an electron from the two metals. If we differentiate (800) we obtain

$$-\epsilon T\frac{\partial^2 V_{12}}{\partial T^2} = \sigma_1 - \sigma_2. \qquad \text{......(801)}$$

In terms of σ_t, Thomson's specific heat of electricity, this reads

$$T\frac{\partial^2 V_{12}}{\partial T^2} = (\sigma_t)_1 - (\sigma_t)_2, \qquad \text{......(802)}$$

a familiar thermodynamic equation.

Though of the nature of a digression it may be noted here that it is natural to see in all thermoelectric phenomena the manifestations of contact potential differences which vary with the temperature. We have already obtained nearly all the usual thermodynamic equations; there remains only the equation for the Peltier heat reversibly absorbed or emitted at a junction of two metals which is

$$\Pi_{12} = T\frac{\partial V_{12}}{\partial T} \qquad \text{......(803)}$$

—a theorem in pure thermodynamics, being an example of the Gibbs-Helmholtz equation. With these equations the electromotive force round any circuit is correctly given by summing (or integrating) a series of "contact" potential differences round the circuit, either for contacts between different metals at the same temperature or the same metal at different temperatures.

§ **11·4**. *Space charge effects. Special electron atmospheres.* It will now be of some interest to examine in detail the equilibrium state of some electron atmospheres in which space charge effects due to the electrons themselves are important and are included in the calculations. As we have shown in § 8·7 the laws governing the equilibrium distribution are

$$\nabla^2 V = 4\pi\epsilon\bar{\nu}, \quad \frac{\bar{\nu}}{\bar{\nu}_0} = e^{\epsilon(V-V_0)/kT}. \qquad \text{......(804)}$$

Not many problems of electron distribution are soluble explicitly in finite terms. The simplest distribution imaginable is a stratification in parallel planes. Such a distribution will be set up between the plates of a parallel plate condenser, and the equations are then soluble exactly. They become

$$\frac{d^2V}{dx^2} = 4\pi\epsilon\bar{\nu}, \quad \bar{\nu} = \bar{\nu}_0 e^{\epsilon V/kT}, \qquad \text{......(805)}$$

if we define V to be zero in the plane where $\bar{\nu} = \bar{\nu}_0$. Hence

$$\frac{\epsilon}{kT}\frac{dV}{dx} = \frac{1}{\bar{\nu}}\frac{d\bar{\nu}}{dx}, \quad 4\pi\epsilon\bar{\nu} = \frac{kT}{\epsilon}\frac{d}{dx}\left\{\frac{1}{\bar{\nu}}\frac{d\bar{\nu}}{dx}\right\}.$$

It will be convenient to introduce a new variable y such that

$$\bar{\nu}\,dx = dy.$$

Then

$$\frac{d^2\bar{\nu}}{dy^2} = \frac{4\pi\epsilon^2}{kT},$$

$$\bar{\nu} = \frac{2\pi\epsilon^2}{kT}y^2 + by + c,$$

where b and c are constants of integration. At the symmetrical plane halfway between the two plates (of the same material at the same potential) we shall have by symmetry $\partial V/\partial x = 0$, $\partial\bar{\nu}/\partial y = 0$. If this plane is $x = 0$ and we choose y so that

$$y = \int_0^x \bar{\nu}\,dx,$$

then $\partial\bar{\nu}/\partial y = 0$ for $y = 0$ and $b = 0$. Since $\bar{\nu} > 0$, $c > 0$, and we write

$$\bar{\nu} = \frac{2\pi\epsilon^2}{kT}(y^2 + \lambda^2).$$

so that

$$\frac{dy}{y^2 + \lambda^2} = \frac{2\pi\epsilon^2}{kT}dx,$$

$$y = \lambda \tan \frac{2\pi\epsilon^2\lambda}{kT}x,$$

$$\bar{\nu} = \frac{2\pi\epsilon^2\lambda^2}{kT}\sec^2\frac{2\pi\epsilon^2\lambda}{kT}x.$$

We can now determine λ, in terms of the electron density $\bar{\nu}_0$ in the central plane, by the equation

$$\lambda = \left(\frac{kT\bar{\nu}_0}{2\pi\epsilon^2}\right)^{\frac{1}{2}}, \qquad \text{......(806)}$$

which gives

$$\bar{\nu} = \bar{\nu}_0 \sec^2\left(\left\{\frac{2\pi\epsilon^2\bar{\nu}_0}{kT}\right\}^{\frac{1}{2}}x\right). \qquad \text{......(807)}$$

For the potential V we have

$$\frac{\epsilon V}{kT} = -2\log\cos\left(\left\{\frac{2\pi\epsilon^2\bar{\nu}_0}{kT}\right\}^{\frac{1}{2}}x\right). \qquad \text{......(808)}$$

With these equations any desired details may be investigated. We may observe in the first place that if an ideal non-electrical material may be imagined which neither emits, absorbs nor attracts electrons, then, since $\partial V/\partial x = 0$ for $x = 0$ and the electric intensity vanishes, the plane $x = 0$ may be replaced by an ideal non-electrical wall on which the electrons will act merely in virtue of their mechanical momenta. The distribution laws in $\bar{\nu}$ and V will be unaltered by this replacement. The plane of symmetry, or ideal wall, is a locus of equilibrium points which no lines of force cross. The stress per unit area at the surface of the emitter due to electrostatic forces is a negative pressure equal in amount to $2\pi\sigma^2$, where σ is the surface density of the charge on the emitter or the total atmospheric charge per unit area contained between the emitter and the central plane. If this distance is a, then

$$\sigma = \epsilon \int_0^a \bar{\nu}\, dx = \epsilon\bar{\nu}_0 \int_0^a \sec^2 \left\{ \left(\frac{2\pi\epsilon^2\bar{\nu}_0}{kT} \right)^{\frac{1}{2}} x \right\} dx,$$

$$= \left(\frac{kT\bar{\nu}_0}{2\pi} \right)^{\frac{1}{2}} \tan \left\{ \left(\frac{2\pi\epsilon^2\bar{\nu}_0}{kT} \right)^{\frac{1}{2}} a \right\}.$$

The electrical negative pressure is

$$kT\bar{\nu}_0 \tan^2 \left\{ \left(\frac{2\pi\epsilon\bar{\nu}_0}{kT} \right)^{\frac{1}{2}} a \right\},$$

or

$$kT\,(\bar{\nu}_a - \bar{\nu}_0).$$

At the same time the positive pressure due to the transport of momentum is

$$kT\bar{\nu}_a.$$

The net pressure on the surface of the conductor is therefore $kT\bar{\nu}_0$, which is also of course the pressure at the plane of symmetry or ideal wall, as it must be for mechanical equilibrium.

The distribution of electrons will be unaltered if we suppose the parallel emitters are finite, equal and similarly situated plates connected by non-electrical walls which are normal to them. In that case the pressure at any point on these side walls will be entirely due to the mechanical transport of momentum—there is no electrical stress acting across an element of the wall surface. The pressure at any point will therefore be simply $kT\bar{\nu}_x$ and in particular close to the emitter $kT\bar{\nu}_a$. It is of some importance for thermodynamic arguments to observe that this simple mechanical pressure $kT\bar{\nu}_a$ acts on a realizable wall surface. It is therefore possible to give a simple derivation of the differential form of (787) or (789) by a thermodynamic cycle without ignoring electrostatic effects and without explicit calculation of them.

§ **11·41**. *Further details of electron atmospheres.* If further details of the distribution are required it is natural to follow a classical exposition by von Laue*. We begin by studying the form of the distribution (807) and (808) near $x = a$, particularly for large T. Using (790) for the density at the surface of the metal we have

$$\bar{\nu}_a = \bar{\nu}_0 \sec^2\left\{\left(\frac{2\pi\epsilon^2\bar{\nu}_0}{kT}\right)^{\frac{1}{2}} a\right\} = A'T^{\frac{3}{2}}e^{-\chi/kT}, \qquad \text{......(809)}$$

where normally $A' = 4{\cdot}86 \times 10^{15}$. It follows that so long as T is large enough for $e^{-\chi/kT}$ not to swamp A' the right-hand side of (809) is a large number—there are plenty of electrons per unit volume. In order to evaluate $\bar{\nu}_0$ for given T we have therefore to solve (809) for $\bar{\nu}_0$ when the right-hand side is (usually) numerically large. The nature of the root will depend on whether or not, as $\bar{\nu}_0$ increases, $2\pi\epsilon^2\bar{\nu}_0 a^2/kT$ approaches $\pi^2/4$ before $\bar{\nu}_0$ approaches the constant on the right of (809). Since the former condition is

$$1{\cdot}04 \times 10^{-2}\,\frac{\bar{\nu}_0 a^2}{T} \to \frac{\pi^2}{4},$$

it is obvious that this happens first unless T is quite small. The first approximation to the root of (809) is therefore

$$\bar{\nu}_0 = \frac{\pi^2}{4a^2}\,\frac{kT}{2\pi\epsilon^2}, \qquad \text{......(810)}$$

and the second

$$\bar{\nu}_0 = \frac{\pi^2}{4a^2}\,\frac{kT}{2\pi\epsilon^2} - \alpha, \qquad \text{......(811)}$$

where

$$\bar{\nu}_0 \operatorname{cosec}^2 \frac{2a^2\epsilon^2}{kT}\,\alpha = A'\,T^{\frac{3}{2}}\,e^{-\chi/kT},$$

$$\alpha = \frac{\pi}{2a}\left(\frac{k}{2\pi\epsilon^2 A'}\right)^{\frac{1}{2}}\frac{kT}{2a^2\epsilon^2}\,\frac{e^{\chi/2kT}}{T^{\frac{1}{4}}}. \qquad \text{......(812)}$$

Inserting numerical values for the atomic constants,

$$\bar{\nu}_0 = 96\,\frac{\pi^2 T}{4a^2} - 4{\cdot}22 \times 10^{-5}\,\frac{\pi T^{\frac{3}{4}}}{2a^3}\,e^{\chi/2kT}.$$

For our immediate purpose the form of V near $x = a$ is more important. By (808) we have approximately after reduction

$$\frac{\epsilon V}{kT} = -\,2\log\left\{\tfrac{1}{2}\pi\,\frac{a' - x}{a}\right\}, \qquad \text{......(813)}$$

where

$$a' = a\left\{1 + \frac{1}{a}\left(\frac{k}{2\pi\epsilon^2 A'}\right)^{\frac{1}{2}}\frac{e^{\chi/2kT}}{T^{\frac{1}{4}}}\right\}. \qquad \text{......(814)}$$

Inserting numerical values

$$a' = a\left\{1 + 1{\cdot}40 \times 10^{-7}\,\frac{1}{a}\,\frac{e^{\chi/2kT}}{T^{\frac{1}{4}}}\right\}.$$

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* von Laue, *Jahrb. der Rad. u. Elektronik*, vol. xv, pp. 205, 257 (1918), or later, *Handbuch der Radiologie*, vol. vi, p. 452 (1925). This paper is summarized by Richardson, *loc. cit.*, who gives much additional information. The reader should also refer to Schottky, *Jahrb. der Rad. u. Elektronik* (1915), p. 199.

Thus for normal values of T and for all practical purposes except for regions in the immediate neighbourhood of the metal surface we may identify a' and a and assert that V behaves as if it had a logarithmic infinity

$$V \sim -\frac{2kT}{\epsilon}\log(a-x) \qquad \text{......(815)}$$

as $x \to a$. The strict behaviour is that V behaves as if it had a similar logarithmic infinity as x approaches a surface just inside the actual metal by an extremely small distance which tends to zero as $T \to \infty$.

The behaviour of V can be exhibited in its most general aspect by introducing the transformation

$$\psi = \frac{\epsilon V}{kT} + \log\frac{4\pi\epsilon^2\bar{\nu}_0}{kT}. \qquad \text{......(816)}$$

Then ψ satisfies the differential equation

$$\nabla^2\psi = e^{\psi}, \qquad \text{......(817)}$$

and the approximate boundary condition

$$\psi \sim -2\log(a'-x) + \log 2. \qquad \text{......(818)}$$

To the accuracy with which a' can be identified with a both the differential equation and the boundary conditions for ψ are absolute—independent of the temperature, of atomic constants and potentials and of the dimensions of the apparatus. We have only established this by a study of the detailed solution for a parallel plate condenser, but it is clear from the form of the result, which concerns only the immediate neighbourhood of the metal surface, that this boundary condition will continue to hold for all metal surfaces plane or curved, so that all electron atmospheres in enclosures entirely surrounded by metal emitters at a sufficiently high temperature can be studied by solving (817) for the enclosure subject to the boundary condition

$$[\psi \sim -2\log\delta], \qquad \text{......(819)}$$

where δ is the normal distance from the boundary.

It does not appear to have been rigorously established that equations (817) and (819) suffice to determine ψ uniquely. For physical reasons one may guess that they must do so, and we shall assume it in the rest of the discussion. Some interesting general theorems then follow at once.

Theorem (11·41). *In any enclosure entirely surrounded by hot electrodes all at the same temperature, the electron density at any point not too near the walls is independent of the material of the walls and proportional to the absolute temperature provided this temperature is sufficiently high.*

The electron density depends of course on the size and shape of the enclosure. Equation (810) provides an example.

Theorem (11·42). *For two similar enclosures at the same temperature, for which Theorem* (11·41) *holds, the electron density at corresponding points is inversely proportional to the square of the linear dimensions.*

Theorem (11·43). *The equilibrium state of the electron atmosphere is characterized by a minimum value of the ratio of the electrostatic energy to the kinetic energy of translation of the electrons.*

The proofs of these theorems are simple and are left to the reader*.

At fairly high temperatures and for not too small a $\bar{\nu}_a$ will be very large compared with $\bar{\nu}_0$. In that case near the emitter there is a large normal electrical stress (tension) and a large mechanical pressure which practically balance since $\bar{\nu}_0$ is trivial. Across a plane, however, normal to the emitting surface there is an electrostatic pressure numerically equal to the tension along the lines of force which therefore just doubles the usual pressure. These considerations will of course continue to hold for surfaces of reasonable curvature, not merely for the plane surfaces of a condenser.

The electron repulsions cause the electron atmosphere to behave near the surface like a surface film of negative surface tension. To examine this more exactly it is necessary to cast (817) into curvilinear coordinates suitable for the discussion of the immediate neighbourhood of the metal. If the curvature is small it is not difficult to show that equation (817) takes the form

$$\frac{\partial^2\psi}{\partial\delta^2}+\left(\frac{1}{R_1}+\frac{1}{R_2}\right)\frac{\partial\psi}{\partial\delta}=e^{\psi}, \qquad \ldots\ldots(820)$$

which is valid in the immediate neighbourhood of the surface if δ is the normal distance from the boundary reckoned positive into the enclosure and R_1 and R_2 are the principal radii of curvature of the boundary, reckoned positive when the centres of curvature lie outside the enclosure. Correct to terms of order $\left(\frac{1}{R_1}+\frac{1}{R_2}\right)$ this equation has a first integral

$$\frac{\partial\psi}{\partial\delta}=-\sqrt{2}\,e^{\frac{1}{2}\psi}-2\left(\frac{1}{R_1}+\frac{1}{R_2}\right)$$

of the correct form. On writing $\frac{1}{2}\psi=\log x$ this equation is easily integrated completely and the required solution is

$$\psi\sim-2\log\left\{\frac{1}{\sqrt{2}}\left(\frac{e^{\left(\frac{1}{R_1}+\frac{1}{R_2}\right)\delta}-1}{\frac{1}{R_1}+\frac{1}{R_2}}\right)\right\}. \qquad \ldots\ldots(821)$$

With the help of (816) equation (821) determines V and so $\bar{\nu}$ in the neighbourhood of any surface of moderate curvature. Equation (821) reduces

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* The reader may refer to von Laue, *loc. cit.*, for further information.

to (818) when $\frac{1}{R_1} + \frac{1}{R_2} \rightarrow 0$. For the further development of the properties of the quasi surface film of electrons we refer the reader to von Laue.

In all the foregoing discussion we have ignored the effects of the so-called *image forces* which will alter the distribution laws near the metal surface, so that our conclusions are only valid under conditions and in regions in which these image forces can be neglected. We return to a fuller consideration of this effect in § 11·8.

§ **11·5**. *Thermionic phenomena as surface or volume properties of the emitter.* We have so far considered the electrons of the assembly as belonging either to the interior of the hot metal or to the electron gas. From the point of view of statistical mechanics there are therefore just two sets of independent systems—free electrons and the metal crystals with a variable number of electrons; from the point of view of thermodynamics the assembly consists of two phases, gas and solid. We could, however, have included formally a third phase—the metal surface—which is perhaps the most important phase of all, since the thermionic emission is very sensitive to the surface properties of the metal and both A and b_0 in (794) vary in a marked manner with the nature of the surface film. We have also seen that the electron atmosphere builds a quasi-film of electrons in the gas phase. In view of these facts it therefore perhaps seems somewhat illogical to ignore the surface phase or statistically the "system" which consists of the metal surface in our discussion. This illogicality is only apparent, but the treatment remains perhaps physically unsatisfactory. That our procedure was not really illogical follows at once from the thermodynamic properties of the ξ's as partial potentials. The ξ of an electron pursues it through all systems in which it appears and in equilibrium

$$\xi_{\text{solid}} = \xi_{\text{surface}} = \xi_{\text{gas}}.$$

Thus we must get formally the correct result from $\xi_{\text{solid}} = \xi_{\text{gas}}$, although from a physical point of view the fundamental equation may rather be $\xi_{\text{surface}} = \xi_{\text{gas}}$. A change in the nature of the surface which changes ξ_{surface} directly reacts on the state of the electrons in the interior so that ξ_{solid} changes in harmony. The method adopted here is therefore correct so far as it goes and may be used in default of better and more direct ways of calculating ξ as ξ_{surface}, which are at present entirely lacking. A complete theory of the variation of the thermionic effect with variation of the surface film can (it is true) only be attempted when we have a reliable direct method of calculating ξ_{surface}*. A satisfactory beginning has, however, been made by Nordheim† by studying the laws of reflection of electrons in a film of steep potential gradient.

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[*] This point has recently been made by v. Raschevsky, *Zeit. für Phys.* vol. XXXIX, p. 159 (1926).

[†] Nordheim, *Zeit. für Phys.* vol. XLVI, p. 833 (1928).

§ **11·6**. *The emission of positive ions.* In certain cases incandescent solids have been observed to emit positive ions as well as electrons. It is therefore necessary to study the equilibrium theory of an atmosphere of a mixture of positive and negative ions and neutral atoms in equilibrium with the hot solid, which is a simple extension of the work of this chapter*. Theoretically, we must expect to have, for example, an atmosphere of electrons, tungsten ions and neutral tungsten atoms in equilibrium with the solid tungsten, and so on in all similar cases. Actually, the atmosphere in equilibrium with a pure metal will never contain a significant number of ions of that metal at any temperature (below the melting point of the metal) at which experiments can be carried out. The effects actually observed are due to the emission of ions of impurities contained in the metal. When spurious effects due to surface adsorption of gaseous layers have been eliminated the remaining effects are generally due to the emission of singly charged positive ions of the alkali metals. We will present the analysis in such a way that the positive ions are explicitly shown as due to an impurity. It will be sufficient to contemplate an atmosphere of electrons, one type of singly charged positive ion, and the corresponding neutral atom together with the impure solid. Metal atoms and ions will be assumed to be absent from the atmosphere. They can be added if required. In considering an atmosphere of ions, electrons and atoms in equilibrium we anticipate in a simple case the general discussion of Chapter XIV. We require here nothing beyond simple reinterpretations of Chapter V.

The formal expression for the number of weighted complexions of this assembly will be, generalizing (378),

$$C = \frac{N\,!\,P\,!\,Q\,!}{(2\pi i)^4}\iiiint \frac{dx\,dy\,dw\,dz}{x^{N+1}y^{P+1}w^{Q+1}z^{E+1}}\,K(x, y, w, z)$$
$$\times \exp\{xf(z) + yg(z) + xyh(z)\}, \quad \ldots\ldots(822)$$

where w and Q refer in the usual way to the metal atoms only present effectively in the crystal. N refers to electrons and P to positive ions. Then we have the usual formulae

$$\overline{N}_{\text{free}} = \xi f(\vartheta),\ \overline{P}_{\text{free}} = \eta g(\vartheta)\ \ \overline{NP}_{\text{free}} = \xi\eta\, h(\vartheta), \quad \ldots\ldots(823)$$

and from the fact that the electrons and the positive ions are effectively present in the solid

$$\xi = 1/\kappa_1(\vartheta),\ \ \eta = 1/\kappa_2(\vartheta). \quad \ldots\ldots(824)$$

We shall expect no alteration in form† for $\kappa_1(\vartheta)$ due to the impurity and only slight alterations in the magnitude of σ. We shall therefore still have

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[*] For a general account of the phenomena, see Richardson, *loc. cit.* The general thermodynamic theory of such atmospheres has been given by von Laue, *Berl. Sitz.* (1923), p. 334.

[†] The surface conditions may of course be such that we have an entirely different numerical value of χ.

(787), (789) or (790) for the density of free electrons in the atmosphere in the immediate neighbourhood of the metal. For $\kappa_2(\vartheta)$ we shall have the same *form* as for $\kappa_1(\vartheta)$, but the magnitude of σ may be entirely different. In fact, at the temperatures concerned it is reasonable to suppose that the specific heat of the solid is "normal" and has the value $3k$ per atom whether metal or impurity. We may go further in fact and assume with sufficient accuracy that $\sigma_2(T) = 3k$ over the whole temperature range for $T > T_0$. In that case

$$\exp\left\{-\int_0^T \frac{dT'}{kT'^2}\int_0^T \sigma\, dT''\right\} \sim \text{const.} \times T^{-3},$$

and

$$\bar{\nu}_+ = \frac{\bar{P}}{V} = \text{const. } T^{-\frac{3}{2}}\, e^{-\chi_2/kT}. \qquad \text{......(825)}$$

The constant is only determinable if more explicit assumptions can be made about $\kappa_2(\vartheta)$. If we may assume, for example, that adding an atom of the impurity to the solid is equivalent to adding a single three-dimensional harmonic oscillator of frequency of ν_0, the weight of all its states being $\kappa_2(0)$, then

$$\kappa_2(\vartheta) = \kappa_2(0)/(1 - e^{-h\nu_0/kT})^3,$$

$$\bar{\nu}_+ = \frac{\varpi_+}{\kappa_2(0)} \frac{(2\pi m_+ kT)^{\frac{3}{2}}}{h^3} (1 - e^{-h\nu_0/kT})^3\, e^{-\chi_2/kT}. \qquad \text{......(826)}$$

There is little point in expanding these formulae further in the absence of exact measurements to compare them with. We note only that if we measure the current carried by the positive ions, we should expect to find

$$I_+ = BT^{-1} e^{-\chi_2/kT}, \qquad \text{......(827)}$$

where B is a constant. We may note that the indices of T in (827) and (793) add up to 1 and the indices of T in (825) and (789) add up to zero. This will always be the case so long as we assume that the neutral atom in the metal has 3 practically classical degrees of freedom yielding 6 square terms and the ion and electron in the gas also 3 square terms each or 6 in all. Owing to the fact that we must assume that ionization and recombination are possible in the solid the product $\xi\eta$ or $\kappa_1(\vartheta)\,\kappa_2(\vartheta)$ must be the same as $\kappa(\vartheta)$, the corresponding function for the neutral atom in the solid. This secures the relation just mentioned.

By eliminating ξ and η between the three equations (823) we obtain

$$\frac{\overline{N}_{\text{free}}\overline{P}_{\text{free}}}{\overline{NP}_{\text{free}}} = \frac{f(\vartheta)\, g(\vartheta)}{h(\vartheta)}. \qquad \text{......(828)}$$

This is a particular case of the formulae for the ionization equilibrium of a gas at high temperature and is of course independent of properties of the solid phase. It is mentioned here because some beautiful thermionic measurements by Langmuir* have established the correctness of the theory

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* Langmuir and Kingdom, *Proc. Roy. Soc.* A, vol. CVII, p. 61 (1925).

as applied to the equilibrium between caesium atoms, ions, and electrons The simple form of (828), valid in the case to be discussed, is

$$\frac{\bar{\nu}_\epsilon \bar{\nu}_+}{\bar{\nu}_0} = \frac{\varpi_\epsilon \varpi_+}{\varpi_0} \frac{(2\pi mkT)^{\frac{3}{2}} (2\pi m_+ kT)^{\frac{3}{2}}}{h^3 (2\pi (m_+ + m) kT)^{\frac{3}{2}}} e^{-\chi_0/kT}, \qquad \ldots\ldots(829)$$

where ϖ_ϵ, ϖ_+ and ϖ_0 are the weights of the normal states of free electrons, positive caesium ions and neutral caesium atoms respectively and χ_0 is the ionization potential. Since $\varpi_\epsilon = \varpi_0 = 2$, $\varpi_+ = 1$, $\chi_0 = 3{\cdot}88$ electron volts and m is negligible compared with m_+, this reduces to

$$\frac{\bar{\nu}_\epsilon \bar{\nu}_+}{\bar{\nu}_0} = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} e^{-\chi_0/kT} = K_n, \qquad \ldots\ldots(830)$$

so that

$$\log_{10} K_n = 15{\cdot}385 + \tfrac{3}{2} \log_{10} T - \frac{19530}{T}. \qquad \ldots\ldots(831)$$

Langmuir's test of this equation proceeds as follows. He considers an enclosure in equilibrium with pure tungsten at 1200° K., containing caesium vapour at a measured pressure (ions plus atoms) of (say) 0·001 bar. The number of free electrons in equilibrium with tungsten at this temperature is deduced from the electron emission of pure tungsten by (793), taking $A = 60$. The actual value is 9·25 per cm.³ At this temperature $K_n = 5340$, so that $\bar{\nu}_+/\bar{\nu}_0 = 577$ according to theory. This means that practically all the caesium must be present as ions, which is what is observed, for it is found that above about 1200° K. the positive saturation current flowing to a collecting electrode in given caesium vapour is independent of the temperature of the tungsten, so that presumably above this temperature the tungsten converts every caesium atom that strikes it into an ion and emits only caesium ions at a rate naturally depending only on the caesium vapour density. On the other hand, with thoriated tungsten the equilibrium electron density is $6{\cdot}0 \times 10^7$ and $\bar{\nu}_+/\bar{\nu}_0 = 8{\cdot}9 \times 10^{-5}$. This means that only an insignificant fraction (1 in 11,000) of caesium atoms leaving the thoriated surface is an ion and no positive current should flow. None is observed.

By somewhat different arguments a rough quantitative test of (830) can be achieved. A pure tungsten filament was raised to 1177° K. in a bulb of caesium vapour at 70° C. at the vapour pressure of pure caesium for that temperature. The positive and negative ion currents were measured. The electron emission from the tungsten at 1177° K. was $2{\cdot}22 \times 10^{-6}$ amperes per cm.² and the positive ion emission $2{\cdot}06 \times 10^{-6}$. The electron emission is some 10^6 times greater than from pure tungsten at this temperature, so that we are really dealing with a caesiated tungsten surface. This, however, does not alter the arguments. On raising the filament temperature to 1300° K. or more the positive ion current increased to $2{\cdot}43 \times 10^{-3}$ and then remained independent of the filament temperature. This saturation current is therefore a measure of the rate at which caesium atoms and ions strike (and are emitted as ions from) the surface and corresponds to $1{\cdot}52 \times 10^{16}$ atoms or ions per sec. per cm.² At the lower filament temperature (1177° K.) the atoms still strike the filament at the same rate for the conditions in the vapour are unaltered, but the positive ion current is only 1/1180 of its saturation value. This means that of the caesium evaporating 1 in 1180 is an ion. The conditions at the surface of the filament are essentially the same as if it were surrounded by caesium vapour at 1177° K. and at such a concentration as to provide $1{\cdot}52 \times 10^{16}$ impacts per sec. per cm.² This concentration would be

$$\bar{\nu}_0 = 1{\cdot}40 \times 10^{12}.$$

If, then, the filament were in an enclosure at 1177° K. in equilibrium with this concentration of caesium it would emit electrons and caesium ions at the rates measured $2{\cdot}22 \times 10^{-6}$ and $2{\cdot}06 \times 10^{-6}$ respectively. From these observed currents the corresponding equilibrium concentrations are

$$\bar{\nu}_\epsilon = 2{\cdot}60 \times 10^6, \quad \bar{\nu}_+ = 1{\cdot}19 \times 10^9.$$

From these three values the observed value of the equilibrium constant is

$$K_n = 2210,$$

while the value calculated from (831) is

$$K_n = 2500.$$

This is excellent agreement. If we express it by examining what temperature makes K_n equal to its observed value we find $T = 1174°$ K. instead of 1177° K., a difference within the uncertainties of the temperature scale.

§ **11·7**. *Space charge effects with positive and negative ions.* The equations so far given for positive ions refer to assemblies of negligible space charge or to the immediate neighbourhood of the emitting surfaces. The general laws for the atmosphere can be studied by an extension of § 11·4. By § 8·7 the average electrostatic density and potential in the atmosphere ρ and V will satisfy the equations

$$\nabla^2 V = -4\pi\rho, \quad \rho = \epsilon\{-(\nu_\epsilon)_0 e^{\epsilon V/kT} + (\nu_+)_0 e^{-\epsilon V/kT}\}. \quad \ldots\ldots(832)$$

This is the *average* potential. In addition, there will be polarization fields round each positive and negative ion like those considered in § 8·8, which will give rise to small additional effects. These, however, are negligible unless the space charge is zero or very small, when they give rise to the only surviving terms in the electrostatic energy. They are probably never of importance here.

We observe first that

$$\nu_\epsilon \nu_+ = (\nu_\epsilon)_0 \, (\nu_+)_0,$$

and that ν_0 is unaffected by the electrostatic field. This is an example of the general theorem that if the condition of dissociative equilibrium is satisfied at any point of an atmosphere in equilibrium under long-range potentials, then it is in dissociative equilibrium everywhere. The equilibrium constant is independent of position. If we write

$$\alpha = \frac{kT}{2\epsilon} \log \frac{(\nu_+)_0}{(\nu_\epsilon)_0} \quad \left(\frac{\kappa}{kT} = 8\pi \sqrt{(\nu_\epsilon \nu_+)}\right), \qquad \text{......(833)}$$

the equation for V becomes

$$\nabla^2 V = \frac{\epsilon\kappa}{kT} \sinh \frac{\epsilon\,(V - \alpha)}{kT}. \qquad \text{......(834)}$$

We naturally only expect to be able to solve this explicitly (if at all) for plane parallel condensers or their equivalent. If, then, V depends only on x

$$\frac{d^2 V}{dx^2} = \frac{\epsilon\kappa}{kT} \sinh \frac{\epsilon\,(V - \alpha)}{kT}.$$

This can be integrated once giving

$$\left(\frac{dV}{dx}\right)^2 = 2\kappa \left[\cosh \frac{\epsilon\,(V - \alpha)}{kT} - A\right], \qquad \text{......(835)}$$

where A is a constant of integration. We may notice that κ has a very simple form. It satisfies

$$\kappa = 8\pi \sqrt{(p_\epsilon p_+)} = 8\pi \sqrt{(K_n p_0)}, \qquad \text{......(836)}$$

where K_n is the equilibrium constant and p_0 the partial pressure of the neutral atoms.

Equation (835) can be integrated completely in terms of Weierstrass's $\wp$-function. It can be integrated in finite terms with elementary functions when $A = 1$. This case will serve for the general study of the behaviour of V in the neighbourhood of the emitting surfaces, since there the argument of the cosh will in general be large. We then have

$$\frac{dV}{dx} = \pm\, 2\sqrt{\kappa} \sinh \frac{\epsilon\,(V - \alpha)}{2kT},$$

which integrates in the form

$$-\log\left\{\pm \tanh \frac{\epsilon\,(V - \alpha)}{4kT}\right\} = \frac{\epsilon\sqrt{\kappa}}{kT}\, x,$$

if x is measured from the emitting surface.

§ **11·8.** *Image forces**. Our treatment hitherto has been based on mean potentials and mean densities according to the analysis of § 8·7. But our averaging has been based only on averaging the electrons and ions in the gas phase of the assembly and not on averaging *all* the movable charges in the *assembly*. This latter of course would be the correct procedure and lead to an unexceptionable result for V. But such a procedure seems to be far

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* Based on von Laue, *loc. cit.* (twice), and Langmuir and Kingdom, *loc. cit.*

beyond our resources at present, and a correction is necessary for the polarizing effect of the individual ion on the neighbouring metal surface. If we assume, as seems reasonable, that the metal surface remains in the mean a surface of constant potential, then the polarizing effect is equivalent to the formation of the usual electrical image, and the ion will be attracted to the (plane) surface at a distance δ with a force $\epsilon^2/4\delta^2$, which is in addition to the force arising from the average potential V. Also, unlike V, the image force affects ions of either sign equally. Both are attracted to the metal.

The image force can be derived from a potential energy function $-\epsilon^2/4\delta$. We must suppose, therefore, that the correct atmospheric density law for electrons is

$$\bar{\nu}_\epsilon = (\bar{\nu}_\epsilon)_0 \, e^{[\epsilon(V-V_0)+\epsilon^2/4\delta]/kT}, \qquad \text{......(837)}$$

and for positive ions

$$\bar{\nu}_+ = (\bar{\nu}_+)_0 e^{[-\epsilon(V-V_0)+\epsilon^2/4\delta]/kT}. \qquad \text{......(838)}$$

The corresponding equation that V must satisfy is

$$\nabla^2 V = -4\pi\epsilon \left[-(\bar{\nu}_\epsilon)_0 e^{\epsilon(V-V_0)/kT} + (\bar{\nu}_+)_0 e^{-\epsilon(V-V_0)/kT}\right] e^{\epsilon^2/4\delta kT}. \qquad \text{......(839)}$$

We have not given a rigorous proof of these equations. As we have indicated, this could only come from a proper averaging treatment of all the movable charges, not only of those in the atmosphere. It seems clear, however, that the equations must be of this form, and that the true correction for the inadequate averaging will not be widely different from that proposed. Equation (839) of course follows logically from (837) and (838). The correction cannot hold good indefinitely as $\delta \to 0$. As soon as the specified electron gets within distances of the walls comparable with their departure from an ideal plane conducting surface the polarizing effect will depend on the nature of the surface, the roughness of its microstructure and so on, and finally will reduce to an effect on individual atoms. Thus the apparent infinity in the correcting factor is spurious and the formula suggested cannot hold for values of $\delta < 5 \times 10^{-8}$ cm., or perhaps 10^{-7} cm. Obviously at these distances the discussion fails altogether and we need only pay attention to greater values of δ.

For values of δ of the order of 10^{-4}, 10^{-5} cm. the correction has become quite insensible and our preceding results will hold unaltered. For on inserting numerical values we see that the extra term is

$$4{\cdot}15 \times 10^{-4}/\delta T.$$

At room temperatures ($T = 300°$ K.) this is entirely negligible for $\delta > 3 \times 10^{-5}$ and at the more usual thermionic temperatures of the order of 1000° K. when $\delta > 10^{-5}$. These are outside limits. Closer investigation shows that marked effects do not even extend so far. Consider for simplicity the case of atmospheres without positive ions. Ignoring the image effect we found in (815) that

$$V \sim -\frac{2kT}{\epsilon} \log \delta.$$

This was derived from an equation

$$\nabla^2 V = Ae^{\epsilon V/kT}$$

instead of from the equation

$$\nabla^2 V = Ae^{\epsilon V/kT + \epsilon^2/4\delta kT},$$

or, in other words, by neglecting $\epsilon^2/4\delta kT$ compared with $-2 \log \delta$. At 300° K. and $\delta = 10^{-6}$ these quantities are 1·4 and 27·6 respectively; for $\delta = 10^{-7}$, 14 and 30. At higher temperatures the main term is unaffected and the image effect proportionally less. We see, therefore, that it is only in the region less than 10^{-6} cm. from the wall that the image force will really alter the solutions already given and at the higher temperatures marked alterations are only caused near $\delta = 10^{-7}$ cm. It must be remembered of course that these neglected terms occur in an exponent and are not simply additive.

When there are positive ions as well the image forces can make much more marked qualitative differences, for they lead to the formation of a sheath of positive ions round the emitting surfaces which would be entirely absent were it not for this image effect. The image effect only alters the *ratio* of the concentrations of electrons and positive ions indirectly through its effect on V. The sign of any space charge will be unaltered.

Since all the image effects are confined to thin layers in the immediate neighbourhood of the emitting surfaces this layer may really be included in the "surface phase" from the point of view of thermodynamic or statistical treatment of volume effects. All our previous arguments are therefore unaffected, if by the "surface of the metal" we mean not so much the actual last fixed metallic atoms as the immediate outside of the surface film at about 10^{-5}, 10^{-6} cm. or so from the last metal atoms. The potential at some such point must then be taken to be the potential of the metal, and the differences of these potentials is the contact potential difference of two different emitters. The question then arises whether the work apparently done against the image forces in the surface layer of the atmosphere is to be included in χ. The answer of course is yes, but caution is required. If we consider two perfectly pure pieces of the same metal, one with a smooth and the other with a rough surface, the work done *in the atmosphere* against the image force would on the average be different for the two pieces. If there were no compensating effect such pieces of metal should have a contact potential difference which there is no evidence for and no reason to expect. There must therefore be some compensation in the surface layer *in the metal*, and it seems necessary to suppose, to avoid spurious contact potential differences, that the compensation is exact or at least that there is exact compensation for all variations due to the mechanical state of the surface*. The same argument for compensation of

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* These conclusions may have to be modified if we should include here the active centres of recent catalytic theories. See for example Constable, *Proc. Roy. Soc.* A, vol. CVIII, p. 355 (1925), vol. CX, p. 283 (1926).

mechanical states holds for any surface of given composition, whatever impurities are present in or adsorbed on the surface of the pure metal.

Let us summarize this discussion by recalling the complete laws for the equilibrium of the atmosphere which we have obtained.

Immediately outside the surface layer ($G\,(\vartheta)$ is the electron's partition function without the V-factor)

$$\bar{\nu}_\epsilon = (\bar{\nu}_\epsilon)_s = \frac{G_1\,(\vartheta)}{\kappa_1\,(\vartheta)}, \tag{840}$$

$$\bar{\nu}_+ = (\bar{\nu}_+)_s = \frac{G_2\,(\vartheta)}{\kappa_2\,(\vartheta)}. \tag{841}$$

The forms of G_1 and κ_1 are discussed in § 11·2 and of G_2 and κ_2 in § 11·6. Elsewhere, outside the surface layers

$$\bar{\nu}_\epsilon = (\bar{\nu}_\epsilon)_s e^{\epsilon(V-V_s)/kT}, \tag{842}$$

$$\bar{\nu}_+ = (\bar{\nu}_+)_s e^{-\epsilon(V-V_s)/kT}, \tag{843}$$

where V is an electrostatic potential satisfying

$$\nabla^2 V = 4\pi\epsilon\,(\bar{\nu}_\epsilon - \bar{\nu}_+). \tag{844}$$

Inside the surface layer at δ from the metal surface (844) continues to hold, but (842) and (843) are replaced by

$$\bar{\nu}_\epsilon = (\bar{\nu}_\epsilon)_s e^{\epsilon(V-V_s)/kT+\epsilon^2/4\delta kT}, \tag{845}$$

$$\bar{\nu}_+ = (\bar{\nu}_+)_s e^{-\epsilon(V-V_s)/kT+\epsilon^2/4\delta kT}. \tag{846}$$

It will be well to call attention to one last point. Inside the surface layer $\bar{\nu}_\epsilon\bar{\nu}_+$ is no longer constant, but

$$\bar{\nu}_\epsilon\bar{\nu}_+ = (\bar{\nu}_\epsilon)_s\,(\bar{\nu}_+)_s\,e^{\epsilon^2/2\delta kT}. \tag{847}$$

At the same time $\bar{\nu}_0$, the concentration of the neutral atoms, is unaffected by the image forces so that

$$\frac{\bar{\nu}_\epsilon\bar{\nu}_+}{\bar{\nu}_0} = \frac{(\bar{\nu}_\epsilon)_s\,(\bar{\nu}_+)_s}{\bar{\nu}_0}\,e^{\epsilon^2/2\delta kT} = K_n\,e^{\epsilon^2/2\delta kT}. \tag{848}$$

It might therefore be thought at first sight that the neutral atoms, ions and electrons are no longer in dissociative equilibrium inside the layer. It seems probable*, however, that this is not the case and that the equilibrium is still complete, the effect of the image forces being merely to decrease the work of dissociation χ by $\epsilon^2/2\delta$. Consider a quasi-Born cycle in which a neutral atom is taken from δ inside the layer to outside the layer, dissociated there (work χ required), brought back to the layer at δ as two ions (work $\epsilon^2/2\delta$ done) and there allowed to recombine (work χ' done). This is a reversible isothermal cycle, and we must therefore have

$$\chi = \chi' + \epsilon^2/2\delta \tag{849}$$

in agreement with (848) and the preceding argument.

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* Langmuir and Kingdom, *loc. cit.*

CHAPTER XII

THE DIELECTRIC AND DIA- AND PARAMAGNETIC CONSTANTS OF GASES

§ **12·1**. *The classical theory of the dielectric constant.* The theory of the dielectric constant of a gas is part of course of the theory of its refractivity, for the dielectric constant is the limit of the refractivity for very long wave lengths. The theory falls into two parts. In the first, which belongs to electromagnetic theory, we trace the connection between the applied electric force, the polarization and the total electric displacement in the medium, assuming that the medium consists entirely of molecules of some given type. In the second, which alone is statistical, we derive the connection between the electric force and the polarization when the molecules present are distributed in equilibrium in the field of force acting.

It is not necessary here to consider the details of the electromagnetic part of the theory†. Let Π be the (average) strength of the doublet produced in a single molecule by a field of electric force F. The main part of this will in simple cases be proportional and parallel to F and we have

$$\Pi = \theta^* F. \qquad \text{......(850)}$$

The calculation of θ^* forms the subject of the second (statistical) part of the theory. If there are N such molecules per unit volume, then the *polarization* P of the medium (doublet strength per unit volume) is given by

$$P = N\Pi = N\theta^* F. \qquad \text{......(851)}$$

The total electric force F acting on a single molecule is not however equal to the external electric force applied to the medium, but is reinforced by the effect of the polarization itself. It is shown in fact by Lorentz that the total electric force acting on any molecule is $F + \frac{4}{3}\pi P$ for any arrangement of the individual molecules with cubical symmetry. This result will therefore be valid for the random arrangements in a gas. We have therefore the equation

$$P = N\theta^* \left(F + \tfrac{4}{3}\pi P\right) \qquad \text{......(852)}$$

to combine with the equation

$$4\pi P + F = \epsilon F \qquad \text{......(853)}$$

defining the dielectric constant ϵ. From these equations we obtain the well-known law of Lorenz-Lorentz

$$\frac{\epsilon - 1}{\epsilon + 2} = \tfrac{4}{3}\pi N\theta^*. \qquad \text{......(854)}$$

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† See for example Lorentz, *The theory of electrons*, chap. IV; or Livens, *The theory of electricity*, § 237, ed. 1.

It is obvious at once that this extends to gaseous mixtures in the form

$$\frac{\epsilon - 1}{\epsilon + 2} = \tfrac{4}{3}\pi\Sigma_r N_r \theta_r^*. \qquad \text{......(855)}$$

If ϵ is replaced by μ^2, the square of the refractive index, then it can be shown similarly that μ^2 obeys an equation of the same form

$$\frac{\mu^2 - 1}{\mu^2 + 2} = \tfrac{4}{3}\pi\Sigma_r N_r \theta_r^*. \qquad \text{......(856)}$$

The function θ_r^* now of course depends on the molecular frequencies ν_r and on the frequency of the exciting radiation ν and (856) takes the form

$$\frac{\mu^2 - 1}{\mu^2 + 2} = \tfrac{4}{3}\pi\Sigma_r N_r \frac{f_r}{\nu_r^2 - \nu^2}. \qquad \text{......(857)}$$

All these formulae will be assumed to be familiar.

We now approach the statistical part of the problem. The chief interest at this stage lies in the calculation of θ^* rather than f. The result will depend on the particular assumption made as to the structure of the molecules. It was first shown by Debye† that the facts are satisfactorily accounted for, for a large variety of gases, if we assume that the gas molecules are rigid dipoles of approximately constant electric moment and in addition have ordinary polarizable isotropic electronic structures. On this assumption the classical theory of θ^* proceeds as follows.

Consider as the model molecule a rigid solid of revolution without axial spin, of moment of inertia A free to turn about its centre of mass, with an electric doublet of strength α directed along its axis of symmetry. Let the body be subject to an electric field intensity F. Then the Hamiltonian function for the motion of the rigid body is

$$H = \frac{1}{2A}\left(p_\theta^2 + \frac{1}{\sin^2\theta} p_\phi^2\right) - \alpha F \cos\theta.$$

The angle θ is so measured that $\theta = 0$ when the positive direction of the dipole points along the field of force F. The partition function for the rotations and orientations of such molecules will therefore be

$$\begin{aligned} R(T) &= \frac{1}{h^2}\iiiint \exp\left[-\frac{1}{kT}\left\{\frac{1}{2A}\left(p_\theta^2 + \frac{1}{\sin^2\theta} p_\phi^2\right) - \alpha F\cos\theta\right\}\right] dp_\theta dp_\phi d\theta d\phi, \\ &= \frac{2\pi A kT}{h^2}\, 2\pi\int_0^\pi \exp\left(\frac{\alpha F\cos\theta}{kT}\right)\sin\theta\, d\theta, \qquad \text{......(858)} \\ &= \frac{8\pi^2 AkT}{h^2}\frac{\sinh(\alpha F/kT)}{\alpha F/kT}. \qquad \text{......(859)} \end{aligned}$$

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† Debye, *Phys. Zeit.* vol. XIII, p. 97 (1912).

The fraction of molecules with their coordinate θ between θ and $\theta + d\theta$ will therefore be

$$\frac{\exp\left(\dfrac{\alpha F\cos\theta}{kT}\right)\sin\theta\,d\theta}{\displaystyle\int_0^\pi \exp\left(\dfrac{\alpha F\cos\theta}{kT}\right)\sin\theta\,d\theta}. \qquad \text{......(860)}$$

The average polarization $\vartheta^* F$ is the resolved part of α along the direction of the field averaged over all molecules distributed according to (860), and is therefore given by

$$\theta^* = \frac{\dfrac{\alpha}{F}\displaystyle\int_0^\pi \exp\left(\dfrac{\alpha F\cos\theta}{kT}\right)\cos\theta\sin\theta\,d\theta}{\displaystyle\int_0^\pi \exp\left(\dfrac{\alpha F\cos\theta}{kT}\right)\sin\theta\,d\theta},$$

$$= \frac{kT}{F^2}\left[\frac{\alpha F}{kT}\coth\frac{\alpha F}{kT} - 1\right]. \qquad \text{......(861)†}$$

In all or nearly all practical cases $\alpha F/kT$ is very small, so that this reduces to

$$\theta^* = \tfrac{1}{3}\frac{\alpha^2}{kT}. \qquad \text{......(862)}$$

The coefficient $\tfrac{1}{3}$ arises as the average value of $\cos^2\theta$ over a sphere.

Two restrictions in the foregoing account are easily removed. We have first to introduce a term for the polarizability of the electronic structure of the molecule. This obviously might depend on the orientation θ, ϕ, and we should then have the Hamiltonian function

$$H = \frac{1}{2A}\left(p_\theta{}^2 + \frac{1}{\sin^2\theta}p_\phi{}^2\right) - \alpha F\cos\theta - \tfrac{1}{2}\beta(\theta, \phi) F^2,$$

and the polarization $\alpha\cos\theta + \beta(\theta, \phi) F$ instead of $\alpha\cos\theta$. We therefore find for the average polarization

$$\theta^* = \frac{\dfrac{1}{F}\displaystyle\int_0^\pi\int_0^{2\pi} \exp\left(\dfrac{\alpha F\cos\theta + \frac{1}{2}\beta F^2}{kT}\right)(\alpha\cos\theta + \beta F)\sin\theta\,d\theta\,d\phi}{\displaystyle\int_0^\pi\int_0^{2\pi} \exp\left(\dfrac{\alpha F\cos\theta + \beta F^2}{kT}\right)\sin\theta\,d\theta\,d\phi}.$$

The leading terms reduce to

$$\theta^* = \tfrac{1}{3}\frac{\alpha^2}{kT} + \bar{\beta}, \qquad \text{......(863)}$$

where

$$\bar{\beta} = \frac{1}{4\pi}\int_0^\pi\int_0^{2\pi}\beta\sin\theta\,d\theta\,d\phi.$$

Secondly it is obviously unnecessary to restrict ourselves to a rigid body with an axis of symmetry without axial spin. Any rigid body with moments of inertia A, B, C, spinning in any manner, may be considered,

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† This formula is more familiar in the theory of paramagnetism and is there due to Langevin, *Jour. de Phys.* ser. 4, vol. IV, p. 678 (1905). See also § 12·7.

which contains an electric doublet fixed in it and is also of polarizable structure. We shall equally obtain (863)*. Thus the general classical result is

$$\frac{\epsilon - 1}{\epsilon + 2} = \tfrac{4}{3}\pi N\left(\tfrac{1}{3}\frac{\alpha^2}{kT} + \bar{\beta}\right). \qquad \ldots\ldots(864)$$

The contributions of different molecular species on the right are additive.

§ **12·2**. *Comparison with experiment.* The formulae of § 12·1 were compared with experiment with marked success by Debye†, and in recent times excellent new comparisons have been rendered possible by the observations of Zahn‡. It is obvious that the classical theory cannot be correct at very low temperatures, but the quantum theory agrees, as we shall see, with (864) at temperatures covering all observations.

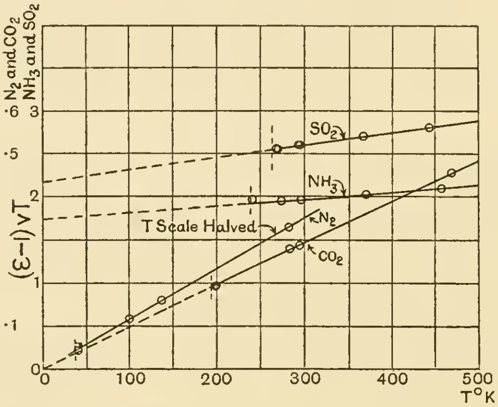

Fig. 19. The analysis of dielectric constants by Debye's equation.

In observations on gases ϵ is very nearly unity and therefore very accurate observations of ϵ are required to establish the value of $\epsilon - 1$ with satisfactory precision. The necessary accuracy can be obtained by the use of the modern technique of oscillating circuits. The variation of capacity of a condenser containing the gas under observation as dielectric is detected and measured by its effect on the electrical beats of two high frequency circuits slightly out of tune. In analysis of the observations $\epsilon + 2$ can be taken to be equal to 3. Referring to (864) we see that

$$(\epsilon - 1)\, T/N = 4\pi\left(\tfrac{1}{3}\frac{\alpha^2}{k} + \bar{\beta}T\right),$$

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* This case and still more general classical cases are discussed by Van Vleck, *Phys. Rev.* vol. XXX, p. 31 (1927), especially § 6.

† Debye, *loc. cit.*

‡ Zahn, *Phys. Rev.* vol. XXIV, p. 400 (1924); *ibid.* vol. XXVII, p. 329 (1926); Smyth and Zahn, *Jour. Amer. Chem. Soc.* vol. XLVII, p. 2501 (1925). See also K. Compton, *Science*, vol. LXIII, p. 53 (1926).

or in terms of gas pressure

$$(\epsilon - 1)\, T^2 = \frac{4\pi p}{k}\left(\frac{1}{3}\frac{a^2}{k} + \bar{\beta} T\right). \qquad \text{......(865)}$$

We therefore plot $(\epsilon - 1)\, T^2$ or better $(\epsilon - 1)\, vT$, where v is the specific volume, against the temperature and expect to find a straight line whose slope determines $\bar{\beta}$ and whose intercept on the axis of $(\epsilon - 1)\, vT$ the value of a. The principal interest centres in a. The polarizability $\bar{\beta}$ can also be directly determined in this way, but better and more generous information is provided by refractivities.

Fig. 19, taken from K. Compton*, shows typical examples of such plots, which are excellent straight lines, and Table 40 shows the values of dipole moments for a variety of gases so determined.

TABLE 40.

Dipole moments of gaseous molecules from Debye's equation.

Gas	$a \times 10^{18}$	Gas	$a \times 10^{18}$	Gas	$a \times 10^{18}$
HCl	1·03	H_2O	1·87	CH_4	0·00
HBr	0·79	C_2H_2	0·00	CH_3Cl	1·97
HI	0·38	C_2H_4	0·00	CH_2Cl_2	1·59
NH_3	1·44 [1·53]	C_2H_6	0·00	$CHCl_3$	0·95
PH_3	0·55	aC_2H_8	0·37	CCl_4	0·00
AsH_3	0·15	N_2	0·00	NO	—
SO_2	1·61	CO_2	0·06	—	—

An elaborate summary of recent work is given by Blüh, *Phys. Zeit.* vol. XXVII, p. 226 (1926), supplementing Debye, *Handbuch der Radiologie*, vol. VI (1924). These values are from K. Compton, *loc. cit.*, except AsH_3, PH_3 and NH_3 [ ] which are from Watson, *Proc. Roy. Soc.* A, vol. CXVII, p. 43 (1927), and the group CH_4–CCl_4 from Sänger, *Phys. Zeit.* vol. XXVII, p. 556 (1926).

The large value for water vapour confirms and in fact demands the triangular model for this molecule which we have already accepted in Chapter III. The small but definitely non-zero value for carbon dioxide confirms the slightly bent model of Dennison also used in that chapter.

Formula (864) in its complete form also applies fairly successfully to many liquids†, though for these a more elaborate theory of the effect of neighbouring molecules may be necessary.

§ **12·3**. *Thermodynamic relations and the approach to the quantum theory of dielectric polarization*‡. We have so far presented the theory of dielectrics in the most familiar way, but there is much to be gained by a more general thermodynamic treatment. We recall that $R\,(T)$ is a partition function and as such equivalent to a thermodynamic potential, and all relevant

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* K. Compton, *loc. cit.*

† Debye, *loc. cit.*

‡ This section is based on Debye, *Phys. Zeit.* vol. XXVII, p. 67 (1926).

molar equilibrium properties, for example P, should be derivable from $R(T)$ by differentiation. Comparing (859) and (861) we see at once that

$$P = N\theta^* F = NkT \frac{\partial}{\partial F} \log R(T). \qquad \text{......(866)}$$

This equation is not merely true in this particular case but is perfectly general. It is simple to give a general proof of (866) similar to the proof of (336) for $\overline{Y}$ which holds for quantized or (in the limit) equally for classical systems. For if the N systems are distributed among a set of possible states of unperturbed energies ϵ_u and if α_u is the average dipole moment of the state u in the specified direction of F, then the perturbation energy is $-\alpha_u F$ and

$$P = \Sigma_u \overline{a_u} \alpha_u = \xi \Sigma_u \varpi_u \alpha_u \vartheta^{\epsilon_u - \alpha_u F}.$$

Since
$$\xi = N/f(\vartheta), \quad f(\vartheta) = \Sigma \varpi_u \vartheta^{\epsilon_u - \alpha_u F},$$

$$P = \frac{N}{\log 1/\vartheta} \frac{\partial}{\partial F} \log f(\vartheta), \qquad \text{......(867)}$$

which is (866). Only the orientational part of $f(\vartheta)$ will be relevant. The extra energy of the molecules is given at once as $-\overline{P}F$ by the usual formula $\vartheta \partial \log f(\vartheta)/\partial\vartheta$. The extended formula (863) can be obtained in the same way by retaining also corrections to ϵ_u of order F^2.

It is next necessary to examine in detail the form of (867) in the most general case required, namely with

$$f(\vartheta) = \Sigma_u \varpi_u \vartheta^{\epsilon_u - \alpha_u F - \frac{1}{2}\beta_u F^2}. \qquad \text{......(868)}$$

We may suppose that the terms in F have had the effect of breaking up a set of degenerate states of the same energy into less degenerate sets of different energies, and write

$$f(\vartheta) = \Sigma_j \vartheta^{\epsilon_j} (\Sigma_s \varpi_s \vartheta^{-\alpha_s F - \frac{1}{2}\beta_s F^2}). \qquad \text{......(869)}$$

We may suppose further that $\alpha_s F + \frac{1}{2}\beta_s F^2$ is so small that only the lowest order terms need be retained so that

$$f(\vartheta) = \Sigma_j \vartheta^{\epsilon_j} (\Sigma_s \varpi_s + \log 1/\vartheta\, F \Sigma_s \alpha_s \varpi_s$$
$$+ \tfrac{1}{2}F^2 \{(\log 1/\vartheta)^2 \Sigma_s \varpi_s \alpha_s^2 + \log 1/\vartheta\, \Sigma_s \varpi_s \beta_s\}).$$

In this equation we may replace $\Sigma_s \varpi_s$ by ϖ_j the weight of the jth degenerate state, and $\Sigma_j \varpi_j \vartheta^{\epsilon_j}$ by $f_0(\vartheta)$ the partition function for zero external field. We may also suppose that

$$\Sigma_s \alpha_s \varpi_s = 0. \qquad \text{......(870)}$$

If (870) were not true, there would be a polarization effect independent of field strength;—no such effect is known, or predicted either by the classical or quantum theory of the effect. Then

$$f(\vartheta) = f_0(\vartheta) + \tfrac{1}{2}F^2 \Sigma_j \vartheta^{\epsilon_j} \{(\log 1/\vartheta)^2 \Sigma_s \varpi_s \alpha_s^2 + \log 1/\vartheta\, \Sigma \varpi_s \beta_s\}, \quad \text{...(871)}$$

$$P = \frac{NF}{f_0(\vartheta)} \Sigma_j \vartheta^{\epsilon_j} \{\log 1/\vartheta\, \Sigma_s \varpi_s \alpha_s^2 + \Sigma_s \varpi_s \beta_s\}. \qquad \text{......(872)}$$

It is easy to recover the classical formula from (872) for classically $\alpha_s = \alpha \cos\theta$ and $\Sigma_s \varpi_s \cos^2\theta = \frac{1}{3}\varpi_j$ so that

$$P = \frac{NF}{f_0(\vartheta)} \Sigma_j \varpi_j \vartheta^{\epsilon_j} \{\tfrac{1}{3}\alpha^2 \log 1/\vartheta + \bar{\beta}\} = NF\left\{\tfrac{1}{3}\frac{\alpha^2}{kT} + \bar{\beta}\right\},$$

as before, α and $\bar{\beta}$ being assumed independent of j.

In the quantum theory the classical "states" that have appeared in the foregoing calculations are of course regrouped into the true quantum states. We must not expect all the details of the classical calculation to be repeated, and in fact we shall find that in the quantum theory it may be that $\alpha_s = 0$ and the whole effect comes from β. All we can demand is that for large T the quantum theory shall agree with (864). Being a second and not a first order effect the older quantum theory never succeeded in giving a correct account satisfying the limiting condition, and we must use the correct modern theory.

§ **12·4**. *Application of the modern quantum theory**. It is never possible in this monograph to give the detailed solutions of quantum-mechanical problems whose results we require for statistical applications. It would be necessary, especially in the case of the modern theory, to develop the solution at far too great a length and we must reluctantly content ourselves with quoting results, or with very brief summaries of arguments in wave or matrix form as may be convenient.

The unperturbed energies of the simple rotator without axial spin are (as already quoted in Chapter II)

$$\epsilon_j = \frac{h^2}{8\pi^2 A} j(j+1) \quad (j = 0, 1, 2, \ldots), \qquad \ldots\ldots(873)$$

and the weights of these states are $2j+1$. The $(2j+1)$ characteristic functions satisfying Schrödinger's equation and corresponding to the jth state are the familiar spherical harmonics†

$$\psi_{j,s} = P_j^s(\mu) \begin{matrix}\cos \\ \sin\end{matrix} s\phi \quad (\mu = \cos\theta) \ (0 \leqslant s \leqslant j).$$

We can now proceed to find the values of ϵ_j when perturbed by an external field F, in which the rigid dipole α has a potential energy $-\alpha F\mu$. It is at

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* Correct versions have been given by Mensing and Pauli, *Phys. Zeit.* vol. XXVII, p. 509 (1926), Kronig, *Proc. Nat. Acad. Sci.* vol. XII, pp. 488, 608 (1926), in abstract by Van Vleck, *Nature*, Aug. 14, 1926, and Manneback, *Phys. Zeit.* vol. XXVIII, p. 72 (1927). The solution of the underlying problem of the free rotator or the symmetrical top in the matrix or wave mechanics will be found in Oppenheimer, *Proc. Camb. Phil. Soc.* vol. XXIII, p. 327 (1926), Mensing, *Zeit. für Phys.* vol. XXXVI, p. 814 (1926), Dennison, *Phys. Rev.* vol. XXVIII, p. 318 (1926), Reiche, *Zeit. für Phys.* vol. XXXIX, p. 444 (1926). More recently a general proof of the Langevin-Debye formula applying to a wide range of molecular models has been given by Van Vleck, *Phys. Rev.* vol. XXIX, p. 727 (1927); vol. XXX, p. 31 (1927).

† Schrödinger, *Ann. der Phys.* vol. LXXIX, p. 489 (1926) (esp. p. 520).

once obvious that there is no first order change in energy for any state, because (after Schrödinger's perturbation theory) the first order energy changes are linear combinations of the integrals

$$\int_{-1}^{+1}\int_{0}^{2\pi} \psi_{j,s}\psi_{j,s'}\mu\, d\mu\, d\phi.$$

These all vanish when $s \neq s'$ owing to the ϕ integration and, when $s = s'$,

$$\int_{-1}^{+1} \mu\, \{P_j^s(\mu)\}^2\, d\mu$$

always vanishes because $\{P_j^s(\mu)\}^2$ is an even function of μ. All the integrals therefore vanish and *there are no first order changes in the energy*. This is in agreement with observation on the infra-red bands of HCl. These show no linear Stark effect[†].

The quadratic terms have also been evaluated[‡]. It is found at once that for the possible values $0 \leqslant s \leqslant j$

$$\beta_s = \frac{8\pi^2 A\alpha^2}{h^2}\, \frac{3s^2 - j(j+1)}{j(j+1)(2j-1)(2j+3)} \quad (j \neq 0), \qquad \text{......(874)}$$

$$\beta_0 = \frac{8\pi^2 A\alpha^2}{3h^2} \quad (j = s = 0). \qquad \text{......(875)}$$

[In the limit of large quantum numbers this goes over into the form

$$\beta_s \sim \frac{4\pi^2 A\alpha^2}{h^2 j^2}\left(\frac{3s^2}{2j^2} - \tfrac{1}{2}\right), \qquad \text{......(876)}$$

which is the classical result for a dipole rotating with total angular momentum $jh/2\pi$ and a resolved momentum $sh/2\pi$ about the direction of the field.]

The degeneracy has not been completely resolved. There are two states of equal energy when $s \neq 0$ and only one when $s = 0$. Therefore $\varpi_s = 2$, $s \neq 0$, and $\varpi_0 = 1$, from which it follows that

$$\Sigma_s \varpi_s \beta_s = 0 \quad (j \neq 0), \qquad \text{......(877)}$$

since

$$\sum_{s=-j}^{s=+j} \{3s^2 - j(j+1)\} = 0. \qquad \text{......(878)}$$

It follows at once that

$$\theta^* = \frac{3}{4\pi}\, \frac{\epsilon - 1}{\epsilon + 2}\, \frac{1}{N} = \frac{8\pi^2 A\alpha^2}{3h^2}\, \frac{1}{f_0(\vartheta)}. \qquad \text{......(879)}$$

In this account we have of course treated *rigid* dipoles. There will still be an extra approximately constant term arising from the distortion of the electronic structures, and we therefore write the complete formula for *rigid polarizable dipoles without axial spin*

$$\theta^* = \frac{3}{4\pi}\, \frac{\epsilon - 1}{\epsilon + 2}\, \frac{1}{N} = \frac{8\pi^2 \mathrm{A}\alpha^2}{3h^2}\, \frac{1}{f_0(\vartheta)} + \overline{\beta}. \qquad \text{......(880)}$$

[†] Barker, *Astroph. Jour.* vol. LVIII, p. 201 (1923).

[‡] Kronig or Mensing and Pauli, *loc. cit.* Both authors calculate the average electric moment parallel to F rather than the energy term, but the analysis is of course equivalent.

The value of $f_0(\vartheta)$ or

$$\sum_{j=0}^{\infty} (2j+1)\, e^{-\sigma j(j+1)} \quad \left(\sigma = \frac{h^2}{8\pi^2 AkT}\right)$$

has already been given in § 3·3. For sufficiently large T

$$f_0(\vartheta) = \frac{1}{\sigma} = \frac{8\pi^2 AkT}{h^2},$$

with a numerical error about $\frac{1}{3}\sigma$ of this. Thus on substituting for $f_0(\vartheta)$ in (880) we recover the classical value. The error in the classical value for the temperatures of Zahn's and similar experiments is at most of the order of 0·5 per cent. and so insensible.

The quantum theory of gaseous dielectric polarization contains the remarkable feature that only molecules in their quantum states $j = 0$ contribute to the polarization. This has a strict classical analogy as has been pointed out by Pauli*. If we group together all orbits of equal classical moment of momentum $jh/2\pi$ and average classically *by integration* over all orientations the average value of s^2/j^2 is $\frac{1}{3}$ and the average value of β_s is still zero. Thus classically all *rotating* molecules make no contribution. The sole contribution comes from those few molecules which execute small vibrations about a position of rest.

§ **12·5**. *The isotropic character of the dielectric constant.* We have so far considered that the direction of the electric field itself serves to define a definite origin of spherical polar coordinates for the molecules. The electrical effects are however second order and small at that, and a small magnetic field may have an overriding orientational effect. Whatever the relative directions of the electric and magnetic fields the first order electric effect vanishes ($\alpha_s = 0$) as before. To see this it is only necessary to verify that

$$\int_{-1}^{+1}\int_0^{2\pi} \cos\gamma\, \psi_{j,s}\psi_{j,s'}\, d\mu\, d\phi = 0 \quad (\textit{all } s, s'),$$

where $$\cos\gamma = \cos\theta\cos\chi + \sin\theta\sin\chi\cos\phi$$

and χ is the angle between the electric and magnetic fields. The quadratic effect β_s will continue to be given by (874) when the direction s of the electric and magnetic fields coincide. When they do not a different value might perhaps be expected, but if they are at right angles the same values of β_s and β_0 are found as before. Thus the response to the electric field is exactly the same whether the molecules are orientated along or across the field, and therefore, as easily follows, *in whatever direction they are orientated or even if their precessional axes are not orientated at all but distributed uniformly in all directions*. This result of course only holds neglecting terms

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* Pauli, *Zeit. für Phys.* vol. VI, p. 319 (1921).

depending on H the strength of the orientating magnetic field. It implies in accordance with observation that there is no magnetic double refraction for long waves independent of the strength of the magnetic field. Similar arguments show that such double refraction must be absent for all wave lengths.

The model treated in this section represents adequately the halogen hydrides and probably N_2, and the conclusions of the theory apply directly to these gases. The results are however far more general as we shall see in § 12·61.

§ **12·6**. *More complex molecules. The symmetrical top model*†. For other molecules a more complicated model is essential and the necessary analysis can be carried through for the symmetrical rigid top. We may assume, in accordance with the symmetry, that the dipole moment lies along the axis of symmetry, and shall indicate the calculations for the case in which the electric field itself removes the degeneracy. The system is then characterized by three quantum numbers j, r, s, of which s defines the (trivial) precession of the resultant angular momentum about the field. The unperturbed energies (neglecting this precession) are

$$\epsilon_{j,r} = \frac{h^2}{8\pi^2}\left\{\frac{1}{A} j (j+1) + \left(\frac{1}{C} - \frac{1}{A}\right) r^2 + \text{const.}\right\}, \quad \text{......(881)}$$

the subsidiary quantum numbers r and s are subject to its restrictions $| r | \leqslant j$, $| s | \leqslant j$. It is then found that

$$\alpha_{r,s} = \frac{rs}{j (j+1)} \alpha, \quad \text{......(882)}$$

$$\beta_{r,s} = -\frac{8\pi^2 A \alpha^2}{h^2}\left\{\frac{(j^2 - r^2)(j^2 - s^2)}{j^3 (2j-1)(2j+1)} - \frac{\{(j+1)^2 - r^2\}\{(j+1)^2 - s^2\}}{(j+1)^3 (2j+1)(2j+3)}\right\}. \quad \text{......(883)}$$

The degeneracy is fully resolved and $\varpi_s = 1$. Substituting in (872), remembering that Σ_j and ϵ_j are now $\Sigma_{j,r}$ and $\epsilon_{j,r}$, we find $\Sigma_s \varpi_s \alpha_s = 0$, as it must, and

$$\theta^* = \frac{\alpha^2}{f_0(\vartheta)} \Sigma_{j,r}\, \vartheta^{\epsilon_{j,r}} \left\{\log 1/\vartheta \frac{r^2 (2j+1)}{3j (j+1)} + \frac{8\pi^2 A}{h^2} \frac{r^2 (2j+1)}{3j^2 (j+1)^2}\right\}. \quad \text{......(884)}$$

We notice that the polarization is contributed quite differently for this model and that for which $r = 0$. There are linear terms as well as quadratic—there should be a linear Stark effect on all states except those for which $r = 0$. We notice also that when $r = 0$ (884) reduces to (879), the only contribution arising when $j = 0$ also, and then only from the quadratic terms.

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† Kronig, *loc. cit.* (2).

To find the limiting form of θ^* for large T we replace the sums by integrals in the usual manner. With the abbreviations

$$\sigma = \frac{h^2}{8\pi^2 AkT}, \quad \tau = \frac{h^2}{8\pi^2 kT}\left(\frac{1}{C} - \frac{1}{A}\right),$$

the sum in the numerator is

$$\frac{1}{3kT}\int_0^\infty e^{-\sigma j(j+1)}\left\{\frac{2j+1}{j(j+1)} + \frac{1}{\sigma}\frac{2j+1}{j^2(j+1)^2}\right\} dj \int_{-j}^{+j} e^{-\tau r^2} r^2 dr,$$

and in the denominator

$$\int_0^\infty e^{-\sigma j(j+1)}(2j+1)\,dj \int_{-j}^{+j} e^{-\tau r^2}\,dr.$$

These can be simplified by integration by parts to the forms

$$\frac{1}{3kT}\frac{2}{\sigma}\int_0^\infty e^{-\sigma j(j+1)-\tau j^2}\frac{j}{j+1}\,dj$$

and

$$\frac{2}{\sigma}\int_0^\infty e^{-\sigma j(j+1)-\tau j^2}\,dj.$$

Since σ and τ are small the important parts of the former of these integrals arises for large j and $j/(j+1) \sim 1$. Their ratio is therefore $1/3kT$, and we find again the classical result

$$\theta^* = \frac{\alpha^2}{3kT},$$

to which a constant deformation term may be added.

§ **12·61**. *General theory of a complex molecule carrying a permanent dipole*†. In view of §§ 12·4, 12·6 which lead to the same result, the Langevin-Debye formula, for different models by entirely different routes, it is natural to suppose that this result is of great generality for ordinary temperatures, as it is in the classical theory. This has now been proved by Van Vleck to be a simple consequence of the summation rules, and the spectroscopic stability rules of the quantum mechanics, that hold quite generally for those molecular systems which when unperturbed have orientational degeneracy. We can hardly digress here sufficiently far to give an adequate account of Van Vleck's proof, though it is in fact quite simple, and must be content with a precise statement of his result and a discussion of its consequences.

In order that the Langevin-Debye formula should hold for sufficiently large T it is only necessary to assume that the dipole carrier (atom or molecule) has a "permanent" electric (or magnetic) dipole moment which is the same for all the group of normal states, and that these normal states have energy steps from one to the next among themselves small compared with kT, or in other words that the precessional frequencies of *all* the

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† This section describes the results of Van Vleck, *loc. cit.*

moments of momenta in the normal state are small compared with kT/h. At the same time this group of normal states must be separated from all other (excited) states by energy steps large compared with kT. These conditions are usually strictly complied with by all simple atoms and molecules. When they are complied with it does not matter whether the normal atom is originally strictly degenerate or already perturbed by a field of any strength weak enough for *second* order perturbations to be neglected. It is unnecessary to specify precisely the degree of complication of the normal group of states. The group may be built up by the composition of any number of moments of momenta with *slow* rates of precession, so that the proof applies equally to rigid molecules, and to molecules in which the orbital and electronic moments of momenta play an important part. Under these conditions formula (863) for θ^* will still be true, α and $\overline{\beta}$ being independent of the direction of the field even when another field in some other direction is already orientating the molecules. In short α and $\overline{\beta}$ are independent of the degeneracy and of the manner in which it is removed. We obtain the same value for θ^* for any type of spatial quantization or if there is no spatial quantization at all. All the molecules in Table 40 are covered by Van Vleck's theorem, and the dipole moments may be legitimately deduced in the manner of § 12·2.

The general proof includes a proof that both terms in the dielectric constant of a gas are independent of the effect of a magnetic field H so far as first order terms in H are concerned. This is in agreement with observation. It has been shown that θ^* for He, O_2 and air changes by less than 10, 0·4, 0·4 per cent. respectively in fields up to 8000 gauss, and for NO and HCl by less than 8 per cent. and 1 per cent. up to 4800 gauss†. There might be an effect depending on H^2 observable only in very large fields, but this has not been investigated either theoretically or experimentally.

These generalities also hold in general for the refractive index just as for the dielectric constant.

In Van Vleck's proof and the foregoing discussion it is assumed that a relation equivalent to (870) holds in general, even when there is an already existing magnetic field. It is conceivable that cases might exist of a kind of magneto-electric directive effect in which the equivalent of (870) fails. There would then be a state of electric polarization produced by a magnetic field and *vice versa*. The energy term concerned is still really quadratic in the perturbations. It is of type HF, but linear therefore in H and F. The foregoing theory would continue to hold in such cases, but only for the additional polarization produced by the electric field itself. The effect could only be found with molecules which possess permanent

† Weatherby and Wolf, *Phys. Rev.* vol. XXVII, p. 769 (1926); Mott-Smith and Daily, *Phys. Rev.* vol. XXVIII, p. 976 (1926). To reach even these accuracy limits requires of course extreme accuracy of measurement of ϵ; 1 in 500,000 for He, O_2, 1 in 100,000 for NO, HCl.

non-zero electric and magnetic moments which are more or less rigidly bound together and not at right angles to each other, so that the orientation of one produces a net orientation of the other*. There is no known example of such a gas, though the effect might be expected for NO†.

A sufficient formal example of the nature of the effect is provided by the classical rigid rotator of § 12·1 with both an electric doublet of strength α and a magnetic doublet of strength μ along its axis of symmetry, in parallel fields F and H. Then the rotational partition function is an obvious extension of (889), namely

$$R(T) = \frac{8\pi^2 AkT}{h^2} \frac{\sinh\{(\alpha F + \mu H)/kT\}}{(\alpha F + \mu H)/kT}. \qquad \text{......(885)}$$

Using (867) and retaining only the largest terms, the polarization P is given by

$$P = \frac{N\alpha\mu H}{3kT}. \qquad \text{......(886)}$$

A simple extension of this result to a model in which the electric and magnetic dipoles are fixed in any directions in the rotator making an angle χ with each other leads to

$$P = \frac{N\alpha\mu\cos\chi\, H}{3kT}. \qquad \text{......(887)}$$

The explanation of the absence of this effect in NO is interesting. An explanation by assuming that $\cos\chi = 0$ is impossible, for the dipole moment must lie along the figure axis, and it is almost certain from the evidence of the band spectrum that the orbital moment of momentum and therefore the magnetic moment has an axial component. The proper explanation probably is that NO molecules are of two kinds, right- and left-handed, of equal energies and therefore of equal concentrations, so that for half of them the axial component of μ is parallel to α and for the other half anti-parallel.

§ **12·7**. *Para- and diamagnetism of gases and of ions in solution.* The foregoing theory can of course be transferred bodily from electric to magnetic effects and becomes the statistical theory of para- and diamagnetism. There is one simplification. The magnetic force inside the medium is by definition determined at the centre of a small needle-like cavity and is independent of the induced magnetization of the medium. The relation between the magnetic force H and the magnetization I is

$$I = \kappa H,$$

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* When the magnetic moment is entirely due to the spins of the electrons, a magnetic field orientating the magnetic moment might be practically without effect on the molecular framework carrying the electric moment. This explanation might hold for the normal states of atoms and molecules whenever these are S-terms, but does not apply to NO whose normal state is a P-term.

† Debye, *Zeit. für Phys.* vol. XXXVI, p. 300 (1926); Huber, *Phys. Zeit.* vol. XXVII, p. 619 (1926).

where κ is the *magnetic susceptibility*, and the susceptibility is connected to the average molecular magnetic moment $\kappa^* H$ by the equation

$$\kappa = N\kappa^*.$$

The calculation of κ^* is identical in form with the calculation of θ^*. We have merely to substitute H for F and μ (magnetic moment) for α. The whole of our formulae then hold otherwise unaltered. We can for example construct a partition function for the rotations and orientations of any molecule including magnetic effects in the form

$$f(\vartheta) = \Sigma \varpi_u \vartheta^{\epsilon_u - \mu_u H - \frac{1}{2}\delta_u H^2} \qquad \text{......(888)}$$

and find at once

$$I = \frac{N}{\log 1/\vartheta} \frac{\partial}{\partial H} \log f(\vartheta). \qquad \text{......(889)}$$

Any rigid body model with fixed magnetic moment μ treated classically leads at once to an extra factor

$$\frac{\sinh(\mu H/kT)}{\mu H/kT}, \qquad \text{......(890)}$$

in the partition function $f(\vartheta)$ and therefore to Langevin's formula

$$\kappa^* = \frac{kT}{H^2}\left[\frac{\mu H}{kT} \coth \frac{\mu H}{kT} - 1\right]. \qquad \text{......(891)}$$

For the common case of $\mu H/kT$ small we have

$$\kappa^* = \tfrac{1}{3}\frac{\mu^2}{kT}. \qquad \text{......(892)}$$

This is the *paramagnetic susceptibility*.

The additional constant term of the dielectric theory reappears here too, but in practice with opposite sign, and represents the *diamagnetic susceptibility*. The complete value of κ^* is therefore

$$\kappa^* = \tfrac{1}{3}\frac{\mu^2}{kT} + \overline{\delta} \quad (\overline{\delta} < 0), \qquad \text{......(893)}$$

but $\overline{\delta}$ is always negligible compared with the other term unless $\mu = 0$, for otherwise μ is comparable with Bohr's magneton, and does not take small non-zero values†.

Paramagnetic moments are always associated with mechanical moment of momentum. So far as we yet know they arise either from unbalanced electronic orbits or unbalanced momenta of the spinning electrons themselves†. The symmetrical top model with its magnetic moment along its axis of figure is then the only not entirely inadequate model which can be

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† These two statements are not strictly accurate. The rotating nuclei of a polar molecule (carrying an electric doublet) give rise to a magnetic moment, which is very small compared with the ordinary μ. The proton also possesses magnetic moment itself, and so do many atomic nuclei, and these moments again are small.

discussed in detail with any simplicity. The analysis of § 12·6 would then apply with obvious changes, and lead to Langevin's formula. The general theory of Van Vleck described in § 12·61 shows however that the applicability of Langevin's formula or the more complete (893) is general, and that too without change in μ or $\overline{\delta}$, whether or not there is spatial quantization. This explains why attempts to repeat Glaser's experiments have failed*. The para- or diamagnetic susceptibilities of air, O_2, CO_2, N_2 and H_2 have been shown to be strictly proportional to the pressure at constant temperature, and therefore to the number of molecules present, over a range of pressures from 5 cm. Hg or less to one atmosphere. The Glaser effect†, or apparent tripling of the susceptibility at the lower pressures, seems to be a secondary effect due to the inadequate drying of the gas used.

§ **12·71**. *Atomic ions.* Similar considerations‡ apply to the para- and diamagnetism of atoms or atomic ions. Generally speaking these must be studied in solutions rather than in gases, but the theory of the effect is the same as it does not matter whether or not there is spatial quantization. The theory of paramagnetism for an atomic ion is simpler than for a molecule, since the magnetic moment is always directly proportional to the mechanical momentum, and the independence of spatial quantization can be established very simply. If the magnetic field lies along the z-axis the atomic paramagnetic susceptibility is easily shown by the argument yielding (872) to be proportional to the average value of M_z^2/kT, where M_z is the z-component of the total angular momentum M. If there is spatial quantization, then according to the quantum mechanics

$$M_z = sh/2\pi \quad (-j \leqslant s \leqslant j).$$

Thus the average value of M_z^2 is

$$\frac{1}{2j+1} \sum_{s=-j}^{s=+j} \frac{s^2h^2}{4\pi^2} = \tfrac{1}{3}j\,(j+1)\frac{h^2}{4\pi^2} = \tfrac{1}{3}M^2, \qquad \text{......(894)}$$

for the square of the total angular momentum is determined in the new mechanics by $j\,(j+1)$. This result holds whether j has integral or half-integral values. The result that $\overline{M_z^2} = \frac{1}{3}M^2$ with spatial quantization means of course that $\overline{M_z^2}$ has the same value as with random orientations, which is Van Vleck's theorem in this special case. In comparing the theory with experiments and determining atomic magnetic moments it must be remembered that M^2 is given by $j\,(j+1)$ and not j^2, and that the magnetic moment associated with M is not M Bohr magnetons but gM magnetons, where g is Landé's splitting factor as determined by the anomalous Zeeman effect for the normal state of the atom or ion in question.

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* Lehrer, *Zeit. für Phys.* vol. XXXVII, p. 155 (1926); Hammer, *Proc. Nat. Acad. Sci.* vol. XII, p. 597 (1926).

† Glaser, *Ann. der Phys.* vol. LXXV, p. 1059 (1924).

‡ Van Vleck, *loc. cit.*

It is well known that any central orbit of area S described in time τ by an electron has a mechanical moment of momentum $2mS/\tau$, and is equivalent to a magnet of moment $\epsilon S/\tau c$. The ratio of magnetic to mechanical momentum has therefore the standard value $\epsilon/2mc$, a ratio which is preserved by the quantum mechanics. For a system of moment of momentum M, purely orbital in origin,

$$\mu = \frac{\epsilon}{2mc} M = \frac{\epsilon h}{4\pi mc} \{j (j + 1)\}^{\frac{1}{2}}. \qquad \text{......(895)}$$

In general

$$\mu = \frac{\epsilon h}{4\pi mc} g \{j (j + 1)\}^{\frac{1}{2}}. \qquad \text{......(896)}$$

The value of $\epsilon h/4\pi mc$, which was μ for the normal one-quantum orbit of hydrogen on the older quantum theory, is usually referred to as Bohr's magneton. Its numerical value is $9{\cdot}23 \times 10^{-21}$ electrostatic units. The empirical unit, Weiss's magneton, is smaller by the factor 4·967. It is easily seen that exact multiples of Bohr's magneton are not to be expected in observations.

A proper comparison of observed and theoretical values of μ for atomic ions in solution is as yet not possible. Qualitatively there is excellent agreement with (896), but the normal states of the free ions in question are mostly still unknown by direct observation, and modifications are possible in solution. We note the following observed and calculated values, the observational data being from Stoner*.

In Table 41 the normal states of the free ions are taken from a table by McLennan and Smith†. It is assumed that in solution the ions have no 4_0 orbits, but that otherwise the normal rules for fixing the normal state apply‡. The entries in square brackets would apply if the normal state were selected from the other extreme of the set of multiple terms composing the normal state.

A comparison of theory and observation for the atomic ions in this table, at first sight unsatisfactory, on deeper consideration is not unpleasing. Whenever we expect an S term for the normal state we find exact agreement between theory and experiment. In other cases the observed value is intermediate between the theoretical extremes and could always be reproduced by a suitable distribution of ions among the terms of the normal multiple state. The distributions among the various states can however hardly be the same as they would be for free ions, and the energy differences of the various states must have been seriously modified in solution, but obviously in a systematic way. This however is not unreasonable and

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* Stoner, *Magnetism and Atomic Structure*, London (1926).

† McLennan and Smith, *Proc. Roy. Soc.* A, vol. CXII, p. 76 (1926).

‡ See Hund, *Linienspektren und periodisches System der Elemente* (1927). No ion with just four 3_2 orbits is known. We should expect a normal term ${}^5D$, but by the rules ${}^5D_0$ rather than ${}^5D_4$.

may be accepted as a probable explanation of the apparent vagaries of the table. A study of the temperature variations of these μ might yield important information*.

TABLE 41.

Observed and calculated magneton numbers of molecules and atomic ions of the iron transition group.

No. of† 3_2 electrons	Atomic ion or molecule	Permanent magnetic moments in Bohr magnetons		g	j	Probable normal state of similar free ion or molecule
		Obs.	Calc., using:			
—	NO	1·85	1·84	—	—	$^2P_{\frac{1}{2}, \frac{3}{2}}$
—	O_2	2·84	2·83	2	1	$^3S_1$
0	K^{+} Ca^{++} Sc^{+++} Ti^{++++}	0	0	—	0	$^1S_0$
1	Ti^{+++}	1·8	1·55	$\frac{4}{5}$	$\frac{3}{2}$	$^2D_{\frac{3}{2}}$
3	V^{++} Cr^{+++} Mn^{++++}	1·8 3·8 4·0	0·77 [6·6	$\frac{2}{5}$ $\frac{4}{3}$	$\frac{3}{2}$ $\frac{9}{2}$	$^4F_{\frac{3}{2}}$ $^4F_{\frac{3}{2}}$]
4	Cr^{++} Mn^{+++}	5·0	6·7	$\frac{3}{2}$	4	$^5D_4$
5	Mn^{++} Fe^{+++}	5·8	5·9	2	$\frac{5}{2}$	$^6S_{\frac{5}{2}}$
6	Fe^{++}	5·2	6·7	$\frac{3}{2}$	4	$^5D_4$
7	Co^{++}	5·0	6·6	$\frac{4}{3}$	$\frac{9}{2}$	$^4F_{\frac{9}{2}}$
8	Ni^{++}	3·2	5·6 [1·63	$\frac{5}{4}$ $\frac{2}{3}$	4 2	$^3F_4$ $^3F_2$]
9	Cu^{++}	1·8	3·55 [1·55	$\frac{6}{5}$ $\frac{4}{5}$	$\frac{5}{2}$ $\frac{3}{2}$	$^2D_{\frac{5}{2}}$ $^2D_{\frac{3}{2}}$]
10	Cu^{+} Zn^{++}	0	0	—	0	$^1S_0$

† Or, in the notation of the older theory, 3_3 electrons.

Turning now to the two paramagnetic diatomic gases, theory and experiment ought here to agree exactly, and agree they do. It is necessary however to use the detailed information which we now possess about the structure of these molecules in their normal states in order to adopt the right model. We must mention here that the electronic states of molecules seem to require exactly the same classifications as the states of atoms —they are merely then overlaid by the vast complication of the states of nuclear vibration and rotation‡. The normal state of O_2 is probably a term $^3S_1$, so that its residual moment of momentum is purely electronic and its

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* Substantially the same conclusions are drawn by Laporte and Sommerfeld, *Zeit. für Phys.* vol. XL, p. 333 (1926), a paper with which I became acquainted after this table was prepared.

‡ We shall not be further concerned in this monograph with the electronic states of molecules. A description of atomic states and notation will be found in Chapter XIV.

magnetic moment necessarily the same as that of an atom with $j = 1$, $g = 2$. Van Vleck's theorem then leads us to the tabulated value derived from (896), irrespective of the precise coupling of this momentum vector to the molecular frame.

The theory of NO is not so simple. The normal electronic state is $^2P_{\frac{1}{2}}$; the other state of the doublet is $^2P_{\frac{3}{2}}$ with a separation (in wave number) of 122. This separation is comparable with kT/hc (= 200) at room temperatures. We have therefore to take account of the equilibrium distribution in the two normal states, and also to make special calculations, since the hypothesis of Van Vleck's theorem that all precessional frequencies are small compared with kT/h is not fulfilled. The detailed calculations have not been published‡, but the result is that given in Table 41.

It is interesting to compare the atomic with the molecular account of paramagnetic theory, considering the atom as a rigid top of vanishingly small moment of inertia. Then terms which contain the factor A all vanish compared with other terms, and the complete account of the effect, using the rigid body model, reduces exactly to the simple atomic account which has just been given.

TABLE 42.

Observed and calculated magneton numbers of atomic ions in the rare earth group.

[Taken from Hund, *loc. cit.* p. 179, Table 78.]

Ion	No. of electrons in 4_3 orbits*	Theoretical normal term	j	g	Magnetons calc.	Magnetons (observed)	
						Cabrera	St Meyer
La^{+++}	0	^1S	0	—	0·00	0	0
Ce^{+++}	1	^2F	$\frac{5}{2}$	$\frac{6}{7}$	2·54	2·39	2·77†
Pr^{+++}	2	^3H	4	$\frac{4}{5}$	3·58	3·60	3·47
Nd^{+++}	3	^4J	$\frac{9}{2}$	$\frac{8}{11}$	3·62	3·62	3·51
—	4	^5J	4	$\frac{3}{5}$	2·68	—	—
Sm^{+++}	5	^6H	$\frac{5}{2}$	$\frac{2}{7}$	0·84	1·54?	1·32
Eu^{+++}	6	^7F	0	—	0·00	3·61	3·12
Gd^{+++}	7	^8S	$\frac{7}{2}$	2	7·9	8·2	8·1
Tb^{+++}	8	^7F	6	$\frac{3}{2}$	9·7	9·6	9·0
Ds^{+++}	9	^6H	$\frac{15}{2}$	$\frac{4}{3}$	10·6	10·5	10·6
Ho^{+++}	10	^5J	8	$\frac{5}{4}$	10·6	10·5	10·4
Er^{+++}	11	^4J	$\frac{15}{2}$	$\frac{6}{5}$	9·6	9·5	9·4
Tu^{+++}	12	^3H	6	$\frac{7}{6}$	7·5	7·2	7·5
Yb^{+++}	13	^2F	$\frac{7}{2}$	$\frac{8}{7}$	4·5	4·4	4·6
Cp^{+++}	14	^1S	0	—	0·00	0	0

* Or, in the notation of the older theory, 4_4 orbits. † For Pr^{++++}.

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‡ Summarized by Van Vleck, *Nature*, vol. CXIX, p. 670 (1927). Published in full, *Phys. Rev.* vol. XXXI, p. 587 (1928).

Data are as yet too scanty for a similar study of the palladium and platinum transition groups, but for the rare earth group a comparison can be made which is still more satisfactory than Table 41. The better agreement here than in Table 41 is to be expected. For the incomplete group of 4_3 electrons lies deeper in the atom than the incomplete group of 3_2 electrons in the iron group, and would be far less liable to modification in solution.

§ **12·8**. *Dissociative Equilibria in magnetic fields.* We take up again a question left over from § 5·8, as to possible effects of magnetic forces on dissociative equilibria, when some or all of the systems concerned possess permanent magnetic moments. A typical example is the dissociation of the halogens, for halogen atoms must be paramagnetic with a normal state $^2P_{\frac{3}{2}}$ ($g = \frac{4}{3}$), while the halogen molecules are known to be diamagnetic. We shall be content to discuss only the simple typical case of the reaction $X_2 \rightleftarrows 2X$, where X is an atom. We shall retain only terms linear in H in the energies used in the partition functions for the atoms, which give the whole paramagnetic effect in this case, and ignore all magnetic effects on the molecules. The atoms may be assumed to be orientated by the field and to be internally in their lowest quantum state. The magnetic states will be assumed to be non-degenerate, of weight unity (§ 14·2).

The partition function (869) must be generalized to include space-variable magnetic fields. Let us start by considering the various magnetic states separately. Then the atom in the sth state will have a potential energy $-\mu_s H$ in the field and therefore a partition function

$$f_s(\vartheta) = F(\vartheta)\, V_s(\vartheta), \qquad \text{......(897)}$$

where
$$F(\vartheta) = \frac{(2\pi m)^{\frac{3}{2}}}{h^3 (\log 1/\vartheta)^{\frac{3}{2}}}, \quad V_s(\vartheta) = \iiint_V \vartheta^{-\mu_s H}\, dq_1 dq_2 dq_3. \qquad \text{......(898)}$$

The partition function for the atoms as a whole will therefore be

$$f(\vartheta) = \Sigma_s f_s(\vartheta) = F(\vartheta)\, V(\vartheta) \quad (V(\vartheta) = \Sigma_s V_s(\vartheta)). \qquad \text{......(899)}$$

The partition function $VG(\vartheta)$ for the molecules is spatially constant and need not be further specified. The numbers of atoms of any magnetic type in a selected volume element will be given by the usual formula of type (370).

In the absence of the magnetic field the dissociative equilibrium is fixed by the equation

$$\frac{\overline{X_2}/V}{(\overline{X}/V)^2} = \frac{G(\vartheta)}{j^2 F^2(\vartheta)}, \qquad \text{......(900)}$$

where j is the number of magnetic states. When the magnetic field is acting

$$\frac{\overline{X_2}}{(\overline{X})^2} = \frac{G(\vartheta)}{F^2(\vartheta)} \times \frac{V}{V^2(\vartheta)}. \qquad \text{......(901)}$$

In any selected volume element δV, let $\overline{x_s}$ be the average number of atoms in the sth magnetic state and $\overline{x_2}$ the number of molecules. Then

$$\frac{\overline{x}}{\delta V} = \frac{\overline{X_s}}{V_s(\vartheta)} \vartheta^{-\mu_s H} = \frac{\overline{X}}{V(\vartheta)} \vartheta^{-\mu_s H},$$

and if

$$\overline{x} = \Sigma_s \overline{x_s},$$

$$\frac{\overline{x_2}/\delta V}{(\overline{x}/\delta V)^2} = \frac{\overline{X_2}/V}{\{\overline{X}/V(\vartheta)\}^2} \frac{1}{(\Sigma_s \vartheta^{-\mu_s H})^2},$$

$$= \frac{G(\vartheta)}{F^2(\vartheta)} \frac{1}{(\Sigma_s \vartheta^{-\mu_s H})^2}. \qquad \text{......(902)}$$

There is nothing to the discredit of this equation, but unlike the corresponding equation (373) it yields a space-variable equilibrium constant. Its form does however suggest that perhaps the fundamental reaction should be regarded as

$$X_2 \rightleftarrows X_s + X_{-s}$$

for the various values of s and not crudely as $X_2 \rightleftarrows 2X$. If this is right, then magnetic and mechanical moment parallel to the field are conserved in recombination or dissociation, and for each fundamental constituent of the reaction we have a space-constant equilibrium constant as before. Equation (902) is of course unaltered by these considerations as to mechanisms of interaction, but the fundamental equations of the dissociative equilibria are

$$\frac{\overline{x_2}/\delta V}{\overline{x_s}/\delta V \,.\, \overline{x_{-s}}/\delta V} = \frac{G(\vartheta)}{F^2(\vartheta)} \quad (\textit{all } s). \qquad \text{......(903)}$$

There is no sufficient reason to believe that the reaction *must* be of this form, but it seems likely. It is difficult to see how *all* processes of dissociation can generate angular momentum parallel to the field, but this is necessary if the dissociation (and recombination) are to be of the more general type.

§ 12·9. *Application to the electron theory of metals.* There remains one very interesting application of paramagnetic theory. Now that electrons have a magnetic moment an electron gas should be paramagnetic. This has a practical application in the revised electron theory of metals, for Pauli* has shown that it accounts most satisfactorily for the residual paramagnetism of the alkali metals which is independent of the temperature. Since however it requires the use of the Fermi-Dirac statistics we postpone an account of it for Chapter XXI.

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* Pauli, *Zeit. für Phys.* vol. LI, p. 81 (1926).

CHAPTER XIII

APPLICATIONS TO LIQUIDS. THE PROPERTIES OF DILUTE SOLUTIONS

§ **13·1.** It is at present far beyond the power of statistical mechanics to deduce the properties of a liquid from a given molecular model. Most liquids of our acquaintance are composed of very complex molecules. Even if we possessed detailed experimental knowledge of the liquid states of the inert gases we could hardly hope as yet to give a satisfactory theoretical interpretation. It is not that the method is not sufficiently clear. It ought to be possible for such simple liquids to give a very satisfactory account of their properties if we take

$$\frac{\Psi}{k} = N\left(\log\frac{F}{N} + 1\right) + \log B(T),$$

$$B(T) = \int_{(V)} \dots \int e^{-W/kT}\, \Pi_\kappa\, (d\omega_\kappa),$$

where W is the complete potential energy of the liquid in any configuration, and F is the ordinary partition function for the constituent molecules lacking the V-factor, presumably much the same as in a gas. It is not a failure of theory but the prohibitive difficulty of calculating $B(T)$ which stands in the way. [It is possible of course that the true theory of liquids does depend essentially on the newer form of statistical mechanics.]

The utmost that statistical mechanics can hope to do at present is to calculate quantitatively the changes in $B(T)$ when certain small changes are made in the force system or the nature of the systems composing the assembly—that is to calculate the properties of more or less dilute solutions, given an empirical knowledge of the properties of the pure solvent. Even this can only be done somewhat tentatively. We shall give here merely a sketch of how the theory of dilute solutions can be approached by an application of the general theorems of statistical mechanics.

§ **13·2.** *Simple solutes.* We will consider first solutions in which the molecules of the solute may be regarded as the simplest possible systems —massive uncharged points without internal structure, or external fields of force. Let the solution consist of N molecules of the solvent and n of the ideal solute in a volume V. Then the contribution to Ψ from the potential energy of the solution is $k \log B(T)$, where

$$B(T) = \int_{(V)} \dots \int \prod_{r=1}^{N} d\Omega_r \int_{(V)} \dots \int e^{-W/kT} \prod_{r=1}^{n} d\omega_r. \qquad \text{......(904)}$$

In the completely ideal solution here contemplated W will be independent of the coordinates of the n dissolved systems so that (904) reduces to

$$B(T) = V^n \int_{(V)} \cdots \int e^{-W/kT} \prod_{r=1}^{N} d\Omega_r, \qquad \text{......(905)}$$

$$= V^n B'(T), \qquad \text{......(906)}$$

where $B'(T)$ is the value of $B(T)$ when the solvent is present pure, in the same volume at the same temperature. The change of Ψ for this assembly or this part of the assembly due to the presence of the solute is therefore an increase of $nk \log V$ from the potential energy term. The translatory energy contributes in this ideal case $nk [\log (F/n) + 1]$, where F is the usual partition function for the free translatory motion of a massive point. The whole increase is therefore

$$nk \left\{ \log \frac{VF}{n} + 1 \right\}, \qquad \text{......(907)}$$

as for a simple perfect gas.

These very simple considerations are sufficient to give us all the laws of ideal dilute solutions. We shall show further in a later section that our hypotheses about the solute sytems are needlessly restrictive, and that the same laws hold rather more generally.

§ **13·21**. *Osmotic pressure.* Suppose an assembly is set up in which there are two fluid phases separated by a semipermeable wall which permits free passage to the solvent but none to the solute. In order that equilibrium may be possible it is known that a pressure P must be applied to the whole of the partition so that the pressure in the solution exceeds the pressure in the solvent by P. This equilibrium excess pressure is called the *osmotic pressure.* Its existence and ideal value follow at once from the theory. For if $N\Psi_0$ is the characteristic function for the pure solvent, then for the solution

$$\Psi = N\Psi_0 + nk \left[\log \frac{VF}{n} + 1 \right], \qquad \text{......(908)}$$

and in equilibrium

$$p_0 = NT \frac{\partial \Psi_0}{\partial V}, \quad p = p_0 + \frac{nkT}{V},$$

or

$$P = p - p_0 = \frac{nkT}{V}. \qquad \text{......(909)}$$

§ **13·22**. *Lowering of the vapour pressure of the solvent.* Let the assembly consist of the solution in equilibrium with its own vapour, the solute being confined entirely to the fluid phase. We must form Ψ for the whole assembly, and in doing so cast $B'(T)$ into the form

$$\log B'(T) = N \log \{Vb(T, V/N)\}, \qquad \text{......(910)}$$

which it must have apart from surface effects. When we add to this the contributions for the internal energy and translational energy of the solvent systems we shall find in all a function of the form

$$N\,[\log\{Q\,(T,\,V/N)\}+1].$$

Therefore

$$\Psi/k = N\Psi_0\,(T,\,V/N) + n\left[\log\frac{VF}{n}+1\right] + M\left[\log\frac{V'G}{M}+1\right], \qquad \text{......(911)}$$

the last term referring to the vapour phase, which is assumed perfect. For equilibrium we must have $\delta\Psi = 0$ for the variation

$$\delta M = -\,\delta N,\quad \delta V = -\,\delta V' = V\delta N/N,\quad \delta T = \delta\,(V/N) = 0,$$

which requires
$$\Psi_0 + \frac{n}{N} = \log\frac{V'G}{M} + \frac{V}{N}\Big/\frac{V'}{M}. \qquad \text{......(912)}$$

For the vapour density of the pure solvent we have

$$\frac{M}{V'}\,e^{-\frac{V}{N}\big/\frac{V'}{M}} = Ge^{-\Psi_0},$$

or, since the density of the vapour is usually negligible compared with that of the solvent, approximately

$$\frac{M}{V'} = Ge^{-\Psi_0}. \qquad \text{......(913)}$$

For the vapour density over the solution

$$\frac{M}{V'} = Ge^{-\Psi_0 - n/N}. \qquad \text{......(914)}$$

Thus
$$p' = pe^{-n/N},\quad \delta p = -\,np/N, \qquad \text{......(915)}$$

which is the standard result. The effect of the solute arises from the fact that it must be compressed when any solvent is evaporated.

§ **13·23**. *Henry's law for dissolved vapours.* We consider an assembly consisting of an ideal solution and a perfect gas phase in which there is present a gas which forms the solute in the solution. Then Ψ/k for the assembly, so far as it depends on the foreign gas, contains just the terms

$$n\left(\log\frac{VF}{n}+1\right) + m\left(\log\frac{V'F'}{m}+1\right),$$

where V' is the volume of the gas phase and F' the partition function for the gas molecules in the gas phase. Then for equilibrium for a variation

$$\delta n = -\,\delta m,\quad \delta T = \delta V = \delta V' = 0,$$

$$\frac{VF}{n} = \frac{V'F'}{m}. \qquad \text{......(916)}$$

Henry's law states that at constant temperature the mass of gas dissolved per unit mass of solvent is proportional to the pressure of the gas on the gas phase, or in symbols

$$\frac{n}{V} = \kappa' p = \kappa \frac{m}{V'},$$

which is (916).

We have given these simple examples, but really once Ψ has been constructed and the thermodynamic properties of the assemblies established the rest is pure thermodynamics, and hardly a genuine illustration of statistical principles. We shall therefore pass on without further reference at this stage to other effects such as the lowering of the freezing point and raising of the boiling point of solutions by solutes which follow by thermodynamic reasoning from the form of Ψ.

§ **13·3**. *Applicability to more extended models.* The form of (905) will be retained for much wider conditions than those contemplated in § 13·2, conditions which represent much better approximations to actual solutes. Suppose that W in (904) now contains terms for the forces between the solute molecules themselves and between the solute and the solvent. If the number of solute molecules is not too great the evaluation of (904) requires merely an extension of the argument applied in § 8·4 in evaluating distribution laws. The expression

$$\int_{(V)} \cdots \int e^{-W/kT} \prod_{r=1}^{N} d\Omega_r \qquad \text{......(917)}$$

will depend only on the relative coordinates of all the solute molecules, and when there are only short-range forces acting it will to a first approximation obviously be independent of these coordinates. Thus we still have

$$B(T) = V^n B'(T), \qquad \text{......(918)}$$

where $B'(T)$ means the value of $B(T)$ for the solvent molecules at the given temperature and in a volume which has a peculiar form, being determined by the geometrical boundaries and the solute molecules fixed in their average positions. The nature of the volume at the disposal of the solvent may lead of course to secondary specific effects depending on the nature of the interaction between the molecules of the solvent and the solute. The natural primary effect is merely that $B'(T)$ will have approximately the same value as it had for the solvent at the same temperature *and at its original volume* V_0 before the solute was added and altered it to V. For dilute solutions the difference between V_0 and V will be insignificant. To a first approximation $V - V_0$ should often be equal or nearly equal to the volume of the molecules dissolved, but this will only be true if there are no marked effects at the surfaces of the molecules of the solute.

The laws of § 13·2 *for ideal solutions* therefore may be expected to continue to hold for dilute solutions of actual molecules as a first approximation. The next approximation would naturally replace the factor V^n in (918) by a more accurate value, which will obviously depend on the sizes of the solute molecules and on their *average fields of force in solution* in exactly the same way as the corrected expression for V^n for a simple gas depends on the sizes of the gas molecules and their ordinary fields of force. We are thus led to *osmotic equations of state* generalizing (909) for ideal solutions as van der Waals' equation of state generalizes the perfect gas laws. Considerable use has been made of such equations, but we shall not stop to consider them here. This side of the theory is satisfactory enough, but we cannot satisfactorily proceed to any further approximation without a more accurate calculation of the effect of the solute molecules on $B'(T)$ which gives rise to the secondary specific effects such as changes of volume differing from solute to solute. This has not yet been done, and would be of the nature of a surface effect.

The general success of van 't Hoff's theory, which the foregoing pages present as a theorem in statistical mechanics, is well known and will not be analysed here.

The theory extends at once to solutions of mixed solutes and to dissociative equilibria among the various solute species, provided that dissociation does not result in ionization as well, or if it does is present to a very slight degree only. The simple osmotic theory can thus account satisfactorily for the properties of weak electrolytes, substances which when dissolved undergo a slight degree of dissociation into pairs of ions (as shown by their conductivity). The number of ions present must be so small that the long-range electrical forces do not contribute seriously to $B(T)$. For solutions of strong electrolytes, for example the common salts which show a far higher conductivity and therefore degree of ionization, the simple theory neglecting electrical effects is inadequate.

§ **13·4**. *Specific heats of solutions of non-electrolytes.* The foregoing theory should predict successfully not merely the commoner osmotic effects but also the specific heat of the solution, or rather the difference of the specific heat of the solution from that of the pure solvent. It follows at once from the general theory applied to (907) that the specific heat of the solution should *exceed* that of the solvent by an amount equal to specific heat of the solute if it could exist as a gas in the same molecular form. It is difficult, if not impossible, to devise satisfactory experimental tests of this, but Zwicky* has shown that theory and experiment are in reasonable agreement by comparing the excess specific heat of the solution per gram-molecule of solute with the specific heat of the solute in the pure solid (or liquid) state. The following table is taken from his paper.

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* Zwicky, *Phys. Zeit.* vol. xxvii, p. 271 (1926).

TABLE 43.

Specific heats of solutes.

[Calories per gram-molecule per degree centigrade.]

T circa 20° C.	Cane sugar $C_6H_{12}O_6$	Lactose $C_{12}H_{22}O_{11}$	Ammonium carbonate $CN_2H_8O_3$	Tartaric acid $C_4H_6O_6$	Glycerine $C_3H_8O_3$
In solution in water	55·2	104·5	24·8	67	56·0
As pure solid or liquid	51·7	98·5	19·3	62	53·0
Diff.	+3·5	+6·0	+5·5	+5	+3·0

The agreement is certainly not exact, but adequate in view of the rough nature of the comparison. The important point is that the simple theory predicts an *increase* in the specific heat when any solute molecules are added, which is roughly that observed for non-electrolytes. The observed change of specific heat for solutions of strong electrolytes in water is however a large *decrease* and must be accounted for in other ways.

§ **13·5**. *Strong electrolytes.* When certain substances such as common salt are dissolved in water, the solution has a comparatively high conductivity, showing that charged ions must be present, and the usual osmotic effects are far larger than can be explained by van 't Hoff's theory if the dissolved substance is present mainly as molecules of NaCl, with or without a charge of either sign. We owe to Arrhenius the suggestion that for such substances, classed as strong electrolytes, at least in dilute and moderately concentrated solution, the solute is composed almost entirely of the systems Na^+ and Cl^-. The evidence for this from the electrolytic side alone is conclusive, but the thermodynamic consequences of this assumption have long given trouble and can only be properly worked out when explicit account is taken of the effect of the long-range electrostatic forces on the value of $B(T)$ or Ψ.

According to the simple theory, if n molecules of a binary electrolyte, such as NaCl, are dissolved in water there will be $2n$ independent solute systems and the ideal osmotic pressure P_0 should be given by

$$P_0 = 2nkT/V. \qquad \text{......(919)}$$

The observed osmotic pressure P is always less than P_0,

$$P = gP_0 \quad (g < 1). \qquad \text{......(920)}$$

Observations are made not so much of P as of the lowering of the freezing point of the solution, etc., but such quantities are all expressible in terms of the same osmotic coefficient g. The object of a correct theory is then to account for the observed departure of g from unity. It is true that $g \to 1$ as the concentration tends to zero, but in a manner which can at once be seen to be impossible of explanation by any type of dissociative equilibrium. The departure of g from unity is known as *the anomaly of strong electrolytes.*

In confirmation of this a simple approximate calculation shows that at moderate concentrations practically all the molecules of the solute should be dissociated. We take the formula (321) putting, for estimates of order of magnitude only,

$$m_1 m_2/(m_1 + m_2) = 2{\cdot}5 \times 10^{-23}, \quad A = 10^{-39}, \quad \text{and} \quad \nu_0 = 3 \times 10^{13}.$$

Then at 300° K. $$\frac{\nu_1 \nu_2}{\nu_{12}} = 3{\cdot}1 \times 10^{24} e^{-40\chi},$$

if χ is the work of dissociation from the normal state of the molecule, measured in electron volts. The molecular densities are reckoned here in number of molecules per cubic centimetre. If we take instead the more usual unit in this connection, gram-molecules per litre solution, we have

$$\frac{c_1 c_2}{c_{12}} = 5 \times 10^3 e^{-40\chi}.$$

If the total solute is C gram-molecules per litre and it dissociates as a simple binary salt into equal numbers of equivalent ions,

$$c_1 = c_2, \quad c_1 + c_{12} = C.$$

Thus $$(C - c_{12})^2 = 5 \times 10^3 e^{-40\chi} c_{12}.$$

To estimate the order of χ we may calculate first the work required to separate to infinity two unit charges *in vacuo* from an initial distance of 2×10^{-8} cm. This is 7·2 electron volts. It is at this point that the dielectric constant of the medium and the polar nature of the normal salt molecule become of dominant importance to the argument. If we may treat these ionic charges as if they were large-scale charges in a medium of dielectric constant D, then the work of separation is only $7{\cdot}2/D$ volts or about 1/11 volts for water. Thus

$$(C - c_{12})^2 = 10^2 c_{12}, \qquad \ldots\ldots(921)$$

and if C is 1 or less, then c_{12} must be less than $10^{-2}C$ and dissociation is practically complete. At first sight this argument might appear to prove too much and suggest that for such values of χ *all* dissociations should be practically complete. But the argument can only hold (even approximately) for strongly polar molecules. If the normal neutral molecule is electrically neutral the medium will hardly affect the work of dissociation or ionization; for the first step it might as well not be there. But for the polar salt molecule in its normal state the medium is already polarized round it by its own field, in such a way as to reduce greatly (though perhaps not really to the normal ratio $1/D$) the effective electrostatic forces.

The calculation we have made assigns to the associated salt molecule classical vibrational energy along its line of centres. Owing to the weak binding energy in solution this is probably a gross overestimate, and the dissociation will be still more complete than that indicated by (921) even for divalent ions and perhaps for some ions of still higher valency.

§ **13·6**. *Electrostatic effects in solutions of strong electrolytes.* We now consider how to extend the analysis of §§ 8·7, 8·8, especially the latter, to a dilute solution of a strong electrolyte, so as to calculate the extra part of $B\,(T)$ due to electrostatic forces. The theory we shall aim at establishing is that of Debye and Hückel, of which we have already given a critical discussion in § 8·8 in the simplest possible case. All that is there said remains true, but we have still to consider the additional difficulties raised by the presence of the solvent.

If we write W in the form $W_s + W_l$, where the suffixes indicate energy terms corresponding to forces of short and long range respectively, the latter being electrostatic, we obtain at once from (530) which defines $W_{\alpha\beta}$,

$$\frac{\partial W_{\alpha\beta}}{\partial x_\beta} = \overline{\frac{\partial W_s}{\partial x_\beta}} + \overline{\frac{\partial W_l}{\partial x_\beta}}. \qquad \text{......(922)}$$

At a distance apart of the α and β sufficient to secure that the short-range forces of the α and β themselves are trivial (the α and β not getting bodily in each other's way) we should expect to have

$$\int_{(V)} \cdots \int \frac{\partial W_s}{\partial x_\beta} e^{-W/kT}\, \Pi_\kappa''\, (d\omega_\kappa)^{N_\kappa} = 0, \quad \overline{\frac{\partial W_s}{\partial x_\beta}} = 0. \qquad \text{......(923)}$$

This result would be exact in the limit of no ionic charges beyond the range of attractive forces of van der Waals' type. It would be modified by such forces, but only trivially compared with the far more powerful electrostatic forces themselves, and this modification will be ignored. There is however a further reason to doubt whether (923) remains exactly valid when the electrostatic forces are acting. In discussing the specific heat of solutions of electrolytes Zwicky has shown reason to believe (see § 13·8) that there is an intense pressure round each ion due to the attraction of the water dipoles by the inhomogeneous field of the ion. It follows that for a water molecule $\overline{\partial W_s/\partial x_\beta} \neq 0$, but must represent a force which acts radially outwards and balances the mean attraction of the ion for the water dipole at that range. Approximately the same force will presumably act on the ions of the solute. It appears on a closer examination that this force is not quite large enough to have a serious effect on the ionic distribution laws. The mean strength μ of the water dipoles is about 5×10^{-19} E.S.U. (less than in the vapour state when it is $1{\cdot}87 \times 10^{-18}$), and the medium near the ion is probably saturated, all the dipoles pointing to the ion. Hence for a water molecule (and so approximately for an ion)

$$\overline{\frac{\partial W_s}{\partial x_\beta}} = \frac{2\mu\epsilon}{Dr^3}.$$

The electrostatic force on an ion at the same place is

$$\frac{\epsilon^2}{Dr^2}.$$

These expressions are both modified by the atmosphere of other ions introducing the factor $e^{-\kappa r}$ and derived terms, but these do not affect the argument for dilute solutions in the important region fairly near the ion. The ratio is

$$\epsilon r/2\mu \quad \text{or} \quad 4{\cdot}8 \times 10^8 r.$$

Since r is always greater than about 2×10^{-8} cm. the pressure term is probably negligible.

We conclude therefore that we have, with sufficient accuracy,

$$\frac{\partial W_{\alpha\beta}}{\partial x_\beta}\int_{(V)}\cdots\int e^{-W/kT}\,\Pi_\kappa''\,(d\omega_\kappa)^{N_\kappa}=\int_{(V)}\cdots\int\frac{\partial W_l}{\partial x_\beta}\,e^{-W/kT}\,\Pi_k''\,(d\omega_\kappa)^{N_\kappa}. \qquad \ldots\ldots(924)$$

This is valid for separations of the α and β above a certain limit. For separations below a certain limit (the mean diameter of the α and β) there can be no pairs of α and β. There might be a transition region of some importance but we shall not attempt to take account of one, and shall identify the two limits just mentioned.

We now differentiate (924) again with respect to x_β and add the two similar equations. We thus find

$$\left\{\nabla_\beta^2\, W_{\alpha\beta}-\frac{1}{kT}\,\Sigma\left(\frac{\partial W_{\alpha\beta}}{\partial x_\beta}\right)^2\right\}\int_{(V)}\cdots\int e^{-W/kT}\,\Pi_\kappa''\,(d\omega_\kappa)^{N_\kappa}$$
$$=\int_{(V)}\cdots\int\left\{\nabla_\beta^2\, W_l-\frac{1}{kT}\,\Sigma\,\frac{\partial W_l}{\partial x_\beta}\left(\frac{\partial W_s}{\partial x_\beta}+\frac{\partial W_l}{\partial x_\beta}\right)\right\}e^{-W/kT}\,\Pi_\kappa''\,(d\omega_\kappa)^{N_\kappa}. \qquad \ldots\ldots(925)$$

It seems reasonable to expect further that

$$\overline{\frac{\partial W_l}{\partial x_\beta}\frac{\partial W_s}{\partial x_\beta}}$$

is zero or at least negligible as in (570), since the correlation between the long- and short-range forces is small. We shall neglect this term in (925) in the rest of the discussion.

We now encounter a difficulty in trying to apply Poisson's equation to $\nabla_\beta^2 W_l$ under the integral sign. The simple direct argument is to say that the ions are immersed in a medium of dielectric constant D which will after averaging for the solvent molecules be the same at least approximately as that for the medium in bulk. For dilute solutions D should therefore be the dielectric constant for the pure solvent. If we make this assumption then

$$\nabla_\beta^2 W_l = -\,4\pi\rho z_\beta \epsilon/D. \qquad \ldots\ldots(926)$$

It is however undeniable that the argument is weak. The main part of D is contributed by the orientation of the water dipoles. In obtaining (926) we have really used an illegitimate averaging process by working the complete averaging implied in $B\,(T)$ in separate stages. Such averaging processes cannot be relied on for numerical accuracy, but any error introduced is not likely to be large. It is the best that we can do here. What is more serious is that most probably D is not really spatially constant round the ion owing to a saturation effect, and the exact form of Poisson's equation

$$\Sigma \frac{\partial}{\partial x_\beta}\left(D\frac{\partial W_l}{\partial x_\beta}\right) = -\,4\pi\rho z_\beta \epsilon$$

should really have been applied. We can only note this deficiency without attempting here a better discussion. Accepting all these somewhat doubtful but as yet unavoidable simplifications we are left with

$$\nabla_\beta{}^2 W_{\alpha\beta} + \frac{4\pi\bar{\rho}z_\beta\epsilon}{D} = \frac{1}{kT}\left\{\Sigma\left(\frac{\partial W_{\alpha\beta}}{\partial x_\beta}\right)^2 - \Sigma\overline{\left(\frac{\partial W_l}{\partial x_\beta}\right)^2}\right\}. \quad \text{......(927)}$$

On the meaning of $\bar{\rho}$ and the importance of the fluctuation term we have already commented at length in § 8·8. There is nothing more to add here. The utmost that we may conclude (and even this is not certain) is that Poisson's equation

$$\nabla_\beta{}^2 W_{\alpha\beta} + \frac{4\pi\bar{\rho}z_\beta\epsilon}{D} = 0 \qquad \text{......(928)}$$

may be used for $W_{\alpha\beta}$ with $\bar{\rho}$ given in terms of $W_{\alpha\beta}$ by Boltzmann's law, see (588) and (589), if

$$\frac{1}{kT}\,\Sigma\left(\frac{\partial W_{\alpha\beta}}{\partial x_\beta}\right)^2$$

is small compared with terms retained, and this must be verified *a posteriori*. Any non-fluctuating part of $W_{\alpha\beta}$ may be removed before applying the test.

§ **13·7**. *The theory of Debye and Hückel.* It was first proposed by Debye and Hückel* to determine the electrostatic terms in the characteristic function of a strong electrolyte by means of the equations above, which may be written

$$\nabla_\beta{}^2 W_{\alpha\beta} = -\,\frac{4\pi\epsilon^2 z_\beta}{D}\,\Sigma_\gamma z_\gamma \frac{N_\gamma}{V}\,e^{-W_{\alpha\gamma}/kT}, \qquad \text{......(929)}$$

$$W_{\alpha\beta} = \epsilon z_\beta \psi_\alpha, \qquad \text{......(930)}$$

ψ_α being then the average electrostatic *potential* round the α-ion of valency z_α. In spite of its insufficient foundation this theory is important, and we shall develop its consequences in this section.

Since ψ_α will be spherically symmetrical we have

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi_\alpha}{\partial r}\right) = -\,\frac{4\pi\epsilon}{D}\,\Sigma_\gamma z_\gamma \frac{N_\gamma}{V}\,e^{-z_\gamma\epsilon\psi_\alpha/kT}. \qquad \text{......(931)}$$

Let us suppose first that the condition that $z_\gamma\epsilon\psi_\alpha/kT$ should be small for

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* Debye and Hückel, *Phys. Zeit.* vol. XXIV, pp. 185, 305 (1923).

all relevant values of r is satisfied for all α and γ. We can then replace the exponentials by their first two terms. The first terms give

$$\Sigma_\gamma z_\gamma \frac{N_\gamma}{V}$$

which is zero, since the solution as a whole is normally electrically neutral. The second terms leave us with the equation

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi_\alpha}{\partial r}\right) = \kappa^2 \psi_\alpha, \quad \kappa^2 = \frac{4\pi\epsilon^2}{DkT} \Sigma_\gamma z_\gamma{}^2 \frac{N_\gamma}{V}. \qquad \ldots\ldots(932)$$

The solution of (932) gives ψ_α for all values of r sufficiently great. Let us suppose for simplicity that all the pairs of ions concerned have the same mean diameter σ (or assume a mean size for them all)*. Then (932) holds for $r > \sigma$, while for $r < \sigma$ there can be no other ion present, and the electric intensity for values of r just less than σ must be $z_\alpha \epsilon / r^2 D$. We have therefore

$$(r \leqslant \sigma) \quad \psi_\alpha = \frac{z_\alpha \epsilon}{rD} + A,$$

$$(r \geqslant \sigma) \quad \psi_\alpha = \frac{1}{r}(Be^{-\kappa r} + Ce^{\kappa r}),$$

where A, B, and C are constants. To satisfy the boundary conditions for $r \to \infty$ we have $C = 0$, and the conditions of continuity of potential and induction at $r = \sigma$ are

$$\frac{z_\alpha \epsilon}{\sigma D} + A = \frac{1}{\sigma} Be^{-\kappa\sigma},$$

$$\frac{z_\alpha \epsilon}{\sigma^2 D} = \frac{1}{\sigma^2} Be^{-\kappa\sigma}(1 + \kappa\sigma).$$

From these equations it follows that

$$B = \frac{z_\alpha \epsilon}{D} \frac{e^{\kappa\sigma}}{1 + \kappa\sigma},$$

$$A = -\frac{z_\alpha \epsilon \kappa}{D} \frac{1}{1 + \kappa\sigma}.$$

The boundary value of ψ_α is

$$(\psi_\alpha)_\sigma = \frac{z_\alpha \epsilon}{\sigma D} \frac{1}{1 + \kappa\sigma}, \qquad \ldots\ldots(933)$$

and the average potential due to the rest of the ions at the centre of a specified α is at the same time

$$-\frac{\kappa z_\alpha \epsilon}{D} \frac{1}{1 + \kappa\sigma}. \qquad \ldots\ldots(934)$$

The maximum value of $z_\beta \epsilon \psi_\alpha / kT$ which should be small to justify (932)

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* In view of other uncertainties a more refined treatment is hardly justified.

can be derived at once from (933). For dilute solutions κ or rather $\kappa\sigma$ is small, so the important term is

$$\frac{z_\alpha z_\beta \epsilon^2}{\sigma D k T}.$$

For water at 0° C. this is $7 \times 10^{-8}\, z_\alpha z_\beta/\sigma$. Since even for univalent ions $z_\alpha z_\beta = 1$, this is hardly small for the expected values of σ, 3 or 4×10^{-8}. It is implied* that there is no serious error committed in using it for ordinary solutions, but this really awaits further investigation using the more accurate equation (931).

We have yet to consider the legitimacy of ignoring the fluctuation term. The fluctuating part of $W_{\alpha\beta}$ is

$$W_{\alpha\beta}' = \frac{z_\alpha z_\beta \epsilon^2}{Dr}\left\{\frac{e^{\kappa(\sigma-r)}}{1+\kappa\sigma} - 1\right\};$$

it is sufficient to ignore $\kappa\sigma$ and examine whether $(\partial W_{\alpha\beta}'/\partial r)^2/kT$ is or is not small compared with a term retained in (931) such as $2\,(\partial W_{\alpha\beta}'/\partial r)/r$ or $\partial^2 W_{\alpha\beta}'/\partial r^2$ or $\kappa^2 W_{\alpha\beta}'$. Comparison with the first is simple. We find the ratio

$$\frac{z_\alpha z_\beta \epsilon^2 \kappa}{2DkT}\left[\frac{1-(1+\kappa r)\,e^{-\kappa r}}{\kappa r}\right].$$

Since for all positive x $\qquad e^x \leqslant 1 + x + xe^x$

it follows that the term [ ] never exceeds unity and the omission of the fluctuation is legitimate if

$$\frac{z_\alpha z_\beta \epsilon^2 \kappa}{2DkT} \qquad \text{......(935)}$$

is small. This is equivalent to the condition that $W_{\alpha\beta}'/kT$ should be small.

Since κ vanishes with the concentration this condition is certainly satisfied for solutions sufficiently dilute. For actual numerical values we write

$$z_\gamma^2 \frac{N_\gamma}{V} = 6{\cdot}06 \times 10^{20}\Gamma_\gamma \quad (\Sigma_\gamma \Gamma_\gamma = \Gamma)$$

so that Γ_γ is the "effective" ionic concentration of γ ions in gram-ions per litre solution. Then

$$\kappa = 0{\cdot}229 \times 10^8 \sqrt{\Gamma}$$

for water at 0° C. With these values of κ, D and T (935) reduces to

$$z_\alpha z_\beta \sqrt{\Gamma},$$

and the condition of smallness may be taken to be satisfied for solutions $\frac{1}{100}$ normal or less.

We conclude that there is a range of fairly dilute solutions in which the combined use of Boltzmann's and Poisson's equations may give an accurate account of the ionic distribution laws, by providing an accurate

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* Hückel, *Ergebnisse der Exakten Naturwiss.* vol. III, p. 214 (1924).

method of approximating to the properties of $B(T)$. It does *not* appear that the use of (932) in place of (931) can be justified strictly and simply. This approximation however is not vital to Debye and Hückel's theory. It merely allows of a simple formal solution in place of the much more complicated one of § 13·72, but a simple solution which may be expected to be a reasonable approximation to the true solution of the equation proposed. Accepting this, the weakest points of the present theory lie in the treatment of D and the use of $\bar{\rho}$.

In order to utilize these results to calculate the electrical contribution Ψ_ϵ to Ψ we must slightly modify and extend the theorem of § 8·91. We have in general

$$B(T) = \int_{(V)} \cdots \int e^{-(W_s + W_l)/kT} \, \Pi_\kappa \, (dw_\kappa)^{N_\kappa},$$

and if the electrostatic energy terms alone are reduced to strength τ

$$B_\tau(T) = \int_{(V)} \cdots \int e^{-(W_s + \tau W_l)/kT} \, \Pi_\kappa \, (dw_\kappa)^{N_\kappa}. \qquad \text{......(936)}$$

The average potential energy $kT^2 \partial \log B_\tau(T)/\partial T$ is then

$$\frac{1}{B_\tau(T)} \int_{(V)} \cdots \int (W_s + \tau W_l) \, e^{-(W_s + \tau W_l)/kT} \, \Pi_\kappa \, (dw_\kappa)^{N_\kappa},$$

of which
$$\frac{\tau}{B_\tau(T)} \int_{(V)} \cdots \int W_l \, e^{-(W_s + \tau W_l)/kT} \, \Pi_\kappa \, (dw_\kappa)^{N_\kappa}$$

is electrostatic. Keeping the distribution laws unaltered but increasing each electrostatic energy term from τ to $\tau + d\tau$ therefore increases the average potential energy of the assembly by

$$-kT d\tau \frac{d}{d\tau} \log B_\tau(T), \qquad \text{......(937)}$$

which is the work required to make this change. On integrating this we verify as before that the increase in the work function, or

$$-kT [\log B_1(T) - \log B_0(T)],$$

is equal to the work required in the reversible isothermal charging process to build up the ionic charges from zero.

The application to the theory of electrolytes is immediate. Let all charges be supposed reduced to a fraction μ. Then $\kappa_\mu = \mu\kappa$ since $\kappa \propto \epsilon$. The work done on the assembly in bringing up a charge $z_a \epsilon d\mu$ to an a ion is therefore by (934)

$$-\left(\frac{\kappa z_a{}^2 \epsilon^2}{D}\right) \frac{\mu^2 d\mu}{1 + \mu\kappa\sigma}.$$

Summed over all ions and integrated for μ from 0 to 1 this gives an expenditure of work

$$-\frac{\kappa\epsilon^2}{D} (\Sigma_a N_a z_a{}^2) \left[\frac{1}{(\kappa\sigma)^3} \{\log(1 + \kappa\sigma) - \kappa\sigma + \tfrac{1}{2}(\kappa\sigma)^2\}\right]. \qquad \text{......(938)}$$

When $\kappa\sigma$ is small this reduces to

$$-\frac{\kappa\epsilon^2}{3D}\Sigma_a N_a z_a^2. \qquad \text{......(939)}$$

We find therefore the standard result

$$\Psi_\epsilon = \frac{\kappa\epsilon^2}{DT}(\Sigma_a N_a z_a^2)\left[\frac{1}{(\kappa\sigma)^3}\{\log(1+\kappa\sigma)-\kappa\sigma+\tfrac{1}{2}(\kappa\sigma)^2\}\right], \qquad \text{......(940)}$$

or for $\kappa\sigma$ small

$$\Psi_\epsilon = \frac{\kappa\epsilon^2}{3DT}(\Sigma_a N_a z_a^2). \qquad \text{......(941)}$$

The isothermal work terms above take account of the work of building up the charges against the field of the other ions. No account is taken of the work of building up the ionic charges themselves against their own field. This work (per ion) does not depend on the concentration and is unimportant in most applications but might affect the specific heat of the solution owing to the temperature variation of D. The contribution will depend on the model adopted for the ion. If we may liken it to a conducting sphere of radius a, then the work of charging is

$$\frac{z_a^2\epsilon^2}{2a_a D},$$

and the term

$$-\frac{\epsilon^2}{2DT}\Sigma N_a\frac{z_a^2}{a_a} \qquad \text{......(942)}$$

must be added to Ψ_ϵ. But this model is probably unreliable, and the calculation would be seriously changed by saturation effects in D.

It is now easy to calculate the osmotic coefficient g. The ideal osmotic pressure P_0 will be given by

$$P_0 = (\Sigma_a N_a)\,kT/V.$$

The actual pressure will be

$$P = P_0 + T\partial\Psi_\epsilon/\partial V.$$

Ψ_ϵ depends on V only through κ, so that by (932)

$$\begin{aligned} V\partial\Psi_\epsilon/\partial V &= -\tfrac{1}{2}\kappa\partial\Psi_\epsilon/\partial\kappa, \\ &= -\frac{\kappa\epsilon^2\Sigma_a N_a z_a^2}{2DT(\kappa\sigma)^3}\left[\frac{\kappa\sigma(2+\kappa\sigma)-2(1+\kappa\sigma)\log(1+\kappa\sigma)}{1+\kappa\sigma}\right]. \end{aligned} \qquad \text{......(943)}$$

Therefore for the osmotic coefficient g we have

$$1-g = \frac{\kappa\epsilon^2}{2DkT}\frac{\Sigma_a N_a z_a^2}{\Sigma_a N_a}\left[\frac{\kappa\sigma(2+\kappa\sigma)-2(1+\kappa\sigma)\log(1+\kappa\sigma)}{(\kappa\sigma)^3(1+\kappa\sigma)}\right]. \qquad \text{......(944)}$$

For small values of $\kappa\sigma$ this reduces to

$$1-g = \frac{\kappa\epsilon^2}{6DkT}\frac{\Sigma_a N_a z_a^2}{\Sigma_a N_a}, \qquad \text{......(945)}$$

which written in full is

$$1 - g = \frac{(4\pi)^{\frac{1}{2}}\,\epsilon^3}{6\,(D\,kT)^{\frac{3}{2}}} \left\{\frac{\Sigma_a N_a z_a{}^2}{\Sigma_a N_a}\right\}^{\frac{3}{2}} \frac{(\Sigma_a N_a)^{\frac{1}{2}}}{V^{\frac{1}{2}}}. \qquad \text{......(946)}$$

If the concentration γ of the electrolyte is given in gram-molecules per litre solution, and if each molecule breaks up into ν ions, then

$$\Sigma_a N_a / V = 6{\cdot}06 \times 10^{20} \nu\gamma.$$

The factor $\{\}^{\frac{3}{2}}$ depends only on the valency of the ions and is unity for univalent binary salts. It is frequently written w. Then inserting numerical values for water at 0° C. we have

$$1 - g = 0{\cdot}\dot{2}63 w \sqrt{(\nu\gamma)}. \qquad \text{......(947)}$$

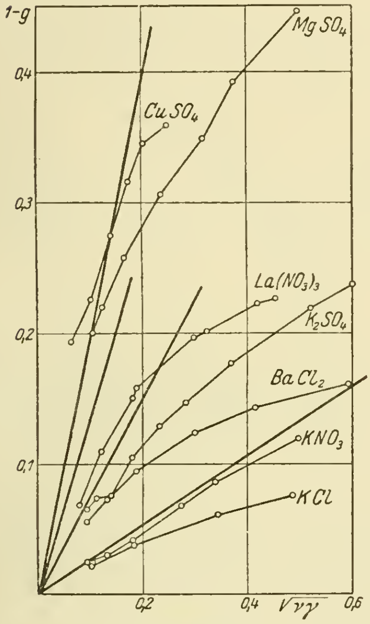

Fig. 20. Osmotic coefficients as functions of the concentration.

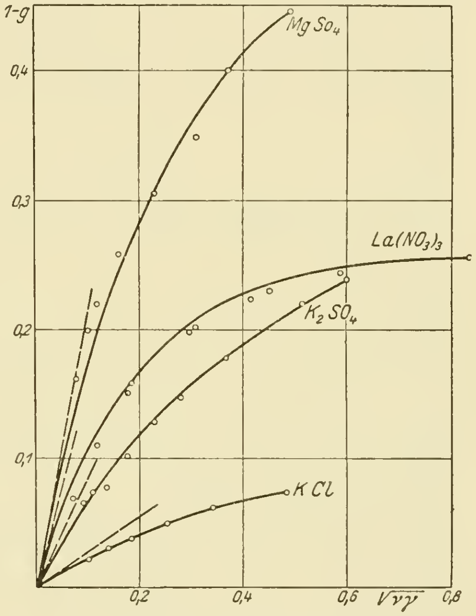

Fig. 21. Osmotic coefficients compared with theoretical values for suitable values of σ.

§ **13·71**. *Comparison of theory and experiment for the osmotic coefficient.* Fig. 20 taken from Hückel's article shows $1 - g$ observed plotted against $\sqrt{(\nu\gamma)}$. The theory, by (947), gives straight lines through the origin which are also shown. The agreement for small concentrations is excellent, and the observed curves approach their theoretical lines as limiting tangents the more rapidly the smaller the valency of the ions. This is as it should be, for the restrictions of the theory are better obeyed the smaller the valency. For somewhat higher concentrations it is found that the full formula (944) with usually reasonable values of σ gives an excellent representation of the observed values. Fig. 21 shows the observed values of $1 - g$ plotted against

$\sqrt{(\nu\gamma)}$, while the curves are theoretical ones calculated from (944) using the following values of σ:

KCl	K_2SO_4	$La(NO_3)_3$	$MgSO_4$
$3{\cdot}76 \times 10^{-8}$	$2{\cdot}69 \times 10^{-8}$	$4{\cdot}97 \times 10^{-8}$	$3{\cdot}55 \times 10^{-8}$

The general agreement is good, but it must be reluctantly admitted that there is no theoretical reason to expect such a success, and that the mean ionic diameters used can bear no simple relation to the diameters of the ions of the solute derived in other ways. The formula is really only acting here as a useful interpolation formula, and σ is correcting for a whole variety of theoretical imperfections which the foregoing discussion should have rendered plain. That the σ obtained in this way as a correction to the laws for very dilute solutions is an omnium gatherum correction and not a true ionic diameter is shown sufficiently clearly by Fig. 22. We see there that the deviations from the simple theory in the series of alkali chlorides are greatest for LiCl and least for CsCl. This requires a greater σ for LiCl than CsCl which is prima facie ridiculous. The deviations here obviously arise because the Li^+ ion is *too small* for the happiness of the theory.

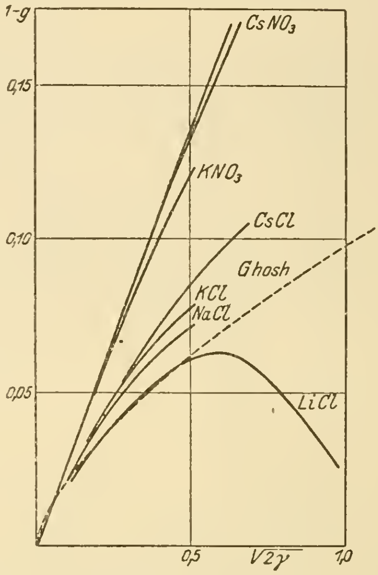

Fig. 22. The effect of ionic sizes on the osmotic coefficient. The broken curve shows $1-g$ according to the theory of Ghosh.

Unreasonably small diameters have also been derived from the Debye-Hückel theory for solutions in water of KNO_3 ($0{\cdot}43 \times 10^{-8}$ cm.) and KIO_3 ($0{\cdot}03 \times 10^{-8}$ cm.)*, while TlCl in a $TlNO_3$ solution† gives a negative (!) diameter of $-\,0{\cdot}93 \times 10^{-8}$ cm.

§ **13·72.** *A more accurate solution of the Debye-Hückel equation.* The impossible diameters mentioned above can in part be ascribed to the inaccuracy of the solution of (931), when the exponent ceases to be small. Gronwall has shown how to improve the solution and found that some of the terms neglected in the rough solution are as large as the terms in $\kappa\sigma$ which are retained‡. Let us consider the simplest case of a symmetrical solute, with two ions of charge $\pm\, z\epsilon$. Then (931) reduces to

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi_a}{\partial r}\right)=\frac{8\pi\epsilon}{D}\,z\,\frac{N}{V}\sinh z\epsilon\psi_a/kT, \qquad \ldots\ldots(948)$$

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* Debye and Hückel, *loc. cit.*; Bjerrum, *Dansk. Vidensk. Selsk.* vol. VII, No. 9 (1926).

† Schärrer, *Phys. Zeit.* vol. XXV, p. 145 (1924).

‡ Gronwall, *Proc. Nat. Acad. Sci.* vol. XIII, p. 198 (1927).

and
$$\kappa^2 = \frac{8\pi\epsilon^2}{DkT} z^2 \frac{N}{V}. \qquad \text{......(949)}$$

It is convenient to introduce the symbols
$$x = \kappa r, \quad a = \kappa\sigma, \quad y = \frac{z\epsilon\psi_\alpha}{kT}, \quad b = \frac{z^2\epsilon^2}{DkT\sigma}. \qquad \text{......(950)}$$

Then
$$\frac{1}{x^2}\frac{d}{dx}\left(x^2 \frac{dy}{dx}\right) = \sinh y, \qquad \text{......(951)}$$

and since at $r = \sigma$
$$\frac{\partial\psi_\alpha}{\partial r} = -\frac{z\epsilon}{D\sigma^2},$$

therefore at $x = a$
$$\frac{dy}{dx} = -\frac{b}{a}. \qquad \text{......(952)}$$

The differential equation may be written
$$\frac{d}{dx}\left(x^2 \frac{dy}{dx}\right) - x^2 y = x^2 \phi\,(y), \qquad \text{......(953)}$$

where
$$\phi\,(y) = \sinh y - y = \sum_{n=1}^{\infty} \frac{y^{2n+1}}{(2n+1)\,!}. \qquad \text{......(954)}$$

We now transform the differential equation into an integral equation by means of the Green's function of the left-hand side*, obtaining
$$y\,(x) = \frac{ba}{1+a}\,\frac{e^{a-x}}{x} - \frac{1}{2x}\int_a^\infty \left\{e^{-|t-x|} - \frac{1-a}{1+a}\,e^{2a-t-x}\right\} \phi\,\{y\,(t)\}\,t\,dt. \qquad \text{......(955)}$$

This equation may be verified by direct differentiation, and attention to the boundary conditions, which are (952) and $y \to 0$ as $x \to \infty$.

The Debye-Hückel solution consists of the first term only. That is, it neglects ϕ entirely. A next approximation may be obtained by substituting the crude solution in ϕ. As κ (and so a) $\to 0$, this term is of the order of a^2. It can be shown (by expanding y in powers of b) that the terms now neglected are of the order of $a^3 \log a$. We write, then,
$$\begin{aligned} y\,(a) &\sim \frac{b}{1+a} - \frac{1}{1+a}\int_a^\infty e^{a-t}\,\phi\left\{\frac{ba}{1+a}\,\frac{e^{a-t}}{t}\right\} t\,dt, \qquad \text{......(956)} \\ &\sim b\,(1 - a + a^2) - \sum_{n=1}^{\infty} \frac{(ba)^{2n+1}}{2n+1\,!}\int_a^\infty e^{2(n+1)(a-t)}\,t^{-2n}\,dt, \\ &\sim b\,(1 - a + a^2) - a^2 \sum_{n=1}^{\infty} \frac{b^{2n+1}}{(2n+1)\,!\,(2n-1)}. \end{aligned}$$

Thus approximately
$$\psi_\alpha\,(\sigma) = \frac{z\epsilon}{D\sigma} - \frac{z\epsilon\kappa}{D}\left(1 - \kappa\sigma + \kappa\sigma \sum_{n=1}^{\infty} \frac{(z^2\epsilon^2/DkT\sigma)^{2n}}{(2n+1)\,!\,(2n-1)}\right). \qquad \text{......(957)}$$

The equation for ψ_β is similar. The potential due to the distribution about the central ion is given by the second term.

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* See Courant-Hilbert, *Methoden der mathematischen Physik*, vol. I, pp. 273–275 (1924).

We now reduce all charges by a fraction μ, and find the work required to increase μ to $\mu + d\mu$. It is

$$-2Nz\epsilon d\mu \,.\, \frac{z\epsilon\kappa\mu^2}{D}\left(1-\kappa\sigma\mu+\kappa\sigma\mu\sum_{n=1}^{\infty}\frac{(z^2\epsilon^2\mu^2/DkT\sigma)^{2n}}{(2n+1)!\,(2n-1)}\right).$$

Integration from $\mu = 0$ to $\mu = 1$ gives the contribution to the work function

$$-kT\Psi_\epsilon = -\frac{2Nz^2\epsilon^2\kappa}{3D}\left(1-\tfrac{3}{4}\kappa\sigma+\tfrac{3}{2}\kappa\sigma\sum_{n=1}^{\infty}\frac{(z^2\epsilon^2/DkT\sigma)^{2n}}{(2n+2)!\,(2n-1)}\right). \qquad \text{......(958)}$$

If σ_0 be the diameter inferred from the crude theory

$$-kT\Psi_\epsilon = -\frac{2Nz^2\epsilon^2\kappa}{3D}\left(1-\tfrac{3}{4}\kappa\sigma_0\right), \qquad \text{......(959)}$$

neglecting powers of κ higher than the square. The two equations for Ψ_ϵ agree if

$$\sigma_0 = \sigma - 2\sigma\sum_{n=1}^{\infty}\frac{(z^2\epsilon^2/DkT\sigma)^{2n}}{(2n+2)!\,(2n-1)}. \qquad \text{......(960)}$$

This agreement holds for any thermodynamic function, such as the osmotic pressure or the free energy, which is obtained from Ψ by differentiation with respect to the volume. For the volume enters into (958) and (959) only through κ, and does not affect (960). The relation between σ_0 and σ may be written

$$\frac{DkT\sigma_0}{z^2\epsilon^2} = \Phi\left(\frac{DkT\sigma}{z^2\epsilon^2}\right), \qquad \text{......(961)}$$

where

$$\Phi(x) = x - \sum_{n=1}^{\infty}\frac{2/x^{2n-1}}{(2n+2)!\,(2n-1)}. \qquad \text{......(962)}$$

These formulae give more reasonable diameters, as appears from the following table taken from Gronwall.

TABLE 44.

Diameters of electrolytic ions by elementary and extended theory.

Solvent	Solute	$10^8\,\sigma_0$ elementary theory	$10^8\,\sigma$ extended theory
$TlNO_3$ in H_2O	TlCl	−0·93	1·77
H_2O	KIO_3	0·03	2·12
H_2O	KNO_3	0·43	2·30

The general case, of N_i ions with valency z_i ($i = 1, 2, \ldots; \Sigma_i N_i z_i = 0$), may be treated in the same manner, but there is now nothing corresponding to σ_0. For instance, we get

$$-kT\Psi_\epsilon = -\tfrac{1}{3}\frac{\epsilon^2\kappa}{D}\Sigma_i N_i z_i^2\left\{1-\tfrac{3}{4}\kappa\sigma-\frac{[z]^2}{4}\frac{\epsilon^2\kappa}{DkT}\left(\log\frac{1}{3\kappa\sigma}-C+\tfrac{1}{6}\right)\right.$$
$$\left.+\tfrac{3}{2}\kappa\sigma\sum_{r=3}^{\infty}\frac{[z^{r-1}]^2\,(-\epsilon^2/DkT\sigma)^{r-1}}{(r+1)!\,(r-2)}\right\}, \qquad \text{......(963)}$$

where C is Euler's constant, and $[z^r] \equiv \Sigma_i N_i z_i^{r+2} / \Sigma_i N_i z_i^2$. As $\kappa \to 0$ the largest terms in the bracket are

$$1 - \frac{[z]^2}{4} \frac{\epsilon^2 \kappa}{DkT} \log 1/\kappa, \qquad \text{......(964)}$$

so that the behaviour of (964) is quite different from that of the crude result

$$-kT\Psi_\epsilon = -\tfrac{1}{3} \frac{\epsilon^2 \kappa}{D} \Sigma_i N_i z_i^2 \left(1 - \tfrac{3}{4}\kappa\sigma_0\right). \qquad \text{......(965)}$$

We may however work with a σ_0 defined by the equation

$$-kT\Psi_\epsilon = -\tfrac{1}{3} \frac{\epsilon^2 \kappa}{D} \Sigma_i N_i z_i^2 \left\{1 - \tfrac{3}{4}\kappa\sigma_0 - \frac{[z]^2}{4} \frac{\epsilon^2 \kappa}{DkT} \left(\log \frac{1}{3\kappa\sigma_0} - C + \tfrac{1}{6}\right)\right\}, \qquad \text{......(966)}$$

neglecting smaller infinitesimals as $\kappa \to 0$. Then

$$\sigma_0 + \frac{[z]^2}{3} \frac{\epsilon^2}{DkT} \log 1/\sigma_0 = \sigma + \frac{[z]^2}{3} \frac{\epsilon^2}{DkT} \log 1/\sigma - 2\sigma \sum_{r=3}^{\infty} \frac{[z^{r-1}]^2 (-\epsilon^2/DkT\sigma)^{r-1}}{(r+1)!\,(r-2)}, \qquad \text{......(967)}$$

that is,

$$\frac{DkT\sigma_0}{[z]^2 \epsilon^2} - \tfrac{1}{3} \log \frac{DkT\sigma_0}{[z]^2 \epsilon^2} = \Theta\left(\frac{DkT\sigma}{[z]^2 \epsilon^2}\right), \qquad \text{......(968)}$$

where

$$\Theta(x) = x - \tfrac{1}{3} \log(x) + \sum_{n=1}^{\infty} \frac{(-)^n\, 2/x^n}{(n+3)!\, n} \frac{[z^{n+1}]^2}{[z]^{2(n+1)}}. \qquad \text{......(969)}$$

Since the relation between σ_0 and σ is again independent of κ, it will hold for all thermodynamic applications as before. The conclusion that there should be this divergence between symmetrical and unsymmetrical electrolytes seems to be supported by the facts.

§ **13·8**. *Specific heats of solutions of electrolytes and indications of necessary theoretical developments.* The considerations advanced in this concluding section are in the main derived from Zwicky*. We shall only attempt a short descriptive account of the nature of the problems and of the tentative solution proposed, for a satisfactory theory requires a theory of the pressure variation of the specific heat of water, which has not yet been developed in quantitative form.

The outstanding fact is that, contrary to the naïve theory of § 13·4, the specific heat of a solution of a strong electrolyte at ordinary temperatures and pressures is appreciably *less* than that of the water in the solution in its pure state. With this we may associate the well-recognized fact that solutions of electrolytes have equations of state which are very close to that of water under high pressure, and that the specific heat of water at

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* Zwicky, *Phys. Zeit.* vol. XXVII, p. 271 (1926).

temperatures from 10° C.–60° C. diminishes with increasing pressure. This variation of the specific heat has not been directly measured but derived from measurements of specific volume and the thermodynamic relation

$$\frac{\partial C_p}{\partial p} = - T \frac{\partial^2 v}{\partial T^2}.$$

This property of water is satisfactorily accounted for in a qualitative way in terms of the formation of complex molecules (polymerization) of large specific volume compared with the simple H_2O. This large specific volume is well known in ice. Since dissociation of these complexes reduces the volume of the constituent molecules in water the degree of dissociation is increased by increasing the pressure. The melting of ice under pressure is simply the extreme case of this phenomenon. It is easy to see that such properties can give rise to a point of maximum density at given pressure. For as the temperature is raised at given pressure there are two processes going on. One is the natural expansion of any fluid (of fixed constituents) due to the increasing kinetic energy of translation and therefore rate of transfer of momentum. The other is the dissociation of large complexes into constituents of smaller total volume. This acts in the opposite sense and a balance point is possible, and, as we know, occurs in water.

Now consider the effect of this polymerization on the specific heat of the water. The specific heat of water at room temperature is by definition 18 calories per gram-molecule, and falls to 16·5 calories at 100° C. If we think of the constituents of water as simple rigid H_2O molecules they have 6 degrees of freedom and, even granting them the full potential energy in each degree of freedom as well as the kinetic energy they must possess, the specific heat could not be more than $12 \times \frac{1}{2}R$ or 12 calories. To this internal molecular energy must be added, to an amount which can be estimated closely from the properties of H_2O vapour at 100° C. It can certainly there not exceed 0·5 calorie, and would be negligible at room temperature. There are thus 6 calories unaccounted for without polymerization, which can (and must) be properly accounted for by the heat of dissociation when polymerization is taken into account. But since pressure decreases the polymerization pressure will decrease C_p at all temperatures at which polymerization still plays a dominant part. This includes room temperatures. At higher temperatures the variation of C_p can change sign in consequence of the entry of other effects.

Zwicky has shown that the specific effects in solution of electrolytes can be at once interpreted at least qualitatively in terms of these bulk properties of water, and the intense pressure field which must surround an ion due to the attraction of its inhomogeneous field for the water dipoles. He estimates the mean dipole for (polymerized) water molecules at 5×10^{-19} (as against $1·87 \times 10^{-18}$ for H_2O in a vapour). He then shows that changes of specific heat can be expected of the following amounts per gram-molecule of simple univalent salt dissolved:

(1) Due to the increase of number of degrees of freedom of the assembly for the dissolved matter

12 calories.

(2) Due to the electrical polarization of the medium round each ion

− 9·8 calories.

In this estimate an attempt is made to allow for the saturation of the polarization round each ion.

(3) Due to the compression of the water round each ion

− 119 calories.

These amounts have to be corrected for overlapping of the ionic fields.

(4) An unknown amount for hydration.

For further details Zwicky's paper should be consulted. The net result is convincing that the explanations offered are on the right lines, and that it only requires a proper elaboration of an exact theory to give complete satisfaction in the explanation of this large group of important facts.

§ **13·9**. *Brownian movement.* In connection with the properties of liquids it is natural to consider the phenomena of Brownian movement. Though the phenomena are observable and similar in all fluids, it is in liquids that the earliest and most striking observations have been made. As we now know the phenomena of Brownian movement are merely the phenomena of molecular agitation, exhibited on a reduced scale by a particle which is very large on the molecular scale—so large that its diffraction effects at least can be seen in an ultramicroscope—and yet so small that its velocity of thermal agitation in the equilibrium state is sufficient to give it visible displacements in reasonable periods of time. This identity was finally established by the experimental work of Perrin* verifying the theories of Einstein. Subsequent investigators have added more accurate measurements in even closer accord with the theory. By the study of suitable particles suspended in a fluid (1) we see the molecular motions going on before our eyes, (2) we can check the assumptions of statistical mechanics in a rather detailed way by proving that the characteristics of the Brownian movement agree with the demands of that theory, and (3) we obtain a direct, though not very accurate, method of measuring molecular magnitudes.

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* Perrin, *La théorie du rayonnement et les quanta* (1912), "Les preuves de la réalité moléculaire". Einstein, *Ann. der Phys.* vol. XVII, p. 549 (1905), vol. XIX, p. 371 (1906).

§ **13·91**. *The particle "atmosphere".* In a liquid in a field of force, containing particles, but so few that their mutual volume interactions may be neglected, we shall find the atmospheric density law

$$\nu = \nu_0 e^{-M'gz/kT}. \qquad \text{......(970)}$$

This follows at once by generalizing (905) in the manner of the concluding paragraphs of § 8·3. M' is the apparent mass of a single grain, that is its mass less the mass of the fluid it displaces. Taking logarithms and introducing the density Δ of the grains and δ of the liquid, we have for spherical grains

$$kT \log (\nu_0/\nu) = \tfrac{4}{3}\pi a^3 (\Delta - \delta)\, gz. \qquad \text{......(971)}$$

In this equation ν_0 and ν can be determined by actually counting the grains visible in the field of a microscope. The other quantities are all easily measurable except a the radius of the grain. This can be fixed in various indirect and independent ways, so that (971) becomes an equation for k, after verification that $T \log (\nu_0/\nu)/z$ is constant. The value obtained by Perrin in this manner was $1·22 \times 10^{-16}$ in sufficiently good agreement with the correct value.

§ **13·92**. *The diffusion movements of a single grain.* If one attempts to follow as closely as possible the actual movements of a single grain and works out an observed "mean velocity of agitation", the value so found is always of the order of 10^{-5} times the value given by the equilibrium theory for the average velocity of a particle of the given mass. Such estimates however are necessarily grossly wrong. We can never follow the details of the movement of the grain, which has a kink at every molecular collision —about 10^{21} times a second in an ordinary liquid*. What we observe in the way of displacements are of the nature of residual fluctuations about a mean value zero and have little direct connection with the actual detailed path of the grain. [To our senses (pushed to their furthest in the form of the best cinematograph taking pictures at 10^5 per sec.) the details of the path are impossibly fine. It may fairly be compared in a crude way to the graph of a continuous function with no differential coefficient. Such a curve has not got a "length", and no idea of length can be obtained from any inscribed polygon.]

A more subtle analysis is necessary. Confining attention to displacements in one direction, let the concentration of the grains at any place and time be $\nu (x, t)$. Of those in any interval $x, x + dx$ let the fraction $f_\tau (x' - x)\, dx'$ be found after a time τ in the interval $x', x' + dx'$. This fraction can depend only on $x' - x$ and not on x' and x separately. By integrating

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* That is, so frequently that it is really wrong to think of separate collisions.

the contributions found in dx' at time $t + \tau$ from all other elements we find

$$\nu(x', t+\tau) = \int_{-\infty}^{+\infty} \nu(x, t) f_\tau(x' - x)\, dx,$$

$$= \int_{-\infty}^{+\infty} \nu(x' - X, t) f_\tau(X)\, dX. \qquad \text{......(972)}$$

This equation must hold for all x', t and τ*. It is satisfied in the equilibrium state in which ν is constant in space and time, since by its definition

$$\int_{-\infty}^{+\infty} f_\tau(X)\, dX = 1.$$

Let us first suppose that τ is small, and expand both functions ν. Then

$$\nu(x', t) + \tau \frac{\partial \nu}{\partial t} + O(\tau^2) = \int_{-\infty}^{+\infty} \left\{ \nu(x', t) - X \frac{\partial \nu}{\partial x'} + \tfrac{1}{2} X^2 \frac{\partial^2 \nu}{\partial x'^2} - \tfrac{1}{6} X^3 \frac{\partial^2 \nu}{\partial x'^3} + O(X^4) \right\} f_\tau(X)\, dX. \qquad \text{......(973)}$$

The odd powers of X may be assumed to vanish on integration by symmetry, and we shall verify *a posteriori* that the $O(\tau^2)$ and $O(X^4)$ terms are negligible for sufficiently small τ. We then find

$$\tau \frac{\partial \nu}{\partial t} = \tfrac{1}{2} \xi^2 \frac{\partial^2 \nu}{\partial x'^2}, \qquad \text{......(974)}$$

where
$$\xi^2 = \int_{-\infty}^{+\infty} X^2 f_\tau(X)\, dX. \qquad \text{......(975)}$$

This is Einstein's diffusion equation for the displacements of single grains.

It is easily verified that ξ^2/τ must be a constant independent of τ and characteristic of the grain, as is really required for (974) to be significant. For if τ is not too small (greater than 10^{-5} sec. will suffice†) the velocity of the grain at the end of the interval τ will be completely independent of the velocity at the beginning. Displacements in consecutive τ-intervals will therefore be independent. This being so if $\tau' = p\tau$ and $x_1, \ldots, x_p$ are p consecutive x-displacements, then

$$x'^2 = \Sigma x_r^2 + 2\Sigma x_i x_j.$$

If then we average x'^2 for a large number n of grains or displacements the product term will vanish‡ and we shall find

$$n\xi'^2 = np\xi^2,$$

or
$$\xi'^2/\tau' = \xi^2/\tau. \qquad \text{......(976)}$$

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[*] Compare the similar treatment of velocities in § 19·5.

[†] This estimate is made by calculating how long the viscosity of the liquid will take to reduce the velocity of a sphere the size of the grain to an insignificant fraction of its initial value. See Perrin, *loc. cit.*

[‡] Strictly, from the independence and the definition of f_τ,

$$\overline{x_i x_j} = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} x \; x_j f_\tau(x_i) f_\tau(x_j)\, dx_i dx_j,$$

which vanishes by symmetry.

The approximation leading to (974) will still be adequate for τ's large enough to satisfy (976).

Unlike the true velocity of agitation the diffusion constant

$$D = \xi^2/2\tau$$

of a grain is directly measurable. It has been shown by Einstein that such measurements may be made to lead at once to a determination of k. We apply the foregoing arguments to an atmosphere of grains in equilibrium in a field of force. The rate of diffusion under the concentration gradient must then just balance the directed effect of the field of force. If a force F acts on the grains, assumed spheres of radius a, they acquire, by Stokes' law, a steady velocity v given by

$$v = \frac{F}{6\pi\mu a},$$

where μ is the viscosity of the fluid. The number crossing unit interface in unit time is therefore $v\nu$ or

$$\frac{\nu F}{6\pi\mu a}.$$

The number crossing by diffusion in the *opposite* direction is $D\partial\nu/\partial x$. If further the grains obey the atmospheric distribution law we have

$$\nu = \nu_0 e^{-\chi/kT},$$

or

$$\frac{1}{\nu}\frac{\partial\nu}{\partial x} = \frac{F}{kT}.$$

Combining these results

$$D = \frac{\xi^2}{2\tau} = \frac{kT}{6\pi\mu a}. \qquad \text{......(977)}$$

This equation has been verified to lead to consistent satisfactory values of k by observation over wide ranges of T, μ and a.

§ **13·93**. *Generalizations. Further deductions from the equation* (972). Equation (972) yields much more information than we have yet obtained, and in fact also fixes the form of $f_\tau(X)$*. On differentiating with respect to τ we find

$$\frac{\partial\nu}{\partial t}(x', t+\tau) = \int_{-\infty}^{+\infty} \nu(x'-X, t)\frac{\partial f_\tau}{\partial\tau}(X)\,dX.$$

But by (974)

$$\frac{\partial\nu}{\partial t}(x', t+\tau) = D\frac{\partial^2\nu(x', t+\tau)}{\partial x'^2},$$

$$= D\frac{\partial^2}{\partial x'^2}\int_{-\infty}^{+\infty} \nu(x'-X, t)f_\tau(X)\,dX,$$

$$= D\int_{-\infty}^{+\infty} \frac{\partial^2}{\partial X^2}\nu(x'-X, t)f_\tau(X)\,dX,$$

$$= \int_{-\infty}^{+\infty} \nu'(x'-X, t)\,D\frac{\partial^2}{\partial X^2}f_\tau(X)\,dX,$$

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* On certain assumptions. See note on p. 332.

assuming the legitimacy of the various inversions of limit operations. We therefore find

$$\int_{-\infty}^{+\infty} \nu(x' - X, t) \left[D \frac{\partial^2}{\partial X^2} - \frac{\partial}{\partial \tau} \right] f_\tau(X)\, dX = 0.$$

This equation is to hold for all x', t and τ, so that it must hold for *any* initial law of density distribution $\nu(x' - X)$. It therefore implies that*

$$\left[D \frac{\partial^2}{\partial X^2} - \frac{\partial}{\partial \tau} \right] f_\tau(X) = 0. \qquad \text{......(978)}$$

The displacement distribution function $f_\tau(X)$ is therefore that solution of (978) which places all the grains near $X = 0$ at $\tau = 0$ (the point-source solution). Hence

$$f_\tau(X) = \frac{1}{2\sqrt{(\pi D \tau)}}\, e^{-X^2/4D\tau}, \qquad \text{......(979)}$$

or

$$f_\tau(X) = \frac{1}{\sqrt{(2\pi)}} \frac{1}{\xi}\, e^{-\frac{1}{2}X^2/\xi^2}. \qquad \text{......(980)}$$

This law, the error law, for the displacements has been exhaustively tested by observation. Perrin gives the following set of counts on the displacements of a grain of radius $2{\cdot}1 \times 10^{-5}$ cm. at 30 sec. intervals. Out of a number N of such observations the number of observed values of x-displacements between x_1 and x_2 should be

$$\frac{N}{\sqrt{(2\pi)}} \int_{x_1}^{x_2} \frac{1}{\xi}\, e^{-\frac{1}{2}X^2/\xi^2}\, dX.$$

TABLE 45.

Observations and calculations of the distribution of the displacements of a Brownian grain.

Range of $x \times 10^4$ cm.	1st set		2nd set		Total	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0 – 3·4	82	91	86	84	168	175
3·4– 6·8	66	70	65	63	131	133
6·8–10·2	46	39	31	36	77	75
10·2–17·0	27	23	23	21	50	44

We observe at this point that the experimental form of $f_\tau(X)$ justifies our preliminary neglect of $O(X^4)$ and $O(\tau^2)$ in (973).

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* We may assert that $\int_{-\infty}^{+\infty} \nu(x' - x)\, \phi(x)\, dx = 0$ for any given ν and all x'. Let $\nu(x) = 1$ from $-\infty$ to 0 and $\nu(x) = 0$ from 0 to ∞. Then $\int_{x'}^{\infty} \phi(x)\, dx = 0$ for all x' and therefore $\phi(x) = 0$.

§ **13·94**. *Einstein's extension of* (977). The argument establishing (977) can be extended to the displacements with respect to any coordinate α (e.g. an angular one) in which the normal equilibrium distribution is uniform. If A^2 is the mean square displacement in this coordinate in time τ due to the molecular agitation then by the old argument A^2/τ is constant. The distribution in α satisfies the same diffusion equation

$$\frac{\partial \nu}{\partial t} = D\frac{\partial^2 \nu}{\partial \alpha^2} \quad (D = A^2/2\tau);$$

and the number of particles passing by diffusion across a given value α of the coordinate in unit time is again

$$D\frac{\partial \nu}{\partial \alpha},$$

in the direction of ν decreasing.

Now suppose an external field of potential energy $\phi(\alpha)$ acts on the grains. In the equilibrium state we should have the distribution law

$$\nu = \nu_0 e^{-\phi(\alpha)/kT}.$$

Suppose further that for an individual grain under a force Ψ we have a steady velocity controlled by viscous resistances and given by

$$\kappa\frac{d\alpha}{dt} = \Psi.$$

Then in the equilibrium state when $\Psi = -\phi'(\alpha)$

$$D\frac{\partial \nu}{\partial \alpha} = -\frac{\nu\phi'(\alpha)}{\kappa}.$$

But
$$\frac{1}{\nu}\frac{\partial \nu}{\partial \alpha} = -\frac{\phi'(\alpha)}{kT}.$$

Therefore
$$D = kT/\kappa = \tfrac{1}{2}A^2/\tau. \qquad \text{......(981)}$$

This is the required generalization of (977). For a sphere rotating in a viscous liquid about a fixed axis

$$\kappa = 8\pi a^3\mu.$$

Therefore for rotational displacements

$$\frac{A^2}{\tau} = \frac{kT}{4\pi a^3\mu}, \qquad \text{......(982)}$$

an equation confirmed experimentally by Perrin.

Footnote to p. 330. The hypothesis that the terms $O(X^4)$ etc. are all $O(\tau^2)$ is essential to § 13·93 and the result is not necessarily true without it. The terms $\overline{X^4}$... *might* contain terms of order τ, when (974) would contain $\partial^4\nu/\partial x^4$, ... If the usual diffusion equation (974) is exact, then the distribution function is Gaussian and conversely as we have shown in the text. But this is not so on the scale of the eddy diffusion in the atmosphere. For Brownian movement Perrin's experiments show that the diffusion equation and the distribution function have their simplest form. Appeal to experiment cannot be dispensed with. I owe this footnote to Mr J. A. Gaunt.

CHAPTER XIV

ASSEMBLIES OF ATOMS, ATOMIC IONS AND ELECTRONS

§ **14·1**. *Introductory.* We have already had occasion to consider incidentally examples of gaseous assemblies in which atoms, ions and electrons are present in dissociative equilibrium. We shall have occasion in the following chapters to discuss systematically assemblies, especially at high and very high temperatures, which are composed entirely of atomic ions and electrons. These discussions of course have reference to the state of matter in stars. It will be necessary to give a general survey of the present state of atomic theory, at least on the formal descriptive side, so that we may be able to write down at will the partition function, or an effective approximate form of it, for the internal energy of any atomic ion. We have then to reformulate the general theory of dissociative equilibrium in terms of atomic ions and electrons instead of atoms and molecules and introduce correcting terms for the electric charges of the particles. This would be a simple matter were it not for the outstanding difficulty of the convergence of the partition functions which must be disposed of in some way during the process.

We shall assume that no molecules are present in the assembly; they can easily be included when required. Let

M_0^z be the (average) number of neutral atoms of atomic number Z in a volume V;

M_r^z be the (average) number of such atoms r-times ionized;

N be the (average) number of free electrons.

In general atoms r-times ionized must be defined to mean nuclei accompanied by $Z-r$ electrons, each of which has insufficient energy to effect an escape. These $Z-r$ electrons combine together to form the stationary states of the ion in which the state of each electron can be described by four quantum numbers. The most convenient state of conventionally zero energy is that state of the assembly in which the only constituents are electrons and bare nuclei at rest at infinite separation. The bare nucleus is assumed to be structureless. This is of course untrue, but unless we are to discuss the break-up and re-formation of nuclei their structure is irrelevant* and it is a legitimate simplification to regard them as structureless massive charged points, for which the standard weight $dp_1 \ldots dq_3/h^3$ is assigned to the element of phase space $dp_1 \ldots dq_3$. The bare nucleus will

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* This is of course only correct because we are not concerned here with formation of molecules. We have seen in the study of H_2 in § 3·4, and again in § 7·41, that the nuclear weights are not only relevant but important.

therefore have a partition function $VF_z^z(T)$ of the usual form (342). The electron is now believed, on spectroscopic evidence, not to be structureless but to have an axis of spin and two possible orientations in a magnetic field. Its spin is invariable in amount and it can otherwise be regarded as a massive charged point, for which when free the weight $2\,(dp_1 \dots dq_3)/h^3$ is assigned to the element of $dp_1 \dots dq_3$. We shall use m for the mass of the electron and m^z for the bare nucleus Z. It will never be necessary to distinguish between m^z and $m^z + rm$ $(r \leqslant z)$. The partition function for the free electron will therefore be $VG(T)$, where

$$G(T) = \frac{2\,(2\pi mkT)^{\frac{3}{2}}}{h^3}, \qquad \text{......(983)}$$

which we have already used in Chapter XI.

Consider next the normal state of each atomic ion. Let the successive ionization energies of the atom Z be $\chi_0^z, \chi_1^z, \dots, \chi^z_{z-1}$ and the weights of the normal states ϖ_r^z. These χ's are all to be defined with reference to a series of normal states or states of least energy so that χ_r^z is the work required to remove one electron from an atom, which has already lost r electrons and is then at rest in the state of lowest energy possible for its remnant of $(Z - r)$ electrons, and leave it again in its state of lowest possible energy for the remnant of $(Z - r - 1)$ electrons, the atom and the extracted electron being at rest at infinite separation. For the r-times ionized atom in its normal state the partition function $VF_r^z(T)$ is therefore given by

$$F_r^z(T) = \frac{(2\pi m^z kT)^{\frac{3}{2}}}{h^3}\, \varpi_r^z\, e^{\{\chi_r^z + \dots + \chi^z_{z-1}\}/kT}. \qquad \text{......(984)}$$

Each ion possesses in addition a set of stationary excited states of greater energy content. If every excited state could be treated formally as a constituent of a perfect gas this would cause ϖ_r^z to be replaced by $b_r^z(T)$, where

$$b_r^z(T) = \sum_{s=0} (\varpi_r^z)_s\, e^{-\{\chi_r^z - (\chi_r^z)_s\}/kT}. \qquad \text{......(985)}$$

The state $s = 0$ is the normal state and we continue to write ϖ_r^z and χ_r^z instead of $(\varpi_r^z)_0$ and $(\chi_r^z)_0$. The energy of excitation is $\chi_r^z - (\chi_r^z)_s$, so that $(\chi_r^z)_s$ is the energy corresponding to the sth spectral *term* (suitably ordered) of the r-times ionized atom Z. In fact $b(T)$ does not converge. The alterations necessary will be discussed at length later in §§ 14·4, 14·5. It is evident from (985) that an application of statistical mechanics to such assemblies requires a working knowledge of or approximation to $(\varpi_r^z)_s$ and $(\chi_r^z)_s$ for all r, s and z.

§ **14·2.** *General features of atomic structure**. We shall start by summarizing the general features of atomic structure which will form the basis

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* We adopt in this paragraph the most modern normalization of the quantum numbers n, k, j, s of an electronic orbit, taking the numbers that are natural to the characteristic solutions of Schrödinger's equation. These are also practically the most convenient for most descriptive

of our discussion. Following Bohr it is now well known that the electrons in the atom can be classified first of all according to their principal quantum number n (1, 2, 3, ...) and azimuthal quantum number k (0, 1, 2, ..., $n-1$) as n_k electrons. The broad outlines of the periodic table of the elements can be at once accounted for in this way if it is assumed that just so many electrons and no more can be packed into each of these groups or subgroups. It was recognized at once that the maximum number of electrons in any atom with principal quantum number n must be $2n^2$ to fit the periodic table. For some time the numbers of electrons in the n_k subgroups were uncertain, but thanks to the work of Stoner and Pauli it was shown that the number must be $2(2k+1)$. We recall of course that

$$2\sum_{0}^{n-1}(2k+1)=2n^2.$$

Pauli in particular was able to show that this maximum number of electrons was an example of a general rule governing the whole structure of atomic stationary states, namely that two electrons in one atom can never occupy orbits described by exactly the same set of quantum numbers. We shall have more to say of this rule later on and shall refer to it meanwhile as Pauli's exclusion principle or simply Pauli's principle. He formulated it on purely empirical grounds, but it has since been shown by Heisenberg and Dirac to possess a natural basis in the new mechanics. As a result the number of electrons $2(2k+1)$ and $2n^2$ in subgroups and groups, which yields at once the general structure of the periodic table, may now be regarded as *a formal deduction* from the new atomic mechanics. When any group or subgroup of electrons is full it forms a symmetrical structure without mechanical or magnetic moment and interacts with other electrons at least to a first approximation like a simple central field of force.

We have started by introducing the closed groups in the atom on account of their descriptive importance, but logically they are complex and are arrived at at a later stage. We turn next therefore to describe the states of a hydrogen-like atom with just one electron, observing that owing to the symmetry of closed groups any atomic ion containing only closed groups behaves qualitatively exactly like a bare nucleus in forming states for the next electron. There are only quantitative energy differences in the states due to the different effective central field.

The states of the hydrogen-like atom containing one spinning electron are described according to the new mechanics by four quantum numbers n, k, j, and s. The principal quantum number n takes (as of old) the values (1, 2, 3, ...). The azimuthal quantum number k takes the values (0, 1, 2, ..., $n-1$). This holds so far equally for a structureless electron. We note also

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purposes and had been used empirically for that purpose by Sommerfeld and others previous to the wave theory. We use s in preference to the commoner m to avoid confusion with the mass of the electron.

that there are no longer *any* artificial exclusions of orbits for mechanical reasons such as "hitting the nucleus". For small quantum numbers at least the mechanical orbits of the older theory have no meaning. *Every* solution of Schrödinger's equation is acceptable and accepted, and we note that for any n there is always one solution (that for which $k = 0$) without "orbital" angular momentum. The spinning electron has a spin of constant magnitude. As we have already seen in Chapter XII, the quantity representing total angular momentum of any isolated system has on the new mechanics the values $(h/2\pi)\{i(i+1)\}^{\frac{1}{2}}$, and its resolved part in the direction of a magnetic or other orientating field the values $+i, \ldots, -i$. For the electron we must assume $i = \frac{1}{2}$. This momentum then compounds with the "orbital" momentum k to give the total angular momentum j of the atom. The j values of the atom are therefore

$$k = 0,\quad j = \tfrac{1}{2};$$

$$k \geqslant 1,\quad j = k \pm \tfrac{1}{2}.$$

The total moment of momentum of the atom is represented as usual by $(h/2\pi)\{j(j+1)\}^{\frac{1}{2}}$. If the atom (or electron and orbit) as a whole is orientated by an external magnetic field, then the possible components of the momentum along the field are $sh/2\pi$, where s takes the $(2j+1)$ values

$$-j \leqslant s \leqslant +j.$$

The complete set of states therefore corresponds to the following sets of values of the four quantum numbers n, k, j, s.

TABLE 46.

The quantum numbers of the states of a one-electron atom.

n	k	j	s	Totals		
1	0	$\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$	2		
2	0	$\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$	2		8
	1	$\frac{3}{2}$	$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$	4	6	
		$\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$	2		
3	0	$\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$	2		18
	1	$\frac{3}{2}$	$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$	4	6	
		$\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$	2		
	2	$\frac{5}{2}$	$\frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, -\frac{5}{2}$	6	10	
		$\frac{3}{2}$	$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$	4		
4	0	$\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$	2		32
	1	$\frac{3}{2}$	$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$	4	6	
		$\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$	2		
	2	$\frac{5}{2}$	$\frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, -\frac{5}{2}$	6	10	
		$\frac{3}{2}$	$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$	4		
	3	$\frac{7}{2}$	$\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, -\frac{5}{2}, -\frac{7}{2}$	8	14	
		$\frac{5}{2}$	$\frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, -\frac{5}{2}$	6		

We see at once that they verify the formulae $2n^2$ and $2(2k+1)=2k+2+2k$ already given, and, assuming Pauli's principle, that the general structure of the periodic table must follow. We note in addition that structurally the spectrum of hydrogen is exactly analogous to that of an alkali; the only difference arises from the accidental coincidence of certain terms in the hydrogen spectrum for different values of k which do not coincide for an alkali owing to the energy variation with k in a non-Coulomb central field. To an approximation which is in general ample for our applications the terms of a true one-electron spectrum depend only on n and are given by the Balmer formula

$$\chi_n = RhcZ^2/n^2. \qquad \text{......(986)}$$

The typical one-electron spectrum is thus (in agreement with observation) what is called a *doublet* spectrum. It consists of sets of terms labelled ^2S, ^2P, ^2D, ^2F, ^2G, ... corresponding to $k = 0, 1, 2, 3, 4, \ldots$, of which the ^2S terms are *single* and all the others *double*. Different terms with the same label correspond to different values of n, but their structure is always independent of n. All the terms are completely resolved by a magnetic field so that no degeneracy remains. We therefore expect that the weight unity should be attached to each magnetic state, and we shall find that this checks up with the limiting principle. The weight of all ^2S terms is therefore 2, of the ^2P terms $4 + 2 = 6$, of the ^2D $6 + 4 = 10$ and so on, or in general the weight of each separate term is $2j + 1$. At the moment this is only justified for strictly hydrogen-like atoms, but we shall see directly that on the same basis all closed configurations have also weight unity and the same set of weights therefore apply to the states of all atoms and ions constructed of closed groups plus one extra electron.

When we come to atoms with more than one extra electron the same principles can still be applied. Subject always to exclusions by Pauli's principle, if we have two electrons in n, k, j, s and n', k', j', s' orbits, originally thought of as independent of each other, we obtain thus one possible atomic state. Subsequent introduction of the mutual perturbations may alter the energy but cannot touch the existence of the state. For given n, k and n', k', for example, the variations of j, s and j', s' are independent and the total number of states found should be

$$2^2\,(2k + 1)\,(2k' + 1). \qquad \text{......(987)}$$

This is in fact correct. If we allow k and k' also to vary the total number of states for given n and n' should be

$$2^2 n^2 n'^2, \qquad \text{......(988)}$$

which is again correct. In practice of course the actual states of an atom with two electrons do not present themselves in this way. The atom as it were constructs itself by compounding the four momentum vectors of the two orbits and the two electrons in a certain order of tightness of binding.

The four vectors have possible components in a specified direction ranging between $\pm k$, $\pm k'$, $\pm \frac{1}{2}$, $\pm \frac{1}{2}$, respectively. It can be shown without much difficulty that the order of compounding is without effect on the total number of terms and total weight or number of magnetic states. The composition commonest in actual two-electron spectra is based on the formation of the vector orbital momentum l from k and k',

$$|k - k'| \leqslant l \leqslant k + k' \quad (l = k \text{ if } k' = 0), \qquad \text{......(989)}$$

and the electronic momentum r from $\frac{1}{2}$ and $\frac{1}{2}$,

$$r = 1, 0. \qquad \text{......(990)}$$

Then l and r combine to give the j-values specifying the total moment of momentum of the atomic system (or rather its maximum resolved part), namely

$$|l - r| \leqslant j \leqslant l + r \quad (j = l \text{ if } r = 0). \qquad \text{......(991)}$$

In the particular case of two electrons we therefore get

$$j = l, \qquad \text{......(992)}$$

$$j = l + 1,\ l,\ l - 1, \qquad \text{......(993)}$$

that is sets of singlets and triplets containing four terms in all for given l of total weight $4(2l + 1)$. If $k' = 0$, $l = k$, and this agrees with (987). If $k, k' \neq 0$, then we may suppose $k' \leqslant k$ (otherwise we interchange them), and the possible l values are $(k + k')$, $(k + k' - 1)$, ..., $(k - k')$. The total number of terms is $4(2k' + 1)$ and the total weight $4\{\sum_{k-k'}^{k+k'} (2l + 1)\}$ or $4(2k + 1)(2k' + 1)$ in agreement with (987). Subject still to exclusions by Pauli's principle the argument can be extended to any number of electrons extra to the closed groups. The total number of states formed by q such electrons in $(n_1)_{k_1}, \ldots, (n_q)_{k_q}$ orbits is always

$$2^q (2k_1 + 1) \ldots (2k_q + 1), \qquad \text{......(994)}$$

or in $n_1, \ldots, n_q$ orbits for any k's

$$2^q n_1^2 \ldots n_q^2. \qquad \text{......(995)}$$

It will be remarked that this number of states is only obtained if we regard the electrons as distinguishable and not allowed to interchange. If we allowed q' distinguishable electrons to be permuted we should expect to get $q'!$ times as many different states.

Let us now try to put the maximum number $2(2k + 1)$ of electrons into any one subgroup of azimuthal quantum number k, remembering Pauli's principle. For all these electrons n and k are the same and therefore one at least of j and s must differ for any pair of electrons. Since there are exactly $2(2k + 1)$ different pairs of possible values of j and s there is one way and one way only in which the electrons can be inserted (permutations being disallowed). There must be one electron in each orbit, and since the values of s are symmetrical about zero the resultant j for the atom is zero, and we have a single state of weight unity. This is the theoretical basis of our previous assertions about the properties of closed groups and subgroups.

There are of course always reductions in the number of states given by (994) and (995) whenever two electrons have the same (n, k) or the same n. This is of particular importance for the smallest possible values of n and k, when it describes the fact that certain otherwise expected spectral terms do not occur. For larger values of n it can usually be ignored, for what will be required is the asymptotic form of (995) for large n, and it is easy to see that (995) remains *asymptotically* true in spite of Pauli's principle. It will be sufficient to consider a simple case of two electrons in states of the same n, and to exclude *all* states of the same k which of course is a gross overestimate. The total number of states by (995) would be $4n^4$. By the other estimate the actual number is at least

$$4\overset{n-1}{\underset{k,k'}{\Sigma_0}}(2k+1)(2k'+1)\quad(k\neq k'),$$

or

$$4n^4-\sum_{0}^{n-1}(2k+1)^2,$$

which is asymptotically still $4n^4$.

In assigning these total weights we have been counting together all states constructed out of so many orbits of given (n, k)'s or given n's. It is often permissible to group the orbits of higher quantum numbers in this way because the differences of the energies of the various states in the group are not significant. For states of lower quantum numbers this will not always be true, though it is often even then legitimate to group together all terms formed out of orbits of given (n, k). We should therefore complete these rules by formulating the corresponding rules for the weights of single states (e.g. *one* of the P or D terms of an alkali spectrum) and for a group of multiple terms (e.g. the *pair* of P or D terms of an alkali spectrum). The necessary analysis has already been implicitly given.

The terms of any atomic spectrum can be conveniently classified into multiple terms and the multiple terms into sets of sequences to which the labels $S, P, D, F, G, \ldots$ are attached. There is just one such set for a one-electron spectrum; in complex cases there may be many more. The labels S, P, D, F, G still correspond to the values $0, 1, 2, \ldots$ of l. The number of components of any multiple term has a maximum value ρ (equal to $2r+1$). The number of components in the multiple $S, P, D, F, G, \ldots$ terms is always the *lesser* of the two numbers $(2l+1, 2r+1)$. A set of terms of maximum multiplicity* ρ is labelled ${}^{\rho}S, {}^{\rho}P, {}^{\rho}D, {}^{\rho}F, \ldots$. In no case can $\rho - 1$ be greater than the number of electrons forming the incomplete group of

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* For this the symbol r (or R or $2R$) is more often used, but we have used r for the associated quantum number.

orbits being compounded together. The individual terms of a multiple term are distinguished by their j values derived from (991) and are labelled

$$^{\rho}S_j,\ ^{\rho}P_j,\ ^{\rho}D_j,\ ^{\rho}F_j,\ \ldots.$$

A number n can be prefixed to this symbol to specify the current number of the term in the sequence, or sets of numbers n_k can be prefixed to specify the quantum numbers of the group of orbits out of which it is constructed. In any case any such term is degenerate and splits into $2j+1$ magnetic states in an external field, so that its weight is $2j+1$.

One other type of grouping is sometimes employed. We may group together all the terms arising from the addition of q electrons in given n_k orbits to an atomic core which is not composed of closed configurations but has some of its electrons in an incomplete group of given $n'_{k'}$ orbits. Remembering the effects of Pauli's principle the set of orbits composing the core will give rise to a countable number of states ϖ_c, which is the weight of the core if its energy differences are insignificant. The result of this is of course that the total number of states of the final system is no longer given by (994) and (995) but is larger by the extra factor ϖ_c.

We collect together the leading results:

(1) The weight of a single term $^{\rho}S_j,\ ^{\rho}P_j,\ ^{\rho}D_j, \ldots$ in any spectrum of any atom is

$$2j+1. \qquad \ldots\ldots(996)$$

(2) The total weight of any multiple term $^{\rho}S,\ ^{\rho}P,\ ^{\rho}D, \ldots$ $(l = 0, 1, \ldots)$ in any spectrum of any atom is

$$(2r+1)(2l+1) \qquad (2r+1=\rho). \qquad \ldots\ldots(997)$$

(3) The total weight of all terms arising from q outer electrons in given n_k orbits attached to a core of total weight ϖ_c is

$$2^q(2k_1+1)\ldots(2k_q+1)\varpi_c. \qquad \ldots\ldots(998)$$

If the core is a bare nucleus or consists of closed groups of electrons, then $\varpi_c = 1$. This formula is subject to reductions when any of the q outer electrons are in orbits of the same n and k.

(4) The total weight of all terms arising from q outer electrons in orbits of given principal quantum numbers n attached to a core of total weight ϖ_c is

$$2^q n_1^2 \ldots n_q^2 \varpi_c. \qquad \ldots\ldots(999)$$

If the core is a bare nucleus or consists of closed groups of electrons, then $\varpi_c = 1$. This formula is also subject to reductions when any of the q outer electrons are in orbits of the same n.

There are no exceptions to these rules.

The foregoing count refers explicitly only to the assumption of non-interchangeable electrons. This however is exactly what we require, if in combining the weights for the whole assembly we multiply as usual the complexions for any particular example of the assembly by

$$\frac{X!\,\Pi_z\,(M^z!)}{N!\,\Pi_{r,z}\,(M_r{}^z!)}, \qquad \text{......(1000)}$$

where X is the total number of electrons, bound or free. The factor $X\,!/N\,!$ is the total number of permutations of all the electrons in the assembly in which a number N, unspecified in order, are free. Permutations of the *free* electrons are allowed for in the calculation of the usual partition function. This factor therefore allows completely for all possible permutations of the individual electrons, now no longer regarded as distinguishable, in a single atom. If we regard certain electrons as permanently bound in specified orbits, they are then simply omitted from X and are no longer counted in the possible permutations in a single atom. The same weights must be used. It seems probable however from the later developments of the new mechanics that all the electrons in any atom must be thought of as continually changing places, and classical mechanics probably requires this too. The method of counting complexions based on the older statistical mechanics which we employ in this monograph would therefore require us to count the states of an atom with q' specified electrons as $q'\,!$ more numerous than those given here. At the same time, since the interatomic permutations are then already allowed for, the symmetry number $\sigma = q'\,!$ must be introduced into the denominator of (1000) to avoid a reduplicated calculation of these permutations. The symmetry number therefore may be allowed to disappear; and the correct count is given by using rules (1)–(4) and (1000). This result is perhaps arrived at in the older theory in a manner not altogether satisfactory. It is comforting to find that it is confirmed in the newer form of statistical mechanics discussed in Chapter XXI. We may embody this conclusion in rule (5):

(5) The weights of rules (1)–(4) are to be combined together as they stand to form the weight of any complexion of any example of any assembly, the number of examples being given by (1000).

In conclusion we shall find it useful in applications to have a table of the weights of the lowest states for a number of atoms. The weight which is of most value in this connection is the sum of the weights of all terms in which all the electrons are in orbits of the normal (least possible) values of n and k. In cases of doubt as to which orbit is normal after $Z = 18$ (e.g. between 3_2 and 4_0) the most useful value refers to states of ions of large core charge. For these there is no doubt which is the normal orbit for the effect of the smaller n overwhelms that of the larger k. In these calculations full account has been taken of Pauli's principle. The weight is the weight of the group of normal terms for the atom named or for any atomic ion with greater nuclear charge and the same (stated) number of electrons. After atomic number 18 the normal state of the atom and singly charged ion with the stated number of electrons may be different, as one or two of the 3_2 orbits may be initially replaced by 4_0 orbits. The atomic symbols are therefore inserted purely as a descriptive reminder, and it is *not* implied that the weights necessarily apply to the normal state of a neutral atom with Z electrons, but only to the normal state of ions of nuclear charge Z and the stated number of electrons provided Z is large enough. In the range of this table it is probably sufficient that Z should exceed the number of electrons by two or more.

TABLE 47.

Electrons in closed and unclosed groups.*

Atom	No. of electrons in groups		Weight	Atom	No. of electrons in groups		Weight
	Closed	Unclosed [type]			Closed	Unclosed [type]	
1 H	0	1 [1_0]	2	19 K	18	1 [3_2]	10
2 He	2	0	1	20 Ca	18	2 [3_2]	45
3 Li	2	1 [2_0]	2	21 Sc	18	3 [3_2]	120
4 Be	4	0	1	22 Ti	18	4 [3_2]	210
5 B	4	1 [2_1]	6	23 V	18	5 [3_2]	252
6 C	4	2 [2_1]	15	24 Cr	18	6 [3_2]	210
7 N	4	3 [2_1]	20	25 Mn	18	7 [3_2]	120
8 O	4	4 [2_1]	15	26 Fe	18	8 [3_2]	45
9 F	4	5 [2_1]	6	27 Co	18	9 [3_2]	10
10 Ne	10	0	1	28 Ni	28	0	1
11 Na	10	1 [3_0]	2	29 Cu	28	1 [4_0]	2
12 Mg	12	0	1	30 Zn	30	0	1
13 Al	12	1 [3_1]	6	31 Ga	30	1 [4_1]	6
14 Si	12	2 [3_1]	15	32 Ge	30	2 [4_1]	15
15 P	12	3 [3_1]	20	33 As	30	3 [4_1]	20
16 S	12	4 [3_1]	15	34 Se	30	4 [4_1]	15
17 Cl	12	5 [3_1]	6	35 Br	30	5 [4_1]	6
18 A	18	0	1	36 Kr	36	0	1

* In the older theory all these suffixes would have been increased by unity.

We have still to consider the form of the term values χ. Except for hydrogen-like atoms exact formulae cannot be given. But in the simpler one- and two-electron spectra most sequences of terms can be put approximately in Rydberg's form

$$\chi_n = \frac{RhC^2}{(n-\alpha)^2}, \qquad \text{......(1001)}$$

where C is the core charge or charge on the rest of the atom other than a single outer electron, and α is a constant, provided we consider terms of one sequence only, in which only the principal quantum number n of a *single* series electron is allowed to vary. It is frequently important to use exact values of the earlier larger χ's. When these are required observed values must be taken. For the later smaller terms (1001) will usually suffice, or sometimes even rougher approximations such as zero.

The only important quantities remaining to be specified before we can handle assemblies of ions and electrons are therefore the ionization energies χ_r^z and to a less extent $(\chi_r^z)_s$ for small s. As we have said, these must in general be taken from observation, but this can only be done directly when the corresponding spectrum has been fully analysed. Thus χ_0^z and χ_1^z (sometimes χ_2^z and χ_3^z or even χ_5^z) have usually been determined in this way, but much work will be required before the higher values are thus determined. It must be remembered that these are the *successive* ionization energies of the atom. The removal of (say) the qth electron often corresponds to a process well known and accurately observed in X-ray spectroscopy, but the energy values derived from X-ray spectroscopy are valueless to us. For these energies are the energies required to remove certain electrons from an intact atom or molecule, while we require to remove the same electron when all the outer more loosely bound electrons are already gone. This often requires twice as much energy—in certain cases it can even be as much as five times as great.

We must fall back therefore on theoretical asymptotic formulae and extrapolations by their means of known results. It has been shown by Hartree* that the majority of the χ_r^z can be fixed with reasonable security in this way. Hartree has constructed tables for oxygen, iron and silver as representative atoms, and others can be constructed by his methods. But most calculations of highly ionized assemblies such as stellar interiors can be carried through for representative atoms or simple mixtures and need not employ large varieties of atoms.

In constructing and using a table of successive ionization energies we must assume a definite order in which the electrons are to be removed (or to return) which is the same as the order of tightness of binding. In accordance with the arguments of the earlier part of this section we assume the order

$$2\ (1_0),\ 2\ (2_0),\ 6\ (2_1),\ 2\ (3_0),\ 6\ (3_1),\ 10\ (3_2),\ 2\ (4_0),\ 6\ (4_1),\ 10\ (4_2),\ 2\ (5_0).$$

There are of course the well-known temporary departures from this order already mentioned, and the two 5_0 orbits do not follow the 4_2 orbits but the 4_3 orbits for the heaviest elements. We shall not usually make calculations explicitly for these. We give below tables taken from Hartree's paper. They were calculated in 1924 and could be made more accurate if revised now in the light of later evidence. But they are amply accurate enough for the purpose for which they are required. Those for oxygen and iron have been so revised in parts.

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* Hartree, *Proc. Camb. Phil. Soc.* vol. XXII, p. 464 (1924).

TABLE 48.

Successive ionization energies for oxygen ($Z = 8$).

Ionization energy			Accuracy
Symbol	ν/R	Electron volts	
χ_7^8	64	865	O
χ_6^8	54	730	B
χ_5^8	10·2	140	A
χ_4^8	7·8	105	C
χ_3^8	5·7	77	C
χ_2^8	4·0	55	O
χ_1^8	2·6	35	O
χ_0^8	1·0	13½	O

TABLE 49.

Successive ionization energies for iron ($Z = 26$).

Ionization energy			Accuracy
Symbol	ν/R	Electron volts	
χ_{25}^{26}	676	9150	O
χ_{24}^{26}	645	8730	A
χ_{23}^{26}	149	2010	A
χ_{22}^{26}	141	1910	A
χ_{21}^{26}	131	1770	A
χ_{20}^{26}	123	1660	A
χ_{19}^{26}	116	1570	A
χ_{18}^{26}	104	1410	B
χ_{17}^{26}	97	1310	B
χ_{16}^{26}	90	1220	B
χ_{15}^{26}	35·7	480	A
χ_{14}^{26}	32·2	435	A
χ_{13}^{26}	29	390	B
χ_{12}^{26}	26	350	C
χ_{11}^{26}	22	300	C
χ_{10}^{26}	21	280	C
χ_9^{26}	—	250	C
χ_8^{26}	16	220	C
χ_7^{26}	11	150	C
χ_6^{26} χ_5^{26} χ_4^{26} χ_3^{26} χ_2^{26} χ_1^{26}	—	Average 80	D
χ_0^{26}	0·60	8·15	O

TABLE 50.

Successive ionization potentials for silver ($Z = 47$).

Ionization energy			Accuracy
Symbol	ν/R	Electron volts	
χ_{46}^{47}	2210	30,000	O
χ_{45}^{47}	2150	29,000	B
χ_{44}^{47}	516	6,980	A
χ_{43}^{47}	500	6,770	A
χ_{42}^{47}	480	6,500	B
χ_{41}^{47}	460	6,200	C
χ_{40}^{47}	440	6,000	C
χ_{39}^{47}	420	5,700	C
χ_{38}^{47}	—	5,500	C
χ_{37}^{47}	390	5,300	C
χ_{36}^{47}	170	2,300	A
χ_{35}^{47}	160	2,160	B
χ_{34}^{47}	154	2,100	C
χ_{33}^{47}	150	2,000	C
χ_{32}^{47}	140	1,900	C
χ_{31}^{47}	135	1,800	C
χ_{30}^{47}	—	1,700	C
χ_{29}^{47}	120	1,600	C
χ_{28}^{47}	105	1,400	C
χ_{27}^{47} χ_{26}^{47} χ_{25}^{47} χ_{24}^{47} χ_{23}^{47} χ_{22}^{47}	—	Average 1,200	D
χ_{21}^{47}	62	850	D
χ_{20}^{47} χ_{19}^{47}	—	Average 800	D
χ_{18}^{47}	36	500	B
χ_{17}^{47}	—	450	C
χ_{16}^{47}	24	350	D
χ_{15}^{47} χ_{14}^{47} χ_{13}^{47} χ_{12}^{47} χ_{11}^{47}	—	Average 300	D
χ_{10}^{47}	11	150	C
χ_{9}^{47} χ_{8}^{47} χ_{7}^{47} χ_{6}^{47} χ_{5}^{47} χ_{4}^{47} χ_{3}^{47} χ_{2}^{47} χ_{1}^{47}	—	Average 80	D
χ_{0}^{47}	0·56	7½	O

In these tables O denotes observed or equally certain values.
A ,, theoretical estimates with error probably less than 3 per cent.
B ,, ,, ,, ,, ,, ,, ,, 10 ,,
C ,, ,, ,, ,, ,, ,, ,, 30 ,,
D ,, estimates quite possibly in error by more than 30 per cent.

§ **14·3**. *The partition function for a single electron, bound or free, in the presence of a nucleus.* It remains to show that the weights assigned in the last section are consistent with the limiting principle so that the quantized partition function

$$\Sigma_s \varpi_s e^{-\chi_s/kT}$$

passes over continuously into the classical form

$$\frac{2^{q'}}{h^{3q'}} \int e^{-\chi/kT}\, dp_1 \ldots dq_{3q'}$$

for large quantum numbers. Since the χ's concerned are all small and tend to zero for large quantum numbers like $1/n^2$ this reduces to showing that

$$\varpi_s \sim \frac{2^{q'}}{h^{3q'}} \int dp_1 \ldots dq_{3q'}, \qquad \ldots\ldots(1002)$$

when the integral is extended over the proper region of phase space. The factor $2^{q'}$ allows for the two orientations of each electron. In the rest of the calculation the electron can be treated as structureless. We shall start by a detailed analysis of the limiting form of the partition function for a single electron bound or free in the presence of a fixed nucleus of charge $Z\epsilon$, which we require in full later in the chapter*.

Consider for simplicity a volume V in the form of a sphere of radius A with the nucleus fixed at its centre. The classical partition function for a single movable electron is, in polar coordinates,

$$f(T) = \frac{2}{h^3}\iiiint e^{-\chi/kT} p^2\, dp\, d\Omega_p\, r^2\, dr\, d\Omega_r, \qquad \text{......(1003)}$$

where

$$\chi = \frac{1}{2m}p^2 - \frac{Z\epsilon^2}{r}. \qquad \text{......(1004)}$$

The elements of solid angle $d\Omega_p$ and $d\Omega_r$ define the directions of the momentum and position vectors respectively. Thus $f(T)$ can be written

$$f(T) = 2\,\frac{8\pi^2(2m)^{\frac{3}{2}}}{h^3}\iint e^{-\chi/kT}(\chi r^2 + Z\epsilon^2 r)^{\frac{1}{2}}\, r\, dr\, d\chi. \text{......(1005)}$$

We will suppose that A is so large that a χ' can be chosen so that

$$Z\epsilon^2/A \ll \chi' \ll kT. \qquad \text{......(1006)}$$

This requirement is usually satisfied in practice with an ample margin. Then the contributions to $f(T)$ can be divided into three parts:

(1) $f_1(T)$. $\infty > \chi > 0$. Electron Free. Classical.

(2) $f_2(T)$. $0 > \chi > -\chi'$. Electron Bound. Effectively Classical†.

(3) $f_3(T)$. $-\chi' > \chi > -\infty$. Electron Bound. Quantized.

In (3) the integral form of the partition function must of course be replaced by the usual sum over the possible stationary states.

Case (1). In $f_1(T)$ we have $\chi \gg Z\epsilon^2/r$ over practically the whole of the effective domain of integration. Hence we replace the factor $(\chi r^2 + Z\epsilon^2 r)^{\frac{1}{2}}$ by $\chi^{\frac{1}{2}}r$ and find

$$f_1(T) = 2\,\frac{(2\pi mkT)^{\frac{3}{2}}\,V}{h^3},$$

the usual formula for the partition function of a free electron. Corrections for the neglect of $Z\epsilon^2/r$ in $f_1(T)$ will be made later by applying Debye and Hückel's theory of ionized media.

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* Planck, *Ann. der Phys.* vol. LXXV, p. 673 (1924).

† If the limiting principle is satisfied, as we shall shortly verify.

Case (2). In $f_2(T)$ we have effectively $\chi/kT = 0$. Putting $\alpha = -\chi$ we find

$$f_2(T) = 2\,\frac{8\pi^2(2m)^{\frac{3}{2}}}{h^3}\int_0^{\chi'} d\alpha \int_0^{a} (Z\epsilon^2 r - \alpha r^2)^{\frac{1}{2}}\, r\,dr, \quad \text{......(1007)}$$

where a is the *smaller* of $Z\epsilon^2/\alpha$ and A.

Case (3). In $f_3(T)$ we have to replace the integral by the quantized sum

$$f_3(T) = \sum_1^{n'} 2n^2 e^{\chi_n/kT} \qquad (\chi_n = RhcZ^2/n^2), \quad \text{......(1008)}$$

and

$$n' \doteq \{RhcZ^2/\chi'\}^{\frac{1}{2}}. \quad \text{......(1009)}$$

We now return to evaluate $f_2(T)$, putting $r = (Z\epsilon^2/\alpha)\sin^2\phi$. Then

$$f_2(T) = 2\,\frac{16\pi^2(2m)^{\frac{3}{2}}}{h^3}\,(Z\epsilon^2)^3 \int_0^{\chi'} \frac{d\alpha}{\alpha^{\frac{5}{2}}} \int_0^{a} \sin^4\phi\cos^2\phi\,d\phi,$$

where a is arc sin $(\alpha A/Z\epsilon^2)^{\frac{1}{2}}$ if this is real or else $\frac{1}{2}\pi$. The double integral therefore divides into

$$\int_0^{Z\epsilon^2/A} \frac{d\alpha}{\alpha^{\frac{5}{2}}} \int_0^{\text{arc sin}\,(\alpha A/Z\epsilon^2)^{\frac{1}{2}}} \sin^4\phi\cos^2\phi\,d\phi + \int_{Z\epsilon^2/A}^{\chi'} \frac{\pi}{32}\frac{d\alpha}{\alpha^{\frac{5}{2}}},$$

or

$$\frac{2}{(Z\epsilon^2/A)^{\frac{3}{2}}}\int_0^{\frac{1}{2}\pi} \frac{\cos\theta\,d\theta}{\sin^4\theta}\int_0^{\theta} \sin^4\phi\cos^2\phi\,d\phi + \frac{\pi}{32}\int_{Z\epsilon^2/A}^{\chi'} \frac{d\alpha}{\alpha^{\frac{5}{2}}}.$$

The repeated integral can be evaluated by integration by parts and is found to have the value $\frac{1}{9} - \frac{1}{96}\pi$. Thus

$$f_2(T) = 2\,\frac{16\pi^2(2m)^{\frac{3}{2}}(Z\epsilon^2)^3}{h^3}\left[\frac{2}{9}\frac{A^{\frac{3}{2}}}{(Z\epsilon^2)^{\frac{3}{2}}} - \frac{\pi}{48}\frac{1}{(\chi')^{\frac{3}{2}}}\right],$$

$$= 2Z^3(Rhc)^{\frac{3}{2}}\left[\frac{32}{9\pi}\frac{A^{\frac{3}{2}}}{(Z\epsilon^2)^{\frac{3}{2}}} - \frac{1}{3}\frac{1}{(\chi')^{\frac{3}{2}}}\right], \quad \text{......(1010)}$$

$$= 2\left\{\frac{32}{9\pi}\frac{(ZRhcA)^{\frac{3}{2}}}{\epsilon^3} - \tfrac{1}{3}n'^3\right\}. \quad \text{......(1011)}$$

We can now see at once that the limiting principle is obeyed for an atom with a single excited electron. For the contribution to the phase integral, corresponding, according to (1009), to energies χ' between $n' \pm \frac{1}{2}$, say, is by (1011) the difference of the values of $f_2(T)$ for $n' \pm \frac{1}{2}$ or

$$\tfrac{2}{3}\{(n' + \tfrac{1}{2})^3 - (n' - \tfrac{1}{2})^3\}$$

which is asymptotically $2n'^2$. This result can be extended at once to the case of a number of electrons each independently in specified orbits of large quantum number $n_1, \ldots, n_q$. The foregoing analysis applies formally to each electron if Z denotes the proper effective nuclear charge. Since Z

disappears from the result, its actual specification is unnecessary. In this calculation the electrons are distinct and permutations are not allowed. Actually in the classical case permutations must certainly occur and the corresponding phase space must be

$$q\,!\,2^q n_1{}^2 \ldots n_q{}^2.$$

This however is still in asymptotic agreement with the weights of the quantum theory, which are equally subject to multiplication by $q\,!$ when the electron permutations are put in at a later stage of complexion counting.

§ **14·4**. *The approximate characteristic function. The method of excluded volumes.* A direct and accurate evaluation of Ψ for the assemblies contemplated in this chapter would be an affair of some difficulty. There are two methods possible for approximations due in essentials to Urey and Planck which are subject to quite different adverse criticisms. The fact that they confirm each other qualitatively and even roughly quantitatively can be regarded as some justification for a belief that the resulting formulae for Ψ/k are a fair approximation to the truth.

In the theory of Urey and Fermi* we treat the various atoms and atomic ions as possessing an actual volume from which they entirely exclude other systems, as in van der Waals' elementary theory of an imperfect gas. We use the formulae of § 8·6 and assume that the ionic volume in an excited state has a radius of the order of the diameter of the central orbit described (after Bohr's theory) by the most highly excited electron. The resulting excluded volumes are therefore really fictitious. Physical reality can only be ascribed to them by the somewhat doubtful argument that they represent that region of space which must be empty for the ion in question to exist in that state at all. To the expression for Ψ/k so obtained we add a correction Ψ_ϵ/k for the till then neglected electrostatic charges.

In the theory of Planck we proceed *initially* more logically by trying to generalize the calculations of the last section into a simplified calculation of $B\,(\vartheta)$. But the simplifications which have to be made are rather severe, and it is satisfactory that the form of the result is checked by the other method using an entirely different type of approximation.

The Ψ/k for the theory of Urey and Fermi, omitting the electrostatic term, has already been given in equation (555). Let us denote the atomic ion of general type (r, s, z) by the suffixes α or β for shortness, and use the suffix ϵ for quantities characteristic of the electron. Σ_β will then mean a summation over all atomic types, and $\Sigma_{\alpha,\,\beta}$ a summation over all pairs of atomic types; free electrons are excluded from either summation. Let the average excluded volume of the (r, s, z)-ion for interaction with an electron

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* Urey, *Astrophys. Jour.* vol. XLIX, p. 1 (1924); Fermi, *Zeit. für Phys.* vol. XXVI, p. 54 (1924).

be $(v_r^z)_{s,\epsilon}$, and for interaction with an atomic ion β, $(v_r^z)_{s,\beta}$. Then in the notation of this chapter we have

$$\Psi/k = N\left(\log\frac{VG}{N}+1\right)+\Sigma_{r,z}M_r^z\left(\log\frac{VF_r^z}{M_r^z}+1\right)+\frac{1}{V}\Sigma_{\alpha,\beta}\frac{M_\alpha M_\beta v_{\alpha\beta}}{\sigma_{\alpha\beta}}, \qquad \text{......(1012)}$$

in which

$$F_r^z=\frac{(2\pi m^z kT)^{\frac{3}{2}}}{h^3}u_r^z(T)\,e^{(\chi_r^z+\dots+\chi^z_{z-1})/kT},\quad G=2\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}, \qquad \text{......(1013)}$$

$$u_r^z(T)=\sum_{s=0}(\varpi_r^z)_s\exp\left[-\{\chi_r^z-(\chi_r^z)_s\}/kT-\{N(v_r^z)_{s,\epsilon}+\Sigma_\beta M_\beta(v_r^z)_{s,\beta}\}/V\right]. \qquad \text{......(1014)}$$

In transforming Ψ/k we have left unmodified the partition function for the free electron. The excluded volume corrections, when not small, are only qualitatively correct. To determine $(M_r^z)_s$ we have

$$\frac{(M_r^z)_s}{(\varpi_r^z)_s\exp\left[-\{\chi_r^z-(\chi_r^z)_s\}/kT-\{N(v_r^z)_{s,\epsilon}+\Sigma_\beta M_\beta(v_r^z)_{s,\beta}\}/V\right]}=\frac{M_r^z}{u_r^z(T)}. \qquad \text{......(1015)}$$

To the Ψ/k of (1012) we must add the contributions of the radiation in the enclosure, and of the electrostatic potentials. The former is properly additive, the latter is not, and if the excluded volumes had a genuine physical existence, the electrostatic and excluded volume effects would interact and ought to be introduced together. Since however we can only aim at qualitative correctness here, we will be content with the rough approximation of adding a separate electrostatic term. If we adopt the approximations of the theory of Debye and Hückel, equations (941) and (932) give us here ($D=1$)

$$\Psi_\epsilon/k=\frac{2\sqrt{\pi}\epsilon^3}{3V^{\frac{1}{2}}(kT)^{\frac{3}{2}}}\{N+\Sigma_{r,z}r^2M_r^z\}^{\frac{3}{2}}. \qquad \text{......(1016)}$$

In calculating this we have assumed that any ion of type (r, s, z) can be treated as a point charge of charge $r\epsilon$.

In proposing this value for the electrostatic term we have ignored the correction of § 2·76 necessary to distinguish between free and bound electrons and the correction of § 13·72 for the complete form of Debye and Hückel's equations. It is a matter for great regret to me that these two corrections have not yet been found amenable to calculation for stellar conditions. The equation (948) can be altered to take account of § 2·76 and Gronwall's method can then be applied to it*. The solution is more difficult than that of § 13·72 and involves interesting points in mathematics and physical interpretation. Results analogous to Gronwall's can be

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* Unpublished work by Gaunt. A summary has since been published, *M.N.R.A.S.* vol. LXXXVIII, p. 369 (1928).

obtained, but unfortunately their region of applicability does not include the average conditions in even the most massive star. We therefore omit the calculations and are forced to content ourselves with (1016) for estimating the order of the electrostatic effects.

In the approximations of Urey and Fermi the excluded volumes are treated as spherical and the radius of the interacting system β is neglected compared with the radius of the (r, s, z)-system itself. This introduces no error at the moderate or low temperatures which they themselves discuss where highly excited orbits are rare. The radius of the (r, s, z)-system is assumed to be the semi-diameter of the orbit of the most highly excited electron or more strictly the aphelion distance when the orbit is not closed. As a result we obtain from (1014) for hydrogen

$$u_0^1\,(T) = \sum_{s=1} 2s^2 \exp\left\{-\frac{\chi_0^1}{kT}\left(1-\frac{1}{s^2}\right) - \alpha s^6\right\}, \quad \text{......(1017)}$$

where

$$\alpha = \frac{4\pi}{3}\frac{N + \Sigma_\beta M_\beta}{V} a^3 = \frac{4\pi}{3}\frac{p_\epsilon + p_a}{kT} a^3. \quad \text{......(1018)}$$

In (1018) a is the radius of the 1-quantum orbit in hydrogen, $5{\cdot}34 \times 10^{-9}$ cm., and χ_0^1 in (1017) its ionization energy, 13·54 volts. More generally at higher temperatures a better approximation to (1014) is obviously provided by replacing s^6 by $(s_0^2 + s^2)^3$, where as_0^2 is the average radius of all the interacting systems. This improvement will not affect orders of magnitude and we shall not investigate it in detail.

To formulate this theory quantitatively for other atoms with one excited electron we obviously replace αs^6 by $\alpha n_s^6/(r+1)^3$, where n_s is the effective quantum number and $(r+1)$ the core charge. Since the excluded volumes are only of importance for states of great excitation it will be sufficiently accurate to group all states of given principal quantum number together with the approximate excluded volume $\alpha s^6/(r+1)^3$ and the weight $2s^2\varpi_c$. For an atom with any number of excited electrons we must presumably replace n_s by $(n_s)_{\max}$, denoting thereby the greatest effective quantum number among the excited electrons in the sth state. In general we shall be able to arrange the states into series in which the quantum defect is roughly constant and n_s increases by unity from term to term. These quantum defects will vary considerably with the k of the greatest orbit and with variations in any of the quantum numbers of the other excited orbits, but as a first approximation it will be legitimate to ignore these variations and group together all the terms in $u\,(T)$ which have a given principal quantum number for the greatest orbit. We can then write

$$u_r^z\,(T) = \Sigma_s\left\{\Sigma_t{}'\,(\varpi_r^z)_t\, e^{-\{\chi_r^z - (\chi_r^z)_t\}/kT}\right\} e^{-\alpha n_s^6/(r+1)^3}, \quad \text{......(1019)}$$

where Σ' is summed over all states in which the principal quantum numbers of every electron are less than or equal to s and one at least is equal to s.

To elucidate (1019) further we must group together the terms that belong to given numbers of highly excited electrons; let there be q of these and $z - r$ electrons in all. Then for these states we can ignore the variations of $(\chi_r^z)_t$ and take $\chi_r^z - (\chi_r^z)_t$ to be effectively

$$\chi_r^z + \dots + \chi^z_{r+q-1},$$

the energy required to remove entirely the q highly excited electrons from their normal orbits. These states contribute to $u_r^z(T)$

$$e^{-\{\chi_r^z+\dots+\chi^z_{r+q-1}\}/kT}\,\Sigma_s\,\{\Sigma_t{}'\,(\varpi_r^z)_t\}\,e^{-\alpha n_s^6/(r+1)^3}.$$

If we ignore reductions in the ϖ's for equivalent orbits, which do not affect the terms of highest order, we find from the rules that, summed over all states with the q principal quantum numbers of the excited electrons less than or equal to s,

$$\Sigma_t\,(\varpi_r^z)_t = \varpi^z{}_{r+q}\,2^q \sum_{t_1, t_2, \dots \leqslant s} t_1^2 t_2^2 \dots t_q^2,$$

$$\sim \varpi^z{}_{r+q}\,\frac{2^q\,s^{3q}}{3^q}.$$

Therefore, by differentiation,

$$\Sigma_t{}'\,(\varpi_r^z)_t \sim \frac{3q\varpi^z{}_{r+q}\,2^q}{3^q}\,s^{3q-1}.$$

These states therefore contribute to $u_r^z(T)$

$$\frac{3q\varpi^z{}_{r+q}\,2^q}{3^q}\,e^{-\{\chi_r^z+\dots+\chi^z_{r+q-1}\}/kT}\,\Sigma_s\,s^{3q-1}\,e^{-\alpha n_s^6/(r+1)^3}.$$

In this summation we shall for this approximation omit the quantum defect and replace the sum by the integral

$$\int_0^\infty s^{3q-1}e^{-\alpha s^6/(r+1)^3}\,ds,$$

or

$$\tfrac{1}{6}\Gamma\,(\tfrac{1}{2}q)\left\{\frac{(r+1)^3}{\alpha}\right\}^{\frac{1}{2}q}.$$

The contribution to $u_r^z(T)$ is therefore

$$\Gamma\,(1+\tfrac{1}{2}q)\,\varpi^z{}_{r+q}\,2^q\left\{\frac{(r+1)^3}{9\alpha}\right\}^{\frac{1}{2}q} e^{-\{\chi_r^z+\dots+\chi^z_{r+q-1}\}/kT}. \quad \text{......(1020)}$$

There is a similar contribution for every possible value of q. The complete result may be written

$$u_r^z(T) = \varpi_r^z + \sum_{q=1}^{q=z-r}\Gamma\,(1+\tfrac{1}{2}q)\,\varpi^z{}_{r+q}\,2^q\left\{\frac{(r+1)^3}{9\alpha}\right\}^{\frac{1}{2}q} e^{-\{\chi_r^z+\dots+\chi^z_{r+q-1}\}/kT}.$$

......(1021)

It will often be found that one term in (1021) is dominant for given values of the density and temperature. In such a case nearly all the atoms

M_r^z present will have just q excited electrons and the rest $z - r - q$ in normal orbits. If there is at most a single excited electron

$$u_r^z\,(T) = \varpi_r^z + \pi^{\frac{1}{2}}\,\varpi^z{}_{r+1}\left\{\frac{(r+1)^3}{9\alpha}\right\}^{\frac{1}{2}} e^{-\chi_r^z/kT}. \qquad \text{......(1022)}$$

This is the simplest generalization of the theory of Urey and Fermi. These authors do not give these approximate summations, whose accuracy is ample for most applications.

It is naturally possible to calculate average values derived from $u_r^z\,(T)$ by the same process. The average energy content of any atom is given by

$$kT^2 \frac{\partial}{\partial T} \log u_r^z\,(T),$$

in which of course only the exponents $\{\chi_r^z - (\chi_r^z)_s\}/kT$ are to be differentiated. We find

$$kT^2 \frac{\partial u_r^z\,(T)}{\partial T} = \sum_{q=1}^{q=z-r} \{\chi_r^z + \ldots + \chi^z{}_{r+q-1}\}\,\Gamma\,(1+\tfrac{1}{2}q)\,\varpi^z{}_{r+q}\,2^q\left\{\frac{(r+1)^3}{9\alpha}\right\}^{\frac{1}{2}q}$$
$$\times\, e^{-\{\chi_r^z + \ldots + \chi^z{}_{r+q-1}\}/kT}. \qquad \text{......(1023)}$$

When the term $q = q^*$ is predominant in (1021) and so also in (1023) we have

$$kT^2 \frac{\partial}{\partial T} \log u_r^z\,(T) = \chi_r^z + \ldots + \chi^z{}_{r+q^*-1}. \qquad \text{......(1024)}$$

The energy content is the same as if these q^* electrons were *free and at rest relative to the ion.*

Other expressions which occur in the general formulae are

$$\frac{1}{V}\,\Sigma_\beta M_\beta v_{\beta,\epsilon}, \quad \frac{1}{V^2}\left[N\Sigma_\beta M_\beta v_{\beta,\epsilon} + \Sigma_{\alpha,\beta}\frac{M_\alpha M_\beta v_{\alpha,\beta}}{\sigma_{\alpha\beta}}\right].$$

These may be evaluated as

$$-\,\Sigma_{r,z} M_r^z \frac{\partial}{\partial N} \log u_r^z\,(T), \quad \tfrac{1}{2}\Sigma_{r,z} M_r^z\left(\frac{\partial}{\partial V} - \frac{N}{V}\frac{\partial}{\partial N}\right) \log u_r^z\,(T)$$

respectively.

The accuracy required in these formulae is reached by retaining only the dominant term $q = q^*$ in (1021). To this approximation

$$\frac{\partial}{\partial N} \log u_r^z\,(T) = -\,\tfrac{1}{2}q^* \frac{\partial}{\partial N} \log \alpha = -\,\frac{\tfrac{1}{2}q^*}{N + \Sigma_\beta M_\beta}, \qquad \text{...(1025)}$$

$$\left\{\frac{\partial}{\partial V} - \frac{N}{V}\frac{\partial}{\partial N}\right\} \log u_r^z\,(T) = \frac{\tfrac{1}{2}q^*}{V}\,\frac{2N + \Sigma_\beta M_\beta}{N + \Sigma_\beta M_\beta}. \qquad \text{......(1026)}$$

In general q^*, the average number of bound but highly excited electrons, will vary with r and z and must be written $(q_r^z)^*$. Then

$$\frac{1}{V}\Sigma_\beta M_\beta v_{\beta,\epsilon} = \tfrac{1}{2}\frac{\Sigma_{r,z}(q_r^z)^* M_r^z}{N+\Sigma_\beta M_\beta}, \qquad \text{......(1027)}$$

$$\frac{1}{V^2}\left[N\Sigma_\beta M_\beta v_{\beta,\epsilon} + \Sigma_{\alpha,\beta}\frac{M_\alpha M_\beta v_{\alpha,\beta}}{\sigma_{\alpha\beta}}\right] = \frac{\Sigma_{r,z}(q_r^z)^* M_r^z}{2V}\,\frac{N+\frac{1}{2}\Sigma_\beta M_\beta}{N+\Sigma_\beta M_\beta}. \qquad \text{......(1028)}$$

§ **14·5**. *Planck's theory.* In the foregoing theory there is an arbitrary element, the choice of excluded volume. This is physically and theoretically unsatisfactory. Instead of attempting to patch up the theory of imperfect gases in this way so as to apply to assemblies of atoms, ions and electrons, Planck has attempted to make a direct simplified calculation of Gibbs' phase integral, and so $B(T)$, for such an assembly by generalizing the calculation of § 14·3.

For an assembly consisting of one electron and one fixed nucleus ($Z\epsilon$) contained in a sphere of radius A about the nucleus, the calculations already given are almost complete. For the electron free we have

$$f(T) = f_1(T) = 2\frac{(2\pi mkT)^{\frac{3}{2}} V}{h^3}.$$

For the electron bound

$$f'(T) = f_2(T) + f_3(T),$$

$$= \sum_{n=1}^{n'} 2n^2 e^{\chi_n/kT} + 2\left\{\frac{32}{9\pi}\frac{(ZRhcA)^{\frac{3}{2}}}{\epsilon^3} - \tfrac{1}{3}n'^3\right\}.$$

Now by familiar arguments we have approximately

$$\sum_{n=1}^{n'} 2n^2 e^{\chi_n/kT} = 2\{e^{\chi_1/kT} + \tfrac{1}{3}n'^3\}.$$

Hence

$$f'(T) = 2e^{\chi_1/kT} + \frac{64}{9\pi}\frac{(ZRhcA)^{\frac{3}{2}}}{\epsilon^3}. \qquad \text{......(1029)}$$

In constructing partition functions hitherto we have found it convenient to take the normal state of lowest energy as standard. With this convention

$$f'(T) = 2 + \frac{64}{9\pi}\frac{(ZRhcA)^{\frac{3}{2}}}{\epsilon^3}e^{-\chi_1/kT}. \qquad \text{......(1030)}$$

In all such approximations it may be necessary to include a finite number of terms besides the first term for the normal state before the terms of high excitation are lumped together with the remainder. Thus the complete form of $f'(T)$ would be

$$f'(T) = \sum_{1}^{s}\varpi_s e^{-\{\chi_1-\chi_s\}/kT} + \frac{64}{9\pi}\frac{(ZRhcA)^{\frac{3}{2}}}{\epsilon^3}e^{-\chi_1/kT}. \qquad \text{......(1031)}$$

In general either the first term ($s = 1$) or the remainder is dominant (the latter for large values of T). When however the remainder is negligible, it is often necessary in discussing fine points, such as the appearance in absorption of lines arising from the first few excited states, to include the first few terms in the former part of $f'(T)$. Only the first term contributes sensibly to the numerical value of $f'(T)$ itself, but the other terms control the distribution of the small fraction of atoms in the early excited states on which the phenomena in question depend.

When the assembly of volume V contains a number of fixed nuclei and one electron, $f(T)$ is still given by (1003) with

$$\chi = \frac{1}{2m}p^2 - \Sigma_a \frac{Z\epsilon^2}{r_a}.$$

It is however now impossible to carry out the exact integration, and the most reasonable simplifying assumption is that when $\chi < 0$ all terms in Σ_a are negligible except the largest. This means that we treat as free all states of the electron in which its energy is greater than the energy of escape from the nearest nucleus when all nuclei have the same charge, and is in a sense equivalent to ignoring molecule formation. This simplification should be reliable so long as the nuclei are not too close together. Each nucleus then makes a contribution to the phase integral like (1005) and therefore like (1030), which may be described by saying that each nucleus has this partition function for a bound electron, if A is so chosen that on the average the bound electron is nearer to the selected nucleus than to any other. If there are M nuclei we must therefore take

$$M\,.\,\tfrac{4}{3}\pi A^3 = V.$$

The essential part of the condition (1006) is then that

$$Z\epsilon^2 \left(\frac{M}{V}\right)^{\frac{1}{3}} \ll kT. \qquad \text{......(1032)}$$

The method can now be generalized for a number of nuclei of different positive charges. The condition that the electron should be bound to nucleus 1 rather than to nucleus 2 is now naturally

$$Z_1/r_1 > Z_2/r_2.$$

This means that to each nucleus $(Z\epsilon)$ we must attach an average volume proportional to Z^3. If we now define a radius A by the equation

$$\tfrac{4}{3}\pi A^3 \Sigma_z Z^3 M^z = V, \qquad \text{......(1033)}$$

then the actual radius A_1 for use with a nucleus $(Z_1\epsilon)$ will be given by

$$A_1{}^3 = Z_1{}^3 A^3 = \frac{3}{4\pi}\frac{Z_1{}^3 V}{\Sigma_z Z^3 M^z}. \qquad \text{......(1034)}$$

The partition function for an electron bound to a nucleus $(Z_1\epsilon)$ may therefore be written

$$2 + e^{-\chi_1/kT}\left[\frac{64}{9\pi}\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\frac{(Rhc)^{\frac{3}{2}}}{\epsilon^3}\right]\frac{Z_1{}^3 V^{\frac{1}{2}}}{(\Sigma_z Z^3 M^z)^{\frac{1}{2}}}. \qquad \text{......(1035)}$$

The permanent constant in [ ] will be written B; it has the numerical value

$$B = 1{\cdot}017 \times 10^{12}\ \text{cm.}^{-\frac{3}{2}}$$

Let us now allow the nuclei their natural freedom of movement. Their mean velocities are very slow compared with the velocities of the electrons, and to a first rough approximation the rule for fixing the particular nucleus to which an electron with negative energy is bound is not affected. It is of course strictly the relative kinetic energy of electron and nucleus which should be used in the binding rule, and we replace this by the kinetic energy of the electron (relative to the centre of mass of the assembly as a whole). A closer approximation here would be of interest. To the approximation at present proposed the foregoing formulae can be regarded as independent of the motion of the nuclei. The calculations of the phase integral of the assembly for the nuclei therefore take their ordinary form and yield the ordinary partition functions for massive particles; the electrostatic forces between the nuclei themselves lead to no complications (being repulsive), and are (or should be) allowed for in the term (1016).

Let us next suppose that there is more than one electron in the assembly, but that no nucleus can catch more than one electron. We can ignore also the repulsive force between the electrons. Then the foregoing analysis suffices to determine the partition function of any nucleus which has caught an electron, and the whole value of $B(T)$ can best be evaluated by the usual combinatory rules of § 5·2. In our notation therefore

$$u^{z_1}{}_{z_1-1}(T) = 2 + B\,\frac{Z_1{}^3 V^{\frac{1}{2}}}{(\Sigma Z^3 M^z)^{\frac{1}{2}}} \exp\left(-\chi^{z_1}{}_{z_1-1}/kT\right), \quad\ldots\ldots(1036)$$

and using (1036) we can apply all the usual formulae.

To extend these arguments to the capture of more than one electron is not difficult, provided rather rough approximations are sufficient. We shall obviously approximate fairly closely to the holding power of an atom r-times ionized by assuming that it holds excited electrons like a point charge $(r + 1)\,\epsilon$. This approximation will be very good when all the electrons except one are in normal or nearly normal orbits. In general it must *underestimate* the efficiency of the ion at holding its last electron. An *overestimate* of the efficiency can be obtained by assuming that the ion holds like a point charge $(r + q)\,\epsilon$, where q is the total number of its electrons in highly excited orbits.

In order to estimate the value of $u_r^z(T)$ we again consider separately the parts arising for various specified numbers q of highly excited electrons. The weight of the remaining core of the atom with electrons in normal orbits is $\varpi^z{}_{r+q}$. This core now catches q electrons in succession into highly excited orbits acting on one assumption like a point charge $(r + 1)\,\epsilon$ and on the other like $(r + q)\,\epsilon$. The contribution to $u_r^z(T)$, estimated according to the foregoing version of Planck's theory, will therefore be the continued product of contributions for each electron in order with an extra factor $\varpi^z{}_{r+q}$ for the weight of the core. According therefore to the holding power assumed we find the following limiting approximations for $u_r{}^z\,(T)$:

$$u_r{}^z\,(T) = \varpi_r{}^z + \sum_{q=1}^{q=z-r} \varpi^z{}_{r+q}\,(r+1)^{3q} B^q \left\{\frac{V}{\Sigma_{r,z}\,(r+1)^3\, M_r{}^z}\right\}^{\frac{1}{2}q} \times e^{-\{\chi_r{}^z+\dots+\chi^z{}_{r+q-1}\}/kT}, \qquad \dots\dots(1037)$$

or

$$u_r{}^z\,(T) = \varpi_r{}^z + \sum_{q=1}^{q=z-r} \varpi^z{}_{r+q}\,(r+q)^{3q} B^q \left\{\frac{V}{\Sigma_{r,z,q}\,(r+q)^3\, (M_r{}^z)_q}\right\}^{\frac{1}{2}q} \times e^{-\{\chi_r{}^z+\dots+\chi^z{}_{r+q-1}\}/kT}. \qquad \dots\dots(1038)$$

In (1038) $(M_r{}^z)_q$ denotes the average number of atomic ions of atomic number Z, r times ionized, with q highly excited electrons. These equations give upper and lower limits for $u_r{}^z\,(T)$. A closer approximation than either can probably be obtained by considering an $(r+q)$-times ionized atom and letting it catch q electrons in succession into excited orbits. If we assume that the number of orbits so obtained is not altered by later captures and that at each stage the ion captures like a point ion of the new net charge, we can replace $(r+q)^q$ in (1038) by $(r+1)\dots(r+q)$ and obtain

$$u_r{}^z\,(T) = \varpi_r{}^z + \sum_{q=1}^{q=z-r} \varpi^z{}_{r+q}\,(r+1)^3 \dots (r+q)^3\, B^q \times \left\{\frac{V}{\Sigma_{r,z,q}\,(r+1)^{3/q}\dots(r+q)^{3/q}\,(M_r{}^z)_q}\right\}^{\frac{1}{2}q} e^{-\{\chi_r{}^z+\dots+\chi^z{}_{r+q-1}\}/kT}. \qquad \dots\dots(1039)$$

If no other considerations entered one should prefer (1039) to (1037) or (1038) in applications. The clustering of the *free* electrons round the positive ion will however decrease its holding power for highly excited electrons, and terms of large q are mainly important for large N/V when this shielding is largest. When as here this shielding is not directly allowed for, formula (1037) is to be preferred. It is undoubtedly at this point, that is in the correct enumeration of bound states, that the present theory is weakest, and a better method of enumeration is greatly to be desired.

These $u_r{}^z\,(T)$ may be used for a direct construction of Ψ, which is formally the Ψ for a mixture of perfect gases with radiation and the electrostatic terms added. There are in this theory as here developed no excluded volumes. The residual atomic cores of electrons in normal orbits do possess volumes which can be taken account of in the usual way. But the effect of these is usually extremely small.

In applications the most important combination is $u^z{}_{r+1}\,(T)/u_r{}^z\,(T)$. It sometimes happens that one term of (1037) is dominant for a given density and temperature, and then the dominant terms of $u^z{}_{r+1}\,(T)$, $u_r{}^z\,(T)$ generally correspond to equal numbers of electrons in normal orbits, and a difference of one highly excited electron. In such a case

$$\frac{u^z{}_{r+1}(T)}{u_r^z(T)} = \frac{e^{\chi_r^z/kT}}{(r+1)^3 B}\left\{\frac{V}{\Sigma_{r,z}(r+1)^3 M_r^z}\right\}^{-\frac{1}{2}}. \qquad \text{......(1040)}$$

If s is the average number of free electrons per atom, then it is defined by

$$\Sigma_{r,z} r M_r^z = s\,\Sigma_{r,z} M_r^z = N.$$

It will then be permissible as a very rough approximation to write

$$\Sigma_{r,z}(r+1)^3 M_r^z = (s+1)^3\,\Sigma_{r,z} M_r^z = \frac{(s+1)^3}{s} N,$$

and so

$$\frac{u^z{}_{r+1}(T)}{u_r^z(T)} = \frac{\{(s+1)^3/s\}^{\frac{1}{2}}\,e^{\chi_r^z/kT}}{(r+1)^3 B\,(V/N)^{\frac{1}{2}}}. \qquad \text{......(1041)}$$

When we now form the equations of dissociative equilibrium the exponential factors vanish. The ratios $M^z{}_{r+1}/M_r^z$ are controlled entirely by the $(r+1)^3$ factor. The χ_r^z only control the numbers of electrons in normal orbits.

As a check on the somewhat speculative approximations which have been necessary at certain stages in this chapter, it is well to compare the formulae for $u_r^z(T)$ given by the two theories in the simplest case of a single excited electron. When the permanent constants are given their numerical values we find:

For the theory of Urey and Fermi,

$$u_r^z(T) = \varpi_r^z + 7{\cdot}40 \times 10^{11}\,\varpi^z{}_{r+1}\,(r+1)^{\frac{3}{2}}\left(\frac{s}{s+1}\right)^{\frac{1}{2}}\left(\frac{V}{N}\right)^{\frac{1}{2}} e^{-\chi_r^z/kT}.$$

For the theory of Planck,

$$u_r^z(T) = \varpi_r^z + 1{\cdot}017 \times 10^{12}\,\varpi^z{}_{r+1}\,\frac{(r+1)^3}{s+1}\left(\frac{V}{N}\right)^{\frac{1}{2}} e^{-\chi_r^z/kT}.$$

These formulae are in substantial agreement.

The following chapters consist largely of applications of these formulae.

CHAPTER XV

ATMOSPHERIC PROBLEMS

§ **15·1.** *Scope of Chapters XV and XVI.* In this chapter and the following we shall set out to apply our general theorems to special problems of the properties of matter in a gaseous state which is nearly perfect. We shall of course discuss only such problems as arise out of the study of equilibrium states of such matter or as can be treated at once by application of the properties of the equilibrium state and the laws of mechanisms detailed in Chapters XVII and XIX. Problems essentially requiring the theory of transport phenomena or of radiative equilibrium are therefore excluded. The problems that present themselves are of two classes, (1) atmospheric problems, this chapter, and (2) problems of the interior of a gaseous star, Chapter XVI. The equilibrium and quasi-equilibrium properties of atmospheres—extensive assemblies of perfect gas constituents in a strong external field of force—consist only of the properties of assemblies which can be treated as isothermal. We have already derived Dalton's law for the distribution of the various constituents in an atmosphere of perfect gases. Until recently the only other problem discussed was the rate of escape of molecules into space from the boundary of the atmosphere of a planet or a star*. Thanks however largely to the work of Milne a number of other interesting atmospheric problems have been proposed and solved at least to a first approximation. The contents of this chapter consist therefore of discussions of the following problems: (1) The equilibrium of an isothermal *ionized* atmosphere and the permanent electrical fields and charges existing in it. (2) The behaviour of the absorption spectra formed by stellar reversing layers. (3) The normal escape of molecules from the atmosphere of the earth or a star. (4) The formation by radiation pressure of tenuous high-level atmospheres (chromospheres). (5) The ejection of atoms and ions from stellar atmospheres at high speeds by abnormal radiation pressure; (4) and (5) in outline only. Of these the first alone refers to a true equilibrium state. The second and third can properly be treated to a first approximation by using equilibrium properties. In the others equilibrium properties play a smaller part. It is however justifiable to give a sketch of them for the sake of a systematic account of this whole group of problems. An account of the third is rendered the more desirable because great advances in treatment have been made since Jeans' account was written, and the theory is now probably in a final form. When all is said however it is obvious that these researches merely deal with special

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* Jeans, *loc. cit.* chap. XV.

features of a stellar atmosphere. A proper theory embracing them all, based as it must be on a study of the assembly subject to the flux of radiation from below, would lie outside our range. But we are spared the temptation to include it, for no such theory yet exists.

In an atmospheric problem the main field of force may be regarded as external to and independent of the assembly discussed. In a star, considered as a whole, this is not so, and the main field arises from the gravitation of the matter of the assembly itself. In Chapter XVI therefore the start corresponding to that of Chapter XV would be a discussion of the isothermal gravitating gas sphere of ionized material. In the absence of electrical forces there is nothing to add to Emden*. We could make some comment following Rosseland† on the effect of electrical forces on the radial distribution of different elements. The applicability of these remarks to an actual (non-isothermal) star is however doubtful. It is obviously outside our province to attempt any discussion of the large scale interior constitution of a star, which depends on many other factors besides the properties of the equilibrium state of a given body of matter. For this the reader will naturally turn to Eddington‡. But whatever the large scale structure of a star, the small scale structure is essentially that of matter in the most complete thermodynamic equilibrium§. The equilibrium properties of stellar material are important, and the main part of Chapter XVI is therefore devoted to an attempt to calculate as accurately as possible the equilibrium state of matter at stellar temperatures and pressures.

§ **15·2**. *The equilibrium of an ionized atmosphere*‖. We start by discussing an atmosphere of a single primary constituent, say Ca, in equilibrium with its ionization products Ca^+ and electrons. We later consider extensions to more complicated atmospheres, but these are not easy to make exactly. By (133) and (375) for the sth constituent

$$\overline{n_s} = (\overline{n_s})_0 \, e^{-(m_s\phi+\epsilon_s\psi)/kT}. \qquad \text{......(1042)}$$

It is necessary to include an electrostatic potential ψ as well as the gravitational ϕ, since Dalton's law entails a separation of the charges. By (572) for each constituent

$$\nabla^2 (m_s\phi + \epsilon_s\psi) = 4\pi m_s G \{\Sigma_s m_s \overline{n_s}\} - 4\pi\epsilon_s \{\Sigma_s \epsilon_s \overline{n_s}\},$$

where G is the constant of gravitation. As these hold for all m_s and ϵ_s we must have

$$\nabla^2\phi = 4\pi G \Sigma_s m_s \overline{n_s}, \qquad \text{......(1043)}$$

$$\nabla^2\psi = -4\pi\Sigma_s \epsilon_s \overline{n_s}. \qquad \text{......(1044)}$$

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* Emden, *Gaskugeln*.

† Rosseland, *M.N.R.A.S.* vol. LXXXIV, p. 729 (1924).

‡ Eddington, *The internal constitution of the stars* (1926), and now also Jeans, *Astronomy and Cosmogony* (1928).

§ Eddington, *loc. cit.* p. 21.

‖ Milne, *Proc. Camb. Phil. Soc.* vol. XXII, p. 493 (1925).

These are the complete equations. Owing however to the smallness of Gm_s^2 compared with ϵ_s^2 we may usually neglect altogether the gravitational field of the atmosphere itself and replace (1043) by $\nabla^2\phi = 0$, so that $\phi = gz$ if the curvature of the atmosphere may be neglected, and otherwise $\phi = -GM/r$, where M is the mass of the central body and r the distance from its centre.

By (376) the ionization constant is constant in space, so that the condition of ionization equilibrium affects only the constants $(\overline{n_s})_0$. The whole equilibrium problem may therefore be solved without reference to this condition, provided the constants of integration $(\overline{n_s})_0$ are adjusted to satisfy it. If the suffixes 1, 2, 3 refer respectively to the neutral atom, the ion and the electron, we have therefore, curvature neglected,

$$\overline{n_1} = (\overline{n_1})_0 \, e^{-m_1 gz/kT}, \qquad \text{......(1045)}$$

$$\overline{n_2} = (\overline{n_2})_0 \, e^{-(m_2 gz + \epsilon\psi)/kT}, \qquad \text{......(1046)}$$

$$\overline{n_3} = (\overline{n_3})_0 \, e^{-(m_3 gz - \epsilon\psi)/kT}, \qquad \text{......(1047)}$$

coupled with

$$\frac{d^2\psi}{dz^2} = -4\pi\epsilon\,(\overline{n_2} - \overline{n_3}). \qquad \text{......(1048)}$$

For an atmosphere stratified in planes ψ will be a function of z alone. We recall also that $m_1 = m_2 + m_3$ and m_3 is very small.

Let us write

$$\epsilon\psi' = -\tfrac{1}{2}(m_2 - m_3)\,g + kTf, \qquad \text{......(1049)}$$

denoting differentiations with respect to z by primes, and differentiate logarithmically (1046) and (1047). Then

$$\left.\begin{aligned} \frac{\overline{n_2}'}{\overline{n_2}} &= -\frac{\frac{1}{2}(m_2 + m_3)\,g}{kT} - f, \\ \frac{\overline{n_3}'}{\overline{n_3}} &= -\frac{\frac{1}{2}(m_2 + m_3)\,g}{kT} + f, \end{aligned}\right\} \qquad \text{......(1050)}$$

$$f' = \frac{4\pi\epsilon^2}{kT}(\overline{n_3} - \overline{n_2}). \qquad \text{......(1051)}$$

We can reintegrate (1050) in the form

$$\begin{aligned} \overline{n_2} &= (\overline{n_2})_0 \exp\left(-az - \int_{z_0}^{z} f\,dz\right), \\ \overline{n_3} &= (\overline{n_3})_0 \exp\left(-az + \int_{z_0}^{z} f\,dz\right), \end{aligned} \quad \left(a = \frac{\frac{1}{2}(m_2 + m_3)\,g}{kT}\right). \qquad \text{......(1052)}$$

From equations (1051) and (1052) we can eliminate $\overline{n_2}$ and $\overline{n_3}$, and from the result eliminate $\int f\,dz$ by differentiation. We find

$$\left\{\frac{f'' + af'}{f}\right\}^2 - f'^2 = 4\left(\frac{4\pi\epsilon^2}{kT}\right)^2 (\overline{n_2})_0 (\overline{n_3})_0 \, e^{-2az}. \qquad \text{......(1053)}$$

With the help of this equation we may determine the behaviour of f and so the general characteristics of the atmosphere.

§ **15·21.** *Form of f for large positive z, at the outside boundary of the atmosphere.* If the resultant charge on the whole body and its atmosphere is zero, then at the outer boundary $\psi' = 0$ and

$$f \to \frac{\frac{1}{2}(m_2 - m_3)\,g}{kT} = f_\infty .$$

We search for an approximate solution of (1053) by replacing f by f_∞ and writing $f' = e^{-\alpha z}\,\xi$. Then ξ satisfies

$$\xi'^2 - f_\infty{}^2\xi^2 = 4\left(\frac{4\pi\epsilon^2}{kT}\right)^2 (\overline{n_2})_0\,(\overline{n_3})_0\,f_\infty{}^2. \qquad \text{......(1054)}$$

Therefore $$\xi = \frac{4\pi\epsilon^2}{kT}\sqrt{(\overline{n_2}\,\overline{n_3})_0}\left\{\gamma e^{f_\infty z} - \frac{1}{\gamma}\,e^{-f_\infty z}\right\},$$

of which the second term is negligible compared with the first; γ is a constant of integration. Returning to f' and integrating, we find

$$\begin{aligned} f &= f_\infty - \frac{4\pi\epsilon^2}{kT}\sqrt{(\overline{n_2}\,\overline{n_3})_0}\,\gamma\,\frac{e^{-(\alpha - f_\infty)z}}{\alpha - f_\infty},\\ &= \frac{\frac{1}{2}(m_2 - m_3)\,g}{kT} - \frac{4\pi\epsilon^2}{m_3 g}\sqrt{(\overline{n_2}\,\overline{n_3})_0}\,\gamma e^{-m_3gz/kT}. \qquad \text{......(1055)}\end{aligned}$$

It is easy to show that the error in this equation is $O\,(e^{-2m_3gz/kT})$. From this it follows that

$$\int^z f dz = \frac{\frac{1}{2}(m_2 - m_3)\,gz}{kT} + \frac{4\pi\epsilon^2 kT}{m_3{}^2g^2}\sqrt{(\overline{n_2}\,\overline{n_3})_0}\,\gamma e^{-m_3gz/kT} + \delta,$$

where δ is a constant of integration. Inserting this in (1052) we find

$$\overline{n_2} = \frac{(\overline{n_2})_0\,e^{-m_2gz/kT}}{D\exp\left[\dfrac{4\pi\epsilon^2 kT}{m_3{}^2g^2}\sqrt{(\overline{n_2}\,\overline{n_3})_0}\,\gamma e^{-m_3gz/kT}\right]}, \qquad \text{......(1056)}$$

$$\overline{n_3} = (\overline{n_3})_0\,e^{-m_3gz/kT}\,D\exp\left[\frac{4\pi\epsilon^2 kT}{m_3{}^2g^2}\sqrt{(\overline{n_2}\,\overline{n_3})_0}\,\gamma e^{-m_3gz/kT}\right], \qquad \text{......(1057)}$$

and in order to satisfy (1051) we must have $D = \gamma\sqrt{(\overline{n_2}/\overline{n_3})_0}$.

We can draw interesting deductions. Since the extra exponentials tend to unity as $z \to +\infty$, we have *ultimately*

$$\begin{aligned}\overline{n_2} &\sim \sqrt{(\overline{n_2}\,\overline{n_3})_0}\,\gamma e^{-m_2gz/kT},\\ \overline{n_3} &\sim \sqrt{(\overline{n_2}\,\overline{n_3})_0}\,\gamma e^{-m_3gz/kT},\end{aligned} \qquad (z\ \textit{very large}), \qquad \text{......(1058)}$$

which is Dalton's law, when the electrostatic forces have become trivial. The "when" is however instructive, for this occurs when

$$\frac{4\pi\epsilon^2 kT}{m_3{}^2g^2}\sqrt{(\overline{n_2}\,\overline{n_3})_0}\,\gamma e^{-m_3gz/kT}$$

is small compared with unity. On using (1058) we see that this condition is

$$\frac{4\pi\epsilon^2 kT\overline{n_3}}{m_3{}^2 g^2} \quad \text{or} \quad \frac{4\pi\epsilon^2 p_3}{m_3{}^2 g^2} \qquad \text{......(1059)}$$

small compared with unity. For electrons on the sun $4\pi\epsilon^2/m_3{}^2g^2$ is $4{\cdot}85 \times 10^{27}$. Thus the partial pressure of the electrons must be well below 10^{-28} dynes/cm.^{2} or 10^{-34} atmospheres before Dalton's law becomes effective. We have then reached a region so tenuous that the density there is far below the probable density in interstellar space! In no region which can be considered as belonging to the atmosphere of the sun or any particular star do we even approach the condition (1059).

§ **15·22**. *The form of f for large negative z, at the base of the atmosphere.* On referring to equation (1053) we see that the right-hand side tends to infinity as $z \to -\infty$, and therefore if f has a limit at all that limit must be zero. There are no physically possible alternatives. For large negative z the equation therefore approximates to

$$f'' + \alpha f' = \frac{8\pi\epsilon^2}{kT}\sqrt{(\overline{n_2}\overline{n_3})_0}\, e^{-\alpha z} f. \qquad \text{......(1060)}$$

This equation must be solved asymptotically as $z \to -\infty$, α and the coefficient of $e^{-\alpha z}f$ being numerically small. By the substitution* $f = \alpha e^{-\eta}$ $(\eta \to +\infty)$ it is easy to show that

$$\eta' = -\left[\frac{8\pi\epsilon^2\sqrt{(\overline{n_2}\overline{n_3})_0}}{kT}\right]^{\frac{1}{2}} e^{-\frac{1}{2}\alpha z} + \tfrac{1}{4}\alpha + O\left(e^{\frac{1}{2}\alpha z}\right).$$

From this it follows that to a sufficient approximation

$$f = \alpha \exp\left[-\frac{2}{\alpha}\left\{\frac{8\pi\epsilon^2\sqrt{(\overline{n_2}\overline{n_3})_0}}{kT}\right\}^{\frac{1}{2}} e^{-\frac{1}{2}\alpha z} + O(\alpha z)\right]. \qquad \text{......(1061)}$$

From this form it follows at once that $\int_{-\infty} f\,dz$ converges, and approximately

$$\int_{-\infty}^{z} f\,dz = \alpha\left[\frac{8\pi\epsilon^2\sqrt{(\overline{n_2}\overline{n_3})_0}}{kT}\right]^{-\frac{1}{2}} e^{\frac{1}{2}\alpha z} \exp\left[-\frac{2}{\alpha}\left\{\frac{8\pi\epsilon^2\sqrt{(\overline{n_2}\overline{n_3})_0}}{kT}\right\}^{\frac{1}{2}} e^{-\frac{1}{2}\alpha z}\right].$$

We can now suppose that $-\infty$ is chosen for z_0 in (1052). Then since $f' \to 0$ $(\overline{n_2})_0 = (\overline{n_3})_0$. For sufficiently large negative z we shall therefore find approximately

$$\overline{n_2} = \overline{n_3} = (\overline{n_2})_0\, e^{-\alpha z}. \qquad \text{......(1062)}$$

The meaning of this distribution law is that the ions and electrons are distributed as if they were both of mass equal to their mean mass—with no tendency to separate out and consequently no electric field. This fusion we have shown to occur at the base of the atmosphere, or in the interior

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* We insert α to take care of the dimensional factor in f.

of the star, but the question of interest is where for this purpose does the interior start. It starts obviously as soon as $\int_{-\infty}^{z} f\,dz$ is small compared with unity, that is to say as soon as

$$\frac{2}{\alpha}\left[\frac{8\pi\epsilon^2\sqrt{(\overline{n_2}\,\overline{n_3})_0}}{kT}\right]^{\frac{1}{2}} e^{-\frac{1}{2}\alpha z}$$

or

$$\frac{8\epsilon}{(m_2+m_3)\,g}\,[2\pi p_3]^{\frac{1}{2}}$$

is fairly large compared with unity. For calcium on the sun this reduces numerically to

$$5{\cdot}4 \times 10^9 \sqrt{p_3},$$

which is large as soon as p_3 the electron pressure is greater than say 10^{-16} dynes/cm.^{2}, or 10^{-22} atmospheres. Even this figure corresponds to a density less than that of interstellar space, so that so far as separation of electrons and ions is concerned, the interior of the star, in which separation is impossible, may be taken to include the whole of the star and any atmosphere that can properly be regarded as private to it. All we have to do in any problem of an ionized atmosphere in equilibrium is to use (1062) instead of Dalton's law. To produce this there is a constant electric field acting outwards of intensity $\frac{1}{2}(m_2 - m_3)\,g/\epsilon$, but the separation of charge necessary to produce this is altogether trivial.

§ **15·23**. *Further observations.* If the charge on the star has a surface density σ, then, as $z \to +\infty$,

$$-\epsilon\psi' \to 4\pi\sigma.$$

This alters slightly the form of the solution as $z \to +\infty$, but does not affect the conditions as $z \to -\infty$, since these are independent of f_∞. Hence the conclusions of § 15·22 are valid whatever the charge on the star.

Again we have shown that $f \to 0$ as $z \to -\infty$ and that

$$f \to \tfrac{1}{2}(m_2 - m_3)\,g/kT,$$

a positive quantity as $z \to +\infty$. From the form of the relation for f', namely

$$f' = A\left[e^{\int_{-\infty}^{z} f dz} - e^{-\int_{-\infty}^{z} f dz}\right] \quad (A > 0),$$

it follows that if f starts positive for large negative z then $f' > 0$, f increases and f' can never vanish. Since f has to be positive for large positive z it follows that f and f' must both always be positive and f steadily increases.

For the uncharged star this implies that the resultant charge down to any level is always negative since as $f > 0$, $\overline{n_3} > \overline{n_2}$. But this negative charge is excessively minute. Applying Gauss' theorem to (1049) we see that the excess charge σ per unit area is given by

$$-4\pi\sigma = -\tfrac{1}{2}(m_2 - m_3)\,g/\epsilon.$$

The excess number of electrons per unit area is therefore

$$(m_2 - m_3)\,g/8\pi\epsilon^2,$$

which for ionized calcium on the sun is 0·3!

§ **15·24**. *Multivalent ions and their compensating free electrons.* The theory for an atmosphere of a single set of positive ions of charge $+v_2\epsilon$ and the corresponding electrons is very similar. In place of the equations (1046)–(1048) we have

$$\overline{n_2} = (\overline{n_2})_0\, e^{-(m_2 gz + v_2\epsilon\psi)/kT}, \qquad \text{......(1063)}$$

$$\overline{n_3} = (\overline{n_3})_0\, e^{-(m_3 gz - \epsilon\psi)/kT}, \qquad \text{......(1064)}$$

$$\psi'' = -4\pi\epsilon\,(v_2\overline{n_2} - \overline{n_3}). \qquad \text{......(1065)}$$

We now define f by the equation

$$\epsilon\psi' = -\frac{(m_2 - m_3)\,g}{v_2 + 1} + kTf,$$

and replace the last equations by

$$\begin{aligned} \overline{n_2} &= (\overline{n_2})_0 \exp\left(-\alpha z - v_2\int_{z_0}^{z} f\,dz\right), \\ \overline{n_3} &= (\overline{n_3})_0 \exp\left(-\alpha z + \int_{z_0}^{z_0} f\,dz\right), \\ f' &= \frac{4\pi\epsilon^2}{kT}\,(\overline{n_3} - v_2\,\overline{n_2}), \end{aligned} \qquad \left(\alpha = \frac{m_2 + v_2 m_3}{v_2 + 1}\frac{g}{kT}\right),$$

the equation satisfied by f being now

$$\left\{\frac{f'' + \alpha f'}{f} - f'\right\}\left\{\frac{f'' + \alpha f'}{f} + v_2 f'\right\}^{v_2} = \left[\frac{4\pi\epsilon^2}{kT}\,(v_2 + 1)\,e^{-\alpha z}\right]^{v_2+1} (\overline{n_3})_0^{\,v_2}\, v_2\,(\overline{n_2})_0. \qquad \text{......(1066)}$$

The conclusions which can be drawn from this equation correspond exactly to those drawn from (1053). The ions and electrons never separate out appreciably in the atmosphere proper, and for large negative z, $f \to 0$, $f' \to 0$. If then z_0 is taken as $-\infty$, we find $(\overline{n_3})_0 = v_2\,(\overline{n_2})_0$ and the distribution laws

$$\overline{n_2} = (\overline{n_2})_0\, e^{-\alpha z}, \qquad \text{......(1067)}$$

$$\overline{n_3} = (\overline{n_2})_0\, v_2 e^{-\alpha z}. \qquad \text{......(1068)}$$

There are just v_2 times as many electrons as ions, and both possess the exponential factor of a neutral particle of mass $(m_2 + v_2 m_3)/(v_2 + 1)$.

§ **15·25.** *Atmospheres with more than one positive ion.* This case is unfortunately much more complicated, and it is of course more typical of actual atmospheres. It is sufficient for illustration to consider two positive ions and electrons. The neutral atoms required by the dissociative equilibrium are also present, but need not be explicitly considered. The equations then are

$$\overline{n_1} = (\overline{n_1})_0\, e^{-(m_1gz+\nu_1\epsilon\psi)/kT},$$
$$\overline{n_2} = (\overline{n_2})_0\, e^{-(m_2gz+\nu_2\epsilon\psi)/kT},$$
$$\overline{n_3} = (\overline{n_3})_0\, e^{-(m_3gz-\epsilon\psi)/kT},$$
$$\psi'' = -\,4\pi\epsilon\,(\overline{n_1}\nu_1 + \overline{n_2}\nu_2 - \overline{n_3}).$$

If it happens that

$$\frac{m_1 - m_3}{\nu_1 + 1} = \frac{m_2 - m_3}{\nu_2 + 1}, \qquad \text{......(1069)}$$

the substitution

$$\epsilon\psi' = -\frac{m_1 - m_3}{\nu_1 + 1}\, g + kTf$$

reduces the leading terms in all three exponentials to equality. We are then led to an equation for f similar to but more complicated than (1066), but from which the same conclusions can be drawn. This equality will never be satisfied by the main constituents of an atmosphere, even approximately.

When (1069) is not satisfied, I have not been able to find any formal approximations to the solution of the set of equations proposed. It is however possible to obtain useful *qualitative* information.

Let us suppose that in a certain region the conditions are dominated by the first constituent. We will suppose this region is fairly deep in the atmosphere so that the conclusions of § 15·22 hold. Then approximately

$$\epsilon\psi = -\left(\frac{m_1 - m_3}{\nu_1 + 1}\right) gz,$$
$$\left.\begin{aligned}\overline{n_1} &= (\overline{n_1})_0\, e^{-\alpha_1 z},\\ \overline{n_3} &= (\overline{n_3})_0\, e^{-\alpha_1 z},\end{aligned}\right\} \quad \alpha_1 = \frac{g}{kT}\,\frac{m_1 + \nu_1 m_3}{\nu_1 + 1},$$
$$\overline{n_2} = (\overline{n_2})_0\, e^{-\alpha_1' z}, \qquad \text{......(1070)}$$

where

$$\alpha_1' = \frac{(\nu_1 + 1)\, m_2 - \nu_2\,(m_1 - m_3)}{\nu_1 + 1}\,\frac{g}{kT}. \qquad \text{......(1071)}$$

We find that $\alpha_1' < \alpha_1$ if

$$\frac{m_2 - m_3}{\nu_2 + 1} < \frac{m_1 - m_3}{\nu_1 + 1},$$

and we shall certainly find a region of control by the first constituent if we can go deep enough into the atmosphere ($z \to -\infty$) without other disturbances. Generalizing we might say that in an isothermal atmosphere the deepest levels will be controlled by the constituent for which

$$(m_1 - m_3)/(\nu_1 + 1)$$

is greatest, but this only holds if the effectively undisturbed isothermal region is extensive enough to differentiate between the various constituents. In the region of control by $\overline{n_1}$ the rate of space variation of $\overline{n_2}$ given by α_1' may even be reversed so that $\overline{n_2}$ increases upwards ($\alpha_1' < 0$).

As we rise in the atmosphere ($z \rightarrow +\infty$) this state of things must reverse and control must pass over to the second constituent. We shall then have

$$\epsilon\psi = -\left(\frac{m_2 - m_3}{\nu_2 + 1}\right) gz,$$

$$\left.\begin{aligned}\overline{n_2} &= (\overline{n_2})_0\, e^{-\alpha_2 z},\\ \overline{n_3} &= (\overline{n_3})_0\, e^{-\alpha_2 z},\end{aligned}\right\} \quad \alpha_2 = \frac{m_2 + \nu_2 m_3}{\nu_2 + 1}\frac{g}{kT},$$

$$\overline{n_1} = (\overline{n_1})_0\, e^{-\alpha_2' z},$$

where
$$\alpha_2' = \frac{(\nu_2 + 1)\, m_1 - \nu_1 (m_2 - m_3)}{\nu_2 + 1}\frac{g}{kT}.$$

We can verify that $\alpha_2' > \alpha_2$ as it should be for this region.

A special case of particular interest is that in which the constituents 1 and 2 are the single and double ions of the same neutral atom 0. Then $m_1 = m_0 - m_3$, $m_2 = m_0 - 2m_3$, $\nu_1 = 1$, $\nu_2 = 2$. Applying these formulae we find that in the deep region

$$\overline{n_0} = (\overline{n_0})_0\, e^{-m_0 gz/kT}, \quad \overline{n_1} = (\overline{n_1})_0\, e^{-\frac{1}{2}m_0 gz/kT},$$
$$\overline{n_2} = (\overline{n_2})_0 \qquad\qquad, \quad \overline{n_3} = (\overline{n_3})_0\, e^{-\frac{1}{2}m_0 gz/kT},$$

so that the concentration of double ions does not alter. In the high region

$$\overline{n_0} = (\overline{n_0})_0\, e^{-m_0 gz/kT}, \quad \overline{n_1} = (\overline{n_1})_0\, e^{-\frac{2}{3}m_0 gz/kT},$$
$$\overline{n_2} = (\overline{n_2})_0\, e^{-\frac{1}{3}m_0 gz/kT}, \quad \overline{n_3} = (\overline{n_3})_0\, e^{-\frac{1}{3}m_0 gz/kT}.$$

Here we leave this application. Our main conclusion is that large scale electrical effects profoundly alter the vertical distribution of the ions and electrons in an atmosphere, in general refusing to let them separate. In effect they alter g for ions and electrons in the way we have attempted to calculate, but the actual fields required to do this are very small, and apart from this modification of g the resulting fields and charges can always be neglected. Certain similar applications to stellar interiors will be made in the next chapter. We should in conclusion record the warning that an actual atmosphere is submitted to a strong one-sided flow of radiation from the photosphere of the star, and that selective action of this radiation may seriously modify any conclusions drawn when gravity is the only external force acting. The atmosphere cannot then be an assembly in statistical equilibrium, but the type of effect which may enter is discussed in § 15·5.

§ **15·3**. *Stellar absorption spectra.* The atmosphere of a star, when we have reached the deeper levels of the last sections, levels still of extreme tenuity, will consist of a mixture of atoms, ions and electrons in a state in which each constituent behaves approximately like a perfect gas. The mixture as a whole is electrically neutral as the separation of electrons and ions in the gravitational field is trivial. We shall verify later that the deviations from the perfect gas laws required by the theory developed in Chapter XIV are insignificant for the regions to be explored in this section. We shall regard this atmosphere to a first approximation as an isothermal homogeneous slab in statistical equilibrium, but subject to a flow of radiation of all wave lengths, corresponding to a higher temperature from the lower levels (*photosphere*) of the star. Such a slab forms an idealized *reversing layer*, forming by specific absorption dark lines in the continuous spectrum. Our object in these sections is to show how the theorems of statistical mechanics can be applied in a general way to explain the behaviour of these *absorption lines*, particularly in regard to the march of their intensities as we pass through the series of spectral types, and to deduce at least rough information as to the temperatures and pressures in the reversing layers of most stars. We shall not enter into great detail, since a recent book by Miss Payne* gives a full account to which the reader should refer. These sections will therefore be confined to a summary, with supplements of her account.

The first successful quantitative application of the theory of statistical (or rather in his case thermodynamic) equilibrium to stellar reversing layers is due to Saha†. An atom absorbs a different optical spectrum for each stage of ionization, and in fact a different set of lines for each stationary state belonging to each stage, and therefore the relative intensities of the absorption lines of its successive spectra in the spectrum of any star must give some indication of the relative numbers of atoms in the various stages of ionization in the reversing layer, and therefore of the temperature and pressure.

The early applications of this idea may be divided into two main groups. The first is typified by comparisons between the spectra of the normal solar reversing layer and sun spots, and between spectra of giants and dwarfs of the same spectral type. It was shown that the intensity differences are largely explained by changes in the degree of ionization resulting either from temperature differences (sun and spot) or from pressure differences (giant and dwarf)‡. A similar successful comparison may be drawn between the spectra of the reversing layer and chromosphere (flash spectrum)‡. In the second group attention is devoted to the general march of the intensity of a line, or group of lines, through the sequence of stellar spectral types, and an attempt is made to deduce the temperature scale from the

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* Miss Payne, *Stellar Atmospheres*, Harvard Monographs, No. 1 (1925).

† Saha, *Phil. Mag.* vol. XL, pp. 472, 809 (1920); *Proc. Roy. Soc.* A, vol. XCIX, p. 136 (1921).

‡ Saha, *loc. cit.* (1) and (2); Russell, *Astrophys. Jour.* vol. LV, p. 119 (1922).

positions in this sequence of the first and last ("marginal") appearances of the line. At such a point the fraction of atoms in the reversing layer capable of absorbing the line must be very small, and if the pressure is known the temperature can be calculated*.

But the precision of the early calculations was questionable owing to the difficulty of formulating the conditions for the marginal appearance of a line†. Firstly we do not know *a priori* how small the "very small" fraction of atoms must be at marginal appearance. Secondly the point of marginal appearance will depend on the relative abundance of the element giving the line—other things being equal lines due to a more abundant element will persist to a smaller fractional concentration. A similar difficulty may arise from different atomic absorption coefficients for different lines‡. Large uncertainties may arise from all these causes.

However, the general qualitative adequacy of the theory carried the conviction that imperfections of this kind were imperfections of our knowledge and not of the theory; it is reasonable both *a priori* and on the evidence to conclude that in the main the intensities of absorption lines vary in the same sense as the numbers of atoms capable of absorbing them. The next step was to formulate this conclusion explicitly: *Other things being equal, the intensity of a given absorption line in a stellar spectrum varies always in the same sense as the concentration of atoms in the reversing layer capable of absorbing the line.* The foregoing difficulties are then in the main avoided, if we devote attention in the first instance to the place in the stellar sequence at which a given line attains its *maximum intensity*. This will be attained at the maximum concentration of atoms capable of absorbing the line, and the conditions therefore only involve the temperature and pressure. We do not now require to know the relative abundance of the various elements, the efficiency of any atomic state as an absorber, or the absolute number of effective atoms required to form a line. The temperature at which, for a given pressure, a given line of known series relationships attains its maximum is simply deducible from the properties of the equilibrium state. A number of such calculations will be given in the following pages. Consequently in the first instance each observed maximum of a line in the stellar sequence relates the temperature and pressure of the reversing layer at that point of the sequence. This appears to be the most satisfactory way to apply Saha's theory quantitatively to fix stellar temperatures and pressures§. We therefore summarize the results of such calculations. But

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* Saha, *loc. cit.* (3), and *Zeit. für Phys.* vol. VI, p. 40 (1921); H. H. Plaskett, "The Spectra of three *O*-type stars," *Pub. Dom. Astrophys. Obs.* vol. I, No. 30 (1922).

† These difficulties were discussed by Milne, *The Observatory*, vol. XLVI, p. 113 (1923).

‡ We now are fairly certain, however, that the atomic absorption coefficients concerned in stellar spectra are all of the same order of magnitude.

§ Such calculations were made by R. H. Fowler and Milne, *M.N.R.A.S.* vol. LXXXIII, p. 403 (1923); vol. LXXXIV, p. 499 (1924); R. H. Fowler, *M.N.R.A.S.* vol. LXXXV, p. 970 (1925).

we can then attempt to refine them in various ways, and show that each observed maximum can probably be made to determine directly a temperature in the stellar sequence, without assuming a pressure. The pressure is itself determined by the theory, being that of the layer in which the absorption line is formed. We find that this refined theory requires the height of this layer to vary in a definite way from line to line. Instead of assuming a pressure, we assume that a certain function of the properties of the atom and its abundance and gravity on the surface of the star may be assumed roughly constant. There is reasonable ground for belief that this assumption is true on the average, so that the derived temperature scale should be reliable. The final step, not here reached, will be to regard each observed maximum in the known temperature scale as fixing the value of this function and to deduce therefrom abundance factors or absolute values of atomic absorption coefficients. For this step we require a quantitative theory of the formation of an absorption line, a synthesis which has hardly yet been made.

Lines absorbed by the neutral atom in its normal state, which we shall call *normal lines*, will be shown theoretically always to decrease in intensity as we traverse the spectral types from M to higher temperatures. This is almost obvious without calculation, for the fraction in the normal state (initially practically unity) can only decrease as the temperature increases. An exception to this absence of maximum could occur if in atmospheres of very low temperature the atoms in question were all removed by condensation or chemical combination. Such considerations are however not usually of importance and will not be referred to again. It is easy to see that all other lines should have a maximum somewhere. Consider first a line absorbed by some excited state of a neutral atom, which we shall refer to as a *subordinate line*. The fraction of atoms in this excited state is the product of two factors: (1) The fraction of the atoms not yet ionized; (2) the fraction of these neutral atoms in the proper state. The first factor decreases steadily from 1 to 0 as T increases, while the second increases steadily from a very small value. This must lead somewhere to a maximum in the product. Similarly for the normal lines of any ion, we start at low temperatures with atmospheres in which there are no such ions, and pass through a stage at which almost all are once ionized, to a final stage in which all are in still higher stages of ionization. Again we find a maximum*.

In the first stage of the discussion we find it convenient to calculate pressures for maxima at a given temperature. The general result of the

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* In identifying this maximum with the observed maximum we assume that the average abundance of this atom changes only very slowly (if at all) along the stellar sequence. There is every *a priori* consideration in favour of this assumption which is of course essential. Otherwise, for example, the maximum of the Balmer lines in A-type stars might be due to a maximum in the absolute abundance of hydrogen there, a barren and unsatisfying conclusion.

comparison with observation is that observed and theoretical maxima can be fitted together into a consistent scheme provided that the pressure in the layers which reverse strongly ordinary subordinate lines is of the order of 10^{-5} atmosphere. Similarly in layers which reverse strongly normal lines of atoms and ions and nearly normal lines of the metallic transition elements the pressure must be of the order 10^{-9}–10^{-10} atmosphere. At the second more refined stage we see that this result is expected and that on the whole all observations fit into a logically consistent whole, leaving outstanding a number of interesting minor discrepancies.

The observational material on the positions of maxima in the sequence of giant stars is mainly due to Miss Payne and Menzel*. For dwarfs there is not the same sequence of material, and we have mainly cross comparisons with the giant sequence at spectral types F and G.

§ **15·31**. *The statistical theory of absorption lines.* To carry out the calculations suggested in § 15·3 we use equations (1015)† and the method of § 8·6 to determine the $(M_r^z)_s/V$, and then differentiate with respect to T to determine maximum values. But the general formulae simplify greatly here. In the first place χ_r^z/χ^z_{r+1} is never greater than about 0·7 for any atomic ions with which we have to deal in reversing layers and is usually nearer 0·5. The successive stages of ionization are thus well separated, and it is found that we never have to consider more than two consecutive stages of any atom at any one time for a subordinate line or three at most for a normal line. Secondly, excluded volumes and the electrostatic energy can be ignored entirely, except of course for the convergency factors due to the former in $u_r^z(T)$. We shall find further that in all calculations of maxima $u(T)$ reduces to its first or at most its first two or three terms, for which the excluded volumes can be ignored, and that the highly excited states make no effective contribution. We shall therefore start the calculations with these simplifications, which are easily justified *a posteriori*.

It is convenient to express the laws of dissociative equilibrium in terms of p_ϵ the partial pressure of the free electrons, and $x_0, x_1, \ldots, x_s$ the fractions of any atom present in the neutral, singly ionized, or s-times ionized states. Then the equations of dissociation (333), generalized as in § 8·6, reduce to

$$\frac{x_{r+1}}{x_r}\, p_\epsilon = \frac{2\,(2\pi m)^{\frac{3}{2}}\,(kT)^{\frac{5}{2}}}{h^3}\,\frac{u_{r+1}(T)}{u_r(T)}\, e^{-\chi_r/kT}, \qquad \ldots\ldots(1072)$$

with $$\Sigma_r x_r = 1.$$

We need not here retain the affix z. Let $(n_r)_s$ be the fraction of all the atoms

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* Miss Payne, Harvard Circular, No. 258 (1924); *loc. cit.* chap. VIII; Menzel, Harvard Circular, Nos. 252, 256 (1924).

† It is here a matter of indifference whether we use Urey's or Planck's form for $u_r^z(T)$, since the states of high excitation prove negligible.

of one type which are r-times ionized and in their sth state. Then (1015) reduces to

$$(n_r)_s = x_r\,(\varpi_r)_s\,e^{-\{\chi_r-(\chi_r)_s\}/kT}/u_r\,(T).$$

For discussing the *maxima* of the states of the neutral atom we may ignore x_r for $r \geqslant 2$ owing to the rapidly increasing χ's. Inserting numerical values in (1072) we find*

$$x_0 = \frac{u_0\,(T)\,e^{\chi_0/kT}}{u_0\,(T)\,e^{\chi_0/kT} + 0{\cdot}664\,u_1\,(T)\,T^{\frac{5}{2}}/p_\epsilon}, \qquad \text{......(1073)}$$

$$(n_0)_s = \frac{(\varpi_0)_s\,e^{(\chi_0)_s/kT}}{u_0\,(T)\,e^{\chi_0/kT} + 0{\cdot}664\,u_1\,(T)\,T^{\frac{5}{2}}/p_\epsilon}. \qquad \text{......(1074)}$$

The maximum value of $(n_0)_s$ for given pressure occurs where $\partial\,(n_0)_s/\partial T = 0$, or where

$$p_\epsilon = \frac{0{\cdot}664\,u_1\,(T)}{u_0\,(T)}\left\{\frac{(\chi_0)_s + \frac{5}{2}kT + kT^2 u_1'/u_1}{\chi_0 - (\chi_0)_s - kT^2 u_0'/u_0}\right\} T^{\frac{5}{2}}\,e^{-\chi_0/kT}. \qquad \text{......(1075)}$$

This gives the pressure in dynes/cm.^{2} which can be converted to atmospheres with sufficient accuracy by multiplication by 10^{-6}. We have also

$$(x_0)_{\max} = \frac{(\chi_0)_s + \frac{5}{2}kT + kT^2 u_1'/u_1}{\chi_0 + \frac{5}{2}kT + kT^2\,(u_1'/u_1 - u_0'/u_0)}, \qquad \text{......(1076)}$$

$$\{(n_0)_s\}_{\max} = (x_0)_{\max}\,\frac{(\varpi_0)_s\,e^{-\{\chi_0-(\chi_0)_s\}/kT}}{u_0\,(T)}. \qquad \text{......(1077)}$$

The same formulae hold for the maxima of the subordinate lines of the r-times ionized atom, when we replace the suffix 0 by r and ignore all stages of ionization except r and $r + 1$. A simple verification, which we omit, is required first to show that for the relevant temperatures $x_r + x_{r+1} = 1$ approximately.

We conclude that any subordinate line should have a maximum given by these formulae. For any normal line of a neutral atom $(\chi_0)_s = \chi_0$ and $(n_0)_s$ has no maximum for $kT^2 u_0'/u_0$ reduces to zero, and (1075) merely gives $T = 0$. Formula (1076) reduces to $(x_0)_{\max} = 1$ in this case.

We must next examine the numerical values of $u_0\,(T)$, $u_1\,(T)$ and their differential coefficients. From (1075) it follows that near the maximum $p_\epsilon/T^{\frac{5}{2}}$ and $e^{-\chi_0/kT}$ must be approximately equal, and we shall find that the actual orders of both are about 10^{-8}. For the approximate form of $u_r\,(T)$ we take (1021), in which a is given by (1018). We may take $p_\epsilon = p_a$ approximately. The numerical value of

$$[(r+1)^3/9a]^{\frac{1}{2}}$$

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* The numerical factor here is twice that (0·332) used in the work of R. H. Fowler and Milne, because we have here corrected for the weight 2 of the free electron. All the weights used in the two papers (*loc. cit.*) are wrong, though the results are hardly affected. Effectively correct weights were used by R. H. Fowler, *loc. cit.*

is therefore of the order 2×10^5 at most in a reversing layer. It follows at once from (1021) that we have at most one highly excited electron, and that the states of high excitation of even this one electron make a negligible contribution to $u_r(T)$ (less than one per cent.). In reversing layer problems therefore it is only the first few terms of $u_r(T)$ which need be considered, and usually only the first (constant) term and the term to which the subordinate line under discussion belongs. We verify in the same way that the contributions of highly excited terms to $kT^2 u_r'(T)/u_r(T)$ are equally negligible in the equations for the maxima.

Returning now to the early terms, suppose that for simplicity

$$u_0(T) = \varpi_0 + (\varpi_0)_1 \, e^{-\{\chi_0 - (\chi_0)_1\}/kT}. \qquad \text{......(1078)}$$

Then

$$\frac{kT^2 u_0'(T)}{u_0(T)} = \{\chi_0 - (\chi_0)_1\}\left[1 - \frac{\varpi_0}{u_0(T)}\right]. \qquad \text{......(1079)}$$

Unless $\chi_0 - (\chi_0)_1$, the energy of excitation, is small compared with kT, the effect of the second term in $u_0(T)$ is negligible both in (1078) and (1079). Even if $\chi_0 - (\chi_0)_1$ is small, $u_0'(T)$ will still be of no importance in the formula for p_ϵ unless this second state of small energy of excitation is also the state in which the atoms must be in order to absorb the line in question. In that special case $(\chi_0)_s = (\chi_0)_1$ and the denominator of p_ϵ becomes

$$\{\chi_0 - (\chi_0)_1\} \, \varpi_0,$$

instead of $\{\chi_0 - (\chi_0)_1\} \, u_0(T)$, which is the value when $u_0'(T)$ is ignored. When the excited states are nearly normal this correction may be considerable. No effect of this sort can be produced by $kT^2 u_1'(T)/u_1(T)$, which can always be neglected. We can therefore replace (1075) by

$$p_\epsilon = \frac{0{\cdot}664 \, u_1(T)}{\varpi_0} \, \frac{(\chi_0)_s + \frac{5}{2}kT}{\chi_0 - (\chi_0)_s} \, T^{\frac{5}{2}} \, e^{-\chi_0/kT}, \qquad \text{......(1080)}$$

which in this form is always valid if ϖ_0 is taken to mean the sum of the weights of just those states which differ in energy from the normal state by an amount which is very small compared with $\chi_0 - (\chi_0)_s$. In calculating $(x_0)_{\max}$ we can always ignore $u_0'(T)$ and $u_1'(T)$ so that

$$(x_0)_{\max} = \frac{(\chi_0)_s + \frac{5}{2}kT}{\chi_0 + \frac{5}{2}kT}. \qquad \text{......(1081)}$$

To discuss a normal line of the ionized atom we must retain three stages. Then

$$\frac{x_2}{x_1} = \frac{0{\cdot}664}{p_\epsilon} \, \frac{u_2(T)}{u_1(T)} \, T^{\frac{5}{2}} \, e^{-\chi_1/kT},$$

$$\frac{x_1}{x_0} = \frac{0{\cdot}664}{p_\epsilon} \, \frac{u_1(T)}{u_0(T)} \, T^{\frac{5}{2}} \, e^{-\chi_0/kT},$$

$$x_0 + x_1 + x_2 = 1, \quad n_1 = \varpi_1 x_1 / u_1(T).$$

If we solve these equations for n_1 we find that

$$n_1 = \frac{\varpi_1}{u_1(T) + u_0(T)\dfrac{p_\epsilon}{0\cdot 664} T^{-\frac{5}{2}} e^{\chi_0/kT} + u_2(T)\dfrac{0\cdot 664}{p_\epsilon} T^{\frac{5}{2}} e^{-\chi_1/kT}}. \qquad \ldots\ldots(1082)$$

Thus the maximum of n_1 will occur when

$$kT^2 u_1'(T) - \frac{p_\epsilon}{0\cdot 664}\{\chi_0 + \tfrac{5}{2}kT - kT^2 u_0'/u_0\} u_0(T) T^{-\frac{5}{2}} e^{\chi_0/kT}$$

$$+ \frac{0\cdot 664}{p_\epsilon}\{\chi_1 + \tfrac{5}{2}kT + kT^2 u_2'/u_2\} u_2(T) T^{\frac{5}{2}} e^{-\chi_1/kT} = 0. \qquad \ldots\ldots(1083)$$

If we can ignore the term in $u_1'(T)$ we then find

$$p_\epsilon = 0\cdot 664 \left\{\frac{\chi_1 + \frac{5}{2}kT + kT^2 u_2'/u_2}{\chi_0 + \frac{5}{2}kT - kT^2 u_0'/u_0} \cdot \frac{u_2(T)}{u_0(T)}\right\}^{\frac{1}{2}} T^{\frac{5}{2}} e^{-\frac{1}{2}(\chi_0+\chi_1)/kT}. \qquad \ldots\ldots(1084)$$

The order of the two terms retained from (1083) is $(u_0 u_2)^{\frac{1}{2}} e^{-\frac{1}{2}(\chi_1-\chi_0)/kT}$ at the maximum, and this maximum occurs at a lower temperature than that at which the maxima of any subordinate lines of the ionized atom occur. The conclusions as to the negligibility of the terms of high excitation hold therefore *a fortiori*. The order of $kT^2 u_1'(T)$ will therefore be

$$\{\chi_1 - (\chi_1)_1\} e^{-\{\chi_1 - (\chi_1)_1\}/kT},$$

which may be important in (1083) if there is an excitation potential of the ionized atom comparable with $\frac{1}{2}(\chi_1 - \chi_0)$. When this is the case (1083) must be solved as a quadratic for p_ϵ. At the maximum, if $u_1'(T)$ can be ignored

$$(n_1)_{\max} = \frac{\varpi_1}{u_1(T) + O\{(u_0 u_2)^{\frac{1}{2}} e^{-\frac{1}{2}(\chi_1-\chi_0)/kT}\}}, \qquad \ldots\ldots(1085)$$

which is approximately equal to $\varpi_1/u_1(T)$ and therefore nearly unity.

If, as can happen, the term in $u_1'(T)$ is of larger order than the other two terms at the suggested maximum (1084), then the third term in (1083) can be ignored and we have

$$p_\epsilon = \frac{0\cdot 664\, kT^2 u_1'(T)}{u_0(T)\{\chi_0 + \frac{5}{2}kT - kT^2 u_0'/u_0\}} T^{\frac{5}{2}} e^{-\chi_0/kT}. \qquad \ldots\ldots(1086)$$

The maximum is due in this case to the switch over of the majority of the atoms from the normal state to the first excited state as the temperature rises, and in the determination of the maximum we can ignore second stage ionization entirely. If for simplicity we write here

$$u_1(T) = \varpi_1 + (\varpi_1)_1 e^{-\{\chi_1 - (\chi_1)_1\}/kT},$$

then

$$p_\epsilon = \frac{0\cdot 664\, (\varpi_1)_1 \{\chi_1 - (\chi_1)_1\}}{u_0(T)\{\chi_0 + \frac{5}{2}kT - kT^2 u_0'/u_0\}} T^{\frac{5}{2}} e^{-\{\chi_0 + \chi_1 - (\chi_1)_1\}/kT}. \qquad \ldots\ldots(1087)$$

In this case $$(n_1)_{\max} = \frac{\varpi_1}{u_1\,(T) + O\,\{(\varpi_1)_1\,e^{-\{\chi_1-(\chi_1)_1\}/kT}\}}, \qquad \text{......(1088)}$$

which again differs only a little from $\varpi_1/u_1\,(T)$ or unity.

In certain cases in calculating maxima of subordinate lines of an ionized element of very small energy of excitation it may be necessary to use the apparatus of these paragraphs taking account of *three* successive stages of ionization. But no general discussion of the negligibility of the various $u\,(T)$ and $u'\,(T)$ can expect to cover all cases, and when doubt arises it is always a simple matter to write down an explicit 2- or 3-term formula for the whole relevant part of $u\,(T)$ and use the exact values of $u\,(T)$ and $u'\,(T)$.

§ **15·32.** *Numerical calculations.* We present in this section numerical applications to a selection of the available observational material. To do more would take up too much space, and the selection is wide enough to justify the theory. It is obvious from a cursory inspection of the rest of the material that it will fit into the same scheme. Except where otherwise recorded the data are taken from Menzel or Miss Payne or from Hund*, but the calculations given here are revised, as we now know the correct forms of $u\,(T)$ which were not available for earlier calculations.

Throughout the calculations we group together all the lines of a multiplet, ignoring the energy differences in the initial and in the final state. This is legitimate, and our discussion therefore refers to the maximum of the multiplet as a whole rather than the maxima of its component lines, but these are indistinguishable. The only noteworthy inaccuracy in this simplification is that the fraction of atoms at maximum is that capable of absorbing *some* line of the multiplet. The fraction capable of absorbing one given line is naturally less, and in some applications this point may need attention. We tabulate for each element or each group of lines of each element the data† used in the calculations. This is followed by the observed position of the maximum, and then by a few calculations for a series of maximum temperatures of the electron pressure, the fraction of atoms in the required stage of ionization, the fraction in the required stationary state, and the product of this last fraction by the electron pressure.

(i) V. $1\,{}^6D - {}^6F$ (part); λλ 4395, 4390, 4385, 4379; $\chi_0 = 6{\cdot}30$, $(\chi_0)_1 = 6{\cdot}02$;

$$u_0\,(T) = 28 + 30e^{-0{\cdot}28/kT} + 20e^{-1{\cdot}05/kT},\quad u_1\,(T) = 25 + 35e^{-0{\cdot}32/kT}.$$

For the least blended lines no maximum is observed. It lies below $M\,3$.

$T_{\max}$	p_ϵ atmos.	$(x_0)_{\max}$	$\{(n_0)_1\}_{\max}$	$(n_0)_1\,p_\epsilon$
2500	$1{\cdot}07 \times 10^{-9}$	0·96	$2{\cdot}17 \times 10^{-1}$	$2{\cdot}32 \times 10^{-10}$
3000	$2{\cdot}44 \times 10^{-7}$	0·96	$2{\cdot}54 \times 10^{-1}$	$6{\cdot}2 \times 10^{-8}$

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* Hund, *Linienspektren und periodisches System der Elemente* (1927). This is supplemented by private information kindly supplied to me by A. Fowler.

† Energies in electron volts.

(ii) Ba$^+$. $1\,^2S - 1\,^2P$; $\lambda\lambda$ 4934, 4554; $\chi_0 = 5{\cdot}18$, $\chi_1 = 9{\cdot}95$;

$$\tfrac{1}{2}(\chi_1 - \chi_0) = 2{\cdot}385 > 1{\cdot}512 = \chi_1 - (\chi_1)_1;$$

$$u_0(T) = 1 + 5e^{-1{\cdot}41/kT}, \quad u_1(T) = 2 + 10e^{-1{\cdot}512/kT}, \quad u_2(T) = 1.$$

[Variations of $u_0(T)$ may be ignored.] The maximum must lie at *M* 3 or just below. $(n_1)_{\max} = 1$.

$T_{\max}$	p_ϵ atmos.	$(n_1)\,p_\epsilon$
2500	$1{\cdot}66 \times 10^{-11}$	$1{\cdot}66 \times 10^{-11}$
3000	$4{\cdot}6 \times 10^{-9}$	$4{\cdot}6 \times 10^{-9}$
3500	$2{\cdot}72 \times 10^{-7}$	$2{\cdot}72 \times 10^{-7}$

(iii) Cr. $1\,^5S - {}^5P$; $\lambda\lambda$ 4497; $\chi_0 = 6{\cdot}75$, $(\chi_0)_1 = 5{\cdot}81$;

$$u_0(T) = 7 + 5e^{-0{\cdot}94/kT} + 25e^{-1{\cdot}00/kT}, \quad u_1(T) = 6 + 30e^{-0{\cdot}40/kT} + 20\,e^{-1{\cdot}20/kT}.$$

The observed maximum lies at *M* 1 (Menzel).

$T_{\max}$	p_ϵ atmos.	$(x_0)_{\max}$	$\{(n_0)_1\}_{\max}$	$(n_0)_1\,p_\epsilon$
2500	$5{\cdot}0 \times 10^{-11}$	$0{\cdot}87$	$7{\cdot}8 \times 10^{-3}$	$3{\cdot}9 \times 10^{-13}$
3000	$1{\cdot}74 \times 10^{-8}$	$0{\cdot}87$	$1{\cdot}60 \times 10^{-2}$	$2{\cdot}78 \times 10^{-10}$
3500	$1{\cdot}21 \times 10^{-6}$	$0{\cdot}87$	$2{\cdot}66 \times 10^{-2}$	$3{\cdot}2 \times 10^{-8}$

(iv) Sr$^+$. $1\,^2S - 1\,^2P$; $\lambda\lambda$ 4216, 4078; $\chi_0 = 5{\cdot}665$, $\chi_1 = 10{\cdot}97$;

$$\tfrac{1}{2}(\chi_1 - \chi_0) = 2{\cdot}652 > 1{\cdot}815 = \chi_1 - (\chi_1)_1,$$

$$u_0(T) = 1, \quad u_1(T) = 2 + 10e^{-1{\cdot}815/kT}, \quad u_2(T) = 1.$$

The observed maximum lies at *M* 0 (Menzel) or *K* 2 (Payne), the latter is probably the more reliable. $(n_1)_{\max} = 1$.

$T_{\max}$	p_ϵ atmos.	$(n_1)\,p_\epsilon$
3000	$2{\cdot}42 \times 10^{-10}$	$2{\cdot}42 \times 10^{-10}$
3500	$2{\cdot}02 \times 10^{-8}$	$2{\cdot}02 \times 10^{-8}$
4000	$6{\cdot}8 \times 10^{-7}$	$6{\cdot}8 \times 10^{-7}$

(v) Mg. $1\,^3P - 1\,^3S$; $\lambda\lambda$ 5184, 5173, 5167; $\chi_0 = 7{\cdot}61$, $(\chi_0)_1 = 4{\cdot}92$;

$$u_0(T) = 1, \quad u_1(T) = 2; \quad (\varpi_0)_1 = 9.$$

Observed maximum at *K* 2–5 but poorly determined.

$T_{\max}$	p_ϵ atmos.	$(x_0)_{\max}$	$\{(n_0)_1\}_{\max}$	$(n_0)_1\,p_\epsilon$
3500	$2{\cdot}42 \times 10^{-8}$	$0{\cdot}68$	$8{\cdot}1 \times 10^{-4}$	$1{\cdot}95 \times 10^{-11}$
4000	$7{\cdot}2 \times 10^{-7}$	$0{\cdot}68$	$2{\cdot}47 \times 10^{-3}$	$1{\cdot}78 \times 10^{-9}$
4500	$1{\cdot}14 \times 10^{-5}$	$0{\cdot}69$	$5{\cdot}7 \times 10^{-3}$	$6{\cdot}4 \times 10^{-8}$
5000	$1{\cdot}08 \times 10^{-4}$	$0{\cdot}69$	$1{\cdot}19 \times 10^{-2}$	$1{\cdot}28 \times 10^{-6}$

(vi) Fe. $1\,{}^3F - {}^3X$; $X = D, F, G$; some 16 lines in all; $\chi_0 = 8{\cdot}15$, $(\chi_0)_2 = 6{\cdot}59$;

$$u_0(T) = 25 + 35e^{-0{\cdot}95/kT} + 21e^{-1{\cdot}56/kT},\ u_1(T) = 30 + 28e^{-0{\cdot}33/kT} + \dots.$$

The observed maximum is well determined at $K2$.

T_{max}	p_ϵ atmos.	$(x_0)_{\text{max}}$	$\{(n_0)_2\}_{\text{max}}$	$(n_0)_2\, p_\epsilon$
3500	$4{\cdot}0 \times 10^{-9}$	0·82	$3{\cdot}7 \times 10^{-3}$	$1{\cdot}47 \times 10^{-11}$
4000	$1{\cdot}67 \times 10^{-7}$	0·83	$6{\cdot}8 \times 10^{-3}$	$1{\cdot}13 \times 10^{-9}$
4500	$3{\cdot}3 \times 10^{-6}$	0·83	$1{\cdot}10 \times 10^{-2}$	$3{\cdot}6 \times 10^{-8}$

(vii) Ca⁺. $1\,{}^2S - 1\,{}^2P$; $\lambda\lambda$ 3968, 3934; $\chi_0 = 6{\cdot}08$, $\chi_1 = 11{\cdot}82$;

$$\tfrac{1}{2}(\chi_0 - \chi_1) = 2{\cdot}87 > 1{\cdot}69 = \chi_1 - (\chi_1)_1;$$

$$u_0(T) = 1,\ u_1(T) = 2 + 10e^{-1{\cdot}69/kT},\ u_2(T) = 1.$$

There are observations of a maximum at $K0$ (Menzel), but it is possible that there is no maximum before $M0$ (Payne). $(n_1)_{\text{max}} = 1$.

T_{max}	p_ϵ atmos.	$(n_1)\, p_\epsilon$
3000	$6{\cdot}8 \times 10^{-11}$	$6{\cdot}8 \times 10^{-11}$
3500	$7{\cdot}4 \times 10^{-9}$	$7{\cdot}4 \times 10^{-9}$
4000	$2{\cdot}56 \times 10^{-7}$	$2{\cdot}56 \times 10^{-7}$
4500	$3{\cdot}9 \times 10^{-6}$	$3{\cdot}9 \times 10^{-6}$

(viii) Zn. $1\,{}^3P - 1\,{}^3S$; $\lambda\lambda$ 4810, 4722 (4680); $\chi_0 = 9{\cdot}34$, $(\chi_0)_1 = 5{\cdot}33$; $u_0(T) = 1, u_1(T) = 2$; $(\varpi_0)_1 = 9$. The observed maximum is well determined at $G0$.

T_{max}	p_ϵ atmos.	$(x_0)_{\text{max}}$	$(n_0)_{1\,\text{max}}$	$(n_0)_1\, p_\epsilon$
5000	$1{\cdot}38 \times 10^{-6}$	0·61	$4{\cdot}9 \times 10^{-4}$	$6{\cdot}8 \times 10^{-10}$
6000	$8{\cdot}4 \times 10^{-5}$	0·62	$2{\cdot}52 \times 10^{-3}$	$2{\cdot}12 \times 10^{-7}$

There are well-determined maxima of many lines of Fe⁺ and Ti⁺ at $F5$, some rising to $F0$ and some falling to $G0$, but we unfortunately do not yet know χ_1 for certain for either of these elements. The steps from Fe to Fe⁺ and Fe⁺ to Fe⁺⁺ both involve the loss of a 4_0-electron, and from our knowledge of the ratio of the first and second ionization potentials in similar cases (He, Mg, Ca, Sr, Ba) we should guess χ_1 here to be about 15 volts. The following calculation for Fe⁺ is therefore speculative.

(ix) Fe⁺. $2\,{}^4P - 1\,{}^4F, {}^4D'$; $\lambda\lambda$ 4173·3, 4179, 4417; approximately $\chi_1 = 15$, $(\chi_1)_s = 12{\cdot}3$; $u_1(T) = 60$, $u_2(T) = 37$; $(\varpi_1)_s = 12$. There is a well-observed maximum at $F5$.

T_{max}	p_ϵ atmos.	$(x_1)_{\text{max}}$	$(n_1)_{1\,\text{max}}$	$(n_1)_1\, p_\epsilon$
6000	$1{\cdot}37 \times 10^{-9}$	0·83	$8{\cdot}9 \times 10^{-4}$	$1{\cdot}22 \times 10^{-12}$
7000	$1{\cdot}30 \times 10^{-7}$	0·84	$1{\cdot}89 \times 10^{-3}$	$2{\cdot}46 \times 10^{-10}$

(x) Mg^+. $1\,{}^2D - 1\,{}^2F$; λλ 4481; $\chi_1 = 15{\cdot}00$, $(\chi_1)_1 = 6{\cdot}15$; $u_1(T) = 2$, $u_2(T) = 1$; $(\varpi_1)_1 = 10$. There is a well-observed maximum at $A\,2$.

T_{max}	p_ϵ atmos.	$(x_1)_{max}$	$(n_1)_{1\,max}$	$(n_1)_1\,p_\epsilon$
9,000	$9{\cdot}0 \times 10^{-6}$	0·48	$2{\cdot}58 \times 10^{-5}$	$2{\cdot}30 \times 10^{-10}$
10,000	$8{\cdot}2 \times 10^{-5}$	0·48	$8{\cdot}2 \times 10^{-5}$	$6{\cdot}8 \times 10^{-9}$
11,000	$5{\cdot}3 \times 10^{-4}$	0·49	$2{\cdot}12 \times 10^{-4}$	$1{\cdot}12 \times 10^{-7}$

(xi) H. Balmer series; λλ 4861, etc.; $\chi_0 = 13{\cdot}54$, $(\chi_0)_1 = 3{\cdot}385$; $u_0(T) = 2$, $u_1(T) = 1$; $(\varpi_0)_1 = 8$. The maximum is at $A\,0$, by definition of the type.

T_{max}	p_ϵ atmos.	$(x_0)_{max}$	$(n_0)_{1\,max}$	$(n_0)_1\,p_\epsilon$
9,000	$3{\cdot}3 \times 10^{-5}$	0·34	$2{\cdot}76 \times 10^{-6}$	$9{\cdot}2 \times 10^{-11}$
10,000	$2{\cdot}62 \times 10^{-4}$	0·35	$1{\cdot}05 \times 10^{-5}$	$2{\cdot}75 \times 10^{-9}$
11,000	$1{\cdot}44 \times 10^{-3}$	—	—	—

(xii) Si^+. $1\,{}^2D - 1\,{}^2F$; λλ 4131, 4128; $\chi_1 = 16{\cdot}27$, $(\chi_1)_1 = 6{\cdot}47$; $u_1(T) = 6$, $u_2(T) = 1$; $(\varpi_1)_1 = 10$. The observed maximum is well defined at $A\,0$.

T_{max}	p_ϵ atmos.	$(x_1)_{max}$	$(n_1)_{1\,max}$	$(n_1)_1\,p_\epsilon$
10,000	$5{\cdot}9 \times 10^{-6}$	0·47	$8{\cdot}8 \times 10^{-6}$	$5{\cdot}2 \times 10^{-11}$
11,000	$4{\cdot}3 \times 10^{-5}$	0·47	$2{\cdot}51 \times 10^{-5}$	$1{\cdot}08 \times 10^{-9}$

(xiii) C^+. $1\,{}^2D - 1\,{}^2F$; λλ 4267; $\chi_1 = 24{\cdot}28$, $(\chi_1)_1 = 6{\cdot}31$; $u_1(T) = 6$, $u_2(T) = 1$; $(\varpi_1)_1 = 10$. The observed maximum is well defined at $B\,3$.

T_{max}	p_ϵ atmos.	$(x_1)_{max}$	$(n_1)_{1\,max}$	$(n_1)_1\,p_\epsilon$
14,000	$1{\cdot}96 \times 10^{-6}$	0·34	$1{\cdot}88 \times 10^{-7}$	$3{\cdot}7 \times 10^{-13}$
16,000	$3{\cdot}7 \times 10^{-5}$	0·35	$1{\cdot}25 \times 10^{-6}$	$4{\cdot}6 \times 10^{-11}$
18,000	$3{\cdot}7 \times 10^{-4}$	0·36	$5{\cdot}5 \times 10^{-6}$	$2{\cdot}02 \times 10^{-9}$

(xiv) He. Sharp and diffuse series of par- and ortho-helium; λλ 4712, 4471, 4922, etc.; $\chi_0 = 24{\cdot}47$, $(\chi_0)_1 = 3{\cdot}48$ (mean); $u_0(T) = 1$, $u_2(T) = 2$; $(\varpi_0)_1 = 3$ (par-He) or 9 (ortho-He). The observed maximum is well defined at $B\,2$–3.

T_{max}	p_ϵ atmos.	$(x_0)_{max}$	$(n_0)_{1\,max}$ [par-He]	$(n_0)_1\,p_\epsilon$
16,000	$2{\cdot}68 \times 10^{-4}$	0·248	$1{\cdot}76 \times 10^{-7}$	$4{\cdot}7 \times 10^{-11}$
18,000	$2{\cdot}76 \times 10^{-3}$	0·259	$1{\cdot}00 \times 10^{-6}$	$2{\cdot}76 \times 10^{-9}$

(xv)* N^+. $1\,{}^1P' - 1\,{}^1P$; λ 3995; $\chi_1 = 29{\cdot}48$, $(\chi_1)_s = 11{\cdot}06$; $u_1(T) = 9$, $u_2(T) = 6$; $(\varpi_1)_s = 3$. The observed maximum is at $B\,3$–5.

T_{max}	p_ϵ atmos.	$(x_1)_{max}$	$(n_1)_{s\,max}$	$(n_1)_s\,p_\epsilon$
18,000	$8{\cdot}5 \times 10^{-5}$	0·45	$1{\cdot}03 \times 10^{-6}$	$8{\cdot}7 \times 10^{-11}$
20,000	$1{\cdot}35 \times 10^{-3}$	0·45	$3{\cdot}4 \times 10^{-6}$	$4{\cdot}6 \times 10^{-9}$

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* A. Fowler and Freeman, *Proc. Roy. Soc.* A, vol. CXIV, p. 662 (1927).

(xvi) Si^{++}. $1\,{}^3S - 2\,{}^3P$; $\lambda\lambda$ 4552, 4567, 4574; $\chi_2 = 33{\cdot}35$*, $(\chi_2)_s = 14{\cdot}40$; $u_2(T) = 1$, $u_3(T) = 2$; $(\varpi_2)_s = 3$. There is a well-defined maximum at $B\,1$–2.

$T_{\max}$	p_ϵ atmos.	$(x_2)_{\max}$	$(n_2)_{s\,\max}$	$(n_2)_s\,p_\epsilon$
18,000	$2{\cdot}48 \times 10^{-5}$	0·49	$7{\cdot}1 \times 10^{-6}$	$1{\cdot}77 \times 10^{-10}$
20,000	$2{\cdot}82 \times 10^{-4}$	0·50	$2{\cdot}44 \times 10^{-5}$	$6{\cdot}9 \times 10^{-9}$

(xvii) O^{+}. $1\,{}^2P - 1\,{}^2D$; $\lambda\lambda$ 4417, 4415; $\chi_1 = 35{\cdot}00$, $(\chi_1)_s = 11{\cdot}53$; $u_1(T) = 4 + 10e^{-3{\cdot}34/kT} + 6e^{-5{\cdot}04/kT}$, $u_2(T) = 9$; $(\varpi_1)_s = 6$. There is a well-defined maximum at $B\,1$. [A number of other O^{+} lines with $(\chi_1)_s$ varying down to 8·5 volts have maxima at B_1 or perhaps at slightly higher temperatures towards $B\,0$.]

$T_{\max}$	p_ϵ atmos.	$(x_1)_{\max}$	$(n_1)_{s\,\max}$	$(n_1)_s\,p_\epsilon$
18,000	$4{\cdot}7 \times 10^{-6}$	0·40	$1{\cdot}13 \times 10^{-7}$	$5{\cdot}3 \times 10^{-13}$
20,000	$5{\cdot}7 \times 10^{-5}$	0·40	$5{\cdot}0 \times 10^{-7}$	$2{\cdot}84 \times 10^{-11}$
22,000	$4{\cdot}5 \times 10^{-4}$	0·41	$1{\cdot}65 \times 10^{-6}$	$8{\cdot}2 \times 10^{-10}$

(xviii) Si^{+++}. $2\,{}^2S - 2\,{}^2P$; $\lambda\lambda$ 4089, 4116; $\chi_3 = 44{\cdot}94$, $(\chi_3)_s = 20{\cdot}98$; $u_3(T) = 2$, $u_4(T) = 1$; $(\varpi_3)_s = 2$. The observed maximum occurs in O-type stars at Plaskett's $O\,9$.

$T_{\max}$	p_ϵ atmos.	$(x_3)_{\max}$	$(n_3)_{s\,\max}$	$(n_3)_s\,p_\epsilon$
24,000	$1{\cdot}14 \times 10^{-5}$	0·52	$4{\cdot}7 \times 10^{-6}$	$5{\cdot}4 \times 10^{-11}$
26,000	$7{\cdot}4 \times 10^{-5}$	0·52	$1{\cdot}16 \times 10^{-5}$	$8{\cdot}7 \times 10^{-10}$

(xix) C^{++}. $3\,{}^3S - 3\,{}^3P$; $\lambda\lambda$ 4649, 4651, 4653; $\chi_2 = 46{\cdot}35$, $(\chi_2)_s = 18{\cdot}05$; $u_2(T) = 1$, $u_3(T) = 2$; $(\varpi_2)_s = 3$. There is a well-defined maximum near that of Si^{+++} at $O\,9$.

$T_{\max}$	p_ϵ atmos.	$(x_2)_{\max}$	$(n_2)_{s\,\max}$	$(n_2)_s\,p_\epsilon$
24,000	$1{\cdot}73 \times 10^{-5}$	0·45	$1{\cdot}52 \times 10^{-6}$	$2{\cdot}62 \times 10^{-11}$
26,000	$1{\cdot}20 \times 10^{-4}$	0·46	$4{\cdot}3 \times 10^{-6}$	$5{\cdot}3 \times 10^{-10}$

(xx) N^{++}. $1\,{}^2S - 2\,{}^2P_2$; λ 4098; $\chi_2 = 47{\cdot}19$, $(\chi_2)_s = 19{\cdot}20$; $u_2(T) = 6$, $u_3(T) = 1$; $(\varpi_2)_s = 2$. The maximum has not been reached among the O-type stars investigated.

$T_{\max}$	p_ϵ atmos.	$(x_2)_{\max}$	$(n_2)_{s\,\max}$	$(n_2)_s\,p_\epsilon$
26,000	$7{\cdot}3 \times 10^{-6}$	0·47	$5{\cdot}7 \times 10^{-7}$	$4{\cdot}2 \times 10^{-12}$
28,000	$4{\cdot}1 \times 10^{-5}$	0·47	$1{\cdot}49 \times 10^{-6}$	$6{\cdot}1 \times 10^{-11}$
30,000	$1{\cdot}82 \times 10^{-4}$	0·48	$3{\cdot}1 \times 10^{-6}$	$5{\cdot}7 \times 10^{-10}$

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* A recent correction by Paschen and Sawyer, *Ann. der Phys.* vol. LXXXIV, p. 1 (1927). Their value has been further corrected by A. Fowler.

(xxi) He^+. "4686 series"; λ 4686; $\chi_1 = 54{\cdot}16$, $(\chi_1)_s = 6{\cdot}02$; $u_1(T) = 2$, $u_2(T) = 1$; $(\varpi_1)_s = 18$.

"Pickering series"; $\lambda\lambda$ 5412, etc.; $(\chi_1)_{s'} = 3{\cdot}39$; $(\varpi_1)_{s'} = 32$.

The lines seem nearly to have reached their maximum at the end of Plaskett's sequence of *O*-stars. The observed maximum may be taken to occur at *O* 5. The calculations are for the 4686 series.

$T_{\max}$	p_ϵ atmos.	$(x_1)_{\max}$	$(n_1)_{s\,\max}$ ["4686"]	$(n_1)_s p_\epsilon$
30,000	$1{\cdot}06 \times 10^{-5}$	0·206	$1{\cdot}45 \times 10^{-8}$	$1{\cdot}54 \times 10^{-13}$
36,000	$5{\cdot}9 \times 10^{-4}$	0·222	$3{\cdot}5 \times 10^{-7}$	$2{\cdot}03 \times 10^{-10}$
40,000	$4{\cdot}7 \times 10^{-3}$	0·233	$1{\cdot}76 \times 10^{-6}$	$8{\cdot}3 \times 10^{-9}$

In addition to these maxima the observations show no maximum for any normal lines of any neutral atom in the sequence of giants, in full accord with the theory. To illustrate the way in which the concentration of atoms in a given state in a reversing layer varies with the temperature according to statistical theory, using merely the equation (1074), we reproduce a figure* showing typical curves. These are based on inaccurate weights and must only be regarded now as qualitatively correct.

§ **15·33.** *Discussion and theoretical developments.* It will be evident from a survey of these tables that there is excellent general agreement between theory and observation as to the positions of the maxima in the sequence of giants, on certain conditions. We have to suppose that the partial pressure of the electrons in the layer in which the lines originate is of the order 10^{-9}–10^{-10} atmosphere for the normal lines of the ionized atoms Ca^+, Sr^+, and Ba^+, and the nearly normal lines of very small energy of excitation such as those of V, Cr (and Ti); we suppose further that it increases steadily as the energy of excitation increases (compared with the energy of ionization) until it reaches 10^{-5} atmosphere for subordinate lines of average excitation energy such as those of Mg, Mg^+ and Si^{+++}, and finally perhaps 10^{-3} atmosphere for the lines of exceptionally great excitation energy such as those of He and He^+. The elementary theory of the maxima was based on a given value of p_ϵ. This is confirmed by the more complete data so long as we confine ourselves to lines of similar depth in the various atoms. The variation of the necessary p_ϵ with variation of depth, which is the same thing as variation with $(n_s)_{\max}$, suggests the next stage in a more refined investigation.

Consider any slab of atmosphere in equilibrium at a mean temperature T. The concentration of any atomic species of mass m and charge $\nu\epsilon$ is given approximately by

$$\nu = \nu_0 e^{-mgz/kT - \nu\epsilon\psi/kT}.$$

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* Fowler and Milne, *loc. cit.* (1).

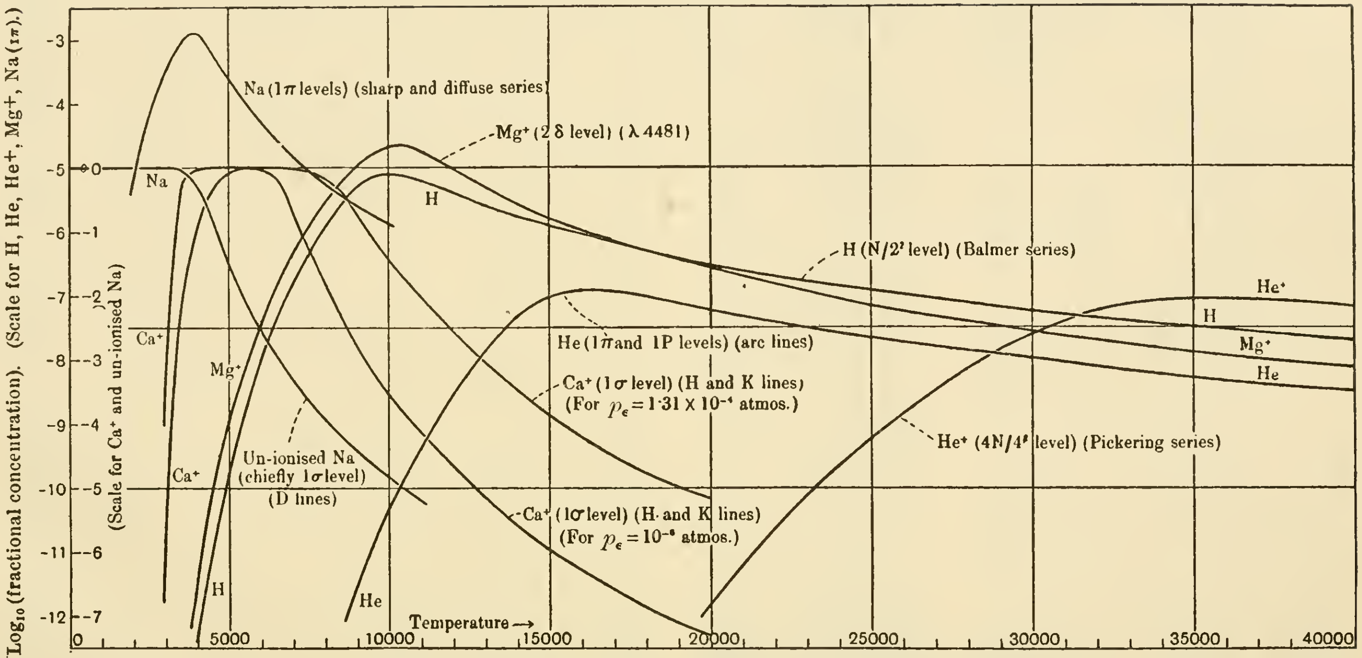

Fig. 23. Showing typical curves of atomic fractional concentrations.

We have already seen that the electrostatic term ψ may profoundly modify the equilibrium distribution of ions. We must be content to assume that

$$\nu = \nu_0 e^{-m'gz/kT}, \qquad \text{......(1089)}$$

where m' is used for the effective atomic mass. Consider the variation of homologous slabs of these atmospheres along the stellar sequence. Homologous slabs will be determined by equal changes in the exponent in (1089), and therefore the thickness of a given slab will be fixed by an equation like

$$\left[\frac{m'gz}{kT}\right]_0^1 = \alpha,$$

where α is some constant such as 1 or 10, and 0 and 1 refer to the bottom and top of the slab. Thus the thickness of homologous slabs varies as $T/m'g$ from star to star, and atom to atom. The number of any atomic species per cm.^{2} of the stellar surface therefore also varies like $T/m'g$. [In an atmosphere perfectly mixed by large-scale convections, such as the lower atmosphere of the earth, m' will have a common mean value for all atoms.]

If p_ϵ is the partial pressure of the electrons at any level in the slab, then the concentration of electrons ν_ϵ is given by

$$\nu_\epsilon = p_\epsilon / kT.$$

If ω is the abundance factor for the element in question, defined by the equation

$$\omega = \frac{\text{Number of nuclei of given atomic number per cm.}^3}{\text{Number of free electrons per cm.}^3},$$

then the concentration ν of these atomic nuclei satisfies

$$\nu = \omega \nu_\epsilon = \omega p_\epsilon / kT,$$

and the number of these nuclei per cm.^{2} of the stellar surface in a given slab will vary as

$$\frac{\omega p_\epsilon}{kT} \times \frac{T}{m'g}, \text{ or } \frac{\omega p_\epsilon}{m'g}.$$

If $(n_r)_s$ is the fraction of these nuclei which provide atoms r times ionized in state s, then the number of atoms per cm.^{2} of the stellar surface in a state to absorb a given line will vary as

$$\frac{\omega p_\epsilon (n_r)_s}{m'g}. \qquad \text{......(1090)}$$

In (1090) ω, $(n_r)_s$, and m' are functions of Z the atomic number.

We must now consider rather more closely the conditions under which a strong absorption line is formed. There must be enough suitable atoms per cm.^{2} to form it. It cannot therefore be formed at too low a pressure, or too high in the reversing layer. But at the same time it must be formed as high as possible in the reversing layer in order that the temperature difference between the absorbing material and the photosphere may be as great as possible. The actual position of the effective layer will be fixed by the balancing of these two factors. Viewed from the outside we may regard an absorption line as a particular wave length at which the absorption coefficient of the stellar atmosphere is abnormally great, so that we can only see into the star down to an abnormally small depth, a depth which is that of the effective slab for this line.

In our elementary calculations we start by determining maxima by $d(n_r{}^z)_s/dT = 0$, that is for a given value of $\omega p_\epsilon/m'g$. This means that for the selected value of (effectively) p_ϵ/g we get the best absorption at the temperature so determined. It remains to examine how to choose or fix the proper value of p_ϵ for use in this way. The *maximum* concentration of suitable atoms per cm.² in the slab of the chosen p_ϵ varies as

$$\frac{\omega\,\{(n_r{}^z)_s\}_{\max}\,p_\epsilon}{m'g}.$$

The value of p_ϵ for use here must be large enough to give enough suitable atoms but no larger. Now it seems probable from general evidence that to produce a strong absorption line one needs about the same number per cm.² of any sort of atom in the suitable state—or more generally that the number one will require will vary as $1/(\kappa_r{}^z)_s$, where κ is the atomic absorption coefficient for selective absorption of this line by atoms in the suitable state. The argument therefore suggests that

$$\frac{\omega\,\{(n_r{}^z)_s\}_{\max}\,p_\epsilon}{m'g} = \frac{\alpha}{(\kappa_r{}^z)_s}, \qquad \text{......(1091)}$$

where α is a constant, which this elementary reasoning cannot fix. There is considerable evidence that $(\kappa_r{}^z)_s$ is of the order 10^8 and not subject to much variation from state to state or atom to atom for the lines of stellar importance.

In equation (1091) there are several factors which it is legitimate to ignore in a first approximation, for the argument is not sufficiently refined to take account of their probable variations. We have already made some comment on m', or rather $m'g$. This really represents the force of gravity on the atom as modified by electrostatic fields and radiation pressure, in particular for the pressure due to the selective absorption forming the line. Gravity itself increases along the giant sequence approximately as T^4, but it is very doubtful if this variation will remain effective in $m'g$. Again ω must decrease as T and therefore ν_ϵ increases, but this is a slow variation, and it will vary by unknown amounts from atom to atom. It seems reasonable to conclude *that* $\{n_r{}^z\}_{s\,\max}\,p_\epsilon$ *as calculated in the last section should have a roughly constant value for all the maxima of absorption lines in stellar spectra*. This conclusion is tentative and is only put forward in so far as it is supported by observation and until an exact theory has been worked out to replace the vague generalities of this section.

This conclusion, it will be seen, at once accounts for the variations of p_ϵ required by the calculations on which we commented before. We see now that if the constant value of $\{(n_r^z)_s\}_{\max} p_\epsilon$ is say 2×10^{-10} (p_ϵ in atmospheres), the theoretical maxima fit coherently with the observations, and determine with some precision and convincingness a stellar temperature scale. We give below the resulting temperatures derived by interpolation from the tables. It will be observed that the equation

$$\{(n_r^z)_s\}_{\max} p_\epsilon = 2 \times 10^{-10}$$

determines $T_{\max}$ directly, without explicit assumption as to p_ϵ, as the root of the equation (for subordinate lines)

$$2 \times 10^{-10} = \frac{0·664\, (\varpi_r^z)_s \{(\chi_r^z)_s + \frac{5}{2}kT\}^2\, u^z{}_{r+1}(T)}{\{\chi_r^z - (\chi_r^z)_s\}\{\chi_r^z + \frac{5}{2}kT\}\{u_r^z(T)\}^2}\, T^{\frac{5}{2}} e^{-\{2\chi_r^z - (\chi_r^z)_s\}/kT}. \qquad \text{......(1092)}$$

There are of course slight modifications when u_r' and u'_{r+1} are included. We derive maxima from (1092) by assuming that $m'g/\omega\kappa$ is roughly constant from atom to atom and star to star, and have fixed its mean value by a rough average over all the stellar material.

TABLE 51.

The stellar temperature scale derived from absorption line maxima.

Atom	Temperature of maximum	Spectral type of observed maximum
V	2,500	Below *M* 3
Ba$^+$	2,700	*M* 3 or below
Cr	2,900	*M* 1
Sr$^+$	3,000	*M* 0 [*K* 5]
Mg	3,700	*K* 2–5
Fe	3,800	*K* 2
Ca$^+$	3,100	*K* 0 [? *M* 0]
Zn	4,800	*G* 0
Fe$^+$	7,000	*F* 5
Mg$^+$	9,000	*A* 2
H	9,250	*A* 0 [*A* 2]
Si$^+$	10,500	*A* 0
N$^+$	18,400	*B* 3–5
C$^+$	16,800	*B* 3
He	16,800	*B* 2–3
Si^{++}	18,000	*B* 1–2
O$^+$	21,100	*B* 0–1
Si^{+++}	25,000	*O* 9
C^{++}	25,400	*O* 9
N^{++}	29,100	Not observed
He$^+$	36,000	Not observed

This scale is eminently satisfactory, and there are few anomalies in the individual entries. When the uncertainties in the material are remembered, there remains only one glaring inconsistency, the value for N$^+$. It must be admitted that, for whatever cause, this maximum does not fit in with the theory. If the H and K lines of Ca^+ really have a maximum at $K0$ then the temperature for Ca^+ is also wrong, but the position of the maximum is doubtful. There is also an important theoretical modification in this case of which we shall speak later.

§ **15·34**. *Giants and dwarfs of the same spectral type.* Statistical theory can be effectively applied to a number of other problems in stellar atmospheres. The most interesting would be a similar analysis of the temperature scale for the sequence of dwarfs, but not enough material is yet available for such a discussion. Certain cross-connections can however be made between the two series, and appear to be in full agreement with statistical theory. Menzel* has shown this qualitatively by a comparison of the spectra of ϵ Indi and α Tauri, a typical dwarf and giant of type $K5$. From the point of view of a stellar atmosphere the difference between a giant and a dwarf must primarily be the different value of g, which is much less for the giant. Absorption lines will therefore be formed at lower pressures in the giant, and given maxima will occur at lower temperatures. This may be expressed by saying that for given spectral type giants will be colder than dwarfs, which is a well-known fact of observation.

The theory here given accounts for this temperature difference satisfactorily. According to (1091) the maxima of a given line should occur in the two sequences where

$$\left[\frac{n_{\max}\, p_\epsilon}{g}\right]_{\text{giant}} = \left[\frac{n_{\max}\, p_\epsilon}{g}\right]_{\text{dwarf}}, \qquad \text{......(1093)}$$

or after (1092) where

$$\left[\frac{T^{\frac{5}{2}}\, e^{-\{2\chi_r{}^z - (\chi_r{}^z)_s\}/kT}}{g}\right]_{\text{giant}} = \left[\frac{T^{\frac{5}{2}}\, e^{-\{2\chi_r{}^z - (\chi_r{}^z)_s\}/kT}}{g}\right]_{\text{dwarf}}. \qquad \text{......(1094)}$$

We may calculate the temperature difference in this way for giants and dwarfs of type $G0$ by using as typical examples the sun and Capella to give the values of g, and by assuming that a spectrum of type $G0$ may be specified with sufficient accuracy by making the lines of zinc have their maximum there. In that case for the reversing layer of the giant Capella we have nearly enough, $T = 4800$, $2\chi_r - (\chi_r)_s = 13{\cdot}35$, $g = 0{\cdot}067 \times 10^4$. For the sun $g = 2{\cdot}73 \times 10^4$. Thus the reversing layer temperature for a dwarf of type $G0$, such as the sun, ought to be the root of the equation

$$T^{\frac{5}{2}}\, e^{-13\cdot35/kT} = 40{\cdot}7\,(4800)^{\frac{5}{2}}\, e^{-13\cdot35/4800k},$$
$$= 6{\cdot}3 \times 10^{-4}.$$

The root is approximately 5400°, a temperature difference of 600°, in excellent agreement with solar conditions, but the success of the theory must only be regarded as provisional, pending a more exact theory replacing (1091).

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* *Loc. cit.*

§ **15·35.** *The points of marginal appearance. Decay of lines past their maxima.* When the stellar temperature scale is known, with or without the help of the positions of the maxima of absorption lines, it is possible to draw some information about the factor $\omega\kappa$ from the temperatures of the points of marginal appearance of an absorption line. When a line is just visible we may suppose that the concentration of suitable atoms required to form it must reach a certain minimum value proportional to $1/\kappa$; that is $\kappa\ (n_r)_s$ has some fairly definite value. Since we know p_ϵ and T we can derive from this a corresponding value of $\omega\kappa$. Since the values of κ are all much the same, we can thus derive values of ω or rather relative values of ω for different elements—that is their relative abundance. The result is of course admittedly only a rough approximation. Such calculations have been begun by Miss Payne (*q.v.*) with interesting results.

In connection with these and future calculations there is one important observation to be made from the statistical side. It will be observed that the typical curves of the concentration of atoms in given states shown in Fig. 23 are markedly unsymmetrical about the maximum. The rise to the maximum is much steeper than the fall off for higher temperatures. So far as the suggested argument goes the value of $\omega\kappa$ derived from first and last appearance should be the same, and the theoretical curves suggest that lines should fade out much more slowly than they come in. For many lines this is directly contrary to observation. The observed rise and fall in intensity are reasonably symmetrical about the maximum. There is however one well recognized exception, the Balmer series which unlike most other lines has not faded out even in the hottest stars.

While the theory can perhaps hardly claim to be able to explain completely the symmetry of the observed curves, the marked difference between the behaviour of the Balmer lines and the lines say of Si or Si^+ and metallic lines generally is accounted for by the simple theory when the calculations are made so as to allow for successive ionizations. This was not done for Fig. 23. Any line of the spectra H I, He II, etc., is a line of the last spectrum the atom can emit, for it has no further electrons to lose. Spectra such as Si I, Fe I, Si II, etc., belong on the other hand to atoms that can lose a regular sequence of further electrons at not too widely spaced ionization potentials. Spectra such as Si IV, Mg II and probably Na I will be effectively the last spectra of these atoms, for the next electron is separated by a big step in ionization potential, and will not become effectively removable at the temperatures of stellar reversing layers. The numerically different behaviour of "last" and "not last" spectra can at once be established.

The behaviour of any state of a "last" spectrum will continue to be given for temperatures far beyond $T_{\max}$ by equation (1074), for no further stage of ionization is reached. The behaviour of a state of a "not last" spectrum is determined on the contrary by (1072) and (1073) as before, but with

$$x_0 + x_1 + \dots + x_r + x_{r+1} = 1, \qquad \dots\dots(1095)$$

if the $(r+1)$th state is the last ever relevant. This leads to (1074) near the maximum of a line of the neutral atom where (1095) reduces to $x_0 + x_1 = 1$. But at higher temperatures we have successively $x_1 + x_2 = 1, \dots x_r + x_{r+1} = 1$, approximately, and $(n_0)_s$ will be substantially diminished. The physical reason for this decrease is easily seen. So long as the commonest ion has merely to catch one electron to get into the required state, the chance of doing so diminishes as the temperature rises, it is true, but not excessively rapidly. But if it has to catch two or more electrons, its chance of being in the proper state diminishes more or less like the square or higher power of the former chance. In the case specified we have

$$\frac{x_r}{x_0} p_\epsilon{}^r = (0{\cdot}664)^r T^{\frac{5}{2}r} e^{-\{\chi_0 + \dots + \chi_{r-1}\}/kT} \frac{u_r(T)}{u_0(T)},$$

and so

$$(n_0)_s = \frac{x_r}{u_r(T)} \frac{(\varpi_0)_s e^{-\{\chi_0 - (\chi_0)_s\}/kT}}{\left(\frac{0{\cdot}664}{p_\epsilon}\right)^r T^{\frac{5}{2}r} e^{-\{\chi_0 + \chi_1 + \dots + \chi_{r-1}\}/kT}}. \qquad \dots\dots(1096)$$

At high temperatures, far past the maximum, this can be combined with $x_r + x_{r+1} = 1$ and the usual relation (1072) between x_r and x_{r+1}. We thus find

$$(n_0)_s = \frac{(\varpi_0)_s e^{-\{\chi_0 - (\chi_0)_s\}/kT}}{u_r(T) + \frac{0{\cdot}664}{p_\epsilon} T^{\frac{5}{2}} e^{-\chi_r/kT} u_{r+1}(T)} \times \frac{1}{\left(\frac{0{\cdot}664}{p_\epsilon}\right)^r T^{\frac{5}{2}r} e^{-\{\chi_0 + \chi_1 + \dots + \chi_{r-1}\}/kT}}. \qquad \dots\dots(1097)$$

This equation holds through the region in which $x_r + x_{r+1} = 1$ sufficiently nearly. It holds also for spectra other than the first if we replace the suffixes 0 by t and the *index* r by $r - t$.

Simple calculation for an idealized case will best show the effect of the extra term in (1097). We will compare the spectrum H I with an idealized Si I of the same term values and ionization potential, 13·54 volts, followed by successive ionization potentials at 20, 31·5, and 45 volts, and carry through the calculations for a temperature of 25,000° K. and $p_\epsilon = 4 \times 10^{-5}$ atmosphere, roughly the maximum of the Si IV lines. For simplicity we will ignore differences of weight and take $(\varpi_0)_s$ and $u_r(T)$ all unity. Dropping factors the same for both atoms we find

$$\text{H I} \quad (n_0)_s \propto \frac{1}{1 + \frac{0{\cdot}664}{p_\epsilon} T^{\frac{5}{2}} e^{-13{\cdot}54/kT}} = 10^{-6{\cdot}48}.$$

$$\text{Si I} \quad (n_0)_s \propto \frac{1}{1 + \frac{0{\cdot}664}{p_\epsilon} T^{\frac{5}{2}} e^{-45/kT}} \times \frac{1}{\left(\frac{0{\cdot}664}{p_\epsilon}\right)^3 T^{\frac{15}{2}} e^{-65/kT}} = 10^{-14{\cdot}89}.$$

There is thus an extra factor $10^{-8\cdot4}$ at 25,000° K. reducing the lines of the idealized Si I compared with those of H I. The fraction of H atoms capable of absorbing the Balmer lines at maximum is about 4×10^{-6}, which is only reduced by an extra factor of $10^{-2\cdot3}$ at 25,000° K. The reduction factor of similar Si I atoms is therefore $10^{-10\cdot7}$.

These purely typical calculations at once explain the complete disappearance of all metallic lines at higher temperatures compared with the striking persistence of the Balmer lines. For in all metals of the Fe group, up to and including Cu, there is always an adequately long series of ionization potentials not too far apart, and the foregoing arguments hold. They also hold for Si, S, and Al and to a less extent for O and N. The rate of disappearance of the He I lines will hardly be reinforced in this way before a temperature of 30,000° K. Lines of Ca I and Mg I and similar spectra, followed by one near ionization potential, will have their rate of decay considerably amplified, though not to the degree calculated above. The *H* and *K* lines of Ca^+ should behave like a last spectrum. There remain certain cases of fairly rapid disappearance which cannot be accounted for in this way. The best example is given by the lines of Mg II which disappear fairly rapidly, but belong to a spectrum which is followed by an ionization potential of the order of 60 volts.

§ **15·4**. *The escape of molecules from the boundary of an isothermal atmosphere.* Recent work by Milne* and Lennard-Jones† has greatly improved the theoretical basis of the calculations on this sixty-year-old‡ problem, which have now for the first time been given a precise form. The earlier calculations, of which a sufficient account is given by Jeans§, contain an unsatisfactory feature in the arbitrary choice of a "ceiling" to the atmosphere. The rate of flow of molecules past the ceiling, possessing more than the velocity of escape, is then enumerated and taken to be the rate of loss of molecules from the atmosphere. A numerical result can only be reached at all by this method for the molecular distribution law typical of an isothermal gas in a constant field of force.

The first advance on these calculations was made by Milne by introducing the idea of the "cone of escape". For simplicity he regarded all the other molecules as fixed except those whose escape is in question, and for a given position in the atmosphere calculated the solid angle above the moving molecule, not screened by other molecules. The restriction of fixing the other molecules is not very serious, and he also evaluates in some detail the atmospheric distribution laws under the assumption $T \propto r^{-n}$, where r

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* Milne, *Trans. Camb. Phil. Soc.* vol. XXII, p. 483 (1923).

† J. E. Jones, *ibid.* p. 535 (1923).

‡ Johnstone Stoney.

§ Jeans, *loc. cit.* chap. XV.

is the distance from the centre of the star or planet. He then shows that the number of molecules moving past a given level into the cone of escape has a fairly sharp maximum at a particular level in the atmosphere—the level of escape—and takes this maximum value as equal to the rate of escape.

In spite of the advance made in this calculation, which defines properly the hitherto undefined level of escape or ceiling, there are still not entirely satisfactory features, for obviously the number of escaping molecules crossing a given level must continually increase as the level rises, starting from zero at the surface of the planet. Though the maximum Milne calculates may and in fact does represent fairly accurately the escaping molecules integrated for all levels we may reasonably ask for a still better theory, and the remedy lies in a more accurate enumeration of the molecules starting off at a given level into the cone of escape. Incidentally we can remove the restriction that the other molecules are fixed. These are the final improvements due to Lennard-Jones. We shall give some account of his work here, which is carried out for isothermal atmospheres. An extension to Milne's general case has not been made. It would be laborious and lie outside our scope. For the isothermal case Milne's approximate theory is satisfactorily confirmed, so that his results are probably reliable in general. We make these applications the occasion for presenting a general calculation of the mean free path and the general method of enumerating molecules by the volume element in which they last suffered a collision—matter which we have not found place for elsewhere, but which is of great importance in many applications of statistical mechanics which lie just beyond our scope.

All calculations are of course made on the assumption that the extremely slow rates of escape are without sensible effect on the equilibrium distribution laws.

§ **15·41**. *The free paths of molecules in a uniform or non-uniform gas.* In accurate calculations of the type that follow the important quantity is not so much the average distance between consecutive collisions (free path) travelled by all molecules as the free path for a molecule of given velocity, or what is the same thing, the chance that in time dt a molecule of velocity c will suffer a collision. This idea was introduced by Tait*. The molecules are supposed to be rigid elastic spheres of diameter σ.

Consider a molecule of velocity c. The chance of collision with a second molecule of velocity c' in an element of time dt is equal to the number of molecules of this type contained in a cylinder of cross-section $\pi\sigma^2$ and length Vdt, where V is the relative velocity. If the direction of c' with respect to c be described by the usual Eulerian angles θ, ϕ, then the number

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* Tait, *Edin. Trans.* vol. XXXIII, p. 74 (1886).

of molecules in this cylinder having velocities between c' and $c' + dc'$ and moving in $d\omega$ about θ, ϕ is

$$\nu \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}mc'^2/kT} c'^2 dc' \sin\theta \, d\theta d\phi \times \pi\sigma^2 V dt. \quad \text{......(1098)}$$

The relative velocity V is of course given by

$$V^2 = c^2 + c'^2 - 2cc' \cos\theta. \quad \text{......(1099)}$$

If we denote by $\Theta(c)\,dt$ the average number of collisions in time dt (the chance of a collision in dt) with any other molecule, then

$$\Theta(c) = \pi\nu\sigma^2 \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_0^\infty \int_0^\pi \int_0^{2\pi} e^{-\frac{1}{2}mc'^2/kT} c'^2 V dc' \sin\theta \, d\theta d\phi. \quad \text{......(1100)}$$

The ϕ-integration is immediate; the θ-integration can be carried out by transforming to the variable V (c and c' fixed). By (1099)

$$\sin\theta \, d\theta = V dV / cc'.$$

The limits of integration for V are $|c - c'|$ and $c + c'$. We are thus left with

$$\Theta(c) = \tfrac{4}{3}\pi^2\nu\sigma^2 \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \left[\int_c^\infty e^{-\frac{1}{2}mc'^2/kT} c'(c^2 + 3c'^2)\, dc' + \frac{1}{c}\int_0^c e^{-\frac{1}{2}mc'^2/kT} c'^2 (c'^2 + 3c^2)\, dc'\right]. \quad \text{......(1101)}$$

The first integral can, the second cannot, be evaluated in finite terms. We find after simple reductions,

$$\Theta(c) = \frac{2\sqrt{\pi}\nu\sigma^2 kT}{mc} \psi\left\{c\sqrt{\left(\frac{m}{2kT}\right)}\right\}, \quad \text{......(1102)}$$

where

$$\psi(x) = xe^{-x^2} + (2x^2 + 1)\int_0^x e^{-y^2} dy. \quad \text{......(1103)}$$

The average number of collisions in a small path length dl is therefore

$$\Theta(c)\, dl/c.$$

This is therefore the chance of the free path terminating in dl. The chance of continuing unaffected is therefore

$$1 - \frac{\Theta(c)}{c} dl.$$

Let $f(l)$ be the fraction of c-molecules projected in a given direction from a given origin that describe without a collision a path greater than l. The fraction of these molecules that survive a further distance dl without a collision is $f(l + dl)$, and therefore by the last argument

$$f(l + dl) = f(l)\left(1 - \frac{\Theta(c)}{c} dl\right),$$

$$\frac{1}{f}\frac{\partial f}{\partial l} = -\frac{\Theta(c)}{c}. \quad \text{......(1104)}$$

It follows generally that

$$f(l) = e^{-\int_0^l \frac{\Theta(c)}{c}\,dl}; \qquad \text{......(1105)}$$

in this equation at the worst both c and ν in $\Theta(c)/c$ may depend on l and the direction of projection and ν also on the origin. If we ignore changes of c and write

$$\theta(c) = \Theta(c)/\nu c,$$

a function of c only, then

$$f(l) = e^{-\theta(c)\int_0^l \nu(x_0, y_0, z_0, l, \theta, \phi)\,dl}. \qquad \text{......(1106)}$$

It follows that the fraction of c-molecules with a path length between l and $l + dl$ before a collision is

$$\theta(c)\,\nu\,dl\,e^{-\theta(c)\int_0^l \nu\,dl}. \qquad \text{......(1107)}$$

When ν is constant (1106) reduces to

$$f(l) = e^{-\nu l\theta(c)} = e^{-\Theta(c)l/c} = e^{-l/\lambda(c)}, \qquad \text{......(1108)}$$

defining *the mean free path* $\lambda(c)$. The fraction of paths between l and $l + dl$ reduces to

$$\frac{dl}{\lambda(c)}\,e^{-l/\lambda(c)}. \qquad \text{......(1109)}$$

These are well-known formulae. The name mean free path is justified by the equation

$$\int_0^\infty \frac{l\,dl}{\lambda(c)}\,e^{-l/\lambda(c)} = \lambda(c). \qquad \text{......(1110)}$$

Similar arguments hold in the general case using (1105). The mean free path of the molecules may then be defined by putting

$$\int_0^{\lambda(c)} \frac{\Theta(c)}{c}\,dl = 1,$$

or

$$\int_0^{\lambda(c)} \frac{\psi\left\{c\sqrt{\left(\frac{m}{2kT}\right)}\right\}}{c^2}\,\nu\,dl = \frac{m}{2\sqrt{\pi\sigma^2 kT}}. \qquad \text{......(1111)}$$

If c is large compared with the average molecular velocity, so that the argument of ψ is large,

$$\frac{\psi(x)}{x^2} \to 2\int_0^\infty e^{-y^2}\,dy = \sqrt{\pi},$$

and formula (1111) becomes

$$\int_0^{\lambda(\infty)} \nu\,ds = \frac{1}{\pi\sigma^2}. \qquad \text{......(1112)}$$

This equation gives the length of a cylinder of base $\pi\sigma^2$ which contains on the average just one molecule, and the free path is that which we get by regarding all the other molecules as fixed. For uniform density we have the well-known result

$$\lambda(\infty) = 1/\pi\nu\sigma^2. \qquad \ldots\ldots(1113)$$

The integral in (1105) or (1106) may, and in atmospheric problems does, converge when $l \to \infty$. In that case the definition of $\lambda(c)$ by (1108) or (1111) fails—it would make $\lambda(c)$ infinite, and the integral in (1110) diverges. This means that as the path increases $f(l) \to f(\infty)$ so that a non-zero fraction of the original molecules survives to execute infinite free paths. The fraction which so survives is

$$e^{-\int_0^\infty \frac{\Theta(c)}{c}\,dl}, \qquad \text{or} \qquad e^{-\theta(c)\int_0^\infty \nu\,dl},$$

if variations of c may be neglected.

§ **15·42**. *The number of molecules with specified velocities which cross or strike a given area in given time.* We have already had occasion in § 11·2 to use such a formula, and it will be considered in greater detail in § 17·8. The formula (1277) there obtained is

$$\nu\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} c^3 e^{-\frac{1}{2}mc^2/kT} \cos\theta \, dc\, d\omega\, dS. \qquad \ldots\ldots(1114)$$

This is the number of c-molecules which strike an area dS moving within a solid angle $d\omega$ making an angle θ with the normal to dS. The number which cross a geometrical interface is the same, and similarly obtained. The molecular density at the wall or interface is ν.

Since this is also the number reflected from such an element of surface in the equilibrium state, the formula (1114) must hold for all equilibrium states, whatever the fields of force in the gas. It applies therefore in atmospheric problems for atmospheres *in equilibrium*, even when the free paths are very long. It is however of some interest to obtain this formula in a more special way, using the idea of the free path, so as to see what contributions the various elements of the gas make to the actual number.

The molecules in (1114) must have had their origin, that is their last collision, somewhere in a cylinder of infinite length on the base dS with generators parallel to the molecular velocity. If the molecules move in a field of force the "cylinder" becomes a tube of flow enclosed by the family of free trajectories passing through the perimeter of dS. In accounting for the molecules which cross dS we shall *associate all the molecules with the volume element in which they last collided*, a classification which is important in many applications. Molecules which cross dS with velocity c in $d\omega$ start from their last collision as c_0-molecules moving in $d\omega_0$.

When the gas is in equilibrium the number of collisions per unit volume *after* which one molecule has specified velocities must be equal to the number *before* which one molecule had the same specified velocities. Hence in a length dl of such a cylinder or tube there will be

$$\nu_0 \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}mc_0^2/kT}\, c_0^2 dc_0 d\omega_0 \Theta\,(c_0)\, dl \cos\theta_0 dS_0$$

such collisions per unit time, since $\Theta\,(c_0)\,dt$ is the fraction of c_0-molecules that suffer a collision in time dt. This can be written

$$\nu_0^2 \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}mc_0^2/kT}\, c_0^3 \theta\,(c_0) \cos\theta_0\, dc_0 d\omega_0 dl dS_0. \quad \text{......(1115)}$$

This is the number of proper molecules which are shot off per unit time from an element at distance l along the tube from dS so as to cross dS if undisturbed. Not all of these reach dS. The number which succeed is reduced by collisions to the fraction

$$e^{-\int_0^l \theta\,(c_0)\,\nu_0\, dl}.$$

The total number of c-molecules crossing dS in the specified direction in unit time is therefore

$$\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_0^\infty \nu_0^2 e^{-\frac{1}{2}mc_0^2/kT}\, c_0^3 \theta\,(c_0) \cos\theta_0\, d\omega_0 dS_0 dc_0 e^{-\int_0^l \theta\,(c_0)\,\nu_0\, dl}\, dl. \quad \text{......(1116)}$$

Such formulae can sometimes be used in non-equilibrium states provided Maxwell's law remains valid. To see how in equilibrium (1116) reduces to (1114) we consider the simplest case of a uniform field of force at right angles to dS. Then

$$dS_0 = dS,\ \tfrac{1}{2}mc_0^2 = \tfrac{1}{2}mc^2 + mgz_0,$$

$$c_0^2 dc_0 d\omega_0 = du_0 dv_0 dw_0 = J\left(\frac{u_0,\ v_0,\ w_0}{u,\ v,\ w}\right) c^2 dc\, d\omega,$$

$$= \frac{\partial w_0}{\partial w}\, c^2 dc\, d\omega = \frac{w}{w_0}\, c^2 dc\, d\omega.$$

Also $$\nu_0 e^{-mgz_0/kT} = \nu.$$

Hence (1116) reduces to

$$\nu \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} c^3 e^{-\frac{1}{2}mc^2/kT} \cos\theta\, dc\, d\omega\, dS \int_0^\infty \nu_0 \theta\,(c_0)\, e^{-\int_0^l \theta\,(c_0)\,\nu_0\, dl}\, dl,$$

which is (1114). This reduction holds equally in the general case.

§ **15·43.** *Free paths in an upper atmosphere.* We will now apply these results to an upper atmosphere where the free paths are very long, so that the change of ν along the path cannot always be neglected. When account is taken of the decrease of gravity with height we have, at a distance r from the centre of the planet,

$$\nu = \nu_0 e^{-\frac{mg}{kT}\frac{a(r-a)}{r}}, \qquad \text{......(1117)}$$

where ν_0 is the density at the base of the isothermal part of the atmosphere, g is the value of gravity and a is the radius of the planet (both strictly for the base of the isothermal atmosphere). As is well known this formula leads to a finite atmospheric density at infinity. The "atmosphere" would then fill space and there would be no problem of escape. It is not however consistent with obvious physical facts to regard such an extensive atmosphere as belonging in any sense to a particular body. The atmosphere has effectively ended at distances comparable with the planet's radius at most. The chief difficulty in (1117) arises from neglecting the mass of the atmosphere itself and treating g as constant. Milne* has shown that when this is taken into account an appropriate formula applicable at all distances is

$$\nu = \nu_0 \left(\frac{r_0}{r}\right)^2 e^{-q_0(1-r_0/r)} \quad (q_0 = mgr_0/kT - 2), \qquad \text{......(1118)}$$

where r_0 refers to any convenient level in the atmosphere. This gives an atmosphere of zero density at infinity though of infinite mass. The mass of the atmosphere does not really seriously affect the distribution law in any important region or the rate of escape, but the use of (1118) avoids troublesome difficulties in the calculations.

We shall now investigate in such an atmosphere the free paths of c-molecules, with the simplification that we shall ignore the effect on the free path of the change of c in the gravitational field and the curvature of the path. The first of these steps is justified because for the molecules that will interest us (escaping molecules) c must be large compared with $(2kT/m)^{\frac{1}{2}}$ in any region in which collisions matter. In the integrand of (1105) ψ/c^2 is only slowly variable and we may use (1106). The second is justified because the length of the exact hyperbolic path is sufficiently represented by its asymptote.

If the c-molecule starts at radius r at θ to the vertical and proceeds to R after a path s, then the exponent in (1106) is

$$-\theta(c)\int_0^l \nu(R)\,ds,$$

where with sufficient accuracy $R = r + s\cos\theta$. This neglects terms due to the curvature of the layers of the atmosphere of order $(s\sin\theta/R)^2$. Using (1118) this reduces to

$$-\frac{\nu_0 r_0 \theta(c)}{q_0 e^{q_0}\cos\theta}\{e^{q_0 r_0/r} - 1\}. \qquad \text{......(1119)}$$

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* Milne, *loc. cit.* equation (25).

The fraction of c-molecules projected from a level r at an angle θ with the vertical which could escape to infinity without a further collision is given by taking the exponential of (1119).

§ **15·44**. *The loss of molecules from a simple isothermal atmosphere.* By a trivial adaptation* of (1115) we see that the number of c-molecules shot off in unit time from a spherical shell of radius r and thickness dr at an angle between θ and $\theta + d\theta$ with the vertical is

$$2\pi\nu^2\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}mc^2/kT}\, c^3\theta\,(c)\sin\theta\, d\theta dc \times 4\pi r^2 dr. \quad \ldots\ldots(1120)$$

We have hitherto been studying only the conditions for avoiding further collisions. We must now introduce the further condition for escape that $c > c_g$, where

$$c_g = 2ga^2/r. \quad \ldots\ldots(1121)$$

We find therefore at once that dL, the total number of escaping molecules produced by the level r, is

$$dL = 8\pi^2\nu^2 r^2 dr\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\int_{c_g}^{\infty} e^{-\frac{1}{2}mc^2/kT}\, c^3\theta\,(c)\,dc$$
$$\times\int_0^{\frac{1}{2}\pi}\exp\left[-\frac{\nu_0 r_0\theta\,(c)}{q_0 e^{q_0}\cos\theta}\{e^{q_0 r_0/r}-1\}\right]\sin\theta\,d\theta. \quad \ldots\ldots(1122)$$

To find L, the total rate of escape, dL must be integrated with respect to r from the surface of the planet to infinity.

There is no need to give the further work in detail since no further question of principle arises, and the calculations are somewhat laborious. Molecules of course theoretically escape from all levels, but owing to the exponential factor in (1122) only effectively when the exponent does not much exceed unity. In order to obtain a concrete picture we may usefully simplify (1122) by replacing the exponential by zero when its exponent is greater than unity and unity when its exponent is less than unity. In fact since only orders of magnitude are of interest this simplification may be used in computations. This is the method used by Lennard-Jones (*q.v.*).

To obtain an idea of the level at which escape effectively begins we quote the results obtained by this simplified method of calculation for the outer helium† atmosphere of the earth, for which $g = 981$, $r_0 = 6{\cdot}39 \times 10^8$, $T = 219°$ K., $k/m = 2{\cdot}08 \times 10^7$. We have therefore $q_0 = 135{\cdot}6$. We may take further $\sigma = 2{\cdot}0 \times 10^{-8}$, $\nu_0 = 7{\cdot}46 \times 10^{12}$ (base of the stratosphere assumed to lie at 20 km. height). We then find that the exponent falls to unity for the most favourable conditions $c = \infty$, $\theta = 0$ at a critical height r_c given by

$$r_c = 1{\cdot}085\, r_0.$$

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* In (1115) the volume element was $\cos\theta_0 dl dS_0$, which here becomes $4\pi r^2 dr$.

† Chapman and Milne, *Quart. J. Roy. Met. Soc.* vol. XLVI, p. 357 (1920). This paper is the source of all the meteorological data in the discussion here.

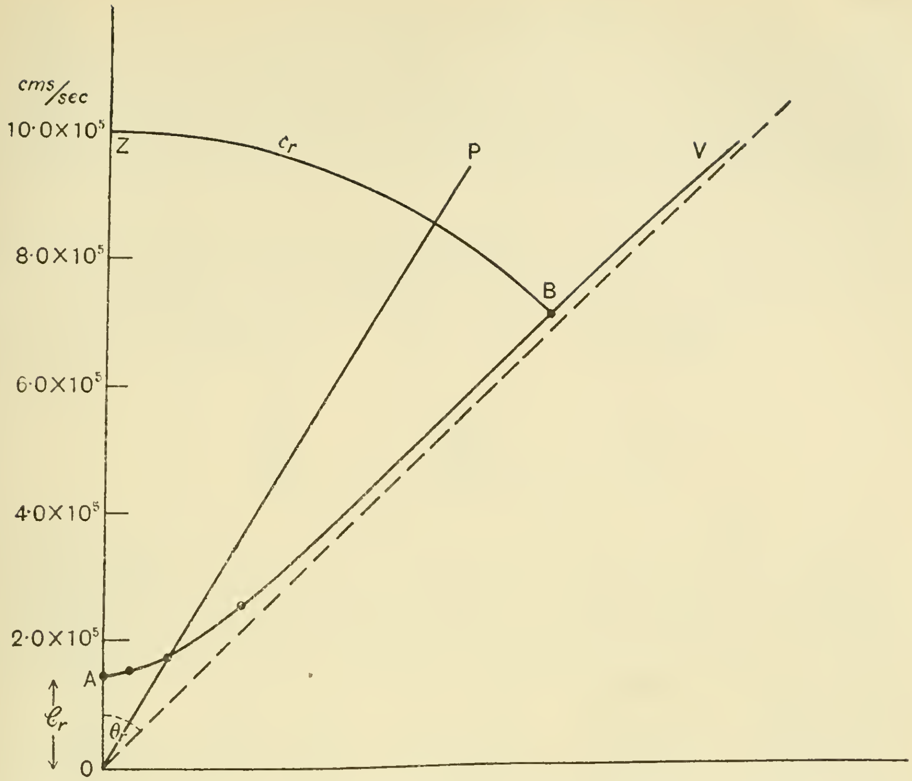

Fig. 24. Showing the variation of the velocity of escape with angle for a level in the earth's atmosphere at which the least velocity of escape $\mathscr{C}_r$ is $1{\cdot}6 \times 10^5$ cm./sec.

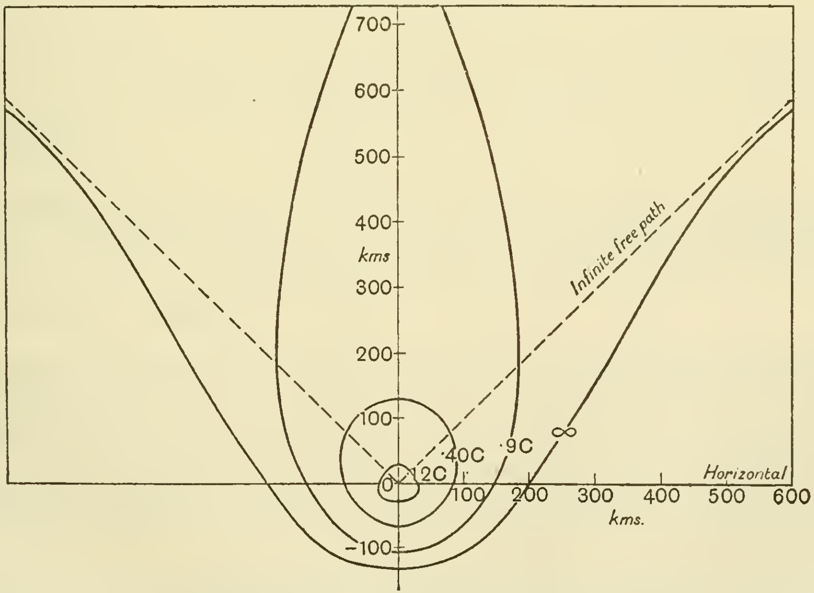

Fig. 25. Showing the variation of free paths with direction in the earth's upper atmosphere.

The critical level is about 540 km. above the base of the stratosphere. Above this height we can define a rapidly expanding cone of escape in such a way that the exponent becomes less than unity inside a cone of given semi-vertical angle about the vertical for $c = \infty$ as soon as r reaches the values given in the table below.

TABLE 52.

Variation of cone of escape with height. (Earth's helium.)

Semi-vertical angle of cone	$r_c/r_0 = 1{\cdot}085$ $(r - r_c)/r_0$	$r - r_0$ km.
0°	0	540
25°	0·00086	545
45°	0·0030	559
65°	0·0075	588
85°	0·0212	676

Inside the cone of escape for given r and θ the velocity must exceed a certain lower limit to reduce the exponent to unity. The variation of this with angle is shown in Fig. 24. The variation of finite free path with direction (defined as the distance required to reduce the undeflected beam to $1/e$ of its initial strength) at a point in the upper atmosphere is shown in Fig. 25.

In terms of the critical level r_c so defined it can be shown by treatment of (1122) that with sufficient accuracy

$$L = \frac{2\pi\sigma^2\nu_0{}^2 r_0{}^4 e^{-2q_0} e^{q_0 r_0/r_c}}{r_c}\left(\frac{2\pi kT}{m}\right)^{\frac{1}{2}}. \qquad \text{......(1123)}$$

The critical level r_c as we have defined it makes the exponent in (1122) unity for $\cos\theta = 1$, $c = \infty$, $\theta(c) = \pi\sigma^2$ (see (1102), etc.). Hence

$$e^{q_0 r_0/r_c} - 1 = \frac{q_0 e^{q_0}}{\pi\nu_0\sigma^2 r_0}, \qquad \text{......(1124)}$$

an equation in which, owing to the size of q_0, 1 may be neglected. The use of this reduces (1123) to

$$L = \frac{2\nu_0 q_0 r_0{}^3 e^{-q_0}}{r_c}\left(\frac{2\pi kT}{m}\right)^{\frac{1}{2}} = \frac{2\nu_0 g r_0{}^4 e^{-mgr_0/kT}}{r_c}\left(\frac{2\pi m}{kT}\right)^{\frac{1}{2}}. \qquad \text{......(1125)}$$

The equation (1125) will hold so long as r_c is free to be fixed by (1124), that is until r_c falls to the solid surface of the planet. After that, when r_c is so fixed, the equation (1123) can be shown to hold. Equation (1125) makes L proportional to ν_0 and independent of σ. The independence of σ is interesting and might have been foreseen. For the rate of production of possible escaping molecules is proportional to σ^2, and the rate at which these are thwarted by collisions is inversely proportional to σ^2.

Table 53 gives various calculations of the rate of escape by these formulae for various gases from various bodies. The rates are in all cases slower than those given by Jeans, so that the interest lies rather in the cases which are regarded by him as critical. The table also includes calculations for mixed atmospheres for which the original paper should be consulted. The much greater rate of loss of the lightest constituent from a mixed atmosphere in the final stages is due to the effect of collisions with the other constituents in keeping up the supply of faster moving molecules. The calculations for mixed atmospheres give of course a better representation of the facts for the later stages, but the later stages are not of much astronomical importance.

TABLE 53.

(1) *Rate of escape of helium from Mars.*

Isothermal atmosphere. Time in years.

Density at the planet's surface after years shown	173° K.		273° K.	
	Helium atmosphere	Mixed atmosphere	Helium atmosphere	Mixed atmosphere
10^{15}	0	0	0	0
10^{12}	$2{\cdot}97 \times 10^{9}$	$2{\cdot}97 \times 10^{9}$	$1{\cdot}58 \times 10^{4}$	$1{\cdot}58 \times 10^{4}$
10^{9}	$5{\cdot}94 \times 10^{9}$	$5{\cdot}94 \times 10^{9}$	$3{\cdot}16 \times 10^{4}$	$3{\cdot}16 \times 10^{4}$
10^{6}	$9{\cdot}77 \times 10^{11}$	$8{\cdot}91 \times 10^{9}$	$2{\cdot}08 \times 10^{6}$	$4{\cdot}74 \times 10^{4}$
10^{5}	$9{\cdot}77 \times 10^{12}$	$1{\cdot}19 \times 10^{10}$	$2{\cdot}08 \times 10^{7}$	$6{\cdot}32 \times 10^{4}$
10^{4}	$9{\cdot}77 \times 10^{13}$	$1{\cdot}49 \times 10^{10}$	$2{\cdot}08 \times 10^{8}$	$7{\cdot}90 \times 10^{4}$
10^{3}	$9{\cdot}77 \times 10^{14}$	$1{\cdot}79 \times 10^{10}$	$2{\cdot}08 \times 10^{9}$	$9{\cdot}48 \times 10^{4}$

(2) *Earth's hydrogen.*

	219° K.		300° K.	
$1{\cdot}89 \times 10^{13}$	0	0	0	0
$1{\cdot}89 \times 10^{8}$	2×10^{24}	2×10^{24}	$2{\cdot}68 \times 10^{16}$	$2{\cdot}68 \times 10^{16}$

Applications of these formulae may also be made to determine the limits of the electrostatic potential of a star set by the possibilities of escape in this way of electrons or positive nuclei. For these reference should be made to Milne's paper*.

§ **15·5**. *Problems of the calcium chromosphere.* Observations at eclipses of the spectrum of the high level gases surrounding the sun show that the *H* and *K* lines of ionized calcium are emitted up to very great heights above the apparent limb. Heights of 14,000 km. above the limb were recorded in 1905 by Mitchell†, and still greater heights have been recorded in more recent work. This means of course that calcium ions must exist

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* Milne, *loc. cit.*

† Mitchell, *Astrophys. J.* vol. XXXVIII, p. 407 (1913).

continually (presumably more or less in an equilibrium state) up to such heights, and the problem at once arises as to how they are supported. A simple calculation shows at once that no such extensive atmosphere can possibly exist in ordinary statistical equilibrium. Beyond the apparent limb of the sun we should expect the atmosphere to consist of matter which in equilibrium would have the properties of a perfect gas, and therefore we should expect the atmospheric density law to hold—that is

$$\nu = \nu_0 e^{-mgz/kT},$$

and g has its solar value $2{\cdot}73 \times 10^4$. Even if we assume a temperature of 6000° K. (the actual temperature must be less), we find that this means a density ratio at the top and bottom of a 10,000 km. layer of 10^{800}. This would be somewhat reduced by the electrostatic fields as in § 15·2. If the atmosphere were a simple mixture of calcium ions and electrons the factor would be 10^{400}, but in no case can we suppose that the index of the factor is reduced much below this order. If therefore we suppose that we have a calcium atmosphere in ordinary equilibrium the density ratio must fall off at this prodigious rate. The density at the sun's limb may not be exactly known, but it is certain that it is not excessively large. The pressure is certainly not of order much greater than one atmosphere, and if this were all due to calcium atoms, the density would be 10^{18}. A reduction of this to 10^{-382} leaves us practically no calcium atoms at all, certainly not enough to be visible. In fact the thickness of the effective calcium atmosphere would be of the order of 100 km. at most, rather than 10,000 km. or more.

This has long been recognized, and the consequence admitted that the calcium atoms seen at eclipses which constitute the permanent calcium chromosphere cannot be matter in approximately thermodynamic equilibrium. They cannot therefore be matter supported by the ordinary material pressure gradient of which the underlying mechanism is molecular collisions, and the only other possible mechanism of support is radiation pressure. This idea has been developed in quantitative form by Milne* in a recent series of important papers, with the result that much new light has been thrown on the nature of such atmospheres supported by radiation and many allied questions, and the observed facts satisfactorily explained. We shall give an account here of so much of these researches as does not require a study of the general laws of the flux of radiation, and summarize the rest. We must naturally make free use of the laws of radiative processes which are collected in Chapter XIX, to which we shall refer forward here.

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* Milne (1). "An astrophysical determination of the average life of an excited calcium atom," *M.N.R.A.S.* vol. LXXXIV, p. 354 (1924), (2), (3) and (4). "The equilibrium of the calcium chromosphere," *M.N.R.A.S.* vol. LXXXV, p. 111 (1924), vol. LXXXVI, pp. 8, 578 (1925, 26), (5). "On the possibility of the emission of high speed atoms from the sun and from the stars," *M.N.R.A.S.* vol. LXXXVII, p. 459 (1926).

If the pressure arising from the reaction of the atom to the flow of radiation from the photosphere is to balance the force of gravity, the pressure must, on the atomic scale, be very large indeed. An atom of course interacts with light of all frequencies, but only strongly with light of the frequency of its own absorption lines (§ 19·2) or of a frequency great enough to ionize it (§ 19·3). For Ca^+ near the sun there will be practically no photo-ionization since the absorption edge lies too far in the ultra-violet, so that the calcium chromosphere must be supported (at least mainly) by the radiation pressure due to the formation of the *H* and *K* absorption lines themselves.

The *H* and *K* lines of Ca^+ form a close doublet $1\,^2S - 1\,^2P$. It will obviously be legitimate in a first survey to imagine that the two lines are fused to form a single one of their united strength. The states of the atom concerned are then to be thought of as two only of weights 2 and 6. We shall find that any Ca^+ atom is only in the excited ^2P state for a very short fraction of all time, so that multiple absorptions to still higher states will be comparatively infrequent and may be disregarded. From the $1\,^2P$ state the excited Ca^+ atom can return either to the normal $1\,^2S$ state emitting *H* and *K* or to the intermediate metastable $1\,^2D$ state emitting the lines $\lambda\lambda$ 8498, 8542, 8662, which may also be regarded as fused, and the ^2D state a single state of weight 10. It follows that this group known to astrophysicists as *X* should be visible in the sun's chromosphere wherever *H* and *K* are visible and with closely connected intensities. Owing to photographic difficulties in the deep red and infra-red region of these lines this has not yet been established observationally, but the *X* lines have been traced to great heights by Curtis and Burns*. The existence of this metastable ^2D state is a complication to the analysis, which however may be avoided at first by the following considerations. Since the state is metastable and the densities in the region to be discussed turn out to be extremely low, a Ca^+ atom in the ^2D state will remain there permanently until it reabsorbs one of the *X* lines and returns to $1\,^2P$. Consequently for present purposes the ^2D state acts like an extra normal state. If the wave lengths of *H* and *K* and *X* were approximately equal we could even regard the $1\,^2S$ and $1\,^2D$ states as fused into a state of weight 12. Though this cannot be done, it is clear that a first discussion omitting all reference to the $1\,^2D$ state will be correct in essentials, liable merely to subsequent numerical correction.

We propose therefore the simplified problem of the formation of a high level chromosphere of Ca^+ atoms (and electrons) supported by the pressure of the absorbed *H* and *K* radiation, the atoms being idealized systems of

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* Eclipse of 1928, Jan. 24. Curtis and Burns, *Pub. Allegheny Obs.* vol. VI, p. 95 (1925). More recently Davidson, *M.N.R.A.S.* vol. LXXXVIII, p. 30 (1927), has recorded preliminary comparisons of *H*, *K*, and *X* by observations without an eclipse.

two stationary states only of weights 2 and 6. The problem is not an equilibrium one, but the state of the matter in this atmosphere must be determined by enumerating and balancing all the atomic events, using the atomic formulae of the equilibrium theory of § 19·2. The only atomic events of importance are absorption and emission of H and K, satisfying Einstein's laws.

Consider the state of an atom at the upper boundary of the chromosphere—that is so high that there are too few atoms above it to alter effectively the outflowing H and K radiation or to return radiation to the atom from above. We may suppose that the sun's continuous photospheric radiation $I(\nu)$ is that of a black body at temperature T (about 6000° K.)*. From the point of view of the Ca^+ atom this may to a first approximation be regarded as uniformly distributed over the hemisphere below it and reduced by absorption below to a fraction r of the photospheric value. Such an atom must on the whole be in equilibrium so that the average rate of absorption of upward momentum from the radiation must exactly balance the rate of increase of downwards momentum due to gravity. Spontaneous emission of radiation by the atom is isotropic and so contributes nothing on the average to the momentum. Stimulated emissions are directed, but for the frequencies in question too rare to need inclusion.

By (1321) the chance of absorption by a normal atom in time dt is $B_1{}^2 I(\nu)\, d\nu dt$ in isotropic ν-radiation. The chance is reduced here to

$$\tfrac{1}{2} r B_1{}^2 I(\nu)\, d\nu dt.$$

The average time τ' that a normal atom remains in the normal state before absorbing† is therefore given by

$$1/\tau' = \tfrac{1}{2} r B_1{}^2 I(\nu)\, d\nu. \qquad \text{......(1126)}$$

Neglecting stimulated emissions, the chance of emitting in time dt and the average life τ in the excited state are given by $A_2{}^1$ and $\tau = 1/A_2{}^1$. Using (1326) and Planck's law for $I(\nu)$ we find

$$\frac{\tau}{\tau'} = \frac{\tfrac{1}{2} r B_1{}^2 I(\nu)\, d\nu}{A_2{}^1} = \frac{\varpi_2}{\varpi_1} \frac{\tfrac{1}{2} r}{e^{h\nu/kT} - 1}. \qquad \text{......(1127)}$$

Now the average life in both states together, during which the atom absorbs just one quantum, is $\tau + \tau'$, and the upward momentum absorbed with this quantum is $h\nu \cos\theta/c$ which averaged over the hemisphere has the value $\tfrac{1}{2} h\nu/c$. It follows that for equilibrium

$$mg\,(\tau + \tau') = \tfrac{1}{2} h\nu/c. \qquad \text{......(1128)}$$

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* Fabry and Buisson, *C.R.* vol. CLXXV, p. 156 (1922); H. H. Plaskett, *Pub. Domin. Astrophys. Obs.* vol. II, p. 253 (1923).

† The argument from the chance in time dt to the fraction not having absorbed after time t and the mean life τ' is that of § 15·41.

For the numerical values $T = 6000°$ K., $\lambda = 3950$, $h\nu/kT = 6{\cdot}05$, $m = 40 \times 1{\cdot}65 \times 10^{-24}$ and $g = 2{\cdot}73 \times 10^4$, $\varpi_2/\varpi_1 = 3$, we find

$$\tau/\tau' = r \times 3{\cdot}54 \times 10^{-3},$$
$$\tau + \tau' = \tau' = 4{\cdot}6 \times 10^{-5},$$
$$\tau = r \times 1{\cdot}62 \times 10^{-7}.$$

The Ca^+ atoms here considered on the upper boundary of the chromosphere will be almost ideally undisturbed and their absorption lines will have their natural narrow width. The observed *H* and *K* lines of the sun and many stars are broad, but it can only be the centre of the line with which we are concerned in the upper chromosphere. The observed value of r for the centre of the *H* and *K* lines averaged over the sun's disc is about 0·11. We thus find

$$\tau = 1{\cdot}8 \times 10^{-8}, \quad A_2{}^1 = 5{\cdot}5 \times 10^7.$$

The simplicity of the argument and the data leading to this result are noticeable, and give this determination of τ great weight*.

A number of interesting deductions may be drawn from these formulae. Equations (1127) and (1128) may be used to derive a formula for r, namely

$$r = \frac{\varpi_1}{\varpi_2}\frac{4mgc\tau}{h\nu}\left(e^{h\nu/kT} - 1\right). \qquad \text{......(1129)}$$

If $F(\nu)$ is the residual central intensity in the line, $rI(\nu)$, this can be expressed very simply in the form

$$F(\nu) = \frac{\varpi_1}{\varpi_2}\frac{8mg\nu^2\tau}{c}. \qquad \text{......(1130)}$$

If the right-hand side of equation (1129) is greater than unity there can be no absorption line, and the type of high level chromospheric equilibrium here contemplated cannot occur. This will happen if the atom is too heavy, if g is too large, if ν/T is too large, or if τ is too large. Using the value of τ deduced from the sun for Ca^+ the critical photospheric temperature below which a calcium chromosphere cannot be formed is 4400° K. for a star with the same surface value of gravity as the sun.

If the right-hand side of (1129) is less than unity a calcium chromosphere may still be impossible for the photospheric ν-radiation will be reduced below $I(\nu)$ in the lower absorbing layers (reversing layer). But so long as the r of (1129) is less than r_1, the reduction ratio when the ν-radiation is free of the pressure-supported layers, a chromosphere will be

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* An important contribution to the theory has just been made by Unsold, *Zeit. für Phys.* vol. XLIV, p. 793 (1927). He points out that we now know $A_2{}^1$ and τ theoretically with some certainty, for the strength of the combined *H* and *K* absorption coefficient is almost exactly the same as if each atom carried one classical electron vibrating with this frequency. The true value of τ is slightly less than the value derived by Milne. The atoms are more absorptive. The discrepancy may be accounted for by the proportion of doubly ionized calcium atoms which must be supported in equilibrium by the radiation pressure of the *H* and *K* lines alone.]

formed at once, for equilibrium for Ca^+ atoms at the top of the reversing layer is impossible, and they will be driven out by the radiation pressure until a screen is formed sufficiently deep to cut down the finally emergent ν-radiation to the fraction r.

Values of r for various stars have been given by Milne as follows:

TABLE 54.

Residual intensities in the centre of the H and K lines.

Star	Mass [Sun's mass = 1]	g	T	r
Capella	4·2	$0·067 \times 10^4$	5,500	0·010
Sirius	2·43	$1·73 \times 10^4$	11,000	0·0043
Plaskett's massive *O*-star	86	$0·56 \times 10^4$	24,000	0·00019

This table shows that for hot stars the residual intensity in the centre of the line must be very small indeed if a calcium chromosphere in equilibrium is formed. It is probable that the formation in these cases is never complete for two reasons. Firstly there must always be a loss of Ca^+ atoms from the chromosphere for a variety of causes of which the most important may be photo-ionization. For stars with a hot photosphere this will be no longer negligible. Secondly there will be a loss by radiative ejection from the star into space which will be continually going on especially during the attempted formation of a chromosphere of a hot star.

The simple arguments so far presented essentially fix only *the upper boundary conditions* for the calcium chromosphere. They apply only to the normal absorption lines of an atom (or ion) whose ionization potential is so high that photo-ionization hardly occurs. All that we have said of Ca^+ applies also to Sr^+ and Ba^+ but probably to no other atoms whose radiations we can observe in stellar spectra. For example the *D*-lines of sodium are found in the chromosphere only to 1000 km. They could be supported like Ca^+ by radiation pressure if the ionization potential (5·1 volts) were probably not too low. Hydrogen and helium extend to considerable heights in the chromosphere but mainly by absorption of light in the visible region from excited not from normal states. For helium certainly there is a metastable state concerned, the lowest state of the triplet system ^3S, which is almost certainly the reason for the occurrence of the lines of the triplet system much higher in the chromosphere than the singlets. In general however the discussion of the support of such atoms is much more complicated.

In all the arguments above we may suppose that the calcium ions are accompanied by an equal number of free electrons, since the electrostatic fields will prevent any separation of the charges as in § 15·2.

We have yet to show that the density distribution in space of the calcium chromosphere set up in this way is such that the chromosphere can extend to the great heights at which it is observed. For this the reader must refer to the original papers*. The result of this investigation is that the pressure of radiation at any given level is proportional to $F(\nu)$ defined above and to $(n_1 - n_2)/(n_1 + n_2)$. The ratio n_2/n_1 decreases outwards and

$$(n_1 - n_2)/(n_1 + n_2)$$

increases outwards and at great heights tends to a limit fixed by the boundary conditions already discussed. The density ρ of the chromosphere at height x is given by

$$\rho = \frac{8\pi k T_0 h\nu^3 \Delta\nu}{mg^2c^3 (x + x_0)^2} \frac{\varpi_1}{\varpi_1 + \varpi_2}. \qquad \text{......(1131)}$$

In this formula T_0 is the "temperature" of the chromosphere assumed uniform, as measured by its pressure, that is by the mean kinetic energy of its constituent systems, $\Delta\nu$ is the effective width of the absorption line of residual intensity $F(\nu)$ and x_0 a constant fixed by the theory, equal to the height of the equivalent homogeneous atmosphere. Heights are measured from an assumed level at which the intensity of ν-radiation has its photospheric value. Curvature of the layers and change of g with height have been neglected†.

Milne discusses also the case in which at the upper boundary the radiation pressure supports a fraction $1 - \mu$ of the weight of the atom and shows that the distribution law changes over rapidly to the exponential type as if the atoms had an effective mass μm. Such chromospheres he calls "partially supported", and those with $\mu = 0$ above "fully supported". In the case of partial support, remembering the electrostatic effects (equation (1062)), we have

$$\rho = \rho_0 e^{-\mu m g x/2kT_0}. \qquad \text{......(1132)}$$

The theory therefore gives just the type of extended atmosphere required. For calcium on the sun the density decreases in a fully supported chromosphere by 1/23 in 14,000 km., compared with 10^{-800} when radiation pressure is neglected or 10^{-8} and 10^{-80} for $\mu = 0{\cdot}01$ or $0{\cdot}1$. Values of μ as great as 0·01 must be impossible on the sun.

In a later paper‡ the doublet character of the ^2P level is taken explicitly into account. It is shown that the residual intensity calculated as above as though the level were single is equal to the weighted mean of the residual intensities in the two components, the weights being naturally the ϖ's of the two ^2P states. The relative residual intensities should vary inversely as the weights—that is the strength of the absorption lines directly as the

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* Milne, *loc. cit.* (2).

† An extension of the theory to a spherical sun has recently been made by P. A. Taylor, *M.N.R.A.S.* vol. LXXXVII, p. 605 (1927).

‡ Milne, *loc. cit.* (3).

weights, in agreement with the general rules for intensities in multiplet spectra.

In this paper the metastable ^2D state is also taken into account and the relation between the residual intensity in H and K and the X group investigated. It is shown that the existence of the ^2D state means that the formula for r for the H and K lines (1129) has to contain an extra factor

$$\frac{1}{1+\nu'\tau/\nu\tau'}.$$

In this factor the ordinary symbols refer to the line $1\,^2S - 1\,^2P$ and the primed symbols to $1\,^2D - 1\,^2P$. If ν' were equal to ν we should simply have replaced the mean life τ for the H and K switch by the true mean life of the excited atom $\tau\tau'/(\tau+\tau')$. This factor does not alter the order of the estimates already made. The further implications of the theory cannot be considered here.

§ **15·51**. *Anomalies in the behaviour of the absorption lines of* Ca^+, Si^+, *and* Ba^+. We are now in a position to consider the places of the maxima of these lines in Table 51 of § 15·33 and their behaviour for higher temperatures. The theory seems to place the maxima at temperatures rather lower than the general run of other temperatures, perhaps 400° too low in the case of Sr^+ which is the best determined. It is tempting to suggest that these delayed maxima are due to the formation of a strontium (or other) chromosphere of increasing depth, and so to increasing chromospheric absorption in hotter stars. Since the residual intensity in the centre of the absorption line is fixed as a function of $g\tau$ and m and independent of the photospheric temperature, the observed strength of the centre of the line will increase with increasing T due to this extra absorption beyond the reversing layer.

Again lines that are past (on the hot side of) their maximum are normally weakened when we pass from dwarfs to giants, and lines that are short of (on the cold side of) their maximum are normally strengthened. To this rule the normal lines of Sr^+ (and to some degree also the same lines of Ca^+ and Ba^+) are noteworthy exceptions. There is no doubt that the lines of Sr^+ are stronger in giants than dwarfs on the hot side of their maximum*. It is extremely tempting to suppose that this is due to a superposed chromospheric effect. In the giants with the smaller g a more extensive chromosphere is formed with a smaller absolute residual intensity. This strengthens the line in a way which is impossible for non-chromospheric absorption and may well outweigh the normal reversing layer effect.

§ **15·6**. *The velocity distribution of atoms in the chromosphere and the escape of atoms from the sun by radiative expulsion.* We have hitherto

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* Payne, *loc. cit.* p. 151.

ignored in this discussion of the chromosphere the fluctuations in the velocity of a single Ca$^+$ atom, and have been content with seeing that its radial velocity shall be zero on the average. Milne has however pushed his enquiry further* so as to establish the details of the velocity distribution law in the upper chromosphere. The method necessary is a simple extension of § 19·5. There we consider the preservation of Maxwell's law by line absorption and emission in isotropic equilibrium radiation. Here we have merely to generalize this for non-isotropic radiation of which the average transfer of momentum due to the anisotropy is balanced by gravity. The state of the matter will not be statistical equilibrium, but the radiative interactions are dominant, and the steady state set up must be practically that demanded by this one-sided application of the laws of § 19·5, assumed to act alone.

It is at once evident that Theorem 19·5 will apply to the radial velocities. The radial velocity distribution will therefore be Maxwellian with a mean square velocity $\overline{v^2}$ given by

$$\overline{v^2} = \tfrac{1}{2} \operatorname*{Lt}_{\tau \to 0} \frac{\overline{u^2}}{\lambda\tau}.$$

The evaluation of $\overline{u^2}$ and λ proceeds exactly as in § 19·52 and requires nothing new in principle, but a knowledge of the details of the radiative anisotropy into which we cannot go. In place of (1373) we find in fact for radiation uniformly distributed over a hemisphere

$$\tfrac{1}{2}m\overline{v^2} = \frac{\tfrac{5}{16}h\nu}{3 - \dfrac{\nu}{I\ (\nu)}\dfrac{\partial I\ (\nu)}{\partial\ (\nu)}} \qquad \text{......(1133)}$$

approximately, with other similar forms with different numerical constants for other (more accurate) assumptions as to the intensity distribution of the radiation. At the bottom of the absorption line $\partial r/\partial\nu = 0$ (maximum reduction in intensity ratio) so that as usual

$$\frac{\nu}{I\ (\nu)}\frac{\partial I\ (\nu)}{\partial\nu} = 3 - \frac{h\nu}{kT_1}$$

approximately, where T_1 is the photospheric temperature. Thus

$$\tfrac{1}{2}m\overline{v^2} = \tfrac{5}{16}kT_1.$$

The distribution of radial velocities is therefore Maxwellian with a temperature T_0 (*temperature meaning now only the parameter of the radial velocity distribution*) given by

$$T_0 = \tfrac{5}{8}T_1. \qquad \text{......(1134)}$$

This T_0 is the temperature which gives the radial pressure and so must be used above in the study of the equilibrium of the chromosphere. More

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* Milne, *loc. cit.* (4).

accurate evaluations lead to values of T_0 rather nearer to and somewhat greater than $\frac{1}{2}T_1$.

Milne has in addition evaluated the temperature parameter T_0' for the tangential velocity distribution. It is interesting to find that this is different from T_0. The distribution is still Maxwellian in these components as we should expect, but in the simple case leading to (1134) above $T_0' = T_1$.

§ **15·61**. *Limitations of the foregoing analysis. Radiative expulsions.* In the arguments of § 19·5 we assume (and follow tacitly the same assumptions here) that the relevant velocities of the atoms are small compared with the velocity of light, and in fact so small that the change from $I(\nu)$ to $I(\nu')$, where $\nu' - \nu$ is the Doppler shift of frequency, can be regarded as equal to $(\nu' - \nu)\,\partial I/\partial\nu$. The black body curve $I(\nu)$ is a smooth curve without sharp local changes, and no question arises as to the legitimacy of these approximations. In the present problem however we are not concerned with the ordinary black body curve, but with $r(\nu)\,I(\nu)$—that is the black body curve cut by a sharp deep absorption line. The foregoing arguments will still hold but really only for atoms which have velocities so small that the Doppler shift is small compared with the width of the absorption line itself. The average velocity $\overline{v}$ for Ca$^+$ atoms in the sun's chromosphere is about $1{\cdot}3 \times 10^5$ and the corresponding Doppler change of wave length about $1{\cdot}5 \times 10^{-10}$. A velocity of $10\overline{v}$ will still only shift the line by 0·1 Ångström and leave the central absorption intensity of these atoms on the flat part at the bottom of the observed contours of H and K. This is sufficient to justify the full procedure adopted above. But once the velocity of an atom exceeds some such value the approximation for $I(\nu)$ in terms of $I(\nu')$ is inadequate within a strong absorption line.

Milne has shown that a convenient and sufficiently accurate form of the equation (1359) for the average radiative retardation adapted to the present calculations for radiation uniformly distributed over a hemisphere is

$$\frac{1}{g}\frac{dv}{dt} = -\frac{2v}{c}\left(1 - \frac{1}{3}\frac{\nu'}{I(\nu')}\frac{\partial I(\nu')}{\partial(\nu')}\right). \qquad\text{......(1135)}$$

This however must be replaced by something like

$$\frac{1}{g}\frac{dv}{dt} = -\frac{2v}{c}\left(1 - \frac{1}{3}\frac{\nu'}{I(\nu')}\frac{\Delta I}{\Delta\nu}\right), \qquad\text{......(1136)}$$

if the velocity is sufficient for the Doppler shift to bring the absorption frequency of the moving atom into the wing of the absorption line. For small velocities in either direction (1135) and (1136) give equally the retardation which we have already discussed, and (1136) continues to give a retardation for an inward moving atom for any value of $\Delta\nu$. But for an outward moving atom of considerable velocity equation (1136) may not only not give a retardation, but may even give an acceleration large compared with $2v/c$. For example if $v = 300$ km./sec. $\Delta\lambda = 4$ Ångströms and the absorption frequency of the atom has moved right out of the absorption line to the ultra-violet side. Then

$$\tfrac{2}{3}\frac{v}{c}\frac{\nu'}{I(\nu')}\frac{\Delta I}{\Delta\nu} = \tfrac{2}{3}\frac{\Delta I}{I},$$

which is about 6 and therefore very large compared with $2v/c$.

The fast outward moving atom is heavily accelerated, nearly enough according to the equation

$$\frac{dv}{dt} = \tfrac{2}{3}g\frac{v}{c}\frac{\nu'}{I(\nu')}\frac{\Delta I}{\Delta\nu} = \tfrac{2}{3}g\frac{\Delta I}{I}. \qquad \text{......(1137)}$$

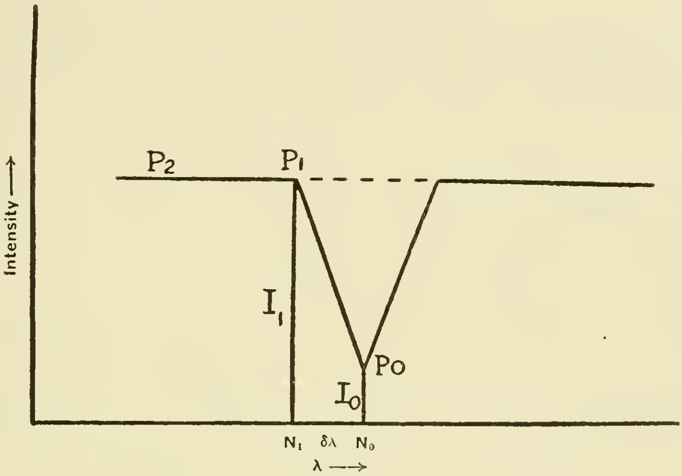

Fig. 26.

This refers to an atom at the top of the chromosphere, and the factor $\frac{2}{3}$ arises from the different directions of the outflowing radiation. For more distant atoms the factor $\frac{2}{3}$ will approach 1 and the general intensity of the radiation and gravity will fall off like $1/r^2$, so that to apply approximately for all distances (1137) may be taken in the form

$$\frac{dv}{dt} = g\frac{a^2 v}{r^2 c}\frac{\nu'}{I(\nu')}\frac{\Delta I}{\Delta\nu} = g\frac{a^2}{r^2}\frac{\Delta I}{I}, \qquad \text{......(1138)}$$

where a is the radius of the sun.

Milne has given an estimate* of the limiting velocity of a particle expelled by radiation pressure in this way by taking a simplified V-shaped contour for the absorption line and $I(\nu)$ constant outside it. The residual intensity I_0 in the line is supposed to be just able to support the atom against gravity.

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* Milne, *loc. cit.* (5).

For velocities of the atom such that the Doppler shift lies between P_0 and P_1 we have obviously the equation of motion

$$r'' = \frac{I_1 - I_0}{I_0}\frac{a^2 g}{V}\frac{r'}{r^2}, \qquad \text{......(1139)}$$

where V is the velocity corresponding to a Doppler shift from P_0 to P_1, half the width of the line. Integrating this for an initial velocity v_0 when $r = a$ we find

$$v - v_0 = \frac{I_1 - I_0}{I_0}\frac{ag}{V}\left(1 - \frac{a}{r}\right). \qquad \text{......(1140)}$$

This holds until $r = r_1$, say, when $v = V$ so that

$$V - v_0 = \frac{I_1 - I_0}{I_0}\frac{ag}{V}\left(1 - \frac{a}{r_1}\right). \qquad \text{......(1141)}$$

If V_∞ is the critical velocity of escape from the sun's gravitational field $\frac{1}{2}V_\infty{}^2 = ag$ so that this may be written

$$2V\,(V - v_0) = \frac{I_1 - I_0}{I_0}\,V_\infty{}^2\left(1 - \frac{a}{r_1}\right). \qquad \text{......(1142)}$$

After P_1 the equation of motion is obviously

$$r'' = \frac{I_1 - I_0}{I_0}\frac{ga^2}{r^2},$$

which gives on integration

$$v^2 - V^2 = \frac{I_1 - I_0}{I_0}\,V_\infty{}^2\left(\frac{a}{r_1} - \frac{a}{r}\right). \qquad \text{......(1143)}$$

Adding (1142) and (1143) to eliminate r_1 we find

$$v^2 + V\,(V - 2v_0) = \frac{I_1 - I_0}{I_0}\,V_\infty{}^2\left(1 - \frac{a}{r}\right).$$

We may now let $r \to \infty$ and neglect v_0, so that we find

$$v_\infty{}^2 = V_\infty{}^2\left[\frac{I_1 - I_0}{I_0} - \frac{V^2}{V_\infty{}^2}\right].$$

For the sun's calcium $V_\infty = 615$ km./sec. the H and K lines are very broad so that, as it happens, V/V_∞ is about 1.

$$(I_1 - I_0)/I_0 = 8,\ v_\infty{}^2 = 7V_\infty{}^2,\ v_\infty = 1{\cdot}63 \times 10^8 \text{ cm./sec.}$$

These very large velocities of repulsive escape are extremely interesting and have a number of astrophysical and geophysical applications for which the original paper should be consulted.

CHAPTER XVI

APPLICATIONS TO STELLAR INTERIORS*

§ **16·1**. *Rosseland's theorem.* We shall start this chapter with some comment on an application by Rosseland† of the theorems of §§ 15·2–15·25 to the far interior of a star. He there discusses the effect of electrical fields on the relative distribution of different elements in the interior of a star, as we have done for atmospheres in the sections quoted.

It will be sufficient to consider the assembly of § 15·25, but we must now use the general equations (1042), (1043) and (1044), since both gravitational and electrical fields arise from the matter of the assembly itself. The point made by Rosseland is that, if (1069) is satisfied, then the substitution

$$\psi = -\frac{m_1 - m_3}{v_1 + 1}\phi = -\frac{m_2 - m_3}{v_2 + 1}\phi \qquad \text{......(1144)}$$

reduces all the exponential factors in the three distribution laws to the common value

$$E = e^{-\frac{\phi}{kT}\left(\frac{m_1 + v_1 m_3}{v_1 + 1}\right)} = e^{-\frac{\phi}{kT}\left(\frac{m_2 + v_2 m_3}{v_2 + 1}\right)}. \qquad \text{......(1145)}$$

The equation for ϕ remains

$$\nabla^2\phi = 4\pi GE\,\{m_1\,(\overline{n_1})_0 + m_2\,(\overline{n_2})_0 + m_3\,(\overline{n_3})_0\},$$

and the equation for ψ becomes

$$\nabla^2\psi = \frac{4\pi\epsilon^2\,(v_1 + 1)}{m_1 - m_3}E\,\{v_1\,(\overline{n_1})_0 + v_2\,(\overline{n_2})_0 - (\overline{n_3})_0\}.$$

These two equations are consistent and the relation (1144) a possible solution of the problem if the values of $(\overline{n_1})_0$, $(\overline{n_2})_0$, $(\overline{n_3})_0$ are suitably fixed, that is if the ratio of the mass density and charge density at a particular point has the correct value. The analysis of §§ 15·2–15·25 shows however that in that simple case even if the initial condition is not satisfied the exact solution approaches the corresponding particular one with extreme rapidity, and one may safely assume that it does so here too. In the interior therefore of a star composed of any number of mixed ions, if the conditions (1069) equivalent to (1144) are satisfied for each pair, the gravitational and electrostatic potentials will be everywhere in the ratio (1144) and the constituents will be everywhere mixed in the same proportions. The space variation common to all components is given by (1145).

Interesting conclusions could be drawn if this uniform constitution could be established even in the restricted isothermal case. It is therefore

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* I have to thank Dr Hartree for the numerical calculations in this chapter.

† Rosseland, *M.N.R.A.S.* vol. LXXXIV, p. 720 (1924).

necessary to examine (1069) with some care to see how closely it could be satisfied in a star. Since atoms are largely reduced to nuclei and free electrons, and since the masses and charges of nuclei are very nearly proportional, it seems at first sight as if (1069) would be very nearly satisfied for stellar material, and Rosseland's theorem might apply. But the satisfaction is not exact. For oxygen, iron and silver nuclei, for example, the values of $(m_1 - m_3)/(v_1 + 1)$ are 1·78, 2·08, 2·25. In order to assert that the electrical forces really maintain the isothermal stellar material at a constant constitution, an almost exact equality would be required. We may conclude that this effect will very much reduce the rate at which the relative concentrations of the heavier elements increase towards the centre, but on the stellar scale the concentration to the centre *in an isothermal star* would still be overwhelmingly great.

As we have said, further consideration of large scale effects is beyond our scope, and we pass on to the study of the properties of matter in equilibrium at stellar temperatures and densities.

§ **16·2**. *Stellar material.* In the radiative theory of the steady states of a star the important quantity that must be provided by statistical theory is the equation of state of the stellar material. The material consists of atomic ions and electrons in dissociative equilibrium, and the equations of Chapter XIV permit this equilibrium state to be calculated so long as the density is not too high.

To a first approximation stellar material behaves like a perfect gas of that number of constituents which is required by the dissociative equilibrium. It is therefore customary to write its equation of state as the perfect gas equation in terms of the temperature, density and *the mean molecular weight* μ. In the first instance this is calculated from the number of atomic ions and free electrons, but any corrections to the pressure, for example for electrostatic effects, can be incorporated as corrections to the mean molecular weight. It is this corrected mean molecular weight μ^* which is required in stellar theory.

In addition to the mean molecular weight, the pulsation theory of Cepheid variables requires a knowledge of the ratio γ of the specific heats of the material together with the radiation it contains—or in other words of its adiabatic curves in p, V coordinates.

Both μ^* and γ can be derived at once from the formulae of statistical theory given in Chapter XIV. The calculations however are somewhat intricate and have not been completed on any reliable theory† except for

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† Fairly extensive calculations were made by R. H. Fowler and Guggenheim, *M.N.R.A.S.* vol. LXXXV, p. 939 (1925), using an earlier less accurate version of the theory. Their results have been used by Eddington, *loc. cit.*, especially § 180, to check the more elementary approximations. The alterations made in their results for μ^* by the more exact theory will therefore be noted here.

μ^*, for which some results are given in this chapter. Finally stellar theory requires a calculation of the mean absorption coefficient of stellar material in the state specified for the radiation passing through it, which is practically black body radiation of its own temperature. This calculation leads us far afield into atomic theory and we shall not attempt to give it here.

We will now summarize the formulae to be used, with the notation of Chapter XIV:

$$\frac{\Psi}{k} = N\left\{\log \frac{VG}{N} + 1\right\} + \Sigma_{r,z}\, M_r{}^z \left\{\log \frac{VF_r{}^z}{M_r{}^z} + 1\right\} + \frac{8\pi^5 k^3 V T^3}{45 c^3 h^3} + \frac{\Psi_\epsilon}{k}. \qquad \ldots\ldots(1146)$$

The electrostatic contribution Ψ_ϵ/k is not accurately known. Debye and Hückel's theory (1016) gives

$$\frac{\Psi_\epsilon}{k} = \frac{2\sqrt{\pi}\epsilon^3}{3V^{\frac{1}{2}}(kT)^{\frac{3}{2}}}\{N + \Sigma_{r,z}\, r^2 M_r{}^z\}^{\frac{3}{2}}. \qquad \ldots\ldots(1147)$$

We have also, repeating former equations,

$$G(T) = 2\frac{(2\pi m kT)^{\frac{3}{2}}}{h^3}, \qquad \ldots\ldots(1148)$$

$$F_r{}^z(T) = \frac{(2\pi m^z kT)^{\frac{3}{2}}}{h^3}\, u_r{}^z(T)\, e^{\{\chi_r{}^z + \cdots + \chi^z{}_{z-1}\}/kT}, \qquad \ldots\ldots(1149)$$

$$u_r{}^z(T) = \varpi_r{}^z + \sum_{q=1}^{q=z-r} \varpi^z{}_{r+q}\,(r+1)^{3q} B^q \left\{\frac{V}{\Sigma_{p,z}\,(p+1)^3 M_p{}^z}\right\}^{\frac{1}{2}q} \times e^{-\{\chi_r{}^z + \cdots + \chi^z{}_{r+q-1}\}/kT}, \qquad \ldots\ldots(1150)$$

$$B = 1{\cdot}017 \times 10^{12},\quad N = \Sigma_{r,z}\, r M_r{}^z. \qquad \ldots\ldots(1151)$$

We define s^z, the average number of free electrons per atom of type Z, by the equation

$$s^z M^z = s^z \Sigma_r M_r{}^z = \Sigma_r r M_r{}^z, \qquad \ldots\ldots(1152)$$

so that

$$N = \Sigma_z s^z M^z. \qquad \ldots\ldots(1153)$$

The pressure p is given by

$$p = T\partial\Psi/\partial V, \qquad \ldots\ldots(1154)$$

the material (as opposed to the radiation) pressure by (1154) in which the term arising from the radiative term $\sigma V T^3$ in (1146) is omitted. The density ρ is given by

$$\rho = \Sigma_z M^z m^z / V. \qquad \ldots\ldots(1155)$$

If the dependence of $F_r{}^z$ on V is ignored, so that the gas mixture is perfect, we should have

$$p = \frac{R\rho T}{\mu},\quad \mu = \frac{\Sigma_z M^z m_*{}^z}{N + \Sigma_z M^z}, \qquad \ldots\ldots(1156)$$

where R is the gram-molecular gas constant and m_*^z the chemical atomic weight. As it is we have

$$p = \frac{R\rho T}{\mu^*}, \qquad \text{......(1157)}$$

defining μ^*.

The equations of dissociative equilibrium are obtained by making $d\Psi = 0$ for all variation of the type

$$\delta N = \delta M^z{}_{r+1} = -\,\delta M_r{}^z = \delta a. \qquad \text{......(1158)}$$

If T, ρ and the ratios of the various M^z are then given (matter of given chemical constitution, temperature and density) the equations can be solved completely.

The actual procedure is rather to assume values for N/V and T, and solve by successive approximations. It must be remembered that Planck's theory is only shown to give a valid approximation to $B(T)$ so long as in all cases the private catching region of each ion is so large that on its boundary the potential energy of an electron due to the central nucleus is small compared with kT. This condition is (1032) in the simple case there considered. It easily extends to

$$\epsilon^2 \left\{\frac{\Sigma_{r,z}\,(r+1)^3\, M_r{}^z}{V}\right\}^{\frac{1}{3}} \ll kT,$$

which may be taken with sufficient accuracy to be

$$\frac{s+1}{s^{\frac{1}{3}}}\,\epsilon^2 \left(\frac{N}{V}\right)^{\frac{1}{3}} \ll kT. \qquad \text{......(1159)}$$

It must be remembered also that Ψ_ϵ is not accurately given by (1147). There are besides other electrical effects, such as the screening of the nuclei by *free* electrons for which it makes no allowance. This effect can be important, and will be opposite to the direct effect of Ψ_ϵ itself. We have to conclude at present that as soon as the terms arising from Ψ_ϵ become important in evaluating μ^* the present theory ceases to be reliable.

For simplicity in the actual calculations the equations of dissociative equilibrium have been taken in their perfect gas form, ignoring the effect of the variations on the $u_r{}^z(T)$. It is easily verified that the omitted factors never differ much from unity; the greatest value they take is about $10^{0\cdot 1}$. Therefore their omission can hardly affect seriously or give an undue bias to the calculated values of μ^*. It is not worth while including them until we have a proper theory of the screening effect of the free electrons.

Calculations have so far been made only for stars composed of iron which are given below in Table 55, and are shown plotted in Fig. 27.

The first six columns in Table 55 need no comment. The seventh gives the μ^* of (1157). When we apply (1154) to (1146) we find

$$p = \frac{kT}{V}\left(N + \Sigma_{r,z} M_r{}^z + \Sigma_{r,z} M_r{}^z V \frac{\partial}{\partial V} \log u_r{}^z\right).$$

Now the various terms in u_r^z correspond to different numbers of excited electrons, and therefore $V\partial \log u_r^z/\partial V$ takes the simple form

$$\frac{\Sigma_q \tfrac{1}{2} q\,(M_r^z)_q}{\Sigma_q\,(M_r^z)_q} = \tfrac{1}{2}\overline{q_r^z}.$$

It follows that
$$p = \frac{kT}{V}\{N + \Sigma_{r,z} M_r^z\,(1 + \tfrac{1}{2}\overline{q_r^z})\},$$

and therefore that

$$\mu^* = \frac{\Sigma_z M^z m_*^z}{N + \Sigma_{r,z} M_r^z\,(1 + \tfrac{1}{2}\overline{q_r^z})} = \frac{\Sigma_z M^z m_*^z}{N + \Sigma_z M^z\,(1 + \tfrac{1}{2}\overline{q})},$$

when electrostatic effects are neglected.

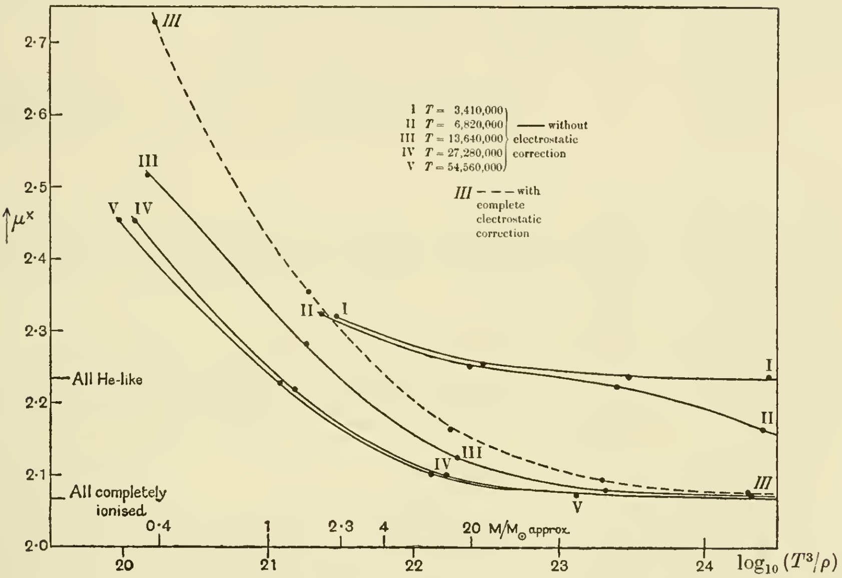

Fig. 27. The mean molecular weight μ^* of stellar material (iron).

On inspection of these results we see that the values of μ^* seem to differ in a rather irregular way (but not seriously) from the old results of Fowler and Guggenheim except for the highest densities, where the new values are higher as they should be. The irregular differences arise from a number of partially compensating changes in the data and the theory used, and are not significant. It is satisfactory to record that the old values are not far wrong at least for the more massive stars.

The control calculation with the estimated electrostatic correction has only been made for one temperature, but this is sufficient, for its importance can be seen to depend almost entirely on the mass of the star, that is on T^3/ρ, and hardly at all on T or ρ separately for given T^3/ρ. The following comments therefore apply sufficiently nearly to all temperatures. The estimated correction becomes sensible ($1\tfrac{1}{2}$ per cent. in μ^*) at a mass about

TABLE 55.

Equilibrium states of matter in stars of iron ($m_* = 55{\cdot}84$).

(Electrostatic corrections are omitted except where specially recorded.)

T °K.	ρ gm./c.c.	Number of electrons			Mean molecular weight μ	μ^*	μ^* with electrostatic correction for same N/V and T	μ' assuming no excited electrons same N/V and T	μ^* Fowler and Guggenheim same ρ and T
		Free per c.c. $= N/V$	Free per atom $= s$	Highly excited per atom $= \bar{q}$					
$3{\cdot}41 \times 10^6$	$1{\cdot}286 \times 10^{-5}$	$3{\cdot}32 \times 10^{18}$	23·96	0·04	2·237	2·235	—	2·234	—
	$1{\cdot}291 \times 10^{-4}$	$3{\cdot}32 \times 10^{19}$	23·87	0·13	2·245	2·239	—	2·234	—
	$1{\cdot}307 \times 10^{-3}$	$3{\cdot}32 \times 10^{20}$	23·58	0·40	2·272	2·253	—	2·235	2·33
	$1{\cdot}385 \times 10^{-2}$	$3{\cdot}32 \times 10^{21}$	22·25	1·59	2·402	2·322	—	2·251	2·36
$6{\cdot}82 \times 10^6$	$1{\cdot}244 \times 10^{-4}$	$3{\cdot}32 \times 10^{19}$	24·78	0·04	2·166	2·164	—	2·169	—
	$1{\cdot}282 \times 10^{-3}$	$3{\cdot}32 \times 10^{20}$	24·04	0·13	2·230	2·224	—	2·219	—
	$1{\cdot}307 \times 10^{-2}$	$3{\cdot}32 \times 10^{21}$	23·57	0·45	2·273	2·252	—	2·232	2·32
	$1{\cdot}398 \times 10^{-1}$	$3{\cdot}32 \times 10^{22}$	22·05	1·93	2·422	2·325	—	2·235	2·33
$1{\cdot}364 \times 10^7$	$1{\cdot}188 \times 10^{-3}$	$3{\cdot}32 \times 10^{20}$	25·93	0·06	2·073	2·071	2·075	2·069	—
	$1{\cdot}196 \times 10^{-2}$	$3{\cdot}32 \times 10^{21}$	25·77	0·17	2·085	2·079	2·092	2·073	—
	$1{\cdot}235 \times 10^{-1}$	$3{\cdot}32 \times 10^{22}$	24·95	0·60	2·151	2·127	2·161	2·105	2·28
	1·383	$3{\cdot}32 \times 10^{23}$	22·28	2·42	2·398	2·280	2·353	2·185	2·30
	$1{\cdot}702 \times 10$	$3{\cdot}32 \times 10^{24}$	18·18	5·97	2·911	2·519	2·729	2·239	—
$2{\cdot}728 \times 10^7$	$1{\cdot}195 \times 10^{-1}$	$3{\cdot}32 \times 10^{22}$	25·80	0·20	2·083	2·076	—	2·068	—
	1·222	$3{\cdot}32 \times 10^{23}$	25·22	0·74	2·130	2·100	—	2·072	2·18
	$1{\cdot}364 \times 10$	$3{\cdot}32 \times 10^{24}$	22·59	3·16	2·367	2·218	—	2·098	2·22
	$1{\cdot}689 \times 10^2$	$3{\cdot}32 \times 10^{25}$	18·25	7·04	2·901	2·452	—	2·193	2·26
$5{\cdot}456 \times 10^7$	1·196	$3{\cdot}32 \times 10^{23}$	25·77	0·23	2·086	2·077	—	2·068	—
	$1{\cdot}227 \times 10$	$3{\cdot}32 \times 10^{24}$	25·11	0·87	2·138	2·103	—	2·070	—
	$1{\cdot}384 \times 10^2$	$3{\cdot}32 \times 10^{25}$	22·27	3·60	2·400	2·227	—	2·084	—
	$1{\cdot}707 \times 10^3$	$3{\cdot}32 \times 10^{26}$	18·05	7·45	2·931	2·452	—	2·194	—

$$\mu^* = m^*/(s + 1 + \tfrac{1}{2}\bar{q}).$$

twenty times the sun's mass, and has increased to $3\frac{1}{2}$ per cent. for a mass about 1·7 times the sun's mass. The average number of highly excited electrons per atom is here about 2·4, calculated of course neglecting the screening power of free electrons. Comparing μ^* and μ' we see that we have reached a mass at which the number of highly excited electrons has an appreciable effect on μ^*. For the reasons given we cannot claim that our theory gives a reliable value for $\bar{q}$ (the true value being less), so that we have here reached the limit of safety; the next entries show that $\bar{q}$ and the electrostatic correction are beginning to increase rapidly. We may conclude that the values of μ^* as calculated without electrostatic corrections are sufficiently reliable down to masses twice the mass of the sun. By a cancellation of neglected effects the values given for μ^* without electrostatic correction are probably nearly correct down to masses equal to the mass of the sun. Below that mass none of our calculations can be relied upon.

§ **16·3**. *Matter of great density.* We have not yet investigated whether matter of the densities and temperatures appearing in Table 55, or of still greater densities, can really exist and still more behave approximately like a gas of mixed dissociating constituents approximately perfect. We have omitted all mention of excluded volumes in the foregoing discussion. It is these, and the fields of force arising from permanent electronic structures, which will make the mixture depart from perfection—in particular reduce largely its very high compressibility. The highly excited electrons and the electrostatic corrections do not have any such effect, and can be ignored in this connection.

A complete formulation of the problem might have started by assigning to every possible type of electronic structure with its electrons in their lowest or at least in tightly bound orbits a definite field of force—with sufficient accuracy an excluded volume, such that no part of any pair of such excluded volumes may overlap. The characteristic function for such an assembly can be written down to a first approximation, using § 8·6. It is easy to see however that such elaboration is unnecessary, for the large volumes of the more complex electronic structures will make them occur on the average still less often than in the assembly for which the calculations have been made, where their excluded volumes are all zero. If therefore we take the simplified assembly for which the calculations have been made, estimate reliable excluded volumes for the dominant tightly bound electronic structures, and show that such excluded volumes are insignificant, the existence of perfect gas matter at such densities will be established, and the foregoing procedure fully justified.

On examining the details of the calculations it appears that the most important surviving electronic structure contains two electrons only in their normal orbits—that is helium-like iron. Apart from the excess nuclear charges which contribute only to the electrostatic correction (the complete electrostatic correction *increases* the compressibility) we may be certain that the helium-like iron ions will interact as if the radius of their excluded volumes bore the same ratio to the radius of the excluded volume of two ordinary helium atoms as do the radii of the corresponding Bohr orbits of the two electrons*. Allowing for screening, the ratio of the radii of the orbits of helium-like iron and normal helium is about 1·7/25·7. The excluded volumes for helium-like iron are therefore smaller than those of helium by a factor $(1\cdot7/25\cdot7)^3$ or, say, $1/(15)^3$.

For a gas of M helium-like iron ions in a volume V and N $(= 24M)$ free electrons we shall have to a first approximation an equation of state

$$\frac{pV}{kT} = N + M + \frac{1}{V}\{NMv_{\epsilon c} + \tfrac{1}{2}M^2 v_{cc}\}.$$

The electrons are practically without volume. The excluded volume for a free electron and a core is $v_{\epsilon c}$ and for two cores v_{cc}. It is perhaps legitimate to suppose that $v_{\epsilon c} = \frac{1}{8}v_{cc}$ on the average. The ratio of the correcting term to the main term is therefore nearly enough $Mv_{\epsilon c}/V$. In the same way the ratio of the correcting term to the main term for normal helium is (say) $\frac{1}{2}M'v_{cc}'/V$. The excluded volumes affect the pressure of ordinary helium gas by 1 per cent. at a density of about 0·0043 gm./cc. The 1 per cent. correction will therefore be reached in a gas of helium-like iron plus electrons at a density of

$$0\cdot0043 \times \tfrac{56}{4} \times (15)^3 \times 4 = 840.$$

In two important respects we have probably underestimated the density for a 1 per cent. correction in this calculation. The greater temperature of the stellar material must diminish rather than increase corresponding excluded volumes, and it is likely that the volume excluded to free electrons may not be comparable with $\frac{1}{8}v_{cc}$. We may conclude that stellar material will in general reach densities of the order of 1000 gm./cc. or more before we find any departures from the compressibility of a perfect gas due to those properties of finite extension of the constituent systems which make the ordinary gases of our experience imperfect.

Whether we can go further than this—to densities of 10,000 or 100,000 with the same compressibility—the theory we have developed is unable to say. Such matter can only be discussed when we have a proper method of including electrostatic effects. At present there is only one further contribution we can make to the nature of matter in white dwarfs, or rather to its ultimate fate when they become black dwarfs. This however involves the new statistics and is postponed to Chapter XXI.

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* The radius of an orbit of the old quantum theory is a reliable guide to the position of maximum density of electricity (the important region) in the new quantum mechanics.

CHAPTER XVII

MECHANISMS OF INTERACTION. COLLISION PROCESSES

§ 17·1. *The nature of the equilibrium state.* We have pointed out in the introductory chapter that the equilibrium theory of statistical mechanics is essentially of a thermodynamic nature. Its laws are independent of all mechanisms of interaction. It has merely to be supposed that the necessary interactions can occur. It is only when we begin to discuss the far more difficult theory of (non-equilibrium) steady states of flow, that the actual laws of the mechanisms acting become relevant, or can be deduced from the experimental facts. It was pointed out further that the laws of equilibrium, being thus in some sense universal, must be conformed to by the laws of any mechanism. The actual details of the laws of interaction between molecular systems and such systems and radiation are still somewhat obscure. The best help that statistical mechanics can give at the moment towards the development of the theory of steady states is to analyse carefully the restrictions that its laws impose on the laws of interaction, so as to leave vague for further determination as little as possible in these laws. This is valuable help, and this chapter gives an account of such help as can be thus given to the study of the laws of interaction by collision in assemblies of perfect gases, or between perfect gases and solid walls. The laws of interaction with radiation are treated in Chapter XIX. The modifications introduced by the newer forms of statistical mechanics conforming to the newer quantum theory are discussed shortly in Chapter XXI.

It may be argued that, since the equilibrium laws (and therewith the detailed relations of the laws of interaction) have been changed by the new mechanics, the equilibrium laws are not the absolute things that we have hitherto represented them to be and do in fact depend on the laws of interaction of molecular systems. This argument is of course correct, but it remains of the greatest value for a clear grasp of the equilibrium theory to regard the equilibrium state as the primary thing and to use it to analyse the form of the relationships among the processes of interaction.

In the classical kinetic theory the laws of interaction of structureless molecules are all that interest us; we visualize molecular encounters as purely conservative collisions either of elastic spheres or point centres of force. This conception has of course long proved fruitful in the study of transport phenomena initiated by the work of Maxwell. By way of introduction to this chapter we shall present the classical theorems of Maxwell and Boltzmann, including the latter's famous H-theorem, from this slightly unusual angle.

In the equilibrium state of a perfect gas the positions and velocities of each set of molecules satisfy Maxwell's law. The distribution function for any one set is, let us say,

$$f(u, v, w)\, du\,dv\,dw \qquad \text{......(1160)}$$

per unit volume, and the function f must be the same *whatever the mechanism by which it is set up*. This is the position at which we are left by the general mechanismless equilibrium theory. It remains to examine whether the usual mechanism of classical conservative collisions is a possible mechanism which will preserve (1160). Now if a certain type of collision between molecules 1 and 2 with velocities u_1, v_1, w_1 and u_2, v_2, w_2 transforms these into u_1^*, v_1^*, w_1^* and u_2^*, v_2^*, w_2^*, then the number of such collisions per unit volume per unit time is

$$f_1 f_2 du_1 \dots dw_2 V p\,dp\,d\psi. \qquad \text{......(1161)}$$

In this expression V is the relative velocity of the two molecules before the encounter begins, and p and ψ are polar coordinates, in a plane through one molecule normal to the direction of V, which define the position of the initial asymptote of the necessary relative orbit. The symbol f_1 is short for $f(u_1, v_1, w_1)$, etc. These collisions all *destroy* molecules of velocities u_1, v_1, w_1 and u_2, v_2, w_2 and *create* molecules of velocities u_1^*, v_1^*, w_1^* and u_2^*, v_2^*, w_2^*. Conversely, since any conservative orbit can also be travelled in the reverse sense there are a set of reverse collisions, in number

$$f_1^* f_2^* du_1^* \dots dw_2^* V^* p^* dp^* d\psi^*, \qquad \text{......(1162)}$$

which *destroy* molecules of velocities u_1^*, v_1^*, w_1^* and u_2^*, v_2^*, w_2^* and create molecules of velocities u_1, v_1, w_1 and u_2, v_2, w_2. The relation between (1161) and (1162) can be simplified. By applying Liouville's theorem to the element of phase space of the conservative system formed by the two molecules we find that

$$du_1 \dots dw_2 V p\,dp\,d\psi = du_1^* \dots dw_2^* V^* p^* dp^* d\psi^*. \text{......(1163)}†$$

The proposed collision mechanism will therefore certainly conserve the equilibrium state if this requires that

$$f_1 f_2 = f_1^* f_2^*, \qquad \text{......(1164)}$$

a relation equivalent to Maxwell's law.

The classical collision mechanism is therefore a possible one, for (1164) is a *sufficient* condition for the preservation of equilibrium. It is important to observe that (1164) has also wider implications, for it asserts that there is a *detailed balancing* of all the individual types of collision, as specified by

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† Since the systems are conservative we have also $V = V^*$. If the relative orbit is described under a central force and so is plane and symmetrical about the apse $d\psi = d\psi^*$, $p = p^*$, $dp = dp^*$. Thus in this simple case $du_1 \dots dw_2 = du_1^* \dots dw_2^*$.

the velocity exchanges. According to (1164) just the same number of collisions of any one type and the reverse type must occur per unit volume per second. This condition of detailed balancing is naturally sufficient for *the preservation of equilibrium.* It does not necessarily follow without further investigation that detailed balancing is also *necessary* and therefore equivalent to the demand for the preservation of equilibrium. On certain assumptions however it is possible to prove this equivalence, and the proof, given in the next section, constitutes Boltzmann's H-theorem. Thus for the particular mechanism of classical conservative collisions with central forces the two requirements of

(*a*) Detailed balancing,

(*b*) Preservation of equilibrium,

are equivalent. For other mechanisms it is not always possible to prove this equivalence, and examples will be given where conditions for (*b*) are definitely less restrictive than for (*a*). The two hypotheses provide alternative bases on which we may attempt to analyse the laws of any proposed mechanism, and both should usually be kept in mind. The more restrictive hypothesis of detailed balancing has a simplicity and inherent probability which strongly recommend it, until, if ever, its consequences can be shown to be in disagreement with experiment or with the requirements of the new mechanics.

In classical kinetic theory molecules are structureless. In the extensions now required their electronic structure becomes relevant and in general more than one mechanism may be causing a specified change of state in any system. The question then presents itself whether or not we can discuss separately the effects of the separate mechanisms. The arguments that follow are those of the classical radiation theory. Suppose we have a system X which can undergo a specified change by interaction with other systems Y or Z. Suppose we can effectively change the concentrations $[Y]$ and $[Z]$ independently of each other, of $[X]$ and of the temperature. This will be the case if Y and Z are separable in the equilibrium state from each other and from X. They will be so separable for example if they refer to different atoms, but not if they refer to different states of the same atom. Interactions between X and Y and X and Z will then certainly occur with unconnected frequencies. This still applies if Y means the temperature radiation in the assembly, with the proviso that then the "concentration" —the density of the radiation—cannot be varied in equilibrium independently of the temperature. Let P_Y be the frequency with which (X, Y) interactions occur per unit volume at unit concentrations, converting X from a state 1 to a state 2, and Q_Y be the corresponding frequency of the reverse process, for an assembly in full statistical equilibrium. We consider now only an assembly of effectively perfect gases, and suppose that the systems are distributed entirely independently of each other, in accordance with the ideas of classical statistical mechanics. Then we see that for equilibrium we must have

$$\begin{aligned}[X_1]\{P_{\text{rad}} + [Y]\,P_Y + [Z]\,P_Z + \ldots &+ [Y]^2\,P_{YY} + \ldots + [Y]\,[Z]\,P_{YZ} + \ldots \\ &+ [Y]\,P_{Y,\text{rad}} + \ldots\} \\ = [X_2]\{Q_{\text{rad}} + [Y]\,Q_Y + [Z]\,Q_Z + \ldots &+ [Y]^2\,Q_{YY} + \ldots + [Y]\,[Z]\,P_{YZ} + \ldots \\ &+ [Y]\,Q_{Y,\text{rad}} + \ldots\}. \qquad \ldots\ldots(1165)\end{aligned}$$

We have here allowed for all sorts of interactions, radiative, simple and multiple collision processes, and mixed radiative and collision processes. Now so long as $[Y]$, $[Z]$, ... are independent variables, and there is a unique equilibrium relationship between $[X_1]$ and $[X_2]$, this equation has important consequences. If the ratio $[X_1]/[X_2]$ is independent of $[Y]$, $[Z]$, ... and so is a function of the temperature only, then

$$\begin{aligned}\frac{P_{\text{rad}}}{Q_{\text{rad}}} = \frac{P_Y + P_{Y,\text{rad}}}{Q_Y + Q_{Y,\text{rad}}} = \frac{P_Z + P_{Z,\text{rad}}}{Q_Z + Q_{Z,\text{rad}}} = \ldots \\ = \frac{P_{YY}}{Q_{YY}} = \ldots = \frac{P_{YZ}}{Q_{YZ}} = \ldots = \frac{[X_2]}{[X_1]}. \qquad \ldots\ldots(1166)\end{aligned}$$

The effects of plain interactions by collision between X and Y and interaction by collision accompanied by the absorption or emission of radiation cannot be separated, and such terms really occur in every fraction. Apart from this however we see that the ratio of the frequencies of each separate process and its reverse process must be equal to a definite function of the temperature $[X_1]/[X_2]$. We can go still further than this later. For the present we can be content to note the independence of the different processes, whose laws therefore can be separately analysed.

If the change from X_1 to X_2 is one of dissociation, the arguments are the same, though the form is a little different. Suppose for example that X_1 dissociates into X_2 and Y. Then $[X_2]\,[Y]/[X_1]$ is a function of the temperature only, and we have

$$\begin{aligned}\frac{0}{Q_{\text{rad}}} = \frac{0}{Q_Z + Q_{Z,\text{rad}}} = \ldots = \frac{P_{\text{rad}}}{Q_Y + Q_{Y.\text{rad}}} = \frac{P_Y + P_{Y,\text{rad}}}{Q_{YY} + Q_{YY\ \text{rad}}} = \ldots \\ = \frac{P_Z + P_{Z,\text{rad}}}{Q_{YZ} + Q_{YZ,\text{rad}}} = \ldots = \frac{[X_2]\,[Y]}{[X_1]}. \qquad \ldots\ldots(1167)\end{aligned}$$

Thus, naturally enough, no process in which no Y is concerned can make up an X_1 from an X_2. The Q's of all such processes must vanish. More generally every process must pair off with a reverse process in which one more Y is concerned—the Y in fact which is to be caught by the X_2 to make it into an X_1. The pairing off is therefore such that it is possible as a dynamical reversal of the original process, and the laws for such pairs can in general be discussed separately.

It remains impossible by these general arguments to separate the effects of, for example, two different states of the same atom, and these must be considered together in any further analysis. We have however shown that it follows merely from the assumption of a unique equilibrium state that the laws of interaction between any molecule and radiation or any molecule and any other group of atoms or molecules must lead separately to the laws of statistical equilibrium. The precise *forms* (1166) and (1167) in which these conclusions are embodied are those for perfect gases. There are analogous forms for the interaction of solids and gases which we shall also discuss. The conclusions can be extended in slightly different forms to imperfect gases, but these we shall not discuss here.

§ **17·2.** *The numbers of collisions of given type in a gas.* The general form of the number of collisions of a given type per unit volume per unit time has already been given in (1161). To derive it we recall that $f_1 du_1 dv_1 dw_1$, which we shall here contract to $f_1 do_1$, is the number of molecules of the first type in unit volume at any time, and near each of them there is a volume $Vpdpd\psi$ in which the centre of the molecule of the second type must lie in order to effect contact within the specified time. The number of such molecules is $f_2 do_2$ per unit volume; hence the formula. For elastic spheres of diameter σ, if θ is the angle between V and the line of centres at collision, we have $p = \sigma \sin\theta$ and $dp = \sigma\cos\theta d\theta$. The element $pdpd\psi$ can then be conveniently replaced by

$$\sigma^2 \cos\theta d\Omega,$$

where $d\Omega$ is an element of solid angle about a direction specifying the line of centres at the instant of collision. The number of collisions then becomes

$$f_1 f_2 \sigma^2 V \cos\theta do_1 do_2 d\Omega. \qquad \ldots\ldots(1168)$$

This is the number of collisions which destroy a pair of molecules u_1, v_1, w_1 and u_2, v_2, w_2 and create a pair u_1^*, v_1^*, w_1^* and u_2^*, v_2^*, w_2^*. Since $do_1 do_2 = do_1^* do_2^*$ and $d\Omega = d\Omega^*$, the corresponding number of reverse collisions creating a pair u_1, v_1, w_1 and u_2, v_2, w_2 and destroying u_1^*, v_1^*, w_1^* and u_2^*, v_2^*, w_2^* is

$$f_1^* f_2^* \sigma^2 V \cos\theta do_1 do_2 d\Omega. \qquad \ldots\ldots(1169)$$

In these collisions the velocities after collision are given in terms of the velocities before and the direction cosines of the line of centres by the equations

$$\left.\begin{aligned} u_1^* &= u_1 + lV\cos\theta, \quad u_2^* = u_2 - lV\cos\theta,\\ v_1^* &= v_1 + mV\cos\theta, \quad v_2^* = v_2 - mV\cos\theta,\\ w_1^* &= w_1 + nV\cos\theta, \quad w_2^* = w_2 - nV\cos\theta,\\ V^2 &= (u_2-u_1)^2 + (v_2-v_1)^2 + (w_2-w_1)^2,\\ V\cos\theta &= l(u_2-u_1) + m(v_2-v_1) + n(w_2-w_1).\end{aligned}\right\} \ldots\ldots(1170)$$

We shall confine attention in this section to properties of the equilibrium state deducible from (1168) when f has Maxwell's form

$$f = \nu\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}m(u^2+v^2+w^2)/kT}, \qquad \text{......(1171)}$$

and ν is the molecular density. The number of collisions per unit volume per unit time in which the relative velocity lies between V and $V + dV$ is an important quantity. If the velocity of the centre of gravity of the pair is U, V, W, and the velocity of 2 relative to 1 ξ, η, ζ, then

$$\mathsf{U} = \tfrac{1}{2}(u_1 + u_2), \quad \xi = u_2 - u_1, \text{ etc.}$$

If we transform (1168) to these new variables we find

$$do_1\, do_2 = d\mathsf{U}\, d\mathsf{V}\, d\mathsf{W}\, d\xi\, d\eta\, d\zeta,$$

$$\tfrac{1}{2}m(u_1{}^2 + v_1{}^2 + w_1{}^2) + \tfrac{1}{2}m(u_2{}^2 + v_2{}^2 + w_2{}^2) = m(\mathsf{U}^2 + \mathsf{V}^2 + \mathsf{W}^2) + \tfrac{1}{4}mV^2,$$

and the number of collisions of the specified type is

$$\nu^2\left(\frac{m}{2\pi kT}\right)^3 e^{-\{m(\mathsf{U}^2+\mathsf{V}^2+\mathsf{W}^2)+\frac{1}{4}mV^2\}/kT}\, \sigma^2 V \cos\theta\, d\mathsf{U} \ldots d\zeta\, d\Omega. \qquad \text{......(1172)}$$

If we integrate this for all values of the motion of the centre of gravity of the system, which is always unimportant in questions of collisions, we find

$$\nu^2\left(\frac{m}{4\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{4}mV^2/kT}\, \sigma^2 V \cos\theta\, d\xi\, d\eta\, d\zeta\, d\Omega. \qquad \text{......(1173)}$$

If we express the relative velocity in spherical polar coordinates V, θ, ϕ, with the direction of the line of centres for axis, we find

$$\nu^2\left(\frac{m}{4\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{4}mV^2/kT}\, \sigma^2 V^3 \sin\theta \cos\theta\, dV\, d\theta\, d\phi\, d\Omega. \qquad \text{......(1174)}$$

For a given direction of the line of centres θ can range from 0 to $\frac{1}{2}\pi$, and ϕ from 0 to 2π, and

$$\int_0^{\frac{1}{2}\pi}\int_0^{2\pi} \sin\theta\cos\theta\, d\theta\, d\phi = \pi.$$

The direction of the line of centres can then range over the whole sphere, but every collision is then counted twice over, since every collision is counted separately with the molecules interchanged. Dividing by 2 to correct for this, we find the total number of collisions per unit volume per unit time, with relative velocity between V and $V + dV$, to be

$$2\pi^2\nu^2\sigma^2\left(\frac{m}{4\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{4}mV^2/kT}\, V^3\, dV. \qquad \text{......(1175)}$$

This is the important result. If we finally integrate over all relative velocities we obtain for the total number of collisions per unit volume per second the well-known formula

$$\nu^2\sigma^2\left(\frac{4\pi kT}{m}\right)^{\frac{1}{2}}. \qquad \text{......(1176)}$$

We shall require also similar formulae for collisions of unlike molecules. Suppose these have masses m_1 and m_2, diameters σ_1 and σ_2. The distance apart of the centres on collision is now σ_{12}, say, where

$$\sigma_{12} = \tfrac{1}{2}(\sigma_1 + \sigma_2).$$

If σ is replaced by σ_{12} the form of (1168) is then still valid. The reduction to the motion of the centre of gravity and the relative motion now however requires the equations

$$(m_1 + m_2)\,\mathsf{U} = m_1 u_1 + m_2 u_2, \quad \xi = u_2 - u_1, \text{ etc.}$$

In these variables

$$do_1\,do_2 = d\mathsf{U}\,d\mathsf{V}\,d\mathsf{W}\,d\xi\,d\eta\,d\zeta,$$

$$\tfrac{1}{2}m_1(u_1^2 + v_1^2 + w_1^2) + \tfrac{1}{2}m_2(u_2^2 + v_2^2 + w_2^2) = \tfrac{1}{2}(m_1 + m_2)(\mathsf{U}^2 + \mathsf{V}^2 + \mathsf{W}^2) + \tfrac{1}{2}\frac{m_1 m_2}{m_1 + m_2}V^2.$$

Formula (1173) is therefore replaced by

$$\nu_1\nu_2\left(\frac{m_1 m_2}{2\pi(m_1 + m_2)kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}\frac{m_1 m_2}{m_1 + m_2}V^2/kT}\,\sigma_{12}^2 V\cos\theta\,d\xi\,d\eta\,d\zeta\,d\Omega, \qquad \text{......(1177)}$$

and formula (1175) by

$$4\pi^2\nu_1\nu_2\sigma_{12}^2\left(\frac{m_1 m_2}{2\pi(m_1 + m_2)kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}\frac{m_1 m_2}{m_1 + m_2}V^2/kT}\,V^3\,dV. \qquad \text{......(1178)}$$

Since the molecules are now distinct, collisions are not counted twice over as before. The total number of collisions is now

$$2\nu_1\nu_2\sigma_{12}^2\left\{\frac{2(m_1 + m_2)\pi kT}{m_1 m_2}\right\}^{\frac{1}{2}}. \qquad \text{......(1179)}$$

It is frequently convenient in applications to rewrite (1171), (1175) and (1178) in terms of kinetic energy, or kinetic energy of the relative motion. If we write

$$\tfrac{1}{2}m(u^2 + v^2 + w^2) = \eta,$$

then Maxwell's law for the number of molecules per unit volume with kinetic energy between η and $\eta + d\eta$ becomes

$$\frac{2\pi\nu}{(\pi kT)^{\frac{3}{2}}}e^{-\eta/kT}\,\eta^{\frac{1}{2}}\,d\eta. \qquad \text{......(1180)}$$

This will frequently be written $\mu(\eta)\,d\eta$, and the molecules with this kinetic energy will be called η-molecules. Similarly, if

$$\tfrac{1}{4}mV^2 = \eta,$$

the number of collisions per unit volume per unit time in which the kinetic energy of the relative motion lies between η and $\eta + d\eta$ is

$$\frac{2\nu^2\sigma^2}{(kT)^{\frac{3}{2}}}\left(\frac{\pi}{m}\right)^{\frac{1}{2}} e^{-\eta/kT}\,\eta\, d\eta. \qquad \text{......(1181)}$$

If

$$\tfrac{1}{2}\frac{m_1 m_2}{m_1 + m_2}\, V^2 = \eta,$$

the number of collisions between molecules of different types per unit volume per unit time in which the kinetic energy of the relative motion lies between η and $\eta + d\eta$ is

$$\frac{2\nu_1\nu_2\sigma_{12}{}^2}{(kT)^{\frac{3}{2}}}\left(\frac{2\pi\,(m_1 + m_2)}{m_1 m_2}\right)^{\frac{1}{2}} e^{-\eta/kT}\,\eta\, d\eta. \qquad \text{......(1182)}$$

§ **17·3**. *Boltzmann's H-theorem for a simple gas.* We have examined in § 17·1 the logical position of this famous theorem in the equilibrium theory as here developed. We may enunciate it most satisfactorily thus.

Theorem 17·3. *Boltzmann's H-theorem. In an assembly of perfect gases in which the only interactions between the systems are conservative collisions with central forces, the preservation of an equilibrium state requires detailed balancing.*

Since detailed balancing ($f_1 f_2 = f_1{}^* f_2{}^*$), which is equivalent to Maxwell's law, obviously preserves the equilibrium state, the theorem tells us that detailed balancing, Maxwell's law and the preservation of an equilibrium state are in the case of this mechanism all equivalent. The idea of Boltzmann's proof is of course to construct a function H (practically the entropy) whose constancy requires detailed balancing. We start with the simplest case of a gas of a single kind of hard elastic spherical molecule of diameter σ in the absence of external fields.

For such a gas f can be changed only by molecular collisions†, so that we can combine (1168) and (1169) and integrate over all the velocities of the second molecule to give its time variation in the form

$$\frac{df_1}{dt} = \sigma^2 \iint (f_1{}^* f_2{}^* - f_1 f_2)\, V \cos\theta\, do_2\, d\Omega. \qquad \text{......(1183)}$$

The integrand is considered to be expressed as a function of $u_1, \ldots, w_2$ by means of equations (1170).

It will be observed that it is essential to the argument that the same molecular distribution laws of the equilibrium state, whatever they may be, should hold for specified volume elements near selected molecules as for the gas as a whole. This is true according to the general equilibrium

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† Except by the boundary fields or collisions with the walls. For the effect of these see § 17·8. They are there shown not to affect the argument.

theory. In discussions which seek to avoid the use of the general theory it becomes a necessary explicit assumption.

Consider now the function

$$H = \int f_1 \log f_1 do_1, \qquad \text{......(1184)}$$

an expression depending only on the number of molecules and the form of f, and therefore constant in the equilibrium state. Then

$$\frac{dH}{dt} = \int (1 + \log f_1) \frac{df_1}{dt} do_1,$$

$$= \sigma^2 \iiint (1 + \log f_1)(f_1{}^* f_2{}^* - f_1 f_2) V \cos\theta \, do_1 do_2 d\Omega. \qquad \text{......(1185)}$$

But it is equally true that

$$H = \int f_2 \log f_2 do_2,$$

and that
$$\frac{df_2}{dt} = \sigma^2 \iint (f_1{}^* f_2{}^* - f_1 f_2) V \cos\theta \, do_1 d\Omega;$$

combining these we find an expression similar to (1185) with $\log f_2$ in place of $\log f_1$, and combining this with (1185) we find

$$\frac{dH}{dt} = \tfrac{1}{2}\sigma^2 \iiint (2 + \log f_1 f_2)(f_1{}^* f_2{}^* - f_1 f_2) V \cos\theta \, do_1 do_2 d\Omega. \qquad \text{......(1186)}$$

But by precisely similar arguments we can start with

$$H = \int f_1{}^* \log f_1{}^* do_1{}^*$$

and find

$$\frac{dH}{dt} = \tfrac{1}{2}\sigma^2 \iiint (2 + \log f_1{}^* f_2{}^*)(f_1 f_2 - f_1{}^* f_2{}^*) V^* \cos\theta^* \, do_1{}^* do_2{}^* d\Omega^*. \qquad \text{......(1187)}$$

The variables of integration may now be changed from the starred variables back to the old variables, and

$$V^* \cos\theta^* do_1{}^* do_2{}^* d\Omega^* = V \cos\theta \, do_1 do_2 d\Omega.$$

If we make this change and combine (1186) and (1187) we find

$$\frac{dH}{dt} = -\tfrac{1}{4}\sigma^2 \iiint (\log f_1 f_2 - \log f_1{}^* f_2{}^*)(f_1 f_2 - f_1{}^* f_2{}^*) V \cos\theta \, do_1 do_2 d\Omega, \qquad \text{......(1188)}$$

$$\leqslant 0, \qquad \text{......(1189)}$$

because the integrand is never negative. The equilibrium state is possible if and only if

$$f_1 f_2 = f_1{}^* f_2{}^*,$$

that is if there is detailed balancing.

We include for completeness the familiar proof that

$$\log f_1 + \log f_2 = \text{const. (coll)}$$

implies that f is Maxwell's distribution function. Let $\chi\,(u, v, w)$ be any function of the velocities of a molecule such that $\chi_1 + \chi_2$ is constant in a collision. Then

$$\log f = \chi$$

is a solution of the equation for the distribution function, and $\log f - \chi$ satisfies the same equation. The most general solution is therefore

$$\log f = \alpha_1\chi' + \alpha_2\chi'' + \alpha_3\chi''' + \dots,$$

where the χ's are all the functions of u, v, w such that $\chi_1 + \chi_2$ is constant in a collision. We know of five such functions, energy, three components of momentum, and mass. There are no others possible, for the four constant relations involving velocities give four independent relations between the six $u_1^*, \dots, w_2^*$ and the old $u_1, \dots, w_2$. Two relations must be left unfixed in this way to depend essentially on the direction cosines of the line of centres at impact. Thus

$$\log f = \alpha_1 + \alpha_2 mu + \alpha_3 mv + \alpha_4 mw + \alpha_5\,\tfrac{1}{2}m\,(u^2 + v^2 + w^2),$$

$$f = Ae^{-jm\{(u-u_0)^2+(v-v_0)^2+(w-w_0)^2\}},$$

where A, j, u_0, v_0, w_0 are constants, which is of the required form.

It will be observed that the detailed collision relations hardly enter into this proof. It is only necessary that there should be some relations giving the $u^*, \dots,$ in terms of the $u, \dots,$ which conserve, momentum, energy and the extension of the element of phase space of the system.

§ **17·31**. *Extensions of Boltzmann's H-theorem.* The extension to the case of a number of different types of molecules is very simple. In place of equation (1183), when classical collisions are the only mechanism acting, we find a set of equations of the form

$$\frac{df_r}{dt} = \Sigma_s\,\sigma_{rs}^2 \iint (f_r^* f_s^* - f_r f_s)\, V \cos\theta\, do_s\, d\Omega. \quad \dots\dots(1190)$$

If we now define the function H by the equation

$$H = \Sigma_s \int f_s \log f_s\, do_s$$

and apply the same analysis we find

$$\frac{dH}{dt} = -\,\tfrac{1}{4}\,\Sigma_r \Sigma_s \sigma_{rs}^2 \iiint (\log f_r f_s - \log f_r^* f_s^*)\,(f_r f_s - f_r^* f_s^*) \times V\cos\theta\, do_r\, do_s\, d\Omega. \quad \dots\dots(1191)$$

From this it follows that H is constant if and only if

$$f_r f_s = f_r^* f_s^* \quad (\textit{all } r, s),$$

that is to say if we have detailed balancing for every choice of a pair of molecules in collision. From the equation for a pair of similar molecules Maxwell's law follows as before. From the dissimilar pairs it follows by the same argument that the mass motion and temperature of each species of gas must be the same.

Let us finally extend the theorem to general classical encounters under central forces between molecules subjected to an external field of force. The distribution function now depends on the position in the gas and we may write it explicitly for a volume element $d\omega$ $(= dxdydz)$,

$$f(u, v, w, x, y, z, t)\, d\omega,$$

so that $\iint f\, do\, d\omega$ extended to a unit volume is the molecular density there. We will assume that force components X_r, Y_r, Z_r per unit mass act on the molecule of the rth kind, so that its equations of motion are

$$\dot{x}_r = u_r, \quad \dot{u}_r = X_r, \text{ etc.}$$

If we now consider all the molecules of the rth type in the element $do\,d\omega$ at u, v, w, x, y, z, t, we see that, *apart from collisions*, after a time dt these molecules will lie in an equal cell of the same space and velocity ranges as before but centred about the point

$$u_r + X_r dt, \quad v_r + Y_r dt, \quad w_r + Z_r dt, \quad x_r + u_r dt, \quad y_r + v_r dt, \quad z_r + w_r dt, \quad t + dt.$$

Moreover since the motion is determinate these molecules are the only ones (apart from collisions) which at time $t + dt$ have the u, v, w, x, y, z so specified. The number of such molecules is by definition

$$f_r(u_r + X_r dt, \ldots, z_r + w_r dt, t + dt)\, do_r\, d\omega,$$

and we have just seen that this differs from $f_r do_r d\omega$ only by the collision term. Thus proceeding to the limit $dt \to 0$,

$$\frac{\partial f_r}{\partial t} = -\left(X_r \frac{\partial}{\partial u_r} + Y_r \frac{\partial}{\partial v_r} + Z_r \frac{\partial}{\partial w_r} + u_r \frac{\partial}{\partial x_r} + v_r \frac{\partial}{\partial y_r} + w_r \frac{\partial}{\partial z_r}\right) f_r + \left[\frac{\partial f_r}{\partial t}\right]_{\text{coll}}. \quad \ldots\ldots(1192)$$

For general classical encounters under central forces we have

$$\left[\frac{\partial f_r}{\partial t}\right]_{\text{coll}} = \Sigma_s \iiint (f_r{}^* f_s{}^* - f_r f_s)\, V p\, dp\, d\psi\, do_s, \quad \ldots\ldots(1193)$$

where the starred velocities are given in terms of the initial velocities (and p and ψ) by the detailed laws derived from the central orbit. Equations (1192) and (1193) together form a very important integro-differential equation for f which should be satisfied for all states (not merely equilibrium ones) of a gas of molecules undergoing classical encounters. It is known as *Boltzmann's equation*.

§ **17·32.** *The equations of mean values.* To derive the general form of the H-theorem we must introduce the equations of mean values. These equations form the starting point for all accurate investigations of transport phenomena in gases†, but these lie outside the range of this monograph and we shall formulate them only to lead up to the H-theorem.

Let $\phi\,(u, v, w, x, y, z, t)$ be any function of the arguments specified, such that all the integrals in the following arguments are absolutely convergent. If we multiply every term in Boltzmann's equation for f_r by $\phi_r do_r$ and integrate for all velocities of the molecules in any specified volume element, we obtain

$$\begin{aligned}\int \phi_r \frac{\partial f_r}{\partial t}\, do_r + \Sigma_x \int u_r \phi_r \frac{\partial f_r}{\partial x_r}\, do_r + \Sigma_x X_r \int \phi_r \frac{\partial f_r}{\partial u_r}\, do_r \\ = \Sigma_s \iiiint \phi_r\,(f_r{}^* f_s{}^* - f_r f_s)\, V p\, dp\, d\psi\, do_r\, do_s, \\ = \Sigma_s \Delta_{sr}\,(\phi_r),\end{aligned}$$

say. In this notation $\Delta_{sr}\,(\phi_r)$ denotes the rate of change in the average value of ϕ_r in the given volume element for molecules of type r produced by collisions with molecules of type s. We can express the last equation more simply in terms of mean values if we remember that

$$\int f_r \psi_r do_r = N_r \overline{\psi_r},$$

where $\overline{\psi_r}$ is the mean value of ψ_r and N_r the total number of molecules of type r in the given volume element. Then

$$\begin{aligned}\int \phi_r \frac{\partial f_r}{\partial t}\, do_r &= \frac{\partial}{\partial t}\,(N_r \overline{\phi_r}) - N_r \overline{\frac{\partial \phi_r}{\partial t}}, \\ \int u_r \phi_r \frac{\partial f_r}{\partial x_r}\, do_r &= \frac{\partial}{\partial x_r}\,(N_r \overline{u_r \phi_r}) - N_r \overline{u_r \frac{\partial \phi_r}{\partial x_r}}, \\ \int \phi_r \frac{\partial f_r}{\partial u_r}\, do_r &= -\int f_r \frac{\partial \phi_r}{\partial u_r}\, do_r = -N_r \overline{\left(\frac{\partial \phi_r}{\partial u_r}\right)}.\end{aligned}$$

Inserting all these expressions we obtain

$$\begin{aligned}\frac{\partial}{\partial t}\,(N_r \overline{\phi_r}) + \Sigma_x \frac{\partial}{\partial x_r}\,(N_r \overline{u_r \phi_r}) = N_r \left\{\overline{\frac{\partial \phi_r}{\partial t}} + \Sigma_x \overline{u_r \frac{\partial \phi_r}{\partial x_r}} + \Sigma_x X_r \overline{\frac{\partial \phi_r}{\partial u_r}}\right\} \\ + \Sigma_s \Delta_{sr}\,(\phi_r). \quad \text{......(1194)}\end{aligned}$$

These are the equations of mean values. Putting

$$\phi_r = \log f_r$$

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† A general account in Jeans, *loc. cit.* chaps. VIII–XIV. The main recent detailed investigations are Chapman, *Phil. Trans.* vol. CCXI, p. 433 (1911), vol. CCXVI, p. 279 (1916), vol. CCXVII, p. 115 (1917); Enskog, *Inaug. Diss. Upsala* (1917), *Arkiv för Matematik*, vol. XVI, No. 16 (1921), *Kungl. Svenska Akad.* vol. LXIII, No. 4 (1922); J. E. Jones, *Phil. Trans.* vol. CCXXIII, p. 1 (1922).

we obtain for the right-hand side of (1194)

$$\int f_r \left[\frac{\partial}{\partial t} + \Sigma_x u_r \frac{\partial}{\partial x_r} + \Sigma_x X_r \frac{\partial}{\partial u_r}\right] \log f_r do_r + \Sigma_s \Delta_{sr} (\log f_r),$$

or

$$\int \left[\frac{\partial}{\partial t} + \Sigma_x u_r \frac{\partial}{\partial x_r} + \Sigma_x X_r \frac{\partial}{\partial u_r}\right] f_r do_r + \Sigma_s \Delta_{sr} (\log f_r). \quad \ldots\ldots(1195)$$

On referring to Boltzmann's equation, (1192) and (1193) we see that (1195) can be written

$$\int \left\{\Sigma_s \iiint (f_r{}^* f_s{}^* - f_r f_s)\, V p dp d\psi do_s\right\} do_r + \Sigma_s \Delta_{sr} (\log f_r),$$

and the first terms obviously vanish. The equation of mean values reduces here to

$$\frac{\partial}{\partial t}(N_r \overline{\log f_r}) + \Sigma_x \frac{\partial}{\partial x_r}(N_r \overline{u_r \log f_r}) = \Sigma_s \Delta_{sr} (\log f_r), \quad \ldots\ldots(1196)$$

which is to hold for every volume element. Written at length this becomes

$$\frac{\partial}{\partial t}\int f_r \log f_r do_r + \Sigma_x \frac{\partial}{\partial x_r}\int u_r f_r \log f_r do_r$$
$$= \Sigma_s \iiiint \log f_r\, (f_r{}^* f_s{}^* - f_r f_s)\, V p dp d\psi do_r do_s. \quad \ldots\ldots(1197)$$

When there are space variations the function H is naturally defined by

$$H = \Sigma_r \iint f_r \log f_r do_r d\omega.$$

Multiplying (1197) by $d\omega$, integrating over the whole gas and summing for all types of molecule, we find

$$\frac{dH}{dt} + \Sigma_r \Sigma_x \int \frac{\partial}{\partial x_r} \int u_r f_r \log f_r do_r d\omega$$
$$= \Sigma_r \Sigma_s \iiiiint \log f_r\, (f_r{}^* f_s{}^* - f_r f_s)\, V p dp d\psi do_r do_s d\omega,$$

and by the usual repetitions

$$= -\tfrac{1}{4}\Sigma_r \Sigma_s \iiiint (\log f_r f_s - \log f_r{}^* f_s{}^*)\,(f_r f_s - f_r{}^* f_s{}^*)\, V p dp d\psi do_r do_s d\omega.$$

The last terms on the left must vanish on integration, for the integration includes the whole gas and therefore extends to regions in which the molecular density vanishes. In a volume element in which the molecular density vanishes f_r must also vanish and therewith $\int u_r f_r \log f_r do_r$. We therefore end by obtaining

$$\frac{dH}{dt} = -\tfrac{1}{4}\Sigma_r \Sigma_s \iiiiint (\log f_r f_s - \log f_r{}^* f_s{}^*)\,(f_r f_s - f_r{}^* f_s{}^*)\, V p dp d\psi do_r do_s d\omega. \quad \ldots\ldots(1198)$$

This is the general H-theorem and requires as before detailed balancing for the equilibrium state.

§ **17·33.** *The general form of Maxwell's law for equilibrium states.* It is not without interest to complete the argument and see how the laws of the most general equilibrium state follow from $f_r f_s = f_r^* f_s^*$ and Boltzmann's equation (1192) which in this case reduces to

$$\Sigma_x u_r \frac{\partial f_r}{\partial x_r} + \Sigma_x X_r \frac{\partial f_r}{\partial u_r} = 0. \qquad \text{......(1199)}$$

The form of f_r for detailed balancing in each volume element is of course still

$$f_r = \nu_r \left(\frac{jm_r}{\pi}\right)^{\frac{3}{2}} e^{-jm_r\{\Sigma(u_r-u_0)^2\}},$$

but so far as detailed balancing is concerned ν_r, j, u_0, v_0, w_0 may all be functions of x, y, z. We may substitute this value of f_r in (1199) and require the equation to be satisfied for all u_r, v_r, w_r. On equating coefficients we find

$$\frac{\partial j}{\partial x} = \frac{\partial j}{\partial y} = \frac{\partial j}{\partial z} = 0,$$

$$\frac{\partial u_0}{\partial x} = \frac{\partial v_0}{\partial y} = \frac{\partial w_0}{\partial z} = 0,$$

$$\frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y} = \frac{\partial w_0}{\partial y} + \frac{\partial v_0}{\partial z} = \frac{\partial u_0}{\partial z} + \frac{\partial w_0}{\partial x} = 0.$$

The first three of these equations require that the temperature shall be constant throughout the assembly. The next six are the equations which characterize a rigid body. They specify that, though the mass motion may vary from point to point in the assembly in the equilibrium state, the variation is such that the assembly moves as a rigid body, with a certain uniform rotation superposed on a translation. These equations being satisfied we are left with

$$\Sigma_x u_r \left\{\frac{1}{\nu_r}\frac{\partial \nu_r}{\partial x} - 2jm_r X_r\right\} + 2jm_r \Sigma_x X_r u_0 \equiv 0.$$

This can only be satisfied if $X_r Y_r Z_r$ are derived from a potential function χ_r, so that

$$\nu_r = (\nu_r)_0\, e^{-2jm_r\chi_r} \qquad ((\nu_r)_0 \textit{ constant}),$$

and finally

$$\Sigma_x X_r u_0 = 0.$$

The last equation demands that the lines of force and the lines of flow must be everywhere at right angles.

The complete specification of the general equilibrium state is therefore that *the gas moves as a rigid body, with temperature everywhere the same, in a field of force of potential* χ_r, *with a molecular distribution function*

$$f_r = (\nu_r)_0 \left(\frac{m_r}{2\pi kT}\right)^{\frac{3}{2}} e^{-\{\frac{1}{2}m_r\Sigma(u_r-u_0)^2 + m_r\chi_r\}/kT},$$

in which $(\nu_r)_0$ *is constant and* u_0, v_0, w_0 *the velocity components of a rigid body motion such that the lines of flow are everywhere normal to the gradient of* χ_r.

§ **17·4.** *Collisions of the first and second kind**. The next mechanism which we shall examine in detail is that of inelastic impacts between electrons and atoms. It is well known from a variety of evidence that such collisions are possible as soon as the energy of the electron exceeds a certain minimum energy, which is that required to change the atom hit from one stationary state to the next state of greater energy. It follows by the foregoing arguments that any such process can only occur if it is accompanied by a corresponding reverse process, the two together preserving the equilibrium laws. In this case the reverse process turns out to be a superelastic collision, called by Klein and Rosseland a collision of the second kind.

The frequency of occurrence of any sort of collision can be expressed in terms of a certain coefficient, of the dimensions of an area, which must be a function solely of the atom and the relative velocity and line of impact of the electron hitting it. This coefficient, which represents the chance of a successful collision, may also depend in an individual collision on the orientation of the atomic axis relative to the line of impact and on the phase constants of the electronic motions in the atom. The average coefficient however, which is usually all that matters, will be obtained by integration over all these variables which are therefore no longer effective.

The electrons are so light and therefore their equilibrium velocities so high that in a first treatment the velocities of the atoms can be neglected and they may be regarded as fixed (or of infinite mass). If ν_1 is the density of the type of atom or molecule under discussion, then the number of collisions per unit volume per second between these atoms and η-electrons, in which the line of impact lies at a distance between p and $p + dp$ from the atomic nucleus (or centre of mass of the molecule), is by (1180)

$$\nu_1 \, . \, 2\pi p dp \, . \left(\frac{2\eta}{m}\right)^{\frac{1}{2}} \mu(\eta)\, d\eta. \qquad \text{......(1200)}$$

If $\Sigma_1{}^2(p, \eta)$ is the probability that such a collision will be successful in exciting the atom from state 1 to state 2 the number of such successful collisions is

$$\nu_1 \, . \, 2\pi p dp \, . \, \Sigma_1{}^2(p, \eta) \left(\frac{2\eta}{m}\right)^{\frac{1}{2}} \mu(\eta)\, d\eta. \qquad \text{......(1201)}$$

If we now introduce the new function

$$S_1{}^2(\eta) = 2\pi \int_0^\infty p \Sigma_1{}^2(p, \eta)\, dp, \qquad \text{......(1202)}$$

we find the total number of successful collisions of the first kind by η-electrons in the equilibrium state to be

$$\nu_1 S_1{}^2(\eta) \left(\frac{2\eta}{m}\right)^{\frac{1}{2}} \mu(\eta)\, d\eta. \qquad \text{......(1203)}$$

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* Klein and Rosseland, *Zeit. für Phys.* vol. IV, p. 46 (1921).

This expression is only relevant when $\eta \geqslant \eta_{12}$, where η_{12} is the extra energy of the atom in state 2 over that in state 1. When $\eta < \eta_{12}$, $S_1^2(\eta) = 0$.

By the general discussion of § 17·1 the reverse process can only be one which occurs with a frequency proportional to ν_2 and to the electron density. It must therefore be some sort of collision. It is hardly possible to suppose that any other sort of collision can be concerned except those which are the direct reverse of the inelastic impacts. These are collisions in which an η-electron interacts with an excited atom and removes its superfluous energy, leaving it in its normal state. The energy removed is carried off by the electron as extra kinetic energy of translation, so that the collision may be termed superelastic. The total number of successful superelastic collisions by η-electrons per unit volume per second can be written

$$\nu_2 S_2^1(\eta) \left(\frac{2\eta}{m}\right)^{\frac{1}{2}} \mu(\eta)\, d\eta, \qquad \text{......(1204)}$$

where ν_2 is the density of the atoms in the state 2. It is possible that $S_2^1(\eta) > 0$ for any value of η.

It must be noted that $S_1^2(\eta)$ and $S_2^1(\eta)$ have a purely atomic significance; they may be called the mean effective target areas of the atom for η-electrons. It is important to observe that these areas by definition cannot depend on any statistical parameter such as temperature or density*.

By considering the conditions for the preservation of the $\mu(\eta)$-law for the velocity distribution of the electrons a fundamental relation can be established between $S_1^2(\eta)$ and $S_2^1(\eta)$. The concentrations ν_1 and ν_2 are connected by the relation (see (131))

$$\nu_2/\nu_1 = (\varpi_2/\varpi_1)\, e^{-\eta_{12}/kT}. \qquad \text{......(1205)}$$

The number η-electrons destroyed by inelastic collisions is

$$\nu_1 S_1^2(\eta) \left(\frac{2\eta}{m}\right)^{\frac{1}{2}} \mu(\eta)\, d\eta \quad (\eta \geqslant \eta_{12}),$$

$$0 \qquad\qquad (\eta < \eta_{12}).$$

The number of η-electrons created by inelastic collisions is

$$\nu_1 S_1^2(\eta + \eta_{12}) \left\{\frac{2(\eta + \eta_{12})}{m}\right\}^{\frac{1}{2}} \mu(\eta + \eta_{12})\, d\eta \quad (\eta > 0).$$

The number of η-electrons destroyed by superelastic collisions is

$$\nu_2 S_2^1(\eta) \left(\frac{2\eta}{m}\right)^{\frac{1}{2}} \mu(\eta)\, d\eta \qquad (\eta > 0).$$

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* It should of course be remembered that if we experiment with directed electron streams and atoms orientated by magnetic fields (e.g. Skinner and Appleyard, *Proc. Roy. Soc.* A, vol. CXVII, p. 224 (1927)) the target areas for a given switch may well be different from those for unorientated collisions. It is obvious that this is in no way contradictory to the statements in the text.

The number of η-electrons created by superelastic collisions is

$$\nu_2 S_2^{\,1}(\eta-\eta_{12})\left(\frac{2(\eta-\eta_{12})}{m}\right)^{\frac{1}{2}}\mu(\eta-\eta_{12})\,d\eta \quad (\eta \geqslant \eta_{12}),$$

$$0 \quad (\eta < \eta_{12}).$$

Putting in the equilibrium values of $\mu(\eta)$ and ν_2/ν_1 we see at once that the action will balance and leave the equilibrium undisturbed if and only if

$$e^{-\eta_{12}/kT}F_1^{\,2}(\eta) - F_1^{\,2}(\eta-\eta_{12}) = 0,$$

where $F_1^{\,2}(\eta) = \alpha\,[\varpi_1(\eta+\eta_{12})\,S_1^{\,2}(\eta+\eta_{12}) - \varpi_2\eta S_2^{\,1}(\eta)] \quad (\eta \geqslant 0),$

$= 0 \quad (\eta < 0),$

and α is a constant. But by a step by step argument this condition can be shown only to be satisfied if

$$F_1^{\,2}(\eta) = 0 \quad (\mathit{all}\ \eta).$$

Hence $$\varpi_1(\eta+\eta_{12})\,S_1^{\,2}(\eta+\eta_{12}) = \varpi_2\eta S_2^{\,1}(\eta). \qquad \text{......(1206)}$$

This is Klein and Rosseland's result. It guarantees the preservation of the equilibrium distribution law of electron velocities for all T. It also guarantees the preservation of the distribution law of atomic states (1205). For the rate of destruction of atoms in state 1 by this mechanism is

$$\nu_1\int_{\eta_{12}}^{\infty} S_1^{\,2}(\eta)\left(\frac{2\eta}{m}\right)^{\frac{1}{2}}\mu(\eta)\,d\eta,$$

and the rate of creation

$$\nu_2\int_0^{\infty} S_2^{\,1}(\eta)\left(\frac{2\eta}{m}\right)^{\frac{1}{2}}\mu(\eta)\,d\eta.$$

These rates will balance when

$$\varpi_1\int_0^{\infty}(\eta+\eta_{12})\,S_1^{\,2}(\eta+\eta_{12})\,e^{-\eta/kT}\,d\eta = \varpi_2\int_0^{\infty}\eta S_2^{\,1}(\eta)\,e^{-\eta/kT}\,d\eta, \qquad \text{......(1207)}$$

which is satisfied for all values of T in virtue of (1206).

It should be observed in passing that conversely (1206) can be deduced directly from the fact that (1207) must hold for all T. Equation (1207) is of the general form

$$\int_0^{\infty} f(\eta)\,e^{-\eta/kT}\,d\eta = 0 \quad (\mathit{all}\ T), \qquad \text{......(1208)}$$

and there exists the following

Lemma. If $f(\eta)$ is a continuous function of η for $\eta \geqslant 0$ and satisfies the general conditions of Fourier's integral theorem, and if

$$\int_0^{\infty} f(\eta)\,e^{-\eta/kT}\,d\eta = 0 \quad (\mathit{all}\ T),$$

then $$f(\eta) = 0 \quad (\eta \geqslant 0).$$

This lemma is a direct corollary of Fourier's integral theorem. There is no physical reason to question the applicability of the conditions of the lemma to the function $f(\eta)$ derived from the atomic target areas in (1207).

The relation (1206) just obtained on the hypothesis of the preservation of the equilibrium state can be obtained at once on the hypothesis of detailed balancing by equating (1203), with η replaced by $\eta + \eta_{12}$, to (1204). Thus for this simple mechanism of interaction between electrons and atoms with only two stationary states the hypotheses of preservation and detailed balancing are again equivalent.

One might naturally hope to be able to deduce from the preservation hypothesis that a relation of the form (1206) holds for the frequencies of every possible switch by collision in an atom with n levels. It appears however that no such deduction can be drawn. An atom with n possible levels has $\frac{1}{2}n(n-1)$ possible switches, all of which we must regard as forming a single mechanism.

A detailed presentation of the case $n = 3$ is instructive. There are three switches (to and fro) to consider. *Sufficiently slow* η-electrons are created only by collisions of the first kind at a rate

$$\nu_1 S_1^2(\eta+\eta_{12})\left\{\frac{2(\eta+\eta_{12})}{m}\right\}^{\frac{1}{2}}\mu(\eta+\eta_{12})\,d\eta$$
$$+\nu_1 S_1^3(\eta+\eta_{13})\left\{\frac{2(\eta+\eta_{13})}{m}\right\}^{\frac{1}{2}}\mu(\eta+\eta_{13})\,d\eta$$
$$+\nu_2 S_2^3(\eta+\eta_{23})\left\{\frac{2(\eta+\eta_{23})}{m}\right\}^{\frac{1}{2}}\mu(\eta+\eta_{23})\,d\eta. \quad \text{......(1209)}$$

They are destroyed only by collisions of the second kind at a rate

$$\{\nu_2 S_2^1(\eta)+\nu_3 S_3^1(\eta)+\nu_3 S_3^2(\eta)\}\left(\frac{2\eta}{m}\right)^{\frac{1}{2}}\mu(\eta)\,d\eta. \quad \text{......(1210)}$$

The condition for the preservation of the equilibrium state can be written

$$e^{-\eta_{12}/kT}F_1^2(\eta)+e^{-\eta_{13}/kT}\{F_1^3(\eta)+F_2^3(\eta)\}=0 \quad (\textit{all } T), \text{......(1211)}$$

an equation valid only when η is less than the least of η_{12}, η_{13} and η_{23}. When η is unrestricted the first terms in (1209) and (1210) continue to give the numbers of η-electrons created by the switch 1 → 2 and destroyed by the switch 2 → 1. There are now in addition

$$\nu_1 S_1^2(\eta)\left(\frac{2\eta}{m}\right)^{\frac{1}{2}}\mu(\eta)\,d\eta$$

η-electrons *destroyed* by the switch 1 → 2 and

$$\nu_2 S_2^1(\eta-\eta_{12})\left\{\frac{2(\eta-\eta_{12})}{m}\right\}^{\frac{1}{2}}\mu(\eta-\eta_{12})\,d\eta$$

η-electrons created by the switch 2 → 1. There are similar terms for the other two switches. The complete form of (1211) is therefore

$$-\{F_1{}^2(\eta-\eta_{12})+F_1{}^3(\eta-\eta_{13})\}+e^{-\eta_{12}/kT}\{F_1{}^2(\eta)-F_2{}^3(\eta-\eta_{23})\}$$
$$+e^{-\eta_{13}/kT}\{F_1{}^3(\eta)+F_2{}^3(\eta)\}=0\quad(all\ T,\eta).\quad\ldots\ldots(1212)$$

This is equivalent to the three equations

$$\begin{aligned}F_1{}^2(\eta-\eta_{12})&+F_1{}^3(\eta-\eta_{13})=0,\\ F_1{}^2(\eta)&-F_2{}^3(\eta-\eta_{23})=0,\\ F_1{}^3(\eta)&+F_2{}^3(\eta)=0,\end{aligned}$$

of which only two are independent. They reduce to

$$F_1{}^2(\eta)=F_2{}^3(\eta-\eta_{23})=-F_1{}^3(\eta-\eta_{23}).\quad\ldots\ldots(1213)$$

We can infer that equation (1206), $F_1{}^2(\eta)=0$, still holds for $\eta<\eta_{23}$, but we can infer nothing more as to the vanishing of the F's. The assumption of only two stationary states is equivalent to making η_{23} infinite. If we were to exclude all switches by collision of types 2 → 3 and 3 → 2 then $F_2{}^3(\eta)=0$, and we can infer that $F_1{}^2(\eta)=0$ and $F_1{}^3(\eta)=0$ for all η. This would be the expected generalization of (1206). But it can only be made when by an arbitrary limitation we rule out the possibility of the cyclic process 1 → 2, 2 → 3, 3 → 1. Such processes seem quite natural*, and are not incompatible with the hypothesis of preservation.

It remains to determine the conditions under which the distribution of atoms between the three states is preserved. For state 1 this can be written

$$e^{-\eta_{12}/kT}\int_0^\infty F_1{}^2(\eta)\,e^{-\eta/kT}\,d\eta+e^{-\eta_{13}/kT}\int_0^\infty F_1{}^3(\eta)\,e^{-\eta/kT}\,d\eta=0,$$

and finally reduced to the form

$$\int_0^\infty\{F_1{}^2(\eta)+F_1{}^3(\eta-\eta_{23})\}\,e^{-\eta/kT}\,d\eta=0\quad(all\ T).\quad\ldots\ldots(1214)$$

Condition (1214) is equivalent to one of the equations (1213) and gives us nothing new. In the same way for states 2 and 3 we get

$$\int_0^\infty\{-F_1{}^2(\eta)+F_2{}^3(\eta-\eta_{23})\}\,e^{-\eta/kT}\,d\eta=0\quad(all\ T),$$

$$\int_0^\infty\{F_1{}^3(\eta)+F_2{}^3(\eta)\}\,e^{-\eta/kT}\,d\eta=0\quad(all\ T),$$

which are also equivalent to components of (1213). Equations (1213) are therefore necessary and sufficient for the preservation of the equilibrium state. In the general case we shall obtain on the preservation hypothesis just $n-1$ necessary and sufficient relations between $\frac{1}{2}n(n-1)$ functions F.

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* In all atoms this particular cycle might be ruled out by selection rules, but other cycles such as 1 → 2, 2 → 3, 3 → 4, 4 → 1 will always be possible.

This example is of some logical importance, since it is a simple case in which the hypotheses of preservation and of detailed balancing are not equivalent. On the latter the number of stationary states and possible switches between them are irrelevant. The old argument will apply to each pair of switches $n \to n'$ and $n' \to n$ giving the old result (1206) for each separate pair. The hypothesis of detailed balancing can however be very strongly supported as likely to be generally valid*, and its probability is untouched by this example which impugns only its necessity. In attempting to get a survey of the laws of mechanisms we shall therefore sometimes be content with a discussion on the basis of detailed balancing alone.

§ **17·41**. *Inelastic and superelastic collisions between heavy systems.* Owing to the small mass and high average velocity of the electron compared with an atom it was legitimate to ignore the momentum of the electron and the velocity of the atom in the last section. When both the interacting systems are of comparable mass the calculations must be revised. The action must now depend only on the relative velocity V of the interacting systems. There are now obviously two sorts of interaction possible—(*a*) An atom of type 1 may play the part of an electron and excite an atom of type 0 with expenditure of energy $(\eta_0)_{12}$. (*b*) An excited atom of type 1 may excite an atom of type 0 with the expenditure of its energy of excitation returning itself to its normal state. Such a collision may be either inelastic or superelastic according as energy is taken up from or surrendered to the relative motion of the systems.

Case (*a*). *Ordinary inelastic collisions between heavy systems.* If we replace the $\pi\sigma_{12}^2$ of (1182) by the more general $S_1^2(\eta)$ for the effective target area for excitation, then the number of successful collisions per unit volume per second will be

$$\frac{4\nu_0^{(1)}\nu_1}{(kT)^{\frac{3}{2}}}\left(\frac{m_0+m_1}{2\pi m_0 m_1}\right)^{\frac{1}{2}} e^{-\eta/kT}\,\eta\, S_1^2(\eta)\, d\eta. \qquad \text{......(1215)}$$

We use $\nu_0^{(1)}$ to denote the concentration of systems 0 in state 1. We recall that

$$\eta = \tfrac{1}{2}\frac{m_0 m_1}{m_0+m_1}V^2,$$

the kinetic energy of the relative motion. This is the number of collisions per unit volume which destroy members of $\nu_0^{(1)}$, create members of $\nu_0^{(2)}$, destroy pairs of molecules of relative velocity V and create other pairs for which the energy of the relative motion is

$$\eta' = \eta - \eta_{12}, \qquad \text{......(1216)}$$

and the relative velocity

$$V'^2 = V^2 - 2\frac{(m_0+m_1)}{m_0 m_1}\eta_{12}.$$

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* G. N. Lewis, *Proc. Nat. Acad. Sci.* vol. XI, pp. 179, 422 (1925).

The number of reverse processes creating $\nu_0^{(1)}$ out of $\nu_0^{(2)}$ by collisions with relative energy η' will be

$$\frac{4\nu_0^{(2)}\nu_1}{(kT)^{\frac{3}{2}}}\left(\frac{m_0+m_1}{2\pi m_0 m_1}\right)^{\frac{1}{2}} e^{-\eta'/kT}\,\eta' S_2^{\,1}(\eta')\,d\eta'. \qquad \text{......(1217)}$$

On the hypothesis of detailed balancing if η and η' are connected by (1216) the expressions (1215) and (1217) must be equal. This gives on reduction

$$\varpi_1(\eta+\eta_{12})\,S_1^{\,2}(\eta+\eta_{12}) = \varpi_2\eta S_2^{\,1}(\eta), \qquad \text{......(1218)}$$

which is (naturally) the same relation as (1206). Here again if there are only two states of the system of type 0 concerned and no other complications it can be shown that, since S may not depend on T, (1218) is necessary and sufficient on the hypothesis of preservation only. Relations similar to (1218) may be expected to hold when the systems of type 0 have a number of stationary states.

We observe finally that

$$S_1^{\,2}(\eta) = 0 \quad (\eta < \eta_{12}), \qquad \text{......(1219)}$$

that is when the energy of the motion relative to the centre of gravity is less than η_{12}. If momentum as well as energy is to be conserved, it is of course only the energy of this relative motion which is available for excitation. It is moreover easy to see that simple conditions for the preservation of the laws of equilibrium are impossible unless they conserve momentum as well as energy.

Case (*b*). *Transference of excitation.* This case is very similar, but the direct and reverse processes are now practically identical. We start with the system of type 0 normal ($\nu_0^{(1)}$), and the system of type 1 excited ($\nu_1^{(2)}$), and end with the system of type 0 excited ($\nu_0^{(2)}$), and type 1 normal ($\nu_1^{(1)}$), and conversely. The equation of relative energy is now

$$\eta' + (\eta_0)_{12} = \eta + (\eta_1)_{12}, \qquad \text{......(1220)}$$

and the condition of detailed balancing as before

$$(\varpi_0)_1(\varpi_1)_2\eta S_1^{\,2}(\eta) = (\varpi_0)_2(\varpi_1)_1\eta' S_2^{\,1}(\eta'), \qquad \text{......(1221)}$$

subject to (1220). One or other of the S's will be zero for a range of relative energies less than a definite limit depending on the relative sizes of $(\eta_0)_{12}$ and $(\eta_1)_{12}$. As before these relations follow from the preservation hypothesis only, if there are no added complications.

§ **17·5.** *Practical applications of the theory of inelastic collisions.* The direct consequences of the suggestion of Klein and Rosseland have been formally developed in the foregoing sections. It is hardly possible even now to make quantitative applications, for until we have a quantitative knowledge of one of a pair of S's or target areas, we can get nothing further from equilibrium theory. But even before any quantitative knowledge is available the mere qualitative knowledge that one S is not zero implies that the other S is also different from zero, and this leads to the recognition of the existence of processes which might otherwise have been overlooked. In the hands of Franck and others the theory, mainly used qualitatively, has been of first-class importance in the interpretation of a variety of phenomena, some of which we shall mention briefly.

The most striking of such qualitative confirmations of the theory is provided by the work of Cario* on the excitation of special lines in the spectra of thallium and silver by illuminating a mixture of the vapours of mercury and thallium or silver with the resonance radiation (λ 2536) of mercury. It was possible to show with certainty that the thallium or silver lines were excited when and only when excited mercury atoms were present in the mixed vapour, and the energy relations were such that this may be regarded as a complete proof of the process (b) of excitation discussed in § 17·41. It was shown further that the thallium lines must be emitted by abnormally swiftly moving thallium atoms, in virtue of their very small absorption in the thallium vapour. This confirms in a general way the laws of conservation of momentum in the process of excitation. For some energy is left over when the excitation is transferred and can only be used up in increasing the relative kinetic energy, and so on the average the actual kinetic energy of both atoms. These studies of excitation have also been extended to other atoms such as Cd, Na, In, Sb, and As.

In addition to this it has been shown by Franck, and Cario and Franck, in other papers that excited mercury atoms can probably dissociate H_2. These authors have also thus accounted for many of the effects of pressure, in particular the effects of foreign inert gases on the resonance spectra of mercury, sodium and the iodine molecule. The strength of the resonance radiation emitted in these gases is greatly reduced by too high a pressure or by the presence of an inert gas. The energy of excitation is used up in superelastic collisions instead of in re-emission of the resonance line. The same authors have also given a theory of the red sensitization of photographic plates by a red-absorbent dye. All these phenomena are intimately connected with the foregoing principles†. The same ideas are of importance in a discussion of the mechanism of excitation underlying so-called unimolecular gas reactions.

§ **17·6**. *The process of ionization by electronic impacts.* We shall again start with fixed atoms, equivalent to atoms of infinite mass. We know that processes exist in which an η-electron (or α-particle) can knock another electron out of an atom provided that $\eta > \eta_0$, where η_0 is the energy neces-

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* Cario, *Zeit. für Phys.* vol. x, p. 185 (1922); Cario and Franck, *Zeit. für Phys.* vol. xvii, p. 202 (1923); Donat, *Zeit. für Phys.* vol. xxix, p. 345 (1924).

† Franck, *Zeit. für Phys.* vol. ix, p. 259 (1922); Franck and Cario, *Zeit. für Phys.* vol. xi, p. 161 (1922).

sary to remove this electron. This process of ionization can certainly occur when η only just exceeds η_0, so that there is no reason to suppose that radiation plays any essential part. It seems probable from a study of β-ray tracks, as photographed in Wilson's apparatus, that we must suppose that the rest of the energy $\eta - \eta_0$ can be distributed in any manner between the two electrons after the collision, and that, whatever η, we may suppose that a process of this sort can occur without the emission or absorption of any radiation. Coupled with this process of ionization there must be some process of capture which for all values of the temperature and concentrations will preserve the laws of dissociative equilibrium. The only possible (suitable) process of capture is, after § 17·1, a collision of three bodies, two electrons and one ionized atom in which the two electrons so interact that one of them is bound by the atom and the other is thrown off with the kinetic energy of both before collision and the ionization energy η_0 thrown in. If the superfluous energy is not to be radiated it can only be carried off by at least one other material body!

The number of impacts by η-electrons on atoms with their line of impact between p and dp is given by (1200). Let us suppose that the only possible result (other than trivial elastic collisions) is ionization (provided $\eta > \eta_0$), after which there will be two free electrons, a new ζ-electron and the old one, now an $(\eta - \eta_0 - \zeta)$-electron. It is necessary that $\eta - \eta_0 - \zeta \geqslant 0$. Let $\Sigma_1{}^2(p, \zeta, \eta)\,d\zeta$ be the probability that such an encounter gives rise to a new ζ-electron. If we introduce the function

$$S_1{}^2(\zeta, \eta) = 2\pi \int_0^\infty p\Sigma_1{}^2(p, \zeta, \eta)\,dp, \qquad \text{......(1222)}$$

then we find that the total number of such collisions is

$$\nu_1 \left(\frac{2\eta}{m}\right)^{\frac{1}{2}} \mu(\eta)\,d\eta \,.\, S_1{}^2(\zeta, \eta)\,d\zeta. \qquad \text{......(1223)}$$

The total rate of production of ions in this way must be obtained by integrating with respect to ζ from 0 to $\eta - \eta_0$, and then with respect to η from η_0 to infinity. There is a simple physical meaning for

$$\int_0^{\eta-\eta_0} S_1{}^2(\zeta, \eta)\,d\zeta.$$

It is the mean effective collision area for ionization by η-electrons.

The reverse three-body process can be similarly formulated. Consider first of all an ionized atom in process of being hit by a ζ-electron on a line of impact between p_1 and $p_1 + dp_1$. There are

$$\nu_2 \,.\, 2\pi p_1 dp_1 \,.\, \left(\frac{2\zeta}{m}\right)^{\frac{1}{2}} \mu(\zeta)\,d\zeta$$

of these occurrences per unit volume per second. The other electron is to enter into collision on a path on which (if undisturbed) it would reach its apse at a time between τ and $\tau + d\tau$ seconds after the first electron reached its apse. With every collision with a ζ-electron there is therefore associated a volume

$$\left(\frac{2\xi}{m}\right)^{\frac{1}{2}} d\tau \,.\, 2\pi p_2 dp_2$$

in which a ξ-electron may lie, whose passage through its apse on a p_2-line of impact would occur in the specified interval. The number of ξ-electrons in such a volume is

$$d\tau \,.\, 2\pi p_2 dp_2 \,.\left(\frac{2\xi}{m}\right)^{\frac{1}{2}} \mu\,(\xi)\, d\xi.$$

The number of three-body collisions in which ζ-electrons and ξ-electrons on p_1- and p_2-lines of impact and time difference τ are concerned is therefore

$$\nu_2 \left(\frac{2\zeta}{m}\right)^{\frac{1}{2}} \mu\,(\zeta)\, d\zeta \,.\left(\frac{2\xi}{m}\right)^{\frac{1}{2}} \mu\,(\xi)\, d\xi \,.\, 2\pi p_1 dp_1 \,.\, 2\pi p_2 dp_2 \,.\, d\tau. \qquad \text{......(1224)}$$

This number has been so specified that it disregards the relative directions of the line of impact of the electrons and the atomic orientation. Averaged over all such directions and orientations there will be a certain definite probability

$$\Sigma_2^1\,(p_1, p_2, \tau, \zeta, \xi)$$

that any one of these collisions will lead to a successful interaction in which the ζ-electron is bound and the ξ-electron thrown off as a $(\xi + \zeta + \eta_0)$-electron. Writing

$$4\pi^2 \int_0^\infty p_1 dp_1 \int_0^\infty p_2 dp_2 \int_{-\infty}^{+\infty} \Sigma_2^1\,(p_1, p_2, \tau, \zeta, \xi)\, d\tau = S_2^1\,(\zeta, \xi), \qquad \text{......(1225)}$$

which will then be a purely atomic function of dimensions $[L]^4\,[T]$, we can express the number of successful triple collisions in which a ζ-electron is bound by the interaction of a ξ-electron in the form

$$\nu_2 \left(\frac{2\zeta}{m}\right)^{\frac{1}{2}} \mu\,(\zeta)\, d\zeta \,.\left(\frac{2\xi}{m}\right)^{\frac{1}{2}} \mu\,(\xi)\, d\xi \,.\, S_2^1\,(\zeta, \xi). \qquad \text{......(1226)}$$

These collisions each create a neutral atom and a $(\xi + \zeta + \eta_0)$-electron at the expense of an ion, a ξ-electron and a ζ-electron.

The appropriate law of dissociative equilibrium is, after (333) and (1013),

$$\frac{\nu_2 \nu_\epsilon}{\nu_1} = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \frac{2\varpi_2}{\varpi_1} e^{-\eta_0/kT}. \qquad \text{......(1227)}$$

If the suggested processes form a possible mechanism they must preserve (1227) subject only to a purely atomic relation between S_1^2 and S_2^1, which turns out to be very simple. On the hypothesis of detailed balancing we must equate at once, subject to (1227), the numbers (1223) and (1226), with the proper relation between η, ζ and ξ. This means that we must write $\eta_0 + \zeta + \xi$ for η in (1223) and identify the ζ's in the two expressions. We then find after a simple reduction that the relation between $S_1{}^2$ and $S_2{}^1$ must be

$$(\eta_0+\zeta+\xi)\,S_1{}^2\,(\zeta,\eta_0+\zeta+\xi)=\frac{16\pi m\varpi_2}{\varpi_1 h^3}\,\xi\zeta S_2{}^1\,(\zeta,\xi)\quad(all\ \zeta,\xi).\ \ldots(1228)$$

$$S_1{}^2\,(\zeta,\eta)=0\quad(\eta<\eta_0+\zeta).$$

It is however not without interest to see once again how far one can get on the simple preservation hypothesis, supposing that this process of ionization is the only process of the type that is acting.

Consider first the preservation of the electron distribution law for ζ-electrons, $\zeta<\eta_0$. By the process of ionization new ζ-electrons are produced by η-electrons at the rate (1223) and the old η-electrons are converted to ζ-electrons when these new ones are $(\eta-\eta_0-\zeta)$-electrons. The combined rate of production of ζ-electrons in ionization by η-electrons is therefore

$$\nu_1\left(\frac{2\eta}{m}\right)^{\frac{1}{2}}\mu\,(\eta)\,d\eta\,\{S_1{}^2\,(\zeta,\eta)+S_1{}^2\,(\eta-\eta_0-\zeta,\eta)\}\,d\eta\quad(\eta>\eta_0+\zeta),$$

and otherwise zero. The total rate of creation of ζ-electrons is therefore

$$\nu_1 d\zeta\int_{\eta_0+\zeta}^{\infty}\left(\frac{2\eta}{m}\right)^{\frac{1}{2}}\{S_1{}^2\,(\zeta,\eta)+S_1{}^2\,(\eta-\eta_0-\zeta,\eta)\}\,\mu\,(\eta)\,d\eta,\quad\ldots\ldots(1228)'$$

per unit volume, by the ionization process. This holds for all ζ, but when $\zeta<\eta_0$ there is no destruction of ζ-electrons by this process.

Taking now the capture process we see at once that it creates no ζ-electrons $(\zeta<\eta_0)$, for the resulting free electron has always an energy greater than η_0. It destroys each time both a ζ- and a ξ-electron. The number of ζ-electrons destroyed by binding (ζ-type) is therefore

$$\nu_2\left(\frac{2\zeta}{m}\right)^{\frac{1}{2}}\mu\,(\zeta)\,d\zeta\int_0^{\infty}\left(\frac{2\xi}{m}\right)^{\frac{1}{2}}S_2{}^1\,(\zeta,\xi)\,\mu\,(\xi)\,d\xi.$$

The corresponding number destroyed by conversion into fast electrons (ξ-type) is

$$\nu_2\left(\frac{2\zeta}{m}\right)^{\frac{1}{2}}\mu\,(\zeta)\,d\zeta\int_0^{\infty}\left(\frac{2\xi}{m}\right)^{\frac{1}{2}}S_2{}^1\,(\xi,\zeta)\,\mu\,(\xi)\,d\xi.$$

The total rate of destruction of ζ-electrons per unit volume is therefore

$$\nu_2\left(\frac{2\zeta}{m}\right)^{\frac{1}{2}}\mu\,(\zeta)\,d\zeta\int_0^{\infty}\left(\frac{2\xi}{m}\right)^{\frac{1}{2}}\{S_2{}^1\,(\zeta,\xi)+S_2{}^1\,(\xi,\zeta)\}\,\mu\,(\xi)\,d\xi,\quad\ldots\ldots(1229)$$

for all values of ξ. For preservation of the distribution laws for $\zeta<\eta_0$ we must therefore equate (1228)′ and (1229). When we use the laws of the equilibrium state the resulting equation reduces to

$$\int_0^\infty e^{-\alpha/kT}(\eta_0+\zeta+\alpha)\{S_1{}^2(\zeta,\eta_0+\zeta+\alpha)+S_1{}^2(\alpha,\eta_0+\zeta+\alpha)\}\,d\alpha$$
$$=\frac{16\pi m\varpi_2}{\varpi_1 h^3}\int_0^\infty e^{-\alpha/kT}\,\alpha\zeta\,\{S_2{}^1(\zeta,\alpha)+S_2{}^1(\alpha,\zeta)\}\,d\alpha\quad(\zeta<\eta_0).\qquad\ldots\ldots(1230)$$

This holds for all T, and it follows at once from the Lemma that we must have

$$(\eta_0+\zeta+\alpha)\{S_1{}^2(\zeta,\eta_0+\zeta+\alpha)+S_1{}^2(\alpha,\eta_0+\zeta+\alpha)\}$$
$$=\frac{16\pi m\varpi_2}{\varpi_1 h^3}\,\alpha\zeta\,\{S_2{}^1(\zeta,\alpha)+S_2{}^1(\alpha,\zeta)\}\qquad\ldots\ldots(1231)$$

for all α and all $\zeta<\eta_0$.

It is necessary in addition that the rates of production and destruction of atomic ions should balance. The condition is easily obtained. It is

$$\nu_1\int_{\eta_0}^\infty\left(\frac{2\eta}{m}\right)^{\frac{1}{2}}\mu(\eta)\,d\eta\int_0^{\eta-\eta_0}S_1{}^2(\zeta,\eta)\,d\zeta$$
$$=\nu_2\int_0^\infty\int_0^\infty\left(\frac{2\zeta}{m}\right)^{\frac{1}{2}}\left(\frac{2\xi}{m}\right)^{\frac{1}{2}}\mu(\zeta)\,\mu(\xi)\,S_2{}^1(\zeta,\xi)\,d\zeta d\xi,\qquad\ldots\ldots(1232)$$

which reduces with the aid of the lemma, and the laws of the equilibrium state, to

$$(\eta_0+\alpha)\int_0^\alpha S_1{}^2(\zeta,\eta_0+\alpha)\,d\zeta=\frac{16\pi m\varpi_2}{\varpi_1 h^3}\int_0^\alpha\zeta(\alpha-\zeta)\,S_2{}^1(\zeta,\alpha-\zeta)\,d\zeta\quad(\textit{all }\alpha).$$
$$\ldots\ldots(1233)$$

This condition however is not entirely new. For if we write $\alpha-\zeta$ for α in (1231) that equation becomes

$$(\eta_0+\alpha)\{S_1{}^2(\zeta,\eta_0+\alpha)+S_1{}^2(\alpha-\zeta,\eta_0+\alpha)\}$$
$$=\frac{16\pi m\varpi_2}{\varpi_1 h^3}\,\zeta(\alpha-\zeta)\,\{S_2{}^1(\zeta,\alpha-\zeta)+S_2{}^1(\alpha-\zeta,\zeta)\}.$$

If both sides of this equation are integrated with respect to ζ from 0 to α, it reduces to (1233), which will therefore be satisfied in virtue of (1231) when (1231) has been established for unlimited ζ.

It remains to consider the electron balance for $\zeta>\eta_0$. Expressions (1228)′ and (1229) still give the rates of creation by ionization and destruction by capture. There is now in addition a destruction of ζ-electrons by ionization at a rate

$$\nu_1\left(\frac{2\zeta}{m}\right)^{\frac{1}{2}}\mu(\zeta)\,d\zeta\int_0^{\zeta-\eta_0}S_1{}^2(\alpha,\zeta)\,d\alpha,\qquad\ldots\ldots(1234)$$

equal of course to the rate of formation of ions by ζ-electrons. There is also creation by capture. The first argument of $S_2{}^1(\alpha,\xi)$ refers to the electron that is bound. The energy of the electron left free on binding an α-electron in interplay with a ξ-electron is $\xi + \alpha + \eta_0$. If therefore $\xi + \alpha + \eta_0 = \zeta$, we have to sum over all triple encounters of the type

$$\alpha,\ \zeta - \alpha - \eta_0 \quad (0 < \alpha < \zeta - \eta_0),$$

and shall so find that ζ-electrons are created at a rate

$$\nu_2 d\zeta \int_0^{\zeta - \eta_0} \left(\frac{2\alpha}{m}\right)^{\frac{1}{2}} \left\{\frac{2(\zeta - \alpha - \eta_0)}{m}\right\}^{\frac{1}{2}} \mu(\alpha)\, \mu(\zeta - \alpha - \eta_0)\, S_2^{\,1}(\alpha, \zeta - \alpha - \eta_0)\, d\alpha. \qquad \ldots\ldots(1235)$$

The electron equation now contains four terms, and equates (1228)′ and (1235) to (1229) and (1234). But on account of (1233) the extra terms (1234) and (1235) balance by themselves. For they will so balance if

$$\zeta \int_0^{\zeta - \eta_0} S_1^{\,2}(\alpha, \zeta)\, d\alpha = \frac{16\pi m \varpi_2}{\varpi_1 h^3} \int_0^{\zeta - \eta_0} \alpha (\zeta - \alpha - \eta_0)\, S_2^{\,1}(\alpha, \zeta - \alpha - \eta_0)\, d\alpha,$$

which is (1233).

The hypothesis of preservation therefore demands only the necessary and sufficient condition* (1231) for all α and ζ; the hypothesis of detailed balancing requires the somewhat more restrictive (1228). In the further analysis of collision processes we shall be content to employ only the hypothesis of detailed balancing. The foregoing examples will be sufficient to put the reader on his guard against ascribing logical necessity to this natural and sufficient hypothesis.

§ **17·61**. *The evidence of β-ray results for the form of $S_1^{\,2}(\zeta, \eta)$ and $S_2^{\,1}(\zeta, \eta)$*. The values of $S_1^{\,2}(\zeta, \eta)$ and $S_2^{\,1}(\zeta, \eta)$ should in principle be directly calculable on the new mechanics, but as yet the actual calculations can only be formulated for the collisions of electrons with hydrogen atoms, and even in this case they have not yet been carried through. It is still necessary therefore to use elementary theory and experimental evidence of some kind or other to estimate these quantities, and it is possible to estimate the mean collision area $S_1^{\,2}(\zeta, \eta)$ for ionization with the ejection of a ζ-electron by a study of the theory of, and experiments on, the passage of β-rays through gases. The classical theory of this phenomenon, developed by J. J. Thomson† and Bohr‡, seems to apply with quite considerable accuracy. It leads to a V^4-law for ranges, which is fairly closely obeyed, though the absolute value of the numerical coefficient in the stopping power to which it leads is somewhat too small§. A further slight extension of the theory by the present writer||, in which we require to know only the

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* This result was first given completely correctly by R. Becker, *Zeit. für Phys.* vol. XVIII, p. 325 (1923), eq. (34).

† J. J. Thomson, *Phil. Mag.* vol. XXIII, p. 449 (1912).

‡ Bohr, *ibid.* vol. XXIV, p. 10 (1913); vol. XXX, p. 581 (1915).

§ C. T. R. Wilson, *Proc. Roy. Soc.* A, vol. CIV, pp. 1, 192 (1923), especially pp. 196, 199.

|| R. H. Fowler, *Proc. Camb. Phil. Soc.* vol. XXI, p. 521 (1923).

ratio $S_1^2(\zeta, \eta)/S_1^2(\zeta', \eta)$, leads to the result that the average expenditure of energy by the β-ray, per pair of ions made, should be four-thirds of the ionization potential. An analysis of the ionization made by α-particles in helium, which is of course mainly due to secondary ionization by the slow electrons (δ-rays) emitted along the track, confirms this estimate. The average energy spent by the α-particle is 33 volts per ion pair made*, and four-thirds of the ionization potential is 32·7 volts. Lehmann has in fact measured directly the average number of ions made by slowish electrons with velocities between 200 and 1000 volts and found in helium that the average loss of energy per pair of ions is still just 33 volts. This is the only gas in which a comparison can be made which is free from all complications.

These experimental confirmations refer mainly to high velocities of the electron, but it is really the lower velocities, especially those just greater than η_0, which are of the main interest. In this region information is still very scanty. It is shown in the next paragraph that the effective target for ionization is on the classical theory

$$\frac{\pi\epsilon^4}{\eta}\left(\frac{1}{\eta_0}-\frac{1}{\eta}\right) \quad (\eta \geqslant \eta_0)$$

for each electron of ionization potential η_0. This has a maximum for $\eta = 2\eta_0$ when its value is $\pi\epsilon^4/4\eta_0^2$. For an atom for which

$$\eta_0 = 10 \text{ volts} = 1{\cdot}591 \times 10^{-11} \text{ erg}.$$

this area works out at $1{\cdot}56 \times 10^{-16}$ cm.^{2}, which is comparable with the area of the whole atom, as determined from its behaviour as an imperfect gas. This result fits in satisfactorily with the work of Franck and others on the determination of ionization potentials. A point of great uncertainty however is whether the target area really tends to zero as $\eta \rightarrow \eta_0$. Certain experiments by Lehmann† on gases such as argon, which lead to energy losses per pair of ions much greater than four-thirds of the *first* ionization potential, seem to indicate that perhaps the target area has a non-zero limit as $\eta \rightarrow \eta_0$ or even perhaps its maximum value there. This would probably be in accord with the target area for ionization by the photoelectric effect. One may hope for more light on this important point shortly. In the meantime in a rough survey it seems legitimate to take the classical theory as it stands for both high and low velocities, as giving correctly the relative frequency of ejection of ζ- and ζ'-electrons and an absolute numerical coefficient of the right order.

If then for the moment p denotes the distance of the line of impact of

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* Lehmann, *Proc. Roy. Soc.* A, vol. cxv, p. 624 (1927); Lehmann and Osgood, *ibid.* p. 609.

† Lehmann, *loc. cit.*

the η-electron from the electron which it is to knock out of the atom, there is a precise relation between this p and ζ, namely*

$$p^2 = \frac{\epsilon^4}{\eta^2}\left(\frac{\eta}{\zeta + \eta_0} - 1\right), \qquad \ldots\ldots(1236)$$

$$-\,2\pi p\,dp = \frac{\pi\epsilon^4}{\eta}\,\frac{d\zeta}{(\zeta + \eta_0)^2}. \qquad \ldots\ldots(1237)$$

This is the average effective target of the present theory for each electron of ionization potential η_0. In the present notation $\Sigma_1{}^2\,(p, \zeta, \eta)\,d\zeta = 1$ for this area and is otherwise zero. Thus

$$S_1{}^2\,(\zeta, \eta) = \frac{\pi\epsilon^4}{\eta}\,\frac{1}{(\zeta + \eta_0)^2}, \qquad \ldots\ldots(1238)$$

for each electron with some doubts as to the numerical factor π. For the process of capture

$$\frac{16\pi m\varpi_2}{\varpi_1 h^3}\,\alpha\zeta S_2{}^1\,(\zeta, \alpha) = (\eta_0 + \zeta + \alpha)\,S_1{}^2\,(\zeta, \eta_0 + \zeta + \alpha) = \frac{\pi\epsilon^4}{(\zeta + \eta_0)^2},$$

$$S_2{}^1\,(\zeta, \alpha) = \frac{\varpi_1 h^3}{16\pi m\varpi_2}\,\frac{1}{\alpha\zeta}\,\frac{\pi\epsilon^4}{(\zeta + \eta_0)^2}. \qquad \ldots\ldots(1239)$$

This makes the mean effective collision "time-(area)^2" for capture tend to infinity as $\alpha \to 0$ or $\zeta \to 0$. This is perhaps unexpected, but in no way physically impossible. It merely means that very slow electrons are very good at being caught or at helping others to be caught.

§ **17·62**. *The general nature of elastic collisions between electrons and atoms.* It seems convenient to introduce at this point a few remarks about the nature of collisions in general according to the new quantum theory, and collisions between electrons and atoms in particular with reference also to experimental facts such as Ramsauer's experiments. In our discussions hitherto of collisions of atoms with atoms we have treated the action as if it were a determinate motion in some particular field of force. In the discussion of the collisions of electrons with atoms we have formulated the interaction more generally, by introducing a probability coefficient for the production of a given result by a given type of encounter. From the classical point of view this is merely an indication that we have not wished (or been able) to make a closer analysis, and it is true that in § 17·61 we have made such a closer analysis in a simple case and reduced the action to a determinate motion. But from the point of view of the newer quantum theory the formulation in terms of probability coefficients is probably fundamental, and does not appear likely to be removed by further analysis. The spirit of § 17·6 would appear to be a proper spirit, and the other discussions should perhaps be recast into similar forms. For example, our whole discussion

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* See, for example, Fowler, *loc. cit.*

of the familiar elastic collisions of the kinetic theory leading up to Boltzmann's theorem was based on determinate dynamical encounters. It is likely that this should be discarded and the interaction reformulated in terms of probability coefficients for a given exchange of momentum. It will be easy to derive the necessary and sufficient relations between pairs of probability coefficients for detailed balancing which will then also preserve the same equilibrium state. It does not however appear worth while to undertake such an analysis until we have more *a priori* knowledge as to what functional forms the probability coefficients may be expected to take.

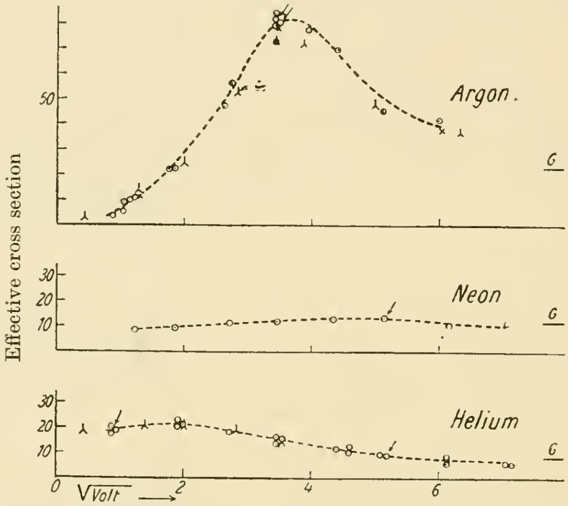

Fig. 28. The Ramsauer effect. The curves show the relative effective cross-section of the atoms named for collisions with electrons, as a function of the accelerating voltage. The line marked G shows the cross-section deduced from ordinary transport phenomena.

In the case of elastic collisions between electrons and atoms however it is already clear from Ramsauer's experiments that some such radical reformulation of the classical collision theory is necessary, at least for very slow electrons. Ramsauer measures in effect the mean free path of directed electrons as a function of their velocity—that is to say the average distance they go before they suffer an appreciable loss of their initial momentum. The determination of the mean free path is of course equivalent to the determination of the target area in any atom for deflecting the electron appreciably. The target area for an atom like an elastic sphere is a constant independent of the electron velocity. The target area for a classical centre of force varies with the velocity, but always so that the target area increases as the velocity of the electron diminishes. The actual variation with velocity observed by Ramsauer is shown in Fig. 28. Actually the target area for some atoms becomes rapidly very small for small velocities. There would be no formal difficulty in specifying a consistent set of probability coefficients for electronic deflections based on these and similar experimental results, but at present they only fix the integral of the probability coefficient taken over all angles above a certain minimum.

§ **17·7**. *General frequency relations for 2- and 3-body encounters leading to dissociation and recombination.* We will now reformulate the results of the last few sections accurately for bodies of comparable masses. We have already sufficiently analysed a 2-body encounter; we have now to extend this analysis to 3-body encounters.

The nature of any encounter can only be a function of the *relative* motion of the systems, and the motion of the centre of gravity of the systems will be unaltered by any interaction in which momentum is conserved. For an encounter of 3-bodies we therefore write

$$\left.\begin{aligned}(m_0+m_1+m_2)\,\mathbf{U} &= m_0u_0+m_1u_1+m_2u_2\\ \xi_1 &= u_1-u_0\\ \xi_2 &= u_2-u_0\end{aligned}\right\},\ \text{etc.} \qquad \ldots\ldots(1240)$$

These equations can be solved at once for u_0, u_1, u_2, and we find

$$\left|\frac{\partial\,(\mathbf{U},\xi_1,\xi_2)}{\partial\,(u_0,u_1,u_2)}\right| = 1, \qquad \ldots\ldots(1241)$$

$$m_0u_0^2+m_1u_1^2+m_2u_2^2 = (m_0+m_1+m_2)\,\mathbf{U}^2 + \frac{1}{m_0+m_1+m_2}\{m_1(m_0+m_2)\,\xi_1^2 - 2m_1m_2\xi_1\xi_2 + m_2(m_0+m_1)\,\xi_2^2\}. \qquad \ldots\ldots(1242)$$

We shall use similar equations for the other components, and θ for the angle between V_1, (ξ_1, η_1, ζ_1) and V_2, (ξ_2, η_2, ζ_2).

Now the number of triple combinations in which systems of types 0, 1, 2, masses m_0, m_1, m_2 and velocity components u_0, u_1, u_2, etc., lie simultaneously in volume elements $d\omega_0$, $d\omega_1$, $d\omega_2$ is by the usual formula

$$\nu_0\nu_1\nu_2\frac{(m_0m_1m_2)^{\frac{3}{2}}}{(2\pi kT)^{\frac{9}{2}}}\,e^{-\eta/kT}\,do_0\,do_1\,do_2\,d\omega_0\,d\omega_1\,d\omega_2, \qquad \ldots\ldots(1243)$$

where

$$\eta = \tfrac{1}{2}m_0(u_0^2+v_0^2+w_0^2)+\tfrac{1}{2}m_1(u_1^2+v_1^2+w_1^2)+\tfrac{1}{2}m_2(u_2^2+v_2^2+w_2^2).$$

Using the substitutions of the preceding paragraph this reduces to

$$\nu_0\nu_1\nu_2\frac{(m_0m_1m_2)^{\frac{3}{2}}}{(2\pi kT)^{\frac{9}{2}}}\exp\left[-\frac{1}{2kT}\left\{(m_0+m_1+m_2)(\mathbf{U}^2+\mathbf{V}^2+\mathbf{W}^2) + \frac{1}{(m_0+m_1+m_2)}[m_1(m_0+m_2)\,V_1^2 - 2m_1m_2V_1V_2\cos\theta + m_2(m_0+m_1)\,V_2^2]\right\}\right]d\omega_0\,d\omega_1\,d\omega_2\,d\mathbf{U}\ldots d\zeta_2. \qquad \ldots\ldots(1244)$$

General 3-body collisions may be classified according to the position of the lines of impact of bodies 1 and 2 on body 0 (asymptotes of orbits) and the time interval between the instants at which the undisturbed relative orbits of (1, 0) and (2, 0) would bring these pairs closest together. To obtain the number of triple collisions per unit volume per unit time in which the lines of impact of 1 and 2 on 0 lie between p_1 and $p_1 + dp_1$ and p_2 and $p_2 + dp_2$ with a time interval between τ and $\tau + d\tau$ we take

$$d\omega_0 = 1, \quad d\omega_1 = 2\pi p_1 dp_1 V_1, \quad d\omega_2 = 2\pi p_2 dp_2 V_2 d\tau. \quad \text{......(1245)}$$

We next change (1244) into spherical polar coordinates for the relative velocities, using the direction of V_1 as the polar axis from which to specify the angles defining the direction of V_2. Then

$$d\xi_1 \ldots d\zeta_2 = V_1^2 dV_1 \sin\psi\, d\psi\, d\chi\, V_2^2 dV_2 \sin\theta\, d\theta\, d\phi. \quad \text{......(1246)}$$

We are only interested in the relative configurations of the orbits, specified by p_1, p_2, τ, V_1, V_2, and θ. The other variables may be eliminated by integration. We then find that the number of collisions so specified is

$$8\pi^2\nu_0\nu_1\nu_2 \frac{\{m_0 m_1 m_2/(m_0 + m_1 + m_2)\}^{\frac{3}{2}}}{(2\pi kT)^3}$$
$$\times \exp\left[-\frac{m_1(m_0 + m_2)V_1^2 - 2m_1 m_2 V_1 V_2 \cos\theta + m_2(m_0 + m_1)V_2^2}{2(m_0 + m_1 + m_2)kT}\right]$$
$$\times 2\pi p_1 dp_1 2\pi p_2 dp_2 d\tau V_1^3 V_2^3 \sin\theta\, dV_1 dV_2 d\theta. \quad \text{......(1247)}$$

The process of capture is a triple encounter of this type resulting in a radiationless union of the bodies 0 and 2. The relative motion of (0, 2) and 1 is to take off the superfluous energy. If $\Sigma_2^1(p_1, p_2, \tau; V_2, \theta, V_1)$ is the probability of this event, and

$$S_2^1(V_2, \theta, V_1) = 4\pi^2 \int_0^\infty p_1 \int_0^\infty p_2 \int_{-\infty}^{+\infty} \Sigma_2^1 dp_1 dp_2 d\tau, \quad \text{......(1248)}$$

then the rate of captures per unit volume of the (V_2, θ, V_1) type is

$$8\pi^2\nu_0\nu_1\nu_2 \frac{\{m_0 m_1 m_2/(m_0 + m_1 + m_2)\}^{\frac{3}{2}}}{(2\pi kT)^3} S_2^1(V_2, \theta, V_1) e^{-\eta/kT} V_1^3 V_2^3 \sin\theta\, dV_1 dV_2 d\theta.$$
$$\text{......(1249)}$$

In this formula η is the energy of the relative motion before the event, which is given explicitly in [ ] in (1247). The energy of the relative motion of the 2-body system (0, 2) and 1 after the event is $\eta + \eta_0$, where η_0 is the energy of dissociation of (0, 2).

By analogy with (1178) the number of 2-body collisions of type (p, V) between (0, 2) and 1 per unit volume per second is

$$4\pi\nu_{02}\nu_1 \left\{\frac{(m_0 + m_2)m_1}{2\pi kT(m_0 + m_1 + m_2)}\right\}^{\frac{3}{2}} \exp\left[-\frac{m_1(m_0 + m_2)V^2}{2(m_0 + m_1 + m_2)kT}\right] 2\pi p\, dp\, V^3 dV.$$
$$\text{......(1250)}$$

The suffix 02 refers to the body (0, 2). These collisions are effective if they result in the dissociation of (0, 2) into 0 and 2. There are then three bodies moving with certain relative velocities and the type of collision depends on the distribution of the available energy. Let

$$\frac{m_0 m_2}{m_0 + m_2} \Sigma_1^2 (p; V_2, \theta, V)\, V_2 \sin \theta\, dV_2 d\theta \qquad \text{......(1251)}$$

be the probability that a body 1 with relative velocity V will so break up (0, 2) that 2 is thrown off with velocity between V_2 and $V_2 + dV_2$ relative to 0, and in such a direction that the angle between V_2 and the velocity V_1 of the body 1 relative to the body 0 after collision lies between θ and $\theta + d\theta$. If V_2 and θ are arbitrarily specified, then V_1 is determined by the conservation of energy, which is

$$\tfrac{1}{2} \frac{m_1 (m_0 + m_2)}{m_0 + m_1 + m_2} V^2 = \eta_0$$
$$+ \tfrac{1}{2} \frac{m_1 (m_0 + m_2) V_1^2 - 2 m_1 m_2 V_1 V_2 \cos \theta + m_2 (m_0 + m_1) V_2^2}{m_0 + m_1 + m_2}. \qquad \text{...(1252)}$$

We now write as usual

$$S_1^2 (V_2, \theta, V) = 2\pi \int_0^\infty p \Sigma_1^2 dp. \qquad \text{......(1253)}$$

The number of dissociations of type (V_2, θ, V) per unit volume per unit time is therefore

$$4\pi \nu_{02} \nu_1 \left\{ \frac{(m_0 + m_2)\, m_1}{2\pi kT\, (m_0 + m_1 + m_2)} \right\}^{\frac{3}{2}} \frac{m_0 m_2}{m_0 + m_2} S_1^2 (V_2, \theta, V)$$
$$\times \exp \left[- \frac{m_1 (m_0 + m_2)\, V^2}{2\, (m_0 + m_1 + m_2)\, kT} \right] V^3 V_2 \sin \theta\, dV dV_2 d\theta. \qquad \text{......(1254)}$$

Let us now assume that there is detailed balancing. Then we must assert here that if the V's are related by (1252) the expressions (1254) and (1249) must be equal. The resulting relation between S_2^1 and S_1^2 refers only to the process $(0, 2) \rightleftarrows 0 + 2$, each body being in a unique internal state before and after the interaction. To see that the process preserves the equilibrium laws with a purely atomic relation between S_2^1 and S_1^2, we must consider the equilibrium laws for just such a reaction. For bodies with more than one internal state, including in this strictly speaking both internal oscillations and rotations, the equilibria of the separate states must be discussed with separate coefficients to S. For the bodies here considered the law of dissociative equilibrium, after (333) and (1013), takes the form

$$\frac{\nu_0 \nu_2}{\nu_{02}} = \left\{ \frac{m_0 m_2}{m_0 + m_2} \right\}^{\frac{3}{2}} \frac{(2\pi kT)^{\frac{3}{2}}}{h^3} \frac{\varpi_0 \varpi_2}{\varpi_{02}} e^{-\eta_0/kT}. \qquad \text{......(1254)}'$$

Inserting this value of $\nu_0\nu_2/\nu_{02}$ in the equation balancing (1254) and (1249) we find

$$V^3 S_1^2 (V_2, \theta, V)\, dV = \left(\frac{m_0 m_2}{m_0 + m_2}\right)^2 \frac{2\pi\varpi_0\varpi_2}{\varpi_{02} h^3} V_1^3 V_2^2 S_2^1 (V_2, \theta, V_1)\, dV_1. \qquad \ldots\ldots(1255)$$

On differentiating (1252) we find

$$V dV = V_1 dV_1 \left(1 - \frac{m_2}{m_0 + m_2} \frac{V_2}{V_1} \cos\theta\right), \qquad \ldots\ldots(1256)$$

and, using this in (1255),

$$V^2 S_1^2 (V_2, \theta, V) \left\{1 - \frac{m_2}{m_0 + m_2} \frac{V_2}{V_1} \cos\theta\right\}$$
$$= \left(\frac{m_0 m_2}{m_0 + m_2}\right)^2 \frac{2\pi\varpi_0\varpi_2}{\varpi_{02} h^3} V_1^2 V_2^2 S_2^1 (V_2, \theta, V_1). \qquad \ldots\ldots(1257)$$

An important special process of this type is *ionization*, in which m_2 is negligibly small compared with m_0. In that case when the body 1 is of atomic (not electronic) mass classical dynamics requires that $V_2 < 2V$, while V_1 and V are only slightly different. Thus V_2/V_1 is of the order unity at most, $\varpi_2 = 2$ and the $\{\}$ reduces to unity. Thus (1257) becomes with sufficient accuracy

$$V^2 S_1^2 (V_2, \theta, V) = \frac{4\pi\varpi_0 m_2^2}{\varpi_{02} h^3} V_1^2 V_2^2 S_2^1 (V_2, \theta, V_1), \qquad \ldots\ldots(1258)$$

with the energy relation

$$\tfrac{1}{2} \frac{m_0 m_1}{m_0 + m_1} V^2 = \eta_0 + \tfrac{1}{2} \frac{m_0 m_1}{m_0 + m_1} V_1^2 + \tfrac{1}{2} m_2 V_2^2. \qquad \ldots\ldots(1259)$$

These equations are the result of ignoring the momentum of the electron in the equations of conservation.

Now that θ no longer appears explicitly in (1258) and (1259), it is possible and often convenient to reformulate these relations more in accord with the relations of the earlier sections, where both the bodies 1 and 2 were electrons. We recall that $\Sigma_2^1 (p_1, p_2, \tau;\, V_2, \theta, V_1)$ is the fraction of all $(p_1, p_2, \tau;\, V_2, \theta, V_1)$-collisions that result in capture. The derived function $S_2^1 (V_2, \theta, V_1)$ is the "target" ($[L]^4\,[T]$) for (V_2, θ, V_1)-collisions to be successful, and so leads to the number of successful (V_2, θ, V_1)-collisions when these are distributed at random in p_1, p_2, and τ. If $S_2^{1*} (V_2, V_1)$ is the mean value of this with respect to θ, so that

$$S_2^{1*} (V_2, V_1) = \tfrac{1}{2} \int_0^\pi S_2^1 (V_2, \theta, V_1) \sin\theta\, d\theta, \qquad \ldots\ldots(1260)$$

then S_2^{1*} is the $[L]^4[T]$ "target" for successful (V_1, V_2)-collisions distributed at random in p_1, p_2, τ and θ.

In a similar way $\Sigma_1^2 (p;\, V_2, \theta, V)\, m_2 V_2 \sin\theta\, dV_2\, d\theta$ is that fraction of (p, V)-collisions which result in (V_2, θ, V_1)-relative motions after causing dissociation. Then

$$S_1^2 (V_2, \theta, V)\, m_2 V_2 \sin\theta\, dV_2\, d\theta$$

is the $[L]^2$ target for V-collisions distributed at random in p to have the result specified. If finally

$$S_1{}^{2*}(V_2, V) = \int_0^{\pi} S_1{}^2(V_2, \theta, V)\sin\theta\, d\theta, \qquad \text{......(1261)}$$

then $S_1{}^{2*} m_2 V_2 dV_2$ is the target for V-collisions distributed at random in p to have (V_2, V_1) relative velocities after dissociation. The complete ionization target for V-collisions distributed at random in p is

$$\int_0^{(V_2)\max} S_1{}^{2*}(V_2, V)\, m_2 V_2 dV_2. \qquad \text{......(1262)}$$

The relation between $S_1{}^{2*}$ and $S_2{}^{1*}$ must be

$$V^2 S_1{}^{2*}(V_2, V) = \frac{8\pi\varpi_0 m_2{}^2}{\varpi_{02}h^3} V_1{}^2 V_2{}^2 S_2{}^{1*}(V_2, V_1) \qquad \text{......(1263)}$$

with the energy relation (1259). Expressed in terms of energy (1263) is identical with the formula (1228) for electron impact. We shall not in future distinguish these S's by an asterisk.

§ **17·71**. *Experimental evidence for the form of* $S_1{}^2(V_2, V)$. The evidence available for the form of $S_1{}^2(V_2, V)$ is provided almost entirely by the phenomena exhibited by α- and β-particles and so refers only to rather high values of V. For definiteness we will suppose that the body 1 is a nucleus of charge $Z\epsilon$ (atomic mass) and velocity V, the body 2 an electron and the body 0 any particular atom or molecule, neutral or ionized, at rest, at concentration ν_0, containing a set of electrons any one of which may be removed with expenditure of energy η_0. Then

(1) The number of *primary* pairs of ions extracted from this group by the body 1 in a length of track dx is

$$\nu_0 dx \int_0^{(V_2)\max} S_1{}^2(V_2, V)\, m_2 V_2 dV_2. \qquad \text{......(1264)}$$

(2) The energy spent on this type of ionization is

$$\nu_0 dx \int_0^{(V_2)\max} (\eta_0 + \tfrac{1}{2}m_2 V_2{}^2)\, S_1{}^2(V_2, V)\, m_2 V_2 dV_2. \qquad \text{......(1265)}$$

(3) The *total* resulting ionization is

$$\nu_0 dx \int_0^{(V_2)\max} g(V_2)\, S_1{}^2(V_2, V)\, m_2 V_2 dV_2, \qquad \text{......(1266)}$$

where $g(V_2)$ is the average number of (pairs of) ions made by a single electron of velocity V_2, which is itself counted as one in $g(V_2)$. Under certain assumptions it can be shown that†

$$g(V_2) = \tfrac{3}{4}\frac{\eta_0 + \tfrac{1}{2}m_2 V_2{}^2}{\eta_0} \qquad \text{......(1267)}$$

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† R. H. Fowler, *Proc. Camb. Phil. Soc.* vol. XXI, p. 531 (1923).

approximately, if the only removable electrons are in the η_0-group. If there are other groups of electrons, η_0 has to be replaced by a mean ionization potential, and it is not yet known how this is to be calculated.

(4) The ratio of the number of V_2-primaries to V_2'-primaries is

$$\frac{S_1^2(V_2, V)\, V_2 dV_2}{S_1^2(V_2', V)\, V_2' dV_2'}. \qquad \text{......(1268)}$$

Generally speaking only integrated effects of S_1^2 are observed from which the form must be estimated as best one may. It is therefore necessary to start with some form of S_1^2 given *a priori*, and all we possess at present are the results of the classical theory of Thomson and Bohr. In this theory the energy q actually transferred to an electron in the process of ionization is identified with the energy q which would be transferred to a free electron initially at rest in a similar encounter, obeying in full the classical laws. If p denotes for a moment the distance of the line of impact from the relevant electron*

$$q = \frac{Z^2\epsilon^4}{\frac{1}{2}m_2 V^2 (p^2 + Z^2\epsilon^4/m_2^2 V^4)}.$$

Since $q = \eta_0 + \frac{1}{2}m_2 V_2^2$ it follows that

$$2p\,dp = -\frac{Z^2\epsilon^4}{V^2}\frac{2V_2 dV_2}{(\eta_0 + \frac{1}{2}m_2 V_2^2)^2}.$$

It follows at once as in § 17·61 that

$$S_1^2(V_2, V) = \frac{\pi Z^2\epsilon^4 n}{\frac{1}{2}m_2 V^2}\frac{1}{(\eta_0 + \frac{1}{2}m_2 V_2^2)^2}, \qquad \text{......(1269)}$$

where n is the number of equivalent electrons in the group, and that the maximum energy transferable is $2m_2V^2$, so that

$$(V_2^2)_{\max} = 4V^2 - 2\eta_0/m_2.$$

When $V_2 > (V_2)_{\max}$, $S_1^2 = 0$. These formulae are naturally practically the same as those for ionization by electron impact, the only difference being in $(V_2)_{\max}$. This formula for S_1^2 is not particularly successful in describing the facts associated with the ionization and rate of loss of energy of α- and β-particles passing through matter. The form of dependence on V_2 is the most successful part†. Even when corrected by Thomas‡ for the motion of the electrons in the atom the results, though much better, are still somewhat unsatisfactory. The form is probably correct for very large V (β-particle velocities), and we might perhaps put

$$S_1^2(V_2, V) = \frac{Z^2 n f(V^2)}{(\eta_0 + \frac{1}{2}m_2 V_2^2)^2}, \qquad \text{......(1270)}$$

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* See, for example, R. H. Fowler, *Proc. Camb. Phil. Soc.* vol. XXI, p. 526 (1923).

† R. H. Fowler, *Proc. Camb. Phil. Soc.* vol. XXII, p. 253 (1924).

‡ L. H. Thomas, *Proc. Camb. Phil. Soc.* vol. XXIII, p. 713 (1927).

where $f(V^2)$ is some function of the velocity V which is practically independent of V_2, η_0, Z and n, and approaches (1269) as $V \to \infty$. More than this we cannot do at present and must await the development of the new mechanics. The corresponding form of S_2^1 is

$$S_2^1(V_2, V_1) = \frac{n\varpi_{02}h^3Z^2}{8\pi\varpi_0 m_2^2} \frac{\left\{\frac{2\eta_0(m_0+m_1)}{m_0m_1} + V_1^2 + \frac{m_2(m_0+m_1)}{m_0m_1}V_2^2\right\}}{V_1^2V_2^2}$$

$$\times \frac{f\left\{\frac{2\eta_0(m_0+m_1)}{m_0m_1} + V_1^2 + \frac{m_2(m_0+m_1)}{m_0m_1}V_2^2\right\}}{(\eta_0 + \frac{1}{2}m_2V_2^2)^2}. \quad \text{......(1271)}$$

§ **17·72**. *The laws of detailed balancing for general collisions.* It is perhaps worth while in conclusion to consider a very general formulation of the laws of detailed balancing for collisions given by Dirac*, which brings out the main features better than the discussion of § 17·7.

We start by observing that in its ordinary form Maxwell's law for the density-in-velocity or density-in-momentum of systems per unit volume is invariant for a transformation from any set of axes to another moving relatively to the former with constant velocity. For relative to the old axes the density-in-momentum is

$$f = Ae^{-(p_1^2+p_2^2+p_3^2)/2mkT},$$

and if the transformation is $p_1' = p_1 + \delta$, then relative to the second set the density-in-momentum is

$$f' = Ae^{-\{(p_1'-\delta)^2+p_2'^2+p_3'^2\}/2mkT}$$

which is unaltered $(f = f')$.

We then consider a general encounter between n material systems in which the rth system has initially a momentum in a region $(dp_1dp_2dp_3)_r$, and in which as a result of the encounter n' material systems leave the scene of action, the rth having a momentum in a region $(dp_1'dp_2'dp_3')_r$. A material system may be of course any molecule, atom, or ion in any specified stationary state, or a free electron, but not here a quantum of radiation. The n' systems must have the same material constituents, but recombined in any manner whatever. The velocity of the centre of gravity of the systems both before and after is V. We then transform to a frame of reference in which the centre of gravity is at rest, and use a zero suffix to distinguish quantities measured in this frame, which we call the normal frame. If we assume for the present that the momenta before and after the encounter are all independent, the number of such encounters per unit volume per second will be of the form

$$\left[\prod_1^n f_r\,(dp_1dp_2dp_3)_r\right]_0 . \,\phi\, . \prod_1^{n'} (dp_1'dp_2'dp_3')_r, \quad \text{......(1272)}$$

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* Dirac, *Proc. Roy. Soc.* A, vol. cvi, p. 581 (1924).

where ϕ is an atomic probability coefficient which must be independent of T and V and depend only on the momenta of the systems in the normal frame of reference both before and after the encounter. It is unnecessary here to analyse ϕ further. It must be supposed to contain the velocity factors for the speeds with which the various systems approach the scene of action. In the same way the corresponding number of reverse encounters is

$$\left[\prod_1^n f_r' \, (dp_1'dp_2'dp_3')_r\right]_0 . \, \phi' \, . \prod_1^n (dp_1dp_2dp_3)_r. \qquad \text{......(1273)}$$

By the principle of detailed balancing we may equate these two expressions, and obtain

$$[f_1 \cdots f_n]_0 \, \phi = [f_1' \cdots f_{n'}']_0 \, \phi'. \qquad \text{......(1274)}$$

Our provisional assumption that all the momenta are independent is not true. There are at least seven relations (energy, and zero momenta in the normal frame before and after the encounter), and there may be more in special cases. We can allow for this most simply by making ϕ and ϕ' zero except when these necessary conditions are fulfilled. There will then be fewer differentials in (1272), but on account of the complete reversibility the same differentials will drop out of (1273), and (1274) will remain generally true. If we now transform back to the frame in which the whole assembly is at rest, owing to the invariance property of Maxwell's law, we find the general collision relation

$$f_1 f_2 \cdots f_n \phi = f_1' f_2' \cdots f_n' \phi'. \qquad \text{......(1275)}$$

Now if $F_1, \ldots, F_n$ are the partition functions for the internal energies of the corresponding systems, and $\nu_1, \ldots, \nu_n$ their total concentrations, then, in the equilibrium state,

$$f_1 f_2 \cdots f_n = \frac{\varpi_1 \ldots \varpi_n}{F_1 \ldots F_n} \frac{\nu_1 \ldots \nu_n}{\prod_1^n (2\pi m_r kT)^{\frac{3}{2}}} e^{-\Sigma\left\{\epsilon_r + \frac{1}{2m_r}(p_1^2+p_2^2+p_3^2)_r\right\}/kT},$$

with a corresponding expression for $f_1'f_2' \ldots f_n'$. There is also the equation of dissociative equilibrium

$$\frac{\nu_1 \ldots \nu_n}{\nu_1' \ldots \nu_n'} = \frac{F_1 \ldots F_n}{F_1' \ldots F_n'} \prod_1^n \frac{(2\pi m_r kT)^{\frac{3}{2}}}{h^3} \Big/ \prod_1^{n'} \frac{(2\pi m_r' kT)^{\frac{3}{2}}}{h^3},$$

and the energy equation

$$\sum_1^n \left\{\epsilon_r + \frac{1}{2m_r}(p_1^2 + p_2^2 + p_3^2)_r\right\} = \sum_1^{n'} \left\{\epsilon_r' + \frac{1}{2m_r'}(p_1'^2 + p_2'^2 + p_3'^2)_r\right\}.$$

Combining these equations we find the relation

$$\frac{\phi'}{\phi} = \frac{\varpi_1 \ldots \varpi_n}{\varpi_1' \ldots \varpi_{n'}'} (h^3)^{n'-n}. \qquad \text{......(1276)}$$

The relationships of the preceding sections are special cases of (1276) in which the coefficients S have been defined somewhat differently from ϕ and ϕ'.*

§ **17·8.** *Laws of interaction of gaseous molecules with solid walls.* We can apply the general arguments of § 17·1 to show that collisions of molecules with the walls of the containing vessel must separately be capable of preserving the equilibrium state. For the equilibrium state of the gas is independent of the shape of the enclosure containing the gas, and by varying the shape of the enclosure the relative importance of the *surface* can be varied independently of all other parameters. Collisions with the walls vary in frequency as the surface multiplied by the molecular density and therefore differently from collisions between molecules ([density]^2) or radiative effects (density).

We have already made use of this principle in discussing the relation between the emission and absorption of electrons at a metal surface in § 11·2. It will therefore only be necessary to generalize the analysis of that section here. If the gaseous phase is practically perfect, and contains a set of systems (atoms, molecules or electrons) at concentration ν, then the number of such systems with velocities between c and $c + dc$ which strike unit area of any solid surface per unit time in a direction within a solid angle $d\Omega$ at an angle θ with the normal to the surface is

$$\nu \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} c^3 e^{-mc^2/2kT} \cos\theta \, dc d\Omega. \qquad \text{......(1277)}$$

This is the number of such systems which are destroyed in unit time by unit area of wall. By the same reasoning an equal number *moving in the reverse direction* must be thrown off by the wall in unit time in order to preserve equilibrium.

As we are no longer dealing with single atoms and molecules we can no longer argue that elementary processes must be independent of the temperature.

In very high vacua collisions with walls are all important in controlling the equilibrium state, and a series of researches notably by Knudsen† Millikan‡ and Langmuir§ have been undertaken to elucidate the properties of the equilibrium state and steady non-equilibrium states under such conditions. These investigations have thrown much light on the nature of the mechanism which we call "collision with a wall". The conclusion is

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[*] Dirac, *loc. cit.*, presents the argument somewhat differently and derives the equations of dissociative equilibrium, etc., from the principle of detailed balancing by substantially the reverse of the foregoing argument. The principle of the invariance of f which must be then known *a priori* can, he shows, be deduced from the properties of the Lorentz transformation.

[†] Knudsen, *Ann. der Phys.* vol. XXVIII, pp. 75, 999 (1909), and a series of other papers up to vol. XXXIV, p. 593 (1911).

[‡] Millikan, *Phys. Rev.* vol. XXI, p. 217, vol. XXII, p. 1 (1923).

[§] Langmuir, *Trans. Faraday Soc.* vol. XVII, pp. 607, 621 (1921).

that in general the greater part of the molecules striking a solid surface actually condense on the surface (stick to it) for a limited period and are then thrown off again. Their direction and velocity of ejection will then naturally have no connection with their direction and velocity of incidence. If this idea of complete lack of correlation is correct, then the molecules evaporating must be thrown off by the wall at a rate given by (1277). This is a conclusion of considerable importance in the researches quoted. It embodies what is known as *Lambert's law of diffuse reflection*. It contains however more information than Lambert's law which refers only to distribution with angle. When we study steady states in which we have no longer a temperature equilibrium, the T in (1277) ceases to have a definite meaning. The general form of the molecular emission law may be expected to hold good, but T becomes a parameter determined by the temperature of the incident molecules and the temperature and other properties of the wall. A great part of Knudsen's researches deals with particular cases of this type.

In other cases we have evidence, from the rate of transfer of momentum to the walls during steady states of flow, that an appreciable fraction of the incident molecules do not condense, or at least do not communicate momentum to the wall on impact. In such cases it is usual (and probably adequate) to describe the interaction by means of an accommodation coefficient f which is such that the interaction proceeds as if the fraction f of all the incident molecules condenses on impact and $1-f$ is reflected according to the laws of reflection of light ("specular reflection"). It is easy to see that specular reflection also conserves (1277). It is usually assumed that f is independent of c and θ.

There is good evidence for condensation and consequent uncorrelated re-emission obeying (1277). Beside this perfectly diffuse reflection the only simple types of reflection which preserve (1277) are perfectly specular reflection and reflection by direct reversal of path. The latter is physically unacceptable. The former has undoubtedly been used to supplement perfectly diffuse reflection on the ground of its simplicity. A more correct analysis would doubtless fuse both the perfectly diffuse and perfectly specular reflections together into a single law with a varying correlation between the direction of incidence and all possible directions of re-emission. It would present no difficulty to formulate such laws satisfying (1277), but at present they do not appear to be of interest.

CHAPTER XVIII

CHEMICAL KINETICS IN GASEOUS SYSTEMS

§ **18·1**. *General nature of reactions in gaseous assemblies**. When gases which undergo a chemical reaction are mixed, it is natural to look to the collisions between the reacting molecules for the source of the rearrangements that occur. The ideas and the formulae of the last chapter should therefore enable a satisfactory account to be given of those gaseous reactions which do not depend observably on radiation†, and proceed sufficiently slowly for the calculation of collisions by the equilibrium theory to be applicable. We shall see that this expectation is in general fulfilled, but there is at least one quite exceptional example in explaining which the theory is strained to the uttermost. It is probable that some other considerations must enter.

Let us start by defining more closely what we mean by "sufficiently slow" for the reactive collisions not to upset the numbers of collisions calculated on the equilibrium theory. All reactions of course proceed to their equilibrium point, at which all the considerations of the equilibrium theory must apply. But in chemical kinetics we are concerned with the speed of unbalanced reactions proceeding primarily in one direction, and it is these which we try to record by observation. In order to calculate such speeds from the equilibrium theory we have to assume that certain types of collisions are effective, and that these types occur (in spite of the one-sided reaction) with a frequency corresponding to that which would be deduced from the properties of an equilibrium state. It will be best to examine the requirements of this condition in the various special cases discussed.

In the examination of a gaseous reaction the first point to be established is that it *is* a reaction between gases (homogeneous reaction) and not a reaction occurring primarily between gas molecules condensed on the walls of the containing vessel—catalysed by the walls—(a heterogeneous reaction). We shall only discuss homogeneous gas reactions here: heterogeneous reactions are more naturally discussed as part of the kinetic theory of surfaces. There are not many simple homogeneous gas reactions known. Catalysis by the walls dominates the vast majority of apparently homo-

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* For a general account see Hinshelwood, *The Kinetics of Chemical Change in Gaseous Systems* (1926). This chapter is based almost entirely on Hinshelwood's account and later work, except that there is one of his *quantitative* interpretations which I do not accept.

† The best known example of a photo-sensitive reaction, or photo-chemical change, in gases is the reaction $H_2 + Cl_2 \rightarrow 2HCl$ under the influence of visible light.

geneous reactions. Those that are known to be simple and homogeneous, for which the velocity of a perfectly definite molecular event can be and has been observed, are all described in detail by Hinshelwood*.

Having established the homogeneity of a reaction, its velocity is studied as a function of the temperature and the concentrations. The dependence on the concentration at once classifies the reactions into different orders of which we need only consider two here, namely:

First order or unimolecular reactions, with a velocity proportional to the concentration so that

$$-\frac{d\nu}{dt}=\kappa\nu, \qquad \text{......(1278)}$$

where κ depends only on the temperature.

Second order or bimolecular reactions, with a velocity proportional to the square or product of the concentrations so that

$$-\frac{d\nu}{dt}=\kappa\nu^2 \text{ or } -\frac{d\nu_1}{dt}=-\frac{d\nu_2}{dt}=\kappa\nu_1\nu_2, \qquad \text{......(1279)}$$

and κ again depends only on the temperature. This function κ is called *the velocity constant* of the reaction. These equations of course only hold before the products of the reaction interfere in any way such as by beginning the reverse reaction. But κ is usually measured† under conditions in which (1278) and (1279) are sufficiently exhaustive. We shall not discuss the methods by which the κ of these equations is determined in practice.

When we compare the observed rates of reaction expressed in numbers of molecules per second with the numbers of collisions per molecule per second we find that at most one collision in 10^8 can lead to a reaction. Gaseous reactions cannot ordinarily be quantitatively studied if the initial concentration of reactants fall to half value in a time as short as one second, and the usual time to half value is of the order of at least a minute. But by (1176) the number of collisions per molecule per second is

$$\nu\sigma^2\left(\frac{4\pi kT}{m}\right)^{\frac{1}{2}}.$$

Inserting numerical values with $\sigma = 3\times10^{-8}$, $k = 1{\cdot}37\times10^{-16}$, $T = 273$, $\nu = 2{\cdot}7\times10^{19}$, $m = 1{\cdot}65\times10^{-24}\,A$, where A is the chemical molecular weight, this reduces to

$$\frac{1{\cdot}3\times10^{10}}{\sqrt{A}}.$$

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* Hinshelwood, *loc. cit.* Recent additions to his list are: (1) "Decomposition of Acetone", Hinshelwood and Hutchison, *Proc. Roy. Soc.* A, vol. cxi, p. 245 (1926). (2) "Decomposition of Propionic Aldehyde", Hinshelwood and Thompson, *Proc. Roy. Soc.* A, vol. cxiii, p. 221 (1926). (3) "Decomposition of Diethyl Ether", Hinshelwood, *Proc. Roy. Soc.* A, vol. cxiv, p. 84 (1927). (4) "Decomposition of Dimethyl Ether", Hinshelwood and Askey, *Proc. Roy. Soc.* A, vol. cxv, p. 215 (1927).

† See Hinshelwood, *loc. cit.* p. 48, for a more general case.

This is to be compared with a number of reactive collisions at most of the order one per second. Thus reactive collisions are completely exceptional.

The clue to this behaviour is provided by the strikingly large temperature variation of the velocity constant κ. Whereas the total number of collisions varies as $\sqrt{T}$, that is hardly at all over wide ranges of temperature, the velocity constant ordinarily doubles itself for a rise of temperature of about 10° C. This suggests at once that the effective collisions are selected not from all collisions, but only from all collisions with more than a certain large minimum of distributable energy.

The actual form of κ which can be successfully compared with observation is suggested by equilibrium considerations. Consider for definiteness a bimolecular reaction between unlike molecules of types 1 and 2 which combine to form two other molecules of types 3 and 4. There is an equilibrium point which is given by

$$\frac{\nu_1\nu_2}{\nu_3\nu_4}=\frac{f_1(T)f_2(T)}{f_3(T)f_4(T)}=\mathrm{K}, \qquad \text{......(1280)}$$

where K is commonly spoken of as the equilibrium constant. For *all* concentrations we know from the velocity measurements that the rate of destruction of systems 1 and 2, with creation of systems 3 and 4, is $\kappa\nu_1\nu_2$. By the arguments of § 17·1 the rate of creation of systems 1 and 2 and destruction of 3 and 4 must be of the form $\kappa'\nu_3\nu_4$, and at the equilibrium point these are equal, so that

$$\mathrm{K}=\kappa'/\kappa. \qquad \text{......(1281)}$$

Now it follows thermodynamically* from the definition of K that

$$\frac{d\log \mathrm{K}}{dT}=\frac{q}{kT^2}=\frac{Q}{RT^2}, \qquad \text{......(1282)}$$

where Q is the "heat of the reaction". Therefore

$$\frac{d\log\kappa'}{dT}-\frac{d\log\kappa}{dT}=\frac{q}{kT^2}.$$

The form of this equation suggests putting

$$\frac{d\log\kappa}{dT}=\frac{\zeta}{kT^2},\quad \frac{d\log\kappa'}{dT}=\frac{\zeta'}{kT^2},$$

where

$$\zeta-\zeta'=-q$$

and the known approximate constancy of q suggests that perhaps ζ and ζ' are also roughly constant. In that case we find after integration

$$\kappa=Ae^{-\zeta/kT}. \qquad \text{......(1283)}$$

This is the well-known empirical equation of Arrhenius for the velocity constant of a homogeneous gaseous reaction. As so far presented it is purely

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* Or from equation (449) or its equivalent.

tentative, but by plotting log κ against $1/T$ for observations over a sufficient range of temperatures, it is found that (1283) with A and ζ constant gives an entirely adequate representation of the facts. The energy ζ is called *the heat of activation of the reaction*, for, as we shall see, it is closely related to the necessary minimum disposable energy present in a possibly effective collision. We shall show in the following sections how the collision mechanism gives an entirely adequate account of the phenomena we have described.

§ **18·2.** *Simple theory of bimolecular reactions.* Equation (1182) gives us the number of collisions per unit volume per unit time in which the kinetic energy of the relative motion lies between η and $\eta + d\eta$ for simple unlike molecules. Let us suppose that $\sigma(\eta)$ is the fraction of these collisions that lead to reaction. Then

$$\kappa = \frac{2\sigma_{12}^2}{(kT)^{\frac{3}{2}}}\left\{\frac{2\pi(m_1+m_2)}{m_1 m_2}\right\}^{\frac{1}{2}}\int_0^\infty \sigma(\eta)\, e^{-\eta/kT}\,\eta\, d\eta. \quad \ldots\ldots(1284)$$

In order to mimic (1283) the simplest assumption is that

$$\sigma(\eta) = 0 \quad (\eta \leqslant \zeta), \qquad \sigma(\eta) = \alpha \quad (\eta > \zeta),$$

where α is a constant less than or equal to unity. On this assumption

$$\kappa = 2\alpha\sigma_{12}^2\left\{\frac{2\pi(m_1+m_2)}{m_1 m_2}\,kT\right\}^{\frac{1}{2}} e^{-\zeta/kT}\left(\frac{\zeta}{kT}+1\right). \quad \ldots\ldots(1285)$$

This is very nearly of the prescribed form. It is to be observed that the T-variation of κ is so dominated by the exponential term when (as in all actual examples) ζ/kT is fairly large, that the experiments cannot possibly distinguish between

$$Ae^{-\zeta/kT} \text{ and } A'T^s e^{-\zeta/kT}$$

for any moderate value of s. The same difficulty has been already encountered in Richardson's thermionic formulae. This simple assumption therefore yields a formula for fairly large values of ζ/kT,

$$\kappa = A'T^{-\frac{1}{2}}e^{-\zeta/kT}, \quad \ldots\ldots(1286)$$

in which

$$A' = 2\alpha\sigma_{12}^2\left\{\frac{2\pi k(m_1+m_2)}{m_1 m_2}\right\}^{\frac{1}{2}}\frac{\zeta}{k}. \quad \ldots\ldots(1287)$$

The theory thus gives us at once a satisfactory form for κ. We have no *a priori* knowledge of ζ/k, and it must therefore be determined from Arrhenius' equation. When this has been done the theory gives us κ completely in terms of a coefficient α which must be less than unity, and a "molecular diameter" σ_{12}. For like molecules the first factor 2 drops out and $m_1 = m_2$.

To proceed further we must consider an actual example, and choose the decomposition of HI discussed by Hinshelwood. This is primarily homogeneous and bimolecular from 550° K. to 780° K., and its temperature variation satisfies Arrhenius' equation accurately with $\zeta/k = 22{,}000$ ($Q = 44{,}000$ calories). With $\sigma = 2 \times 10^{-8}$, $m_1 = m_2 = 128 \times 1{\cdot}65 \times 10^{-24}$, and $\sqrt{T} = 25$ this gives

$$A' = 2{\cdot}5 \times 10^{-8}\,\alpha,\quad \kappa = 10^{-9}\,\alpha e^{-22{,}000/T}.$$

From the definition of κ
$$\frac{1}{\nu}\frac{d\nu}{dt} = -\kappa\nu.$$

Therefore the fraction of molecules reacting in one second at a concentration of one gram-molecule per litre ($\nu = 6{\cdot}06 \times 10^{20}$) and a temperature 556° T is

$$4 \times 10^{-6}\alpha.$$

The observed value is $3{\cdot}52 \times 10^{-7}$. The observed value is thus obtained* if $\alpha = 1/11$.

This is entirely satisfactory so far as it goes. It only remains for us to verify that this fraction of reactive collisions is small enough for the calculation of collisions with energy more than ζ to be substantially unaffected, i.e. to verify that the reaction is "sufficiently slow". A certain proportion of collisions with relative energy more than ζ will concern at least one molecule whose last collision was also one of the same class. This is the phenomenon *of the persistence of velocities*†. In default of an exact theory of transport phenomena, correction for persistence of velocities was successful in removing the greater part of the numerical error in the simpler theory of these phenomena. In order to be certain that the equilibrium calculations are adequate it is sufficient to assure oneself that allowance for persistence of velocities is unimportant here. The proportion of collisions affected can be fairly high, but even if it is nearly unity only the fraction α at most will be removed by the reaction and the effect on numerical values cannot possibly reach 10 per cent. At the same time the numerical values might begin to be seriously affected if α were larger. The interpretation given by Hinshelwood to his result $\alpha = 1$ is therefore hardly acceptable. It is necessary for α to be small for the simple theory to apply at all. But of course the results of a more exact theory are not likely to be widely different, and will only differ in a numerical factor.

Summing up, we may say that the simple theory of homogeneous bimolecular reactions, namely that *they are reactions by collision which can only occur in a fairly small fraction of collisions in which the relative kinetic energy of the molecules exceeds a certain lower limit determined by Arrhenius' equation*, gives a most satisfying account of the observed facts. We have discussed it only with reference to the reaction

$$(1)\quad 2\mathrm{HI} \rightarrow \mathrm{H_2} + \mathrm{I_2},$$

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* Hinshelwood, *loc. cit.*, concludes that approximately $\alpha = 1$, but he has used an inaccurate formula for the number of collisions.

† Jeans, *loc. cit.* pp. 260, 275, 312.

but the following other reactions have been shown by Hinshelwood to fit equally well into the same theory:

(2) $H_2 + I_2 \rightarrow 2HI$,
(3) $2O_3 \rightarrow 3O_2$,
(4) $2N_2O \rightarrow 2N_2 + O_2$,
(5) $2Cl_2O \rightarrow 2Cl_2 + O_2$,

with other more complicated examples in which the homogeneous bimolecular reaction must be disentangled from other simultaneous effects.

It is at the same time to be remarked that there is not much margin in the above theory as it stands. A different form for $\sigma(\eta)$ might at once require $\alpha > 1$. For example, if $\sigma(\eta) = \alpha\zeta/\eta$ the number of effective collisions is practically unchanged, but if in conformity with some of the collision targets of the last chapter we have, say,

$$\sigma(\eta) = \frac{\alpha\zeta^2}{\eta}\left(\frac{1}{\zeta} - \frac{1}{\eta}\right)$$

we find the number of collisions smaller by loss of the factor ζ/kT. Effective collisions in which the relative kinetic energy of translation exceeds ζ may therefore be somewhat scarce, and it seems to my mind better to recognize even here that there are other sources of energy as yet unexplored in this connection. We proceed therefore in the next section to develop formulae for the number of collisions with given transferable energy in which the transferable energy from all sources is taken into account.

§ **18·3**. *The transferable energy in collisions, including internal energy of the molecules.* It is hardly possible to obtain simple formulae if we consider the rotations and internal vibrations of the molecules as quantized. It will however be sufficiently accurate for present purposes to assume that the molecules are equivalent to molecules whose Hamiltonian function contains s square terms (kinetic or potential) associated with such low frequencies that the classical mechanics apply. Then the classical partition function for the internal energy of such a molecule is

$$\int \dots \int e^{-\eta/kT}\, dp_1 \dots dq_t,$$

where $p_1, \dots, p_t, q_1, \dots, q_t$ are a complete set of Hamiltonian coordinates and

$$\eta = \sum_1^s \alpha_t \mu_t^2,$$

μ being either a p or q; all the p's must occur. The integration is extended over all values from $-\infty$ to $+\infty$ for any μ, and with respect to the other geometrical variables over their proper ranges. To find the fraction with energy between η_1 and $\eta_1 + d\eta_1$ we have to take out that part of the complete integration which corresponds to

$$\eta_1 \leqslant \sum_1^s \alpha_t \mu_t^2 \leqslant \eta_1 + d\eta_1.$$

The number of molecules per unit volume with this internal energy is therefore

$$\nu_1 \frac{\int \cdots \int e^{-\eta/kT}\, d\mu_1 \cdots d\mu_{s\,[\eta_1 \leqslant \Sigma\alpha_t \mu_t^2 \leqslant \eta_1 + d\eta_1]}}{\int \cdots \int e^{-\eta/kT}\, d\mu_1 \cdots d\mu_{s\,[-\infty \leqslant \mu_t \leqslant +\infty]}}. \qquad \text{......(1288)}$$

By the well-known procedure of Dirichlet* this can be reduced to

$$\nu_1 \frac{\eta_1^{\frac{1}{2}s-1}\, e^{-\eta_1/kT}\, d\eta_1}{\int_0^\infty \eta^{\frac{1}{2}s-1}\, e^{-\eta/kT}\, d\eta}, \qquad \text{......(1289)}$$

or

$$\frac{\nu_1}{\Gamma(\frac{1}{2}s)} \left(\frac{\eta_1}{kT}\right)^{\frac{1}{2}s-1} e^{-\eta_1/kT} \frac{d\eta_1}{kT}. \qquad \text{......(1290)}$$

The number of molecules with internal energy greater than η_0 is

$$\frac{\nu_1}{\Gamma(\frac{1}{2}s)} \frac{1}{(kT)^{\frac{1}{2}s}} \int_{\eta_0}^\infty \eta^{\frac{1}{2}s-1}\, e^{-\eta/kT} d\eta, \qquad \text{......(1291)}$$

which, for η_0/kT large, is approximately†

$$\frac{\nu_1}{\Gamma(\frac{1}{2}s)} \left(\frac{\eta_0}{kT}\right)^{\frac{1}{2}s-1} e^{-\eta_0/kT}. \qquad \text{......(1292)}$$

Let us now combine (1290) with (1182). We find that the number of collisions per unit volume per second between a molecule of type 1 with energy η_1 and a molecule of type 2 with energy η_2 and relative kinetic energy ξ is

$$\frac{2\nu_1\nu_2\sigma_{12}^2}{\Gamma(\frac{1}{2}s_1)\,\Gamma(\frac{1}{2}s_2)} \left\{\frac{2\pi(m_1+m_2)}{m_1 m_2}\right\}^{\frac{1}{2}} \frac{e^{-(\eta_1+\eta_2+\xi)/kT}}{(kT)^{\frac{1}{2}s_1+\frac{1}{2}s_2+\frac{3}{2}}}\, \eta_1^{\frac{1}{2}s_1-1}\, \eta_2^{\frac{1}{2}s_2-1}\, \xi\, d\eta_1 d\eta_2 d\xi. \qquad \text{......(1293)}$$

So far as energy considerations go it is conceivable that any collision in which $\eta_1 + \eta_2 + \xi \geqslant \eta_0$ may have a non-zero probability of producing an active molecule or causing a reaction. The total number of such collisions

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* Whittaker and Watson, *Modern Analysis*, p. 258 (ed. 3).

† It may be emphasized that s in these equations is the number of square terms in the energy, not the number of degrees of freedom, so that any harmonic oscillation contributes 2 to s, and any rotation 1.

is therefore obtained by integrating (1293) over all η_1, η_2 and ξ satisfying $\eta_1 + \eta_2 + \xi \geqslant \eta_0$. This number thus reduces by simple substitutions* to

$$\frac{2\nu_1\nu_2\sigma_{12}^2}{\Gamma\left(\frac{1}{2}s_1 + \frac{1}{2}s_2 + 2\right)}\left\{\frac{2\pi\,(m_1 + m_2)}{m_1 m_2}\right\}^{\frac{1}{2}} \frac{1}{(kT)^{\frac{1}{2}s_1 + \frac{1}{2}s_2 + \frac{3}{2}}}\int_{\eta_0}^{\infty} e^{-\lambda/kT}\,\lambda^{\frac{1}{2}s_1 + \frac{1}{2}s_2 + 1}\,d\lambda, \qquad \ldots\ldots(1294)$$

which, for η_0/kT large, is approximately

$$\frac{2\nu_1\nu_2\sigma_{12}^2}{\Gamma\left(\frac{1}{2}s_1 + \frac{1}{2}s_2 + 2\right)}\left\{\frac{2\pi\,(m_1 + m_2)}{m_1 m_2}\,kT\right\}^{\frac{1}{2}}\left(\frac{\eta_0}{kT}\right)^{\frac{1}{2}s_1 + \frac{1}{2}s_2 + 1} e^{-\eta_0/kT}. \qquad \ldots\ldots(1295)$$

If the two molecules are of the same species then of course $m_1 = m_2$ and $\sigma_{12} = \sigma$ and the factor 2 must be removed, for every collision will as usual be found to have been counted twice over in all the foregoing formulae.

The fraction of all collisions with "enough" available energy is easily seen to be

$$\frac{(\eta_0/kT)^{\frac{1}{2}s_1 + \frac{1}{2}s_2 + 1}\, e^{-\eta_0/kT}}{\Gamma\left(\frac{1}{2}s_1 + \frac{1}{2}s_2 + 2\right)}, \qquad \ldots\ldots(1296)$$

which may be very large indeed compared with the fraction $e^{-\eta_0/kT}$, often used in error in this connection.

If it is denied (as is perhaps natural in certain applications) that the internal energy of the second molecule is ever available to serve towards the activation energy of the first, then the formulae (1294) and (1295) will still apply if we put $s_2 = 0$. In fact more generally we can in these formulae always use s_1 and s_2 for the number of square terms in the internal energy *whose energy content is available for redistribution in the collision.*

The total number of reactions can of course only be expressed in terms of a probability coefficient $\sigma(\eta_1, \eta_2, \xi)$. Thus on multiplying (1293) by $\sigma(\eta_1, \eta_2, \xi)$ and integrating we find

$$\kappa = \frac{2\sigma_{12}^2}{\Gamma\left(\frac{1}{2}s_1\right)\Gamma\left(\frac{1}{2}s_2\right)}\left\{\frac{2\pi\,(m_1 + m_2)}{m_1 m_2}\right\}^{\frac{1}{2}} \frac{1}{(kT)^{\frac{1}{2}s_1 + \frac{1}{2}s_2 + \frac{3}{2}}}$$

$$\times \iiint_{\eta_1 + \eta_2 + \xi \geqslant \eta_0} e^{-(\eta_1 + \eta_2 + \xi)/kT}\,\sigma(\eta_1, \eta_2, \xi)\,\eta_1^{\frac{1}{2}s_1 - 1}\,\eta_2^{\frac{1}{2}s_2 - 1}\,\xi\,d\eta_1 d\eta_2 d\xi; \qquad \ldots\ldots(1297)$$

the last few formulae arise from putting $\sigma = 1$ when $\eta_1 + \eta_2 + \xi \geqslant \eta_0$.

When internal energies are taken into account a more accurate investigation of the precise use of Arrhenius' equation is necessary. In practice the observations are used to plot $\log \kappa$ against $1/T$ and determine a slope, which defines the activation energy ζ of the equation

$$\frac{d \log \kappa}{dT} = \frac{\zeta}{kT^2}.$$

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* Whittaker and Watson, *loc. cit.*

The theoretical κ derived by putting simple forms for σ in (1297) is however generally of the form

$$\kappa = B\left(\frac{\eta_0}{kT}\right)^t e^{-\eta_0/kT},$$

so that

$$\frac{d\log\kappa}{dT} = \frac{\eta_0}{kT^2} - \frac{t}{T}.$$

Thus η_0 of the theory and ζ determined by observation are connected by the equation

$$\eta_0 = \zeta + tkT. \qquad \text{......(1298)}$$

The apparent constancy of the experimental ζ in no way prevents ζ being really of the theoretical form (1298), for the experiments could not detect these variations, tkT being small compared with η_0. In calculating whether there are sufficient energetic collisions to give the observed rate of reaction with a small efficiency α we must use the η_0 of (1298) with the observed ζ and a mean value of T. We thus retain the correct temperature variation of κ.

If we now examine how these considerations affect the typical homogeneous bimolecular reaction between simple molecules we see that for a molecule such as HI we must have at least $s = 2$, or for a triatomic molecule $s = 3$ at least. Thus for the reaction $2\mathrm{HI} \rightarrow \mathrm{H}_2 + \mathrm{I}_2$ ($s = 2$ say) we have to replace the factor

$$\frac{\zeta}{kT}\, e^{-\zeta/kT}$$

of (1285) by the factor

$$\tfrac{1}{6}\left(\frac{\eta_0}{kT}\right)^3 e^{-\eta_0/kT}$$

of (1295), with $\eta_0 = \zeta + 3kT$, ζ having its observed value. There are therefore substantially more collisions with enough energy than the simple theory indicates, the extra factor being about 13, which leaves an ample margin.

§ **18·4**. *Homogeneous unimolecular reactions.* There are well-known difficulties in the theory of those unimolecular reactions which are apparently insensitive to radiation. The simplest assumption which will account in any way for the facts is to suppose that the reaction is not elementary but consists of bimolecular activation and deactivation processes which by themselves would keep up a normal equilibrium between activated and inert molecules, while superposed on this there is a definite chance for the spontaneous disintegration of the activated molecules. Provided this disintegration is slow compared with the activation process the equilibrium concentration of activated molecules will be unaffected. This concentration will therefore be proportional to the total concentration and the reaction will apparently obey the unimolecular law. If this theory is correct then there should come a concentration for any unimolecular reaction below which its rate begins to fall below the expected unimolecular rate, for the underlying bimolecular process is there beginning to work too slowly. This form of collision theory for unimolecular reactions is usually associated with the name of Lindemann*.

The state of affairs according to this theory is formally very simple. Let x and y be the concentrations of activated and inert molecules at any time. Let the total number of activations and deactivations in time dt be $Z'y\,dt$ and $Zx\,dt$ respectively. Let $Bx\,dt$ be the number of disintegrations of activated molecules. Then the differential equations which control the process are

$$\left.\begin{aligned}\frac{dx}{dt} &= Z'y - (Z+B)\,x,\\ \frac{dy}{dt} &= -Z'y + Zx.\end{aligned}\right\}\qquad \text{......(1299)}$$

On Lindemann's theory B is a molecular constant and Z and Z' themselves proportional to $x + y$ or perhaps rather of the form $Ax + By + Cz$, where z is the concentration of any diluents plus the gaseous products of reaction.

If we solve equations (1299), assuming that Z and Z' are constants, the general solution takes the form

$$x = L_1e^{-\lambda_1 t} + L_2e^{-\lambda_2 t},\quad y = M_1e^{-\lambda_1 t} + M_2e^{-\lambda_2 t},\quad \text{......(1300)}$$

where λ_1 and λ_2 are the roots of the equation

$$D^2 - D\,(Z + Z' + B) + BZ' = 0.\qquad \text{......(1301)}$$

Using the initial condition that the equilibrium is undisturbed by disintegration, which is $(Z'y)_0 = (Zx)_0$, we find that the coefficients in (1300) satisfy

$$\frac{L_1}{Z'-\lambda_1} = \frac{M_1}{Z} = \frac{M_2}{-Z\lambda_1/\lambda_2} = \frac{L_2}{-(Z'-\lambda_2)\,\lambda_1/\lambda_2}.$$

This is exact and the rate is of course not that of a unimolecular reaction. If now we suppose that B/Z is small the values of λ_1 and λ_2 reduce approximately to

$$\lambda_1 = BZ'/(Z+Z'),\quad \lambda_2 = Z + Z'.$$

Since $(x/y)_0$ is in general rather small, Z'/Z will also be rather small and at any rate less than unity. Then $L_2/L_1 = O\,(B/Z)$ and $M_2/M_1 = O\,(BZ'/Z^2)$ which is still smaller. Therefore the second terms in (1300) are negligible even initially and *a fortiori* at all later times owing to their much more powerful exponential factor. They are still negligible initially and so always if $(x/y)_0$ is altered by terms of order B/Z. The solution then reduces to

$$x = X_0e^{-BZ't/(Z+Z')},\quad y = Y_0e^{-BZ't/(Z+Z')},\qquad \text{......(1302)}$$

which is of unimolecular form.

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* Lindemann, *Trans. Faraday Soc.* vol. XVII, p. 599 (1921).

A more exact treatment of equations (1299) or more general forms can be given by treating them as of the form

$$\left.\begin{aligned}\frac{dx}{dt} &= f(t)\,y - \{g(t) + B\}\,x,\\ \frac{dy}{dt} &= -f(t)\,y + g(t)\,x,\end{aligned}\right\} \qquad \text{......(1303)}$$

the coefficients $f(t)$ and $g(t)$ being slowly varying functions of the time. The precise variation of $f(t)$ and $g(t)$ is only assignable *a posteriori*, but this does not affect the argument. We can then apply the general theory of such equations, which is equivalent to the theory of the asymptotic forms of solutions of such equations for large values of a parameter*. It follows from this theory that the first approximation to the solutions of (1303) is of the form

$$x = L_1 e^{-\int \lambda_1 dt} + L_2 e^{-\int \lambda_2 dt}, \quad y = M_1 e^{-\int \lambda_1 dt} + M_2 e^{-\int \lambda_2 dt},$$

where λ_1 and λ_2 are functions of t which are the roots of (1301) with Z and Z' replaced by $f(t)$ and $g(t)$. Since $\lambda_1 = BZ'/(Z + Z') = Bx/(x + y)$, λ_1 is independent of the concentrations and therefore of t when B/Z is small. The L_1, L_2, M_1, M_2 are constants to this approximation. We obtain the same unimolecular form as before, with an accuracy dependent on the slowness of the variation of $f(t)$ and $g(t)$. The fundamental condition for the validity of the unimolecular forms is that B/Z should be small, or $Bx/Z'y$ small, that is that the number of disintegrations in time dt should be small compared with the total number of activations or deactivations in the same time.

From equations (1299)

$$\frac{1}{\nu}\frac{d\nu}{dt} = \frac{1}{x + y}\frac{d(x + y)}{dt} = \frac{Bx}{x + y} = \frac{BZ'}{Z + Z'} = \kappa.$$

Thus in this theory κ is B times the fraction of activated molecules. If these are molecules with more internal energy than η_0, then by (1292)

$$\kappa = \frac{B}{\Gamma(\frac{1}{2}s)}\left(\frac{\eta_0}{kT}\right)^{\frac{1}{2}s-1} e^{-\eta_0/kT}. \qquad \text{......(1304)}$$

This will therefore fit the observed form of Arrhenius' equation if

$$\eta_0 = \zeta + (\tfrac{1}{2}s - 1)\,kT. \qquad \text{......(1305)}$$

For the correctness of the theory there is also the over-riding condition that Bx or $\kappa\nu$ is small compared with Zx or the number of activating collisions. The maximum number of such collisions is given by (1295), and the actual number should be a small fraction of this.

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* Schlesinger, *Math. Ann.* vol. LXIII, p. 277 (1907); Birkhoff, *Trans. Amer. Math. Soc.* vol. IX, p. 219 (1908); Fowler and Lock, *Proc. Lond. Math. Soc.* vol. XX, p. 127 (1922).

We will now discuss shortly, in the order of the severity of their demands on the theory, the five reactions already known to be homogeneous and (apparently) unimolecular. References have been given in § 18·1.

(1) *Decomposition of gaseous diethyl ether.* This reaction proceeds at a convenient rate between 700°–860° K. and is homogeneous and unimolecular down to pressures of 200 mm. Hg. Below that pressure of the reactant the reaction proceeds more slowly and approximates to a bimolecular type. The final result of the reaction is roughly

$$C_2H_5.O.C_2H_5 \rightarrow CO + 2CH_4 + \tfrac{1}{2}C_2H_4,$$

though of course this does not represent the primary process which is probably the formation of CO and two unstable hydrocarbons. Sufficient admixture of H_2, for example a partial pressure of 300 mm. Hg at 800° K., will preserve the unimolecular rate unaltered down to a pressure of 40 mm. Hg of the reactant. He, N_2 and the reaction products have no marked effects. The velocity constant observed is

$$\log \kappa = 26{\cdot}47 - 53{,}000/RT. \qquad \text{......(1306)}$$

(2) *Decomposition of gaseous dimethyl ether.* This is very similar. The final result of the reaction is

$$CH_3.O.CH_3 \rightarrow CH_4 + H_2 + CO,$$

proceeding at a convenient rate in the range 700°–825° K. unimolecularly down to a pressure of 400 mm. Hg. A pressure of 400 mm. Hg of admixed H_2 at 775° K. will preserve the unimolecular rate to a pressure of 30 mm. Hg of the reactant. N_2, He, CO and CO_2 have no such effect. The velocity constant observed is

$$\log \kappa = 30{\cdot}36 - 58{,}500/RT. \qquad \text{......(1307)}$$

(3) *Decomposition of gaseous propionic aldehyde.* The main feature of the reaction is

$$C_2H_5CHO \rightarrow CO + [\text{various hydrocarbons}],$$

of convenient speed for 725°–875° K., and unimolecular down to a pressure of about 80 mm. Hg. No effect of admixed gases has been detected. The velocity constant observed is

$$\log \kappa = 28{\cdot}56 - 55{,}000/RT. \qquad \text{......(1308)}$$

These three reactions can be discussed together.

The molecules concerned are all fairly complicated and have a rather large number of degrees of freedom which might have their classical energies. We shall find in all these cases that Lindemann's theory gives a completely satisfactory explanation of the observations even if we only take into account the internal energy of the molecule to be activated and put $s_2 = 0$. By way of making the calculations precise we shall take $\sigma_{12} = 10^{-7}$, $s_2 = 0$, and determine for what value of s_1 the number of collisions given by (1295) falls to 100 times the value of $\kappa\nu$ for the least value of ν for which the reaction remains unimolecular. Since we deal with collisions of like molecules $m_1 = m_2$ and the factor 2 falls out.

We find that this condition is fulfilled:

For $C_2H_5.O.C_2H_5$, $\nu = 2{\cdot}4 \times 10^{18}$, with s_1 between 6 and 7.

For $CH_3.O.CH_3$, $\nu = 5 \times 10^{18}$, with s_1 between 10 and 11.

For C_2H_5CHO, $\nu = 1 \times 10^{18}$, with s_1 about 8.

These values of s_1 are all acceptable. The molecules may be thought of as consisting of at least three loosely bound structural units. The first of these gives a rigid framework to which the others are fitted. Ignoring tortional oscillations each of the others has 3 freedoms in this framework yielding 6 square terms, and the rotations of the whole complex another 3. Values of s_1 up to 15 at least are thus to be expected. There is thus an ample margin for an activation rate slow compared with the number of sufficiently energetic collisions and a disintegration rate slow compared with the rate of activation, even when we do not admit that any of the internal energy of the other molecule is available.

In the case of the two reactions maintained by a sufficient pressure of H_2, the activating collisions must be supplied by collisions between H_2 and the reacting molecule. There is no theoretical difficulty in this. The difficulty is rather to understand why all diluent molecules do not act in the same way. This point lies much deeper than the simple collision theory. It appears as though similar molecules, and only in exceptional cases other molecules, had specific powers of activation. One is tempted to expect that considerations analogous to the resonance theory of Heisenberg will be found to be important here*.

We now pass to two entirely different cases.

(4) *Decomposition of gaseous acetone*. This reaction is homogeneous and unimolecular and of convenient speed for the temperatures 780°–900° K. and shows no signs of deviation from the unimolecular law down to pressures of 100 mm. Hg. No diluents tested have been found to have any effect. The nature of the reaction is

$$CH_3.CO.CH_3 \rightarrow CO + [\text{hydrocarbons}],$$

and the velocity constant observed is

$$\log \kappa = 34{\cdot}95 - 68{,}500/RT. \qquad \ldots\ldots(1309)$$

On carrying out the same calculations as before we find if we take $\nu = 10^{18}$ and $s_1 = 15$ that there are only just about twice as many possible activations as disintegrations. The unimolecular law could not possibly be maintained on this margin. Even if we assume $s_1 = 24$ (24 square terms) we have only a marginal factor of about 30. There might well be 15 relevant

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* Heisenberg, *Zeit. für Phys.* vol. XXXVIII, p. 411 (1926).

square terms in the acetone molecule, or even so many as 24, but this is hardly enough, and there is no evidence that the reaction does not remain unimolecular to still lower pressures.

We have hitherto confined attention to the internal energy of the molecule which is to be activated in the collision. But this is arbitrary, for there is no *a priori* reason why some or indeed all of the energy in certain coordinates of the other molecule may not in certain circumstances be available for activation. The consequences of such an assumption of availability are considered in the next section in the light of the theory of detailed balancing. Such an assumption makes a large difference, for the fraction of activated molecules in equilibrium depends only on s_1 and is unaltered, but the number of possible activating collisions is largely increased. If we take $s_1 = s_2 = 15$ there is a marginal factor of $3 \cdot 6 \times 10^4$ which is probably ample. A comparatively small value of s_2 will increase the previous margin substantially.

(5) *Decomposition of nitrogen pentoxide.* This, the best known and most exhaustively investigated homogeneous unimolecular reaction, also shows no signs of deviation from the unimolecular law but now down to pressures of 0·05 or even 0·01 mm. Hg. The convenient temperature range is from 273°–340° K. No effect of any diluent has been recorded. The nature of the reaction is

$$N_2O_5 \rightarrow N_2O_4 + \tfrac{1}{2}O_2,$$

and the velocity constant observed*

$$\log \kappa = 33 \cdot 17 - 24{,}700/RT. \qquad \ldots\ldots(1310)$$

For $\nu = 3 \cdot 55 \times 10^{14}$, $\sigma_{12} = 10^{-7}$, and $s_1 = s_2 = 15$ we find a maximum rate of activation 40 times the observed rate of disintegration. It is quite feasible to suppose that at these temperatures the energy content of N_2O_5 is even greater than is represented by 15 square terms, so that there is still an ample margin. But the conditions for obtaining such a margin are extreme. It is impossible practically speaking unless all the internal energy in both molecules is available for the activation energy of one, and such activations occur in something more than one per cent. of all sufficiently energetic collisions.

§ **18·5**. *The requirements of detailed balancing.* In view of the extreme form of the theory required to account for the decomposition of N_2O_5 it is desirable to examine the consequences of the assumption we have been driven to, that all the energy in a large number of freedoms in both molecules is available for the activation of one, and is actually so used in a fraction of all sufficiently energetic collisions which may be as large as 1/100 or even possibly 1/10. Obviously not *all* "collisions with enough energy" can be activations, for the class must include all deactivations as well.

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* Hurst and Rideal, *Proc. Roy. Soc.* A, vol. CIX, p. 526 (1925).

When $\eta_1+\eta_2+\xi \geqslant \eta_0$ a collision with the initial conditions η_1, η_2, ξ *can* yield a pair of molecules with energies between $\eta_1^*, \eta_1^*+d\eta_1^*$ $(\eta_1^*>\eta_0)$ and $\eta_2^*, \eta_2^*+d\eta_2^*$, the rest of the energy being absorbed in ξ^*. The effective target for such an exchange, in conformity with the notation of the last chapter, will be taken to be

$$S(\eta_1, \eta_2, \xi; \eta_1^*, \eta_2^*)\, d\eta_1^* d\eta_2^*.$$

Then in the equilibrium state (or other state not seriously disturbed from this) the number of collisions per unit volume and unit time which convert η_1, η_2, ξ into $\eta_1^*, \eta_2^*, \xi^*$ is proportional to

$$\eta_1^{\frac{1}{2}s_1-1}\,\eta_2^{\frac{1}{2}s_2-1}\,\xi e^{-(\eta_1+\eta_2+\xi)/kT}\, d\eta_1 d\eta_2 d\xi \times S(\eta_1, \eta_2, \xi; \eta_1^*, \eta_2^*)\, d\eta_1^* d\eta_2^*. \quad \text{......(1311)}$$

By the same argument the number of collisions which convert $\eta_1^*, \eta_2^*, \xi^*$ into η_1, η_2, ξ is

$$(\eta_1^*)^{\frac{1}{2}s_1-1}\,(\eta_2^*)^{\frac{1}{2}s_2-1}\,\xi^*\, e^{-(\eta_1^*+\eta_2^*+\xi^*)/kT}\, d\eta_1^* d\eta_2^* d\xi^* \times S(\eta_1^*, \eta_2^*, \xi^*; \eta_1, \eta_2)\, d\eta_1 d\eta_2. \quad \text{......(1312)}$$

By the principle of detailed balancing these must be equal. Moreover, since $\eta_1+\eta_2+\xi=\eta_1^*+\eta_2^*+\xi^*$, for given η's, $d\xi=d\xi^*$. Hence

$$(\eta_1^*)^{\frac{1}{2}s_1-1}\,(\eta_2^*)^{\frac{1}{2}s_2-1}\,\xi^*\, S(\eta_1^*, \eta_2^*, \xi^*; \eta_1, \eta_2) = \eta_1^{\frac{1}{2}s_1-1}\,\eta_2^{\frac{1}{2}s_2-1}\,\xi\, S(\eta_1, \eta_2, \xi; \eta_1^*, \eta_2^*). \quad \text{......(1313)}$$

If now it is to be possible for the number of activations to be comparable with the number of collisions with enough energy we must have

$$\iint S(\eta_1, \eta_2, \xi; \eta_1^*, \eta_2^*)\, d\eta_1^* d\eta_2^*$$

of the same order as $\pi\sigma_{12}^2$ (equal to $\alpha\pi\sigma_{12}^2$ say), when $\eta_1+\eta_2+\xi \geqslant \eta_0$ and $\eta_1^*>\eta_0$. For the sake of investigating orders of magnitude we will take S constant over the ranges of η_1^* and η_2^* in which it has a non-zero value. Then, very roughly,

$$S(\eta_1, \eta_2, \xi)\int_{\eta_0}^{\eta_1+\eta_2+\xi} d\eta_1^* \int_0^{\eta_1+\eta_2+\xi-\eta_1^*} d\eta_2^* = \alpha\pi\sigma_{12}^2,$$

or

$$S(\eta_1, \eta_2, \xi) = 2\alpha\pi\sigma_{12}^2/(\eta_1+\eta_2+\xi-\eta_0)^2. \quad \text{......(1314)}$$

There is nothing unacceptable in (1314). Then by (1313)

$$S(\eta_1^*, \eta_2^*, \xi^*; \eta_1, \eta_2) = \frac{2\alpha\pi\sigma_{12}^2}{(\eta_1+\eta_2+\xi-\eta_0)^2}\left(\frac{\eta_1}{\eta_1^*}\right)^{\frac{1}{2}s_1-1}\left(\frac{\eta_2}{\eta_2^*}\right)^{\frac{1}{4}s_2-1}\frac{\xi}{\xi^*}. \quad \text{......(1315)}$$

To find the corresponding total collision area for deactivations we have to integrate with respect to η_1 and η_2, the ranges being respectively 0 to η_0 and 0 to η_0 or $\eta_1^*+\eta_2^*+\xi^*-\eta_1$ whichever is the lesser. It is not necessary however to carry out this integration explicitly. We can see at once from (1315) that in certain circumstances the deactivation target must be very large compared with the activation target $\alpha\pi\sigma_{12}^2$. Such a molecular property is not entirely impossible and dismissible on *a priori* grounds. Formula (1315) means that a very slow molecule or a molecule with exceptionally little energy finds it exceptionally easy to bring about deactivation. In the present state of molecular theory all we can do is to bear such possibilities constantly in mind*.

§ **18·6**. We have confined the foregoing account of homogeneous gaseous reactions to the simplest collision mechanism. Interesting and important questions are raised by following up the subsequent history of the products of reaction which may often contain excessive amounts of energy, especially when the reaction is thermodynamically exothermic with a large heat of activation. In these cases we shall expect to find the formation of reaction chains and explosion waves. It is however hardly yet possible to discuss such phenomena with precision from the kinetic standpoint, and such discussion as is possible would take us too far afield. Nor have we in this chapter discussed photo-sensitive gaseous reactions. Some account of these is given in the next chapter. It should be mentioned that the homogeneous unimolecular gaseous reactions of this chapter have frequently been considered to be due primarily to a radiative process on account of their unimolecular character. It is however almost impossible to maintain such a theory in the face of the abnormal molecular absorption coefficients which it requires†, which would have to manifest themselves in the absorption of external radiation. When the attempt is made to modify such a theory by claiming that these abnormal coefficients are only typical of the interaction of two molecules in resonance with one another‡, we are really abandoning the radiative theory altogether and again groping after a theory of molecular interaction, probably of the nature of Heisenberg's resonance theory, which may just as properly be regarded as a collision process. This is no doubt the direction in which the better deeper theory of the future will be found.

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* A valuable critique of the extreme collision theory here presented has recently been published by Tolman, Yost and Dickinson, *Proc. Nat. Acad. Sci.* vol. XIII, p. 188 (1927).

† Christiansen and Kramers, *Zeit. für phys. Chem.* vol. CIV, p. 451 (1923).

‡ G. N. Lewis and Smith, *Jour. Amer. Chem. Soc.* vol. XLVII, p. 1508 (1925), G. N. Lewis, *Proc. Nat. Acad. Sci.* vol. XIII, p. 623 (1927).

CHAPTER XIX

MECHANISMS OF INTERACTION. RADIATIVE PROCESSES

§ 19·1. *The nature of radiative processes.* The analysis of § 17·1 was arranged to cover both collisions and radiative processes. We recapitulate the conclusions as to the latter. If X_1 and X_2 denote two different states of the same system such that the equilibrium ratio of the concentrations $[X_1]$ and $[X_2]$ is a function of the temperature only, and if P_{rad} and Q_{rad} are the frequencies with which an X_1 is converted to an X_2 and an X_2 to an X_1 by interaction with equilibrium radiation alone, then

$$\frac{P_{\text{rad}}}{Q_{\text{rad}}}=\frac{[X_2]}{[X_1]}. \qquad \text{......(1316)}$$

If the change from X_1 to X_2 is one of dissociation, so that an expression such as $[X_2][Y]/[X_1]$ is a function of the temperature only, then

$$\frac{P_{\text{rad}}}{Q_Y+Q_{Y,\text{rad}}}=\frac{[X_2][Y]}{[X_1]}. \qquad \text{......(1317)}$$

Here Q_Y means the frequency of interaction of an X_2 and a Y to form an X_1 *without* any radiative action, and $Q_{Y,\text{rad}}$ that of the similar interaction *with* radiative action.

It is now possible to analyse this result a little further and see that in general

$$Q_Y=0.$$

In general there will be a difference of energy between the free X_2+Y and the combined X_1. Consequently no interaction between X_2 and Y is possible resulting in X_1 and conserving energy. We have still every reason to believe as heretofore that energy and momentum are conserved in every atomic as in every molar process. In general therefore $Q_Y=0$, and we have

$$\frac{P_{\text{rad}}}{Q_{Y,\text{rad}}}=\frac{[X_2][Y]}{[X_1]}. \qquad \text{......(1318)}$$

In this interaction of course the radiation can adjust the energy balance. We proceed to examine in detail the consequences of (1316) and (1318).

§ 19·2. *Interaction of radiation with the stationary states of fixed atoms.* This problem was the first of such problems to be discussed in this way —by Einstein* in a classical paper. Consider first an atom with only two stationary states 1 and 2, of negative energies χ_1 and χ_2, $\chi_1>\chi_2$, and weights ϖ_1 and ϖ_2. The atom can proceed from state 1 to state 2 with absorption

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* Einstein, *Phys. Zeit.* vol. xviii, p 121 (1917).

of radiation and from state 2 to state 1 with emission of radiation. According to Bohr's theory this radiation will be monochromatic, of frequency ν given by $h\nu = \chi_1 - \chi_2$, *Bohr's frequency condition.* The equilibrium ratio of the numbers of atoms in the two states from the properties of their partition function is (Boltzmann's law)

$$\frac{\varpi_1}{\varpi_2 e^{-(\chi_1-\chi_2)/kT}}. \qquad \text{......(1319)}$$

We have now to make some natural assumption as to the dependence of the rates of emission and absorption of the atoms in the proper state on the intensity of the radiation of frequency ν. Let $I(\nu)\,d\nu$ be the intensity of radiation of frequency between ν and $\nu + d\nu$, that is the quantity of energy in radiation of this type which crosses unit area normal to its path per unit solid angle per second. It is connected with the density of this radiation $\rho(\nu)\,d\nu$ by the equation

$$I(\nu) = \frac{c}{4\pi}\rho(\nu). \qquad \text{......(1320)}$$

We will then assume that the chance of absorption of one quantum by an atom in state 1 in time dt is

$$B_1{}^2 I(\nu)\,d\nu dt, \qquad \text{......(1321)}$$

and that the chance of emission of one quantum by an atom in state 2 in time dt is

$$(A_2{}^1 + B_2{}^1 I(\nu)\,d\nu)\,dt, \qquad \text{......(1322)}$$

the A's and B's being atomic constants. They are commonly referred to as Einstein's A's and B's or Einstein's coefficients. The form of (1321) is the obvious one to choose, that of (1322) is more obscure and the second term might *a priori* be overlooked. It is necessary as we shall see for the mechanism to preserve Planck's law for $\rho(\nu)$, and it can be seen to be necessary *a priori* by a deeper consideration of classical radiation theory*.

In equilibrium the absorption and emission of quanta and the numbers of switches from 1 → 2 and 2 → 1 must be equal. Using therefore (1319), Bohr's frequency condition, (1321) and (1322) this necessary and sufficient equality is equivalent to

$$\varpi_1 B_1{}^2 I(\nu)\,d\nu = \varpi_2 e^{-h\nu/kT}(A_2{}^1 + B_2{}^1 I(\nu)\,d\nu). \qquad \text{......(1323)}$$

Solving for $I(\nu)$ we find

$$I(\nu)\,d\nu = \frac{A_2{}^1}{(\varpi_1/\varpi_2)\,B_1{}^2\,e^{h\nu/kT} - B_2{}^1}. \qquad \text{......(1324)}$$

On comparing this with Planck's law,

$$I(\nu)\,d\nu = \frac{2h\nu^3 d\nu}{c^2}\frac{1}{e^{h\nu/kT}-1}, \qquad \text{......(1325)}$$

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* Van Vleck, *Phys. Rev.* vol. xxiv, pp. 330, 347 (1924).

we see that the form is correct and equilibrium will be preserved if

$$\varpi_1 B_1{}^2 = \varpi_2 B_2{}^1 = \varpi_2 A_2{}^1 \frac{c^2}{2h\nu^3 d\nu}. \qquad \ldots\ldots(1326)$$

These relations are extremely important.

Some comment is called for on other arrangements of the foregoing argument. It has been arranged here purely to derive the relations (1326) and to verify that our assumptions form a possible mechanism. We may note too that there is here no difference between preservation of equilibrium and detailed balancing.

In the first place the forms (1321) and (1322), though the only forms consistent with classical radiation theory, are not the only forms which satisfy (1325). If we replace them by $f_a\,(I\,(\nu)\,d\nu)$ and $f_e\,(I\,(\nu)\,d\nu)$ respectively the functions f_a and f_e have only to satisfy the necessary and sufficient relation

$$f_e\,(x) = \frac{2h\nu^3 d\nu/c^2 + x}{x} f_a\,(x). \qquad \ldots\ldots(1327)$$

In the next place we have actually assumed more results of the equilibrium theory and atomic theory than are strictly necessary for the proof. Einstein, in his original presentation, assumed the forms (1321) and (1322), Wien's displacement law (a theorem of pure thermodynamics) and Boltzmann's law, and *deduced* from these premises Bohr's frequency condition and Planck's law. Eddington* has recast the discussion and taken as his premises Wien's law and Bohr's frequency condition, and *deduced* Boltzmann's law and Planck's law. These theorems however are of interest from points of view different from that adopted in this monograph.

The discussion extends at once to atoms with any number of stationary states. For each pair of stationary states which are connected by a radiative transition there is a set of relations identical with (1326). Moreover this is true whether we work on the hypothesis of preservation or of detailed balancing. The difficulty of § 17·4 does not arise here, for in general we may assume that every possible transition affects radiation of a different frequency.

§ **19·21**. *Numerical values.* The connection between $B_1{}^2$ and the mass absorption coefficient is obtained as follows. Of the energy of radiation

$$I\,(\nu)\,d\nu d\omega \cos\theta dS dt$$

incident in time dt at an angle θ within a pencil $d\omega$ on a slab of area dS and thickness dx, the fraction

$$k_\nu \rho\, dx \sec\theta$$

will be absorbed, ρ being the mass density of the atomic distribution. This

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* Eddington, *Phil. Mag.* vol. L, p. 803 (1925).

expression defines the mass absorption coefficient k_ν. In terms of $B_1{}^2$ the energy absorbed is

$$\overline{a_1}\,dx\,dS \times B_1{}^2 I(\nu)\,d\nu\,dt\,\frac{d\omega}{4\pi} \times h\nu,$$

where $\overline{a_1}$ is the number of atoms in the state 1 per unit volume. Equating the two amounts we find

$$k_\nu = \frac{B_1{}^2\overline{a_1}h\nu}{4\pi\rho}. \qquad \text{......(1328)}$$

We can write $\rho = ma$, where m is the atomic mass and a the total concentration. Then

$$k_\nu = \frac{B_1{}^2 h\nu\overline{a_1}}{4\pi ma}. \qquad \text{......(1329)}$$

Unless $\overline{a_1}/a$ is small the mass absorption coefficients are extremely large. The direct experimental evidence for the Hg line λ 2536 ($1\,{}^1S - 2\,{}^3P$), the Ca^+ lines H, K $\lambda\lambda$ 3968, 3933 ($1\,{}^2S - 2\,{}^2P$) of the chromosphere and the Na lines D, ($1\,{}^2S - 2\,{}^2P$), all lines for which in the conditions of observation $\overline{a_1}/a = 1$, is that k_ν is of the order 10^9. Einstein's absorption coefficient is then of the order 0·1 to 0·5.

In order to evaluate $A_2{}^1$ numerically we have to know the value of $d\nu$. The meaning of this is of course that $B_1{}^2$ is a sort of mean absorption coefficient integrated through the line, no line of any set of atoms (even if all at rest) being of mathematically zero breadth. The total absorption is therefore the mean absorption coefficient $B_1{}^2$ multiplied by the mean breadth $d\nu$, and it is $B_1{}^2 d\nu$ or more strictly $\int_{\nu_0-\infty}^{\nu_0+\infty} \alpha_\nu d_\nu$ which is correlated with the emission coefficient $A_2{}^1$. If we estimate on observational evidence the ordinary line breadth at 10^{-10} cm., then for $\lambda = 3000$ $\delta\nu = 3 \times 10^9$, $B_1{}^2 d\nu = 1{\cdot}5 \times 10^9$. The numerical order of $A_2{}^1$ is then 2×10^7. There is direct experimental confirmation of such a value, for we observe that $1/A_2{}^1$ is the mean life of the atom in the excited state 2 before it spontaneously radiates and returns to the state 1. This mean life τ is therefore approximately

$$\tau = 5 \times 10^{-8} \text{ secs.}$$

Mean lives of this order or rather shorter are determined by experiments such as Wien's on the light emitted by streams of positive rays and by the theory of the chromosphere. This is also the mean time of radiation suggested by classical radiation theory.

The stimulated emissions are often of negligible importance numerically. The ratio of stimulated to spontaneous emissions is

$$\frac{B_2{}^1 I(\nu)\,d\nu}{A_2{}^1} = \frac{c^2 I(\nu)}{2h\nu^3} = \frac{1}{e^{h\nu/kT} - 1}.$$

For the region of the spectrum near $\lambda_{\max}$ $h\nu/kT$ is about 5, so this fraction is negligible and *a fortiori* for all higher frequencies. For very low frequencies the fraction approximates to $kT/h\nu$ and the stimulated emissions become important.

The latest theoretical advances have enabled direct calculations of the A's and B's to be made for the hydrogen atom and to some extent for helium and the atoms of the alkalis*, and have suggested the general order of the coefficients for other elements, the exact evaluation of which is only a matter of time. The results are in full account with the foregoing experimental evidence and crude calculations.

§ **19·3**. *The photo-electric liberation of electrons from fixed atoms*†. Besides the line emission and absorption spectrum of an atom, associated with transitions between stationary states, there is also a continuous emission and absorption spectrum associated with capture and loss of electrons. We will again consider the atoms as fixed, and at first for simplicity as possessing a single stationary state of negative energy χ and weight ϖ_0. The process to be analysed consists of absorption of radiation of frequency ν such that $h\nu > \chi$ with the ejection of an electron of velocity v or energy η such that

$$\eta = \tfrac{1}{2}mv^2 = h\nu - \chi, \qquad \text{......(1330)}$$

which is Einstein's law of the photo-electric effect. The relic of the atom is an ion in its normal (at present sole) stationary state of weight ϖ_1. If y is the concentration of free electrons and x_0, x_1 the concentrations of (single state) atoms and ions, the equilibrium state is characterized after (333) and (1013) by

$$\frac{x_1 y}{x_0} = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \frac{2\varpi_1}{\varpi_0} e^{-\chi/kT}. \qquad \text{......(1331)}$$

The mechanism is controlled by (1318) and the reverse process is the encounter of an ion and a free electron resulting in capture with emission of radiation.

Let $\psi(\nu) I(\nu)\, d\nu dt$ be the chance that a neutral atom will in time dt, under the influence of isotropic ν-radiation of intensity $I(\nu)\, d\nu$, become ionized by absorption of a quantum $h\nu$. The total number of ν-quanta absorbed in time dt will therefore be (per unit volume)

$$x_0 \psi(\nu) I(\nu)\, d\nu dt. \qquad \text{......(1332)}$$

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* See, among other authors, Schrödinger, *Ann. der Phys.* vol. LXXX, p. 437 (1926), Heisenberg, *Zeit. für Phys.* vol. XXXIX, p. 499 (1926), Sugiura, *Jour. de Phys.* vol. VIII, p. 113 (1927), and *Phil. Mag.* vol. IV, p. 495 (1927).

† Milne, *Phil. Mag.* vol. XLVII, p. 209 (1924). This is the most complete original account. See also, Kramers, *Phil. Mag.* vol. XLVI, p. 836 (1923), and R. Becker, *Zeit. für Phys.* vol. XVIII, p. 325 (1923).

By (1200) the number of collisions in time dt between η-electrons and ions in which the line of impact lies between p and $p + dp$ is

$$x_1 \,.\, 2\pi p\,dp \,.\, \left(\frac{2\eta}{m}\right)^{\frac{1}{2}} \mu(\eta)\, d\eta\, dt.$$

Let the probability that such an encounter results in capture with emission of ν-radiation be

$$f(p, \eta) + I(\nu)\, g(p, \eta).$$

We shall find that stimulated captures are necessary here as for line emission and absorption in order to conserve Planck's law. Then the total number of captures with emission of ν-radiation in time dt is

$$x_1 \,.\, 2\pi p\,dp \,.\, \{f(p, \eta) + I(\nu)\, g(p, \eta)\} \left(\frac{2\eta}{m}\right)^{\frac{1}{2}} \mu(\eta)\, d\eta\, dt.$$

In order to conserve energy η and ν are connected by (1330) so that we have also

$$d\eta = h\,d\nu.$$

Inserting the equilibrium value of $\mu(\eta)$ from (1180) and writing

$$F(\eta) = 2\pi \int_0^\infty pf(p, \eta)\, dp, \quad G(\eta) = 2\pi \int_0^\infty pg(p, \eta)\, dp,$$

we find the total number of captures of η-electrons in time dt with emission of ν-radiation to be

$$\frac{2\pi x_1 y}{(\pi kT)^{\frac{3}{2}}} \{F(\eta) + I(\nu)\, G(\eta)\} \left(\frac{2}{m}\right)^{\frac{1}{2}} \eta\, e^{-\eta/kT}\, d\eta\, dt. \quad \text{......(1333)}$$

Either for preservation or detailed balancing (1332) and (1333) must be equated. On using (1331), (1330) and its resulting differential relation this gives

$$\eta F(\eta) = \frac{2h\nu^3}{c^2} \eta G(\eta) = \frac{h^3\nu^3}{4\pi mc^2} \frac{\varpi_0}{2\varpi_1} \psi(\nu), \quad \text{......(1334)}$$

or

$$\psi(\nu) = \frac{4\pi mc^2}{h^3\nu^3} \frac{2\varpi_1}{\varpi_0} \eta F(\eta) \quad (\eta = h\nu - \chi). \quad \text{......(1335)}$$

Of course

$$\psi(\nu) = 0 \quad (\nu < \chi/h).$$

The ratio of stimulated to spontaneous captures is again $1/(e^{h\nu/kT} - 1)$, and is still less important than for line emission, since in this process we are never concerned with frequencies less than χ/h.

§ **19·31**. *Extensions to complicated atoms.* If we consider more complicated atoms with more than one stationary state, then we can always write the equilibrium relation between single states of the neutral atom and ion in the form*

$$\frac{(x_1)_t\, y}{(x_0)_s} = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \frac{2\,(\varpi_1)_t}{(\varpi_0)_s} e^{-\chi_s{}^t/kT}, \quad \text{......(1336)}$$

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* First pointed out explicitly by Milne, *Phil. Mag.* vol. L, p. 547 (1925).

where $\chi_s{}^t$ is the ionization energy required to remove an electron from the neutral atom in its sth state and leave the ion in its tth state. This can be effected by radiation of frequency ν ejecting an η-electron, provided now that

$$h\nu = \eta + \chi_s{}^t.$$

We introduce exactly the same coefficients $F(\eta)$, $G(\eta)$, and $\psi(\nu)$ as before for each such photo-electric process. On the principle of detailed balancing it follows at once that the relations (1334) hold for each set of these coefficients. On the preservation hypothesis matters are rather complicated and it is hardly of sufficient interest to discuss them in detail. The balancing of ν-quanta and η-electrons involves in general more than one set of coefficients. Only the atomic balance involves a single set (and then only when the ion is assumed to have only a single state), and the condition of atomic balance for all T does not imply so much as (1334). We may be content to expect that, as in § 17·4, preservation could be shown to demand less restrictive conditions than detailed balancing.

It is obvious that the foregoing argument applies to any two consecutive stages of ionization.

§ **19·32**. *Free-free transitions.* In addition to radiative captures there is ample reason to believe that transitions from one free orbit to another are possible with emission or absorption of radiation. The greater part of "white" X-radiation is undoubtedly of this nature. The new quantum theory should enable us to calculate the probability of these transitions at least for atoms with one electron. In the meantime the laws for such processes can easily be formulated, but do not give much significant information, since the process and its reverse are essentially the same, with change of sign of ν.

By (1200) and (1180) the number of encounters per atom per unit time with (η, p)-electrons is

$$2\pi p dp \,.\left(\frac{2}{m}\right)^{\frac{1}{2}} \frac{2\pi\nu_\epsilon}{(\pi kT)^{\frac{3}{2}}} e^{-\eta/kT}\, \eta\, d\eta.$$

The chance of a switch to an (η', p')-electron with absorption of ν-radiation, $h\nu = \eta' - \eta$, is naturally taken to be

$$I(\nu)\, \sigma(\eta, p; \eta', p')\, d\eta' \,.\, 2\pi p' dp'.$$

If
$$S_a(\eta, \eta') = 4\pi^2 \int_0^\infty \int_0^\infty pp'\sigma(\eta, p; \eta', p')\, dp dp',$$

then the number of switches of η-electrons to η'-electrons per atom per unit time with absorption of ν-radiation is

$$\left(\frac{2}{m}\right)^{\frac{1}{2}} \frac{2\pi\nu_\epsilon}{(\pi kT)^{\frac{3}{2}}} e^{-\eta/kT}\, I(\nu)\, \eta\, S_a(\eta, \eta')\, d\eta d\eta'. \qquad \text{......(1337)}$$

In exactly the same way we must then take the number of switches of η'-electrons to η-electrons per atom per unit time with emission of ν-radiation to be

$$\left(\frac{2}{m}\right)^{\frac{1}{2}} \frac{2\pi\nu_e}{(\pi kT)^{\frac{3}{2}}} e^{-\eta'/kT} \{1 + aI(\nu)\} \eta' S_e(\eta', \eta)\, d\eta\, d\eta'. \quad \text{......(1338)}$$

On the principle of detailed balancing we must equate (1337) and (1338) obtaining

$$e^{h\nu/kT} \eta S_a(\eta, \eta') = \eta' S_e(\eta', \eta) \{1 + aI(\nu)\}. \quad \text{......(1339)}$$

If $I(\nu)$ is to satisfy Planck's law, then we must have

$$a = c^2/2h\nu^3, \quad \text{......(1340)}$$

$$\eta S_a = \frac{c^2}{2h\nu^3} \eta' S_e. \quad \text{......(1341)}$$

The analogous process to this in Chapter XVII would be merely a simple 3-body encounter with energy exchanges between the 3 bodies, from which we should have derived little of importance.

§ **19·33**. *Numerical values of continuous absorption coefficients.* Little is known experimentally or from direct astrophysical evidence as to the numerical values of the mass absorption coefficient which is derived from $\psi(\nu)$ by the equation analogous to (1329),

$$k_\nu = \frac{h\nu}{4\pi m} \frac{\Sigma\psi^{(s)}(\nu)\, \overline{a_s}}{a}. \quad \text{......(1342)}$$

We do know that the continuous absorption grades off continuously into the massed line absorption at the series limit and that there is no infinity at the limit itself. Hence $\operatorname*{Lt}_{\eta \to 0} \eta F(\eta)$ must be finite and non-zero. This means that the chance of capture of a very slow electron must ultimately vary like $1/\eta$ or $1/v^2$. It does not imply however that $\psi(\nu) \propto \nu^{-3}$ and $k_\nu \propto \nu^{-2}$, and in fact these relations do not seem to be true. The X-ray evidence is that $k_\nu \propto \nu^{-2\cdot 6} - \nu^{-3}$. We have however direct calculations of $\psi(\nu)$ and so k_ν for atoms with one electron, which probably apply to the absorption of X-rays and roughly to the optical absorption by any simple atom or ion*. It is now merely a matter of time before these coefficients are calculated theoretically. Complications but not difficulties of principle are the only remaining obstacles.

§ **19·4**. *General processes involving emission and absorption of radiation.* We have considered hitherto only simple radiative processes in which a single quantum is absorbed or emitted. In order to generalize these considerations on the basis of detailed balancing to apply to processes involving two or more quanta such as the Compton effect (scattering of radiation

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* Oppenheimer, *Zeit. für Phys.* vol. XLI, p. 268 (1927); Sugiura, *loc. cit.*

by free electrons) a convenient way is to generalize the method of § 17·72 to include radiation*, at first a single quantum only. To define the encounters we must now specify in addition the solid angle $d\Omega$ in which the radiation is to proceed, and also when continuous ranges of frequencies are concerned the frequency range $d\nu$. These specifications are first required in the normal frame of reference ($d\Omega_0$, $d\nu_0$), the momentum of the radiation being taken into account if it is significant. As before the probability coefficients ϕ and ϕ' are to be independent of V and therefore also of $I(\nu)$, though they may of course depend on the direction of the radiation. We find as before that the only simple assumption is that, in the normal frame, the frequency of the absorption process is proportional to $I_0(\nu_0)$ and the frequency of the emission process to $\{1 + \alpha I_0(\nu_0)\}$. The equation of detailed balancing, see (1274), now reduces in the normal frame to

$$I_0(\nu_0)\,[f_1 f_2 \cdots f_n]_0\,\phi = \{1 + \alpha I_0(\nu_0)\}\,[f_1' f_2' \cdots f_{n'}']_0\,\phi'.$$

Since $I(\nu)/\nu^3$ is invariant under a Lorentz transformation† this reduces, in the original frame in which the assembly as a whole is at rest, to

$$\frac{1}{\alpha} f_1 f_2 \cdots f_n\,\phi = \left\{\frac{\nu^3}{\alpha\nu_0{}^3 I(\nu)} + 1\right\} f_1' f_2' \cdots f_{n'}'\,\phi'. \qquad \text{......(1343)}$$

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* Dirac, *loc. cit.* (2). First discussed from the present point of view by Pauli, *Zeit. für Phys.* vol. XVIII, p. 272 (1923).

† See, for example, Einstein, *Phys. Zeit.* vol. XVIII, p. 121 (1917).

The proof is simple and may be repeated here for reference. In the original frame K, in which the assembly as a whole is at rest, the radiation is isotropic in all frequencies and of intensity in a given range and direction

$$I(\nu)\,d\nu d\omega.$$

Consider a system at rest in a frame K' moving with velocity v in the frame K along the x-axis. A given bundle of radiation of intensity $I(\nu)\,d\nu d\omega$ in K will belong to an interval $d\nu'$ and solid angle $d\omega'$ and be of intensity

$$I'(\nu', \theta')\,d\nu' d\omega'$$

in K', where θ' is the angle between the x'-axis and $d\omega'$. Obviously in K', I' is not isotropic but depends on θ', not on ϕ'.

Between these two expressions for the intensity or energy density of a given beam there must obviously be the same relation as between the squares of the corresponding frequencies, so that

$$\frac{I'(\nu', \theta')\,d\nu' d\omega'}{I(\nu)\,d\nu d\omega} = \left(\frac{\nu'}{\nu}\right)^2.$$

The transformation equations (1355) give us at once Doppler's law and the aberration in the form

$$\nu' = \frac{\nu\{1 - (v/c)\cos\theta\}}{(1 - v^2/c^2)^{\frac{1}{2}}}, \quad \cos\theta' = \frac{\cos\theta - v/c}{1 - (v/c)\cos\theta}.$$

It follows that
$$\frac{d\nu'}{d\nu} = \frac{\nu'}{\nu}, \quad \frac{d\omega'}{d\omega} = \frac{d\cos\theta'}{d\cos\theta} = \left(\frac{\nu}{\nu'}\right)^2.$$

Therefore (to all orders)
$$\frac{I'(\nu', \theta')}{I(\nu)} = \left(\frac{\nu'}{\nu}\right)^3.$$

The full expression for $I'(\nu', \theta')$ in terms of ν' and θ' correct to v/c is

$$I'(\nu', \theta') = \left\{I(\nu') + \frac{v}{c}\nu' \cos\theta' \frac{\partial I}{\partial \nu'}\right\}\left(1 - 3\frac{v}{c}\cos\theta'\right). \qquad \text{......(1343)}'$$

An alternative method is to apply the general theorem used by Dirac (see footnote to § 17·72, p. 455).

It is of course only this form for the ratios of the emission and absorption coefficients which it is necessary and sufficient to postulate. Writing Planck's law in the form

$$\frac{2h}{c^2}\frac{\nu^3}{I(\nu)}+1=e^{h\nu/kT},$$

we see that, if

$$\alpha=\frac{c^2}{2h\nu_0{}^3}, \qquad \text{......(1344)}$$

the equation (1343) of detailed balancing reduces to

$$\frac{2h\nu_0{}^3}{c^2}f_1f_2\dots f_n\phi=e^{h\nu/kT}f_1'f_2'\dots f_{n'}'\phi'. \qquad \text{......(1345)}$$

In this form only can the relation be satisfied with coefficients ϕ and ϕ' independent of T and V. It will be observed that ν_0, the frequency of the necessary radiation, is measured in the normal frame and so is a constant of the process independent of V. The rest of the argument proceeds exactly as in § 17·72 except that the energy relation is

$$h\nu+\sum_1^n\left\{\epsilon_r+\frac{1}{2m_r}(p_1{}^2+p_2{}^2+p_3{}^2)_r\right\}=\sum_1^{n'}\left\{\epsilon_r'+\frac{1}{2m_r'}(p_1'^2+p_2'^2+p_3'^2)_r\right\}.$$

The final result of the introduction of the equations of equilibrium is now

$$\frac{\phi'}{\phi}=\frac{2h\nu_0{}^3}{c^2}\frac{\varpi_1\dots\varpi_n}{\varpi_1'\dots\varpi_{n'}'}(h^3)^{n'-n}. \qquad \text{......(1346)}$$

We have considered above a process and its reverse in which a single quantum is absorbed and emitted respectively. It is easy to generalize the argument to cover processes in which any number of quanta are absorbed and emitted with the corresponding emissions and absorptions in the reverse

that for any set of systems (here quanta) the law of density-in-momentum is invariant for a Lorentz transformation. If the density-in-momentum of ν-quanta per unit volume in K is

$$\mu(\nu,\theta,\phi)\,\nu^2d\nu d\omega,$$

then $\mu(\nu,\theta,\phi)$ is invariant. But since we are reckoning in quanta $\mu(\nu,\theta,\phi)\,\nu^2d\nu d\omega$ and $(I(\nu)/\nu)\,d\nu d\omega$ are proportional. Therefore $I(\nu)/\nu^3$ is invariant.

We therefore give a proof of this general invariance theorem, which is of course only a rearrangement of the proof above. Let the four space-time momenta of the particle of rest mass m_0 be m_1, m_2, m_3 and m_4 connected by the relation

$$m_4{}^2-(m_1{}^2+m_2{}^2+m_3{}^2)=m_0{}^2c^2.$$

The density-in-momentum per unit volume of a set of particles is $\mu(m_1,m_2,m_3)\,dm_1dm_2dm_3$. This is the number per unit volume of a specified group of particles and therefore transforms according to the same law as the reciprocal of a volume moving with the velocity of the particles, that is, the same law as m_4. Hence

$$\frac{\mu(m_1,m_2,m_3)\,dm_1dm_2dm_3}{m_4}$$

is invariant. But by the equations of transformation

$$J\left(\frac{m_1',m_2',m_3'}{m_1,m_2,m_3}\right)=\frac{m_4'}{m_4}.$$

Therefore $dm_1dm_2dm_3/m_4$ is invariant, so that $\mu(m_1,m_2,m_3)$ is invariant, which is the theorem.

process. In the normal frame the equation of detailed balancing must obviously take the form

$$\Pi_s \{I_0\,(\nu_0{}^{(s)})\}\,\Pi_t\,\{1 + \alpha_t\,I_0\,(\nu_0{}^{(t)})\}\,[f_1 f_2 \cdots f_n]_0\,\phi$$
$$= \Pi_s\,\{1 + \alpha_s\,I_0\,(\nu_0{}^{(s)})\}\,\Pi_t\,\{I_0\,(\nu_0{}^{(t)})\}\,[f_1'f_2' \cdots f_{n'}']_0\,\phi', \quad \ldots\ldots(1347)$$

which reduces in the original frame to

$$\Pi_s\left(\frac{1}{\alpha_s}\right)\Pi_t\left\{\frac{(\nu^{(t)})^3}{\alpha_t\,(\nu_0{}^{(t)})^3\,I_0\,(\nu^{(t)})} + 1\right\}f_1 f_2 \cdots f_n\,\phi$$
$$= \Pi_s\left\{\frac{(\nu^{(s)})^3}{\alpha_s\,(\nu_0{}^{(s)})^3\,I_0\,(\nu^{(s)})} + 1\right\}\Pi_t\left(\frac{1}{\alpha_t}\right)f_1'f_2' \cdots f_{n'}'\,\phi'. \quad \ldots\ldots(1348)$$

Provided that all the "coefficients of stimulation" α satisfy

$$\alpha_s = \frac{c^2}{2h\,(\nu_0{}^{(s)})^3}, \quad \alpha_t = \frac{c^2}{2h\,(\nu_0{}^{(t)})^3}, \quad \ldots\ldots(1349)$$

equation (1348) reduces, on using Planck's law, to

$$\Pi_s\,\frac{2h\,(\nu_0{}^{(s)})^3}{c^2}\,e^{h\,(\Sigma_t\nu^{(t)})/kT}\,f_1 f_2 \cdots f_n\,\phi$$
$$= \Pi_t\,\frac{2h\,(\nu_0{}^{(t)})^3}{c^2}\,e^{h\,(\Sigma_s\nu^{(s)})/kT}\,f_1'f_2' \cdots f_{n'}'\,\phi'. \quad \ldots\ldots(1350)$$

The energy equation is

$$\Sigma_s h\nu^{(s)} + \sum_1^n\left\{\epsilon_r + \frac{1}{2m_r}\,(p_1{}^2 + p_2{}^2 + p_3{}^2)\right\}$$
$$= \Sigma_t h\nu^{(t)} + \sum_1^{n'}\left\{\Sigma_r' + \frac{1}{2m_r'}\,(p_1'^2 + p_2'^2 + p_3'^2)\right\},$$

and the final relation between the ϕ's,

$$\frac{\phi'}{\phi} = \frac{\Pi_s\,\dfrac{2h\,(\nu_0{}^{(s)})^3}{c^2}}{\Pi_t\,\dfrac{2h\,(\nu_0{}^{(t)})^3}{c^2}}\,\frac{\varpi_1 \ldots \varpi_n}{\varpi_1' \ldots \varpi_{n'}'}\,(h^3)^{n'-n}. \quad \ldots\ldots(1351)$$

It is easily seen that in no other way can we eliminate T and V from the equation of detailed balancing and so obtain a statistically acceptable relation between the ϕ's. It is not necessary to take the exact form chosen for the various emission and absorption coefficients as functions of $I_0\,(\nu_0)$. Only the ratio of each pair is relevant and determinate. If however the form chosen is accepted, then we must accept also the following general law:

Any atomic process which results in the emission of one or more quanta of radiation is stimulated by external incident radiation of the same frequency as that of any of the emitted quanta, the ratio of the stimulated to the spontaneous emission being proportional to the intensity of the incident radiation divided by the cube of its frequency and independent of the nature of the process concerned, the direction of the stimulated radiation being the same as that of the incident radiation.

§ **19·41**. *The Debye-Compton effect**. Compton's process of the scattering of radiation by free electrons is an example of a process to which the foregoing general theory will apply. In this case there is one material system, $n' = n = 1$, one quantum of frequency ν is absorbed and one quantum of frequency ν' is emitted, the difference between ν and ν' being of course controlled by the laws of conservation of energy and momentum. The weights ϖ_1 and ϖ_1' are equal. Consequently the scattering process will preserve the equilibrium state (Maxwell's law for the electrons and Planck's law for the radiation) if

$$\frac{\phi'}{\phi} = \left(\frac{\nu_0}{\nu_0'}\right)^3. \qquad \text{......(1352)}$$

Here ν_0 and ν_0' are the frequencies in the normal frame of the incident and scattered radiation respectively. By (1347) the chance of one electron scattering ν_0-radiation into ν_0'-radiation must be

$$\left\{I_0(\nu_0) + \frac{c^2}{2h\nu_0'^3} I_0(\nu_0) I_0(\nu_0')\right\}\phi, \qquad \text{......(1353)}$$

which is the result first given by Pauli. Reduced to the ordinary frame, the chance of the elementary scattering process must be

$$\left\{\frac{I(\nu)}{\nu^3} + \frac{c^2}{2h}\frac{I(\nu)}{\nu^3}\frac{I(\nu')}{\nu'^3}\right\}\phi\nu_0^3. \qquad \text{......(1354)}$$

Further details of the interaction are not necessary for formulating its laws, but it is perhaps desirable to summarize the details here for reference. In the original frame we have initially a quantum with energy $E = h\nu$, and (vector) momentum $\boldsymbol{\Gamma} = h\nu/c$ and an electron with (vector) momentum

$$\mathbf{G} = m_0 \mathbf{v} (1 - \beta^2)^{-\frac{1}{2}} \quad (\beta = |\mathbf{v}|/c),$$

and energy

$$U = m_0 c^2 \left\{1 + \frac{\mathbf{G}^2}{m_0^2 c^2}\right\}^{\frac{1}{2}} = \frac{m_0 c^2}{(1 - \beta^2)^{\frac{1}{2}}}.$$

The quantum and the electron "collide" and go off with a new frequency ν' and new velocity $\mathbf{v}'$ in new directions; energy and momentum are conserved, so that

$$\mathbf{G} + \boldsymbol{\Gamma} = \mathbf{G}' + \boldsymbol{\Gamma}', \quad E + U = E' + U'.$$

We are not concerned here with the distribution of scattering with angle. If the electron is initially at rest in the ordinary frame we derive at once Compton's formula for the change of frequency of the scattered radiation with angle θ from the direction of the primary beam,

$$\nu\nu'(1 - \cos\theta) = \frac{m_0 c^2}{h}(\nu - \nu'),$$

or

$$\lambda' - \lambda = \frac{h}{m_0 c}(1 - \cos\theta).$$

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* A. H. Compton, *Phys. Rev.* vol. XXI, p. 483 (1923); Debye, *Phys. Zeit.* vol. XXIV, p. 161 (1923).

In order to understand the nature of the interaction we reduce to the normal frame. The transformation equations are of course typified by

$$(\Gamma_x)_0 = \frac{\Gamma_x - VE/c^2}{(1-\mathrm{B}^2)^{\frac{1}{2}}},\ (\Gamma_y)_0 = \Gamma_y,\ (\Gamma_z)_0 = \Gamma_z,\ E_0 = \frac{E - V\Gamma_x}{(1-\mathrm{B}^2)^{\frac{1}{2}}}\quad (\mathrm{B} = V/c), \qquad \text{......(1355)}$$

with similar equations for **G** and U. In the normal frame there is no resultant momentum, so that

$$\mathbf{G}_0 + \boldsymbol{\Gamma}_0 = \mathbf{G}_0' + \boldsymbol{\Gamma}_0' = 0.$$

To reduce to the normal frame we choose the x-axis in the direction of $\mathbf{G} + \boldsymbol{\Gamma}$ and take

$$V = c^2\,|\mathbf{G} + \boldsymbol{\Gamma}|/(E + U).$$

When the total momentum is zero

$$h\nu_0 = m_0 c^2 \beta_0/(1 - \beta_0^2)^{\frac{1}{2}},$$

and from the energy relation ($E_0 + U_0 = W_0$)

$$\beta_0 = \frac{(W_0/m_0c^2)^2 - 1}{(W_0/m_0c^2)^2 + 1}.$$

It follows that β_0, and therefore v_0, and therefore ν_0 are fixed by W_0, so that in the normal frame

$$\nu_0 = \nu_0',\ v_0 = v_0'.$$

The nature of the interaction in the normal frame is thus simply that the quantum and the electron make a head-on collision and rebound with directly reversed momenta. The chance of the scattering process in the normal frame must be

$$\left\{\frac{I\,(\nu_0)}{\nu_0^3} + \frac{c^2}{2h}\left(\frac{I\,(\nu_0)}{\nu_0^3}\right)^2\right\}\phi\nu_0^3.$$

§ **19·42**. *Further inferences from Dirac's discussion.* The discussion of § 19·4 proceeds throughout on the basis of detailed balancing, and the requirement that the atomic laws in the normal frame shall be independent of T and V. Certain of the conclusions implicitly drawn there deserve further emphasis.

(1) Every quantum of radiation concerned in every process must possess *both energy and momentum.* For every one must transform according to the usual Lorentz transformation in order that the atomic laws may be independent of V. Thus all emitted quanta are directed.

(2) All processes, radiative or not, contemplated in § 19·4 preserve Maxwell's law for the density-in-momentum of material systems and Planck's law for the radiation. Thus in particular if we generalize the discussions of § 19·2 and § 19·3 and allow the atoms to move (thereby exchanging momentum as well as energy with the quanta), the atoms will take up (as they must) Maxwell's distribution law.

We have arrived at these important results on the basis of detailed balancing and the use of very general arguments. On account of their importance it is worth while to pause here and consider the more specialized but more direct arguments by which Einstein in his original investigation was led to the conclusion that in the process of line absorption and emission every quantum must be directed (have momentum), and that then Maxwell's velocity distribution law for the atoms would be preserved. Einstein considered only the mean square atomic velocity. We shall give the discussion as completed by Milne*. From the present point of view this discussion may be regarded as a study of the process of line absorption and emission by atoms free to move on the assumption of the preservation hypothesis. It is satisfactory to confirm all the conclusions on this narrower hypothesis in the simple case of an atom with one pair of stationary states.

§ **19·5**. *Extensions of Einstein's argument to free atoms and the conditions for the preservation of Maxwell's law by line absorptions and emissions.* In a frame in which an atom is at rest the radiation is as we have seen not isotropic. The atom meets more radiation from ahead than behind, so that absorption tends to slow it up while the emission (in this frame) is isotropic and without mean effect. There is therefore on the average a deceleration to the first order proportional to v, so that

$$\frac{dv}{dt} = -\lambda v.$$

The actual value of λ will be investigated later. We might at first suppose that each atom, apart from atomic collisions, would ultimately come to rest, but this is not so. Superposed on the steady deceleration there will be in any given time interval τ a net gain of velocity u, arising from fluctuations in the directions of absorption and emission. The mean value of u by definition is zero, and obviously to the first order in v independent of the slight anisotropy of the radiative field—that is independent of v. It is then clear that a necessary condition for the equilibrium state is that

$$\overline{(ve^{-\lambda\tau} + u)^2} = \overline{v^2}, \qquad \text{......(1356)}$$

which means that $\overline{v^2}$ is unaltered after time τ by the two radiative effects. The equation (1356) reduces to

$$\overline{u^2} = \overline{v^2}\,(1 - e^{-2\lambda\tau}), \qquad \text{......(1357)}$$

or for small τ

$$\overline{v^2} \doteqdot \overline{u^2}/2\lambda\tau. \qquad \text{......(1358)}$$

The direct calculation of $\overline{u^2}$ is also simple, but is temporarily postponed. In the foregoing, velocities may be interpreted everywhere as velocity components in any given direction.

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* Milne, *Proc. Camb. Phil. Soc.* vol. XXIII, p. 465 (1926). Compare the discussion of *displacements* in § 13·8.

When u^2 and λ have been calculated directly from the properties of the assumed mechanism $\overline{v^2}$ is determined by (1358), and Einstein showed that it had its proper equilibrium value. This verification is not however, as Einstein pointed out, a complete solution to the problem. But further detailed investigation of this particular mechanism is rendered unnecessary by the following general theorem*.

Theorem 19·5. *If the centre of mass of the atoms moving with velocity* (*or velocity component*) v *moves according to the equation*

$$\frac{dv}{dt} = -\lambda v, \qquad \text{......(1359)}$$

and if in addition in any small interval τ *each atom acquires a velocity* (*or velocity component*) *increment* u, *independent of* v, *such that* $\overline{u} = 0$, *then in the steady state the velocity* (*or velocity component*) *distribution function* $f(v)\,dv$ *is given by*

$$f(v) = ce^{-\frac{1}{2}v^2/\overline{v^2}}, \qquad \text{......(1360)}$$

where $\overline{v^2}$ *is given by* (1358) *and c is a constant.*

This theorem is of somewhat wide importance since it applies under the conditions stated, which need not correspond to statistical equilibrium. In the present application it justifies confining a discussion of the particular mechanism to the values of λ and $\overline{u^2}$. We take its proof next, confining the discussion to one dimension, or one velocity component.

Of the atoms moving with velocity v at a given instant let the fraction $\phi(v, w)\,dw$ acquire increments of velocity between w and $w + dw$ during the succeeding interval τ. Consider the atoms at the end of this interval which are moving with velocities between v' and $v' + dv'$. Those of them which were originally v-atoms have had an increment w, where

$$w = v' - v, \quad dw = dv';$$

they therefore form the fraction $\phi(v, v' - v)\,dv'$ of the v-atoms, which were originally a fraction $f(v)\,dv$ of the whole. Hence if $F(v')\,dv'$ is the new distribution function,

$$F(v')\,dv' = dv' \int_{-\infty}^{+\infty} f(v)\,\phi(v, v' - v)\,dv. \qquad \text{......(1361)}$$

The condition for the preservation of equilibrium (or more generally a steady state) is $F \equiv f$ or

$$f(v') = \int_{-\infty}^{+\infty} f(v)\,\phi(v, v' - v)\,dv. \qquad \text{......(1362)}$$

The increment w is given by

$$w = (ve^{-\lambda\tau} - v) + u,$$

or for τ small

$$w \doteqdot -\lambda\tau v + u.$$

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* Milne, *loc. cit.*, whose account we follow. See also Fokker, *Ann. der Phys.* vol. XLIII, p. 810 (1914); Planck, *Berl. Sitz.* p. 324 (1917).

The function $\phi\,(v, -\lambda\tau v + u)\,du$ is by definition the fraction of v-atoms which acquire by fluctuations increments between u and $u + du$ in time τ. By hypothesis this fraction is independent of v, and we therefore write

$$\phi\,(v, -\lambda\tau v + u) = \psi\,(u). \qquad \text{......(1363)}$$

The function $\psi\,(u)$ satisfies

$$\psi\,(u) = \psi\,(-u), \quad \int_{-\infty}^{+\infty} \psi\,(u)\,du = 1, \quad \int_{-\infty}^{+\infty} u\psi\,(u) = \overline{u} = 0,$$

and we shall write

$$\int_{-\infty}^{+\infty} u^2\psi\,(u)\,du = \overline{u^2}.$$

In order to make use of (1363), and this is the point of Milne's proof, we make the substitution

$$v = (v' - x)/(1 - \lambda\tau).$$

Then equation (1362) becomes

$$f\,(v') = \int_{-\infty}^{+\infty} f\left(\frac{v' - x}{1 - \lambda\tau}\right)\phi\left(\frac{v' - x}{1 - \lambda\tau}, -\lambda t\,\frac{v' - x}{1 - \lambda\tau} + x\right)\frac{dx}{1 - \lambda\tau},$$

and after using (1363) this becomes

$$f\,(v') = \frac{1}{1 - \lambda\tau}\int_{-\infty}^{+\infty} f\left(\frac{v' - x}{1 - \lambda\tau}\right)\psi\,(x)\,dx. \qquad \text{......(1364)}$$

We can now for small τ expand f in powers of x and integrate term by term. We find

$$-f\,(v') = \frac{1}{\lambda\tau}\left[f\left(\frac{v'}{1 - \lambda\tau}\right) - f\,(v') + \frac{\frac{1}{2}\overline{u^2}}{(1 - \lambda\tau)^2}f''\left(\frac{v'}{1 - \lambda\tau}\right) + \dots\right].$$

It is necessary to assume that $\overline{u^4}$, $\overline{u^6}$, ... are of a higher order in τ than $\overline{u^2}$. Letting now $\tau \to 0$ we find that

$$\tfrac{1}{2}f''\,(v') + [f\,(v') + v'f'\,(v')]\,\underset{\tau \to 0}{\mathrm{Lt}}\,\frac{\lambda\tau}{\overline{u^2}} = 0. \qquad \text{......(1365)}$$

Let us now put $$\underset{\tau \to 0}{\mathrm{Lt}}\,\frac{\lambda\tau}{\overline{u^2}} = \mu.$$

Then the complete solution of the differential equation (1365) is

$$f\,(v') = e^{-\mu v'^2}\left[A\int_0^{v'} e^{\mu q^2}\,dq + B\right].$$

Since $$\int_{-\infty}^{+\infty} f\,(v')\,dv' = 1$$

and the A-contribution does not converge, we must have

$$A = 0, \quad B = (\mu/\pi)^{\frac{1}{2}}.$$

Then $$\overline{v'^2} = \left(\frac{\mu}{\pi}\right)^{\frac{1}{2}}\int_{-\infty}^{+\infty} v^2 e^{-\mu v^2}\,dv = \frac{1}{2\mu},$$

and finally

$$f(v) = \left(\frac{1}{2\pi\overline{v^2}}\right)^{\frac{1}{2}} e^{-\frac{1}{2}v^2/\overline{v^2}}, \quad \left(\overline{v^2} = \tfrac{1}{2}\mathop{\mathrm{Lt}}_{\tau=0} \frac{\overline{u^2}}{\lambda\tau}\right). \qquad \text{......(1366)}$$

§ **19·51**. *Corollaries and extensions of Theorem* 19·5. A more exact treatment of the theorem, not confined to small τ, is of considerable interest, at least mathematical. The ψ defined in (1363) though independent of v, depends on τ, as of course does $\overline{u^2}$. When τ is no longer restricted to be small we must everywhere replace $1 - \lambda\tau$ by the exact $e^{-\lambda\tau}$. Equation (1364) then takes the exact form

$$f(v') = e^{\lambda\tau}\int_{-\infty}^{+\infty} f[(v'-x)\,e^{\lambda\tau}]\,\psi(x,\tau)\,dx. \qquad \text{......(1367)}$$

This equation must hold for all v' and τ and the right-hand side must be independent of τ. We can show that these conditions serve to determine not only $f(v')$ but also $\psi(x,\tau)$, that is both the steady distribution law and the law of diffusion of random velocity among a subgroup of atoms, moving initially all with the same velocity.

By the study of small τ we have already shown that

$$f(v) = \left(\frac{\mu}{\pi}\right)^{\frac{1}{2}} e^{-\mu v^2}.$$

Inserting this in (1367) and changing the variable of integration we find

$$e^{-\mu v'^2} = \int_{-\infty}^{+\infty} e^{-\mu v^2}\,\psi(v' - ve^{-\lambda\tau}, \tau)\,dv.$$

If we differentiate this with respect to τ and simplify by integration by parts we find

$$\int_{-\infty}^{+\infty}\left\{\frac{\frac{1}{2}\lambda e^{-2\lambda\tau}}{\mu}\psi_{xx} - \psi_\tau\right\} e^{-\mu v^2}\,dv = 0,$$

in which the variable x has the value $v' - ve^{-\lambda\tau}$ after differentiation. This equation thus reduces for fixed τ to the form

$$\int_{-\infty}^{+\infty} g(v'' - v)\,e^{-\mu v^2}\,dv = 0 \quad \textit{(all } v''\textit{)}$$

which requires that $g = 0$.* We thus have

$$\frac{\frac{1}{2}\lambda e^{-2\lambda\tau}}{\mu}\psi_{xx} = \psi_\tau, \qquad \text{......(1368)}$$

which (on the proper time scale) is equivalent to the standard equation of diffusion. It is reducible to the ordinary form by the change of variable

$$t = 1 - e^{-2\lambda\tau}.$$

* For a proof see footnote on p. 496.

Its solution for a "point source", that is for an initial concentration of all the particles at the origin of x, is, when the constant is adjusted so that

$$\int_{-\infty}^{+\infty} \psi(x, \tau)\, dx = 1,$$

$$\psi(x, \tau) = \left(\frac{\mu}{\pi}\right)^{\frac{1}{2}} \frac{e^{\lambda\tau}}{(e^{2\lambda\tau} - 1)^{\frac{1}{2}}} e^{-\frac{\mu e^{2\lambda\tau} x^2}{e^{2\lambda\tau} - 1}}. \qquad \text{......(1369)}$$

This function exhibits the growth of the distribution law for the random velocities. Its initial value is zero except for $x = 0$, and as $\tau \rightarrow \infty$,

$$\psi(x, \tau) \sim \left(\frac{\mu}{\pi}\right)^{\frac{1}{2}} e^{-\mu x^2}.$$

Thus the subgroup of atoms moving initially with a given velocity ultimately acquires a Maxwellian distribution, which is naturally independent of its initial velocity.

§ **19·52**. *Einstein's calculation of* λ *and* $\overline{u^2}$. We proceed next to the calculation of λ. By (1321) the number of absorptions of isotropic radiation per atom in state 1 per unit time is

$$B_1{}^2 I(\nu)\, d\nu.$$

This can be generalized for radiation in a given solid angle, thus applying to anisotropic cases. The number of absorptions is then

$$B_1{}^2 I'(\nu', \theta')\, d\nu' d\omega'/4\pi,$$

measured in the frame K' moving with the atom. The coefficient $B_1{}^2$ cannot depend on orientation unless there is a field orientating the atoms. The number of absorptions per atom in unit time averaged over all the atoms is therefore*

$$\frac{\varpi_1 e^{\chi_1/kT}}{f(T)} B_1{}^2 I'(\nu', \theta')\, d\nu' d\omega'/4\pi. \qquad \text{......(1370)}$$

Every such absorption conveys to the atoms X'-momentum to the amount

$$\frac{h\nu'}{c}\cos\theta'.$$

The stimulated emissions must also be anisotropic for they must take place always in the direction of the incident radiation. We have as yet not considered this point, but it is required by the classical analogy discussed by Van Vleck†. More forcibly, unless the stimulated emissions are in the same direction as the incident radiation, they will not concern light of the same frequency in all frames of reference, and the whole argument of

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* We recall that χ_1 and χ_2 are negative energies and $f(T) = \varpi_1 e^{\chi_1/kT} + \varpi_2 e^{\chi_2/kT}$.

† Van Vleck, *loc. cit.* in § 19·2.

§ 19·4 applied to this process must break down. Due to the radiation incident in $d\omega'$ there are

$$\frac{\varpi_2 e^{\chi_2/kT}}{f(T)} B_2^1 I'(\nu', \theta')\, d\nu' d\omega'/4\pi$$

such emissions per atom per unit time, each contributing to the atom the recoil momentum

$$-\frac{h\nu'}{c}\cos\theta'.$$

In the frame K' the natural emissions must be isotropic and contribute nothing to λ.

If now we collect these results and recall that $\varpi_1 B_1^2 = \varpi_2 B_2^1$ we find that the total average momentum contributed by the radiation to each atom per unit time is

$$\frac{h\nu'}{4\pi c f(T)} \varpi_1 B_1^2 \{e^{\chi_1/kT} - e^{\chi_2/kT}\}\, d\nu' \int I'(\nu', \theta') \cos\theta'\, d\omega'.$$

Using (1343)′ and carrying out the integration we find that this rate of transfer of momentum is

$$-v\frac{h\nu'}{c^2 f(T)}\left\{I(\nu') - \tfrac{1}{3}\nu' \frac{\partial I(\nu')}{\partial \nu'}\right\} \varpi_1 B_1^2 d\nu'\, (e^{\chi_1/kT} - e^{\chi_2/kT}).$$

The coefficient of $-v$ is by definition $m\lambda$, and the formula now contains only the isotropic $I(\nu')$. Using Planck's law and the relation $h\nu' = \chi_1 - \chi_2$ we reduce this to

$$\lambda = \frac{h^2\nu'^2}{c^2}\frac{\varpi_1 e^{\chi_1/kT}}{f(T)}\frac{B_1^2 I(\nu')\, d\nu'}{3mkT}. \qquad \text{......(1371)}$$

We may observe that in this calculation we have for simplicity used a frame K' and neglected the change of mass of the atom on absorbing $h\nu$. This is sufficiently accurate here, but the exact method is of course that of § 19·4.

We have finally to calculate $\overline{u^2}$, the fluctuational increment of velocity in time τ, to an approximation which ignores the slight anisotropy and treats the atom as at rest. A single absorption or emission exerts at an angle θ_r an impulse $(h\nu'/c)\cos\theta_r$ on the atom in the X-direction. Thus for any atom

$$mu = (h\nu'/c)\, \Sigma_r \cos\theta_r,$$

and averaged over all atoms $\overline{u} = 0$, and

$$m^2\overline{u^2} = \frac{h^2\nu'^2}{c^2}\overline{(\Sigma_r \cos^2\theta_r + 2\Sigma_r \cos\theta_r \cos\theta_s)}.$$

The average value of the product term is obviously zero. The average value of the square terms is $\frac{1}{3}n$, where n is the total number of emissions and absorptions in time τ, that is double the number of the absorptions. Thus by (1370)

$$n = \tau \frac{2\varpi_1 e^{\chi_1/kT}}{f(T)} B_1{}^2 I(\nu')\, d\nu',$$

and finally
$$\overline{u^2} = \frac{h^2\nu'^2}{c^2} \frac{\varpi_1 e^{\chi_1/kT}}{f(T)} \frac{2B_1{}^2 I(\nu')\, d\nu'}{3m^2} \tau. \qquad \text{......(1372)}$$

Comparing (1371) and (1372) we find

$$\frac{\overline{u^2}}{2\lambda\tau} = \frac{kT}{m},$$

so that by (1358)
$$\tfrac{1}{2} m\overline{v^2} = \tfrac{1}{2} kT,$$

as required for preservation of the equilibrium state.

If we did not assume Planck's law for $I(\nu)$ in reducing (1371) and (1372) we should eventually find

$$\tfrac{1}{2} m\overline{v^2} = \frac{m\overline{u^2}}{4\lambda\tau} = \frac{\tfrac{1}{2} h\nu'}{(1 - e^{-h\nu'/kT})\left(3 - \dfrac{\nu'}{I}\dfrac{\partial I}{\partial \nu'}\right)}. \qquad \text{......(1373)}$$

§ **19·6.** *The emission and absorption of solids.* A solid body, or for that matter a liquid or a sufficiently dense gas, can generally be regarded as emitting light of all wave lengths (e.g. incandescent filaments, electric arcs, the sun). In an assembly in equilibrium this is a surface effect, and therefore must preserve equilibrium independently of all volume effects.

In unit time the energy of ν-radiation within a solid angle $d\omega$ at an angle θ with the normal to a unit surface which strikes the unit surface is

$$I(\nu) \cos\theta \, d\nu \, d\omega.$$

In order to preserve equilibrium (isotropic radiation) the same amount of ν-radiation must be sent back in the reverse direction. This must hold for all ν and all T. The surfaces of condensed bodies are usually described by an absorption coefficient $k(\nu, \theta)$, which is the fraction of ν-radiation incident at an angle θ that they absorb. The rest of the radiation, the fraction $1 - k(\nu, \theta)$, is reflected in some manner, but with a definite phase relation to the incident light. The existence of a phase relation is the defining property of reflection, and forces us to distinguish between the reflected radiation and the radiation re-emitted after absorption for which there is no such phase relation. It is this point which leads (at least on classical theories) to a discussion somewhat more complicated than that required for the impact of particles on walls. If there is absorption there must of course be emission as well, and the emission coefficient $\epsilon(\nu, \theta)$ is so defined that the ν-radiation emitted in unit time by unit area into a solid angle $d\omega$ at an angle θ with the normal to the surface is

$$\epsilon(\nu, \theta) \cos\theta \, d\nu \, d\omega.$$

The radiation reflected from *all* incident beams into the same solid angle may be defined to be

$$r(\nu, \theta) \cos\theta \, d\nu \, d\omega.$$

The hypothesis of the preservation of equilibrium requires that

$$I(\nu) = \epsilon(\nu, \theta) + r(\nu, \theta). \qquad \text{......(1374)}$$

According to the hypothesis of detailed balancing we should be entitled to assert separately the equality of the absorbed and re-emitted fractions and of the unabsorbed and total reflected fractions, i.e. that

$$r(\nu, \theta) = \{1 - k(\nu, \theta)\} I(\nu), \qquad \text{......(1375)}$$

$$\epsilon(\nu, \theta) = k(\nu, \theta) I(\nu). \qquad \text{......(1376)}$$

This is a familiar result of the classical radiation theory. It will be true on the hypothesis of preservation alone if for example the reflection is perfectly specular or perfectly diffuse, or obeying any mixture of these two laws, or if the surface is such that Helmholtz's reciprocal theorem on definite beams of light holds*. It does not seem that Helmholtz's theorem can extend to the most general condition of reflective scattering contemplated here, but it is undoubtedly true for most reflections actually found in practice.

A body for which $k(\nu, \theta) = 1$ is usually called *a black body*, or, since

$$\epsilon(\nu, \theta) = I(\nu),$$

a full radiator. A body for which $k(\nu, \theta)$ is a constant (less than unity) is called *a grey body*. It emits radiation distributed according to Planck's law, but at less than the normal rate.

The surface coefficients actually depend on the state of polarization of the incident beam. It is necessary to imagine $I(\nu)$ broken up into two plane polarized components, one in the plane of incidence and the other at right angles to it. The theory is easily extended to cover this distinction.

§ **19·7**. *Photo-electric emission of solids.* There is a well-known mechanism, apparently completely distinct from the radiationless thermionic emission of Chapter XI, by which electrons are ejected from solids when illuminated by light of a suitable frequency. The elementary process is undoubtedly that a quantum of energy $h\nu$ strikes a solid surface and is absorbed by an electron in the solid which is then ejected from the solid with an energy η given by Einstein's equation

$$\eta = h\nu - \chi, \qquad \text{......(1377)}$$

where χ is a constant. If $\nu < \chi/h$ there is no effect. In practice electrons are apparently ejected with all velocities up to a maximum of η, but this is naturally accounted for by losses in collisions on the way out and will not be further considered here. The threshold potential χ bears no close relation

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[*] See Lorentz, *Problems of Modern Physics*, Note 17 (1927)

to the potentials of the atoms composing the solid when in a free state, so that the phenomenon may properly be classed as a solid and not an atomic property.

The phenomenon (in particular the value of χ) is extremely sensitive to surface impurities, as are thermionic phenomena. The thermionic work function and the photo-electric threshold potential are on the evidence obviously closely related and it is probably a legitimate induction to identify them. The conditions of observation are different, for the temperatures of the solid are different in the two classes of experiment, and the observed mean χ can change slowly with the temperature.

The converse of this effect is the emission of ν-radiation when an electron of energy $h\nu - \chi$ strikes the solid. Such effects have never been recorded and are too scarce and too difficult ever to observe. That radiation is emitted in stopping the electrons striking a metal target (X-ray emission) is familiar enough. The radiation of continuous frequency so obtained is probably almost entirely atomic in origin, arising from free-free transitions in the field of a single atom; the characteristic radiations are obviously atomic. The interest of the converse photo-electric effect would lie in $h\nu$ exceeding (by a few volts) the energy of the impacting electron.

We shall not give the details in this case, but it follows at once by arguments now familiar and the use of (789) that if ϕ is the chance that a ν-quantum striking the solid shall produce a photo-electron, and

$$\phi'\left(1+\frac{c^2}{2h\nu^3}I(\nu)\right)$$

is the chance that an η-electron ($\eta = h\nu - \chi$) striking the solid shall be absorbed with the production of a ν-quantum of radiation, then

$$\phi = \frac{1}{\kappa(0)}\frac{mc^2}{h^2\nu^2}\eta\phi'. \qquad \ldots\ldots(1378)$$

In the region of λ 3000 ϕ may be numerically comparable with unity, but ϕ' is then of the order 10^{-5}–10^{-6}. The converse effect is very small. It must also be remembered that the calculations leading to (1378) refer to the equilibrium state, and that a solid is no longer (like an atom in a given state) a definite system, but itself depends on the temperature. The solid may be capable at high temperatures of capturing impinging electrons in this way with the calculated frequency, but it does not follow that the same solid cold, bombarded by electrons, will be able to achieve the same fraction of captures. There may be no vacant orbits for the electrons to occupy.

§ **19·8.** *Photo-chemical reactions and chemi-luminescence.* It is a familiar fact that certain gaseous reactions are initiated by the absorption of external radiation—usually light of the visible region or nearby. It is however very difficult to find simple unambiguous examples, in which we can be perfectly sure of what is happening, so that we shall be content to discuss such mechanisms and their converses in general terms without attempting precise applications of any theoretical results.

In the photo-chemical mechanism the primary action is the absorption of a single quantum of ν-radiation. There is no known case of dependence on a power of $I(\nu)$ higher than the first, so that only a single quantum can normally be concerned. The result of this absorption may be either

(1) An activated molecule.

(2) Immediate dissociation.

In either case we may expect (and find) a threshold frequency ν_0 below which radiation is ineffective. We may observe further that, whether $\nu > \nu_0$ or $\nu < \nu_0$, ν-radiation must be ineffective unless it is absorbed by the molecule and therefore that only the lines and continuous stretches (if any) of the absorption spectrum of the molecule can be effective photo-chemically. This point is well brought out by the practice of sensitizing photographic plates to red light by staining them with red-absorbent dyes. The plates are normally insensitive to red light not because $\nu_{\mathrm{red}} < \nu_0$ but because they do not absorb the red light. Once absorbed the energy of the red light is transferable by other mechanisms, and the photographic reaction occurs.

In simple cases we shall expect to find with either mechanism (1) or (2) that just one molecule is transformed for each quantum of effective light absorbed. This is called *Einstein's law of photo-chemical equivalence*. There is however no reason to expect its universal validity, owing to secondary effects such as the formation of reaction chains carried on by the products of the primary photo-chemical act. Einstein's law is found to hold in many cases, but there are marked exceptions, such as the reaction

$$H_2 + Cl_2 \rightarrow 2HCl,$$

in which the number of reacting pairs is many million times the number of light quanta absorbed.

The converse reactions are either

(1) Emission of ν-radiation and deactivation.

(2) Recombination of two free atoms or molecules with emission of ν-radiation to get rid of the excess energy.

Experiments will certainly be able to distinguish between (1) and (2) and no doubt will do so soon, but owing to subsidiary effects this is never easy. In the meantime we may be certain that examples of both types of mechanism occur in nature. A quantum of visible light represents a heat of activation per gram-molecule of 50,000 calories, more or less, which is just of the order of the heats of activation with which we are familiar in reactions proceeding by collision. On the other hand, examples of the converse mechanism (2) are known, though not in the gaseous state. This is the phenomenon of chemi-luminescence[*].

Here, as to some extent in Chapter XVIII, detailed application of the theory must await more precise experimental facts.

[*] See, for example, Noddack, *Handb. der Phys.* vol. XXIII, p. 631, art. *Photochemie* (1926).

Footnote to p. 489. A simple proof of this theorem can be given under sufficiently wide conditions by connecting it with Fourier's integral theorem. We assume that g is differentiable and that $\int_{-\infty}^{+\infty} |g|\, dx$ exists. Then from the hypothesis of the theorem to be proved

$$0 = \int_{-\infty}^{+\infty} dx \int_0^\infty e^{ixt} g(x-v)\, e^{-v^2}\, dv = \int_{-\infty}^{+\infty} d\xi \int_0^\infty e^{i(\xi+v)t\xi} g(\xi)\, e^{-v^2}\, dv,$$

$$= \left(\int_0^\infty e^{-v^2+ivt}\, dv\right)\left(\int_{-\infty}^{+\infty} g(\xi)\, e^{i\xi t}\, d\xi\right).$$

The first integral factor is equal to $\frac{1}{2}\sqrt{\pi}e^{-\frac{1}{4}t^2}$ and never vanishes. Therefore

$$\int_{-\infty}^{+\infty} g(\xi) \begin{matrix}\cos\\ \sin\end{matrix} (\xi t)\, d\xi = 0 \qquad (\textit{all } t).$$

But by Fourier's integral theorem (Hobson, *Functions of a Real Variable*, vol. II, p. 727)

$$g(x) = \frac{1}{\pi} \int_0^\infty dv \int_{-\infty}^{+\infty} g(t) \cos\{v(t-x)\}\, dt = 0,$$

since the inner integral vanishes.

CHAPTER XX

FLUCTUATIONS

§ **20·1.** We have hitherto, in calculating average values and asserting that they represent properties of the assembly, normally observed in or characterizing the equilibrium state, generally ignored the fact that actual examples of the assembly will all deviate more or less from the average value. From the definition of average value the average of these deviations must of course vanish, but the average numerical value of the deviation will not vanish, and will be a measure of the closeness with which the assembly really conforms to the theoretical equilibrium state. It was necessary for the logical development to point out at once, as we did in Chapter II, that in general these average deviations are insignificant compared with the average values themselves. This at once justifies our treatment of the equilibrium state and the possession of all its average values as a normal property of the assembly in the sense familiarized by Jeans. We have also had occasion to prove certain theorems, particularly in Chapter XIX in connection with Einstein's discussion of the interaction of radiation and atoms, which are closely concerned with fluctuation problems and will be applied further.

It is therefore our primary object here to develop systematic methods of calculating such average deviations, (*a*) for the sake of the logical development of the whole subject, and (*b*) for direct application where possible to physical observations such as Brownian movement and opalescence near the critical point. In taking up these calculations we find at once that the average value of the numerical deviation is awkward to handle and is naturally replaced by a calculation of the average of the square of the deviation. This is moreover the quantity ordinarily required in applications, and we have usually spoken of this quantity hitherto as the *fluctuation*. If P is any quantity whose average value is $\overline{P}$, then the fluctuation in this sense is $\overline{(P-\overline{P})^2}$. In devising general methods of calculating these fluctuations, we find it almost equally simple to calculate $\overline{(P-\overline{P})^n}$ for any positive integral value of n. We shall therefore speak of all such quantities in this chapter as fluctuations, and refer to particular ones as fluctuations of order n, the "fluctuations" of other chapters being here fluctuations of the second order. Fluctuations of orders other than the second are not of much immediate physical importance, but the results are elegant and perhaps not without intrinsic interest. They generalize in many cases the corresponding results due to Gibbs*.

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* Gibbs, *Elementary Principles in Statistical Mechanics*, chap. VII. The results for non-dissociating assemblies were given by Darwin and Fowler, *Proc. Camb. Phil. Soc.* vol. XXI, p. 391 (1922), but the discussion there given for dissociating assemblies is inadequate and is here revised.

§ **20·2**. *General fluctuations in the partition of energy.* We start by discussing fluctuations of energy, and can obviously achieve full generality by considering an assembly of two types of quantized systems. The results extend at once to any number of types quantized or classical, in the absence of dissociation which we consider separately later.

In the notation of § 2·6, and by a repetition of the arguments there given, we have at once

$$C\overline{E_A{}^n} = \frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}\left\{\left(z\frac{d}{dz}\right)^n [f(z)]^M\right\}[g(z)]^N. \qquad \text{......(1379)}$$

We could at once evaluate the dominant term or terms in $\overline{E_A{}^n}$ from (1379) by the usual application of steepest descents. But what we really require is the dominant term in $\overline{(E_A - \overline{E_A})^n}$, and in passing to this by expansion and use of $\overline{E_A{}^n}$ a number of the leading terms will cancel and a more or less complete expansion of $\overline{E_A{}^n}$ must be used. We avoid this difficulty by first constructing an exact integral for $C\,\overline{(E_A - \overline{E_A})^n}$, which can be simply evaluated in the usual way.

A change of notation is expedient. Put

$$z = e^u, \; f(z) = e^{F(u)}, \; g(z) = e^{G(u)}.$$

We shall usually omit the arguments of F and G. Then

$$C\overline{E_A{}^n} = \frac{1}{2\pi i}\int_{\gamma'} e^{NG-Eu}\left\{\left(\frac{d}{du}\right)^n e^{MF}\right\}du, \qquad \text{......(1380)}$$

where the contour γ' is now the straight line from $\log\vartheta - i\pi$ to $\log\vartheta + i\pi$. This contour is of course that required in the application of steepest descents. To form the integral for $C\,\overline{(E_A - \overline{E_A})^n}$ we replace E by $\overline{E_A} + \overline{E_B}$ and use Leibnitz's theorem; thus

$$\begin{aligned} C\,\overline{(E_A - \overline{E_A})^n} &= C\,[\overline{E_A{}^n} - {}_nC_1\overline{E_A{}^{n-1}}\,\overline{E_A} + {}_nC_2\overline{E_A{}^{n-2}}(\overline{E_A})^2 - \dots (-)^n(\overline{E_A})^n], \\ &= \frac{1}{2\pi i}\int_{\gamma'} e^{NG-Eu}\,du\left[\begin{matrix}\left(\frac{d}{du}\right)^n - {}_nC_1\overline{E_A}\left(\frac{d}{du}\right)^{n-1} + {}_nC_2\,(\overline{E_A})^2\left(\frac{d}{du}\right)^{n-2} \\ - \dots (-)^n(\overline{E_A})^n\end{matrix}\right]e^{MF}, \\ &= \frac{1}{2\pi i}\int_{\gamma'} e^{NG-\overline{E_B}u}\left[\left(\frac{d}{du}\right)^n e^{MF-\overline{E_A}u}\right]du. \qquad \text{......(1381)} \end{aligned}$$

This is the desired integral. We know that effectively the whole value of this integral is provided by a small element of the contour near $u = \log\vartheta$. We therefore write $u = \log\vartheta + i\zeta$ and F for $F(\log\vartheta)$, etc., and recall that in this notation

$$\overline{E_A} = \left[M\frac{dF(u)}{du}\right]_{\log\vartheta} = MF'.$$

Then

$$MF - \overline{E_A}u = M\,(F - \log\vartheta\, F') - \tfrac{1}{2}MF''\zeta^2 - \tfrac{1}{6}iMF'''\zeta^3 + \dots,$$

with a similar expression for $NG - \overline{E_B}u$. The integration is now with respect to ζ, and while ζ is still small we may suppose that $(MF'' + NG'')^{\frac{1}{2}}\,\zeta$ ranges effectively from $-\infty$ to $+\infty$, while all other terms such as $MF'''\,\zeta^3$ remain small. Thus

$$C\,\overline{(E_A - \overline{E_A})^n} = \frac{(i)^{-n}}{2\pi}\exp\left[M\,(F - \log\vartheta\, F') + N\,(G - \log\vartheta\, G')\right]$$
$$\times \int_{-\infty}^{+\infty} e^{-\frac{1}{2}NG''\zeta^2}\{1 + O\,(N\zeta^3)\}\left(\frac{d}{d\zeta}\right)^n \left[e^{-\frac{1}{2}MF''\zeta^2}\{1 + O\,(M\zeta^3)\}\right] d\zeta,$$

in which the O-terms may be differentiated. If we take the special case $n = 0$ we obtain C, and the O-terms cannot contribute to the leading term in the integral, which is

$$\int_{-\infty}^{+\infty} e^{-\frac{1}{2}(MF'' + NG'')\zeta^2}\,d\zeta = \left(\frac{2\pi}{MF'' + NG''}\right)^{\frac{1}{2}}.$$

Thus

$$\overline{(E_A - \overline{E_A})^n} = (i)^{-n}\left(\frac{MF'' + NG''}{2\pi}\right)^{\frac{1}{2}}\int_{-\infty}^{+\infty} e^{-\frac{1}{2}NG''\zeta^2}\{1 + O\,(N\zeta^3)\}$$
$$\times \left(\frac{d}{d\zeta}\right)^n \left[e^{-\frac{1}{2}MF''\zeta^2}\{1 + O\,(M\zeta^3)\}\right] d\zeta. \quad \dots\dots(1382)$$

The further approximation to (1382) depends on the parity of n. It is clear in any case that the first differentiation of the bracket $\{1 + O\,(M\zeta^3)\}$ does not alter the order of the integral. Instead of the leading term 1 we have then $M\zeta^2$. But every time we differentiate $e^{-\frac{1}{2}MF''\zeta^2}$ we multiply the integrand by $M\zeta$ and increase its order after integration by $\sqrt{M}$. Thus the highest order term arises from differentiating the exponential n times and the O-terms are both of lower order, *provided that this highest order term does not happen to vanish identically on integration.* It does not vanish for n even, but does vanish for n odd, when further consideration is required to which we return. If we now put $n = 2v$ we find for the required asymptotic form of $\overline{(E_A - \overline{E_A})^{2v}}$,

$$\overline{(E_A - \overline{E_A})^{2v}} = (-)^v\left(\frac{MF'' + NG''}{2\pi}\right)^{\frac{1}{2}}\int_{-\infty}^{+\infty} e^{-\frac{1}{2}NG''\zeta^2}\left(\frac{d}{d\zeta}\right)^{2v} e^{-\frac{1}{2}MF''\zeta^2}\,d\zeta. \quad \dots\dots(1383)$$

To evaluate this integral let us write

$$I_v = (-)^v\int_{-\infty}^{+\infty}\phi_2\phi_1^{(2v)}\,d\zeta = (-)^{v+r}\int_{-\infty}^{+\infty}\phi_2^{(r)}\phi_1^{(2v-r)}\,d\zeta,$$

the latter form following by repeated integration by parts, and ϕ_1 and ϕ_2

being short for $e^{-\frac{1}{2}MF''\zeta^2}$ and $e^{-\frac{1}{2}NG''\zeta^2}$ respectively. Then since $\phi_1' = -MF''\zeta\phi_1$, $\phi_2' = -NG''\zeta\phi_2$ we find that

$$\frac{MF''+NG''}{MF''NG''}I_v = (-)^v \int_{-\infty}^{+\infty} \zeta\,(\phi_2\phi_1^{(2v-1)} + \phi_1\phi_2^{(2v-1)})\,d\zeta.$$

On integration by parts the right-hand side becomes

$$2I_{v-1} + (-)^{v-1}\int_{-\infty}^{+\infty} \zeta\,(\phi_2'\phi_1^{(2v-2)} + \phi_1'\phi_2^{(2v-2)})\,d\zeta,$$

and by continued repetition

$$2vI_{v-1} + \int_{-\infty}^{+\infty} \zeta\,(\phi_2^{(v)}\phi_1^{(v-1)} + \phi_1^{(v)}\phi_2^{(v-1)})\,d\zeta,$$

or

$$(2v-1)\,I_{v-1}.$$

Thus

$$I_v = (2v-1)\ldots 3\,.\,1\left(\frac{MF''NG''}{MF''+NG''}\right)^v I_0 \quad \left(I_0 = \left\{\frac{2\pi}{MF''+NG''}\right\}^{\frac{1}{2}}\right), \qquad \ldots\ldots(1384)$$

$$\overline{(E_A-\overline{E_A})^{2v}} = (2v-1)\ldots 3\,.\,1\left(\frac{MF''NG''}{MF''+NG''}\right)^v,$$

$$= (2v-1)\ldots 3\,.\,1\,\{\overline{(E_A-\overline{E_A})^2}\}^v. \qquad \ldots\ldots(1385)$$

Finally

$$\overline{(E_A-\overline{E_A})^2} = \frac{MF''NG''}{MF''+NG''} = \vartheta\frac{d\overline{E_A}}{d\vartheta}\left(1 - \frac{\vartheta\,d\overline{E_A}/d\vartheta}{\vartheta\,dE/d\vartheta}\right). \qquad \ldots\ldots(1386)$$

Fluctuations of the energy of all even orders are thus completely determined.

We now return to the odd orders. To an equivalent approximation these all vanish, and they are actually of order lower by $\sqrt{M}$ or $\sqrt{N}$ than the corresponding even orders. We must retain the exact $M\zeta^3$ and $N\zeta^3$ terms in (1382), the $M\zeta^4$ and $N\zeta^4$ and higher terms being negligible. We then find after simple reductions

$$\overline{(E_A-\overline{E_A})^{2v-1}} = \frac{(-)^v}{6}\left(\frac{MF''+NG''}{2\pi}\right)^{\frac{1}{2}}$$

$$\times\left[MF'''\int_{-\infty}^{+\infty} e^{-\frac{1}{2}NG''\zeta^2}\left(\frac{d}{d\zeta}\right)^{2v-1}\{\zeta^3 e^{-\frac{1}{2}MF''\zeta^2}\}\,d\zeta\right.$$

$$\left. + NG'''\int_{-\infty}^{+\infty}\zeta^3 e^{-\frac{1}{2}NG''\zeta^2}\left(\frac{d}{d\zeta}\right)^{2v-1} e^{-\frac{1}{2}MF''\zeta^2}\,d\zeta\right].$$

But

$$\zeta^3 e^{-\frac{1}{2}MF''\zeta^2} = \left[-\frac{1}{M^3F''^3}\left(\frac{d}{d\zeta}\right)^3 - \frac{3}{M^2F''^2}\frac{d}{d\zeta}\right]e^{-\frac{1}{2}MF''\zeta^2}.$$

Therefore

$$\overline{(E_A - \overline{E_A})^{2v-1}} = \frac{(-)^{v-1}}{6}\left(\frac{MF'' + NG''}{2\pi}\right)^{\frac{1}{2}}$$

$$\times \left[MF''' \int_{-\infty}^{+\infty} \left(\frac{1}{M^3F''^3}\,\phi_2\phi_1^{(2v+2)} + \frac{3}{M^2F''^2}\,\phi_2\phi_1^{(2v)}\right) d\zeta \right.$$

$$\left. + NG''' \int_{-\infty}^{+\infty} \left(\frac{1}{N^3G''^3}\,\phi_2^{(3)}\phi_1^{(2v-1)} + \frac{3}{N^2G''^2}\,\phi_2'\phi_1^{(2v-1)}\right) d\zeta\right],$$

$$= (2v-1) \ldots 3\,.\,1 \left(\frac{MF''NG''}{MF'' + NG''}\right)^v \left[\frac{NG'''}{6N^2G''^2}\left\{3 - (2v+1)\,\frac{MF''}{MF'' + NG''}\right\}\right.$$

$$\left. - \frac{MF'''}{6M^2F''^2}\left\{3 - (2v+1)\,\frac{NG''}{MF'' + NG''}\right\}\right]. \quad \ldots\ldots(1387)$$

This expression is of order $(v-1)$ in M or N, that is $\frac{1}{2}(2v-1) - \frac{1}{2}$, while the order of $\overline{(E_A - \overline{E_A})^{2v}}$ is $\frac{1}{2}(2v)$.

When the systems of type A are in a bath of B's, that is when N is very large compared with M, (1387) reduces to

$$\overline{(E_A - \overline{E_A})^{2v-1}} = \tfrac{1}{3}(v-1)(2v-1) \ldots .\, 3\,.\,1\,(MF'')^{v-2}MF'''. \quad \ldots\ldots(1388)$$

The corresponding formula in the even case is

$$\overline{(E_A - \overline{E_A})^{2v}} = (2v-1) \ldots 3\,.\,1\,(MF'')^v. \quad \ldots\ldots(1389)$$

We recall that

$$MF'' = \vartheta\,\frac{d\overline{E_A}}{d\vartheta}, \quad MF''' = \left(\vartheta\,\frac{d}{d\vartheta}\right)^2 \overline{E_A}. \quad \ldots\ldots(1390)$$

These formulae give the dominant terms of the formulae given by Gibbs*, which alone are relevant when M is large. The general formulae (1386) and (1387) hold for all values of the ratio $N : M$.

We may observe in conclusion that

$$C\,\overline{(E_A - \overline{E_A})^v\,(E_B - \overline{E_B})^w}$$

$$= \frac{1}{2\pi i}\int_{\gamma'} \left\{\left(\frac{d}{du}\right)^v e^{MF - \overline{E_A}u}\right\}\left\{\left(\frac{d}{du}\right)^w e^{NG - \overline{E_B}u}\right\} du, \quad \ldots\ldots(1391)$$

which can be evaluated in a similar way.

§ **20·3**. *General fluctuations of $\bar{a}_r$.* A similar but slightly more complicated investigation evaluates $\overline{(a_r - \bar{a}_r)^n}$, where $\bar{a}_r$ is as usual the number of systems of type A in the assembly in their rth state or cell. By § 2·6

$$C\,\overline{(a_r - \bar{a}_r)^n} = \Sigma_{a,b}\,\frac{M\,!}{a_1\,!\,a_2\,!\ldots}\,\varpi_1^{a_1}\varpi_2^{a_2}\ldots\,\frac{N\,!}{b_1\,!\,b_2\,!\ldots}\,\rho_1^{b_1}\rho_2^{b_2}\ldots(a_r - \bar{a}_r)^n.$$

$$\ldots\ldots(1392)$$

There are only a finite number of terms in (1392) so that $C\,\overline{(a_r - \bar{a}_r)^n}$ is

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* Gibbs, *loc. cit.* p. 78.

$(n\,!)$ times the coefficient of x^n in the expression obtained by replacing $(a_r - \bar{a}_r)^n$ in (1392) by $e^{x(a_r - \bar{a}_r)}$. This relationship is conveniently expressed by the notation

$$C\,\overline{(a_r - \bar{a}_r)^n} = \text{Coef}_n\, \Sigma_{a,b} \frac{M\,!}{a_1\,!\,a_2\,!\,\ldots}\, \varpi_1^{a_1} \varpi_2^{a_2} \ldots \frac{N\,!}{b_1\,!\,b_2\,!\,\ldots}\, \rho_1^{a_1} \rho_2^{a_2} \ldots e^{x(a_r - \bar{a}_r)}.$$

The series $\Sigma_{a,b}$ is now of the standard type with ϖ_r replaced by $\varpi_r e^x$ and an extra factor $e^{-\bar{a}_r x}$. Therefore in the usual integral the partition function $f(z)$ is replaced by

$$f(z) + \varpi_r z^{\epsilon_r} (e^x - 1).$$

We therefore find at once in the notation of the last section

$$C\,\overline{(a_r - \bar{a}_r)^n} = \text{Coef}_n \frac{1}{2\pi i} \int_{\gamma'} e^{-Eu + MF + NG - \bar{a}_r x} \{1 + \varpi_r e^{\epsilon_r u - F} (e^x - 1)\}^M \, du. \quad \text{......(1393)}$$

The terms containing x in (1393) can be written

$$\exp\left[-\bar{a}_r x + M \log\{1 + \varpi_r e^{\epsilon_r u - F} (e^x - 1)\}\right], \quad \text{......(1394)}$$

and x can be fixed as small as we please. On γ' $u = \log\vartheta + i\zeta$, where ζ is small on the only effective part of the contour. If x is sufficiently small the presence of the x terms does not affect the choice of the u-contour. Inserting

$$\bar{a}_r = M\varpi_r e^{\epsilon_r \log\vartheta - F(\log\vartheta)}$$

in (1394) we obtain after reduction

$$\exp\{i\zeta x\,\bar{a}_r(\epsilon_r - F') + \tfrac{1}{2}x^2(\bar{a}_r - (\bar{a}_r)^2/M) + O(M\zeta^2 x) + O(M\zeta x^2) + O(Mx^3)\}.$$

When $n = 0$ we can at once put $x = 0$ in (1393) and obtain C. Using this fact, and approximating as in the last section, we find that

$$\begin{aligned}
\overline{(a_r - \bar{a}_r)^n} &= \text{Coef}_n \left(\frac{MF'' + NG''}{2\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} e^{-\frac{1}{2}\zeta^2(MF'' + NG'') + i\zeta x \bar{a}_r(\epsilon_r - F') + \frac{1}{2}x^2(\bar{a}_r - (\bar{a}_r)^2/M)} \\
&\quad \times \{1 + O(M\zeta^3) + O(M\zeta^2 x) + O(M\zeta x^2) + O(Mx^3)\}\, d\zeta \\
&= \text{Coef}_n \exp\left\{\tfrac{1}{2}x^2\left[\bar{a}_r - \frac{(\bar{a}_r)^2}{M} - \frac{(\bar{a}_r)^2(\epsilon_r - F')^2}{MF'' + NG''}\right]\right\} \\
&\quad \times \{1 + O(M^{-\frac{1}{2}}) + O(x) + O(M^{\frac{1}{2}}x^2) + O(Mx^3)\}. \quad \text{......(1395)}
\end{aligned}$$

We require the highest order term in (1395), and it is obvious that when n is even all the O-terms are negligible. Thus

$$\begin{aligned}
\overline{(a_r - \bar{a}_r)^{2v}} &= \text{Coef}_{2v} \exp\left\{\tfrac{1}{2}x^2\left[\bar{a}_r - \frac{(\bar{a}_r)^2}{M} - \frac{(\bar{a}_r)^2(\epsilon_r - F')^2}{MF'' + NG''}\right]\right\}, \\
&= \frac{2v\,!}{2^v v\,!}\left[\bar{a}_r - \frac{(\bar{a}_r)^2}{M} - \frac{(\bar{a}_r)^2(\epsilon_r - F')^2}{MF'' + NG''}\right]^v,
\end{aligned}$$

$$\overline{(a_r - \bar{a}_r)^{2v}} = (2v - 1)\,\ldots.\,3\,.\,1\left[\bar{a}_r - \frac{(\bar{a}_r)^2}{M}\left(1 + \frac{M(\epsilon_r - \overline{E_A}/M)^2}{\vartheta\, dE/d\vartheta}\right)\right]^v, \quad \text{......(1396)}$$

$$= (2v - 1)\,\ldots.\,3\,.\,1\left[\bar{a}_r - \frac{(\bar{a}_r)^2}{M} - \frac{(\vartheta\, d\bar{a}_r/d\vartheta)^2}{\vartheta\, dE/d\vartheta}\right]^v, \quad \text{......(1397)}$$

$$= (2v - 1)\,\ldots.\,3\,.\,1\,\{\overline{(a_r - a_r)^2}\}^v. \quad \text{......(1398)}$$

When n is odd the approximation must be carried one stage further to obtain $\overline{(a_r - \bar{a}_r)^{2v-1}}$, but we shall not give the analysis. By an obvious extension we can also calculate all such expressions as

$$\overline{(a_r - \bar{a}_r)^v (a_s - \bar{a}_s)^w}, \quad \overline{(a_r - \bar{a}_r)^v (b_s - \bar{b}_s)^w}$$

by evaluating the coefficients of $x^v y^w$ in the integrals

$$\frac{1}{2\pi i}\int_{\gamma'} du\, e^{-Eu+MF+NG-\bar{a}_r x-\bar{a}_s y}\left[1 + \varpi_r e^{\epsilon_r u-F}(e^x - 1) + \varpi_s e^{\epsilon_s u-F}(e^y - 1)\right]^M,$$

$$\frac{1}{2\pi i}\int_{\gamma'} du\, e^{-Eu+MF+NG-\bar{a}_r x-\bar{b}_s y}\left[1 + \varpi_r e^{\epsilon_r u-F}(e^x - 1)\right]^M\left[1 + \rho_s e^{\eta_s u-G}(e^y - 1)\right]^N,$$

respectively. We content ourselves with giving the results required in calculating second order fluctuations in the external reactions of the assembly. They are

$$\begin{aligned}\overline{(a_r - \bar{a}_r)(a_s - \bar{a}_s)} &= -\,\bar{a}_r\bar{a}_s\left[\frac{1}{M} + \frac{(\epsilon_r - F')(\epsilon_s - F')}{MF'' + NG''}\right],\\ &= -\,\frac{\bar{a}_r\bar{a}_s}{M} - \frac{(\vartheta\, d\bar{a}_r/d\vartheta)(\vartheta\, d\bar{a}_s/d\vartheta)}{\vartheta\, dE/d\vartheta}. \qquad \text{......(1399)}\end{aligned}$$

$$\begin{aligned}\overline{(a_r - \bar{a}_r)(b_s - \bar{b}_s)} &= -\,\bar{a}_r\bar{b}_s\,\frac{(\epsilon_r - F')(\eta_s - G')}{MF'' + NG''},\\ &= -\,\frac{(\vartheta\, d\bar{a}_r/d\vartheta)(\vartheta\, d\bar{b}_s/d\vartheta)}{\vartheta\, dE/d\vartheta}. \qquad \text{......(1400)}\end{aligned}$$

§ **20·4**. *Fluctuations in the external reactions.* The generalized reaction of the systems of type A on an external body is given by

$$Y = \Sigma_r\left(-\frac{\partial\epsilon_r}{\partial y}\right)a_r, \qquad \text{......(1401)}$$

where y is the corresponding coordinate defining the position of the external body. The average reaction is

$$\bar{Y} = \Sigma_r\left(-\frac{\partial\epsilon_r}{\partial y}\right)\bar{a}_r = M\Sigma_r\left(-\frac{\partial\epsilon_r}{\partial y}\right)\varpi_r\vartheta^{\epsilon_r}/f(\vartheta), \qquad \text{......(1402)}$$

$$= \frac{M}{\log 1/\vartheta}\,\frac{\partial}{\partial y}\log f(\vartheta), \qquad \text{......(1403)}$$

the usual form. The second order fluctuation of Y is

$$\overline{(Y - \bar{Y})^2} = \Sigma_r\left(\frac{\partial\epsilon_r}{\partial y}\right)^2\overline{(a_r - \bar{a}_r)^2} + 2\Sigma_{r,s}\frac{\partial\epsilon_r}{\partial y}\frac{\partial\epsilon_s}{\partial y}\overline{(a_r - \bar{a}_r)(a_s - \bar{a}_s)}.$$

Applying the formulae (1397) and (1399) we find that

$$\overline{(Y - \bar{Y})^2} = \Sigma_r\left(\frac{\partial\epsilon_r}{\partial y}\right)^2\bar{a}_r - \frac{1}{M}\left(\Sigma_r\frac{\partial\epsilon_r}{\partial y}\bar{a}_r\right)^2 - \frac{1}{\vartheta\, dE/d\vartheta}\left\{\Sigma_r\frac{\partial\epsilon_r}{\partial y}\,\vartheta\,\frac{\partial\bar{a}_r}{\partial\vartheta}\right\}^2.$$

This expression can be simplified, for on differentiating (1401) and (1402) we find

$$\Sigma_r \left(\frac{\partial \epsilon_r}{\partial y}\right)^2 \bar{a}_r - \frac{1}{M}\left(\Sigma_r \frac{\partial \epsilon_r}{\partial y}\bar{a}_r\right)^2 = \left(\frac{\partial \bar{Y}}{\partial y} - \overline{\frac{\partial Y}{\partial y}}\right)\Big/\log 1/\vartheta. \quad \text{......(1404)}$$

Therefore

$$\overline{(Y - \bar{Y})^2} = \left(\frac{\partial \bar{Y}}{\partial y} - \overline{\frac{\partial Y}{\partial y}}\right)\Big/\log 1/\vartheta - \frac{\{\vartheta\, \partial \bar{Y}/\partial \vartheta\}^2}{\vartheta\, dE/\partial \vartheta}. \quad \text{......(1405)}$$

Gibbs* gives a formula for $\overline{(Y - \bar{Y})^2}$ equivalent to (1405) without the last term, which is of course negligible under his condition that N is large compared with M.

With the help of (1400) it is easy to show that (1405) is formally unaltered if Y refers to the total reaction due to all groups of systems instead of to the partial reaction of a single group.

In (1405) all the terms except $\overline{\partial Y/\partial y}$ or $\Sigma_r \bar{a}_r\,(-\,\partial^2\epsilon_r/\partial y^2)$ have an obvious interpretation. This term lies deeper and is compared by Gibbs to an elasticity.

In illustration we shall apply these results to the limiting case in which the reaction is a pressure. It is sufficient to consider the reaction with a part of the wall only, which may be taken to be plane and represented by a movable piston in a cylinder of cross-section A, which completes the enclosure. We cannot progress without *some* definite assumption as to the field of force near the wall. We shall suppose its potential is D/d^s, where d is the distance of the molecule from the wall, and D and s are constants. If D is small and $s > 4$, this will adequately represent an intense local field. If y is the length of the cylinder and x_1, x_2, x_3 rectangular cartesian coordinates, x_1 along the cylinder, then

$$\epsilon_r = \frac{1}{2m}(p_1^2 + p_2^2 + p_3^2)_r + [D/(y - x_1)^s]_r, \quad \text{......(1406)}$$

$$f(\vartheta) = \frac{(2\pi m)^{\frac{3}{2}} A}{h^3 (\log 1/\vartheta)^{\frac{3}{2}}} \int_0^y \exp\left\{-\log 1/\vartheta \frac{D}{(y - x_1)^s}\right\} dx_1. \quad \text{......(1407)}$$

When the field is sufficiently local, or D nearly zero, we have the usual result,

$$f(\vartheta) = \frac{(2\pi m)^{\frac{3}{2}} Ay}{h^3 (\log 1/\vartheta)^{\frac{3}{2}}}. \quad \text{......(1408)}$$

By direct differentiation of (1407) we show further that to the same approximation

$$\frac{1}{f}\frac{\partial f}{\partial y} = \frac{1}{y}. \quad \text{......(1409)}$$

It follows at once from (1403) that as usual

$$\bar{Y} = M/(y \log 1/\vartheta), \quad \bar{Y} y = PV = MkT. \quad \text{......(1410)}$$

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* *Loc. cit.* p. 81.

We see then that we arrive at (1410) whatever the law of force. But when we come to calculate $\overline{\partial Y/\partial y}$ we find that it depends essentially on the form of the law. Thus

$$\overline{\frac{\partial Y}{\partial y}} = \Sigma_r\left(-\frac{\partial^2 \epsilon_r}{\partial y^2}\right)\bar{a}_r = -\frac{M}{y}\int_0^y \frac{Ds\,(s+1)}{(y-x_1)^{s+2}} \exp\left\{-\log 1/\vartheta \frac{D}{(y-x_1)^s}\right\} dx_1,$$

$$= -\frac{(s+1)\,M}{y}\int_{D/y^s}^{\infty}\left(\frac{q}{D}\right)^{1/s} e^{-q\log 1/\vartheta}\,dq.$$

Now D/y^s is the potential of the wall field at the other end of the cylinder, and is indistinguishable from zero. Therefore

$$\overline{\frac{\partial Y}{\partial y}} = -\frac{(s+1)\,M}{yD^{1/s}}\,\frac{\Gamma\,(1+1/s)}{(\log 1/\vartheta)^{1+1/s}}. \qquad \text{......(1411)}$$

This depends essentially on D and s and moreover must tend to infinity if $D \to 0$ or $s \to \infty$. The largeness of $\overline{\partial Y/\partial y}$ and therewith the fluctuation $\overline{(Y-\overline{Y})^2}$ is however then to be expected, for in the limit the reaction of the boundary with a single molecule must itself become infinite, although $\overline{Y}$ retains its usual value. In spite of this, however, if we calculate roughly the order of $\overline{(Y-\overline{Y})^2}/(\overline{Y})^2$ for reasonable values of D and s, we find that it is still negligibly small. Equation (1411) and the usual form for E for a monatomic gaseous assembly lead to

$$\overline{(Y-\overline{Y})^2} = -\tfrac{5}{2}\,\frac{M}{y^2\,(\log 1/\vartheta)^2} + \frac{sM}{yD^{1/s}}\,\frac{\Gamma\,(2+1/s)}{(\log 1/\vartheta)^{2+1/s}},$$

$$\frac{\overline{(Y-\overline{Y})^2}}{(\overline{Y})^2} = \frac{\overline{(p-\overline{p})^2}}{(\overline{p})^2} = \frac{1}{M}\left\{-\tfrac{5}{2} + s\Gamma\,(2+1/s)\,\frac{V}{A\,(D/kT)^{1/s}}\right\}.$$

A reasonable assumption as to the wall field is to take $s = 4$ and suppose that $(D/kT)/(y-x_1)^s$ is small, 10^{-2} say, for $y - x_1 = 10^{-7}$ cm. Thus $D/kT = 10^{-30}$. With $V = 1$, $A = 1$ and $M = 2{\cdot}7 \times 10^{19}$ we have

$$\overline{(Y-\overline{Y})^2}/(\overline{Y})^2 = 4{\cdot}7 \times 10^{-12}.$$

Other second order fluctuations involving reactions, such as

$$\overline{(Y-\overline{Y})\,(Z-\overline{Z})},\quad \overline{(Y-\overline{Y})\,(E_A-\overline{E_A})},$$

both mentioned by Gibbs, may be similarly calculated. We find

$$\overline{(Y-\overline{Y})\,(Z-\overline{Z})} = \left(\overline{\frac{\partial Y}{\partial z}} - \frac{\partial\overline{Y}}{\partial z}\right)\Big/\log 1/\vartheta - \frac{(\vartheta\,\partial\overline{Y}/\partial\vartheta)\,(\vartheta\,\partial\overline{Z}/\partial\vartheta)}{\vartheta\,\partial E/\partial\vartheta}, \qquad \text{......(1412)}$$

$$\overline{(Y-\overline{Y})\,(E_A-\overline{E_A})} = \vartheta\,\frac{\partial\overline{Y}}{\partial\vartheta}\left(1 - \frac{\vartheta\,\partial\overline{E_A}/\partial\vartheta}{\vartheta\,\partial E/\partial\vartheta}\right). \qquad \text{......(1413)}$$

Of course since the forces have a potential

$$\overline{\frac{\partial Y}{\partial z}} = \overline{\frac{\partial Z}{\partial y}},\quad \frac{\partial\overline{Y}}{\partial z} = \frac{\partial\overline{Z}}{\partial y}.$$

§ **20·5**. *Fluctuations of concentration in dissociating assemblies.* If we take for simplicity of exposition the assembly of § 5·3 and transform equation (305) by writing*

$$z = e^u,\ x_1 = e^{v_1},\ x_2 = e^{v_2},\ f_1(e^u) = F_1(u) = F_1, \ldots,$$

we have at once

$$C = \frac{X_1!\,X_2!}{(2\pi i)^3}\iiint_{\gamma'} du\,dv_1\,dv_2 \exp\left[-X_1v_1 - X_2v_2 - Eu + e^{v_1}F_1 + e^{v_2}F_2 + e^{v_1+v_2}G\right]. \quad \ldots\ldots(1414)$$

On comparing (305) and (308) we see that the integral for $C\overline{M}_1$, which in this notation contains the extra factor $e^{v_1}F_1$, was obtained by operating on C with $\Sigma_s \varpi_s^1 \dfrac{\partial}{\partial \varpi_s^1}$. This operator had the effect of inserting the necessary $\Sigma_s a_s^1$ under the original summation sign. Obviously this operation may be repeated any number of times with the same result. The integral for $C\overline{M_1^n}$ is therefore obtained from (1414) by use of the operator $\left[\Sigma_s \varpi_s^1 \dfrac{\partial}{\partial \varpi_s^1}\right]^n$. This can be more simply expressed by observing that the operator acts only on the term $\exp(e^{v_1}F_1)$ and that

$$\left[\Sigma_s \varpi_s^1 \frac{\partial}{\partial \varpi_s^1}\right] \phi(e^{v_1}F_1) = \frac{\partial}{\partial v_1}\phi(e^{v_1}F_1) = \psi(e^{v_1}F_1).$$

It follows at once that

$$C\overline{M_1^n} = \frac{X_1!\,X_2!}{(2\pi i)^3}\iiint_{\gamma'} du\,dv_1\,dv_2 \exp\left[-X_1v_1 - X_2v_2 - Eu + e^{v_2}F_2 + e^{v_1+v_2}G\right]$$
$$\times \left(\frac{\partial}{\partial v_1}\right)^n \exp(e^{v_1}F_1). \quad \ldots\ldots(1415)$$

Therefore, by a familiar argument,

$$C\,\overline{(M_1 - \overline{M}_1)^n} = \frac{X_1!\,X_2!}{(2\pi i)^3}\iiint_{\gamma'} du\,dv_1\,dv_2 \left(\frac{\partial}{\partial v_1}\right)^n \exp(e^{v_1}F_1 - \overline{M}_1 v_1)$$
$$\times \exp\left[-(X_1 - \overline{M}_1)v_1 - X_2v_2 - Eu + e^{v_2}F_2 + e^{v_1+v_2}G\right]. \quad \ldots\ldots(1416)$$

We have now to evaluate (1416) after the plan already adopted in § 20·2 for similar simple integrals, using the methods of § 5·3. The operator $(\partial/\partial v_1)^n$ inserts of course only trivial extra factors which do not affect the determination of the saddle-point. In this notation the values of v_1, v_2, u at the saddle-point are $\log \xi_1$, $\log \xi_2$, $\log \vartheta$, and on γ' we put

$$v_1 = \log \xi_1 + i\alpha_1,\ v_2 = \log \xi_2 + i\alpha_2,\ u = \log \vartheta + i\zeta;$$

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* The reader must remember that this F, the most convenient for dissociating assemblies, is *not* the F of §§ 20·2 *sqq.* They are related so that

$$F\ (\S\ 20{\cdot}5) = \log\{F\ (\S\ 20{\cdot}2)\}.$$

the variables α_1, α_2, ζ range effectively from $-\infty$ to $+\infty$ close to the saddle-point. Carrying out the usual approximations we find that

$$C\,\overline{(M_1-\overline{M}_1)^n} = \exp\left[-X_1\log\xi_1 - X_2\log\xi_2 - E\log\vartheta + \xi_1F_1 + \xi_2F_2 + \xi_1\xi_2G\right]$$
$$\times\frac{(i)^{-n}}{8\pi^3}\iiint_{-\infty}^{+\infty}\exp\left[-\tfrac{1}{2}E_{\vartheta}\zeta^2 - \tfrac{1}{2}\overline{M}_2\alpha_2{}^2 - \tfrac{1}{2}\overline{N}(\alpha_1+\alpha_2)^2 - \overline{E}_2\alpha_2\zeta - \overline{E}_{12}(\alpha_1+\alpha_2)\zeta\right]$$
$$\times\left[1+O\{(\alpha,\zeta)^3F\}\right]\left(\frac{\partial}{\partial\alpha_1}\right)^n\left[\exp\{-\tfrac{1}{2}\overline{M}_1\alpha_1{}^2 - \overline{E}_1\alpha_1\zeta\}\left(1+O\{(\alpha,\zeta)^3F\}\right)\right]. \qquad \text{......(1417)}$$

We have written E_{ϑ} for $\xi_1F_1{}'' + \xi_2F_2{}'' + \xi_1\xi_2G''$ which is $\vartheta\,\partial E/\partial\vartheta$ calculated for constant ξ_1 and ξ_2 and as usual $\overline{E_1}$ for $\xi_1F_1{}'$ and $\overline{E_{12}}$ for $\xi_1\xi_2G'$. As before when n is even the O-terms are negligible. We shall not further investigate the case of n odd.

Certain conclusions as to the form of $\overline{(M_1-\overline{M}_1)^{2n}}$ can be drawn at once without detailed calculation. We first transform from α_1 to $\alpha_1{}'$ so that the differentiated terms take the form

$$\left(\frac{\partial}{\partial\alpha_1{}'}\right)^{2n}\exp\left(-\tfrac{1}{2}\overline{M}_1\alpha_1{}'^2\right).$$

We then transform from α_2 and ζ to $\alpha_2{}'$ and ζ' so that the exponent of the other exponential is a sum of squares of $\alpha_1{}'$, $\alpha_2{}'$ and ζ' without product terms, and carry out the integrations for $\alpha_2{}'$ and ζ'. All these operations are independent of n, and the form of the result must be

$$C\,\overline{(M_1-\overline{M}_1)^{2n}} = (-)^n\,Q\int_{-\infty}^{+\infty}e^{-\frac{1}{2}P\alpha_1{}'^2}\left(\frac{\partial}{\partial\alpha_1{}'}\right)^{2n}e^{-\frac{1}{2}\overline{M}_1\alpha_1{}'^2}\,d\alpha_1{}'.$$

It follows at once that

$$\overline{(M_1-\overline{M}_1)^{2n}} = (-)^n\left(\frac{P+\overline{M}_1}{2\pi}\right)^{\frac{1}{2}}\int_{-\infty}^{+\infty}e^{-\frac{1}{2}P\alpha_1{}'^2}\left(\frac{\partial}{\partial\alpha_1{}'}\right)^{2n}e^{-\frac{1}{2}\overline{M}_1\alpha_1{}'^2}\,d\alpha_1{}',$$
$$= (2n-1)\,\ldots\,.\,3\,.\,1\left\{\frac{P\overline{M}_1}{P+\overline{M}_1}\right\}^n. \qquad \text{......(1418)}$$

This is the familiar form of all such results, but to evaluate any one fluctuation explicitly P must be known, and the foregoing (or equivalent) transformations actually carried out. Perhaps the simplest method is to evaluate C and $C\,\overline{(M_1-\overline{M}_1)^2}$ by direct calculation of (1417) without the O-terms for $n = 0, 2$. The exponential term in both reduces to

$$\exp\left\{-\tfrac{1}{2}\left[E_{\vartheta}\zeta^2 + X_1\alpha_1{}^2 + X_2\alpha_2{}^2 + 2E_{112}\,\alpha_1\zeta + 2E_{212}\,\alpha_2\zeta + 2\overline{N}\alpha_1\alpha_2\right]\right\},$$

in which we have written for shortness

$$E_{112} = \overline{E}_1 + \overline{E}_{12} = (\xi_1\partial E/\partial\xi_1)_{\vartheta,\xi_2},$$
$$E_{212} = \overline{E}_2 + \overline{E}_{12} = (\xi_2\partial E/\partial\xi_2)_{\vartheta,\xi_1}.$$

The extra factor for $n = 2$ is

$$\{\overline{M}_1 - (\overline{M}_1\alpha_1 + \overline{E}_1\zeta)^2\}. \qquad \ldots\ldots(1419)$$

The reduction is of course largely arbitrary. There is some advantage of symmetry and parallelism with § 20·2 in using

$$\left.\begin{aligned} \alpha_1 &= \alpha_1' - \frac{\overline{N}}{X_1}\alpha_2' - \frac{X_2E_{112} - \overline{N}E_{212}}{X_1X_2 - \overline{N}^2}\zeta', \\ \alpha_2 &= \qquad\quad \alpha_2' - \frac{X_1E_{212} - \overline{N}E_{112}}{X_1X_2 - \overline{N}^2}\zeta', \\ \zeta &= \qquad\qquad\qquad\qquad\qquad\quad \zeta'. \end{aligned}\right\} \qquad \ldots\ldots(1420)$$

This reduces the quadratic exponent to

$$-\tfrac{1}{2}\alpha_1'^2X_1 - \tfrac{1}{2}\alpha_2'^2(X_2 - \overline{N}^2/X_1) - \tfrac{1}{2}\zeta^2\left[E_{\vartheta} - \frac{X_2E_{112}^{\ 2} + X_1E_{212}^{\ 2} - 2\overline{N}E_{112}E_{212}}{X_1X_2 - \overline{N}^2}\right]$$

and the value of C can be at once obtained by integration. On applying the transformation (1420) to the extra factor (1419) we obtain

$$\overline{M}_1 - \left(\overline{M}_1\alpha_1' - \frac{\overline{M}_1\overline{N}}{X_1}\alpha_2' + \left\{\overline{E}_1 - \overline{M}_1\frac{X_2E_{112} - \overline{N}E_{212}}{X_1X_2 - \overline{N}^2}\right\}\zeta'\right)^2.$$

It is not necessary to evaluate C. We observe merely that in the ratio of the two integrals a constant term repeats itself, a product term vanishes and a square term appears, divided by the coefficient of the corresponding square in the quadratic exponent. Thus after a little rearrangement

$$\overline{(M_1 - \overline{M}_1)^2} = \frac{\overline{M}_1\overline{M}_2\overline{N}}{X_1X_2 - \overline{N}^2} - \frac{\left\{\overline{E}_1 - \overline{M}_1\dfrac{X_2E_{112} - \overline{N}E_{212}}{X_1X_2 - \overline{N}^2}\right\}^2}{E_{\vartheta} - \dfrac{X_2E_{112}^{\ 2} + X_1E_{212}^{\ 2} - 2\overline{N}E_{112}E_{212}}{X_1X_2 - \overline{N}^2}}. \qquad \ldots\ldots(1421)$$

This is rather complicated, and there is no very simple general form. The last denominator can be cast into the form

$$\left(\vartheta\frac{\partial E}{\partial\vartheta}\right)_{\overline{M},\overline{N}} + \frac{\overline{M}_1\overline{M}_2\overline{N}}{X_1X_2 - \overline{N}^2}\left(\vartheta\frac{\partial}{\partial\vartheta}\log\kappa\right)^2,$$

where κ is the equilibrium constant F_1F_2/G, and the numerator is

$$\left(\frac{\overline{M}_1\overline{M}_2\overline{N}}{X_1X_2 - \overline{N}^2}\right)^2\left(\vartheta\frac{\partial}{\partial\vartheta}\log\kappa\right)^2.$$

We can therefore write (1421) in the form

$$\overline{(M_1 - \overline{M}_1)^2} = \frac{\overline{M}_1\overline{M}_2\overline{N}}{X_1X_2 - \overline{N}^2}\left[1 - \frac{\dfrac{\overline{M}_1\overline{M}_2\overline{N}}{X_1X_2 - \overline{N}^2}\left(\vartheta\dfrac{\partial}{\partial\vartheta}\log\kappa\right)^2}{\left(\vartheta\dfrac{\partial E}{\partial\vartheta}\right)_{\overline{M},\overline{N}} + \dfrac{\overline{M}_1\overline{M}_2\overline{N}}{X_1X_2 - \overline{N}^2}\left(\vartheta\dfrac{\partial}{\partial\vartheta}\log\kappa\right)^2}\right]. \qquad \ldots\ldots(1422)$$

This shows the type of formula we should expect in more complex examples. We note as a check that if there is no "molecule" $\overline{N} = 0$ and the fluctuation vanishes. We may note also that the argument is unaffected by the presence of other sets of systems in the assembly so long as these do not combine with or are not formed out of the systems of the types already under discussion. The only residual effect of such other systems will be to increase $(\vartheta \partial E/\partial \vartheta)_{\overline{M}, \overline{N}}$, which will continue to refer to the whole assembly, though it may not retain this simple form. When the whole assembly is large (bath conditions) we may therefore simplify (1422) by the omission of the last term, and write

$$\overline{(M_1 - \overline{M_1})^2} = \frac{\overline{M_1}\,\overline{M_2}\,\overline{N}}{X_1 X_2 - \overline{N}^2}. \qquad \text{......(1423)}$$

From the symmetry of this result $\overline{(M_2 - \overline{M_2})^2}$ has the same value, as also does $\overline{(N - \overline{N})^2}$, since in this simple case $N - \overline{N} = -(M_1 - \overline{M_1})$.

§ **20·51**. *Fluctuations of energy in dissociating assemblies.* The fluctuations of the energy can be studied in a similar way. To obtain $C\overline{E_1}$ we have to insert the extra factor $\Sigma_s a_s{}^1 \epsilon_s{}^1$ in the original sum for C. This is effected by the operator

$$\Sigma_s \varpi_s{}^1 \epsilon_s{}^1 \frac{\partial}{\partial \varpi_s{}^1}.$$

Similarly, by repetition, $C\overline{E_1{}^n}$ is obtained from C by use of the operator

$$\left(\Sigma_s \varpi_s{}^1 \epsilon_s{}^1 \frac{\partial}{\partial \varpi_s{}^1}\right)^n.$$

In (1414) this operator again acts only on $\exp\{e^{v_1} F_1(u)\}$ and by a similar argument may be replaced by $(\partial/\partial u)^n$. Thus corresponding to (1416) we have

$$C\,\overline{(E_1 - \overline{E_1})^n} = \frac{X_1!\,X_2!}{(2\pi i)^3} \iiint_{\gamma'} du\,dv_1\,dv_2 \exp[-X_1 v_1 - X_2 v_2 - (E - \overline{E_1})\,u + e^{v_2} F_2$$
$$+ e^{v_1+v_2} G]\left(\frac{\partial}{\partial u}\right)^n \exp(e^{v_1} F_1 - \overline{E_1}\,u). \qquad \text{......(1424)}$$

The further study of (1424) follows exactly the same course as before. The form of (1418) is preserved. In the explicit calculations the extra factor for $\overline{(E_1 - \overline{E_1})^2}$ is

$$(\overline{E_1})_\vartheta - \{(\overline{E_1})_\vartheta\, \zeta + \overline{E_1}\,\alpha_1\}^2,$$

where $(\overline{E_1})_\vartheta$ means $\vartheta \partial \overline{E_1}/\partial \vartheta$ calculated for constant ξ's. In the new variables this becomes

$$(\overline{E_1})_\vartheta + \left\{\overline{E_1}\,\alpha_1{}' - \frac{\overline{E_1}\,\overline{N}}{X_1}\,\alpha_2{}' + \left[(\overline{E_1})_\vartheta - \overline{E_1}\,\frac{X_2 E_{112} - \overline{N} E_{212}}{X_1 X_2 - \overline{N}^2}\right]\zeta'\right\}^2.$$

We thus obtain

$$\overline{(E_1-\overline{E_1})^2}=(\overline{E_1})_\vartheta-\frac{X_2\overline{E_1}^2}{X_1X_2-\overline{N}^2}-\frac{\left\{(\overline{E_1})_\vartheta-\overline{E_1}\,\dfrac{X_2E_{112}-\overline{N}E_{212}}{X_1X_2-\overline{N}^2}\right\}^2}{E_\vartheta-\dfrac{X_2E_{112}^2+X_1E_{212}^2-2\overline{N}E_{112}E_{212}}{X_1X_2-\overline{N}^2}}. \qquad \ldots\ldots(1425)$$

To reduce this to a more intelligible form we use

$$\left(\vartheta\frac{\partial\overline{E_1}}{\partial\vartheta}\right)_{M_1},$$

calculated for constant $\overline{M_1}$, which is equal to

$$(\overline{E_1})_\vartheta-(\overline{E_1})^2/\overline{M_1}.$$

Then

$$\overline{(E_1-\overline{E_1})^2}=\left(\vartheta\frac{\partial\overline{E_1}}{\partial\vartheta}\right)_{\overline{M_1}}+\frac{\overline{M_1}\,\overline{M_2}\,\overline{N}}{X_1X_2-\overline{N}^2}\left(\frac{\overline{E_1}}{\overline{M_1}}\right)^2$$
$$-\frac{\left\{\left(\vartheta\dfrac{\partial E_1}{\partial\vartheta}\right)_{\overline{M_1}}+\dfrac{\overline{E_1}}{\overline{M_1}}\,\dfrac{\overline{M_1}\,\overline{M_2}\,\overline{N}}{X_1X_2-\overline{N}^2}\,\vartheta\dfrac{\partial}{\partial\vartheta}\log\kappa\right\}^2}{\left(\vartheta\dfrac{\partial E}{\partial\vartheta}\right)_{\overline{M},\overline{N}}+\dfrac{\overline{M_1}\,\overline{M_2}\,\overline{N}}{X_1X_2-\overline{N}^2}\left(\vartheta\dfrac{\partial}{\partial\vartheta}\log\kappa\right)^2}. \qquad \ldots\ldots(1426)$$

In this form the relationships of the new formula to preceding ones are obvious. If $\overline{N}=0$ it reduces to (1386). If $(\vartheta\partial E/\partial\vartheta)$ is large, so that the whole assembly is large compared with the systems under discussion, then, using (1423),

$$\overline{(E_1-\overline{E_1}^2)}=\left(\vartheta\frac{\partial E_1}{\partial\vartheta}\right)_{\overline{M_1}}+\left(\frac{\overline{E_1}}{\overline{M_1}}\right)^2\overline{(M-\overline{M_1})^2}, \qquad \ldots\ldots(1427)$$

or the energy fluctuation is equal to the energy fluctuation for fixed dissociation plus the fluctuation of energy due to the fluctuation of the dissociation. This additive result is not however true in general, since for not very extensive assemblies the fluctuations in $\overline{M_1}$ and in energy content for fixed $\overline{M_1}$ are not independent.

§ **20·52**. *Other fluctuations.* It should now be sufficiently clear how to construct exact integral expressions for any fluctuation such as

$$\overline{(M_r-\overline{M_r})^m\,(N_s-\overline{N_s})^n},\quad \overline{(M_r-\overline{M_r})^m\,(E_s-\overline{E_s})^n},\ \text{etc.},$$

for the most general gaseous dissociating assembly. We shall not write down these integrals or attempt to evaluate them here, as they are obviously complicated. It is sufficient to have established a simple method by which they can be calculated if required.

It remains however to indicate the changes necessary in § 20·3 to adapt it to dissociating assemblies. These are slight. Using y instead of the x of § 20·3 we find in the same way that

$$C\,\overline{(a_r{}^1-\overline{a_r{}^1})^n}=\text{Coef}_n\frac{X_1\,!\,X_2\,!}{(2\pi i)^3}\iiint_{\gamma'}du\,dv_1\,dv_2\exp\left[-X_1v_1-X_2v_2-Eu\right.$$
$$\left.+e^{v_1}F_1+e^{v_2}F_2+e^{v_1+v_2}G-\overline{a_r}y+\varpi_r{}^1e^{\epsilon_r{}^1u+v_1}(e^y-1)\right].\quad\ldots\ldots(1428)$$

Approximating in the same way as in § 20·3 we find easily that the dominant term for an even order fluctuation is given by

$$C\,\overline{(a_r{}^1-\overline{a_r{}^1})^{2n}}=\text{Coef}_{2n}\frac{X_1\,!\,X_2\,!}{8\pi^3}e^{\frac{1}{2}\overline{a_r}y^2}\iiint_{-\infty}^{+\infty}d\alpha_1\,d\alpha_2\,d\zeta\exp-\tfrac{1}{2}\left[E_3\zeta^2+X_1\alpha_1{}^2\right.$$
$$\left.+X_2\alpha_2{}^2+2E_{112}\alpha_1\zeta+2E_{212}\alpha_2\zeta+2\overline{N}\alpha_1\alpha_2-2i\overline{a_r}{}^1y\,(\epsilon_r{}^1\zeta+\alpha_1)\right].\quad\ldots\ldots(1429)$$

We must remove the linear term from this quadratic form by the usual substitution. When this is done we find at once that as usual

$$\overline{(a_r{}^1-\overline{a_r{}^1})^{2n}}=(2n-1)\ldots.\,3\,.\,1\,\overline{(a_r{}^1-\overline{a_r{}^1})^2},$$

and on carrying through the calculations it can be shown that

$$\overline{(a_r{}^1-\overline{a_r{}^1})^2}=\overline{a_r}{}^1-\frac{(\overline{a_r{}^1})^2X_2}{X_1X_2-\overline{N}^2}-\frac{(\overline{a_r{}^1})^2\left\{\epsilon_r{}^1-\dfrac{F_1{}'}{F_1}+\dfrac{\overline{M}_2\overline{N}}{X_1X_2-\overline{N}^2}\vartheta\dfrac{\partial}{\partial\vartheta}\log\kappa\right\}^2}{\left(\vartheta\dfrac{\partial E}{\partial\vartheta}\right)_{\overline{M},\overline{N}}+\dfrac{\overline{M}_1\overline{M}_2\overline{N}}{X_1X_2-\overline{N}^2}\left(\vartheta\dfrac{\partial}{\partial\vartheta}\log\kappa\right)^2}.\quad\ldots\ldots(1430)$$

Remembering the different meanings of F_1 here in § 20·3 we see that this reduces to (1396) when $\overline{N}=0$.

§ **20·6**. *Formal consequences of general fluctuation theorems.* An interesting consequence of the general form, e.g. (1418), of our fluctuation theorems may be noted here. Retaining only terms of the highest order we may say that if

$$\overline{(P-\overline{P})^2}=\mu,$$

then

$$\overline{(P-\overline{P})^{2n-1}}=O\,(\mu^{n-1})\,\{1+O\,(1/E)\},$$
$$\overline{(P-\overline{P})^{2n}}=1\,.\,3\,.\ldots\,(2n-1)\,\mu^n\,\{1+O\,(1/\mu)+O\,(1/E)\}.\quad\ldots\ldots(1431)$$

We may pass at once from these equations to a general distribution law in P for examples of the assembly with the accuracy of (1431) by means of a theorem due to Pólya*, which we quote here.

Theorem 20·6. *The distribution function $f(x)$ is continuous. The moments t_m of $f(x)$,*

$$t_m=\int_{-\infty}^{+\infty}x^m\,df(x)\quad(m=0,1,2,\ldots),$$

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* Pólya, *Math. Zeit.* vol. VIII, p. 171 (1920). The integrals must be taken as Stieltjes' integrals.

are assumed to satisfy the condition that

$$\overline{\mathop{\mathrm{Lt}}_{m\to 0}}\,\frac{\sqrt[2m]{(t_{2m})}}{m}$$

is finite. If then a sequence of distribution functions $f_1(x), \dots, f_n(x), \dots$ *satisfies the infinite set of limiting conditions*

$$\mathop{\mathrm{Lt}}_{n\to\infty}\int_{-\infty}^{+\infty} x^m df_n(x) = t_m \quad (m = 0, 1, 2, \dots),$$

then

$$\mathop{\mathrm{Lt}}_{n\to\infty} f_n(x) = f(x)$$

uniformly in any interval.

In equations (1431) let us substitute

$$P = \bar{P} + \gamma\sqrt{\mu}.$$

Then we have proved that

$$\overline{\gamma^{2n}} = 1\,.\,3\,.\dots(2n-1)\left\{1 + O\left(\frac{1}{E}\right) + O\left(\frac{1}{\mu}\right)\right\},$$

$$\overline{\gamma^{2n-1}} = O\left(\frac{1}{\sqrt{\mu}}\right) + O\left(\frac{1}{E}\right).$$

Now let E, μ tend to infinity in fixed ratios, which means taking larger and larger assemblies. The γ-moments tend to the moments of the distribution function

$$f(\gamma)\,d\gamma = \frac{1}{(2\pi)^{\frac{1}{2}}}\,e^{-\frac{1}{2}\gamma^2}\,d\gamma.$$

Pólya's theorem applies, and it follows that this is the actual limit of the distribution function of examples of the assembly for infinite assemblies, and that too uniformly in any fixed interval of γ. In terms of P the distribution function therefore tends to the limit

$$f(P)\,dP = \frac{1}{(2\pi\mu)^{\frac{1}{2}}}\,e^{-\frac{1}{2}(P-\bar{P})^2/\mu}\,dP, \qquad \dots\dots(1432)$$

uniformly in any fixed interval $\bar{P} \pm z\sqrt{\mu}$.

This theorem provides us with the simplest means of completing the proof that the possession of $\bar{P}$ is a normal property of a sufficiently large assembly. It will be a normal property provided only

$$\int_{\bar{P}-p}^{\bar{P}+p} f(P)\,dP = 1 - \epsilon(p),$$

where ϵ can be made very small while $p/\bar{P}$ is still itself very small. But this equation is obviously equivalent to

$$\frac{1}{\sqrt{\mu}}\int_p^\infty e^{-\frac{1}{2}x^2/\mu}\,dx = \epsilon(p),$$

of which the left-hand side is $O\left(\frac{1}{p}\, e^{-p^2/2\mu}\right)$. This can be made small compared with unity for small values of $p/\overline{P}$ provided only $(\overline{P})^2/\mu$ is very large, which is the general result of this chapter.

The elegant formula (1432), which we have just obtained from the purely analytical side, really gives no information not already contained in Einstein's quasi-thermodynamical formulae (434) and (435). Taking these in the form (434) and comparing with (1432) we see that these two equations are attempting to assert the same relation and that they succeed if

$$-(\Sigma\Delta S)/k = \tfrac{1}{2}(P-\overline{P})^2/\mu.$$

In this chapter we are only working accurately for comparatively small displacements from the true equilibrium. If we further confine our attention to a small part of a large assembly then this equation is equivalent to

$$\frac{1}{k}\frac{\partial^2 S}{\partial \overline{P}^2} = -\frac{1}{\mu}, \qquad \text{......(1433)}$$

or

$$\overline{(P-\overline{P})^2} = -k\Big/\frac{\partial^2 S}{\partial \overline{P}^2}. \qquad \text{......(1434)}$$

It is easy to verify that (1433) is correct in the simple cases to which alone *all* the calculations apply. For example, if $P = E_A$, then in bath conditions $\mu = kT^2\partial\overline{E_A}/\partial T$ and $\partial S/\partial\overline{E_A} = 1/T$, which verifies (1433). Similarly if $P = a_r$ in a gaseous assembly, then S as a function of $\overline{a_r}$ contains $\overline{a_r}\{\log[f(T)/\overline{a_r}]+1\}$, $\mu = \overline{a_r}$, and (1433) is again verified. A similar verification holds for $\overline{M_1}$.

§ **20·7**. *Special cases.* The special formulae that are of primary importance among those of this chapter refer to bath conditions and are

$$\overline{(E-\overline{E})^2} = \vartheta\frac{\partial\overline{E}}{\partial\vartheta} = kT^2\frac{\partial\overline{E}}{\partial T}, \qquad \text{......(1435)}$$

$$\overline{(a_r-\overline{a_r})^2} = \overline{a_r}\,(1-\overline{a_r}/M), \qquad \text{......(1436)}$$

$$\overline{(M_1-\overline{M_1})^2} = \frac{\overline{M_1}\,\overline{M_2}\,\overline{N}}{X_1X_2-\overline{N}^2}, \qquad \text{......(1437)}$$

and in particular (1435). The form taken by (1435) for special systems should be noted.

(i) A gas of structureless atoms

$$\overline{(E-\overline{E})^2} = \tfrac{3}{2}Nk^2T^2 = (\overline{E})^2/\tfrac{3}{2}N. \qquad \text{......(1438)}$$

(ii) A set of Planck's oscillators

$$\overline{(E-\overline{E})^2} = \frac{Nk^2\nu^2 e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2} = \frac{(\overline{E})^2}{N} + h\nu\overline{E}. \qquad \text{......(1439)}$$

(iii) Temperature ν-radiation in unit volume

$$\overline{(\rho(\nu)\,d\nu - \overline{\rho(\nu)\,d\nu})^2} = \frac{8\pi h^2\nu^4 d\nu\, e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2},$$

$$= h\nu\rho(\nu)\,d\nu + \frac{c^3\{\rho(\nu)\}^2\,d\nu}{8\pi\nu^2}. \qquad \text{......(1440)}$$

Formula (1440) has played an important part in the history of the theory of radiation. It will be observed that $h\nu\rho(\nu)\,d\nu = h^2\nu^2 n(\nu)$, where $n(\nu)$ is the number of ν-quanta in this volume. On referring to (1436) we see that this term gives just the fluctuation we should get if the extreme light-quantum view of radiation as particles could be adopted. On the other hand this term cannot be interpreted on the classical wave theory, for all fluctuations by interference must depend on the square of the energy density. For the second term the reverse is true; the extreme light-quantum view cannot account for it, the classical wave theory accounts for it naturally by interference. These critical remarks of course apply not to the result itself as a property of the equilibrium state, but only to the mechanisms proposed for the maintenance of that state. The new mechanics gives a satisfactory account of the formula.

§ **20·8**. *The scattering of light by liquids and gases. Opalescence near the critical point.* When a beam of light is passed through a homogeneous gas or a liquid, a certain small proportion is scattered out of the beam by the molecules of the gas or liquid in each element of the path. The amount scattered is very small for a gas or a liquid not near its critical point, but still of measurable intensity, e.g. the blue of a clear sky. As a liquid nears its critical point the intensity of the scattered light increases and at the critical point itself the liquid glows strongly with a peculiar shine known as the phenomenon of *critical opalescence.* Owing to its more striking character attention is often concentrated on the phenomenon of critical opalescence, but all the phenomena of the scattering of light by liquids and gases when the wave length of the light is long compared with the average distance apart of the scattering agents (molecules) form a single whole and may be discussed together.*

It can be shown† that the scattering of such light must depend on the irregular spacing of the scattering centres, and that it is therefore a problem of the fluctuations in the distribution of molecules in given small volume elements. If the molecules were regularly spaced at their average spacing as in a crystal there would be no scattering at all. Any scattering actually observed in crystals can be traced to imperfections or foreign bodies. This absence of scattering persists until the wave length falls to molecular

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* Perrin, *La théorie du rayonment et les quanta* (1912); *Les preuves de la réalité moléculaire.*

† For a simple account see Lorentz, *The Problems of Modern Physics* (1927), § 21.

dimensions and we have a true scattering, but only in definite directions, more commonly known as X-ray reflection or diffraction.

From the statistical point of view therefore the phenomena are best approached as an example of molecular fluctuations in the manner of von Smoluchowski*, using the general formula (435). We consider a fluid which in its normal equilibrium state contains n_0 molecules in a volume v_0 at a pressure p_0. The actual volume at any given moment occupied by this body of molecules is v, only small values of $(v - v_0)/v_0$ being important. The rest of the fluid is a large volume, the whole being isothermal. Then by general thermodynamical theorems $\Sigma\Delta A$ is the maximum work which the assembly can do in returning to its normal equilibrium state; since for any body in an isothermal expansion $dA = -\,pdv$,

$$\Sigma\Delta A = \int_v^{v_0} (p - p_0)\, dv.$$

The fraction of examples of the assembly in which we shall find these n_0 molecules at a volume between v and $v + dv$ is therefore

$$W(v)\, dv = \mu e^{-\frac{1}{kT}\int_v^{v_0} (p-p_0)\, dv}\, dv,$$

where μ is a constant, fixed by the condition $\int W dv = 1$. Without specific assumptions as to the equation of state, we may expand $p - p_0$ and write

$$-\int_v^{v_0} (p - p_0)\, dv = \frac{(v-v_0)^2}{2\,!}\frac{\partial p_0}{\partial v_0} + \frac{(v-v_0)^3}{3\,!}\frac{\partial^2 p_0}{\partial {v_0}^2} + \frac{(v-v_0)^4}{4\,!}\frac{\partial^2 p_0}{\partial {v_0}^3} + O\{(v-v_0)^5\}.$$

We write also

$$\gamma = (v - v_0)/v_0,$$

so that γ is the accidental condensation (strictly expansion). Then omitting fifth order terms

$$W(\gamma)\, d\gamma = \mu d\gamma \exp\left[\frac{1}{kT}\left\{\frac{{v_0}^2\gamma^2}{2\,!}\frac{\partial p_0}{\partial v_0} + \frac{{v_0}^3\gamma^3}{3\,!}\frac{\partial^2 p_0}{\partial {v_0}^2} + \frac{{v_0}^4\gamma^4}{4\,!}\frac{\partial^3 p_0}{\partial {v_0}^3}\right\}\right]. \qquad \ldots\ldots(1441)$$

The further development now depends on whether the normal equilibrium state does or does not refer to the critical point. Away from the critical point $\partial p_0/\partial v_0 \neq 0$, and it is sufficiently accurate to take

$$W(\gamma)\, d\gamma = \mu d\gamma \exp\left[\frac{{v_0}^2\gamma^2}{2kT}\frac{\partial p_0}{\partial v_0}\right]. \qquad \ldots\ldots(1442)$$

If the fluid is a perfect gas

$$\frac{\partial p_0}{\partial v_0} = -\frac{n_0 kT}{{v_0}^2},$$

$$W(\gamma)\, d\gamma = \mu d\gamma e^{-\frac{1}{2}n_0\gamma^2}. \qquad \ldots\ldots(1443)$$

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* von Smoluchowski, *Ann. der Phys.* vol. xxv, p. 205 (1908); Einstein, *Ann. der Phys.* vol. xxxiii, p. 1275 (1910).

In this simple case we find a result which we can also obtain at once from (1432). Putting there $P = n$, the number of molecules in a given small volume, we have $\overline{P} = \mu = n_0$,

$$f(n)\, dn = (2\pi n_0)^{-\frac{1}{2}}\, e^{-\frac{1}{2}(n-n_0)^2/n_0}\, dn. \qquad \text{......(1444)}$$

But $\gamma = (v - v_0)/v_0$ for constant n and therefore equally $\gamma = -(n - n_0)/n_0$ for constant v, so that (1443) and (1444) are identical.

The value of $\overline{\gamma^2}$ is easily calculated from (1442). We find

$$\overline{\gamma^2} = -\frac{kT}{v_0{}^2\partial p_0/\partial v_0}\left(=\frac{1}{n_0},\ \textit{perfect gas}\right). \qquad \text{......(1445)}$$

At the critical point $\partial p_0/\partial v_0 = \partial^2 p_0/\partial v_0{}^2 = 0$, so that

$$W(\gamma)\, d\gamma = \mu\, d\gamma \exp\left[\frac{v_0{}^4\gamma^4}{24kT}\frac{\partial^3 p_0}{\partial v_0{}^3}\right].$$

For the sake of a numerical estimate we may use Dieterici's equation of state (606), which yields after reduction

$$W(\gamma)\, d\gamma = \mu\, d\gamma\, e^{-\frac{n_0}{22\cdot 2}\gamma^4};$$

from this we find

$$\overline{\gamma^2} = 1\cdot 6/n_0{}^{\frac{1}{2}}. \qquad \text{....(1446)}$$

The next step is to make use of a formula which dates back to Lord Rayleigh,* and states that if light of unit intensity and wave length λ_0 in a medium of refractive index μ_0 is incident on a small volume v_0 in which the refractive index is μ, the dimensions of v_0 being small compared with λ_0, then the intensity of the light scattered at right angles is

$$\frac{2\pi^2 v_0{}^2}{\lambda_0{}^4}\left(\frac{\mu - \mu_0}{\mu_0}\right)^2.$$

To make use of this formula for the light scattered by spontaneous fluctuations we must combine with it a relation between μ and ρ the density of the fluid in v_0. For gases, and probably with sufficient accuracy for liquids also, we may use Lorentz's law of refraction

$$\frac{1}{\rho}\frac{\mu^2 - 1}{\mu^2 + 2} = \text{const.},$$

from which it follows that for small values of $(\mu - \mu_0)/\mu_0$

$$\frac{\mu - \mu_0}{\mu_0} = \frac{(\mu_0{}^2 - 1)(\mu_0{}^2 + 2)}{6\mu_0{}^2}\gamma.$$

The intensity of the light scattered by a fluctuation to an accidental condensation γ in a volume v_0 is therefore

$$\frac{\pi^2 v_0{}^2 \gamma^2}{18\mu_0{}^4\lambda_0{}^4}(\mu_0{}^2 - 1)^2(\mu_0{}^2 + 2)^2. \qquad \text{......(1447)}$$

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* Rayleigh, *Phil. Mag.* vol. XII, p. 81 (1881); *Scientific Papers*, vol. I, No. 74.

In unit volume of the liquid the number of such scattering volumes is $1/v_0$ and the average value of γ^2 is $\overline{\gamma^2}$ given by (1445). It follows that the average intensity i of the light scattered by unit volume of fluid at right angles to the incident beam of intensity I is given by

$$\frac{i}{I}=\frac{\pi^2}{18\mu_0{}^4\lambda_0{}^4}(\mu_0{}^2-1)^2(\mu_0{}^2+2)^2\left\{-\frac{kT}{v_0\partial p_0/\partial v_0}\right\}. \quad \text{......(1448)}$$

§ **20·81**. *Comparison with observation.* We begin with some qualitative remarks. The great difference in intensity between critical opalescence and ordinary fluid scattering follows from the different orders of $\overline{\gamma^2}v_0$ in the two cases (1445) and (1446). Roughly we may say that this factor is greater at the critical point than in the perfect gas state (or any not nearly critical state) by a factor of the order of $\sqrt{n_0}$. For a volume v_0 small compared with the λ_0 of visible light, say a cube of edge 10^{-5} cm., $n_0 = 10^4$ for a gas at normal pressure and temperature and 10^6–10^7 for a liquid. Again formula (1448) shows that there is a strong selection in favour of the scattering of light of the shorter wave lengths. The scattered light from incident white light should look blue. This is of course in accord with all the facts (blue of sky, etc.). The fact that at the critical point the scattered light becomes white shows that the theory is there breaking down because the scattering elements, that is volumes in which the fluctuations are sensible, are no longer small compared with the wave length. We see in fact from (1445) and (1446) that for a cube of edge 10^{-4} cm. comparable with the wave-length the mean square fluctuation $\sqrt{\overline{\gamma^2}}$ in a perfect gas at normal pressure and temperature is only 2×10^{-4}, whereas at the critical point it is 10^{-2}. A 1 per cent. density change leads to a sensible change of refractive index.

Equation (1448) for a perfect gas in which μ_0 is very nearly unity leads to

$$\frac{i}{I}=\frac{\pi^2}{2\mu_0{}^4\lambda_0{}^4}(\mu_0{}^2-1)^2\frac{kT}{p}. \quad \text{......(1449)}$$

This formula, generalized for intensities at any angle to the original beam and integrated through the atmosphere, can be applied to calculate the nature of the scattered sunlight incident on the eye at an angle α with the vertical and β with the sun. It is completely successful. It can of course be used inversely, treating k as unknown, to determine k from measurements of i, and has been so used with success.*

A complete quantitative test of (1448) is afforded by the experiments of Keesom†. He studied ethylene ($T_c = 11{\cdot}18^\circ$ C.). He verified first that for $p = p_c$ and $T = 13{\cdot}6^\circ$ C. the ratio of the intensities of scattered light of two wave lengths was still proportional to $(\lambda_1/\lambda_2)^4$ so that this tempera-

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* Perrin, *loc. cit.*

† Keesom, *Ann. der Phys.* vol. xxxv, p. 591 (1911).

ture still lies in the region of validity of the theory.* For the same wave lengths i_2/i_1 falls to 1·18 at 11·43° C., showing that by that stage the scattering elements are, as statistical theory requires, no longer small.

Again near the critical point, since $(\partial p/\partial v)_c = (\partial^2 p/\partial v^2)_c = 0$

$$-v_0 \frac{\partial p}{\partial v_0} = -v_0 \left(\frac{\partial^2 p}{\partial v \partial T}\right)_c (T - T_c). \qquad \ldots\ldots(1450)$$

Hence near, but not too near, the critical point the intensity of the scattered light should vary like $1/(T - T_c)$. This prediction is well verified.

TABLE 56.

Scattering of light by ethylene near its critical point ($T_c = 11{\cdot}18°$ C.).

T °C. ($p = p_c$)	i	$i\,(T - T_c)$
13·53	0·190	0·44
12·54	0·337	0·46
11·86	0·671	0·46
11·61	1†	0·43
11·42	2·61	0·63
11·24	6·11	0·37

† Assumed.

Finally having thus verified all the details of the theory Keesom obtained $i/I = 0{\cdot}0007$–$0{\cdot}0008$ for the D lines of sodium at 11·93° C. The known compressibilities of ethylene give $-v_0 \partial p_0/\partial v_0$. All the data are therefore ready for the use of (1448) for an absolute determination of k, which comes out within 15 per cent. (the accuracy of the measurement of i/I) of its accepted value.

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* He found for $(\lambda_1/\lambda_2)^4 = 2{\cdot}13$, $i_2/i_1 = 2{\cdot}00$.

CHAPTER XXI

THE NEW STATISTICAL MECHANICS

§ **21·1**. *Introduction.* We have hitherto developed the whole theory of statistical mechanics in a classical way—that is on the basis of Liouville's theorem and the obvious generalizations imposed by the classical quantum theory. We were led in this way to derive all the equilibrium properties of our assemblies by averaging over the whole of the *accessible* phase space of the assembly. Though our confidence in this principle is partly based on its success in applications and cannot be referred entirely to *a priori* arguments, we have no grounds for loss of confidence in applying it to any assembly which is strictly classical. We have in fact no grounds for questioning the principle at all, provided we can define exactly what parts of the phase space are accessible for the purpose of averaging. In the classical theory we took as accessible the whole phase space of the assembly subject only to the energy (and momentum) integrals and the conditions assigned by given total numbers of the structural units—atoms or electrons and nuclei according to the nature of the problem. This may be wrong even classically, but as we have said we have so far absolutely no theoretical or empirical reason to suspect it. In our exposition hitherto we have taken over this definition of accessibility essentially unaltered into the classical quantum theory. The only modification imposed by the classical quantum theory is to divide up the classical continuous phase space into cells and replace these cells by discrete stationary states. The whole of the accessible classical phase space is replaced by corresponding accessible stationary states.

Even if our definition of accessibility is classically correct, its adoption in the quantum theory was only justified as an experiment, in our complete ignorance of the nature of the laws of interaction of quantized systems prior to the advent of the quantum mechanics. Now that the laws of non-relativistic quantum mechanics are fairly completely known, at least *formally*, it remains to examine the old definition of accessibility in the light of these laws. We find quite simply the interesting and somewhat surprising result that the accessible regions of the phase space must be drastically cut down, in a way which has important consequences for the deduced properties of matter in certain limiting cases.

The difference between the new statistical mechanics and the old is in fact confined to this difference in the accessible regions of phase space over which the averaging must be taken. Once the accessible region has been specified averages are taken in the same way in all forms of the theory.

The arguments from Liouville's theorem which suggest and more or less justify the use of a weight proportional to the extension of phase space in averaging in the classical theory persist in a strictly analogous form in the newer theory, and show that our choice of weights for quantized systems was correct. But we must only include accessible complexions.

After a general account of the corrected form of statistical mechanics required by the new mechanics we give the main applications which have so far (April 1928) been made of it, in completing the theory of temperature radiation, and in reviving in a most promising way the electron theory of metals.

§ 21·2. *Accessibility.* To fix ideas it will be convenient to start by considering an assembly with two different sets of similar systems practically without interactions, as in Chapter II. A gaseous assembly with two different sorts of molecules, which is practically perfect, is an example of the assembly proposed. The statistical state of the assembly was specified in Chapter II by the set of positive numbers $a_1, \ldots, a_t, \ldots, b_1, \ldots, b_t, \ldots$, describing the distribution of the various systems among their possible stationary states. These states would previously have been taken to have energies $\epsilon_1, \ldots, \epsilon_t, \ldots, \eta_1, \ldots, \eta_t, \ldots$, and weights $\varpi_1, \ldots, \varpi_t, \ldots, \rho_1, \ldots, \rho_t, \ldots$, and we shall see that they can continue to be so described. If there are M and N systems in all of the two types and a total energy E, then we have of course in the classical theory

$$\Sigma_t a_t = M,\ \Sigma_t b_t = N,\ \Sigma_t a_t \epsilon_t + \Sigma_t b_t \eta_t = E. \qquad \ldots\ldots(1451)$$

The total number of weighted complexions, equivalent to the extension of the phase space, representing the specified statistical state is

$$\frac{M!\,N!}{a_1!\ldots b_1!\ldots}\,\varpi_1^{a_1}\ldots\rho_1^{b_1}\ldots. \qquad \ldots\ldots(1452)$$

An essential feature in the foundation of these formulae and all those of like nature hitherto used is the *ultimate independence* of each other of the separate similar systems in the assembly. It is used in the enumeration of the possible arrangements $M!/\Pi_t a_t!$ corresponding to a given statistical specification. It is essential to the argument of Boltzmann's H-theorem (Chapter XVII) which establishes Maxwell's distribution law as the necessary and sufficient condition of equilibrium in a gaseous assembly in which the particles possess this ultimate independence of each other and undergo occasional classical collisions. It is precisely this ultimate independence which the newer theories are forced to deny. This denial is in fact the most fundamental feature of the new mechanics, and, as Bohr* in particular has emphasized, it lies behind Heisenberg's principle of uncertainty, according to which a coordinate and its conjugated momentum can never both be determined exactly in the same experiment. We must now examine in

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* Bohr, *Nature*, vol. CXXI, p. 580 (1928).

detail the way in which this denial of ultimate independence affects statistical mechanics. We shall find it acts simply, by severely limiting the region of accessibility over which averages have to be calculated.

Let us consider first a single conservative isolated system whose classical Hamiltonian function would be $H(q, p)$, and energy integral

$$H(q, p) = E.$$

The variables q, p are to be taken as a shortened form of $q, q', q'', \ldots, p, p', p'', \ldots$, being any suitable set of Lagrangian coordinates and their conjugated momenta. Then in order to discuss such a system exactly according to the new mechanics we form Schrödinger's differential equation

$$\left[H\left(q, -i\mathbf{h}\frac{\partial}{\partial q}\right) - E\right]\psi = 0, \qquad \ldots\ldots(1453)$$

in which $\mathbf{h} = h/2\pi$. All the properties of the system are determined by the function ψ and the condition that ψ must be bounded* and one-valued in the q-space (configuration space) of the system. Not every value of E need be admissible. Values of E for which possible values of ψ exist correspond to possible states of the system. These values of E may be discrete or continuous or sometimes one and sometimes the other according to the nature of the system. For the systems for which stationary states were successfully postulated by the old quantum theory, the possible values of E are discrete, and we shall generally be concerned only with discrete values of E in this chapter. These will be supposed to be enumerated by a suffix taking the values 1, 2, ..., so that no two values of E with different suffixes are equal. Corresponding to any possible value ϵ_σ of E there exist one or more proper solutions ψ_σ of equation (1453). The number of such independent solutions may be called ϖ_σ, since we shall see that it corresponds exactly to the weight ϖ which we have previously used. If the system is degenerate ($\varpi_\sigma \neq 1$), we can often reduce it to a non-degenerate one ($\varpi_{\sigma'} = 1$) by including suitable perturbing fields, if it is convenient to do so for purposes of discussion.

Let us suppose next that our assembly is built up of two such similar systems with very weak interactions, so that to a first approximation the Hamiltonian of the pair is the sum of the separate Hamiltonians. Then the complete wave equation is

$$\left[H\left(q_1, -i\mathbf{h}\frac{\partial}{\partial q_1}\right) + H\left(q_2, -i\mathbf{h}\frac{\partial}{\partial q_2}\right) - E\right]\Psi = 0. \quad \ldots\ldots(1454)$$

It is obvious that the equation separates into two parts and that the permissible values of E are $\epsilon_\sigma + \epsilon_\tau$, and the corresponding solutions

$$\Psi = \psi_\sigma(q_1)\,\psi_\tau(q_2), \qquad \ldots\ldots(1455)$$

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* This is probably not quite correct. The correct condition is probably that $\int |\psi|^2 dq$ taken over any finite part of the configuration space should exist, and that ψ should behave suitably at infinity, the precise behaviour there depending on the nature of the system.

where ϵ_σ and ϵ_τ are possible values of E in (1453) and ψ_σ, ψ_τ corresponding proper solutions. Such values of E are called characteristics (*eigenwerte*) and the corresponding solutions characteristic functions (*eigenfunktionen*), or more commonly in view of Schrödinger's interpretation wave-functions. It is of the utmost importance to observe that in the limit of vanishing interaction the pair of systems is essentially degenerate except when $\sigma = \tau$ even if the single systems are not degenerate. For if $\sigma \neq \tau$ at least two wave-functions

$$\Psi_1 = \psi_\sigma(q_1)\,\psi_\tau(q_2),\ \Psi_2 = \psi_\sigma(q_2)\,\psi_\tau(q_1),$$

obtained by permuting the individual systems, correspond to the characteristic $E = \epsilon_\sigma + \epsilon_\tau$. If the single systems are degenerate $(\varpi_\sigma, \varpi_\tau)$ then obviously the total number of distinct wave-functions corresponding to $\epsilon_\sigma + \epsilon_\tau$ is $2\varpi_\sigma\varpi_\tau$ $(\sigma \neq \tau)$ or $\varpi_\sigma{}^2$ $(\sigma = \tau)$.

The argument is quite general. If the assembly consists of M weakly interacting systems, the complete wave equation is

$$\left[H\left(q_1, -i\mathbf{h}\frac{\partial}{\partial q_1}\right) + H\left(q_2, -i\mathbf{h}\frac{\partial}{\partial q_2}\right) + \dots \right.$$
$$\left. + H\left(q_M, -i\mathbf{h}\frac{\partial}{\partial q_M}\right) - E\right]\Psi = 0. \qquad \text{......(1456)}$$

To the characteristic

$$E = \epsilon_\sigma + \epsilon_\tau + \dots + \epsilon_\omega, \qquad \text{......(1457)}$$

no pair of the suffixes $\sigma, \tau, \dots, \omega$ being equal, there corresponds a set of $M!$ wave-functions obtained by permuting the systems $1, 2, \dots, M$ among the suffixes of the characteristics $\sigma, \tau, \dots, \omega$. The simplest wave-function is

$$\Psi_1 = \psi_\sigma(q_1)\,\psi_\tau(q_2)\dots\psi_\omega(q_M). \qquad \text{......(1458)}$$

For degenerate systems the total number of wave-functions corresponding to the characteristic (1457) is

$$M!\,\varpi_\sigma\varpi_\tau\dots\varpi_\omega.$$

If finally we consider the completely general characteristic

$$E = a_1\epsilon_\sigma + a_2\epsilon_\tau + \dots + a_t\epsilon_\omega \quad (a_1 + a_2 + \dots + a_t = M), \qquad \text{......(1459)}$$

where the individual characteristics are equal in groups of $a_1, a_2, \dots, a_t$, then there are sets of

$$\frac{M!}{a_1!\,a_2!\dots a_t!} \qquad \text{......(1460)}$$

distinct wave-functions obtainable by permutation, of which

$$\Psi_1 = \psi_\sigma(q_1)\dots\psi_\sigma(q_{a_1})\,\psi_\tau(q_{a_1+1})\dots\psi_\tau(q_{a_1+a_2})\dots\psi_\omega(q_M) \qquad \text{......(1461)}$$

is typical. The total number of distinct wave-functions in the degenerate case is

$$\frac{M!\,(\varpi_\sigma)^{a_1}(\varpi_\tau)^{a_2}\dots(\varpi_\omega)^{a_t}}{a_1!\,a_2!\dots a_t!}. \qquad \text{......(1462)}$$

If to the assembly thus constructed we add another set of similar systems distinct from the set hitherto considered, we obtain obviously a new set of wave-functions similar to (1461) each of which can be combined by multiplication with each one of (1461) to give an independent wave-function of the complete assembly. We may not of course permute a pair of distinct systems, for we do not so obtain a solution of the wave equation of the assembly. Thus for an assembly of two distinct sets of similar systems the total number of independent wave-functions corresponding to the characteristic

$$E = a_1\epsilon_\sigma + \dots + b_1\eta_{\sigma'} + \dots \qquad \text{......(1463)}$$

is

$$\frac{M!\,N!\,(\varpi_\sigma)^{a_1}\dots(\rho_{\sigma'})^{b_1}\dots}{a_1!\dots b_1!\dots}. \qquad \text{......(1464)}$$

So far no new point has emerged. In fact on comparing these sets of wave-functions with formulae like (1452) we find as we might expect that the numbers exactly correspond. If we define the weights as in this section, then each weighted complexion corresponds to one wave-function of the assembly. If therefore the introduction of weak interactions between systems of the assembly allows the assembly to pass from a state corresponding to any one of these wave-functions to any other, no modification will be introduced into the statistical calculations. But this is not so. It has been shown, principally by Heisenberg*, to whom we owe the first appreciation of the importance of this type of exchange degeneracy†, that the wave-functions (1461) of a set of similar systems, after reorganization into suitable linear combinations, necessarily divide into a number of groups A, B, ..., S. These groups contain between them all the wave-functions belonging to all the characteristics, and they possess the extremely important property that no interaction between the systems, of whatever type or strength, so long as it is symmetrical (as it must be) in the coordinates of the similar systems, can ever change the assembly from a wave-function of one group A to a wave-function of any other group B. Thus if the assembly is originally represented by a wave-function of group A for the first set of systems it will be for ever confined to wave-functions of group A. Only the states corresponding to this group are accessible, and the average equilibrium properties of the assembly must obviously be determined by averaging over the states of group A and not over all states as hitherto.

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* Heisenberg, *Zeit. für Phys.* vol. XXXVIII, p. 411 (1926). See also the references to § 21·21, and Dirac, *Proc. Roy. Soc.* A, vol. CXII, p. 661 (1926).

† It has recently been pointed out by Heitler, *Zeit. für Phys.* vol. XLVII, p. 835 (1928), that one should distinguish between exchange degeneracy (*Austauschentartung*) and resonance degeneracy (*Resonanzentartung*). The type of degeneracy here considered has often been referred to as resonance degeneracy, but the two types of degeneracy are distinct except accidentally in certain of the commonest cases.

§ **21·21**. *Existence theorem for non-combining groups**. The general form of Schrödinger's equation for Ψ, the wave-function of an assembly of M similar systems to the zero order of approximation in which interactions of the systems and external perturbations are neglected, and from which the operator $\partial/\partial t$ has not yet been eliminated, is

$$\left[H\left(q_1, -i\mathbf{h}\frac{\partial}{\partial q_1}\right) + H\left(q_2, -i\mathbf{h}\frac{\partial}{\partial q_2}\right) + \dots + H\left(q_M, -i\mathbf{h}\frac{\partial}{\partial q_M}\right) - i\mathbf{h}\frac{\partial}{\partial t}\right]\Psi^t = 0 \qquad \text{.......(1465)}$$

The wave-function here must retain its time factor $e^{iEt/\mathbf{h}}$; its presence is recorded by the affix t. The solutions of this equation are expressions such as (1458) (with the time factor), or, since the equation is symmetrical in all the systems and linear in Ψ^t, any expression which can be derived from (1458) by permuting the systems and taking linear combinations of any of these permutations. Any such wave-function we will denote for shortness by $\Psi^t(1, 2, \dots, M)$, the order of the suffixes of the systems being in general significant.

If equation (1465) were exact, the assembly, once represented by a given wave-function, would remain so represented for all time. Owing however to interactions and perturbations this permanence does not exist and Ψ^t will pass from (approximately) one zero order form $\Psi_1{}^t$ to another $\Psi_2{}^t$ or rather to one of a number of other forms in a manner which can be best specified by certain probability coefficients. It is not necessary to enter into this here beyond observing that the exact Ψ^t has to satisfy exactly an equation of the form

$$\left[\mathbf{H} - i\mathbf{h}\frac{\partial}{\partial t}\right]\Psi^t = 0, \qquad \text{......(1466)}$$

where **H** *includes the interaction and perturbation terms and is completely symmetrical in all the systems.*

Let P be any operation of permuting the systems in a given wave-function $\Psi^t(1, 2, \dots M)$, and taking given linear combinations of these permutations, and let $P\Psi^t$ be the result of the operation. Then since **H** is completely symmetrical $P\Psi^t$ is also a wave-function. Suppose that at any given time $t = t_0$ $P\Psi^t = 0$. But $[\mathbf{H}]\,0 = 0$, so that

$$\frac{\partial}{\partial t}(P\Psi^t) = 0 \qquad \text{......(1467)}$$

or $P\Psi^t = 0$ for all time. This is all that is required to establish the existence

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* A proof not involving explicit appeal to group theory was first given by Hund, *Zeit. für Phys.* vol. XLIII, p. 788 (1927). See also Heisenberg, *Zeit. für Phys.* vol. XLI, p. 239 (1927), and especially Wigner, *Zeit. für Phys.* vol. XL, pp. 492, 883, vol. XLIII, p. 624 (1927). These detailed investigations of the structure of the non-combining groups are required for the theory of the structure of atomic and molecular spectra, but are not necessary to us here, where all that we require can be obtained very simply as suggested by Ursell, *Proc. Camb. Phil. Soc.* vol. XXIV, p. 445 (1928).

of non-combining groups of wave-functions. We say that Ψ is *symmetrical* in the systems $\alpha_1, \alpha_2, \ldots, \alpha_\lambda$ if Ψ does not alter when any one of these numbers is interchanged. For example, if

$$\Psi(1, 2, 3, \ldots, M) = \Psi(2, 1, 3, \ldots, M),$$

then Ψ is symmetrical in the systems 1, 2. If

$$\Psi(1, 2, 3, 4, \ldots, M) = \Psi(2, 1, 3, 4, \ldots, M) = \Psi(1, 3, 2, 4, \ldots, M),$$

then Ψ is symmetrical in the systems 1, 2, 3 and so on. But then $P_0\Psi = 0$, where P_0 is the operation of interchanging 1 and 2 and taking the difference of these wave-functions, so that the wave-functions representing the assembly if they are ever symmetrical in any pair of systems must always be symmetrical in that pair. In the same way we say that Ψ is *antisymmetrical* in the systems $\alpha_1, \alpha_2, \ldots, \alpha_\lambda$ if Ψ changes to $-\Psi$ when any pair of these numbers is interchanged. It then follows as before that if Ψ is ever antisymmetrical in any pair of wave-functions it is always antisymmetrical in that pair. The different non-combining groups can be specified by the various groups of systems in which they are symmetrical or in which they are antisymmetrical, but we need not examine the structure of these groups here.

§ **21·22**. *The symmetrical and the antisymmetrical group.* From among the various non-combining groups two stand out conspicuous for the simplicity of their properties and their mathematical form. One is the group of wave-functions which are symmetrical in *all* the systems. This group we shall call simply the symmetrical group S. The other is the group of wave-functions which are antisymmetrical in *all* the systems. This we shall call the antisymmetrical group A. These groups are unique in that for non-degenerate systems they alone contain at most one wave-function for any given characteristic $\Sigma\epsilon_\sigma$. There is always exactly one member of the S group, and there is one member of the A group if all the σ's are different or if all the a_t are 0 or 1, and otherwise no member. This is easily verified if we observe that the antisymmetrical wave-function must take the form of the M-row determinant

$$\begin{vmatrix} \psi_\sigma(q_1) & \psi_\sigma(q_2) & \cdots & \psi_\sigma(q_M) \\ \psi_\tau(q_1) & \psi_\tau(q_2) & \cdots & \psi_\tau(q_M) \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \psi_\omega(q_1) & \psi_\omega(q_2) & \cdots & \psi_\omega(q_M) \end{vmatrix},$$

while the symmetrical wave-function is the same expression with all the signs taken positive.

These very simple enumerations for assemblies of non-degenerate systems can be generalized directly to degenerate ones. For example, if $\varpi_\sigma = 2$, the other ϖ's being 1 as before, there are just two alternative ψ_σ which may be used in constructing Ψ. There are therefore in the A group clearly 1, 2, 1 or 0 wave-functions according as $a_1 = 0$, 1, 2 or $a_1 > 2$. In the S group there are $(a_1 + 1)!/a_1!$ or $a_1 + 1$ wave-functions instead of 1 as before. The general formulae can be given, but it is simpler to pass from non-degenerate systems to degenerate ones at a later stage. General formulae are therefore omitted here, and we shall confine attention for the present to non-degenerate systems.

We know as yet no *a priori* reason why wave-functions of only one group or of one group rather than another should be found in nature. To determine the proper group we must appeal to observation, and the proper group may vary from system to system. When the systems are electrons or protons (hydrogen nuclei) it is certain that the proper group is the *antisymmetrical*. For electrons this follows from the fact that the laws of interaction of electrons must embody Pauli's exclusion principle which is fundamental to the interpretation of spectra. According to this principle, as we know, two electrons in an atom may never possess the same set of quantum numbers, or as we should now say may never have the same wave-function. The group A is the only group of wave-functions of the assembly which possesses just this property, that it has no member whenever two systems have the same wave-function. Since the wave-functions for the electrons in any atom belong to the group A one must suppose that this is due to the nature of the electron and that the wave-functions for the electrons in any other assembly will also belong to group A. For protons the evidence is not so extensive, as it depends only on the interpretation of the hydrogen band spectrum and the theory of the specific heat of hydrogen at low temperatures (§ 3·4). It is however sufficient to be convincing.

Since all atoms and molecules are presumably built up out of electrons and protons, the nature of the wave-functions for other material systems should be deducible from the antisymmetrical nature of the wave-functions for assemblies of electrons or of protons. It is of course true that any material assembly may be considered as an assembly of electrons and protons (for which we know already the nature of the wave-functions) and not as an assembly of atom and molecules. But equally of course this is not particularly illuminating for the ordinary nearly perfect gaseous assembly. If therefore we have an assembly of atomic systems which can be treated properly as practically independent we may ask what will be the nature of the wave-functions for groups of similar atoms, molecules or ions, which represent their motions as wholes, not their internal structure. It is easy to see* that these wave-functions must be *antisymmetrical* if the system contains an *odd* number of electrons and protons and *symmetrical* if it contains an *even* number. For when we interchange a pair

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* It is assumed that the same laws govern the structure of the nuclei as govern the external atomic structure, so far at least as the combining properties of the wave-functions are concerned.

of atomic systems we really interchange a number of electrons and protons and therefore subject the wave-function to a number of changes of sign equal to the total number of electrons and protons in the system. In particular the wave-functions for gaseous assemblies of practically independent *neutral* atoms or molecules must be *symmetrical* for each set of similar atoms or molecules.

Besides material systems we have also to consider radiation. As is now well known, while material particles such as electrons have many of the properties of waves, radiation has also many of the properties of particles. We cannot therefore be satisfied unless we can account for the equilibrium properties of radiation both from the wave and from the light-quantum point of view. We have already given an account of temperature radiation in an enclosure based on its wave aspect in § 4·3. In order to treat it satisfactorily as a collection of quanta we must use a modified statistics. We shall find that light quanta must be assumed to behave, in contradistinction to electrons, in such a way that their wave-functions always belong to the symmetrical group S.

§ 21·3. *The analogue of Liouville's theorem and its consequences.* At the close of Chapter I we pointed out that Liouville's theorem guarantees the invariance of any element of volume of the phase space of an assembly during any dynamical motion. This includes the natural motion of the assembly and its motion under any mechanical perturbation from without. We may derive from this some sort of principle of consistency which supports the actual choice of weights proportional to elements of phase space. For if we compare the motions of the perturbed and the unperturbed assembly and consider the regions of phase space in which a group of representative points lies at corresponding times in the two motions, it is natural to expect that the averaging should be unaffected by the perturbation and should attach equal weights to corresponding elements. Liouville's theorem shows that the weights actually chosen have this property. There is an analogue of this invariance in the new quantum mechanics.

In the new quantum mechanics each independent wave-function corresponds to a stationary state of unit weight in the older quantum theory, and this again corresponds to a certain constant extension of classical phase space. It is therefore natural to expect that the proper method of averaging will be to average over all accessible wave-functions *assigning an equal* (*unit*) *weight to each.* Having therefore proposed this convention we require it to satisfy a consistency theorem, similar to that provided by Liouville's theorem in the classical theory. Such a theorem has been given by Dirac*. The proof is as follows.

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* Dirac, *Proc. Roy. Soc.* A, vol. CXII, p. 661 (1926).

Suppose that at some moment ($t = 0$) the assembly is in a state represented by some particular wave-function $(\Psi^t)_{t=0}$ of the set of accessible wave-functions. The assembly then carries on with or without perturbations. If there were no interactions between the systems and no perturbations we should always have the same wave-function. In general however the wave-function will change and at time t we shall have

$$\Psi^t = \Sigma_n a_n(t) \Psi_n^t, \qquad \text{......(1468)}$$

where Σ_n is extended over all the accessible Ψ_n^t.

This equation may be established by the method of variation of parameters. Including interactions and perturbations the wave-equation takes the form

$$\Big[H\left(q_1, -i\mathbf{h}\frac{\partial}{\partial q_1}\right) + H\left(q_2, -i\mathbf{h}\frac{\partial}{\partial q_2}\right) + \dots + H\left(q_M, -i\mathbf{h}\frac{\partial}{\partial q_M}\right)$$
$$- i\mathbf{h}\frac{\partial}{\partial t} + A\left(t, q_1, \dots, q_M, -i\mathbf{h}\frac{\partial}{\partial q_1}, \dots, -i\mathbf{h}\frac{\partial}{\partial q_M}\right)\Big]\Psi^t = 0. \qquad \text{...(1469)}$$

This is written expressly for an assembly of M similar systems when A must be symmetrical in all the M suffixes. The Ψ_n^t are the solutions of (1469) without the term A. It will be obvious that what follows holds equally for assemblies in which there are any number of such groups. On substituting (1468) we see that it satisfies (1469) if

$$\Sigma_n a_n(t)[A]\Psi_n^t = i\mathbf{h}\Sigma_n \dot{a}_n(t)\Psi_n^t. \qquad \text{......(1470)}$$

We shall assume for simplicity that the Ψ_n of equation (1456) which lack the time factor form a complete set of real normal orthogonal functions in the configuration space of the assembly[*]. Then we may assume that $[A]\Psi_n^t$ with its time factor can be expanded in a series

$$\Sigma_m A_{m,n}(t)\Psi_m^t.$$

The equation (1470) is then reduced to

$$\Sigma_{m,n} a_n(t) A_{m,n}(t)\Psi_m^t = i\mathbf{h}\Sigma_n \dot{a}_n(t)\Psi_n^t,$$

which is satisfied if and only if

$$i\mathbf{h}\dot{a}_m(t) = \Sigma_n a_n(t) A_{m,n}(t). \qquad \text{......(1471)}$$

The $A_{m,n}(t)$ are given by the usual integrals which fix the coefficients of any expansion in a series of orthogonal functions, here

$$\int\dots\int[\Sigma_r A_{r,n}(t)\Psi_r^t]\Psi_m dq_1 \dots dq_M = A_{m,n}(t)\, e^{iE_m t/\mathbf{h}}$$
$$= e^{iE_n t/\mathbf{h}}\int\dots\int \Psi_m [A]\Psi_n dq_1 \dots dq_M, \qquad \text{......(1472)}$$

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[*] The consistency theorem we shall prove is true more generally, without the restriction to reality which requires the differential equation for Ψ_n to be self-adjoint. If this equation $[H(1) + \dots + H(M) - E]\Psi_n = 0$ is not restricted to be self-adjoint the expansion of $[A]\Psi_n^t$ must proceed in terms of the characteristic functions of the adjoint equation. This equation may be the conjugate complex of the original equation and its characteristic functions are then the conjugate complexes of the Ψ_n, but it may be still more general. For the modifications in the theorem then required see a forthcoming work by Dirac.

where the $\int \dots \int$ are extended over the configuration space. Equations (1471) and the initial conditions serve to determine the $a_n(t)$ uniquely.

The regular interpretation of any such equation as (1468) proposed by the new quantum mechanics is that $| a_n(t) |^2$ represents the probability that the assembly, initially in a given state at $t = 0$, will be found in the state represented by $\Psi_n{}^t$ at time t. This interpretation requires the consistency theorem

$$\Sigma_n \, | a_n |^2 = 1, \qquad \dots\dots(1473)$$

which is true and is the required analogue of Liouville's theorem. For it shows that if we attach unit weight to the state represented by each wave-function we attach the same unit weight to the group of states that succeed any given state at any time, whether or not there are perturbations.

To establish (1473) we have to show that

$$S = i\mathbf{h} \frac{d}{dt} \Sigma_n \, | a_n(t) |^2 = i\mathbf{h}\Sigma_n \left[a_n(t) \, \dot{a}_n{}^*(t) + \dot{a}_n(t) \, a_n{}^*(t) \right] = 0,$$

where a^* denotes the conjugate complex of a. We restrict ourselves of course to the same special case as before. The conjugate complexes of the a's are defined by

$$\Psi^{t*} = \Sigma_n a_n{}^*(t) \, \Psi_n{}^{t*}$$

and satisfy the differential equations

$$- i\mathbf{h}\dot{a}_m{}^*(t) = \Sigma_n a_n{}^*(t) \, A_{m,n}{}^*(t), \qquad \dots\dots(1474)$$

where $$A_{m,n}{}^*(t) = e^{-i(E_n - E_m)t/\mathbf{h}} \int \dots \int \Psi_m \, [A^*] \, \Psi_n dq_1 \dots dq_M. \qquad \dots(1475)$$

With the help of equations (1471) and (1474) it follows that

$$\begin{aligned} S &= \Sigma_n \left[a_n{}^*(t) \, \Sigma_m a_m(t) \, A_{n,m}(t) - a_n(t) \, \Sigma_m a_m{}^*(t) \, A_{n,m}{}^*(t) \right], \\ &= \Sigma_{n,m} a_n{}^*(t) \, a_m(t) \left[A_{n,m}(t) - A_{m,n}{}^*(t) \right]. \end{aligned}$$

On comparing (1472) and (1475) we see that $A_{n,m}(t) = A_{m,n}{}^*(t)$ whenever A is a function of t and the q's only (when it must be real). The same relation can be shown to hold also when A contains terms in $- i\mathbf{h}\partial/\partial q$ with constant coefficients. These cover all the examples commonly required. Actually the relation $A_{n,m}(t) = A_{m,n}{}^*(t)$ is essential to the interpretation of the quantum mechanics and must be true in general, as it is the analogue of the reality of the interaction or perturbation in the classical problem. Our consistency theorem is thus established.

§ 21·4. *Average values in an assembly obeying general laws of accessibility*†. The result of the foregoing investigations is that in enumerating

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† For the sections immediately following a very useful reference is Uhlenbeck, *Over statistische Methoden in de Theorie der Quanta*, Thesis, Leiden (1927). The general method was given by Fowler, *Proc. Roy. Soc.* A, vol. CXIII, p. 432 (1926).

the accessible complexions of a group of similar non-degenerate systems in an assembly we have to replace the classical

$$\frac{M!}{a_1!\,a_2!\,\ldots\,a_t!} \qquad \ldots\ldots(1476)$$

by 1 when the wave-functions are confined to the group S, and by

$$1\,[a_t \leqslant 1\ (\textit{all}\ t)],\ \ 0\,[a_t > 1\ (\textit{some}\ t)]$$

when the wave-functions are confined to the group A. We shall proceed therefore to study the equilibrium state, using the general expression

$$\Pi_t \gamma\,(a_t) \qquad \ldots\ldots(1477)$$

in place of (1476) in calculating C. This covers at once all the cases yet proposed. It is obvious that we must always take

$$\gamma\,(0) = 1.$$

To make the calculation sufficiently representative we shall consider in detail an assembly of similar systems of two types A and B, which can also exist in combination, type AB. There are then three different groups of similar systems, all at first non-degenerate, of characteristics

$$\epsilon_1, \epsilon_2, \ldots, \epsilon_t, \ldots,\quad \eta_1, \eta_2, \ldots, \eta_t, \ldots,\quad \zeta_1, \zeta_2, \ldots, \zeta_t, \ldots,$$

respectively. The number of systems assigned to each characteristic is specified by

$$a_1, a_2, \ldots, a_t, \ldots,\quad b_1, b_2, \ldots, b_t, \ldots,\quad c_1, c_2, \ldots, c_t, \ldots,$$

respectively. This set of numbers specifies completely the statistical state of the whole assembly which is therefore represented by

$$\Pi_t \gamma\,(a_t)\,\Pi_t \gamma'\,(b_t)\,\Pi_t \gamma''\,(c_t) \qquad \ldots\ldots(1478)$$

complexions or independent wave-functions. It will not necessarily be true that the γ's are the same for the different types.

To see more clearly that (1478) is the proper form when dissociation is going on we may go back for the moment to the classical enumeration for this assembly. We then assigned to the specified statistical state for a single example of the assembly

$$\frac{M!}{\Pi_t\,(a_t!)}\cdot\frac{N!}{\Pi_t\,(b_t!)}\cdot\frac{P!}{\Pi_t\,(c_t!)}$$

complexions, where $\Sigma_t a_t = M$, $\Sigma_t b_t = N$, $\Sigma_t c_t = P$. We also multiplied this number by

$$\frac{X!\,Y!}{M!\,N!\,P!},$$

where $M + P = X$, $N + P = Y$, for the number of such examples. Thus the full number of complexions was

$$\frac{X!\,Y!}{\Pi_t\,(a_t!)\,\Pi_t\,(b_t!)\,\Pi_t\,(c_t!)}, \qquad \ldots\ldots(1479)$$

which apart from the trivial constant factor $X!\,Y!$ is of the form (1478).

We might however have proceeded directly to this form by considering the complete permutations of the systems among all their possible states, without reference to particular examples of the assembly and without distinguishing between the bound and free states of the systems. We can now see that we can do the same thing in the new mechanics. If we enumerate the wave-functions of the assembly corresponding to the (a_t, b_t, c_t) specification as in § 21·2, it is unnecessary to distinguish between states that are bound or free, and we shall again arrive at (1479). When however we consider the symmetry properties of the two sets of systems A and B we find just as before that the wave-functions break up into non-combining groups, there being in particular just as before the groups A and S. If we may assume that the wave-functions of the systems A and B belong to one or other of these two groups, then the wave-functions of the set AB must also belong to one of these groups, and the form (1478) for the number of wave-functions or complexions is correct.

The arguments are obviously quite general and apply to any dissociating assembly such as those discussed in § 5·4. We shall not trouble to repeat the general formulae in this chapter. We need only comment on the question of the symmetry numbers which occur in the general classical discussion. In the new mechanics all questions of molecular symmetry automatically adjust themselves, if the accessible states of the molecule or other system containing numbers of similar parts are correctly enumerated. Of course the considerations which govern the accessibility of complexions of assemblies of similar systems equally apply to the possible intercombinations between the states of an atom or molecule. For example the accessible states of H_2 must be antisymmetrical in the two protons. The number of its accessible states is thereby halved (as we have seen in Chapter III), which is the analogue of the effect of the classical symmetry number $\sigma = 2$. In the same way the states of an atom must be antisymmetrical in all its n electrons, when account is taken of their spin. For this reason its possible states are reduced in number by the similarity of the electrons by the factor $n\,!$, representing a classical symmetry number of this value as we saw in Chapter XIV.

To find the total number of complexions C we have to sum (1478) for all a_t, b_t, c_t subject to the conditions

$$\begin{aligned}\Sigma_t a_t + \Sigma_t c_t &= X,\\ \Sigma_t b_t + \Sigma_t c_t &= Y,\\ \Sigma_t a_t \epsilon_t + \Sigma_t b_t \eta_t + \Sigma_t c_t \zeta_t &= E,\end{aligned}$$

which can obviously be done by the method of § 5·3. The required number of complexions is the coefficient of $x^X y^Y z^E$ in

$$\Sigma \,\{[\Pi_t \gamma(a_t)]\, x^{\Sigma_t a_t} z^{\Sigma_t a_t \epsilon_t}\}\,\{[\Pi_t \gamma'(b_t)]\, y^{\Sigma_t b_t} z^{\Sigma_t b_t \eta_t}\}\,\{[\Pi_t \gamma''(c_t)]\,(xy)^{\Sigma_t c_t} z^{\Sigma_t c_t \zeta_t}\}, \qquad \ldots\ldots(1480)$$

summed over unrestricted positive and zero values of a_t, b_t, c_t for all t. This series can be partially summed. We write

$$\left.\begin{aligned} f(xz^{\epsilon_t}) &= \sum_{n=0}^{\infty} \gamma(n)\, x^n z^{n\epsilon_t}, \\ g(yz^{\eta_t}) &= \sum_{n=0}^{\infty} \gamma'(n)\, y^n z^{n\eta_t}, \\ h(xyz^{\zeta_t}) &= \sum_{n=0}^{\infty} \gamma''(n)\, (xy)^n z^{n\zeta_t}. \end{aligned}\right\} \qquad \ldots\ldots(1481)$$

The new functions so defined may be called the *generating functions* of the systems. Then the series (1480) reduces to

$$\Pi_t f(xz^{\epsilon_t})\, \Pi_t g(yz^{\eta_t})\, \Pi_t h(xyz^{\zeta_t}), \qquad \ldots\ldots(1482)$$

and the total number of complexions is

$$C = \frac{1}{(2\pi i)^3} \iiint \frac{dx\,dy\,dz}{x^{X+1} y^{Y+1} z^{E+1}}\, \Pi_t f(xz^{\epsilon_t})\, \Pi_t g(yz^{\eta_t})\, \Pi_t h(xyz^{\zeta_t}). \quad \ldots(1483)$$

The forms of the generating functions with which we shall have to deal are:

$$\text{Classical};\ f(xz^{\epsilon_t}) = \exp(xz^{\epsilon_t}), \qquad \ldots\ldots(1484)$$

$$\text{Wave-functions of group } S;\ f(xz^{\epsilon_t}) = \Sigma_n x^n z^{n\epsilon_t} = 1/(1 - xz^{\epsilon_t}), \quad \ldots\ldots(1485)$$

$$\text{Wave-functions of group } A;\ f(xz^{\epsilon_t}) = 1 + xz^{\epsilon_t}. \qquad \ldots\ldots(1486)$$

It will now be sufficient to summarize the rest of the development of the revised equilibrium theory and its thermodynamical connections which are strictly parallel to Chapters V and VI. The fundamental first step is the construction of an integral for $C\overline{a_r}$ similar to (1483), where $\overline{a_r}$ is the average number of systems of type A in their rth state. The required number is the coefficient of $x^X y^Y z^E$ in a series differing only from (1480) by the extra factor a_r. This series sums to a result like (1482) except that the single factor $f(xz^{\epsilon_r})$ is different, being replaced by

$$\sum_{n=1}^{\infty} n\gamma(n)\, x^n z^{n\epsilon_r} = x \frac{\partial}{\partial x} f(xz^{\epsilon_r}).$$

Thus

$$C\overline{a_r} = \frac{1}{(2\pi i)^3} \iiint \frac{dx\,dy\,dz}{x^{X+1} y^{Y+1} z^{E+1}}\, x \frac{\partial}{\partial x} \log f(xz^{\epsilon_r})\, \Pi_t f(xz^{\epsilon_t})\, \Pi_t g(yz^{\eta_t}) \times \Pi_t h(xyz^{\zeta_t}). \quad \ldots\ldots(1487)$$

The other integrals required can be similarly constructed, and can all be evaluated by the method of steepest descents. If we write

$$\begin{aligned} Z &= \log \{\Pi_t f(xz^{\epsilon_t})\, \Pi_t g(yz^{\eta_t})\, \Pi_t h(xyz^{\zeta_t})\}, \\ &= \Sigma_t \log f(xz^{\epsilon_t}) + \Sigma_t \log g(yz^{\eta_t}) + \Sigma_t \log h(xyz^{\zeta_t}), \quad \ldots(1488) \end{aligned}$$

$$\Sigma = Z - E \log z - X \log x - Y \log y, \qquad \ldots\ldots(1489)$$

so that Σ is the logarithm of the integrand of C, then the saddle-point of the integrand is given by the unique real positive root λ, μ, ϑ of the equations

$$\frac{\partial \Sigma}{\partial x} = \frac{\partial \Sigma}{\partial y} = \frac{\partial \Sigma}{\partial z} = 0.$$

Theorem 5·5 applies here, and we find as in Chapter v that if $\overline{M}$, $\overline{N}$ and $\overline{MN}$ are the average numbers of free systems of types A, B, and AB,

$$\overline{a_r} = \lambda \frac{\partial}{\partial \lambda} \log f(\lambda \vartheta^{\epsilon_r}), \qquad \text{......(1490)}$$

$$\overline{M} = \Sigma_r \overline{a_r} = \lambda \frac{\partial}{\partial \lambda} \Sigma_r \log f(\lambda \vartheta^{\epsilon_r}), \qquad \text{......(1491)}$$

$$\overline{E_A} = \Sigma_r \overline{a_r}\, \epsilon_r = \vartheta \frac{\partial}{\partial \vartheta} \Sigma_r \log f(\lambda \vartheta^{\epsilon_r}). \qquad \text{......(1492)}$$

Similarly

$$\overline{c_r} = \lambda\mu \frac{\partial}{\partial (\lambda\mu)} \log h(\lambda\mu\vartheta^{\zeta_r}), \qquad \text{......(1493)}$$

$$\overline{MN} = \Sigma_r \overline{c_r} = \lambda\mu \frac{\partial}{\partial (\lambda\mu)} \Sigma_r \log h(\lambda\mu\vartheta^{\zeta_r}), \qquad \text{......(1494)}$$

$$\overline{E_{AB}} = \Sigma_r \overline{c_r}\, \zeta_r = \vartheta \frac{\partial}{\partial \vartheta} \Sigma_r \log h(\lambda\mu\vartheta^{\zeta_r}). \qquad \text{......(1495)}$$

It is obvious that the method is quite general. If there are no molecules possible of type AB, then it is only necessary to omit all terms in $h(xyz^{\zeta_r})$. If other types of molecules are present such as A_2B (chemical notation), then we have only to insert the corresponding additional factors

$$\prod_{r=1}^{\infty} j(x^2yz^{\kappa_r})$$

and terms derived from them, j being constructed for the new systems as h was for the old.

§ 21·41. *External reactions, entropy and absolute temperature.* External forces acting on the assembly can be discussed in the revised theory just as in the old. The ϵ_r depend on parameters α which define the external fields of force, and

$$-\frac{\partial \epsilon_r}{\partial \alpha} \delta\alpha$$

is the reversible work done by the system in the rth state on the external body as α increases from α to $\alpha + \delta\alpha$. This is only a definition conserving energy and is still valid in the new mechanics*. If $\overline{\mathrm{A}}$ is the corresponding average reaction of the whole assembly

$$\overline{\mathrm{A}} = \Sigma_r \overline{a_r} \left(-\frac{\partial \epsilon_r}{\partial \alpha}\right) + \Sigma_r \overline{b_r} \left(-\frac{\partial \eta_r}{\partial \alpha}\right) + \Sigma_r \overline{c_r} \left(-\frac{\partial \zeta_r}{\partial \alpha}\right),$$

$$= \frac{1}{\log 1/\vartheta} \frac{\partial Z}{\partial \alpha}. \qquad \text{......(1496)}$$

We observe next that the intensive parameters, λ, μ, ϑ, which specify the equilibrium state have still exactly those properties which we expect of the partial potentials and the temperature in thermodynamics. To prove

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* For the nature of adiabatic (i.e. slow reversible) variations in the new mechanics see Born, *Zeit. für Phys.* vol. XL, p. 167 (1926).

that these assemblies are thermodynamic systems we have to show that there still exist functions T and S of the state of the assembly such that T is a function of ϑ only and

$$dQ = dE + \Sigma\overline{\mathrm{A}}da = TdS.$$

It is easily verified that these functions exist and have the forms

$$\vartheta = e^{-1/kT}, \quad S - S_0 = k\Sigma, \qquad \ldots\ldots(1497)$$

where Σ is defined by (1489). We can verify also that, omitting trivial terms,

$$S - S_0 = k \log C. \qquad \ldots\ldots(1498)$$

The natural convention is always to take $S_0 = 0$, and there are now no awkward factorials to be omitted from C before we may assert in all cases that

$$S = k\Sigma = k \log C. \qquad \ldots\ldots(1499)$$

It will be seen at once that the contributions of the various sets of systems to S are strictly additive and that the characteristic function Ψ is simpler than S. The typical contribution to Ψ from the free systems of the first type is

$$\Psi = k\left[-\overline{M}\log\lambda + \sum_{r=1}^{\infty}\log f(\lambda\vartheta^{\epsilon_r})\right]. \qquad \ldots\ldots(1500)$$

§ **21·42**. *Degenerate systems.* We can now remove the restriction of non-degeneracy. The equilibrium properties of systems of given type depend only on the function

$$\Sigma_r \log f(\lambda\vartheta^{\epsilon_r}),$$

in which we have supposed that the ϵ_r are all distinct, with one wave-function apiece. If the systems are naturally degenerate we may now remove the necessary perturbations, and the ϵ_r then become equal in groups of number ϖ_r. The logarithm of the generating function is then

$$\Sigma_r \varpi_r \log f(\lambda\vartheta^{\epsilon_r}). \qquad \ldots\ldots(1501)$$

If λ is sufficiently small the logarithm can be expanded and the function (1501) cast into the form used by Einstein*,

$$\sum_{j=1}^{\infty} \alpha(j)\,\lambda^j\,(\Sigma_r \varpi_r \vartheta^{j\epsilon_r}). \qquad \ldots\ldots(1502)$$

If Schrödinger's equation separates into distinct parts so that $\epsilon_r = \epsilon_\rho + \epsilon_\tau$ and $\varpi_r = \varpi_\rho\varpi_\tau$ we shall find for (1502)

$$\sum_{j=1}^{\infty} \alpha(j)\,\lambda^j\,(\Sigma_\rho \varpi_\rho \vartheta^{j\epsilon_\rho})\,(\Sigma_\tau \varpi_\tau \vartheta^{j\epsilon_\tau}). \qquad \ldots\ldots(1503)$$

In classical mechanics (1502) reduces to

$$\lambda\Sigma_r\varpi_r\vartheta^{\epsilon_r} = \lambda f(\vartheta),$$

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* Einstein, *Berl. Sitz.* (1924) p. 261; (1925) p. 3.

where $f(\vartheta)$ is the old partition function. For wave-functions of group S we have

$$-\Sigma_r \varpi_r \log(1-\lambda\vartheta^{\epsilon_r}) = \sum_{j=1}^{\infty} \frac{\lambda^j}{j}(\Sigma_r \varpi_r \vartheta^{j\epsilon_r}), \qquad \text{......(1504)}$$

and for wave-functions of group A

$$\Sigma_r \varpi_r \log(1+\lambda\vartheta^{\epsilon_r}) = \sum_{j=1}^{\infty} \frac{(-)^{j-1}\lambda^j}{j}(\Sigma_r \varpi_r \vartheta^{j\epsilon_r}). \qquad \text{......(1505)}$$

§ **21·43**. *Moving mass-points in a volume V.* If our systems are atoms, molecules, ions or electrons free to move in a volume V, we can discuss their translatory motion apart from their internal motions, since Schrödinger's equation separates into two parts for the two motions. If V has the form of a rectangular box of edges a, b, c, the determination of the ϵ_r is simple. The separated part of Schrödinger's equation reduces to

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - W)\psi = 0, \qquad \text{......(1506)}$$

where W is the potential energy of the system in the local boundary field. A sufficiently representative form for W is to assume that $W = 0$ inside the box* and $W \to \infty$ rapidly as we pass the walls. Then ψ to be a possible wave-function must be one-valued and bounded in V and vanish over the walls†. The possible forms of Ψ are obviously

$$\psi_r = \sin\frac{s\pi x}{a}\sin\frac{t\pi y}{b}\sin\frac{u\pi z}{c}, \qquad \text{......(1507)}$$

where s, t, u are positive integers (not zero), corresponding to the characteristic

$$E = \epsilon_r = \frac{h^2}{8m}\left(\frac{s^2}{a^2}+\frac{t^2}{b^2}+\frac{u^2}{c^2}\right). \qquad \text{......(1508)}$$

There is only the one ψ_r for each characteristic. Any weight factors other than unity enter only in virtue of the internal structure of the systems.

On referring back to (1502) we see that the important series to be summed is

$$\Sigma_r e^{-j\epsilon_r/kT},$$

which on using (1508) breaks up into the product of three series of which

$$\sum_{s=1}^{\infty} \exp\left\{-\frac{jh^2}{8ma^2kT}s^2\right\} \qquad \text{......(1509)}$$

is typical. This series is practically a ϑ-function and its value when $jh^2/(8ma^2kT)$ is small, as it is for all the important terms in (1502) in all

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* For ions or electrons we thus ignore the effects of their charges. If the assembly as a whole is a neutral mixture this is probably a valid but rough first approximation and is in common use.

† The boundary condition on the walls can be established thus: consider the wall $x=0$, near which as $V \to \infty$ $\psi'' \sim V\psi$. By well-known methods [e.g. Jeffreys, *Proc. Lond. Math. Soc.* vol. XXIII, p. 428 (1924)] it follows that $\log\psi \sim \pm\int^x V^{\frac{1}{2}}dx$. We must suppose that for a local boundary field the integral does not converge as $x \to 0$. Hence either $\psi \to 0$ or $\psi \to \infty$. The latter is impossible if ψ is to be bounded or even if only $\int|\psi|^2 dx$ is to exist. Hence $\psi \to 0$ on the boundary.

ordinary applications, can be obtained as accurately as may be required from the transformation theory. We have in fact*

$$\vartheta_3(v,\tau) = 1 + 2\sum_{s=1}^{\infty} e^{\pi i\tau s^2}\cos 2s\pi v,$$

$$= \sqrt{\left(\frac{i}{\tau}\right)}\sum_{n=-\infty}^{\infty} e^{-\frac{\pi i}{\tau}(v+n)^2}. \qquad \text{......(1510)}$$

Putting $v = 0$, and $\tau/i = jh^2/(8\pi ma^2kT)$ we find from (1510), with great accuracy for small values of τ/i,

$$\sum_{s=1}^{\infty}\exp\left\{-\frac{jh^2}{8ma^2kT}s^2\right\} = \tfrac{1}{2}\left\{\left(\frac{8m\pi a^2kT}{jh^2}\right)^{\frac{1}{2}} - 1\right\},$$

which is sufficiently nearly equal for all ordinary values of a and T and early values of j to

$$\frac{(2\pi mkT)^{\frac{1}{2}}}{h}\frac{a}{j^{\frac{1}{2}}}. \qquad \text{......(1511)}$$

Thus
$$\Sigma_r\, e^{-j\epsilon_r/kT} = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}\frac{V}{j^{\frac{3}{2}}}. \qquad \text{......(1512)}$$

For structureless mass-points and sufficiently small values of λ

$$\Sigma_r \log f(\lambda\vartheta^{\epsilon_r}) = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} V \sum_{j=1}^{\infty}\frac{\alpha(j)}{j^{\frac{3}{2}}}\lambda^j. \qquad \text{......(1513)}$$

If the internal motions are included this becomes

$$\Sigma_r \log f(\lambda\vartheta^{\epsilon_r}) = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} V \sum_{j=1}^{\infty}\frac{\alpha(j)}{j^{\frac{3}{2}}}\lambda^j\left(\Sigma_\tau\varpi_\tau e^{-j\epsilon_\tau/kT}\right). \quad \text{...(1514)}$$

The conditions under which the foregoing formulae hold are first that λ shall be sufficiently small for the expansion of the logarithms; on this condition we shall defer further comment. The other condition is that $h^2/(8\pi ma^2kT)$ shall be very small even when multiplied by any integer j which yields a significant term in the j-expansion. This condition is fulfilled for all ordinary enclosures and ordinary temperatures, for if $a = 1$ cm., $T = 1°$ K., the value of this ratio is $1{\cdot}4 \times 10^{-11}$. We shall not discuss (1514) in detail. A single example will be sufficient to illustrate the relationship to the classical formulae of §§ 2·6, 5·3. Let us assume that the moving systems are rigid symmetrical rotators without axial spin. Then as before in § 2·62

$$\epsilon_\tau = \tau(\tau+1)\frac{h^2}{8\pi^2A}, \quad \varpi_\tau = 2\tau + 1 \quad (\tau = 0, 1, 2, \ldots).$$

It was shown in § 3·3 that

$$\sum_{\tau=0}^{\infty}(2\tau+1)\exp\left\{-\frac{jh^2}{8\pi^2AkT}\tau(\tau+1)\right\} \sim \frac{1}{j}\frac{8\pi^2AkT}{h^2}$$

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* Tannery and Molk, *Elliptic Functions*, vol. II, pp. 252, 264.

when the rotations are practically classical, that is when $jh^2/8\pi^2AkT$ is small. Under these conditions (1514) reduces to

$$\Sigma_r \log f(\lambda\vartheta^{\epsilon_r}) = \frac{(2\pi m)^{\frac{3}{2}}(8\pi^2A)(kT)^{\frac{5}{2}}V}{h^5}\sum_{j=1}^{\infty}\frac{\alpha(j)}{j^{\frac{5}{2}}}\lambda^j. \qquad \text{......(1515)}$$

In all these formulae we have for systems whose wave-functions are of the group S

$$\alpha(j) = 1/j.$$

This is called the Einstein-Bose statistics. For systems whose wave-functions are of group A we have

$$\alpha(j) = (-)^{j-1}/j.$$

This is called the Fermi-Dirac statistics.

§ **21·44**. *The value of λ and the approximation to classical statistics.* The value of the foregoing expansions depends on the size of λ which must now be examined. By equations (1491) and (1513), ignoring internal structure, the molecular density ν is given by

$$\nu = \frac{\overline{M}}{V} = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}\sum_{j=1}^{\infty}\frac{\alpha(j)}{j^{\frac{1}{2}}}\lambda^j. \qquad \text{......(1516)}$$

It follows at once that λ is small if

$$\frac{\nu h^3}{(2\pi mkT)^{\frac{3}{2}}} \quad \text{or} \quad 5{\cdot}2 \times 10^{-21}\frac{\nu}{(TM^*)^{\frac{3}{2}}}$$

is small, where M^* is the molecular weight on the (chemical) oxygen scale. Thus even for molecular hydrogen at 1° K. and normal concentration, $\nu = 2{\cdot}7 \times 10^{19}$, λ is still less than 0·1 and the series in (1516) reduces practically to its first term. *A fortiori* for heavier molecules and greater temperatures λ is still smaller, or as small up to higher concentrations. Thus in all applications to actual gases we may assume that λ is small and that (1516) and similar series reduce to their first terms. The only exception will be electron gases at the concentrations at which one would expect to find free electrons in metals, about one per atom, $\nu = 10^{22}$. Such assemblies are still non-classical up to temperatures greater than 2000° K. The expansions are then valueless.

When λ is small the assembly is indistinguishable from a classical one, according to any statistics for which $\alpha(1) = 1$. For (1516) reduces to

$$\nu = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}\lambda, \qquad \text{......(1517)}$$

and the distribution law (1490) to

$$\overline{a_r} = \lambda e^{-\epsilon_r/kT}. \qquad \text{......(1518)}$$

These equations are equivalent to those of § 5·3. The contribution of these systems to the characteristic function is then

$$\overline{M}\left[\tfrac{3}{2}\log T - \log\nu + \log\frac{(2\pi mk)^{\frac{3}{2}}}{h^3} + 1\right], \qquad \text{......(1519)}$$

which is classical, including the value of the constant. Thus all our formulae for the chemical constants are unaffected.

We have shown that in general gaseous assemblies are practically classical in spite of the change of statistics either to type A or S. It is now easy to see the reason, which is that the phase space has so many cells of extension h^3 or the assembly so many corresponding wave-functions that it is extremely improbable that any pair of systems will attempt to occupy the same cell or possess the same wave-function. It does not then matter how those events are enumerated in which two or more systems occupy the same cell.

From (1514) we can derive the result that

$$p = \tfrac{2}{3}\overline{E_{\mathrm{kin}}}/V. \qquad \text{......(1520)}$$

For in (1503) only the ϵ_ρ and not the ϵ_τ depend on the mass motion of the systems, so that to find their mean kinetic energy we have to operate with $\vartheta\partial/\partial\vartheta$ or $kT^2\partial/\partial T$ on the $\vartheta^{\epsilon_\rho}$ terms only and not on the $\vartheta^{\epsilon_\tau}$. These terms give rise to the external $T^{\frac{3}{2}}$ factor in (1514). Therefore

$$\overline{E_{\mathrm{kin}}} = \tfrac{3}{2}kT\,\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}\,V\sum_{j=1}^{\infty}\frac{\alpha(j)}{j^{\frac{3}{2}}}\,\lambda^j\,(\Sigma_\tau\varpi_\tau e^{-j\epsilon_\tau/kT})\text{.......(1521)}$$

On the assumption that the ϵ_τ are independent of V,

$$\begin{aligned} p &= kT\,\frac{\partial}{\partial V}\,\Sigma_r \log f(\lambda\vartheta^{\epsilon_r}),\\ &= kT\,\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}\sum_{j=1}^{\infty}\frac{\alpha(j)}{j^{\frac{3}{2}}}\,\lambda^j\,(\Sigma_\tau\varpi_\tau e^{-j\epsilon_\tau/kT}), \qquad \text{......(1522)}\end{aligned}$$

which yields (1520). This classical result therefore holds in the new statistics so long as (1511) is a legitimate approximation—that is practically always—whatever be the value of λ.*

The equations of dissociative equilibrium can be obtained at once from equations (1491) and (1494) by eliminating λ and μ from these equations and the analogue of (1491) for the other free systems. We have only to solve these equations for λ, μ and $\lambda\mu$ in terms of T and $\overline{M}/V$, $\overline{N}/V$ and $\overline{MN}/V$ respectively. The functions so obtained are proportional to the concentrations in the classical limit when λ and μ are small, and are equivalent to the *activities* of modern thermodynamics.

§ **21·45**. *Space distributions of mass-points in external fields of force.* The distribution laws which we have given are primarily concerned only with distributions over the characteristics, that is with energy distributions. At the same time these must imply some means of deriving the average number of systems "present" in some sense in a given volume element of ordinary space.

The means required are provided by the properties of the wave-

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* That (1520) is true for all values of λ can be more simply proved by using the integrals of the following sections instead of the expansion (1503).

functions themselves. We interpret these wave-functions so that $|\psi_r|^2 dV$ is the probability that a given system with this normalized wave-function will be found in the volume element dV at any time. The average number n of molecules "present" in the volume element dV is therefore given by

$$n/dV = \nu \Sigma_r \bar{a}_r |\psi_r|^2, \qquad \text{......(1523)}$$

$$= \lambda \frac{\partial}{\partial \lambda} \Sigma_r \log f(\lambda \vartheta^{\epsilon_r}) |\psi_r|^2. \qquad \text{......(1524)}$$

We must now study the approximate forms of these wave-functions when the systems move in a field of force in which they possess the potential energy W.* We must restrict ourselves to wave equations for ψ which separate in the variables x, y, z, so that $W = w_1(x) + w_2(y) + w_3(z)$. Actually this restriction proves not to be serious since with a more general W we can always limit the assembly to physically small portions of the gas in which W is sensibly of this form. The equation for the x-factor in ψ_r, namely

$$\frac{d^2\psi(x)}{dx^2} + \kappa^2 [\epsilon_s - w_1(x)]\psi(x) = 0 \qquad \left(\kappa^2 = \frac{8\pi^2 m}{h^2}\right), \text{...(1525)}$$

is then typical of all three factors. It must be solved with the boundary conditions $\psi(0) = \psi(a) = 0$. For convenience we shall assume that $w_1(0) = 0$ and that $dw_1(x)/dx > 0$, but these conditions are inessential. Since κ is very large we can apply the analysis developed by Jeffreys† for such problems. He has shown that if

$$\kappa \gg \int_0^x \frac{d^2}{dx^2}[\epsilon_s - w_1(x)]^{-\frac{1}{4}} \frac{dx}{[\epsilon_s - w_1(x)]^{\frac{1}{4}}}, \qquad \text{......(1526)}$$

then the two solutions of (1525) approximate very closely to

$$[\epsilon_s - w_1(x)]^{-\frac{1}{4}} \exp\left\{\pm\kappa \int_0^x [w_1(x) - \epsilon_s]^{\frac{1}{2}} dx\right\}. \qquad \text{......(1527)}$$

Since κ is large the condition (1526) is satisfied for all but a very few of the possible ϵ_s except near a zero of $\epsilon_s - w_1(x)$, where there is a range very small compared with the total range 0, a in which the condition fails.

We now choose that solution vanishing at $x = 0$ or $x = a$ which can also be made to vanish at $x = a$ or $x = 0$. There are two cases. If $\epsilon_s - w_1(x) > 0$ everywhere in the range the required solution is

$$[\epsilon_s - w_1(x)]^{-\frac{1}{4}} \sin\left\{\kappa \int_0^x [\epsilon_s - w_1(x)]^{\frac{1}{2}} dx\right\}. \qquad \text{......(1528)}$$

The ϵ_s are then those values for which

$$\kappa \int_0^a [\epsilon_s - w_1(x)]^{\frac{1}{2}} dx = n\pi,$$

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* Mott, *Proc. Camb. Phil. Soc.* vol. XXIV, p. 76 (1928).

† Jeffreys, *Proc. Lond. Math. Soc.* vol. XXIII, p. 428 (1924). An independent discussion has been more recently given by Kramers, *Zeit. für Phys.* vol. XXXIX, p. 828 (1926), with results which agree with those of Jeffreys to the order required here, though they do not seem to agree completely.

where n is an integer. If $\epsilon_s - w_1(x) = 0$ at $x = x_0$ in the range we may take that solution which, when $\epsilon_s - w_1(x) < 0$, approximates to

$$[w_1(x) - \epsilon_s]^{-\frac{1}{4}} \exp\left\{- \kappa \int_{x_0}^{x} [w_1(x) - \epsilon_s]^{\frac{1}{2}}\, dx\right\},$$

for this solution decreases very rapidly as x increases and may be taken to be zero for $x > x_0$, and so at $x = a$. When $x < x_0$ this solution has been shown by Jeffreys to approximate to

$$[\epsilon_s - w_1(x)]^{-\frac{1}{4}} \sin\left\{\tfrac{1}{12}\pi + \kappa \int_{x}^{x_0} [\epsilon_s - w_1(x)]^{\frac{1}{2}}\, dx\right\}.$$

These values of ϵ_s are determined by

$$\tfrac{1}{12}\pi + \kappa \int_0^{x_0} [\epsilon_s - w_1(x)]^{\frac{1}{2}}\, dx = n'\pi,$$

where n' is an integer. Since the period of the oscillating function is very short compared with the distances of appreciable variation in $w_1(x)$ the normalizing divisor for this wave-function is

$$N_s = \tfrac{1}{2} \int_0^{x_0} [\epsilon_s - w_1(x)]^{-\frac{1}{2}}\, dx,$$

and for the other type the same with x_0 replaced by a. The interval between two characteristics is given by

$$\kappa \int_0^{x_0'} [\epsilon_{s+1} - w_1(x)]^{\frac{1}{2}}\, dx - \kappa \int_0^{x_0} [\epsilon_s - w_1(x)]^{\frac{1}{2}}\, dx = \pi,$$

so that approximately, if $d\epsilon_s = \epsilon_{s+1} - \epsilon_s$,

$$\kappa N_s d\epsilon_s = \pi.$$

Thus the normalized characteristic functions are approximately

$$\begin{aligned} \psi &= \left(\frac{\kappa d\epsilon_s}{\pi}\right)^{\frac{1}{2}} \frac{1}{[\epsilon_s - w_1(x)]^{\frac{1}{4}}} \sin G \quad && \{\epsilon_s > w_1(x)\}, \\ &= 0 && \{\epsilon_s < w_1(x)\}, \end{aligned}$$

where $\sin G$ oscillates very rapidly when either ϵ_s or x varies. There are similar factors in y and z.

We now insert these values in the series in (1524), and average over a small volume element $dV\ (= dx\,dy\,dz)$ so that factors such as $\sin^2 G$ may be replaced by $\frac{1}{2}$. We find for this series

$$\frac{(2m)^{\frac{3}{2}}}{h^3} \Sigma_r \log f(\lambda e^{-\epsilon_r/kT}) \frac{d\epsilon_s d\epsilon_t d\epsilon_u}{[\{\epsilon_s - w_1(x)\}\{\epsilon_t - w_2(y)\}\{\epsilon_u - w_3(z)\}]^{\frac{1}{2}}}$$
$$(\epsilon_r = \epsilon_s + \epsilon_t + \epsilon_u), \quad \ldots\ldots(1529)$$

summed over all r such that

$$\epsilon_s > w_1(x),\ \epsilon_t > w_2(y),\ \epsilon_u > w_3(z).$$

Using the substitutions $\epsilon_s = w_1(x) + \frac{1}{2} mu^2$, etc., and obvious approximations this sum can be replaced by the integral

$$\left(\frac{2m}{h}\right)^3 \iiint_0^\infty \log f(\lambda e^{-\{W + \frac{1}{2}m(u^2+v^2+w^2)\}/kT})\, du\, dv\, dw. \quad \ldots(1530)$$

Therefore

$$\frac{n}{dV} = \left(\frac{2m}{h}\right)^3 \lambda \frac{\partial}{\partial\lambda} \iiint_0^\infty \log f\left(\lambda e^{-\{W+\frac{1}{2}m\,(u^2+v^2+w^2)\}/kT}\right) du\,dv\,dw. \quad \ldots(1531)$$

The u, v, w are the exact analogues of the velocity components of the classical particle. Thus (1531) gives us the space distribution law in its form integrated over the velocities. By returning to (1529) and taking only those terms which correspond to specified velocity ranges we obtain the complete velocity-space distribution law in the form*

$$n\,(u, v, w, x, y, z)\,du\,dv\,dw\,dV$$

$$= \left(\frac{m}{h}\right)^3 \lambda \frac{\partial}{\partial\lambda} \log f\left(\lambda e^{-\{W+\frac{1}{2}m\,(u^2+v^2+w^2)\}/kT}\right) du\,dv\,dw\,dV, \quad \ldots\ldots(1532)$$

which is the new form of the Maxwell-Boltzmann distribution law. When λ is small the log reduces in all statistics to

$$\lambda e^{-\{W+\frac{1}{2}m\,(u^2+v^2+w^2)\}/kT}.$$

On carrying through the integrations in (1531) we then obtain

$$\frac{n}{dV} = \nu = \frac{(2m\pi kT)^{\frac{3}{2}}}{h^3} \lambda e^{-W/kT},$$

which, λ being constant, is the classical result.

It may be useful to express (1532) in terms of the resultant velocity or total kinetic energy and the direction of motion. We can then put

$$u^2 + v^2 + w^2 = c^2, \quad du\,dv\,dw = c^2 dc\,d\omega,$$

where $d\omega$ is an element of solid angle, so that

$$\frac{n}{dV} = \left(\frac{m}{h}\right)^3 \lambda \frac{\partial}{\partial\lambda} \log f\left(\lambda e^{-(W+\frac{1}{2}mc^2)/kT}\right) c^2 dc\,d\omega. \quad \ldots\ldots(1533)$$

On integrating over all directions, we find an expression for $n\,(c)\,dc$, the average number of systems per unit volume moving with velocities between c and $c + dc$,

$$n\,(c)\,dc = \frac{4\pi m^3}{h^3} \lambda \frac{\partial}{\partial\lambda} \log f\left(\lambda e^{-(W+\frac{1}{2}mc^2)/kT}\right) c^2 dc. \quad \ldots\ldots(1534)$$

Expressed in terms of energies ($\frac{1}{2}mc^2 = \epsilon$) this reduces for the range ϵ, $\epsilon + d\epsilon$ to

$$n\,(\epsilon)\,d\epsilon = \frac{2\pi\,(2m)^{\frac{3}{2}}}{h^3} \lambda \frac{\partial}{\partial\lambda} \log f\left(\lambda e^{-(W+\epsilon)/kT}\right) \epsilon^{\frac{1}{2}} d\epsilon. \quad \ldots\ldots(1535)$$

§ **21·46.** *Distribution of mass-points between different phases or enclosures.* The foregoing result can be obtained under more general conditions by a somewhat different method of treatment which does not contemplate in one survey the whole space V accessible to the systems, but starts instead by breaking it up into parts and treating each part as if it were a

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* A factor 8 drops out from (1532) because only positive values of u, v, w were contemplated in (1531), while the actual u, v, w may have either sign independently of each other.

practically independent enclosure. We know that such a procedure leads to correct results in the classical statistical mechanics, and there is no reason to question its validity here.

Consider for simplicity an assembly of two slightly connected enclosures in each of which the potential energy of the systems is constant. In one enclosure it may be taken to have the value zero, but in the other a different constant value W, which may of course be of either sign. In the former the characteristics have the values already given in (1508) with the corresponding spacing. We thus find, using the same groupings and transformations that lead to (1535),

$$\Sigma_r \log f(\lambda\vartheta^{\epsilon_r}) = \frac{2\pi(2m)^{\frac{3}{2}}}{h^3} V \int_0^\infty \log f(\lambda e^{-\epsilon/kT})\, \epsilon^{\frac{1}{2}} d\epsilon. \quad \ldots\ldots(1536)$$

In the latter enclosure the wave equation is

$$\nabla^2\psi + \kappa^2 (E - W)\psi = 0,$$

and the characteristics are given by

$$E - W = \frac{h^2}{8m}\left(\frac{s^2}{a^2} + \frac{t^2}{b^2} + \frac{u^2}{c^2}\right).$$

We therefore find instead of (1536)

$$\Sigma_r \log f(\lambda\vartheta^{\epsilon_r'}) = \frac{2\pi(2m)^{\frac{3}{2}}}{h^3} V' \int_0^\infty \log f(\lambda e^{-(W+\epsilon)/kT})\, \epsilon^{\frac{1}{2}} d\epsilon. \quad \ldots(1537)$$

If we construct the usual expression for the number of complexions of this two-enclosure assembly we have

$$C = \left(\frac{1}{2\pi i}\right)^2 \iint \frac{dx\,dz}{x^{X+1}z^{E+1}}\, \Pi_r f(xz^{\epsilon_r})\, \Pi_r f(xz^{\epsilon_r'}),$$

and the average numbers of systems in the two enclosures will be given by

$$\overline{M} = \lambda\frac{\partial}{\partial\lambda}\Sigma_r \log f(\lambda\vartheta^{\epsilon_r}), \quad \overline{M'} = \lambda\frac{\partial}{\partial\lambda}\Sigma_r \log f(\lambda\vartheta^{\epsilon_r'}).$$

On using (1536) and (1537) we see that these expressions are equivalent to (1531) which we obtained by discussion of the whole assembly with a simple form for W.

We may note in conclusion that the dependence on T of (1536) and (1537) can be shown in a simple form by the substitution $\epsilon/kT = x$. We then find

$$\Sigma_r \log f(\lambda\vartheta^{\epsilon_r'}) = \frac{2\pi(2mkT)^{\frac{3}{2}} V'}{h^3} \int_0^\infty \log f(\lambda e^{-W/kT} e^{-x})\, x^{\frac{1}{2}} dx, \quad \ldots\ldots(1538)$$

which when $W = 0$ depends on T only through the outside factor.

Whether or not the systems are practically classical in either of the enclosures will depend on the value of $\lambda e^{-W/kT}$. It may happen that λ is small (classical statistics) while $\lambda e^{-W/kT}$ is very large (tight-packed systems). This happens in applications to thermionics.

§ **21·5**. *Applications to the electron theory of metals.* For assemblies in which λ is not small, we require fresh means of evaluating the integrals of the last sections. Series expansions are now useless. As we have already stated such assemblies in practice are only assemblies of electrons so that we may confine attention to the generating function proper to the Fermi-Dirac statistics. All the formulae can be converted when required to the Einstein-Bose statistics by simple changes of sign. We must also remember that the electron has a spin with two orientations, so that in the absence of external magnetic fields it is a degenerate system of weight 2 whatever its translational motion.

Before applying our theorems to assemblies of electrons we must recall that our assemblies have to be composed of practically independent systems, while electrons act on each other with long range fields. It is not possible that these long range fields should be entirely without effect on the characteristics of the assembly, but if the charges of the electrons are neutralized in each volume element by the charges of suitable associated positive systems, as in fact they are, it does seem reasonable to assume that the charges of the electrons can be neglected in constructing a valid approximation of zero order to the wave-function of the assembly. If we make this approximation we smooth out as it were the atomic structure of the charges, so that their only remaining effect from the point of view of the electrons is to create a region of uniform negative potential energy in which the electrons move almost freely. This is the model which (following Sommerfeld) we can apply to explain the leading features of metallic conductors* and perhaps the interiors of ultra-white-dwarf stars.

For an assembly of electrons so treated we find on adapting (1538) that

$$\begin{aligned} Z &= \Sigma_r \log f(\lambda \vartheta^{\epsilon_r}), \\ &= 2\,\frac{(2\pi mkT)^{\frac{3}{2}}\,V}{h^3}\,\frac{2}{\sqrt{\pi}}\int_0^\infty x^{\frac{1}{2}} \log\left(1+\lambda e^{-W/kT-x}\right)dx. \quad \text{...(1539)} \end{aligned}$$

If $W = 0$ for free space, then $W < 0$ for the interior of a metal. We shall write $W = -\chi_0$ to conform to our previous notation and shorten the algebra by writing

$$\mu = \lambda e^{\chi_0/kT}. \qquad \text{......(1540)}$$

We can remove the logarithm if desired by integration by parts, so that

$$Z = 2\,\frac{(2\pi mkT)^{\frac{3}{2}}\,V}{h^3}\,\frac{4}{3\sqrt{\pi}}\int_0^\infty \frac{x^{\frac{3}{2}}\,dx}{1+e^x/\mu}. \qquad \text{......(1541)}$$

For this group of electrons

$$\overline{M} = \mu\frac{\partial Z}{\partial \mu} = 2\,\frac{(2\pi mkT)^{\frac{3}{2}}\,V}{h^3}\,\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{\frac{1}{2}}\,dx}{1+e^x/\mu}, \qquad \text{......(1542)}$$

$$\overline{E} = kT^2\left(\frac{\partial Z}{\partial T}\right)_\lambda = kT^2\left[\frac{\partial Z}{\partial T}+\frac{\partial Z}{\partial \mu}\frac{\partial \mu}{\partial T}\right] = \tfrac{3}{2}kTZ - \overline{M}\chi_0. \quad \text{......(1543)}$$

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* Sommerfeld, *Zeit. für Phys.* vol. XLVII, p. 1 (1928); *Naturwiss.* vol. XV, p. 825 (1927).

Since all the equilibrium results can be derived from Z, it is strictly only necessary here to evaluate Z itself in a form suitable for use when μ is large. Sommerfeld* however has given a somewhat more general result —an asymptotic expansion for the function

$$U_\rho = \frac{1}{\Gamma(\rho+1)} \int_0^\infty \frac{x^\rho\, dx}{1 + e^x/\mu}. \qquad \text{......(1544)}$$

The result is

$$U_\rho \sim \frac{(\log \mu)^{\rho+1}}{\Gamma(\rho+2)} \left[1 + 2\left\{\frac{(\rho+1)\rho c_2}{(\log \mu)^2} + \frac{(\rho+1)\rho(\rho-1)(\rho-2)c_4}{(\log \mu)^4} + \dots\right\}\right], \qquad \text{......(1545)}$$

where $c_\nu = 1 - \frac{1}{2^\nu} + \frac{1}{3^\nu} - \frac{1}{4^\nu} + \dots = \left(1 - \frac{1}{2^{\nu-1}}\right)\left(1 + \frac{1}{2^\nu} + \frac{1}{3^\nu} + \dots\right).$

An elementary proof of the first two terms of the formula for $\rho = \frac{3}{2}$ (i.e. for Z) is easily given. Consider the integral factor in Z in the form

$$I = \frac{2}{\sqrt{\pi}} \int_0^\infty x^{\frac{1}{2}} \log(1 + e^{\beta - x})\, dx \qquad (\beta = \log \mu).$$

By breaking the range at $x = \beta$ this reduces to

$$\tfrac{1}{2}\sqrt{\pi} I = \int_0^\beta x^{\frac{1}{2}} (\beta - x)\, dx + \int_0^\beta (\beta - y)^{\frac{1}{2}} \log(1 + e^{-y})\, dy + \int_0^\infty (\beta + y)^{\frac{1}{2}} \log(1 + e^{-y})\, dy.$$

In either of these integrals the logarithms can be expanded and the resulting series integrated term by term. Thus we get

$$\tfrac{1}{2}\sqrt{\pi} I = \tfrac{4}{15}\beta^{\frac{5}{2}} + \Sigma \frac{(-)^{s-1}}{s} \int_0^\beta e^{-sy} (\beta - y)^{\frac{1}{2}}\, dy + \Sigma \frac{(-)^{s-1}}{s} \int_0^\infty e^{-sy} (\beta + y)^{\frac{1}{2}}\, dy.$$

This is exact. When β is large the square roots in these integrals can both be replaced by $\sqrt{\beta}$ to give the dominant terms. The range of the first series of integrals can then be extended to ∞ without sensible error. Thus

$$\tfrac{1}{2}\sqrt{\pi} I = \tfrac{4}{15}\beta^{\frac{5}{2}} + 2\beta^{\frac{1}{2}} \Sigma \frac{(-)^{s-1}}{s} \int_0^\infty e^{-sy}\, dy,$$

$$= \tfrac{4}{15}\beta^{\frac{5}{2}} + \frac{\pi^2}{6}\beta^{\frac{1}{2}}.$$

The method can easily be extended† to show that the error term is $O(\beta^{-\frac{3}{2}})$. We find therefore that

$$Z = 2\frac{(2\pi mkT)^{\frac{3}{2}} V}{h^3} \frac{2}{\sqrt{\pi}} \left\{\tfrac{4}{15}(\log \mu)^{\frac{5}{2}} + \frac{\pi^2}{6}(\log \mu)^{\frac{1}{2}} + O(\log \mu)^{-\frac{3}{2}}\right\}. \qquad \text{......(1546)}$$

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* Sommerfeld, *loc. cit.* p. 11. This more general result is needed for the discussion of transport phenomena.

† And extended without very much difficulty to give Sommerfeld's complete result.

Beyond this we require only the distribution laws of §§ 21·45, 21·46. The most important are the special forms of (1532) and (1535), namely

$$n\,(u, v, w, x, y, z)\, dudvdwdV = 2\left(\frac{m}{h}\right)^3 \frac{dV\,dudvdw}{1 + e^{\{W+\frac{1}{2}m\,(u^2+v^2+w^2)\}/kT}/\lambda},$$

$$= 2\left(\frac{m}{h}\right)^3 \frac{dV\,dudv\,dw}{1 + e^{\frac{1}{2}m\,(u^2+v^2+w^2)/kT}/\mu}, \quad \ldots\ldots(1547)$$

$$n\,(\epsilon)\, d\epsilon dV = \frac{4\pi\,(2m)^{\frac{3}{2}}}{h^3}\frac{\epsilon^{\frac{1}{2}}\,d\epsilon dV}{1 + e^{\epsilon/kT}/\mu}. \quad \ldots\ldots(1548)$$

Before applying these formulae we must examine whether it is reasonable that $\log \mu$ should be large for metals when $\overline{M}/V$ is of the order of one electron per atom. We shall use n_0 for this electron density inside the metal. It follows from (1546) that

$$n_0 = 2\,\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}\,\frac{2}{\sqrt{\pi}}\left\{\tfrac{2}{3}\,(\log\mu)^{\frac{3}{2}} + \frac{\pi^2}{12}\,(\log\mu)^{-\frac{1}{2}}\right\}. \quad \ldots\ldots(1549)$$

We can solve this equation of $\log \mu$ in terms of n_0 and obtain

$$\log\mu = \frac{h^2}{8m}\left(\frac{3n_0}{\pi}\right)^{\frac{2}{3}}\frac{1}{kT}\left\{1 - \frac{\pi^2}{12}\left(\frac{8m}{h^2}\,\frac{kT}{(3n_0/\pi)^{\frac{2}{3}}}\right)^2\right\}. \quad \ldots\ldots(1550)$$

The first approximation to $\log \mu$ is

$$\frac{h^2}{8m}\left(\frac{3n_0}{\pi}\right)^{\frac{2}{3}}\frac{1}{kT} \quad \text{or} \quad 4{\cdot}2 \times 10^{-11}\,\frac{n_0^{\frac{2}{3}}}{T}.$$

For copper whose density is 8·9 and atomic weight 63 the number of atoms per cc. and therefore n_0 is about $8{\cdot}5 \times 10^{22}$. Thus

$$\log\mu = 8 \times 10^4/T.$$

This is still 80 at 1000° K. and 40 at 2000° K., amply large enough for the use of the foregoing approximations. For metallic caesium, in which the atomic density has the lowest value known for a metal, n_0 is less by a factor of 10 and $\log \mu$ by a factor of 5, but $\log \mu$ is still large enough for the application of these formulae at any temperatures below the melting point of caesium.

§ **21·51.** *Specific heats of metals.* In Chapter IV we were able to give a generally satisfying account of the specific heats of metals, in which we entirely neglected any contribution that might be made by the condensed gas of free electrons which we now explicitly assume a metal to contain. This contribution to the energy per unit volume is, by (1543) and (1550),

$$\overline{E} = -\,n_0\chi_0 + \frac{\pi}{40}\,\frac{h^2}{m}\left(\frac{3n_0}{\pi}\right)^{\frac{5}{3}} + \frac{2\pi^3}{3}\,\frac{m}{h^2}\left(\frac{3n_0}{\pi}\right)^{\frac{1}{3}} k^2T^2. \quad \ldots\ldots(1551)$$

It is natural to start the development of the theory on the assumption that n_0 is constant and to retain a variable n_0 to account if possible for special features in particular examples. For the simpler univalent and bivalent atoms, for which there is a large energy step between the first or first two and the following ionization potentials of the free atom, variations of the number of free electrons per atom certainly seem likely to be small and of secondary importance. Variations of n_0, which is a number per unit volume, and also of χ_0 can also be produced by variations of V, but we shall not consider such effects here. This being so, the only variable part of the electronic energy contribution is the third term in (1551). The first two terms give the zero-point energy of the condensed electron gas. The main contribution C_v^ϵ of the electrons to the specific heat per unit volume is therefore

$$C_v^\epsilon = \frac{4\pi^3}{3}\frac{m}{h^2}\left(\frac{3n_0}{\pi}\right)^{\frac{1}{3}} k^2T, \qquad \text{......(1552)}$$

which may be compared with the equipartition value $\frac{3}{2}n_0k$ given by classical statistics for freely moving particles. The ratio of these quantities is only $4{\cdot}1 \times 10^{-5}\,T$ for copper and therefore quite insensible. The fact of primary importance is that the old difficulties of Drude's electronic theory of metals have now been entirely overcome. Properly treated the electron gas is found not to contribute sensibly to the specific heat of the metal. We are free to apply the idea of this gas to thermionic, photo-electric, thermo-electric and conductivity problems without upsetting our earlier conclusions based on the theory of crystals.

The electron pressure may be noted here for reference. According to (1520) it must be

$$p = \frac{\pi}{60}\frac{h^2}{m}\left(\frac{3n_0}{\pi}\right)^{\frac{5}{3}} + \frac{4\pi^3}{9}\frac{m}{h^2}\left(\frac{3n_0}{\pi}\right)^{\frac{1}{3}} k^2T^2. \qquad \text{......(1553)}$$

§ **21·52**. *Thermionic and photo-electric emission.* Let us consider an assembly of two enclosures of which one is in free space and the other within the metal. In the former the average electron density n_f is very low and $W = 0$ so that λ is very small, and we may write

$$n_f = 2\,\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}\,\lambda. \qquad \text{......(1554)}$$

The value of λ must be the same for both enclosures, so that

$$\mu = \lambda e^{\chi_0/kT}.$$

It follows from (1550) that

$$\lambda = \exp\left\{-\frac{\chi}{kT} - \frac{2\pi^2}{3}\frac{m}{h^2}\frac{kT}{(3n_0/\pi)^{\frac{2}{3}}}\right\}, \qquad \text{......(1555)}$$

where

$$\chi = \chi_0 - \frac{h^2}{8m}\left(\frac{3n_0}{\pi}\right)^{\frac{2}{3}}. \qquad \text{......(1556)}$$

On combining these equations we find to a first approximation

$$n_f = \frac{2\,(2\pi mkT)^{\frac{3}{2}}}{h^3}\,e^{-\chi/kT}, \qquad \text{......(1557)}$$

in agreement with (789). Thus the χ of (1556) is the ordinary thermionic work function. The small extra term in λ corresponds as we shall see in § 21·53 to Richardson's terms in σ. Since the number of electrons emitted by the metal per cm.^{2} must be equal in equilibrium to the number returning to the metal from free space, the saturated thermionic current $-I$ is given by

$$I = \tfrac{1}{4}\bar{c}\,n_f\,\epsilon\,(1-r), \quad \bar{c} = 2\left(\frac{2kT}{\pi m}\right)^{\frac{1}{2}}. \qquad \ldots\ldots(1558)$$

The mean velocity $\bar{c}$ outside the metal will have its Maxwellian value. The fraction r is the average coefficient of reflection of the returning electrons. We thus find

$$I = AT^2 e^{-\chi/kT},$$

where

$$A = \frac{4\pi m k^2 \epsilon}{h^3}(1-r) = 120\,(1-r),$$

when we measure currents in amperes per cm.^{2} This result is in agreement with the best measurements of I and r, as we have already pointed out in Chapter XI.

The revised theory provides an entirely satisfactory explanation of the accepted relation $\chi = h\nu_0$ between the thermionic work function and the photo-electric threshold frequency ν_0. At ordinary temperatures the metallic free electrons are almost completely condensed and practically in the same average state as at the absolute zero. For it follows from (1548) and (1550) that when μ is large

$$n(\epsilon) = \frac{4\pi\,(2m)^{\frac{3}{2}}}{h^3}\,\frac{\epsilon^{\frac{1}{2}}}{1 + e^{(\epsilon-\epsilon^*)/kT}}, \qquad \ldots\ldots(1559)$$

where

$$\epsilon^* = \frac{h^2}{8m}\left(\frac{3n_0}{\pi}\right)^{\frac{2}{3}}. \qquad \ldots\ldots(1560)$$

Thus when $T \to 0$

$$\left.\begin{aligned} n(\epsilon) &= \frac{4\pi\,(2m)^{\frac{3}{2}}}{h^3}\,\epsilon^{\frac{1}{2}} \qquad (\epsilon < \epsilon^*),\\ &= 0 \qquad\qquad\qquad\quad (\epsilon > \epsilon^*),\end{aligned}\right\} \qquad \ldots\ldots(1561)$$

and the greatest kinetic energy normally possessed by any electron is ϵ^*. Now if light of frequency ν shines on the metal and a quantum is picked up by an ϵ-electron, the energy of this electron rises to $\epsilon + h\nu$, and it has a chance of escaping from the metal if

$$h\nu + \epsilon > \chi_0.$$

The least possible value of $h\nu$ satisfying this inequality is

$$h\nu = h\nu_0 = \chi_0 - \epsilon^* = \chi$$

which is the equivalence required.†

The theory demands a fairly definite average negative potential energy

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† Prof. Wentzel informs me by letter that the theory can be successfully carried much further and yields photo-electric efficiency coefficients of the right order of magnitude and varying roughly in the right way with polarization, angle of incidence and frequency—a most striking success.

χ_0 for an electron inside a metal as compared with the outside. For we have $\chi_0 = \chi + \epsilon^*$. The observed values of χ are of the order of 5 electron volts, and the values of ϵ^* can be calculated from (1560). For copper with one electron per atom the value of ϵ^* is 7 electron volts so that χ_0 must be about 12 volts. For two electrons per atom at the same atomic density ϵ^* would be $7 \times 2^{\frac{2}{3}}$ or 11 volts, and χ_0 16 volts. For three electrons per atom ϵ^* would be $14\frac{1}{2}$ volts and χ_0 about $19\frac{1}{2}$ volts. Direct evidence of such energy steps is desirable and is perhaps provided by the analysis of Davison and Germer's experiments† on the diffraction of electron beams by nickel crystals. If it is assumed that the velocity and therefore the wave length of the beams in the metal are the same as that of the beam in free space, no exact agreement can be found between the observed diffracted peaks and those calculated from the crystal spacing. If however it is assumed that the beam is accelerated on entry by 18 volts we obtain excellent agreement. This is shown in the following table prepared for me by Dr Hartree from the latest experimental results.

TABLE 57.

The refraction coefficient for electron waves incident on nickel, chosen to make the observed reflections fit the lattice structure and the free wave lengths of the incident electrons.

V_0 volts, energy of incident electrons	Observed refraction coefficient μ	μ^2	$(\mu^2 - 1)\, V_0 = V$	Calculated refraction coefficient with $V = 18$
64	1·14	1·30	19·2	1·132
130	1·07	1·145	18·8	1·067
216	1·04	1·08	17	1·041
328	1·02	1·04	13	1·027
449	1·01	1·02	9	1·020
586	1·01	1·02	$11\frac{1}{2}$	1·015
Mean, weighted by $\mu - 1$, = 18.				

For nickel $\rho = 8{\cdot}9$, $M^* = 57$, $\epsilon^* = 11{\cdot}8$ volts for two free electrons per atom, $\chi = 5$ volts, so that the theoretical $\chi_0 = 16{\cdot}8$ volts.

Before leaving the subject of thermionic emission, we should mention that much more can be done with Sommerfeld's model and the new quantum mechanics than the purely statistical discussion so far given here. It is possible to calculate the reflection coefficient r as a function of the velocity of the electron impinging on the metal surface either from within or without on various simple assumptions as to the nature of the variation of the potential energy near the surface. This has been done by Nordheim‡ for the ordinary thermionic emission discussed here. It would take us too far

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† Davison and Germer, *Proc. Nat. Ac. Sci.*, April (1928).

‡ Nordheim, *Zeit. für Phys.* vol. XLVI, p. 833 (1928).

from statistical theory to give this work in detail. He finds theoretical values for the reflection coefficients in excellent agreement with the observed values both for clean tungsten surfaces and for tungsten surfaces coated with monatomic films of thorium or other atoms for which the values both of χ and of A are very much reduced. It has also been found possible† to calculate the rate of emission of electrons by cold metals in intense electric fields on the same model. The formula for the current per unit area is then

$$I = \frac{\epsilon}{2\pi h} \frac{\epsilon^{*\frac{1}{2}}}{(\chi + \epsilon^*)\,\chi^{\frac{1}{2}}} F^2 e^{-4\kappa\chi^{\frac{3}{2}}/F} \qquad \left(\kappa^2 = \frac{8\pi^2 m}{h^2}\right), \quad \text{......(1562)}$$

where F is the field strength. This formula seems to be in good agreement with the latest work of Millikan‡.

§ **21·53**. *Thermo-electric effects.* We must now recall the formulae of Chapter XI, particularly (786) for $\kappa(\vartheta)$ in terms of σ and (799) for the contact potential difference of two metals. These were established in a purely formal way so far as the internal structure of the metal was concerned, and are therefore still formally valid here when we use Sommerfeld's model. The new considerations do not alter the distribution laws outside the metals. It follows that the equilibrium treatment which we have given of Sommerfeld's model makes explicit evaluations of σ, V_{12} and Π_{12} by equation (803). From the thermo-electric standpoint we saw that $-\sigma/\epsilon$ is Thomson's specific heat of electricity σ_t, and Π_{12} is the Peltier heat.

The evaluation of σ follows at once by comparing (786) or (787) with (1550) or (1555). We find

$$\sigma = \frac{4\pi^2}{3} \frac{m}{h^2} \frac{k^2 T}{(3n_0/\pi)^{\frac{2}{3}}}. \qquad \text{......(1563)}$$

It will be recalled further (§ 21·41) that λ is equivalent to the partial potential of the electrons in the assembly and in fact is identical with a ξ of § 6·5. It follows from § 6·5 and the laws of thermodynamics that we should have

$$\sigma = \frac{\partial C_v^{\epsilon}}{\partial n_0}, \qquad \text{......(1564)}$$

a relation which can be verified at once from (1552). It follows at once that according to this theory§

$$\sigma_t = -\frac{4\pi^2}{3} \frac{m}{\epsilon h^2} \frac{k^2 T}{(3n_0/\pi)^{\frac{2}{3}}}, \qquad \text{......(1565)}$$

and $$\Pi_{12} = \frac{T\,\partial V_{12}}{\partial T} = \frac{4\pi^2}{3} \frac{m}{\epsilon h^2} k^2 T^2 \left\{\left(\frac{\pi}{3(n_0)_1}\right)^{\frac{2}{3}} - \left(\frac{\pi}{3(n_0)_2}\right)^{\frac{2}{3}}\right\}. \qquad \text{...(1566)}$$

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† Fowler and Nordheim, *Proc. Roy. Soc.* A, vol. CXIX, p. 173 (1928).

‡ Millikan and Eyring, *Phys. Rev.* vol. XXVII, p. 51 (1926); Millikan and Lauritsen, *Proc. Nat. Ac. Sci.* vol. XIV, p. 45 (1928).

§ Sommerfeld, *Zeit. für Phys., loc. cit.*, gives these formulae but with ϵ (or rather e) for the charge on the electron. There is however a real discrepancy to be recorded between (1565), (1566) and

It is not fair to expect Sommerfeld's theory as so far developed to yield values of σ_t exactly comparable with observation. The theory is qualitatively not unsuccessful, for it gives values of σ_t of the right order of magnitude and depending in about the correct manner on the temperature T. The calculated values for the series of metals, copper, silver, gold, fall also into the proper sequence. Abnormally large values such as are found for bismuth or negative values such as are found for iron and lead naturally lie outside the simplest form of the theory.

Since by the thermodynamic equations (800) and (803) the Peltier heats depend only on the temperature variable part of V_{12} which is completely determined by σ_t, a successful theory of σ_t is exactly as successful for Π_{12}, and also of course for the resulting electromotive forces in thermocouples. The theory gives Peltier heats for pairs of simple metals in general of the right sign. The variation with temperature like T^2 is also in reasonable accordance with observation.

TABLE 58.

Comparison of observed and calculated values of the specific heat of electricity.

Metal	Temperature range	$10^{12}\,\sigma_t/T$	
		obs.	calc.
Hg	323–423	80	9·6
Cu	173–773	11–19	5·8
Ag	373–773	21–31	7·4

§ **21·54**. *Residual paramagnetism of an electron gas. The paramagnetism of the alkalis**. We have hitherto treated our electron gas as a collection of degenerate systems of weight 2. It is however possible to remove the degeneracy with a magnetic field. The electrons in each orientation will then form separate parts of the assembly with slightly different sets of energy values, but as usual the equilibrium state must be characterized by values of ϑ and λ common to the two parts. When we carry through the

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Sommerfeld's formulae. Sommerfeld of course is developing a theory of transport phenomena and evaluates σ_t from the term proportional to the current in the complete expression for the evolution of heat when a current is flowing in a conductor whose temperature varies along its length. His formula contains terms in σ_t depending on the variations of the mean free path with velocity which could not be given by an equilibrium theory. This is the distinction between the equilibrium $-\sigma/\epsilon$ and the true σ_t which we have already mentioned. There is no reason to suspect the genuineness of these terms, which may well be concerned with the variation of σ_t with direction in single crystals (Bridgeman, *Phys. Rev.*). The real discrepancy does not lie here, but in the fact that Sommerfeld gives the "equilibrium" terms (1565) and (1566) with an additional factor 2. This part of his σ_t therefore does not satisfy (1564) with my value of C_v^ϵ, which however agrees with Sommerfeld's. I do not know where the mistake lies nor do I understand how such a discrepancy can be permissible.

* Pauli, *Zeit. für Phys.* vol. XLI, p. 81 (1927); Frenkel, *Zeit. für Phys.* vol. XLIX, p. 31 (1928).

calculations we find that for a metallic electron gas there is a residual paramagnetism independent of the temperature and of the order of ordinary diamagnetic effects. This can be very simply explained, for in the condensed gas the N electrons occupy the N states of lowest energy, but under the influence of the magnetic field these N states are not divided into equal halves with the electrons pointing in opposite directions, but a majority of the electrons point along the field, taking advantage of the smaller total energy when so orientated.

In general let us suppose that the constituents of our gas have $2j+1$ orientations in a magnetic field H and that the magnetic energy terms are

$$\epsilon_s = -sg\mu_0 H \quad (-j \leqslant s \leqslant j), \qquad \text{......(1567)}$$

where $\mu_0\,[=\epsilon h/(4\pi mc)]$ is Bohr's magneton and g is Landé's splitting factor. The rest of the energy of the various systems is kinetic and the same as in the preceding sections. We can therefore apply § 21·46 and equation (1542) without the weight factor 2 to each set of systems, so that

$$\overline{M_s} = \frac{(2\pi mkT)^{\frac{3}{2}}\,V}{h^3}\,\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{\frac{1}{2}}\,dx}{1+e^x/\mu_s} \qquad (\mu_s = \lambda e^{-\epsilon_s/kT}). \text{...(1568)}$$

We have also the condition

$$\Sigma_s \overline{M_s} = n_0 \qquad \text{......(1569)}$$

and the equation

$$\mathscr{M}H = -\sum_{s=-j}^{s=+j} \overline{M_s}\,\epsilon_s \qquad \text{......(1570)}$$

for the total magnetization $\mathscr{M}$ of the gas.† We can now use the approximation (1549) for $\overline{M_s}$, and expand on the basis that ϵ_s/kT is small compared with $\log\lambda$. Thus

$$\overline{M_s} = \frac{(2\pi mkT)^{\frac{3}{2}}\,V}{h^3}\,\frac{2}{\sqrt{\pi}}\left[\tfrac{2}{3}(\log\lambda)^{\frac{3}{2}} + \frac{\pi^2}{12}\frac{1}{(\log\lambda)^{\frac{1}{2}}} - \frac{\epsilon_s}{kT}\left\{(\log\lambda)^{\frac{1}{2}} - \frac{\pi^2}{24}\frac{1}{(\log\lambda)^{\frac{3}{2}}}\right\}\right].$$

On inserting these values in (1569) we see that $\log\lambda$ is unaffected (to the first order in ϵ_s) since $\Sigma_s\epsilon_s = 0$. On carrying through the calculations for $\log\lambda$ and for $\mathscr{M}H$ we find

$$\frac{\mathscr{M}H}{V} = \frac{4\pi m}{3h^2}\left(\frac{3n_0}{4\pi(2j+1)}\right)^{\frac{1}{3}}(2j+1)\,j\,(j+1)\,g^2\mu_0{}^2H^2$$
$$\times\left\{1 - \frac{\pi^2}{3}\left(\frac{mkT}{h^2\,[3n_0/4\pi(2j+1)]^{\frac{2}{3}}}\right)^2\right\}. \qquad \text{......(1571)}$$

The temperature-dependent term is negligible at all ordinary temperatures. For an electron gas for which $j=\frac{1}{2}, g=2$ we find from the main term that the paramagnetic susceptibility κ is

$$\kappa = \frac{\mathscr{M}}{VH} = \frac{4\pi m\mu_0{}^2}{h^2}\left(\frac{3n_0}{\pi}\right)^{\frac{1}{3}}. \qquad \text{......(1572)}$$

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† $\mathscr{M}$ can of course be derived by constructing the complete Ψ and using $\mathscr{M} = -(\partial\Psi/\partial H)_{n_0,T,V}$ as in Chapter XII.

The agreement between theory and experiment for the alkalis is shown in Table 59. The order of magnitude is correctly given. The small observed value for rubidium and the negative value for caesium are doubtless due to the diamagnetic susceptibility of these large ions, which we have of course omitted from the calculations.

TABLE 59.

Paramagnetic susceptibilities of the alkali metals.

	Na	K	Rb	Cs
$10^7 \kappa$ calc.	6·57	5·2	4·88	4·54
$10^7 \kappa$ obs.	5·8	5·1	0·6	−0·5

§ **21·6**. *Stellar matter of extreme density.* The foregoing theory of condensed electron gases may perhaps be applied to solve a difficulty in the theory of the ultimate fate of those stars of extreme density which are known as white dwarfs. The difficulty first formulated by Eddington* is as follows. We know that matter in white dwarf stars must exist at densities of at least 100,000 and probably greater. As these stars go on radiating they will if anything condense still further and ultimately may well lose all their superfluous energy and fall to zero temperature. We may perhaps venture to refer to their probable final state as the black dwarf stages. In this state they then consist of matter at low temperature and extremely high density. This can of course only be achieved if their constituents are free nuclei and free electrons forming a neutral mixture, which will probably behave to a first approximation as the condensed gas of these sections. The difficulty observed by Eddington is that according to the classical statistics matter in such a state would contain far less energy than the same matter expanded in the form of free complete atoms at rest at infinite separation. If such matter were removed by any cause from the interior of the black dwarf it could not then resume its ordinary state. If however the condensed gas, which is primarily an electron gas, behaves according to the theory here developed, and this is required by the new mechanics, then the difficulty disappears, for the kinetic energy content of the matter never falls below the zero-point energy given by the second term in (1551). On numerical examination it proves† that this energy is so great that, after allowing for the negative potential energy, the matter (if removed from the black dwarf and so free to expand) could reconstitute itself as an expanded gas of complete atoms at an extremely high temperature. The black dwarf material is best likened to a single gigantic molecule in its lowest quantum state. On the Fermi-Dirac

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* Eddington, *Internal Constitution of the Stars*, § 117.

† R. H. Fowler, *M.N.R.A.S.* vol. LXXXVII, p. 114 (1926).

statistics its high density can be achieved in one way only, in virtue of a correspondingly great energy content. But this energy can no more be expended in radiation than the energy of a normal atom or molecule. The only difference between black dwarf matter and a normal molecule is that the molecule can exist in a free state while black dwarf matter can only so exist under very high external pressure.

§ 21·7. *The statistics of light quanta.* For the sake of completeness and its historical interest we shall now show how Planck's law of temperature radiation may be derived when an extreme light-quanta view of radiation is adopted, provided we apply the Einstein-Bose statistics of the new mechanics to a collection of suitable particles *of indefinite number*.

In order to determine the equilibrium properties of any type of particle it is only necessary to construct the corresponding factor in Z in (1488). Since the assembly contains a number of these particles which is unrestricted, no selector variable such as x is here required. Since the particles obey the Einstein-Bose statistics $f(u) = 1/(1-u)$. Hence

$$Z = -\Sigma_t \log(1 - \vartheta^{\epsilon_t}).$$

There is now a choice of developments. In order to stress the particle analogy to the utmost we shall here follow through the argument (without fields of force) which leads to (1532) in terms of the component velocities of the particle. For particles with this statistics and given velocity components we should have therefore

$$Z = -2\left(\frac{m}{h}\right)^3 V \log(1-\vartheta^{\epsilon})\, du\, dv\, dw. \qquad \text{......(1573)}$$

The factor 2 remains as for electrons to allow for the two states of polarization of the light-particle. This however is non-relativistic, and to apply in the limit to light-quanta we must replace it by its relativistic form. The arguments of § 17·72 and § 19·4 show that the relativistic form is*

$$Z = -\frac{2}{h^3} V \log(1-\vartheta^{\epsilon})\, dp_1 dp_2 dp_3, \qquad \text{......(1574)}$$

where p_1, p_2, p_3 are the exact components of momentum of the particle, and

$$\epsilon = m_0 c^2 \left\{ \frac{1}{\left(1 - \dfrac{u^2+v^2+w^2}{c^2}\right)^{\frac{1}{2}}} - 1 \right\}.$$

We can now proceed to the limit in which $u^2 + v^2 + w^2 \to c^2$, $m_0 \to 0$, $\epsilon \to h\nu$, $p_1 \to h\nu_1/c$, etc., where ν_1, ν_2, ν_3 are the frequencies resolved along the coordinate axes. In terms of the frequency ν and the direction of motion of the particle we find of course

$$d\nu_1 d\nu_2 d\nu_3 = \nu^2 d\nu\, d\omega,$$

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* For a complete account of the new statistics of particles in relativistic form see Jüttner, *Zeit. für Phys.* vol. XLVII, p. 542 (1928).

where ω is an element of solid angle. Thus

$$Z = -\frac{2}{c^3} V \log (1 - \vartheta^{h\nu}) \nu^2 d\nu d\omega.$$

Integrating over all directions we find for the Z of ν-radiation

$$Z_\nu = -\frac{8\pi V\nu^2 d\nu}{c^3} \log (1 - \vartheta^{h\nu}). \qquad \text{......(1575)}$$

The energy content of these particles per unit volume follows at once in the usual way, namely

$$E_\nu \, d\nu = \frac{\vartheta}{V}\frac{\partial Z_\nu}{\partial \vartheta} = \frac{8\pi h\nu^3 d\nu}{c^3} \frac{1}{e^{h\nu/kT} - 1}, \qquad \text{......(1576)}$$

which is Planck's law. The average number of light-quanta of this frequency, obtained by dividing by $h\nu$, is

$$\frac{8\pi\nu^2 d\nu}{c^3} \frac{1}{e^{h\nu/kT} - 1}. \qquad \text{......(1577)}$$

§ **21·8**. *Fluctuations.* The calculus of fluctuations developed in Chapter XX can be applied to the revised statistics of this chapter just as to classical statistics. In fact in certain instances the applications are even easier than before.

The first step is to revise the integrals of Chapter XX for $C\overline{a_r{}^n}$ and $C\overline{E_A{}^n}$. Equation (1487) for $C\overline{a_r}$ can be written in the form

$$C\overline{a_r} = \left(\frac{1}{2\pi i}\right)^3 \iiint_\gamma \frac{dx dy dz}{x^{X+1} y^{Y+1} z^{E+1}} \left[x \frac{\partial}{\partial x} f (xz^{\epsilon_r})\right] \Pi_t' f (xz^{\epsilon_t})$$
$$\times \Pi_t \, g (yz^{\eta_t}) \, \Pi_t \, h (xyz^{\zeta_t}), \qquad \text{......(1578)}$$

where the prime on Π_t denotes that the single factor $f (xz^{\epsilon_r})$ is omitted. On following through the argument leading to (1487) it is easily seen that

$$C\overline{a_r{}^n} = \left(\frac{1}{2\pi i}\right)^3 \iiint_\gamma \frac{dx dy dz}{x^{X+1} y^{Y+1} z^{E+1}} \left[\left(x \frac{\partial}{\partial x}\right)^n f (xz^{\epsilon_r})\right] \Pi_t' f (xz^{\epsilon_t})$$
$$\times \Pi_t \, g (yz^{\eta_t}) \, \Pi_t \, h (xyz^{\zeta_t}). \qquad \text{......(1579)}$$

Similarly

$$C\overline{E_A{}^n} = \left(\frac{1}{2\pi i}{}^3\right) \iiint_\gamma \frac{dx dy dz}{x^{X+1} y^{Y+1} z^{E+1}} \left[\left(z \frac{\partial}{\partial z}\right)^n \Pi_t f (xz^{\epsilon_t})\right]$$
$$\times \Pi_t \, g (yz^{\eta_t}) \, \Pi_t \, h (xyz^{\zeta_t}). \qquad \text{......(1580)}$$

The special device of Chapter XX for $C\overline{a_r{}^n}$ is not here required. The formation of these mean values (and others) is obviously quite general and straightforward and applies to any assembly.

In order to evaluate the fluctuations we make the substitutions

$$x = e^u, \; y = e^v, \; z = e^w,$$
$$f (xz^{\epsilon_t}) = f (e^{u+\epsilon_t w}) = \exp F (u + \epsilon_t w), \qquad \text{......(1581)}$$

etc. These and similar equations (1581) define F, G, H. We then find, as in Chapter XX, that

$$C\,\overline{(E_A - \overline{E_A})^n} = \left(\frac{1}{2\pi i}\right)^3 \iiint_{\gamma'} du\,dv\,dw \exp\left[- Xu - Yv - (E - \overline{E_A})\,w\right.$$

$$\left. + \Sigma_t\, G\,(v + \eta_t w) + \Sigma_t\, H\,(u + v + \zeta_t w)\right]\left(\frac{\partial}{\partial w}\right)^n \exp\left[\Sigma_t\, F\,(u + \epsilon_t w) - \overline{E_A} w\right], \qquad \text{......(1582)}$$

$$C\,\overline{(a_r - \bar{a}_r)^n} = \left(\frac{1}{2\pi i}\right)^3 \iiint_{\gamma'} du\,dv\,dw \exp\left[- (X - \bar{a}_r)\,u - Yv - Ew\right.$$

$$\left. + \Sigma_t' F\,(u + \epsilon_t w) + \Sigma_t G\,(v + \eta_t w) + \Sigma_t H\,(u + v + \zeta_t w)\right]$$

$$\times \left(\frac{\partial}{\partial u}\right)^n \exp\left[F\,(u + \epsilon_r w) - \bar{a}_r u\right]. \qquad \text{......(1583)}$$

Having thus shown how to write down exact integral expressions for any desired fluctuation, which can be evaluated as in Chapter XX, it will be sufficient illustration of the nature of the results as modified by the new mechanics to carry through the calculations for $\overline{(a_r - \bar{a}_r)^2}$ in a non-dissociating gaseous assembly of two types of system. We put $n = 0, 2$ in (1583) and omit the terms H. It will be convenient however to allow the systems to be degenerate. Equations (1582) and (1583) then stand, but in place of (1581) we have

$$F\,(u + \epsilon_t w) = \varpi_t \log f\,(xz^{\epsilon_t}). \qquad \text{......(1584)}$$

The formal working repeats that of Chapter XX and need not be given. Remembering that

$$\bar{a}_r = \varpi_r \lambda \frac{\partial}{\partial \lambda} \log f\,(\lambda \vartheta^{\epsilon_r}) = \frac{\partial}{\partial \log \lambda} F\,(\log \lambda + \epsilon_r \log \vartheta) = F'\,(r) \text{......(1585)}$$

say, we find ultimately

$$\overline{(a_r - \bar{a}_r)^2} = F''(r) - \frac{\{F''\,(r)\}^2}{\Sigma_t F''\,(t)}$$

$$- \frac{\left(\epsilon_r - \dfrac{\Sigma_t \epsilon_t F''\,(t)}{\Sigma_t F''\,(t)}\right)^2 \{F''\,(r)\}^2}{\Sigma_t\,\{\epsilon_t^2 F''\,(t) + \eta_t^2\, G''\,(t)\} - \dfrac{\{\Sigma_t \epsilon_t F''\,(t)\}^2}{\Sigma_t F''\,(t)} - \dfrac{\{\Sigma_t \eta_t G''\,(t)\}^2}{\Sigma_t G''\,(t)}}. \qquad \text{......(1586)}$$

The various terms are easily interpreted. From (1585) and similar equations we find at once that

$$F''\,(r) = \frac{\lambda \partial \bar{a}_r}{\partial \lambda}, \quad \Sigma_t F''\,(t) = \lambda \frac{\partial X}{\partial \lambda}, \quad \Sigma_t G''\,(t) = \frac{\mu \partial Y}{\partial \mu}, \qquad \text{...(1587)}$$

$$\Sigma_t \epsilon_t F''\,(t) = \lambda \frac{\partial E}{\partial \lambda} = \vartheta \frac{\partial X}{\partial \vartheta}, \quad \Sigma_t \eta_t G''\,(t) = \mu \frac{\partial E}{\partial \mu} = \vartheta \frac{\partial Y}{\partial \vartheta}, \qquad \text{...(1588)}$$

$$\Sigma_t\,\{\epsilon_t^2 F''\,(t) + \eta_t^2 G''\,(t)\} = \vartheta \frac{\partial E}{\partial \vartheta}. \qquad \text{......(1589)}$$

In all these differentiations the functions operated on are to be regarded as functions of λ, μ and ϑ, and the other pair are to be kept constant. It is further easily verified that the denominator of the last term in (1586) is

$$\left(\vartheta\frac{\partial E}{\partial\vartheta}\right)_{X,Y}.$$

Inserting all these results we find that

$$\overline{(a_r-\bar{a}_r)^2}=\lambda\frac{\partial\bar{a}_r}{\partial\lambda}-\frac{(\lambda\partial\bar{a}_r/\partial\lambda)^2}{\lambda\partial X/\partial\lambda}-\frac{\left\{\epsilon_r-\dfrac{\lambda\partial\overline{E}_1/\partial\lambda}{\lambda\partial X/\partial\lambda}\right\}^2\left(\dfrac{\lambda\partial\bar{a}_r}{\partial\lambda}\right)^2}{\left(\vartheta\dfrac{\partial E}{\partial\vartheta}\right)_{X,Y}}.\quad\text{...(1590)}$$

Classically $F \equiv \exp$, $F'' = F' = \bar{a}_r$, so that equation (1590) then agrees with (1396) for $v = 1$ as it should. For any other statistics we can evaluate (1590) by inserting the proper values of $\bar{a}_r$, X, and $\overline{E}_1$ from equations such as (1490). Under bath conditions, when E is very large compared with any quantity connected with systems of the first type, (1590) reduces to

$$\overline{(a_r-\bar{a}_r)^2}=\lambda\frac{\partial\bar{a}_r}{\partial\lambda}\left[1-\frac{\lambda\partial\bar{a}_r/\partial\lambda}{\lambda\partial X/\partial\lambda}\right].\qquad\text{......(1591)}$$

The result commonly given* (though not in this general form) is

$$\overline{(a_r-\bar{a}_r)^2}=\lambda\frac{\partial\bar{a}_r}{\partial\lambda},\qquad\text{......(1592)}$$

which is valid as we now see under bath conditions if also $\bar{a}_r$ is small compared with X. For the Fermi-Dirac statistics

$$\bar{a}_r=\frac{\varpi_r}{e^{\epsilon_r/kT}/\lambda+1},$$

$$\overline{(a_r-\bar{a}_r)^2}=\bar{a}_r-(\bar{a}_r)^2/\varpi_r.\qquad\text{......(1593)}$$

This result was first given by Pauli. The fluctuation vanishes when $T \to 0$, since the assembly is then tight packed. For the Einstein-Bose statistics

$$\bar{a}_r=\frac{\varpi_r}{e^{\epsilon_r/kT}/\lambda-1},$$

$$\overline{(a_r-\bar{a}_r)^2}=\bar{a}_r+(\bar{a}_r)^2/\varpi_r.\qquad\text{......(1594)}$$

The last result has been shown by Einstein to yield the correct fluctuation of radiation when applied to the light-quantum theory.

§ **21·9**. *Mechanisms of interaction. Boltzmann's H-theorem.* The modifications required in Chapters XVII and XIX, especially the former, when the laws of the new quantum mechanics are taken into account, have been discussed by various authors† from the point of view adopted in this monograph. More recently this type of discussion has been completed by

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* See, for example, Einstein, *Berl. Sitz.* (1924) p. 261; (1925) p. 3; Pauli, *Zeit. für Phys.* vol. XLI, p. 81 (1927).

† Jordan, *Zeit. für Phys.* vol. XLI, p. 711 (1927); Ornstein and Kramers, *Zeit. für Phys.* vol. XLII, p. 481 (1927); Bothe, *Zeit. für Phys.* vol. XLVI, p. 327 (1928).

Nordheim†. We shall follow his exposition fairly closely in this chapter, and shall confine ourselves to the reformulation of the laws of gas collisions leading up to Boltzmann's H-theorem. The similar reformulation of the other sections of Chapter XVII will present no difficulty to the reader. Great elaboration at the level proposed hardly seems justifiable at present, since the work of Dirac, Jordan, Pauli and Wigner‡ on the emission and absorption of radiation and the quantum mechanics of radiation fields and fields satisfying Pauli's principle has obviously opened up the possibility of a much deeper formulation.

In the classical statistics of Chapters XVII and XIX it is always possible to express the frequency of any given atomic event in terms of certain target areas or probability coefficients and the distribution laws for the systems engaged prior to the given event. The distribution laws for the systems emerging from the event are irrelevant. In the new statistics this is no longer true. For example, in the Fermi-Dirac statistics an event cannot occur at all if it has to produce a system in a state of which the assembly already possesses as many as possible. Again in the Einstein-Bose statistics the presence of other systems in the assembly in the state produced by a given event makes that event correspondingly *more* probable. This is the natural interpretation in light-quantum statistics of Einstein's coefficient of stimulated emission.

Let us now define a collision process in a way which is agreeable to the new mechanics with Heisenberg's principle of uncertainty. We consider a volume element dV, physically small but large compared with atomic dimensions. Through that element two different wave groups or wave packets are supposed to be proceeding, representing particles with velocity components between $u, u + du$, $v, v + dv$, $w, w + dw$ and $u_1, u_1 + du_1$, $v_1, v_1 + dv_1$, $w_1, w_1 + dw_1$. We assume that $du\,dv\,dw\,dV$ $(= do\,dV)$ is large compared with h^3/m^3 so that we do not get entangled with the principle of uncertainty. If there are no other particles in the assembly, the sequence of events can be calculated when the interaction energy of the two particles is given. This sequence can be described in terms of a calculable probability coefficient §

$$\phi\,(u, u_1;\ u^*, u_1^*)$$

which is such that

$$\phi\,(u, u_1; u^*, u_1^*)\,do^* do_1^*$$

is the probability that the interaction results in the production of wave groups representing particles with velocity components in the ranges u^*,

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† Nordheim, *Proc. Roy. Soc.* A, vol. CXIX, p. 689 (1928).

‡ Dirac, *Proc. Roy. Soc.* A, vol. CXIV, p. 243 (1927); Jordan, *Zeit. für Phys.* vol. XLIV, p. 473 (1927); Jordan and Pauli, *Zeit. für Phys.* vol. XLVII, p. 151 (1928); Jordan and Wigner, *Zeit. für Phys.* vol. XLVII, p. 631 (1928).

§ For shortness we shall show only one of each set of velocity components as an argument of ϕ. Of course they are all equally concerned.

$u^* + du^*$, v^*, $v^* + dv^*$, w^*, $w^* + dw^*$ and u_1^*, $u_1^* + du_1^*$, v_1^*, $v_1^* + dv_1^*$, w_1^*, $w_1^* + dw_1^*$. The new velocity components have to satisfy the energy and momentum relations so that only two of them are really independent. We can therefore write this probability

$$\phi\,(u, u_1;\, \sigma^*)\, d\sigma^*,$$

where $d\sigma^*$ is an element of two-dimensional extension on the energy-momentum hyper-surface in the velocity space.

So far we have scarcely diverged from the classical formulation. We have now to enumerate the total number of such events in dV in an assembly in which there are a number of systems similar to the interacting pair. If as usual $f\,(x, y, z, u, v, w)\, do\,dV$ is the number of particles in dV with velocity components in the specified ranges, the classical number of collisions of the specified type is†

$$f dV f_1 dV \phi\,(u, u_1;\, \sigma^*)\, do\, do_1\, d\sigma^*. \qquad \text{......(1595)}$$

In either of the new statistics however the corresponding expression must contain factors depending on f^* and f_1^*. The simplest possible assumptions which fulfil all requirements are as follows. In the Fermi-Dirac statistics the number of events must vanish when $f^* do^* dV$ is equal to the number of available cells of extension h^3 of the phase space in the given velocity ranges. We shall write this number $A do^* dV$. If the systems we are discussing are degenerate freely moving systems of weight ϖ, then the available phase space is $\varpi m^3 do^* dV$ and $A = \varpi m^3/h^3$. The simplest possible extra factor in (1595) is therefore

$$(1 - f^*/A).$$

There is a similar factor for the second system. The number of the specified events becomes therefore

$$f dV f_1 dV \left(1 - \frac{f^*}{A}\right)\left(1 - \frac{f_1^*}{A_1}\right) \phi\,(u, u_1;\, \sigma^*)\, do\, do_1\, d\sigma^*. \qquad \text{......(1596)}$$

It may be necessary to distinguish between the A's for the two systems; for their masses may be different.

The number of reverse events can be similarly specified. The probability that a single pair originally moving in dV with velocities u^*, v^*, w^* and u_1^*, v_1^*, w_1^* should be scattered into the ranges u, $u + du$, ... w_1, $w_1 + dw_1$ is

$$\phi\,(u^*, u_1^*;\, u, u_1)\, do\, do_1, \quad \text{or} \quad \phi\,(u^*, u_1^*;\, \sigma)\, d\sigma,$$

and the number of such events

$$f^* dV f_1^* dV \left(1 - \frac{f}{A}\right)\left(1 - \frac{f_1}{A_1}\right) \phi\,(u^*, u_1^*;\, \sigma)\, do^* do_1^* d\sigma. \qquad \text{...(1597)}$$

We can make one further general assertion—that

$$\phi\,(u, u_1;\, \sigma^*)\, do\, do_1\, d\sigma^* = \phi\,(u^*, u_1^*;\, \sigma)\, do^* do_1^* d\sigma. \qquad \text{......(1598)}$$

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† We write as usual f for $f\,(x, y, z, u, v, w)$ and f_1 for $f\,(x, y, z, u_1, v_1, w_1)$, etc.

These probabilities are calculated as the squares of the moduli of the components of a certain interaction matrix, and the two probabilities in question belong to the (n, m) and (m, n) terms of that matrix. All such matrices are Hermitian so that the (n, m) and (m, n) terms are conjugate complex numbers of equal moduli.

In the Einstein-Bose statistics the simplest possible assumption which allows for the stimulating effect of the systems already present in the final states is to insert factors such as

$$(1 + f^*/A)$$

with positive signs wherever there is a negative sign in (1596) and (1597). This may be regarded as a change of sign of A, so that it is sufficient to carry through the modifications for one of the new statistics only. The calculations also cover collisions between systems one of which obeys the Fermi-Dirac and the other the Einstein-Bose statistics.

The various investigations of Chapter XVII can easily be repeated with these or similar modifications.

We observe first that on the hypothesis of detailed balancing we must equate (1596) and (1597) so that

$$ff_1\left(1-\frac{f^*}{A}\right)\left(1-\frac{f_1^*}{A_1}\right)=f^*f_1^*\left(1-\frac{f}{A}\right)\left(1-\frac{f_1}{A_1}\right). \quad \text{...(1599)}$$

On writing

$$\frac{f}{1-f/A}=g,$$

we see that

$$gg_1 = g^*g_1^*. \quad \text{......(1600)}$$

Therefore as in § 17·3 g has Maxwell's form, which when there is no mass motion may be taken to be

$$g = B' e^{C'(u^2+v^2+w^2)},$$

B' and C' being independent of the velocities. It follows that

$$f=\frac{A}{e^{C'(u^2+v^2+w^2)}/B+1}, \quad \text{......(1601)}$$

which is the usual distribution law.

We observe next that there is still an equation for f in the new statistics of the same form as Boltzmann's integro-differential equation (1192). This follows from the considerations of Darwin† who has shown that the wave packet representing a particle undisturbed by collisions moves in uniform or nearly uniform external fields just as a classical particle. The distribution function f therefore satisfies the equation

$$\frac{\partial f}{\partial t}+X\frac{\partial f}{\partial u}+Y\frac{\partial f}{\partial v}+Z\frac{\partial f}{\partial w}+u\frac{\partial f}{\partial x}+v\frac{\partial f}{\partial y}+w\frac{\partial f}{\partial z}=\left[\frac{\partial f}{\partial t}\right]_{\text{coll}} \quad \text{....(1602)}$$

The revised form of the collision terms can now be written down. We shall

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† Darwin, *Proc. Roy. Soc.* A, vol. CXVII, p. 258 (1927). See also Kennard, *Zeit. für Phys.* vol. XLIV, p. 326 (1927).

be content to consider an assembly of one set of particles only. The revised form is

$$\left[\frac{\partial f}{\partial t}\right]_{\text{coll}} = -\,dV \iint \left[ff_1\left(1-\frac{f^*}{A}\right)\left(1-\frac{f_1{}^*}{A_1}\right) - f^*f_1{}^*\left(1-\frac{f}{A}\right)\left(1-\frac{f_1}{A_1}\right)\right] \times \phi\,(u, u_1;\, \sigma^*)\, do_1 d\sigma^*. \quad \text{......(1603)}$$

This pair of equations should be used in place of (1192) and (1193) in investigations of transport phenomena in condensed electron gases and similar assemblies, and has been so used by Nordheim† in developing Sommerfeld's electron theory of metals.

We conclude by showing that the distribution law (1601) can be derived from the more restricted hypothesis of preservation, confining attention to the element dV of a simple assembly of one type of system, without space variations in f or external fields of force. To do this we have only to construct a modified H-function,‡

$$H = \int [f \log f + (A-f) \log (A-f)]\, do. \quad \text{......(1604)}$$

Then $$\frac{dH}{dt} = \int [\log f - \log (A-f)]\, \frac{\partial f}{\partial t}\, do, \quad \text{......(1605)}$$

and in the example considered $\partial f/\partial t$ is given completely by (1603). Therefore

$$\frac{dH}{dt} = -\,dV \iiint \log \frac{f}{A-f}\, [ff_1\,(A-f^*)\,(A_1-f_1{}^*) - f^*f_1{}^*\,(A-f)\,(A_1-f_1)] \times \frac{\phi\,(u, u_1;\, \sigma^*)}{AA_1}\, do\, do_1 d\sigma^*. \quad \text{......(1606)}$$

By the familiar argument of exchanging the rôles of various types of variable we find

$$\frac{dH}{dt} = -\,\tfrac{1}{4}\, dV \iiint [\log \{ff_1\,(A-f^*)\,(A_1-f_1{}^*)\} - \log\{f^*f_1{}^*\,(A-f)\,(A-f_1)\}] \times [ff_1\,(A-f^*)\,(A_1-f_1{}^*) - f^*f_1{}^*\,(A-f)\,(A-f_1)]\, \frac{\phi\,(u, u_1;\, \sigma^*)}{AA_1}\, do\, do_1 d\sigma^*. \quad \text{......(1607)}$$

Therefore $dH/dt \leqslant 0$ and can only vanish when (1599) is satisfied, which is what we wished to prove.

With this inadequate account of the more recent developments we end this monograph. The new mechanics is perhaps just emerging from what one may call its Newtonian stage. Great developments in the exposition of the new mechanics itself may be expected. Such developments are desirable and perhaps even necessary before a satisfying account can be given of its statistical side.§

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† Nordheim, *loc. cit.*

‡ If A is negative we replace the second log by $\log (A+f)$.

§ The correct basis for the statistical mechanics of quantum-mechanical assemblies (or at least a great step towards such a basis) seems to be provided by the work of v. Neumann, *Gött. Nach.* (1927), pp. 245, 273.

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