Volume 4 *October, 1932* *Number 4*

REVIEWS

OF

MODERN PHYSICS

Statistical Mechanics with Particular Reference to the Vapor Pressures and Entropies of Crystals

By R. H. FOWLER, F.R.S.
Professor of Mathematical Physics in the University of Cambridge
and
T. E. STERNE
National Research Fellow at Harvard University and the Massachusetts Institute of Technology

PREFACE

UNTIL quite recently the theory of "chemical constants"—that part of statistical mechanics which deals with the vapor pressures of crystals and liquids and which yields theoretical results easily comparable with the results of experiments—was none too satisfactory. For substances yielding *monatomic* vapors the agreement between the calculated constants in the vapor pressure equations and the constants actually found by experiment upon the crystalline and liquid substances was in general close; and that part of the theory may be said to have been satisfactory. But when one came to study the mathematical treatments then existing for substances whose vapors were *diatomic*, one found that all sorts of supplementary assumptions and special considerations, more or less plausible, had been made in order to account for the observed constants.

So far at least as diatomic substances are concerned these difficulties seem now to have been overcome. We believe that it is now possible to present the theory of the constants in the vapor pressure equations of such substances in a form which is nearly if not yet quite logically complete and free from *ad hoc* assumptions. In this article therefore we shall indicate how such a theory is to be developed from the comparatively simple yet profound principles which are believed to form the basis of modern statistical mechanics.

In extending the theory from monatomic to diatomic substances we at once encounter explicitly additional complications due to (1) nuclear spins, (2) non-combining sets of ortho- and para- states, and (3) mixtures of isotopes. Complications (1) and (3) are really present in a concealed form even for monatomic substances, but for such they are universally ignored and rightly so, for they are without effect on any results. For diatomic substances all these complications must be explicitly included from the outset. It is found, of course, that in general they do not affect the results even here except in certain outstanding cases, where, however, they are essential to the satisfactory clearing up of the whole subject.

In order that this article may be of an introductory nature and at the same time sufficiently complete in itself we shall include in it a short account of the theory of the "vapor pressure constants" of monatomic substances, even though this simpler part of the theory has been adequately described elsewhere. But this procedure will also have the advantage of allowing us to introduce first in their simplest form those general methods of enumerating states or wave functions which are almost essential in the more complicated discussions of the later sections of this article and which are in fact a most valuable tool of statistical mechanics in general. We shall include in this article therefore a short modern version of the methods of statistical mechanics specially designed with a view to their application to the vapor pressure problem.

Closely associated with "vapor pressure constants" are questions concerned with the entropies of crystals at extremely low temperatures, equations of dissociative equilibria, and the accuracy of Nernst's Heat Theorem. We shall naturally proceed therefore from our discussion of "vapor pressure constants" to discussion of these allied questions. They will occupy us in the closing sections of this article. Since we shall be forced to conclude that Nernst's Heat Theorem is not universally true or at least not when applied straightforwardly to the data of the practical physical chemist, we have felt it necessary to discard altogether the name "chemical constant" for the constant in the vapor pressure equation. This old name for the constant is at best a misnomer, but justifiable on account of the other uses of this constant if Nernst's Heat Theorem were universally true. This failing, a change is forced on us. The constant in question does still appear to be important enough to have a name, and the name *vapor pressure constant* already used is obvious and seems suitable.*

Cavendish Laboratory, R. H. Fowler
Cambridge, England.

Jefferson Physical Laboratory, T. E. Sterne
Cambridge, Massachusetts.

---

* To a considerable extent, this article is based both upon the relevant parts of Fowler's *Statistical Mechanics*, and upon the extensions of them made by Sterne while obtaining his doctor's degree at Cambridge University and summarized in an unpublished dissertation by Sterne in the summer of 1931. The form and content of this article follow to a considerable extent those of the latter dissertation. Thus Chapters V, VI, VII, VIII, Appendix I, and some of the material of Appendix II, have been taken over almost unaltered; while Chapters I, III, IV and IX contain much that was embodied in the dissertation. The Preface, and considerable parts of Chapters I, II, III, IV and IX are additions made by Fowler.

CONTENTS

Chapter I

Introduction to the Study of the Vapor Pressures and Entropies of Crystals

SECTION

Chapter II

Quantum Statistical Mechanics and the Vapor Pressure Constants of Monatomic Vapors

Chapter III

The Vapor Pressure Constant of Hydrogen

Chapter IV

The Symmetric Spherical Oscillator and the Rotational Motion of Molecules in Crystals. The Partition Functions for Free Molecules

Chapter V

The Vapor Pressure Constant of Chlorine

Chapter VI

The Vapor Pressure Constant of Hydrogen Chloride

Chapter VII

Mixed Crystals

Chapter VIII

The Vapor Pressure Constants of Diatomic Vapors

Chapter IX

Entropies and Chemical Equilibria

Appendix I

Crystals in Quantum Mechanics

Appendix II

The Enumeration of the Linearly Independent Wave Functions Capable of Representing Assemblies Containing Crystals

CHAPTER I

INTRODUCTION TO THE STUDY OF THE VAPOR PRESSURES AND ENTROPIES OF CRYSTALS

§1.1. The vapor pressure equation of classical thermodynamics

Consider an assembly containing originally a gram molecule of a condensed substance, at an absolute temperature T_2, and a pressure p_2 which is its natural vapor pressure. The vapor is supposed to be an ideal gas, and hence to obey the simple law for an ideal gas $pV = RT$, where V is the volume of the vapor and R the gas constant. Allow the condensed phase to evaporate completely at temperature T_2. The heat absorbed by the assembly is Λ_2, the heat of evaporation at this temperature per gram molecule. The increase in entropy of the assembly is Λ_2/T_2. Now allow the vapor to expand isothermally to a lower pressure p_1. The heat absorbed by the assembly is $RT_2 \log (p_2/p_1)$, and the increase in the entropy of the assembly is $R \log (p_2/p_1)$. Lower the temperature, keeping the pressure constant at p_1, until condensation starts; the process being so carried out that supercooling does not occur. During the cooling from T_2 to the temperature T_1 at which condensation starts, the heat lost by the assembly is $\int_{T_1}^{T_2} C_p dT$; the loss in entropy is $\int_{T_1}^{T_2} C_p dT/T$. C_p is the specific heat per gram molecule of the vapor, at constant pressure; at what pressure does not matter for an ideal gas. Now decrease the volume until the vapor is entirely condensed, at temperature T_1. The loss of heat by the assembly is Λ_1, and the loss of entropy is Λ_1/T_1. Finally warm the condensed phase, without allowing evaporation and at a pressure always equal to its vapor pressure, to the original temperature T_2. This sequence of pressures will just suffice to prevent evaporation. This gives to the condensed phase an amount of heat $\int_{T_1}^{T_2} (C_p)_{sol}\, dT$. In this integral $(C_p)_{sol}$ is the specific heat of the condensed phase under these conditions, and the integral includes all the heats of transition, if any transitions occur in the condensed phase between T_1 and T_2. The corresponding increase of entropy is $\int_{T_1}^{T_2} (C_p)_{sol}\, dT/T$. The cycle is reversible, and if we apply the second law of thermodynamics we find

$$\frac{\Lambda_2}{T_2} - \frac{\Lambda_1}{T_1} + R \log \frac{p_2}{p_1} - \int_{T_1}^{T_2} [C_p - (C_p)_{sol}] dT/T = 0.$$

This equation can be reduced to an equality between two expressions, the first depending upon T_1 only, and the second upon T_2 only; each of these expressions must therefore be equal to a constant and we find, dropping subscripts,

$$\log p = -\frac{\Lambda}{RT} + \int^{T} \frac{C_p - (C_p)_{sol}}{RT'} dT' + i'' \qquad (1.01)$$

where i'' is some constant.

If we apply the first law of thermodynamics to the same cycle, we find that

$$\Lambda_2 - \Lambda_1 = \int_{T_1}^{T_2} [C_p - (C_p)_{sol}]dT'. \qquad (1.05)$$

If in this equation we let $T_1 = 0$, we have

$$\Lambda_T = \int_0^T [C_p - (C_p)_{sol}]dT' + \Lambda_0$$

where Λ_0 is the work of evaporation per gram molecule at the absolute zero. Combining Eq. (1.01) with the last equation we have

$$\log p = -\frac{\Lambda_0}{RT} - \frac{1}{RT}\int_0^T [C_p - (C_p)_{sol}]dT' + \int_0^T \frac{C_p - (C_p)_{sol}}{RT'} dT' + i''.$$

If we differentiate the second term in the right-hand member and then integrate it again we see that

$$\log p = -\frac{\Lambda_0}{RT} + \int^T \frac{dT'}{RT'^2}\int_0^{T'} [C_p - (C_p)_{sol}]dT'' + i'''.$$

It is convenient to break up the specific heat of the vapor into two parts $(C_p)_0$ and $(C_p)_1$ of which $(C_p)_0$ is a constant part (constant over the temperature range which may be in question) and $(C_p)_1$ a variable part. This can always be arranged so that the double integral in the equation below converges when the lower left-hand limit in the integration is made zero.[1] The term in $(C_p)_0$ integrates and gives $[(C_p)_0/R] \log T$ besides contributions to i'''. We are left finally with

$$\log p = -\frac{\Lambda_0}{RT} + \frac{(C_p)_0}{R}\log T + \int_0^T \frac{dT'}{RT'^2}\int_0^{T'} [(C_p)_1 - (C_p)_{sol}]dT'' + i. \quad (1.1)$$

For reasons mentioned in the Preface, the constant i, formerly known as the *chemical constant*, will be called here the *vapor pressure constant* of the vapor in question. In deriving this equation we have assumed, beyond the first and second laws of thermodynamics, merely that the vapor obeys the ideal gas law $pV = RT$, and that the vapor pressure is so small that the work done by the condensed phase in expanding against it in the last stage of the cycle is trivially small. The last assumption, which it was necessary to make in deriving Eq. (1.05), is found to be true in all the experiments, actually performed, relevant to this discussion. As far as existing vapor pressure measurements are concerned we may neglect the utterly trivial differences between the specific heat of the condensed phase at zero pressure (or at one atmos-

---

[1] The implications of this choice of the lower limit in question are considered in detail in §9.1.

phere) and at the pressure of its own vapor; we shall do so throughout this paper. The Eq. (1.1) then, depends only on the laws of ideal gases and upon classical thermodynamics for its validity. It should hold not only for crystals but also for liquids. It may be used with values of $(C_p)_{sol}$ measured at any convenient standard pressure. About the actual values of Λ_0 and i classical thermodynamics has nothing to say.

§1.2. The experimental determination of i

The Eq. (1.1) has been used in the reduction of observations by many experimenters. In practice common logarithms are used, and the pressure is expressed in atmospheres. The constant term in the new and slightly different equation

$$\log_{10} p = -\frac{\Lambda_0}{RT \log 10} + \frac{(C_p)_0}{R} \log_{10} T + \int_0^T \frac{dT'}{RT'^2 \log 10} \int_0^{T'} [(C_p)_1 - (C_p)_{sol}] dT'' + \left(\frac{i}{\log 10} - 6.006\right) \qquad (1.2)$$

which results may be denoted by i'. The experimenters assume some value for $(C_p)_0$ which corresponds to the constant part of the specific heat of the gas for the range of temperatures used; the value of $(C_p)_0$ thus depends upon the temperature range, and different values of the vapor pressure constant i' will result from the use of different values of $(C_p)_0$. The pioneer in all this field was of course Nernst; perhaps the greatest number of accurate measurements are due to Eucken. The reader is referred to his paper[2] for a description of the way in which he obtains values of i' from his observations of vapor pressures at definite temperatures over a certain temperature range; and it is sufficient to note here that (1) he corrects his i''s for the deviations of his vapors from the ideal gas laws, and (2) he adjusts not only i but also Λ_0 so as to cause his experimental results to have the best fit with the theoretical vapor pressure Eq. (1.2), taking account of imperfections in his gases.

§1.3. The theoretical determination of i

The interest of trying to calculate theoretically what the value of i should be is obvious and has engaged the attention of many workers. Since classical thermodynamics has no bearing on the value of i, it is a matter at least for classical statistical mechanics and in fact, in its usual form, requires considerations derived from the quantum theory. The first successful calculations were those of Sackur[3] and Tetrode[4] and Stern[5] who obtained the correct value of i for a monatomic vapor by arguments which may be regarded as incomplete versions of those we use today, and their theoretical result was first compared with experiment by Nernst.[6] The method of predicting values of i

[2] Eucken, Zeits. f. Physik **29,** 1 (1924).

[3] Sackur, Ann. d. Physik **40,** 67 (1913).

[4] Tetrode, Ann. d. Physik **38,** 434; **39,** 255 (1912).

[5] Stern, Phys. Zeits. **14,** 629 (1913).

[6] A general account is given by Nernst in his *Grundlagen des Neuen Wärmesatzes* (1918).

is to compare an expression for the vapor pressure, which we shall obtain by statistical mechanics, with the thermodynamical Eq. (1.1). As we shall show in the next chapter, this comparison furnishes us with theoretical values of the vapor pressure constants of monatomic vapors which are found to be in good agreement with experiment in the case of a considerable number of substances. The arguments of the next chapter are essentially those which appear in Chapter VII of Fowler's *Statistical Mechanics*, recast into the simpler and more satisfactory form provided by quantum mechanics. The earliest form of these arguments which may claim to be logically complete is due to Ehrenfest and Trkal.[7]

A somewhat more complicated theory is necessary for diatomic gases, and in particular, vapors made up of molecules composed of two atoms of the same element require to be given, in general, a special treatment. No early investigation, not even that of Ehrenfest and Trkal in spite of its formal correctness, yielded results of much value here; for it is essential to examine the details and this can only be done in the light thrown by quantum mechanics. The case of hydrogen vapor was investigated by Fowler,[8] taking account of the existence of the two sorts of hydrogen molecules, first suggested by Dennison[9] to explain the specific heat, namely ortho-hydrogen with odd rotational quantum numbers, and para-hydrogen with even rotational quantum numbers. These molecules retain their type over long periods at very low temperatures. By the use of classical statistics for the vapor, it was possible to show that at very low temperatures hydrogen, as obtained by cooling hydrogen gas from ordinary temperatures, ought to have very nearly the experimentally observed vapor pressure constant. Since Dennison's theory of the rotational specific heat of hydrogen yields correct values at all temperatures, it follows from (1.1) that, at ordinary temperatures also, Fowler's theory would yield a correct value for the vapor pressure constant. In these calculations it was assumed that the molecules of hydrogen were able to rotate in the crystal with very nearly the same energy levels as in the gas.

Fowler's analysis for hydrogen, however, cannot be taken over directly for other diatomic molecules of type X_2. For, though symmetry properties must always be considered in investigating vapor pressures when the molecules of the vapor are made up of two atoms of the same element, it appears from the recent work of L. Pauling[10] that whereas in some crystals, as of hydrogen, the molecules are able to rotate quite freely, in others they cannot; they "oscillate" instead about orientations of equilibrium. The problem is thereby altered, and is further complicated in general by the existence of isotopes of the elements concerned. This semi-classical investigation of the vapor pressure constant of hydrogen yielded a value for the vapor pressure constant of hydrogen in good agreement with experiment. The use of the classical statistics is however theoretically incorrect. We shall show in the

---

[7] Ehrenfest and Trkal, Proc. Sect. Sci. Amsterdam **23**, 162 (1920).

[8] Fowler, Proc. Roy. Soc. **A118**, 52 (1928).

[9] Dennison, Proc. Roy. Soc. **A115**, 483 (1927).

[10] L. Pauling, Phys. Rev. **36**, 430 (1930).

third chapter that by using the correct Einstein-Bose statistics for the vapor precisely the same value,[11] to our order of accuracy, will be obtained for the vapor pressure constant. We prove in short that the classical approximation can *always* be used for the vapor without significant error. In the fourth chapter we shall investigate the nature of the quantum states of diatomic molecules in crystals;[12] we shall need these results in subsequent chapters. In the fifth chapter we shall present in detail an investigation of the vapor pressure of chlorine,[13] taking account of the isotopic composition of chlorine. The investigations of the third, fourth and fifth chapters should, we hope, provide a clear account of how one ought to consider, in statistical mechanics, assemblies containing crystals whose vapors are composed of molecules made up of two atoms of the same chemical element.

The remaining chapters VI–VIII devoted to vapor pressure constants deal firstly with the vapor pressure constants of molecules of type XY such as HCl, which after our discussion of type X_2 are comparatively simple. They then pass on to a study of mixed crystals in general, in which the discussion is no longer limited to the perfect mixing which we have assumed up to this point. Though the generalizations of this chapter are not applied in this article it is desirable to examine carefully the important assumption of perfect mixing, and the generalized formulae of Chapter VII may prove to be of some importance in future investigations. Finally in Chapter VIII we review and tabulate all the available data of reasonable reliability, for diatomic molecules.

CHAPTER II

QUANTUM STATISTICAL MECHANICS AND THE VAPOR PRESSURE CONSTANTS OF MONATOMIC VAPORS

§2.1. The basis of quantum statistical mechanics*

There are few differences between quantum statistical mechanics and the older classical version. We postulate always that the observable properties of any assembly of systems are to be determined by averaging over all the *accessible* states of the assembly. There are two ways in which this average can be taken. We can take a simple average over all accessible states *of given energy*, assigning to each such state an equal weight or *a priori* probability. Or we can follow Gibbs in preferring the more general method of averaging over all accessible states, of no matter what energy E, provided we assign to each such state an *a priori* probability $e^{-E/\theta}$, where θ is a parameter which of course turns out to be proportional to the absolute temperature. It is a matter of little importance, primarily a matter of taste, which method is chosen—they lead to identical results. In this article we shall use the former, and *determine*

---

[11] Sterne, Proc. Roy. Soc. **A130**, 367 (1931); **A133**, 303 (1931).

[12] Sterne, Proc. Roy. Soc. **A130**, 551 (1931).

[13] Sterne, Proc. Roy. Soc. **A131**, 339 (1931).

* For a more complete discussion of matters lightly passed over here, and of the method of considering the wave functions of the molecules in a gas, the reader is referred to Fowler's *Statistical Mechanics*.

all properties of our assemblies by averaging over all accessible states of given energy, assigning equal weights to all distinct states. We have based this procedure on a postulate, but this postulate is capable of analysis and (to some degree at least) of formal justification by deduction from the laws of quantum mechanics. But into this field in which the leaders have been von Neumann[14] and Dirac[15] we shall not attempt to penetrate here. The analogy between the classical and the quantum mechanical versions is very close, and if we replace each accessible state by a corresponding accessible region of phase space we at once regain the classical version.

§2.11. The specification of accessible states

It is however necessary to examine with great care what we mean by an accessible state in quantum mechanics. It is possible, fortunately, to specify the accessible states quite precisely when we have specified the nature of the systems of which our assembly is composed. We are no longer left in doubt about tiresome "symmetry factors" as in the classical theory. By a state we mean of course a stationary state of the whole assembly characterized by a definite value of the energy E and a corresponding wave function Ψ, E_n and Ψ_n, say, which Ψ_n satisfies the complete Schrödinger's equation for all the systems in the assembly taken together for the specified E_n. *Every such distinct wave function Ψ_n is to be counted as a separate state and all Ψ_n's are distinct which are not identically linear combinations of each other.* In all this there is no grave departure from classical considerations—one's tools are merely sharper and simpler. By an accessible state we mean a state in which the assembly *might* be found at some later time, if it starts in a given initial state, and is then left to itself and to random interactions with its surroundings. This however imposes a severe non-classical limitation, because if the assembly contains a number of systems, electrons, protons, atoms X, or molecules XY or X_2, which are indistinguishable among themselves, only those states are accessible from an initial state which have the same symmetry characteristics as the initial state with respect to the indistinguishable systems. And in fact we know that (with certain rare exceptions to which we shall return) *the accessible states of all assemblies are those and only those which are antisymmetrical in all the electrons and also antisymmetrical in all the protons, account being taken of their spins.* Since in fact all assemblies are presumably assemblies of electrons and protons only (usually in equal numbers) these symmetry requirements should be sufficient for all purposes, and so no doubt they are. But for the sake of treating an assembly in a way which corresponds closely to its physical nature it is inconvenient and of little value to regard it as an assembly of electrons and protons when it is in fact an assembly of permanent helium atoms or of permanent hydrogen molecules, and we need secondary derived symmetry rules for these permanent complex systems. Suppose such a complex system contains n protons and m electrons. Then, since interchange of a pair of complex systems means interchange of $(n+m)$

---

[14] von Neumann. Gött. Nach. p. 245 (1927).

[15] Dirac, Proc. Camb. Phil. Soc. **25**, 62 (1928).

pairs of electrons and protons in each of which pairs the wave function is antisymmetrical, the wave function of the assembly will be symmetrical in the complexes if $(n+m)$ is even and antisymmetrical if $(n+m)$ is odd. We have therefore at least these derived symmetry rules and as we shall shortly see these are not only necessary but also sufficient.

We shall therefore be able to turn this difficulty. If we can decide *a priori* from our knowledge of the properties of these secondary systems, atoms, molecules, or nuclei, what systems can be effectively regarded as the permanent population of the assembly, then we can appeal to the following

Lemma: It is sufficient, in enumerating the wave functions characterizing the accessible states of the complete assembly, to construct formally, and so to enumerate, all those linearly independent wave functions which have the correct symmetry properties in the permanent systems, conceived as wholes, of which the assembly is composed. The wave function of any permanent system must have the correct symmetry properties in the electrons and protons of which that system is composed, but the direct analysis of the complete assembly into the electrons and protons of which it is ultimately composed may be omitted, for the total number of admissible wave functions is not thereby altered.

This simplifying lemma is easily established, but as a formal proof would be long and clumsy, we can be content with illustrative examples in which the argument is obviously general. It is a well-known property of the solutions of Schrödinger's equation for an assembly that the neglect of the interactions between various constituent systems can never alter the number or symmetry type of the various stationary states, though of course it alters their energies and can allow new degeneracies to come in. Consider for one example an assembly of two electrons and two protons in a box, for which we are told that the actual permanent systems may be assumed to be two hydrogen atoms. Let $\psi_\alpha(1, \mathrm{I})$ be the wave function of the system electron 1 and proton I in the box, describing a particular stationary state with neglect of the interaction with electron 2 and proton II. This is then the wave function for a freely moving hydrogen atom in a given electronic state and a given state of translatory motion, and we need not specify it further. Let $\psi_\beta(2, \mathrm{II})$ have the obvious similar meaning. Then the wave functions describing a specified state of the assembly (one atom in state α and one atom in state β) are

$$\psi_\alpha(1, \mathrm{I})\psi_\beta(2, \mathrm{II}), \qquad \psi_\alpha(2, \mathrm{II})\psi_\beta(1, \mathrm{I})$$

and the unique wave function *symmetrical* in the two hydrogen atoms as wholes is

$$\psi_\alpha(1, \mathrm{I})\psi_\beta(2, \mathrm{II}) + \psi_\alpha(2, \mathrm{II})\psi_\beta(1, \mathrm{I}). \qquad (A)$$

This wave function is not antisymmetrical in the electrons and protons, but it corresponds to just one such function, as the lemma requires. This function is

$$\{\psi_\alpha(1, \mathrm{I})\psi_\beta(2, \mathrm{II}) + \psi_\alpha(2, \mathrm{II})\psi_\beta(1, \mathrm{I})\} - \{\psi_\alpha(2, \mathrm{I})\psi_\beta(1, \mathrm{II}) + \psi_\alpha(1, \mathrm{II})\psi_\beta(2, \mathrm{I})\}. \qquad (B)$$

Of course we may not argue that to (B) correspond two functions of type (A), namely the two terms $\{\ \}$ in (B), for to admit both these functions denies the permanency of the hydrogen atoms—we must then regard the assembly as one of electrons and protons and we are then driven back to the unique (B) itself.

For one more example consider an assembly of eight electrons and eight protons for which we know that the permanent systems may be regarded as two α particles and four free electrons. Let $\psi_\alpha(1, 2, \mathrm{I}, \cdots, \mathrm{IV})$ and $\psi_\beta(3, 4, \mathrm{V}, \cdots, \mathrm{VIII})$ represent wave functions for the two α complexes each of the proper internal antisymmetry in their own electrons and protons. Let $\psi_\gamma(5)$, $\psi_\delta(6)$, $\psi_\epsilon(7)$ and $\psi_\xi(8)$ be the wave functions for the extra-nuclear electrons. The only wave function Ψ for the complete assembly which is antisymmetrical in the extra-nuclear electrons, symmetrical in the α particles, of the given grouping for the systems grouped in the α complexes, and representative of the specified state of the assembly (α particles in states α and β, free electrons in γ, δ, ϵ, ξ), is

$$\Psi = \left\| \begin{matrix} \psi_\alpha(1, 2, \mathrm{I}, \cdots, \mathrm{IV}), & \psi_\alpha(3, 4, \mathrm{V}, \cdots, \mathrm{VIII}) \\ \psi_\beta(1, 2, \mathrm{I}, \cdots, \mathrm{IV}), & \psi_\beta(3, 4, \mathrm{V}, \cdots, \mathrm{VIII}) \end{matrix} \right\| \times \left| \begin{matrix} \psi_\gamma(5), & \psi_\gamma(6), & \psi_\gamma(7), & \psi_\gamma(8) \\ \psi_\delta(5), & \psi_\delta(6), & \psi_\delta(7), & \psi_\delta(8) \\ \psi_\epsilon(5), & \psi_\epsilon(6), & \psi_\epsilon(7), & \psi_\epsilon(8) \\ \psi_\xi(5), & \psi_\xi(6), & \psi_\xi(7), & \psi_\xi(8) \end{matrix} \right| . \qquad (C)$$

In (C) $\|\cdots\|$ denotes a *permanent*, that is, a determinant but with the signs of all its terms positive, and $|\cdots|$ denotes a determinant. It is easy to see that from any such function we can construct just one Ψ_0 antisymmetrical in all the protons by summation with the proper signs of the terms $P_p\Psi$ over all permutations P_p of the protons which make a significant change in Ψ (such as for example an interchange of I and V but not of I and II). We can then construct just one Ψ_{00} antisymmetrical in both protons and electrons by similar summation of the terms $P_e\Psi_0$ over all significant permutations P_e of the electrons. The order of these operations is irrelevant. Conversely from given elementary ψ's for the electrons and protons, we obviously can construct only one function with the groupings and symmetries of (C). Hence the lemma.

We must not however forget that though this is the way in which the symmetry requirements of the assembly with permanent complexes *ought* to be satisfiable, yet nuclei containing an odd number of electrons, e.g., N_{14}, Li_6, appear to be exceptions and to behave *as if* the nuclear electrons made no contribution to the nuclear symmetry. These are the rare exceptions referred to above. We do not yet understand this, but fortunately, if we accept the fact, it does not cramp our procedure. For we always treat nuclei as permanent complexes in any terrestrial problem and therefore by the lemma we should in any case proceed by satisfying the symmetry requirements of the assembly merely in all sets of equivalent nuclei. Whether or not we are able correctly to analyze this symmetry in terms of component electrons and protons does not in fact matter at all. Permanent complexes may be treated as the primary constituents, by the lemma if they are analyzable into components, by hypothesis if they are not.

We have so far formulated the lemma for the analysis of permanent complexes into electrons and protons, but there is no need so to restrict it. It applies equally to the analysis of permanent complexes X into any permanent component secondary units Y and Z. For example, in an assembly of chlorine atoms Cl_{35} the complete wave functions must be antisymmetrical in the Cl_{35} nuclei. But the assembly will often consist entirely of permanent molecules $(Cl_{35})_2$. Applying the lemma, therefore, we see that the symmetry requirements of the assembly will be satisfied, and that the enumeration of wave functions will be correct, if we make the wave function of each molecule *antisymmetrical* in its nuclei and then make the combined wave function of the assembly *symmetrical* in the molecules.

§2.2. The statistical mechanics of an assembly containing a substance in the crystalline and monatomic gaseous phases. The method of enumerating wave functions

Let us consider an assembly containing in all X atoms of some pure chemical element; and let there be N atoms in the gaseous phase and P atoms in the crystalline phase. We suppose for simplicity that the lattice of the latter is an atomic one, and that in any specified state of vibration or translatory motion the atom is represented by a single wave function; i.e., that the weight of its internal state is unity. For the moment however let us ignore the crystalline phase, and fix our attention upon the vapor. Let us also for the moment neglect completely the internal motions of the atoms, and consider that the energy associated with each atom in the gas is simply its kinetic energy of motion plus its potential energy due to its position outside of the crystal. Let the possible energy levels of each gas atom then be $\epsilon_0, \epsilon_1, \epsilon_2, \cdots$, where the degenerate levels if there are any are written here as many times as there are linearly independent wave functions to represent them.

To a first approximation a complete wave function for the vapor alone is a linear combination of products of the individual wave functions of the N atoms in the gaseous phase, symmetrical or, it may be, antisymmetrical in all the N atoms. Since the atoms are neutral they will require symmetrical wave functions unless we are concerned with one of the exceptions with an odd number of electrons in the nucleus. We have no example of such a vapor and shall omit the antisymmetrical case, the treatment of which however follows exactly the same lines as the treatment of the symmetrical case. Let the r'th wave function of the k'th atom be denoted by $\psi_r(k)$; then such a linear combination, symmetrical in all the atoms, might be for instance the permanent

$$\Psi = \left\| \begin{matrix} \psi_0(1), & \psi_0(2), & \psi_0(3), & \cdots \psi_0(N) \\ \psi_0(1), & \psi_0(2), & \psi_0(3), & \cdots \psi_0(N) \\ \psi_3(1), & \psi_3(2), & \psi_3(3), & \cdots \psi_3(N) \\ \psi_4(1), & \psi_4(2), & \psi_4(3), & \cdots \psi_4(N) \\ \cdot & \cdot & \cdot & \cdots \cdot \\ \cdot & \cdot & \cdot & \cdots \cdot \\ \cdot & \cdot & \cdot & \cdots \cdot \\ \psi_l(1), & \psi_l(2), & \psi_l(3), & \cdots \psi_l(N) \end{matrix} \right\|$$

which is the only combination symmetrical in all the atoms which is representative of the specified state of the gas (two atoms in state 0, one in state 3, and so on). This Ψ corresponds to an energy for the gas of

$$F = 2\epsilon_0 + \epsilon_3 + \epsilon_4 + \cdots + \epsilon_l.$$

It is now easy to see that the total number of linearly independent wave functions with the correct symmetry properties capable of representing the gas of N atoms, when the total energy of the gas is F, is simply the coefficient of $x^N z^F$ in the series $\Pi_j(1-xz^{\epsilon_j})^{-1}$, where the product is taken over all the possible energy levels ϵ_j; for we may write the product in the form

$$\Pi = \left\{ \begin{matrix} (1 + xz^{\epsilon_0} + x^2z^{2\epsilon_0} + x^3z^{3\epsilon_0} + \cdots) \\ \times (1 + xz^{\epsilon_1} + x^2z^{2\epsilon_1} + x^3z^{3\epsilon_1} + \cdots) \\ \times (1 + xz^{\epsilon_2} + x^2z^{2\epsilon_2} + x^3z^{3\epsilon_2} + \cdots) \\ \times (\cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot) \\ \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\ \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \end{matrix} \right\}. \qquad (2.2)$$

Let us now consider the crystal phase alone. The number of linearly independent wave functions symmetrical in all the atoms which can represent the crystal, that is, its number of accessible states, when its total energy is U and it contains P atoms, can be cast into the form of the coefficient of z^U in a function $[\kappa(z)]^P$, which is the partition function corresponding to Debye's analysis of the normal modes of the crystal. In order not to interrupt the argument this analysis is given in Appendix I.

If we regard the atoms in the gas and the crystal as distinct, then of course the total number of accessible states of an assembly composed of N atoms in the gas with total energy F and P atoms in the crystal with total energy U is the product of these coefficients:

$$[\text{coeff } x^N z^F \text{ in } \Pi_j(1 - xz^{\epsilon_j})^{-1}] \times [\text{coeff } z^U \text{ in } [\kappa(z)]^P] \qquad (A)$$

and the representative wave functions are the products of the gas and crystal wave functions already constructed. Such wave functions will of course not have the full symmetry over all atoms. But the lemma of §2.11 applies again, and the number of wave functions so obtained is the correct number of wave functions with the full symmetry.

But now we know in fact, about the energy, merely that the total energy of the assembly is $E=F+U$. To obtain the total number C_N of accessible states of the assembly when its total energy is E, and when there are N atoms in the gas and $P=X-N$ atoms in the crystal, we must sum (A) over all values of F and U subject to the above condition. We thereby obtain the coefficient of $x^N z^E$ in

$$[\kappa(z)]^{X-N}\Pi_j(1-xz^{\epsilon_j})^{-1}. \tag{B}$$

By using Cauchy's theorem for functions of a complex variable we may write this as[16]

$$C_N=\left(\frac{1}{2\pi i}\right)^2\int\int\frac{dxdz\Pi_j(1-xz^{\epsilon_j})^{-1}[\kappa(z)]^{X-N}}{x^{N+1}z^{E+1}}, \tag{2.21}$$

where the integrals are taken along closed contours about the origins in the x and z planes, within the regions in which (B) is holomorphic.

To evaluate these integrals we make use of the method of steepest descents. We shall in this article merely sketch the correct method and its results, referring for a more complete discussion of the method of steepest descents in general to Chapters II, V (excluding §§5.6 and 5.9) and XXI of Fowler's *Statistical Mechanics*. Since a rigorous application of the method to the enumeration of the wave functions capable of representing an assembly containing crystals is nowhere available in print, we shall present such a treatment in Appendix II of this article. Consider the integrand of (2.21) on the positive real axes of x and z. For a value ξ of x between 0 and ∞, and a value θ of z between 0 and 1, the integrand has a unique minimum. For the contours of integration take circles about the origins of radii ξ and θ in the x and z planes, respectively. Then for values of x on the circle in the x plane $x=\xi e^{i\alpha}$ say, $x=\xi$, $\alpha=0$ is a strong *maximum* of the modulus of the integrand. Similarly for values of z on the circle in the z plane $z=\theta e^{i\beta}$ say, $z=\theta$, $\beta=0$ is a strong maximum of the modulus of the integrand. Owing also to the fact that the differential coefficients of the integrand vanish for $\alpha=0$ and $\beta=0$, the complex terms there are trivial and the whole effective contribution to the integral comes from very small values of α and β. The result is that

---

[16] Our procedure in this article for considering assemblies containing crystals is more rigorous than the different procedure used in §5.6 of Fowler's *Statistical Mechanics*. The latter method, although it leads to the correct results, is deficient in rigor and is really incorrect. It depends upon the application of the method of steepest descents to the evaluation of a double integral denoting the number of accessible states corresponding to *all* possible choices of N. The integrand of this integral contains the factor $1-x\kappa(z)$ in the denominator, and the regions of importance in the evaluation of the integral by the method of steepest descents are so close to the singularities of the integrand which result from the presence of this factor that when one reduces the integrand to the form similar to Fowler's Eq. (346), the terms in α^3, etc. and α^4, etc. are as important as the quadratic terms in the exponential. Accordingly, the method of steepest descents does not appear to be applicable to the double integral in §5.6 of Fowler's *Statistical Mechanics*, and we have departed in the text above from this earlier and incorrect treatment. Throughout this article we shall use the new and rigorous treatment.

$$C_N = \frac{1}{2\pi}\,\frac{\Pi_j(1-\xi\theta^{\epsilon_j})^{-1}[\kappa(\theta)]^{X-N}}{\xi^N\theta^E}\left[\frac{1}{V}J_0^{-1/2}+O\left(\frac{1}{V^2}\right)\right], \tag{2.211}$$

where ξ and θ are the unique positive roots of

$$\xi\frac{\partial}{\partial\xi}\sum_j \log(1-\xi\theta^{\epsilon_j})^{-1} = N \tag{2.212}$$

and

$$\theta\frac{\partial}{\partial\theta}\sum_j \log(1-\xi\theta^{\epsilon_j})^{-1} + (X-N)\theta\frac{\kappa'(\theta)}{\kappa(\theta)} = E.$$

Here V is the volume of the gas phase, and J_0 is a certain Jacobian determinant which varies only slowly with N, and which we may in fact treat as a constant in the following discussion. The term $O(1/V^2)$ is an error term which becomes trivial when V becomes large. The parameters θ and ξ, which we have been led to introduce because of the nature of the mathematics, correspond to the absolute temperature and thermodynamic partial potential, respectively. In fact, $\theta = e^{-1/kT}$ where k is Boltzmann's constant.

In these calculations we have thus far kept the number of gas atoms fixed and equal to N. But we know in fact merely that the total number of atoms in both phases, $N+P$, is fixed and equal to X. Therefore the total number of accessible states of the assembly when its energy is E, that is, the total number of linearly independent wave functions with the correct symmetry properties which can represent it, is given by

$$C = \sum C_N \tag{2.213}$$

summed over all values of N from 0 to X. We wish to find the average value $\overline{N}$ of N, defined by

$$C\overline{N} = \sum_0^X NC_N. \tag{2.214}$$

We proceed as follows. The value N^* of N for which C_N is a maximum is obtained by equating to zero the total derivative of $\log C_N$ with respect to N, and if we neglect as we may the nearly constant term $\log(J_0)^{-1/2}$ we have

$$\left[\frac{\partial}{\partial\xi}\sum_j \log(1-\xi\theta^{\epsilon_j})^{-1} - \frac{N}{\xi}\right]\frac{d\xi}{dN} + \left[\frac{\partial}{\partial\theta}\sum_j \log(1-\xi\theta^{\epsilon_j})^{-1} + (X-N)\frac{\kappa'(\theta)}{\kappa(\theta)} - \frac{E}{\theta}\right]\frac{d\theta}{dN} - \log\kappa(\theta) - \log\xi = 0.$$

Since the bracketted expressions vanish, the maximum value of C_N corresponds to a value of ξ given by

$$\xi = 1/\kappa(\theta), \tag{2.215}$$

with a trivial error. The corresponding value N^* of N is given by (2.215) and (2.212). It is easy to show that $\overline{N}$ and N^* are equal. We have merely to observe that the rapidly varying part of the right-hand member of equation (2.211)

$$\frac{\Pi_j(1-\xi\theta^{\epsilon_j})^{-1}[\kappa(\theta)]^{X-N}}{\xi^N\theta^E} = \left[\frac{\Pi_j(1-\xi\theta^{\epsilon_j})^{-1}[\kappa(\theta)]^{X-N}}{\xi^N\theta^E}\right]^*$$

$$\times \exp\left\{-\tfrac{1}{2}[(N-N^*)^2/AN^*] + \text{cubic and higher terms in } (N-N^*)\right\}$$

by Taylor's theorem, since the first derivative vanishes. Here the expression $[\quad]^*$ is to be evaluated for a value of N equal to N^*. To show that the denominator in the exponential is of order N^*, we may use the approximate expression for $\Sigma_j \log(1-\xi\theta^{\epsilon_j})^{-1}$ which we shall introduce shortly for finding $\overline{N}$. The exponential factor in the above expression diminishes with extreme rapidity as $|N-N^*|/N^*$ increases, when N^* is large, and thus the significant contributions to the sums (2.213) and (2.214) come only from terms for which N is very nearly equal to N^*. Thus $\overline{N}=N^*$ with great accuracy when N^* is large. Hence we have finally

$$\overline{N} = \xi\frac{\partial}{\partial\xi}\sum_j \log(1-\xi\theta^{\epsilon_j})^{-1} \tag{2.24}$$

where

$$\xi = 1/\kappa(\theta).$$

Eq. (2.24) gives a value for $\overline{N}$, according to the Einstein-Bose statistics. It is in practice sufficiently accurate to use the classical approximation to these statistics for the gaseous phase. The arguments on pages 535–537 of Fowler's *Statistical Mechanics* show that we may replace the Π in the integrand of (2.21) in all ordinary cases by $e^{xF(z)}$; where $F(z)$ is the ordinary partition function for a gas atom. A partition function $f(\theta)$ of a system is simply the sum

$$f(\theta) = \sum_j \rho_j\theta^{\epsilon_j}$$

where the ϵ_j's are the possible energy levels of the system and ρ_j is the number of linearly independent wave functions capable of representing the system in the j'th level.

Accordingly, we may replace (2.24) by

$$\overline{N} = F(\theta)/\kappa(\theta). \tag{2.25}$$

Still neglecting internal motions, we have for a monatomic gas $(C_p)_0 = 5R/2$, where R is the gas constant, and $(C_p)_1 = 0$. We make use of the relation[17]

$$pV = \overline{N}kT$$

where p is the pressure of the vapor, and V is the volume. Let us take for the state of zero energy of an atom the state in which it is when it is condensed in the crystalline phase at the absolute zero, and is in its lowest quantum state of internal motion. Then $\kappa(0)=1$ and it follows from the corollary to the

---

[17] Fowler, *Statistical Mechanics*, p. 45.

lemma which we shall prove in the next chapter that

$$\log K(T) = \int_0^T \frac{dT'}{RT'^2} \int_0^{T'} (C_p)_{sol}\, dT''$$

where $K(T) = \kappa(\theta)$. Again, the gaseous partition function for such an atom is[18]

$$F(T) = (2\pi mkT)^{3/2} V e^{-\chi/kT}/h^3.$$

It follows from Eq. (2.25) and the subsequent relations, therefore, that

$$\begin{aligned}\log p = &-\frac{\chi}{kT} + \frac{5}{2}\log T - \int_0^T \frac{dT'}{RT'^2} \int_0^{T'} (C_p)_{sol}\, dT'' \\ &+ \log \frac{(2\pi m)^{3/2} k^{5/2}}{h^3}\cdot\end{aligned} \qquad (2.26)$$

Here χ is the work which must be done to remove an atom from the state of zero energy defined above and place it at rest, in its lowest quantum state of internal motion, at infinity. The quantity m is the mass of an atom, and h is Planck's constant.

Now if the reader will compare Eq. (2.26) with Eq. (1.1) of the last chapter, bearing in mind that $Mk = R$ where M is Avogadro's number, he will see that the two equations are identical; and that for our monatomic gas the vapor pressure constant must be given by

$$i = \log\left[(2\pi m)^{3/2} k^{5/2}/h^3\right], \qquad (2.27)$$

the formula of Stern and Tetrode.

Let us now remove the restriction to a unique internal state for the atom (and its nucleus). If internal motions and nuclear orientations are taken account of, the gaseous partition function for an atom is no longer simply $F(T)$, but becomes $F(T)f(T)$ where $f(T)$ is the partition function for the internal motions, including nuclear effects. Similarly, the crystalline partition function $K(T)$ must be replaced by $K(T)f'(T)$ say, where $f'(T)$ is the partition function for the internal motions (including nuclear orientations) of an atom in the crystal.[19] By the same corollary we shall now have

$$\log K(T)f'(T) - \log \omega_0 = \int_0^T \frac{dT'}{RT'^2} \int_0^{T'} (C_p)_{sol}\, dT'',$$

where ω_0 is the statistical weight of the lowest energy state of internal motion and nuclear orientation of the atom in the crystalline phase. More precisely $\omega_0{}^P$ is the number of linearly independent wave functions of proper symmetry which can represent the lowest quantum state of a crystal made up of P atoms. The result is that if we leave the first three terms of Eq. (2.26) unaltered, we must then replace the expression (2.27) for i by

---

[18] Fowler, *Statistical Mechanics*, p. 39.

[19] See Appendix I.

$$i = \log \left[(2\pi m)^{3/2}k^{5/2}/h^3\right] + \log \left[f(T)/\omega_0\right]. \tag{2.28}$$

If the nuclei have a spin with $\tilde{\omega}$ different orientations it is clear that to the present approximation these spins, which are practically independent of the external electronic structure of their own atoms and *a fortiori* of other atoms, serve merely to introduce an extra number of possible wave functions for each atom, there being now just $\tilde{\omega}$ times as many different functions for each atomic state as before. This $\tilde{\omega}$ will enter as a factor into both $f(T)$ and ω_0 and will be without effect on i. We shall ignore it altogether wherever possible, but we shall be required to consider the part that nuclear spins play for diatomic molecules in detail in later chapters.

§2.3. The vapor pressure constants of some monatomic vapors

The observed values of some monatomic vapor pressure constants i' are shown in Table I, with the pressure expressed in atmospheres and the logarithms taken to the base 10, so that

$$i' = [i/\log 10] - 6.006,$$

together with the values calculated from the preceding theory. The lowest spectral terms of free mercury, cadmium zinc, lead, and argon atoms are all of type ${}^1S$ and can therefore be represented by only a single wave function in each case; the other terms are so much higher that $f(T)$ in Eq. (2.28) is in all of these cases the same as ω_0, and therefore only the first term in (2.28) contributes to i. For sodium and potassium, the lowest spectral terms of the free atoms are of type ${}^2S$ and can each be represented by two linearly independent wave functions; at ordinary temperatures the partition function for internal motions of a sodium or potassium atom in the free state

$$f(T) = \sum_j \rho_j e^{-\epsilon_j/kT}$$

is nearly equal to its first term, which is simply 2. To find what ω_0 should be, we observe that both sodium and potassium crystals are metallic conductors, and apply the electron theory of metals in the manner of Sommerfeld. We may think of the atom as being dissociated into electrons, and positive ions; the latter having statistical weights unity (nuclear weights being neglected) since they are formed of perfect closed groups of electrons. The electrons have weight 2 for their spin orientations. The positive ion lattice may be considered by the usual Debye analysis and contributes merely the factor unity to the total number of linearly independent wave functions which can represent our crystal made up of P positive ions and P electrons. The electrons may be considered to form an electron gas, obeying the Fermi-Dirac statistics (i.e., the wave functions for the electron gas must be antisymmetrical in any two electrons), in an enclosure at nearly constant potential. This electron gas is perfectly degenerate: At the absolute zero there exists only one state for the electron gas, namely that in which there is only one electron in each of the P-states of lowest energy, and for this state there is only one possible wave function. Hence, for sodium and potassium, $\omega_0 = 1$. The departure of the potential from uniformity within the metals in no way invalidates this conclusion.

The case of hydrogen at very low temperatures will be considered separately in the next chapter; it is included in Table I merely for the sake of completeness. The monatomic vapor pressure constants of chlorine, bromine and iodine require, however, further discussion here. The lowest spectral term of a free halogen atom is an inverted doublet, ^2P; so that the normal state is a term $^2P_{1\frac{1}{2}}$ of statistical weight 4, while the next higher state is a term $^2P_{1/2}$ of statistical weight 2 which is however but slightly higher. The halogen crystals are in all probability molecular, the atoms being present as diatomic molecules performing spherical oscillations about a direction of equilibrium. It will be necessary to discuss such crystals in detail in Chapter V. It would interrupt the argument too much if we were to proceed otherwise than by

TABLE I. *Some monatomic vapor pressure constants.*

Vapor	Atomic weight	i' calculated	i' observed	Authorities for i' observed
Hg	200.6	1.866	1.83 ± 0.03	(1)
Cd	112.4	1.488	1.45 ± 0.1 1.57	(1) (6)
Zn	65.37	1.135	1.10 ± 0.1	(1)
Pb	207.2	1.887	1.8 ± 0.2 2.27 ± 0.36	(1) (7)
A	39.88	0.813	0.79 ± 0.04	(1)
H_2	2.015	−1.132	-1.09 ± 0.02	(2)
Na	23.0	0.756	0.63 0.78 ± 0.1 0.97	(3) (8) (4)
K	39.1	1.10	0.92 1.13	(3) (4)
Cl	35.46	1.44	1.44 ± 0.2	(5)
Br	79.92	1.87	2.03 ± 0.2	(5)
I	126.9	2.17	2.21 ± 0.2	(5)

AUTHORITIES

(1) Egerton, Proc. Phys. Soc. Lond. **37**, 75 (1925).
(2) Eucken, Zeits. f. Physik **29**, 1 (1924); at very low temperatures only.
(3) Edmonson and Egerton, Proc. Roy. Soc. **A113**, 533 (1927).
(4) Zeidler, Zeits. f. phys. Chem. **123**, 383 (1926).
(5) See Fowler, *Statistical Mechanics*, note (7) on p. 156.
(6) Lange and Simon, Zeits. f. phys. Chem. **134**, 374 (1928).
(7) P. Harteck, Zeits. f. phys. Chem. **134**, 1 (1928).
(8) Ladenburg and Thiele, Zeits. f. phys. Chem. **7**, 161 (1930).

simply using here the results of the discussions of this later chapter. If we suppose that the nucleus of the particular halogen considered has an n quantum spin, then it follows from the discussion of Chapter V, since the ground state of a halogen molecule is probably of type $^1\Sigma$, that at the absolute zero a crystal made up of P atoms of a halogen may be represented by $(2n+1)^P$ linearly independent wave functions. Hence ω_0 in Eq. (2.28), by the general rule for interpreting it given in §2.2, should be simply $2n+1$. If the lattice were atomic we should have obtained the result $\omega_0=4(2n+1)$. For $f(T)$ in Eq. (2.28) we need only consider the ^2P term mentioned above, in this case of the halogens; and this term contributes two terms to the partition function, corresponding to its doublet structure, thus:

$$f(T) = (2n+1)(4+2e^{-\Delta P/kT})$$

where ΔP is the difference between the energies of the components of the inverted doublet. Accordingly the last term in Eq. (2.28) becomes simply

$$\log(4+2e^{-\Delta P/kT})$$

and the nuclear weights disappear as we should expect. The following table is taken from Fowler's *Statistical Mechanics*.

TABLE IA. *Values of* $\log_{10}(4+2e^{-\Delta P/kT})$ *for the ground states of halogen atoms.*

Atom	Mean Temp. °K	ΔP (volts)*	$\Delta P/kT$	$\log_{10}(4+2e^{-\Delta P/kT})$
Cl	1000	0.11	1.28	0.66
	1700		0.752	0.69
Br	1350	0.45	3.88	0.6
I	1200	0.94	9.1	0.6

* Electron volts; values from Turner, Phys. Rev. **27**, 397 (1926).

In calculating the i' in Table I we have used for chlorine the value 0.7 for the last term (to the base 10) in Eq. (2.28), and we have used for bromine and iodine the value 0.6.

As already explained we can ignore here the effects of nuclear spins for Hg, Cd, Zn, Pb, A, Na and K (atomic lattices); for the effects are nil since they merely call for the introduction of equal multipliers in both numerators and denominators of the fraction in the second term of (2.28), for all these substances.

The errors given in Table I in the third column are not probable errors, but are, rather, ranges of error. For instance, in the case of mercury the evidence indicates that i' lies between 1.80 and 1.86 apart from concealed errors in the specific heats used. Owing to difficulties of extrapolation the real uncertainly in i' may well be greater than the range.

CHAPTER III

THE VAPOR PRESSURE CONSTANT OF HYDROGEN[20]

§3.1. The statistical mechanics of assemblies containing hydrogen gas and mixed crystals of para- and ortho-hydrogen

In order to represent the properties of an assembly containing hydrogen, at low and ordinary temperatures, we know that owing to the half quantum spins of hydrogen nuclei we must regard the hydrogen as made up of two sorts of molecules—molecules whose rotational wave functions are symmetrical in the nuclei and whose nuclear spin wave functions are antisymmetrical in the nuclei, called para-hydrogen, and molecules whose rotational wave functions are antisymmetrical in the nuclei and whose nuclear spin wave functions are symmetrical in the nuclei, called ortho-hydrogen. Under ordinary experimental conditions no transitions para→ortho or ortho→para take place, even during times which are long compared with the duration of an experiment.[21] It is therefore correct and necessary to treat the assembly as a mixture of two different constituents, para-hydrogen and ortho-hydrogen, present in the proportions given by the long-time statistical equilibrium ratio to which the hydrogen will have settled down before the experiment began.

A molecule of para-hydrogen in a given state of translation and rotation can be represented by only $(2j+1)$ linearly independent wave functions, where j is the rotational quantum number, corresponding to the $(2j+1)$ possible eigenvalues of the z component of rotational angular momentum. A molecule of ortho-hydrogen, however, can be represented by any one of $3(2j+1)$ linearly independent wave functions, corresponding to the $(2j+1)$ possible eigenvalues of the z component of rotational angular momentum and the three possible eigenvalues of the z component of nuclear spin angular momentum. The pair of nuclei being symmetrical in the spins must have a total spin of $\frac{1}{2}+\frac{1}{2}=1$. The spins and the rotations may for the purposes of this enumeration be assumed to be without interaction. In Dirac's language the observables involved commute with each other so that we may assign these eigenvalues independently. By the lemma of §2.11 it is then sufficient to make the wave function of an assembly of hydrogen molecules symmetrical in all of the molecules. We are interested in the total number of linearly independent wave functions of this type capable of representing the assembly when the total energy of the assembly is E, which we call the total number of accessible states.

We consider that a complete wave function for the crystal is a linear combination, symmetrical in all of the molecules in the crystal, of functions of the form $\psi_m\psi_A$, to a first approximation. Here ψ_m is a wave function representing a set of normal modes of vibration of the crystal lattice, and ψ_A is a wave function representing a set of eigenstates for the molecules in the

---

[20] Sterne, Proc. Roy. Soc. **A130**, 367 (1931).

[21] For the experimental verification of such properties of hydrogen see Bonhoeffer and Harteck, Sitz Preuss. Akad. Wiss., Berlin, 103–108 (1929); Zeits. f. phys. Chem. **B4**, 113–141 (1929). Also A. Eucken, Naturwiss. **17**, 182 (1929).

crystal. The reader is referred to Appendix I for a detailed examination of the wave functions of crystals, and for a more rigorous derivation of the partition function of a mixed crystal than that which we shall present in this chapter.

Let N be the number of molecules of para-hydrogen in the gas and let N' be the number of molecules of ortho-hydrogen in the gas. Let P and P' be the numbers of molecules of the two sorts in the crystalline phase. The partition function for the normal modes of vibration of a mixed crystal containing in all L molecules of both sorts of hydrogen is of the form $[\kappa(z)]^L$, no matter what the ratio P/P' nor how the different types are arranged;[22] and we suppose that the rotational partition functions for the molecules, both in the crystal and in the gas (we defer until later an analysis of this assumption) are for the para-hydrogen

$$f(z) = \sum_{j=0,2,4,\cdots}^{\infty}(2j + 1)z^{j(j+1)\epsilon}$$

and for the ortho-hydrogen

$$f'(z) = \sum_{j=1,3,5,\cdots}^{\infty}(2j + 1)z^{j(j+1)\epsilon}, \tag{3.10}$$

where $\epsilon = h^2/(8\pi^2 I)$, h being Planck's constant and I the moment of inertia of the molecule. The normal modes of vibration of the crystal contribute to the total number of accessible states of the whole assembly a factor equal to the coefficient of z^Q in $[\kappa(z)]^{P+P'}$, when the total energy of the normal modes of vibration of the crystal is Q. We take as the standard reference state of zero energy a state in which all the molecules are condensed in the crystalline phase, at the absolute zero, and in which the molecules are in their lowest electronic and nuclear vibrational states, and are free from nuclear rotation. This last specification means that our standard state is not a possible eigenstate if ortho-molecules are present; but it will suffice as a zero of energy notwithstanding.

We must now obtain an expression for the factor, contributed to the total number of accessible states, by the molecular rotations in the crystal. Consider first, for simplicity, a "crystal" made up of three similar molecules arranged in any manner among the lattice points a, b, c. Two of the molecules are to have rotational wave functions of class A, and the other of class B. There is only one independent wave function of class A, but class B has two linearly independent wave functions B^1 and B^2. Then, if we neglect oscillations, the possible linearly independent wave functions for the crystal, symmetrical in all of the molecules, are to a first approximation the permanents

$$\left\| \begin{matrix} A_a(1), & A_a(2), & A_a(3) \\ A_b(1), & A_b(2), & A_b(3) \\ B_c^1(1), & B_c^1(2), & B_c^1(3) \end{matrix} \right\|,$$

$$\left\| \begin{matrix} A_a(1) \\ A_b(1) \\ B_c^2(1) \end{matrix} \right\|, \quad \left\| \begin{matrix} A_a(1) \\ B_b^1(1) \\ A_c(1) \end{matrix} \right\|, \quad \left\| \begin{matrix} A_a(1) \\ B_b^2(1) \\ A_c(1) \end{matrix} \right\|, \quad \left\| \begin{matrix} B_a^1(1) \\ A_b(1) \\ A_c(1) \end{matrix} \right\|, \quad \left\| \begin{matrix} B_a^2(1) \\ A_b(1) \\ A_c(1) \end{matrix} \right\|;$$

---

[22] Since the masses are the same. See Appendix I.

here for instance $B_c{}^1(2)$ means the first rotational wave function of class B for the second molecule associated with the lattice point c. We have written explicitly only the first columns of the permanents for the last five wave functions. In this enumeration we have made the complete wave function symmetrical in all the molecules 1, 2, 3, and are therefore allowing for complete interchanges of molecules. If however A and B refer to para- and ortho-states, respectively, then in the restricted assembly the individual wave functions of molecules 1 and 2 must remain of class A; and those of molecule 3 of class B. The possible states are then represented by

$$\begin{Vmatrix} A_a(1) \\ A_b(1) \end{Vmatrix} B_c{}^1(3), \quad \begin{Vmatrix} A_a(1) \\ A_b(1) \end{Vmatrix} B_c{}^2(3), \quad \begin{Vmatrix} A_a(1) \\ A_c(1) \end{Vmatrix} B_b{}^1(3)$$

$$\begin{Vmatrix} A_a(1) \\ A_c(1) \end{Vmatrix} B_b{}^2(3), \quad \begin{Vmatrix} A_b(1) \\ A_c(1) \end{Vmatrix} B_a{}^1(3), \quad \begin{Vmatrix} A_b(1) \\ A_c(1) \end{Vmatrix} B_a{}^2(3).$$

We observe that in both enumerations the number of wave functions and therefore the number of distinct accessible states is

$$1^2 2^1 3!/(2!1!) = 6.$$

The identity of these enumerations is another aspect of the lemma of §2.11.

We see at once by generalizing this example that the number of accessible states of the assembly contains as a factor

$$\rho^P \rho'^{P'} (P + P')!/(P!P'!)$$

when the P molecules have one set of wave functions ρ in number and the P' molecules another different set ρ' in number. If these sets are degenerate, these states possess rotational or orientational energy $\rho\epsilon + \rho'\epsilon' = S$, say. If instead of supposing that each set is degenerate we merely restrict the total energy of this type to be S, and if

$$f(z) = \sum \rho z^{\epsilon}, \quad f'(z) = \sum \rho' z^{\epsilon'}$$

are partition functions for the sets of states of the two types of molecule in the crystal, then by a further generalization of the same type we see that the total factor in the number of accessible states due to these possibilities of rotation and orientation is the coefficient of z^S in

$$[f(z)]^P [f'(z)]^{P'} (P + P')!/(P!P'!).$$

If we repeat this argument, after specifying that the total energy $Q+S$ of the crystal, made up of P and P' molecules of the two sorts respectively, is U, we see that the crystal possesses a number of accessible states equal to the coefficient of z^U in

$$[f(z)]^P [f'(z)]^{P'} [\kappa(z)]^{P+P'} (P + P')!/(P!P'!)$$

in complete agreement with the results found more rigorously in §A1.6 of Appendix I.

The vapor, if its energy is F, has a number of accessible states equal to the coefficient of $x^N x'^{N'} z^F$ in

$$\Pi_j(1 - xz^{\epsilon_j})^{-1}\Pi_k(1 - x'z^{\epsilon_k'})^{-1},$$

where the Π's are taken over all the energy levels: The primed and unprimed letters refer as before to ortho- and para-hydrogen. Hence by the arguments of §2.2 the total number of linearly independent wave functions, symmetrical in all the molecules, capable of representing the entire assembly of energy E when there are N and N' molecules of the two sorts in the gas and $P = X - N$ and $P' = X' - N'$ molecules of the two sorts in the crystal, respectively, is the coefficient of $x^N x'^{N'} z^E$ in

$$[(P + P')!/(P!P'!)][f(z)]^P[f'(z)]^{P'}[\kappa(z)]^{P+P'}\Pi_j(1 - xz^{\epsilon_j})^{-1}\Pi_k(1 - x'z^{\epsilon_k'})^{-1}. \quad (A)$$

Hence this number of accessible states $C_{N,N'}$ is given by

$$C_{N,N'} = \left(\frac{1}{2\pi i}\right)^3 \frac{(P + P')!}{P!P'!} \int\!\!\int\!\!\int \left\{ \frac{dx dx' dz [f(z)]^P [f'(z)]^{P'} [\kappa(z)]^{P+P'}}{x^{N+1} x'^{N'+1} z^{E+1}} \right. \\ \left. \times \Pi_j(1 - xz^{\epsilon_j})^{-1}\Pi_k(1 - x'z^{\epsilon_k'})^{-1} \right\}, \tag{3.101}$$

where the integrals are taken along closed contours about the origins in the x, x' and z planes, within the regions in which (A) is holomorphic.

To evaluate these integrals we make use of the method of steepest descents,[23] as we did for the simpler case of a monatomic vapor in §2.2. We find that

$$C_{N,N'} = \frac{(P + P')![f(\theta)]^P[f'(\theta)]^{P'}[\kappa(\theta)]^{P+P'}}{(2\pi)^{3/2}P!P'!\xi^N\xi'^{N'}\theta^E} \\ \times \Pi_j(1 - \xi\theta^{\epsilon_j})^{-1}\Pi_k(1 - \xi'\theta^{\epsilon_k'})^{-1}\left[\frac{1}{V^{3/2}} J_0^{-1/2} + O\left(\frac{1}{V^{5/2}}\right)\right] \tag{3.102}$$

where ξ, ξ' and θ are the unique positive roots of

$$\xi \frac{\partial}{\partial \xi} \sum_j \log (1 - \xi\theta^{\epsilon_j})^{-1} = N \tag{3.103}$$

$$\xi' \frac{\partial}{\partial \xi'} \sum_k \log (1 - \xi'\theta^{\epsilon_k'})^{-1} = N' \tag{3.104}$$

and

$$\theta \frac{\partial}{\partial \theta} \sum_j \log (1 - \xi\theta^{\epsilon_j})^{-1} + \theta \frac{\partial}{\partial \theta} \sum_k \log (1 - \xi'\theta^{\epsilon_k'})^{-1} + P\theta \frac{\partial}{\partial \theta} \log f(\theta) \\ + P'\theta \frac{\partial}{\partial \theta} \log f'(\theta) + (P + P')\theta \frac{\partial}{\partial \theta} \log \kappa(\theta) = E. \tag{3.105}$$

---

[23] For a more complete discussion, see Appendix II.

Here V is the volume of the gas phase, and J_0 is a certain Jacobian determinant which varies only slowly with N and N', and which we may in fact treat as a constant in the following discussion. The parameters ξ, ξ' and θ correspond to the thermodynamic partial potentials and to the temperature, respectively. In fact, $\theta = e^{-1/kT}$ where k is Boltzmann's constant.

If we wish to find the total number of linearly independent wave functions C capable of representing the assembly when we know merely the total energy E and the total numbers of particles of the two sorts X and X', we must sum $C_{N,N'}$ over all values of N and N' from 0 to X and from 0 to X', respectively, thus:

$$C = \sum_{N=0}^{X} \sum_{N'=0}^{X'} C_{N,N'}. \tag{3.106}$$

We wish to find the mean values $\overline{N}$ and $\overline{N}'$ of N and N', respectively, defined by the equations

$$C\overline{N} = \sum_{N=0}^{X} \sum_{N'=0}^{X'} N C_{N,N'}$$

and

$$C\overline{N}' = \sum_{N=0}^{X} \sum_{N'=0}^{X'} N' C_{N,N'}. \tag{3.107}$$

We proceed as in §2.2; the values N^* of N and N'^* of N' for which $C_{N,N'}$ is a maximum are obtained by equating the partial derivatives of $\log C_{N,N'}$ with respect to N and N' to 0. We use Stirling's asymptotic formula $\log P! = P \log P - P$ for approximating with sufficient accuracy to the factorials in the right-hand member of equation (3.102), and we may treat the bracketted expression involving $J_0^{-1/2}$ as a constant. We find, using the relations (3.103), (3.104) and (3.105) that $C_{N,N'}$ is a maximum when

$$\xi = \frac{P}{P+P'} \frac{1}{\kappa(\theta) f(\theta)}, \tag{3.108}$$

$$\xi' = \frac{P'}{P+P'} \frac{1}{\kappa(\theta) f'(\theta)}. \tag{3.109}$$

These two equations, considered simultaneously with the three equations (3.103), (3.104) and (3.105) serve to define N^* and N'^*.

It is possible to show, by a slight generalization of the argument employed in §2.2, that $C_{N,N'}$ diminishes with extreme rapidity from its maximum value C_{N^*,N'^*} as $|N-N^*|/N^*$ or $|N'-N'^*|/N'^*$ increases from zero, provided that N^* and N'^* are large. Accordingly, the significant contributions to the sums (3.106) and (3.107) come only from terms for which N is very nearly equal to N^* and N' is very nearly equal to N'^*. Hence $\overline{N} = N^*$ and $\overline{N}' = N'^*$ with great accuracy when N^* and N'^* are large. It follows that we can obtain $\overline{N}$ and $\overline{N}'$ by inserting in Eqs. (3.103) and (3.104) the values of ξ and ξ' given by (3.108) and (3.109).

We have, because of our choice of the zero of energy, $\kappa(0)=1$, and therefore $\kappa(\theta)\geqq 1$. It follows from the dicussion of R. H. Fowler[24] that we may replace the expression (3.103) for $\overline{N}$ by[25]

$$\overline{N}=\xi\frac{\partial}{\partial\xi}\,\frac{(2\pi mkT)^{3/2}Ve^{-\chi/kT}}{h^3}\sum_{n=1}^{\infty}\frac{\xi^n e^{-(n-1)\chi/kT}}{n^{5/2}}\sum_{j=0,2,4,\cdots}^{\infty}(2j+1)e^{-nj(j+1)\epsilon/kT} \quad (3.14)$$

where m is the mass of a molecule of hydrogen and k is Boltzmann's constant; since it follows from (3.108) that $\xi<1$. χ is the work which must be done to remove a molecule from the zero of energy defined above and place it at rest, at infinity, in its lowest electronic and vibrational state, and in a state without nuclear rotation. Further, although ξ' may be enormously greater than unity, it follows from (3.109) that $\xi'\theta^{\epsilon k'}$ is always less than unity; so that the expansion of the logarithms in series, and the subsequent use of Fowler's discussion, is valid for this case also. Hence

$$\begin{aligned}\overline{N}' &= \xi'\frac{\partial}{\partial\xi'}\,\frac{(2\pi mkT)^{3/2}Ve^{-\chi/kT}}{h^3} \\ &\quad\times\sum_{n=1}^{\infty}\frac{\xi'^n e^{-(n-1)\chi/kT}}{n^{5/2}}\sum_{j=1,3,5,\cdots}^{\infty}3(2j+1)e^{-nj(j+1)\epsilon/kT}.\end{aligned} \quad (3.141)$$

It remains to determine the ordinary temperature ratio of para- to ortho-hydrogen, which is the value of X/X' to be used in applications of these formulae. For this purpose we have merely to consider the equilibrium distribution of hydrogen molecules between the sets of states enumerated by

$$f(z) = \sum_{j=0,2,4,\cdots}^{\infty}(2j+1)z^{j(j+1)\epsilon} \qquad \text{(para-)},$$

and

$$f'(z) = 3\sum_{j=1,3,5,\cdots}^{\infty}(2j+1)z^{j(j+1)\epsilon} \qquad \text{(ortho-)}.$$

This is an ordinary problem of *classical* gas theory, the complete partition function for the rotational and orientational states of a single molecule when ortho-para transitions can occur being $F(z)=f(z)+f'(z)$. At temperature T therefore the long-time equilibrium ratio is given by

$$\begin{aligned}\frac{\text{para-}}{\text{ortho-}} &= \frac{1}{3}\,\frac{\displaystyle\sum_{j=0,2,4,\cdots}^{\infty}(2j+1)e^{-j(j+1)\epsilon/kT}}{\displaystyle\sum_{j=1,3,5,\cdots}^{\infty}(2j+1)e^{-j(j+1)\epsilon/kT}}, \\ &\sim \tfrac{1}{3} \qquad (T\to\infty).\end{aligned}$$

---

[24] R. H. Fowler, *Statistical Mechanics*, pp. 535, 536.

[25] In Sterne's paper, reference 20, he carelessly omitted the factors involving χ from the equations corresponding to (3.14) and (3.141); so that the chemical constant found for hydrogen at very low temperatures was too large by 0.02. Sterne corrected this mistake in a subsequent paper: Proc. Roy. Soc. **A133**, 303 (1931).

For our purposes ordinary temperatures, 300°K and above, are infinite and we have

$$X' = 3X.$$

§3.2. The vapor pressure constant of hydrogen at low temperatures

It is possible to show[26] from the results of the last section that the ratio of ortho-hydrogen molecules to para-hydrogen molecules in the crystal will be, when the system is in equilibrium, very nearly 3:1. Hence, in accordance with (3.108) and (3.109) we have $\xi = 1/[4f(\theta)\kappa(\theta)]$ and $\xi' = 3/[4f'(\theta)\kappa(\theta)]$. It follows from these results and from Eqs. (3.14) and (3.141), with sufficient accuracy when T is small, that

$$\overline{N} + \overline{N}' = \frac{G(T)}{K(T)} \sum_{n=1}^{\infty} \frac{1 + 3^n/9^{n-1}}{4^n n^{3/2}[K(T)e^{\chi/kT}]^{n-1}} \tag{3.20}$$

where

$$G(T) = \frac{(2\pi mkT)^{3/2} V e^{-\chi/kT}}{h^3},$$

the partition function for the translatory motion in the gas, and $K(T) = \kappa(\theta)$. For hydrogen at 17°K, the midpoint of Eucken's range at low temperatures,[27] we find from thermal data[28] that $K(17°) = 1.23$, approximately; and also that $e^{\chi/kT}$ is roughly 225. Using these values in Eq. (3.20) we find that

$$\overline{N} + \overline{N}' = G(T)/K(T) \tag{3.21}$$

very nearly. For hydrogen at these very low temperatures $(C_p)_0 = 5R/2$, where R is the gas constant, and $(C_p)_1 = 0$. We make use of the relation

$$pV = (\overline{N} + \overline{N}')kT$$

and of the corollary to the lemma which we are about to prove, from which it follows that at these low temperatures in the case of hydrogen

$$\log K(T) = \int_0^T \frac{dT'}{RT'^2} \int_0^{T'} (C_p)_{\text{sol}}\, dT''.$$

Hence, at these very low temperatures,

$$\log p = -\frac{\chi}{kT} + \frac{5}{2}\log T - \int_0^T \frac{dT'}{RT'^2}\int_0^{T'} (C_p)_{\text{sol}}\, dT'' + \log\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}.$$

---

[26] Sterne, Proc. Roy. Soc. **A130**, 367 (1931). With the correction of the preceding note, the ratio becomes almost precisely 3:1.

[27] Eucken, Zeits. f. Physik **29**, 1 (1924).

[28] Simon, Zeits. f. Physik **15**, 312 (1923).

Accordingly we find for the vapor pressure constant of hydrogen at these very low temperatures the value

$$i' = -1.13$$

in fair agreement with Eucken's experimental value

$$i' = -1.09 \pm 0.02.$$

It will be observed that at these temperatures i' has the same value as it would have if molecules of hydrogen were ideal structureless *atoms* of mass 2.015.

§3.3

Lemma: Let the state of zero energy of a gram molecule of crystal be defined as its state at the absolute zero of temperature, when it is subjected to zero external pressure. Let the exact partition function for the entire crystal, $H[V, T]$, *be a function only of the volume* V *and temperature* T *of the crystal. Let the specific heat of the whole crystal* C_p *be measured in any manner at all, such that at each stage of the process of measurement the pressure* p *acting on the crystal is a definite function* $p(T)$ *of the temperature, provided that it is zero when* $T=0$. *Then*

$$k \log \frac{H[V(T), T]}{H[V(0), 0]} = \int_0^T \frac{dT'}{T'^2} \int_0^{T'} C_p dT'' + \frac{1}{T} \int_0^T p(T')V'(T')dT',$$

where $V(T)$, *a function of the temperature, is the volume which the crystal must have at the temperature* T *if the pressure acting on it is* $p(T)$.

Proof: The energy of the crystal at a temperature T is

$$\begin{aligned} E[V(T), T] &= \int_0^T C_p dT' - \int_0^T p(T')d\,V(T') \\ &= kT^2 \frac{\partial}{\partial T} \log H[V(T), T] \end{aligned}$$

by the principles of statistical mechanics. Here $\partial/\partial T$ operates only on T, not on $V(T)$. Further,

$$(d/dT)H[V, T] = (\partial/\partial T) \log H[V, T] + V'(T)(\partial/\partial V) \log H[V, T];$$

and by the principles of statistical mechanics

$$p(T) = kT(\partial/\partial V) \log H(V, T).$$

Hence

$$\begin{aligned} k \log \frac{H[V(T), T]}{H[V(0), 0]} &= \int_0^T \frac{dT'}{T'^2} \int_0^{T'} [C_p - p(T'')V'(T'')]dT'' \\ &+ \int_0^T \frac{p(T')}{T'} V'(T')dT', \end{aligned}$$

and by a simple reduction the theorem follows at once.

A simple consequence of this theorem, and one which will be very useful, is that when the measurements are so carried out that $p(T)$ is always zero, then

$$k \log \frac{H[V(T),\, T]}{H[V(0),\, 0]} = \int_0^T \frac{dT'}{T'^2} \int_0^{T'} C_p dT''. \tag{3.31}$$

The reader can readily verify that if the measurements are not carried out at zero pressure, but at the vapor pressure of the crystal, which in practice is small, the errors introduced by the use of Eq. (3.31) with $(C_p)_{\text{sol}}$ instead of C_p will be trivial. A useful corollary of the lemma is:

Corollary: Let the partition function for a gram molecule of crystal be of the form $\{K(T)[f_A(T)]^a\, [f_B(T)]^b \cdots\}^P$ *where* P *is the number of molecules in the crystal. In this approximate expression,* $K(T)$ *is the partition function per molecule for normal modes of oscillation, and* $f_A(T)$, $f_B(T)$, *etc., are partition functions for the quantum states of individual molecules of sorts* A, B, *etc., in the crystal. The reference state of zero energy need not, here, be a possible state of the crystal; but is such that* $K(0)=1$. *The eigenstates of lowest energies will in general have statistical weights* ${}_A\omega_0$, ${}_B\omega_0$, $\cdots$, *and energies* ${}_A\epsilon_0$, ${}_B\epsilon_0$, $\cdots$, *respectively. Then*

$$\int_0^T \frac{dT'}{RT'^2} \int_0^{T'} (C_p)_{\text{sol}}\, dT'' = \log \{K(T)[f_A(T)]^a [b_B(T)]^b \cdots\}$$

$$+ a\frac{{}_A\epsilon_0}{kT} + b\frac{{}_B\epsilon_0}{kT} + \cdots - a \log {}_A\omega_0 - b \log {}_B\omega_0 - \cdots,$$

where $(C_p)_{\text{sol}}$ *is the "specific heat at constant pressure" of the crystal as usually measured, i.e., with* $p(T)$ *equal to the vapor pressure, and* R *is the gas constant. We call* $K(T)[f_A(T)]^a \cdots$, *the partition function of the crystal "per molecule."*

Proof: In order to use the lemma in proving the corollary, we must reduce out partition function to a form corresponding to the same state of zero energy as that defined in the lemma. We can accomplish this by multiplying $f_A(T)$ by $\exp({}_A\epsilon_0/kT)$, $f_B(T)$ by $\exp({}_B\epsilon_0/kT)$, etc., so as to obtain new functions $f_A'(T)$, $f_B'(T)$, etc., where

$$f_A'(T) = eA^{\epsilon_0} \sum_r {}_A\omega_r e^{-A\epsilon_0/kT}$$

$$= {}_A\omega_0 + {}_A\omega_1 e^{-(A^{\epsilon_1} - A^{\epsilon_0})/kT} + \cdots$$

with similar expressions for $f_B'(T)$, etc. Then the expression $\{K(T)[f_A'(T)]^a\, [f_B'(T)]^b \cdots\}^P$ denotes a partition function for the crystal corresponding to the same state of zero energy as that used in the lemma, and we may set the above expression equal to the $H[V,\, T]$ in Eq. (3.31). We find then that

$$Pk \log \frac{\{K(T)[f_A'(T)]^a [f_B'(T)]^b \cdots\}}{\{K(0)[f_A'(0)]^a [f_B'(0)]^b \cdots\}} = \int_0^T \frac{dT'}{T'^2} \int_0^{T'} (C_p)_{\text{sol}}\, dT''$$

very nearly, and the corollary follows at once if we remember that $K(0)=1$, and note that $f_A'(0) = {}_A\omega_0$, $f_B'(0) = {}_B\omega_0$, etc., and that $Pk = R$.

§3.4. The vapor pressure constant of hydrogen at ordinary temperatures

To obtain the vapor pressure constant of hydrogen at ordinary temperatures, when $(C_p)_0$ is equal to $7R/2$ and $(C_p)_1$ is zero, we proceed as follows. At ordinary temperatures rotations become significant in the gas, but vibrations are still unimportant. At ordinary temperatures we may set, with sufficient accuracy for small values of n,

$$\sum_{j=0,2,4,\cdots}^{\infty} (2j+1)e^{-nj(j+1)\epsilon/kT} = kT/(2\epsilon n)$$

and

$$\sum_{j=1,3,5,\cdots}^{\infty} 3(2j+1)e^{-nj(j+1)\epsilon/kT} = 3kT/(2\epsilon n). \tag{3.40}$$

Substituting these values in (3.14) and (3.141) we find, if we replace ξ by $1/[4f(T)K(T)]$ and ξ' by $3/[4f'(T)K(T)]$, that

$$\overline{N} = G(T)\sum_{n=1}^{\infty}\frac{kTe^{-(n-1)\chi/kT}}{2\epsilon n^{5/2}[4f(T)K(T)]^n}$$

and

$$\overline{N}' = G(T)\sum_{n=1}^{\infty}\frac{3kTe^{-(n-1)\chi/kT}}{2\epsilon n^{5/2}}\left[\frac{3}{4f'(T)K(T)}\right]^n.$$

Using Eqs. 3.40 with $n=1$ to evaluate $f(T)$ and $f'(T)$ we obtain

$$\overline{N}+\overline{N}' = \frac{G(T)}{K(T)}\sum_{n=1}^{\infty}\frac{1}{n^{5/2}}\left[\frac{\epsilon e^{-\chi/kT}}{2kTK(T)}\right]^{n-1}. \tag{3.401}$$

At ordinary temperatures the sum is very nearly equal to unity. The denominator $K(T)$ is not yet the complete partition function per molecule for the crystalline phase for all kinds of energy. The required function is $K(T)[f(T)]^{1/4}[f'(T)]^{3/4}$, to which the corollary of the lemma of §3.3 applies. Since to our approximation at these temperatures

$$[f(T)]^{1/4}[f'(T)]^{3/4} = 3^{3/4}kT/2\epsilon$$

we can write

$$\overline{N}+\overline{N}' = \frac{3^{3/4}G(T)\ (kT/2\epsilon)}{K(T)[f(T)]^{1/4}[f'(T)]^{3/4}}, \tag{3.41}$$

and apply the lemma. We therefore find that for hydrogen for ordinary temperatures

$$i = \log\left[(2\pi m)^{3/2}k^{7/2}8\pi^2 I/h^5\right] - \tfrac{3}{4}\log 3 - \log 2$$

and so

$$i' = -3.72.$$

Eucken's published value is $i' = -3.68 \pm 0.03$, and this is in agreement with our result.

§3.5. The rotation of hydrogen molecules in crystalline hydrogen

We have assumed in the above discussion that the molecules of hydrogen in the crystals possess the same rotational partition functions that they have in the gas. Now they can have the same partition functions only if they can rotate freely in the crystal, and also possess the same moment of inertia that they have in the gas. It is by no means obvious *a priori* that molecules in general are able to rotate in crystals. It appears from the theoretical investigations of L. Pauling[29] that in some crystals molecules cannot rotate at all, and in some can rotate in an irregular fashion corresponding to wave functions intermediate between those for pure rotation and for pure oscillation; but that in hydrogen the molecules can really rotate quite freely, in all probability. In fact, the reasonable nature of the results recorded here is itself fairly good evidence for the ability of the molecules of hydrogen to rotate quite freely in the crystal.

If there were a change in the energy levels of the molecules when they condensed from the gaseous phase on to the crystal, we might expect the ratio of the number of ortho-hydrogen to the number of para-hydrogen molecules in the crystal to differ, when the system was in equilibrium, from the ratio of 3:1. This effect has been investigated mathematically,[26] assuming that the difference in energy is caused by a change in the moment of inertia when the molecules condense on to the crystal. But changes in the moment of inertia are not the only ways in which the energy levels can come to be different in the crystal. The presence of fields, even of small amounts, tending to give the molecular axes preferred directions of orientation would cause changes of energy to occur. The changes of energy could be measured if the Raman spectrum of crystalline hydrogen were investigated. Unfortunately, this has not been done. However, J. C. McLennan and J. H. McLeod state[30] that in the case of liquid hydrogen Raman wave numbers 354 cm^{-1} and 588 cm^{-1} corresponding to the transitions $(j=0)\rightarrow(j=2)$, and $(j=1)\rightarrow(j=3)$, respectively, were found to occur. These are to be compared with the wave numbers 347 cm^{-1} and 578 cm^{-1}, respectively, obtained from band spectra. The change in the energy levels would thus seem to be small when hydrogen molecules condense into the *liquid* phase.

CHAPTER IV

THE SYMMETRIC SPHERICAL OSCILLATOR AND THE ROTATIONAL MOTION OF MOLECULES IN CRYSTALS. THE PARTITION FUNCTIONS FOR FREE MOLECULES

§4.1. Introduction

Before proceeding to investigate the vapor pressure constant of chlorine, it would be perhaps advisable to investigate the nature of the quantum states of molecules in crystals. We obtained a satisfactory theory of the vapor pressure of hydrogen by supposing the molecules to be capable of rotation when

---

[29] Pauling, Phys. Rev. **36**, 430 (1930).

[30] McLennan and McLeod, Nature **123**, 160 (1929).

in the crystalline phase. We shall find when investigating chlorine that in all probability the molecules in crystalline chlorine are incapable of free rotation, and possess wave functions corresponding to states of spherical oscillation about possible orientations of stable equilibrium. We could proceed to consider chlorine by the use of Pauling's analysis of the motions of molecules in crystals[31] if we wished, at this point. But Pauling derived his criteria for distinguishing between the cases of "rotation" and "oscillation" by approximate methods. It has been found possible[32] to present a somewhat more accurate account of the motions of molecules made up of two atoms of the same sort, in axially symmetric fields of force. We present the results of this investigation here.

§4.2. The symmetric spherical oscillator

We imagine a molecule of type X_2 free to rotate in a field of force of axial symmetry. Symmetry considerations show that if a certain orientation is one of equilibrium, then the orientation obtained by reversing the molecule end for end will also be one of equilibrium; and we see also, if the orientation of the molecule is specified by the coordinates θ, ϕ (the axis of θ being the axis of symmetry), that the potential function $V(\theta)$ of the homopolar molecule must be symmetric about the equatorial circle $\theta = \frac{1}{2}\pi$. We suppose that our molecule is free from axial spin. If $V(\theta)$ can be expanded in a Fourier series made up of cosines of even multiples of θ—as it can be of course if it can be expanded in a Fourier series at all—then a good first approximation will be obtained by taking only the first two terms of this series; higher terms can be taken account of later, if desired, by a perturbation method. We therefore consider, with Pauling, the potential function

$$V = V_0(1 - \cos 2\theta). \tag{4.20}$$

We desire to find the eigenvalues of the energy and the corresponding solutions of Schrödinger's equation for the rotational motion,

$$\nabla^2\psi + (8\pi^2 I/h^2)(W - V)\psi = 0. \tag{4.21}$$

The solutions are to be in the form

$$\psi = F(\theta)e^{mi\phi} \tag{4.23}$$

and are subject to the conditions that ψ must be single-valued, and that $|\psi|$ must be bounded, over the surface of the θ, ϕ sphere. W is the total energy of the molecule as far as rotations about its center of mass are concerned.

We see at once that m must be an integer which can be positive, zero, or negative in sign. Make the substitutions (4.20), (4.23), and

$$\left.\begin{aligned} x &= \cos\theta \\ \mu &= (W - 2V_0)8\pi^2 I/h^2 \\ \lambda^2 &= 16\pi^2 I V_0/h^2 \end{aligned}\right\} \tag{4.235}$$

---

[31] Pauling, Phys. Rev. **36,** 430 (1930).

[32] Sterne, Proc. Roy. Soc. **A130,** 551 (1931).

in Eq. (4.21). We obtain

$$(1 - x^2)F'' - 2xF' + [\mu + \lambda^2 x^2 - m^2/(1 - x^2)]F = 0. \tag{4.24}$$

Solutions are desired which are finite within the interval $-1 \leqq x \leqq 1$. This equation has been considered by several writers, and by A. H. Wilson in particular.[33] Corresponding to any value of λ there exist certain eigenvalues of μ for which our conditions will be fulfilled. Make the substitution

$$F = (1 - x^2)^{M/2} y$$

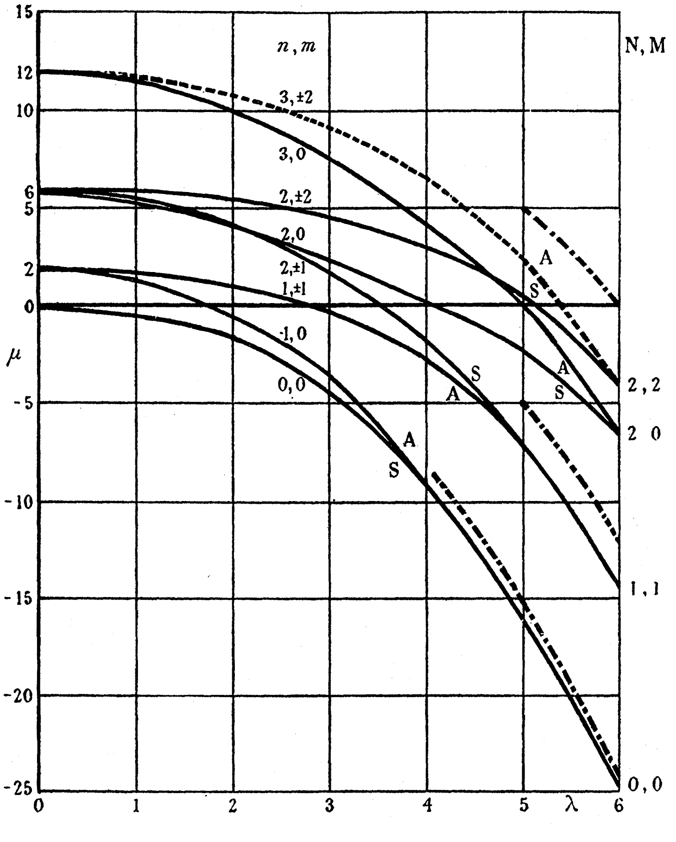

Fig. 1. The seven lowest energy levels of the symmetric spherical oscillator. (Reproduced by kind permission of the Royal Society.)

where $M = |m|$. Then our desired solutions are of two different types. We can represent y by a series of even powers of x, or by a series of odd powers of x. The two types refer in general to different values of μ. Values of μ have been calculated[34] for the first seven eigenstates of the symmetric spherical oscillator, for integral values of λ up to and including six. It was not practicable to calculate values of μ corresponding to large values of λ by that method.

[33] A. H. Wilson, Proc. Roy. Soc. **A118,** 628 (1928).

[34] Sterne, reference 32.

In Fig. 1, which is taken from Sterne's paper, are shown the eigenvalues of μ corresponding to values of λ up to six, for the lowest energy levels. The dotted curve $(3, \pm 2)$ is not accurate, and was drawn merely to complete the second vibrational level. If λ is zero, it is obvious that our Eq. (4.21) is merely that of the spatial rotator; and we find as we expect the corresponding values of μ. Accordingly, the curves may be numbered by the use of n and m, the quantum numbers of the spatial rotator from which they originate at the left-hand side of the diagram for small λ. The symmetry properties of the eigenstates will, of course, not alter when λ is increased, so that we may denote by A and by S the states which are antisymmetrical and symmetrical, respectively, in the reversal of the radius vector θ, ϕ end for end. The component of angular momentum about the axis $\theta=0$ will not change as λ is increased, so that m will remain a good quantum number. On the other hand, n loses its significance for large values of λ. We shall find that there will always be a degeneracy associated with non-zero values of M, corresponding to both positive and negative values of m; and for this reason we use M rather than m as the quantum number for values of λ greater than zero.

As pointed out above, this analysis does not tell us much about the behavior of the solutions for large values of λ. However, from Wilson's asymptotic expansion for μ we find that, for large λ,

$$W = h\nu_0(N+1) \tag{4.25}$$

very nearly, where

$$\nu_0 = (1/\pi)(V_0/I)^{1/2}$$

and

$$N = r + M.$$

Here r can be zero of any even positive integer. Thus when λ is large the molecule behaves rather like a plane oscillator. We find that corresponding to any value N_1, of N, in this case of large λ, there are $2(N_1+1)$ linearly independent wave functions; of these N_1+1 are symmetrical and N_1+1 are antisymmetrical in reversals of the radius vector end for end. The broken curves in Fig. 1 represent the asymptotic solutions which hold for large values of λ. The difference between the energies of those states corresponding to the same N is trivial when λ is large.

§4.3. The spherical oscillatory motion of molecules of type X_2, in $^1\Sigma$ states, in crystals

From here on our investigation is similar to Pauling's. He points out that the molecules can be said to rotate if the difference between the energies of the wave functions for a given N value is large compared with the difference between the energies of consecutive N levels, since the probability of reversals of the molecules end for end is then large; and that the molecule can be said to oscillate about positions of equilibrium if the difference between the energies of the wave functions for a given N is small compared with the difference between the energies of consecutive N levels. The transition between the two cases seems from an inspection of Fig. 1 to occur roughly along the axis $\mu=0$; which corresponds to $W=2V_0$. We might have anticipated this from the form of the potential function. We can obtain exactly the same criteria as Pauling's for distinguishing between the two cases, without difficulty; but it seems to us to be simpler to proceed as follows. For rotation to occur, we are to have $W>2V_0$; and regardless of the nature of the energy levels of the molecules, the molecules will not be likely, statistically, to possess this energy until the temperature T of the crystal becomes comparable with $2V_0/k$, where k is Boltzmann's constant. Therefore, roughly, rotation occurs if

$$T > 2V_0/k$$

and oscillation occurs if

$$T < 2V_0/k.$$

These criteria are exactly equivalent to Pauling's. Actually, the probability that a molecule will rotate is given roughly by

$$p = e^{-2V_0/kT}.$$

In order to make use of this analysis we must be able to find V_0. A rough value for this quantity[31] can be obtained from the observed heat capacity of the solid. If the molecules oscillate about equilibrium orientations the specific heat of the crystal per gram molecule would be given as a first approximation by the sum of a Debye function of parameter $\beta\nu$, corresponding to the translational oscillations, and twice an Einstein function of parameter $\beta\nu_0=h\nu_0/k$, where ν_0 is the characteristic frequency of equation (4.25). It is found that such a curve does not give a very close fit with observed heat capacities since the model is too greatly simplified; but the heat capacity curves do show that $\beta\nu$ and $\beta\nu_0$ are nearly the same for many substances. Hence a rough value for $\beta\nu$ and $\beta\nu_0$ can be obtained by taking three times the temperature at which the heat capacity reaches 5 calories per gram molecule per degree; that is, half the high-temperature value of the specific heat for five degrees of freedom.* V_0 is then given by $V_0=I(\nu_0\pi)^2$. It appears further[35] that for many substances the total heat change accompanying transitions and fusions is approximately equal to $V_0/2$.

If the field of force is not axially symmetrical, then probably the simplest method of investigating the behavior of a homopolar molecule is to consider the problem by a perturbation method, in which the unperturbed state is that of a plane oscillator having the potential function

$$V = ax^2 + by^2$$

and the energy levels

$$W = h\nu_a(N_1 + \tfrac{1}{2}) + h\nu_b(N_2 + \tfrac{1}{2})$$

---

* This procedure is based on the fact that an Einstein function reaches half its maximum value at the temperature $0.33\beta v$.

[35] Pauling, reference 31, Table I, columns 5 and 6.

where N_1 and N_2 can have any zero or positive integral values. But since, as before in the case of fields of axial symmetry, the lowest quantum state of the molecule would still be capable of representation by two wave functions, one symmetrical and the other antisymmetrical, in reversals of the radius vector end for end, the absence of axial symmetry in the orienting field will not introduce anything new into our analyses of vapor pressures.

It is possible that in certain crystals made up of molecules of the type which we are considering, there will be, not one axis of minimum potential energy, but several for the molecule we happen to be considering. If there are, for instance, three axes of minimum potential energy with all of the minima equal, then the lowest quantum state of the molecule considered would have for strong fields a statistical weight of 6; 3 of the linearly independent wave functions being symmetrical and 3 antisymmetrical in reversals of the radius vector end for end. Perturbation methods would probably suffice for an investigation of the general case where there are several axes of minimum potential energy for each molecule. The quantum mechanics of molecules of type X_2 in crystals deserves further consideration; but what we have said will suffice for our purposes in this article, except possibly for oxygen, which we shall consider separately. It should be borne in mind that the statistical weights of this chapter have been thus far merely the weights of the spherical oscillatory and rotational motions alone.

§4.4. The rotational motion of diatomic molecules of type XY in $^1\Sigma$ states in crystals

In this case the wave equation similar to Eq. (4.21) does not seem capable of simple precise treatment; accordingly we consider the nature of the quantum states of molecules like hydrogen chloride in the crystalline phase by perturbation methods. The transitional cases between oscillation and rotation are not likely to be met with in practice—either the molecules will be found to be capable of free rotation or else they will be found to oscillate about orientations of equilibrium. For in a crystal, all the molecules will experience nearly the same strength of fields (though not necessarily in the same direction); and if the molecules in close proximity to a given molecule are rotating, then it would seem from the properties of the wave functions that they could not manage to contribute a significant field to the region occupied by the given molecule, such as might cause it to oscillate. They would either all rotate or else all oscillate; and it is possible that in some cases at low temperatures they all would oscillate, and as the temperatures were raised all start rotating rather suddenly, at a rather definite transition point of the crystal.

If the molecules oscillate, then we can use a perturbation method to show that for a molecule of type XY with only one orientation of minimum potential energy (and, unlike molecules of type X_2, with a potential minimum in only one sense along this axis) the lowest quantum state will have a statistical weight of unity. With N axes of equal minimum potential energy, the lowest quantum state would have a statistical weight of N; but it is hard to see how there could be more than one orientation of minimum potential energy for a molecule of this type, since the potential energy should be a minimum when the axis of the molecule is pointing along the electric field which exists in the region occupied by the molecule.

§4.5. The rotational motion of molecules in states other than $^1\Sigma$ in crystals

We have hitherto considered only those molecules which were without axial spins. However, we shall later have to consider the behavior of nitric oxide, whose ground state in the free state is $^2\Pi$; i.e., a state in which the resultant electron spin is one half a quantum and in which there is a one quantum component of orbital electronic angular momentum about the line joining the nuclei. We shall therefore discuss this molecule briefly. The coupling for an NO molecule in the gas is that known as "Hund's case a." The total orbital angular momentum is not quantized, but that component in the direction of the line of nuclei is quantized, and is denoted by a quantum number Λ which is 1 for a Π state. It may be directed in either sense along the line of nuclei. The resultant electronic spin angular momentum has a quantized component in the direction of the line of nuclei with the quantum number $\frac{1}{2}$ in either sense. The resultant of these two components along the line of nuclei is called Ω, and forms with the angular momentum O a quantized resultant J^* which is the total angular momentum of the molecule; the z component of J^* is quantized. O is the resultant of the nuclear rotational angular momentum and the component normal to the line of nuclei of the electronic orbital angular momentum. In the ground state of the free NO molecule, a $^2\Pi_{1/2}$ state, $\Omega = J^* = \frac{1}{2}$. The lowest state of a free NO molecule has a statistical weight of 4 therefore, since the z component of Ω may be $\pm\frac{1}{2}$ and Ω may be directed in either sense along the line of nuclei. In the crystal, if the molecule oscillated the line of nuclei would be orientated, and the statistical weight of each molecule might be expected to be 2.

However, Johnston and Giauque[36] have measured calorimetrically the difference between the entropy of gaseous nitric oxide at 121.36°K and the entropy of nitric oxide in the crystalline phase at the absolute zero, and have obtained the result 43.0 E.U. per gram molecule. The value which they obtained from spectroscopic data for the entropy of the gas at 121.36°K, referred to a state in which the gas could be represented by only one[37] independent wave function, was 43.75 E.U. per gram molecule. The difference, 0.75 E.U. per gram molecule, is almost exactly $\frac{1}{2}R \log 2$. The difference could therefore be accounted for if, neglecting nuclear spins, each NO molecule has a statistical weight $2^{1/2}$ in the crystal lattice at these lowest temperatures; and this indicates that the molecules of NO are grouped in the crystal into units N_2O_2 each of which has a statistical weight 2. It is known that groups N_2O_2 exist in liquid nitric oxide, so that the result is reasonable. But the discussion of the previous paragraph would not have predicted it; and this

---

[36] J.A.C.S. **51,** 3194 (1929).

[37] If we disregard, as we may, nuclear spins. The precise theoretical meaning of this statement is made clear in Chapter IX.

shows that we should be cautious in trying to predict the statistical weights of molecules in crystals when their free ground states are not Σ.

We find similar difficulties for Σ states which are not $^1\Sigma$. The only such molecule which we shall consider is oxygen whose ground state is $^3\Sigma$. Here the component of electronic orbital angular momentum in the direction of the line of nuclei is zero; but the resultant electronic spin angular momentum is quantized with the quantum number unity. It is difficult to predict theoretically what the statistical weight of an O_2 molecule should be in the crystal lattice at the absolute zero; but Giauque and Johnston[38] have measured calorimetrically the difference between the entropy of gaseous oxygen at 90.13°K and the entropy of oxygen in the crystalline phase at the absolute zero, and have obtained the result 40.7 E.U. per gram molecule. This is in excellent agreement with the value 40.68 E.U. per gram molecule, obtained from spectroscopic data, for the entropy of the gas at 90.13°K, referred to a state in which the gas can be represented by only one independent wave function. We must therefore infer that at the absolute zero each molecule O_2 in the crystalline phase has a statistical weight unity. These inferences however for O_2 and NO are inferences from the observed entropy changes, practically equivalent to observed vapor pressures; we cannot yet deduce these *a priori* and to this extent a complete theory is still lacking.

§4.6. The statistical weights of the lowest quantum states of oscillating molecules in crystals

We are now in a position to tabulate the results of this chapter. We shall need them in subsequent chapters. In constructing this table we have assumed for the reasons mentioned previously in this chapter, that only one direction of minimum potential energy exists for each molecule; with two possible senses for molecules of the type X_2 and but one sense for molecules of type XY. For $^1\Sigma$ molecules of type X_2 with similar nuclei, there will by $(n+1)$ $(2n+1)$ linearly independent wave functions which are symmetrical in the nuclear spins alone, and $n(2n+1)$ which are antisymmetrical; the spin of the nuclei being n quanta of $h/2\pi$. But there is one wave function for spherical oscillations which is symmetrical in reversals of the radius vector

TABLE II. *Weights* $_r\omega_0$ *of the lowest states of oscillating molecules in crystals.*

Type	Para-X_2	Ortho-X_2	Heteronuclear X_2	XY
$^1\Sigma$	$n(2n+1)$	$(n+1)(2n+1)$	$2(2n_1+1)$ $\times(2n_2+1)$	$(2n_1+1)$ $\times(2n_2+1)$
$^3\Sigma$ (O_2)	$n(2n+1)$	$(n+1)(2n+1)$	$2(n_1+1)$ $\times(2n_2+1)$	—
$^2\Pi$ (NO)	—	—	—	$\sqrt{2}(2n_1+1)$ $\times(2n_2+1)$

---

[38] Giauque and Johnston, J.A.C.S. **51,** 2300 (1929).

end for end, and one antisymmetrical; hence the total number of linearly independent wave functions with the proper symmetry properties for the molecule is $(2n+1)^2$. (This is the same as the number one obtains at once by regarding the lattice as composed of atoms which are free from degeneracy in their lowest *electronic* states.)

The enumeration of these wave functions for an X_2 molecule is simple. Let the spin wave functions be $\psi_1^{(a)}, \cdots, \psi_j^{(a)}$ and $\psi_1^{(b)}, \cdots, \psi_j^{(b)}$, $(j=2n+1)$ for the atomic nuclei a and b, respectively. Suppose we have a pair of spin functions $\psi_s^{(a)}, \psi_s^{(b)}$. From these we can form one symmetrical combined function, $\psi_s^{(a)}\psi_s^{(b)}$ only, and there are j such pairs. Suppose on the other hand that we have a pair of spin functions $\psi_r^{(a)}, \psi_s^{(b)}$, $(s\neq r)$. Let us combine with these the pair $\psi_r^{(b)}, \psi_s^{(a)}$. We can form from these one symmetrical and one antisymmetrical combination, $\psi_r^{(a)}\psi_s^{(b)} \pm \psi_s^{(a)}\psi_r^{(b)}$ respectively, and there are $\frac{1}{2}j(j-1)$ such pairs. There are therefore $\frac{1}{2}j(j-1)+j=(n+1)(2n+1)$ symmetrical spin combinations and $\frac{1}{2}j(j-1)=n(2n+1)$ antisymmetrical spin combinations as stated.

For any molecule of type X_2 with different nuclei we can and must neglect all symmetry requirements for interchange of the nuclei. For if we interchange the nuclei we have *not* just interchanged electrons and protons since one nucleus has more component primary systems than the other. In a crystal therefore a heteronuclear molecule of type X_2 and state $^1\Sigma$ has a statistical weight $2(2n_1+1)(2n_2+1)$, being represented by that number of linearly independent wave functions. Here n_1 and n_2 are the spins of the two nuclei which may be unequal, and the factors $(2n_1+1)$ and $(2n_2+1)$ come from the possible independent orientations of each spin. The factor 2 comes from the possibility of end for end reversal which for a heteronuclear molecule gives new states. For molecules of type XY this factor 2 drops out since end for end reversal does not in general lead to a position of equilibrium.

§4.7. The weights of the rotational states and the partition functions for free diatomic molecules

The weights of the states of free diatomic molecules and their partition functions are fairly familiar. We have already used the most important special results for hydrogen in Chapter III, but for convenience we assemble here the principal results required for other molecules.

In the first place the translatory motion of the center of gravity of the molecule is strictly independent of its internal motion, so that any translational wave function can be combined with every wave function for the internal state. The partition function $F(T)$ therefore separates into two factors

$$F(T) = Q(T)M(T)$$

summed respectively over the translational and internal states. As we have already said in Chapter II, $Q(T)$ has the form

$$Q(T) = (2\pi mkT)^{3/2}Ve^{-\chi/kT}/h^3.$$

The states arising from the different orientations of nuclear spins are included in $M(T)$. Since nuclear spins are so lightly coupled to the rest of the molecule they are associated only with insignificant energy differences, small compared with kT at any attainable temperature. They produce therefore only an extra weight factor N for each internal state, obviously the same as the factors depending on n in Table II. Nuclear vibrations and rotations are however not strictly independent of each other though it is usually possible so to treat them. When they cannot be so treated $M(T)$ can and must be computed from the actual energies of the states by numerical summation; but we shall confine ourselves to the separable case. $M(T)$ then breaks up into

$$NV(T)R(T).$$

Here we include any weight factors from the electronic state of the molecule in $R(T)$, and can then so define χ in $Q(T)$ that $V(0)=1$. We shall be always concerned with molecules for which the rotational specific heat has its constant classical value, except for the case of hydrogen at very low temperatures, while the vibrational specific heat is variable. Then just as in §3.3

$$\log V(T) = \int_0^T \frac{dT'}{RT'^2}\int_0^{T'} (C_p)_1 dT''.$$

It will not be necessary to consider further the nature of $V(T)$.

The structure of $R(T)$ will depend on the nature of the normal electronic state of the molecule. For a rigid rotator without axial spin

$$R(T) = \sum_{j=0}^{\infty}(2j+1)e^{-j(j+1)h^2/(8\pi^2IkT)}$$
$$\sim \frac{8\pi^2IkT}{h^2}, \quad \left(kT \gg \frac{h^2}{8\pi^2I}\right).$$

For all the molecules we shall discuss, except hydrogen, the last condition is always fulfilled, and for every type of electronic state this value of $R(T)$ appears as a permanent factor to which others are added. We shall therefore write

$$M(T) = G8\pi^2IkT\cdot V(T)/h^2$$

and tabulate the values of G for various types of molecule.

For molecular states ${}^1\Sigma$ there is no angular momentum about the nuclear axis and no electron spin. The only contributions to G come therefore from N and from symmetry requirements (if any). G has thus the values $(2n_1+1)$ $(2n_2+1)$ for XY or heteronuclear X_2 molecules, but $\frac{1}{2}n(2n+1)$ and $\frac{1}{2}(n+1)$ $(2n+1)$ for para- and ortho-states of homonuclear X_2 molecules, since only half the terms of $R(T)$ occur for each type.

For a normal state ${}^3\Sigma$ such as that of oxygen the coupling between the electronic spin and the nuclear rotation is very weak and the rotational energy levels are not seriously split by the spin.[39] The actual splitting is

---

[39] Mulliken, Rev. Mod. Phys. **2**, 106 (1930). The splitting is of the order of 2 cm^{-1}; see Mulliken, Phys. Rev. **32**, 880 (1928).

small compared with kT for all temperatures at which the vapor pressure of oxygen is sensible, and one may neglect it. The only effect is then to insert a factor 3 in G.[40]

For a normal state $^2\Pi_{1/2}$ such as that of NO we must take into account the upper level $^2\Pi_{3/2}$, which is higher than the $^2\Pi_{1/2}$ level by 124 wave numbers in the free molecule. There is what is known as Λ-type doubling of the rotational levels and the quantum number for the total angular momentum, j, takes half odd integer values split into two groups.[41] The complete function $M(T)$ takes the form

$$M(T) = 2(2n_1 + 1)(2n_2 + 1)V(T)\left\{ \sum_{j=1/2,3/2,\cdots}^{\infty} (2j + 1)e^{-j(j+1)\epsilon/kT} \right.$$
$$\left. + \; e^{3\epsilon-124hc/kT} \sum_{j=3/2,5/2,\cdots}^{\infty} (2j + 1)e^{-j(j+1)\epsilon/kT} \right\}$$

where $\epsilon = h^2/(8\pi^2 I)$. The factors $(2n_1+1)(2n+2_1)$ are nuclear and the factor 2 comes from the two opposite senses relative to the nuclear rotation of the component of the total orbital angular momentum along the nuclear axis. It follows that when $kT \gg \epsilon$

$$M(T) \sim 2(1 + e^{-170/T})(2n_1 + 1)(2n_2 + 1)8\pi^2 IkT/h^2$$

so that

$$G = 2(1 + e^{-170/T})(2n_1 + 1)(2n_2 + 1).$$

We can now prepare Table III.

TABLE III. *The factors G for various types of free diatomic molecules.*

Type	Para-X_2	Ortho-X_2	Heteronuclear X_2	XY
$^1\Sigma$	$\frac{1}{2}n(2n+1)$	$\frac{1}{2}(n+1)(2n+1)$	$(2n_1+1)(2n_2+1)$	$(2n_1+1)(2n_2+1)$
$^3\Sigma$	$\frac{3}{2}n(2n+1)$	$\frac{3}{2}(n+1)(2n+1)$	$3(2n_1+1)(2n_2+1)$	$3(2n_1+1)(2n_2+1)$
$O_{16}O_{16}$	0	$\frac{3}{2}$	—	—
$^2\Pi_{\frac{1}{2},\,1\frac{1}{2}}$ (NO)	—	—	—	$2(2n_1+1)(2n_2+1)$ $\times(1+e^{-170/T})$

CHAPTER V

THE VAPOR PRESSURE CONSTANT OF CHLORINE[42]

§5.1. Introduction. The isotopic constitution of chlorine

We consider chlorine at ordinary temperatures to consist of three sorts[43] of molecules—namely $Cl_{35}Cl_{35}$, $Cl_{35}Cl_{37}$ and $Cl_{37}Cl_{37}$, which we shall denote

---

[40] $R(T)$ for oxygen has been examined more closely in this connection by Giauque and Johnston, J. A. C. S. **51**, 2300 (1929).

[41] Mulliken, Rev. Mod. Phys. **2**, 105, 111 (1930).

[42] "The Chemical Constant of Chlorine Vapor, and the Entropy of Crystalline Chlorine," T. E. Sterne, Proc. Roy. Soc. **A131**, 339 (1931).

[43] There is probably an isotope of mass 39 present in smaller quantities (G. Hettner and J. Böhme, Zeits. f. Physik **72**, 95 (1931)), but this does not invalidate the principles and conclusions of this chapter, which was written before the appearance of the above paper.

respectively by A, B and C. The work of Elliott[44] on the absorption band spectrum of chlorine makes it seem extremely likely that the Cl_{35} nucleus has a 5/2 quantum spin. Elliott was unable to determine the magnitude of the nuclear spin of Cl_{37}. In any case, however, we expect chlorine A and C at ordinary temperatures to consist of two sorts of chlorine; para-chlorine molecules represented by wave functions with even rotational quantum numbers and antisymmetrical in the nuclear spins, and ortho-chlorine molecules with wave functions with odd rotational quantum numbers and symmetrical in the nuclear spins. The normal state of a chlorine molecule appears to be $^1\Sigma$. If the 5/2 quantum spin is correct, then at ordinary temperatures, we should expect para- and ortho-chlorine to exist in chlorine gas in the ratio $n:(n+1)$ or 5:7.

One can determine by statistical mechanics[42] the composition of chlorine gas—the relative numbers of molecules of the different sorts present in the ordinary gas. This has never been measured experimentally; from the atomic weight of chlorine we can obtain directly merely the relative numbers of atoms of the two isotopes. The results found by statistical mechanics differ only trivially from the results obtained by the simple assumption that any atom of chlorine is equally likely to combine with any other atom present to form a molecule of chlorine. Further, it is found that the molecular composition of chlorine gas is independent of the magnitudes of the nuclear spins of Cl_{35} and Cl_{37}. Denoting by a, b and c numbers proportional to the numbers of molecules of sorts A, B and C, respectively, with $a+b+c=1$, it is found that $a=0.5779$, $b=0.3650$, $c=0.0571$.

In calculating the vapor pressure of chlorine crystals we shall carry through the analysis in a general fashion applicable not only to chlorine but also to other diatomic gases of type X_2 which may consist of two or more isotopes. We denote the maximum z component of nuclear angular momentum of Cl_{35} by $n_1h/2\pi$, and that of Cl_{37} by $n_2h/2\pi$. We shall find that the vapor pressure is independent of the values of n_1 and n_2; and we shall obtain a value for the vapor pressure constant of chlorine in moderately good agreement with experiment.

§5.2. The statistical mechanics of assemblies containing gaseous molecules of types para-X_1X_1, ortho-X_1X_1, X_1X_2, para-X_2X_2, and ortho-X_2X_2; as well as mixed crystals of these molecules

We denote the number of molecules of the r'th type in the crystal by P_r, and we suppose that the total number $X_r=P_r+N_r$ of molecules of the sort r in the assembly remains constant. We define a set of quantities D_r by the equations $D_r/X_r=\text{const.}$; $\Sigma D_r=1$; $r=1, 2, 3, 4, 5$. We consider that the molecules retain their identity in the crystal and form a molecular lattice, as they certainly do for iodine and probably for chlorine. There will be the usual Debye normal modes of oscillation of the crystal as a whole and in addition the molecules themselves can be in various quantum states of spherical oscillation or rotation. We may make our enumerations on the

---

[44] Elliott, Proc. Roy. Soc. A127, 638 (1930).

basis that a complete wave function for the crystal is a linear combination, symmetrical in all similar molecules, of functions of the form $\psi_m \psi_A \psi_B \psi_C$ to the first approximation; where ψ_m is a wave function representing a set of normal modes; ψ_A is a wave function representing a set of rotational or spherical oscillatory states of the molecules of sort A; and ψ_B and ψ_C are similar functions for molecules of sorts B and C respectively.[45] Then the normal modes contribute to the total number of linearly independent wave functions capable of representing the assembly a factor equal to the coefficient of z^Q in $[\kappa(z)]^P$; if the total energy of these modes is Q. Here $P=\Sigma P_r$. Let a partition function for a molecule of the r'th sort for rotations or spherical oscillations in the crystal be $f_r(z)$. Then these motions, if their total energy for the whole crystal is S, contribute to the total number of wave functions of the entire assembly a factor equal to the coefficient of z^S in

$$P!\prod_1^5 [f_r(z)]^{P_r} \Big/ \prod_1^5 P_r!.$$

Thus the whole crystal, if its energy is U, contributes a factor equal to the coefficient of z^U in

$$P![\kappa(z)]^P \prod_1^5 [f_r(z)]^P \Big/ \prod_1^5 P_r!.$$

The gas phase, if its total energy is F, contributes a factor equal to the coefficient of $z^F\Pi_1^5 x_r^{N_r}$ in $\Pi_1\, \Pi_2\, \Pi_3\, \Pi_4\, \Pi_5$ where

$$\Pi_r = \Pi_t(1 - x_r z^{r\epsilon_t})^{-1}.$$

Hence the whole assembly, if its energy is E, and if there are N_r molecules of sort r in the vapor and $P_r = X_r - N_r$ in the crystal phase,[46] can be represented by a number of linearly independent wave functions, symmetrical in all the pairs of similar molecules, equal to

$$C(N_1, N_2, N_3, N_4, N_5)$$
$$= \frac{P!}{\prod_1^5 P_r!}\left(\frac{1}{2\pi i}\right)\int\int\int\int\int\int \frac{dz \prod_1^5 dx_r \prod_1^5 [f_r(z)]^{P_r}[\kappa(z)]^P \Pi_1\Pi_2\Pi_3\Pi_4\Pi_5}{z^{E+1}\prod_1^5 x_r^{N_r+1}}. \quad (5.20)$$

At ordinary temperatures and pressures we may replace[47] the product of the Π's in the numerator of the integrand of the above expression by

$$\exp \sum_1^5 x_r F_r(z)$$

---

[45] See Appendix I.

[46] And if we allow all possible arrangements of the sets of molecules P_r among the lattice points. For an analysis of the legitimacy of this procedure, see Chapter VII. The sets of molecules are not constrained to condense on definite sets of lattice points.

[47] Fowler, *Statistical Mechanics*, pp. 534–537. This approximation being valid for H_2 at 20°K is *a fortiori* valid for greater temperatures and masses.

where $F_r(z)$ is the gaseous partition function for a molecule of the r'th sort. We thus use the classical approximation to the Einstein-Bose statistics as far as the molecules in the gas are concerned, but retain sufficient accuracy. By the usual methods we find for the mean values

$$\overline{N}_r = \xi_r F_r(\theta) \tag{5.21}$$

where

$$\xi_r = \overline{P}_r/[\overline{P} f_r(\theta)\kappa(\theta)]. \tag{5.22}$$

If nearly all of the molecules are in the crystal, then

$$\overline{P}_1:\overline{P}_2:\overline{P}_3:\overline{P}_4:\overline{P}_5 = D_1:D_2:D_3:D_4:D_5 \tag{5.23}$$

very nearly, and it follows from this equation and the two preceding ones that

$$\overline{N}_r = D_r F_r(\theta)/[f_r(\theta)\kappa(\theta)]. \tag{5.24}$$

Hence the average value of the total number of molecules in the vapor, $\overline{N}$, is given by

$$\overline{N} = \sum_1^5 \overline{N}_r = \sum_1^5 \frac{D_r F_r(\theta)}{f_r(\theta)\kappa(\theta)}\cdot \tag{5.25}$$

§5.3. The vapor pressure of chlorine

We have the relation $pV = \overline{N}kT$, where p is the pressure. It follows that the vapor pressure is given by

$$p = \sum_1^5 D_r p_r \tag{5.30}$$

where

$$p_r = F_r(\theta)kT/[Vf_r(\theta)\kappa(\theta)], \tag{5.31}$$

which is not the partial pressure of the r'th species, but is the vapor pressure of a crystal made up wholly of the r'th sort of molecules. We take as the zero of energy the state when all of the molecules are condensed in the crystalline phase at the absolute zero of temperature, when the lattice is subjected to zero pressure. In this state of zero energy the molecules, further, are to be in their lowest electronic and nuclear vibrational states, and are to have no spherical oscillation or rotation (this may not be a possible stationary state, but will suffice as a zero of energy). We suppose the partition functions $f_r(\theta)$ to be of the form

$$f_r(\theta) = \sum_{j=0}^{\infty} {}_r\omega_j \theta^{{}_r\epsilon_j}$$

where ${}_r\omega_j$ is the number of linearly independent wave functions capable of representing the j'th eigenstate of a molecule of the r'th species in the crystal, and ${}_r\epsilon_j$ is the energy of the state. We denote by C_r the specific heat per gram molecule at constant pressure of a crystal made up wholly of the r'th sort of molecules. Then it follows from the corollary to the lemma of §3.3 that

$$\int_0^T \frac{dT'}{RT'^2}\int_0^{T'} C_r dT'' = \log K(T)f_r(T) - \log {}_r\omega_0 + \frac{{}_r\epsilon_0}{kT}\cdot \tag{5.32}$$

It follows from this last relation, (5.31) and §4.7, that[48]

$$\log p_r = -\frac{\chi - {}_r\epsilon_0}{kT} + (7/2)\log T + \int_0^T \frac{dT'}{RT'^2}\int_0^{T'}[(C_p{}^r)_1 - C_r]dT'' + \log\frac{(2\pi m_r)^{3/2}k^{7/2}8\pi^2 I_r}{h^5} + \log\frac{G_r}{{}_r\omega_0}\cdot \tag{5.33}$$

Here $(C_p{}^r)_1$ is the vibrational specific heat of the vapor made up of molecules of the r'th sort, and G_r is the G which we studied in the last chapter, for the r'th variety. The quantity χ, which we have taken to be the same for all five sorts of molecules (the differences are trivial) is the work which must be done on a molecule in the crystal in the state of zero energy defined above, in order to remove it to a state of rest at infinity, in its lowest quantum state of electronic and nuclear vibrational motion, and with minimum energy of rotation.

It now becomes necessary to consider the nature of the energy levels of the molecules of chlorine in crystalline chlorine. We use the methods explained in the last chapter. The specific heat of crystalline chlorine becomes equal to 5 calories per gram molecule at approxmately 34°K.[49] By the first method mentioned in the last chapter we therefore find that V_0 is equal roughly to 5.2×10^{-13} ergs. Taking the heat of fusion[49] (there are no transitions below the melting point) to be 1615 calories per gram molecule, we find by the second method mentioned in the last chapter that V_0 is approximately 2.2×10^{-13} ergs. In either case, rotation ought not to occur at absolute temperatures lower than about 3000°K. Thus we may be fairly confident that chlorine molecules in crystalline chlorine, at temperatures at which the latter can exist, are not rotating; but are vibrating instead about orientations of equilibrium, with a set of energy levels much like those of a two-dimensional harmonic oscillator, separated by energy intervals of the order of 100°K in temperature units. X-ray analysis of the structure of iodine crystals[50] shows that the atoms are joined in pairs to form molecules by strong shared-electron-pair bonds, and the molecules are grouped together in such a way that the figure axis for each assumes a definite orientation. This is the equilibrium orientation, with the polar angle $\theta = 0$, say. The symmetry of the molecule requires that there is also another equilibrium orientation at $\theta = \pi$.[31] Unfortunately no x-ray analysis of the crystal structure of chlorine has yet been made, but it is plausible to guess that chlorine, when its structure is finally investigated experimentally, will be found to be similar to iodine in that each molecule is definitely orientated.

---

[48] To have included the partition functions for nuclear vibrations in the analysis of the complete partition function for the crystal would have complicated the demonstration without introducing any features new in principle.

[49] Eucken and Karwat, Zeits. f. phys. Chem. **112,** 478 (1924).

[50] P. M. Harris, E. Mack and F. C. Blake, J.A.C.S. **50,** 1583 (1928).

Assuming that the molecules of chlorine perform spherical oscillations, we can make use of the results given in §§4.6 and 4.7 to calculate the last terms in the five expressions (5.33). We find that in all cases the last term reduces to $\log\frac{1}{2}$. This is the value we should expect from the elementary argument that for molecules of type X_2 there are twice as many states as usual in the crystal owing to the end for end rotations. But it does not seem possible to establish this rigorously without detailed examination.

A detailed examination of the terms in Eqs. (5.32) and (5.33) shows that the different p_r's differ by only about one part in seven from each other at the utmost. We can show therefore that

$$\log p = \log \sum D_r p_r = \sum D_r \log p_r \qquad (5.34)$$

very nearly; with an error of less than 2 percent in p.[51] Further, we can show by using the complete crystalline partition function that if $(C_p)_{\text{sol}}$ is the specific heat at constant pressure of the mixed crystal of chlorine, per gram molecule, then

$$(C_p)_{\text{sol}} = \sum_1^5 D_r C_r. \qquad (5.35)$$

Since

$$(C_p)_1 = \sum_1^5 D_r (C_p{}^r)_1$$

we have, from (5.33), (5.34) and (5.35)

$$\log p = -\frac{\chi''}{kT} + \frac{7}{2}\log T + \int_0^T \frac{dT'}{RT'^2}\int_0^{T'} [(C_p)_1 - (C_p)_{\text{sol}}]dT'' + i, \qquad (5.36)$$

where

$$i = \sum_1^5 D_r i_r;$$

or since $D_1 + D_2 = a$, $D_3 = b$, $D_4 + D_5 = c$, $i_1 = i_2$ and $i_4 = i_5$, we have

$$i = ai_1 + bi_3 + ci_4$$

where

$$i_r = \log 8\pi^2 I_r k^{7/2}(2\pi m_r)^{3/2}/(2h^5). \qquad (5.37)$$

We know the masses of the molecules from Aston's measurements and from a knowledge of Avogadro's number; we know the moments of inertia I of chlorine A and B from the work of Elliott[44] to be 114×10^{-40} and 118×10^{-40} CGS units, respectively. We take as the moment of inertia of chlorine C molecules the value 121×10^{-40} CGS units, obtained from the former value by a simple calculation involving the masses, since the nuclear distances of

---

[51] Define a set of quantities A_r small compared with unity such that $p_r = p(1+A_r)$; $\Sigma D_r A_r = 0$. Then $\Sigma D_r \log p_r = \log p + \Sigma D_r \log(1+A_r)$. If the logarithms in the last term are expressed as power series the truth of (5.34) follows at once, since terms in A_r disappear.

the molecules *A* and *C* may be supposed to be equal, and also the distances to the centers of mass. Hence, using atmospheres as units of pressure and using common logarithms in the vapor pressure equation, we find for the vapor pressure constant of chlorine at ordinary temperatures the value

$$i' = 1.35.$$

This is in fair agreement with Eucken's first published value[49] $i' = 1.51 \pm 0.16$, but in worse agreement with his revised value[52] $i' = 1.66 \pm 0.08$. It would however be well to await verification of these measurements of the vapor pressure of chlorine before regarding the above discrepancies as serious.

Everything we have said here for Cl_2 obviously applies with trivial change to any molecule of the type X_2, and we shall apply the formulae of this chapter to such molecules without further discussion. It is clear that the method extends at once to mixtures of any number of isotopes. We pass on to a molecule of the type XY in the next chapter.

CHAPTER VI

THE VAPOR PRESSURE CONSTANT OF HYDROGEN CHLORIDE[53]

§6.1. The vapor pressure constant of hydrogen chloride

The normal state of the gaseous HCl molecule is $^1\Sigma$. Further, the nuclear vibrational energy levels higher than the ground level are so high (of the order of 4000°K) that in a treatment of the vapor pressure of hydrogen chloride at ordinary temperatures they may be neglected entirely. The pure rotation absorption spectrum, in the extreme infrared, and the lowest rotational-vibration spectrum in the infrared, have both been investigated recently by Czerny,[54] so that our knowledge of the energy levels relevant to the evaluation of the partition function for gaseous HCl molecules is quite complete. More recently still, the two lowest absorption bands have been investigated by Meyer and Levin[55] and the results have been analyzed by Colby[56] who fitted them to the equations derived theoretically by Fues,[57] for the oscillating rotator. It appears that owing to Colby's somewhat unusual though undoubtedly correct analysis it is simpler, in calculating the rotational partition functions, to use the value for the "moment of inertia" of the molecule of hydrogen chloride obtained by Czerny, namely 2.656×10^{-40} CGS units, rather than to use the correct moment of inertia for the molecule at rest obtained by Colby. For we should have to apply just those corrections to the latter value, if we used it, which would give us Czerny's value. When we make calculations for the moments of inertia of the HCl_{35} and HCl_{37} molecules, we find that the difference between their moments of in-

---

[52] Eucken, Phys. Zeits. **31**, 361 (1930).

[53] Sterne, Proc. Roy. Soc. **A133**, 303 (1931).

[54] Czerny, Zeits. f. Physik **44**, 252 (1927).

[55] Meyer and Levin, Phys. Rev. **34**, 44 (1929).

[56] Colby, Phys. Rev. **34**, 53 (1929).

[57] Fues, Ann. d. Physik **80**, 367 (1926); **81**, 281 (1926).

ertia is trivial, owing to the fact that the centers of mass are in both cases very close to the Cl nuclei. These calculations are confirmed by the actual values of the moments of inertia obtained by Colby in his analysis of the experiments of Meyer and Levin. In calculating the gaseous partition functions we may therefore neglect the differences in the moments of inertia. We must, however, consider the differences in the masses when we calculate the translational factors in the gaseous partition functions.

We may use the analysis developed for chlorine, with the greater simplicity that now there are only two sorts of molecules HCl_{35} and HCl_{37} which we call A and B in this chapter, without any non-combining groups of terms since there are no symmetry properties to be obeyed by the molecular wave functions. But there is an even greater simplicity—for when we come to evaluate the last term in (5.33) we find that it now makes no difference to our results whether the HCl molecule oscillates or rotates in its lowest quantum state in the crystalline phase—in either case ω_0 is $(2n_1+1)(2n_2+1)$, and since G has the same value, the last term in (5.33) becomes simply zero. Hence the vapor pressure constant of hydrogen chloride is

$$i = D_A i_A + D_B i_B$$

where

$$i_r = \log\left[(2\pi m_r)^{3/2} k^{7/2} 8\pi^2 I_r / h^5\right], \qquad r = A, B.$$

As we have indicated, both I's may be taken to be the same; we take for the molecular weights of the molecules 36 and 38 with sufficient accuracy; D_A and D_B are equal respectively to 0.760 and 0.240.[58] We find for the vapor pressure constant, therefore, the value

$$i' = -0.42. \tag{6.1}$$

We may be quite confident of the correctness of this value. It does not depend at all upon whether or not the molecules of HCl rotate in the crystal; it should be correct if the molecules perform either spherical oscillations or rotations—provided only that if they oscillate, there is but one orientation of minimum potential energy. That HCl forms a molecular lattice is rendered almost certain by the persistence[59] in the crystalline phase, with but a small change in wave-length, of the absorption band observed in gaseous absorption at about 3.46 microns. The existence of the transition point at 98°K in the crystalline phase, in no way diminishes the validity of the investigations.

The value (6.1) is in excellent agreement with the most recent value given by Eucken,[52] which is -0.40 ± 0.03. It is in poor agreement with Eucken's old value[60] of -0.26 ± 0.04.

---

[58] Sterne, Proc. Roy. Soc. **A131**, 339 (1931).

[59] Unpublished work of the late Fraulein G. Laski at the Reichsanstalt. The writers are indebted to F. I. G. Rawlins for this information.

[60] Eucken, Zeits. f. Physik **29**, 1 (1924).

The discussion of this chapter for HCl applies *mutatis mutandis* to any other molecules of type XY and of normal electronic state $^1\Sigma$.

CHAPTER VII

MIXED CRYSTALS

§7.1. The statistical mechanics of assemblies containing mixed crystals made up of constituents which can mix in all fashions

In Chapters V and VI we have had to consider assemblies containing crystals made up of different sorts of nearly identical molecules—the differences being due to the presence of isotopes and in the former chapter to the presence of non-combining groups of rotational terms as well. In §5.2 in particular, we had to deal with three sorts of chlorine molecules A, B and C of molecular weights 70, 72 and 74, respectively. We there supposed that all distributions of the sets of molecules A, B and C among the lattice points of the crystal were possible distributions which had to be counted in enumerating the total number of linearly independent wave functions capable of representing the entire assembly. Since the only relevant difference between molecules of different sorts was the comparatively small difference in their masses, which might make a difference to the crystalline partition function for the normal modes of oscillation, but which could hardly restrain the different sorts of molecules to condense on definite sets of lattice points, this assumption seemed plausible. But other considerations may tend to make one doubt the legitimacy of the assumption. Even if all distributions of the different sorts of molecules among the lattice points are at the outset, before the crystal is actually formed, equally likely, do we not know that, once the crystal is formed, and after its volume has reached such a value when compared with its surface that only a trivial proportion of its molecules can be concerned in any processes of evaporation and condensation at the surfaces, the interior of the crystal is then arranged fairly permanently in some definite arrangement which can change only very slowly with the time? For we know as an experimental fact that processes of diffusion within a solid—of rearrangements of different sorts of molecules—proceed usually with extreme slowness. We may be ignorant of the precise way in which the different sorts of molecules are distributed among the lattice points. They are nevertheless in fact distributed in some quite definite way in the interior of the crystal—in a way which cannot change appreciably during the time of a physical measurement. Ought we not to count as possible wave functions for the crystal not all of those which we did count, but merely those, much fewer in number, corresponding to rearrangements of only those molecules which are very close to the surfaces? We desire to know the total number of linearly independent wave functions capable of representing the entire assembly, and hence the total number of linearly independent wave functions capable of representing the mixed crystal. This latter seems to depend upon our knowledge of the crystal. How are we to think of it in statistical mechanics?

We must answer these questions which we have asked ourselves as foliows: It is no doubt often true that the interior of a crystal is in a state which can change only very slowly. But we have considered assemblies which contained definite total numbers X_r of molecules of each sort r. For any sort we supposed that if N_r of them were in the gas, then P_r of them, given by $X_r - N_r$, were in the crystal; and quite apart from the different distributions among the lattice points of the molecules of the different sorts in the crystal, the method of enumerating the different possible wave functions allowed for the occurrence of all values of P_r from 0 to X_r. Hence our calculations applied to an assembly such that the X_r molecules of a particular sort could be distributed between the gaseous and crystalline phases in all of these possible ways, and could not be considered to apply to an assembly in which any crystal could be known to be arranged internally in a definite way. For if any of the molecules of a certain sort r were known to be arranged in definite places in a crystal, they would be known not to form part of the set of X_r molecules which could be distributed between the two *phases* in all possible ways. Our procedure in Chapters V and VI was therefore correct, and led to correct values of the vapor pressure. If we wish to apply these methods to an actual assembly in which for instance it *is* known that S_r molecules of sort r are in a crystal and that they occupy a definite set of lattice points, we must ignore these molecules by considering them to be outside of the imagined assembly to which our calculations apply; and we can do this by subtracting S_r from the total number of molecules of sort r in the real assembly in order to get the number X_r which we use in our calculations. In this way we get the correct number of linearly independent wave functions *effectively* representing the assembly.

The situation is similar to that covered by the lemma of §2.11. Instead of regarding the whole crystal as analyzable into its constituent molecules we regard the greater part of the crystal as a permanent system (and even leave it out of the assembly!) and need not then make the wave functions of the assembly symmetrical or antisymmetrical in the molecules which are permanently in the permanent part of the crystal. We now get a different number of accessible states for what remains of the assembly, but this only corresponds to the fact that our assembly is now a different one, and no physical result is altered.

In modern statistical mechanics the entropy of an assembly appears as the sum of a constant, which may be arbitrarily chosen, and the product of Boltzmann's constant and the natural logarithm of the total number of linearly independent wave functions capable of representing the assembly. The considerations of the preceding paragraphs show that in calculating the entropy of a mixed crystal made up of constituent molecules or atoms which can be arranged in all fashions, the correct procedure is to take into account all the different distributions of the sets of molecules P_r among the lattice points, when we calculate the total number of wave functions. For the mixed crystal must have been obtained either by condensation from a mixture of the gaseous phases or of the liquid phases, or else by a process of diffusion in the solid state.

§7.2. The statistical mechanics of assemblies containing mixed crystals made up of constituents which cannot mix in all fashions

If a crystal is made up of P_1 particles (molecules or atoms) of sort 1, P_2 of sort 2, P_3 of sort 3, etc., and if as we supposed in the last section they can mix in all fashions, there will be for the crystal as thus specified

$$(P_1 + P_2 + P_3 + \cdots)!/(P_1!P_2!P_3! \cdots) \tag{7.20}$$

different possible arrangements. If the particles are sufficiently similar (as for instance the different sorts of chlorine molecules were supposed to be in Chapter V) then we see from Chapter V that the total vapor pressure p will be given very nearly by

$$p = \sum_r D_r p_r$$

where p_r is the vapor pressure which a crystal would have if it were made up wholly of the r'th sort of particles, and D_r is the ratio which the number of particles of sort r bears to the total number of particles. If in particular there were but three sorts of molecules for which the p_r's were the same, then p for the mixed crystal would have the same value as these p_r's.

This is only true if the constituent particles can mix in all fashions. For the other extreme case, we suppose that the particles cannot mix at all; or in other words that all the particles P_r of each sort r in the crystal must necessarily occupy a single definite set of lattice points, so that there will be but one possible arrangement for the crystal instead of the number give in (7.20). It is easy to show that in this case, if the particles are sufficiently similar, the total vapor pressure p will be given by

$$p = \sum_r p_r.$$

This is entirely reasonable, since in the case where each sort of particle condensed on its own pure crystal the total vapor pressure would have to be equal to the sum of the partial pressures, which latter are here just the p_r's. If we had supposed in Chapter V that the three different sorts of chlorine molecules could not mix at all in the crystal, we should thus have found three times the vapor pressure[61] very nearly that we did find, and accordingly the vapor pressure constant i' would have been greater than that which we did find by $\log_{10}3$, and would therefore have been equal to 1.83. This last value is considerably greater than even the greatest of the experimental values given by Eucken; and we are provided with experimental evidence, therefore, that the three sorts of chlorine molecules are not completely incapable of mixing in the crystalline phase.

The intermediate cases, for which mixing is possible to intermediate extents, may be of interest. We must introduce a parameter or parameters specifying how "perfect" a mixing can occur. We consider for simplicity the case where there are just two sorts of particles A and B. We denote as usual the

---

[61] Sterne, Proc. Roy. Soc. **A131**, 339 (1931).

numbers in the crystal by P_A and P_B. Let us start from the one extreme case in which the particles can be distributed in all ways among the lattice points of the crystal. Then one simple way to limit the extent of mixing is to require that the particles of sort A must be grouped together in groups of m each and that those of sort B must be grouped together in groups of n each, which groups can then mix perfectly. This is a possibility that may well be realized in real mixed crystals. The total number of possible arrangements is now

$$[(P_A/m) + (P_B/n)]!/[(P_A/m)!(P_B/n)!].$$

We observe that this number of possible arrangements is the same as the number of possible arrangements would be if a fraction $1/m$ of the P_A A-particles in the crystal and a fraction $1/n$ of the P_B B-particles in the crystal could mix in all fashions while the remaining sets of particles of the two sorts in the crystal were constrained to occupy definite sets of lattice points and thus could not enter into the mixing process at all. It is therefore natural to introduce two constants α_A and α_B, such that $0 \leqq \alpha_A \leqq 1$, $0 \leqq \alpha_B \leqq 1$, called the "mixing coefficients" of the A-particles and B-particles, respectively, which specify that the total number of possible different arrangements of the P_A A-particles and the P_B B-particles among the lattice points is

$$[(\alpha_A P_A) + (\alpha_B P_B)]!/[(\alpha_A P_A)!(\alpha_B P_B)!]. \tag{7.21}$$

We have arrived at the notion of mixing coefficients by considering only two special ways in which the extent of mixing can be limited; but as we shall indicate later these mixing coefficients should be sufficient adequately to describe the extent of mixing no matter how it is limited, in all investigations of vapor pressures.

Let us investigate the statistical mechanics of an assembly containing atoms or molecules of two sorts, A and B, in which the total numbers are X_A and X_B, and for which the mixing coefficients are α_A and α_B. We denote the numbers of particles in the gas by N_A and N_B and for convenience we assume that the particles are so similar that we may suppose the crystalline partition function for normal modes of oscillation to be of the form $[\kappa(z)]^{P_A+P_B}$. Then the total number of linearly independent wave functions capable of representing the crystal if its energy is U is the coefficient of z^U in

$$\frac{[(\alpha_A P_A) + (\alpha_B P_B)]!}{(\alpha_A P_A)!(\alpha_B P_B)!}[\kappa(z)]^{P_A+P_B}[f_A(z)]^{P_A}[f_B(z)]^{P_B}.$$

Here $f_A(z)$ and $f_B(z)$ are the partition functions for the individual particles in the crystal. We shall use the classical approximation to the correct quantum statistics for the vapor, and the total number of linearly independent wave functions which can represent the vapor if its energy is F is then the coefficient of $x_A{}^{N_A}\, x_B{}^{N_B}\, z^F$ in

$$\exp [x_A F_A(z) + x_B F_B(z)].$$

Hence the total number of linearly independent wave functions which can represent the entire assembly if the total energy is E, and if there are N_A

and N_B particles of the two sorts respectively in the vapor and $P_A = X_A - N_A$ and $P_B = X_B - N_B$ particles of the two sorts respectively in the crystal, is

$$C_{N_A,N_B} = \frac{(\alpha_A P_A + \alpha_B P_B)!}{(\alpha_A P_A)!(\alpha_B P_B)!}\left(\frac{1}{2\pi i}\right)^3 \int\int\int \left\{ \frac{dx_A dx_B dz}{x_A{}^{N_A+1} x_B{}^{N_B+1} z^{E+1}} \right.$$
$$\left. \times\ [\kappa(z)]^{P_A+P_B}[f_A(z)]^{P_A}[f_B(z)]^{P_B} \exp\,[x_A F_A(z) + x_B F_B(z)] \right\}. \quad (7.22)$$

Using Stirling's asymptotic expression for factorials, we find by the usual methods that the mean values are

$$\overline{N}_A = \xi_A F_A(\theta);\ \overline{N}_B = \xi_B F_B(\theta);$$

where

$$\xi_A = \left(\frac{\alpha_A \overline{P}_A}{\alpha_A \overline{P}_A + \alpha_B \overline{P}_B}\right)^{\alpha_A} \frac{1}{f_A(\theta)\kappa(\theta)}$$

and

$$\xi_B = \left(\frac{\alpha_B \overline{P}_B}{\alpha_A \overline{P}_A + \alpha_B \overline{P}_B}\right)^{\alpha_B} \frac{1}{f_B(\theta)\kappa(\theta)}.$$

If most of the particles are in the crystalline phase, then we have also, very nearly,

$$\frac{\overline{P}_A}{\overline{P}_B} = \frac{X_A}{X_B},$$

and hence

$$\left.\begin{aligned} \overline{N}_A &= \frac{F_A(\theta)}{\kappa(\theta) f_A(\theta)}\left(\frac{\alpha_A X_A}{\alpha_A X_A + \alpha_B X_B}\right)^{\alpha_A} \\ \overline{N}_B &= \frac{F_B(\theta)}{\kappa(\theta) f_B(\theta)}\left(\frac{\alpha_B X_B}{\alpha_A X_A + \alpha_B X_B}\right)^{\alpha_B} \end{aligned}\right\}. \quad (7.23)$$

One sees that when the α's are both zero the total pressure is equal to the sum of the vapor pressures of the two sorts of pure crystal, and that when the α's are both unity the result (7.23) becomes simply the usual one for the case of complete mixing. It is easy to extend these methods to the general case where there may be more than two sorts of particles.

Since appreciable contributions to the sums

$$\sum C_{N_A,N_B},\ \sum N_A C_{N_A,N_B} \text{ and } \sum N_B C_{N_A,N_B}$$

come only from those terms for which N_A and N_B are very close to their equilibrium values $\overline{N}_A$ and $\overline{N}_B$, respectively, it follows that so long as the expression (7.21) gives the correct number of crystalline arrangements when the P's have nearly their equilibrium values, it does not matter to our results whether or not the mixing variables describe the mixing so accurately that this expression still represents the number of arrangements for values of P_A and P_B appreciably different from the equilibrium values $\overline{P}_A$ and $\overline{P}_B$. Thus we see that our parameters α_A and α_B serve to specify the extent of the mixing adequately for discussions of equilibria, provided only that they correctly describe the mixing for values of P_A and P_B very close to $\overline{P}_A$ and $\overline{P}_B$, respectively.

It is of course a tautology to say that the "entropy of mixing" of a mixed crystal, referred to a state of zero entropy where the constituents are completely separated, is

$$S = k \log \frac{(\alpha_A P_A + \alpha_B P_B)!}{(\alpha_A P_A)!(\alpha_B P_B)!}$$

if the α's describe the mixing properly for the actual values of P_A and P_B in question.

CHAPTER VIII

THE VAPOR PRESSURE CONSTANTS OF DIATOMIC VAPORS

§8.1. The general theory of the vapor pressure constants of diatomic vapors

Hydrogen is probably unique among diatomic vapors in that measurements of its vapor pressure can be made at temperatures so low that the rotational specific heat R is not developed and for which, therefore, the constant part of the specific heat of the vapor is $5R/2$. That this is possible is due to a combination of two circumstances; one of which is the very low moment of inertia of the hydrogen molecule which causes its rotational energy levels to be widely separated, and the other of which is the low boiling point of the liquid which allows measurements to be made of its vapor pressure at temperatures so low that the para- and ortho-hydrogen molecules are all in their lowest rotational states. For all other diatomic vapors we may consider $(C_p)_0$ to be $7R/2$. We may then at once generalize the results of §§5.2 and 5.3 of Chapter V. For any chemical compound having a diatomic vapor, the vapor pressure is given by

$$p = \sum D_r p_r$$

if the constituents of the mixed crystals can mix in all fashions, where

$$p_r = F_r(T)kT/[Vf_r(T)K(T)]$$

is the vapor pressure of a pure crystal of the r'th species. Here, in accordance with the discussion of §4.7, $F_r(T)$ can be considered with sufficient accuracy to be

$$G_r V \frac{8\pi^2 I_r kT(2\pi m_r kT)^{3/2}}{h^5} V_r(T) e^{-\chi/kT}$$

where G_r is some number, and where $V_r(T)$ is the partition function for nuclear vibrations in the gas molecules, given experimentally by the equation

$$\log V_r(T) = \int_0^T \frac{dT'}{RT'^2} \int_0^{T'} (C_p^r)_1 \, dT'',$$

in which $(C_p{}^r)_1$ is the vibrational specific heat of the r'th species. The crystalline partition function $[K(T)f_r(T)]$ is definied by the equation

$$\int_0^T \frac{dT'}{RT'^2}\int_0^{T'} C_r dT'' = \log\,[K(T)f_r(T)] - \log{}_r\omega_0 + \frac{{}_r\epsilon_0}{kT},$$

and thus its form is immaterial, as long as $[K(T)f_r(T)]^{P_r}$ is the crystalline partition function of a pure crystal of the r'th species containing P_r diatomic molecules.

Accordingly the vapor pressure constant of the vapor of a pure crystal of the r'th species is

$$i_r = \log\left[(2\pi m_r)^{3/2}k^{7/2}8\pi^2 I_r/h^5\right] + \log\,[G_r/{}_r\omega_0]. \qquad (8.1)$$

This equation is perfectly general. It can be used to find the vapor pressure constant of the diatomic vapor of the pure r'th species even if the structural units in this crystalline phase are not the same molecules as those which exist in the gas, but are groups of molecules, or separate atoms, or even atomic ions and electrons. All that we need to do is always to interpret ${}_r\omega_0$ as being equal to C^{1/P_r}, where C is the number of linearly independent wave functions which can represent the crystal of the r'th species, containing in all $2P_r$ atomic nuclei, at the absolute zero.

If now $K(T)f_r(T)$ really is the product of two functions $K(T)$ and $f_r(T)$ of which the first is the partition function per molecule for the normal modes of vibration and is the same for all the different species (this assumption amounts to neglecting the interaction terms between the thermal oscillations of the crystal lattice and the internal motions of the particles situated at the lattice points), then we have Eq. (5.35) for the mixed crystal

$$(C_p)_{\text{sol}} = \sum_r D_r C_r$$

and in any case we have also for the vapor

$$(C_p)_1 = \sum_r D_r (C_p{}^r)_1.$$

Now the notion of vapor pressure constant has a meaning only when it is applied to a vapor for which the p_r's, of those species present in significant amounts, are nearly the same functions of the temperature—otherwise it will be impossible to find any expression in the form of Eq. (1.1) of Chapter I. But if the p_r's are the same or nearly the same, then we have the equation, as in Chapter V,

$$i = \sum_r D_r i_r. \qquad (8.15)$$

With Eqs. (8.1) and (8.15) we can calculate the vapor pressure constants, with $(C_p)_0 = 7R/2$, of all the diatomic vapors.

We notice from an inspection of Eqs. (8.1) and (8.15) that the *values* of the nuclear spins are without effect upon the vapor pressure constants, for we saw in Chapter IV how the same factors involving n (or n_1 and n_2) occurred in both G_r and ${}_r\omega_0$.

§8.2. The vapor pressure constants of some diatomic vapors

In order to apply the general theory of §8.1 to the calculation of the vapor pressure constants of particular substances, it is necessary to know the value of the last term in Eq. (8.1). G_r is found easily in all cases. To find ${}_r\omega_0$ it is necessary to know something about the nature of the crystalline phase, at the absolute zero, of the substance whose diatomic vapor we are investigating. To begin with, one must know whether or not the molecules exist in the crystalline phase. So far as we have ascertained none of the lattices of the crystalline phases of the substances mentioned in this chapter are likely to be atomic. They are all molecular, and indeed it is possible that in some of them, except crystalline hydrogen, the structural units are groups of several molecules each. Secondly, Pauling's analysis,[31] when applied to the molecules H_2, N_2, O_2, NO, CO, HCl, HBr, HI, Cl_2, Br_2 and I_2 which we consider in this chapter, shows that the only molecule among them which is likely to rotate at temperatures close to the absolute zero is H_2. This is confirmed by the specific heats of the crystals, for we should expect the separations of the rotational levels in the crystals, if rotation occurred, to be of the same order of magnitude as they are in the gaseous phase; and with the exception of hydrogen they would then retain their rotational specific heats R in the crystals for temperatures extending downwards to within a few degrees of the absolute zero. Since the observed specific heats do not show this behavior, we can feel quite confident in assuming that the molecules mentioned above oscillate and do not rotate, at the lowest temperatures in the crystal phase, with the exception of H_2 which rotates. Hydrogen has already been considered. For the other substances, whose molecules cannot rotate at very low temperatures in the crystals, it does not matter whether the structural units of the crystals are individual molecules or groups of molecules, with the two exceptions of oxygen and nitric oxide. For the ground states of the other molecules are all ${}^1\Sigma$, and ${}_r\omega_0$ could not be made any smaller than the values given in Table II in Chapter IV even if the molecules were grouped to form larger units; nor could it be made larger.

The ground state of NO however is a ${}^2\Pi_{1/2}$ and we have shown reasons in §4.6 to believe that ${}_r\omega_0$ is effectively $\sqrt{2(2n_1+1)(2n_2+1)}$ so that combining the results found in §§4.6 and 4.7

$$\frac{G_r}{{}_r\omega_0} = \sqrt{2}(1 + e^{-170/T})$$

and is therefore a function of the temperature.[62] If we use its value for $T=110$°K, the midpoint of Eucken's temperature range, we obtain the first value for the vapor pressure constant i' given in Table IV, which agrees fairly well with the value given by Eucken. Our vapor pressure constant

---

[62] The reason being that to obtain results on the same basis as Eucken's, we have had to include in i what really should be taken account of in the integral term in Eq. (1.2). Eucken took $(C_p)_1$ to be 0, and by so doing he has made his experimental i' liable to error in this case as well as in others.

calculated with the $G_r/_r\omega_0$ above is equal to the correct vapor pressure constant defined in §1.2 plus a term

$$\int_0^T \frac{dT'}{RT'^2} \int_0^{T'} (C_p)_1' \frac{dT''}{\log 10},$$

where $(C_p)_1'$ is the contribution of the multiplicity of the ${}^2\Pi$ levels to the total specific heat of the vapor, and our i' will only be a real constant at temperatures above about 2400°K when it takes the limiting value 0.696. This is the value which one ought to use in the next chapter in investigating high-temperature chemical equilibria. The true constant i' defined by equation (1.2), with $(C_p)_0$ equal to $7R/2$, should be 0.395.

In Table IV are shown the values of i' calculated in accordance with the theory of §8.1. One should not attach great importance to the few discrepancies which remain, because the experimental values are still uncertain. The

TABLE IV. *Some diatomic vapor pressure constants.*

Vapor	Ground state	$I \times 10^{40}$ gm · cm²	Species considered	2) i' Observed	i' Calculated
H_2	${}^1\Sigma$	1) 0.463	Para- $D=\frac{1}{4}$ Ortho- $D=\frac{3}{4}$	-3.68 ± 0.03	-3.722
N_2	${}^1\Sigma$	1) 13.8		-0.16 ± 0.03	-0.177
O_2	${}^3\Sigma$	1) 19.15		0.55 ± 0.02	0.530
NO	${}^2\Pi$	3) 16.4		0.55 ± 0.03 at 110°K	$\left.\begin{array}{r}110°\text{K}\\2400°\text{K}\\\infty°\text{K}\end{array}\right\}\begin{array}{l}0.479\\0.681\\0.696\end{array}$ see text
CO	${}^1\Sigma$	4) 15.0		-0.07 ± 0.05	0.160
HCl	${}^1\Sigma$	5) 2.656	HCl_{35}, $D=0.76$ HCl_{37}, $D=0.24$	-0.40 ± 0.03	-0.419
HBr	${}^1\Sigma$	6) 3.32	HBr_{79}, $D=0.54$ HBr_{81}, $D=0.46$	0.24 ± 0.04	0.197
HI	${}^1\Sigma$	6) 4.31		0.65 ± 0.05	0.608
Cl_2	${}^1\Sigma$	7) $Cl_{35}Cl_{35}$ 114 $Cl_{35}Cl_{37}$ 118 $Cl_{37}Cl_{37}$ 121	$Cl_{35}Cl_{35}$, $D=0.58$ $Cl_{35}Cl_{37}$, $D=0.36$ $Cl_{37}Cl_{37}$, $D=0.06$	1.66 ± 0.08	1.352
Br_2	${}^1\Sigma$	8) 445.		2.59 ± 0.10	2.467
I_2	${}^1\Sigma$	9) 820.		3.08 ± 0.05	3.031

AUTHORITIES

[1] Rosetti, Phys. Rev. **34,** 370 (1929).
[2] Eucken, Phys. Zeits. **31,** 361 (1930).
[3] Snow and others, Proc. Roy. Soc. **A124,** 453 (1929).
[4] Snow and Rideal, Proc. Roy. Soc. **A125,** 462 (1929).
[5] Czerny, reference 54.
[6] *International Critical Tables.*
[7] Elliott, reference 44.
[8] Brown, Phys. Rev. **37,** 1007 (1931), letter.
[9] Mecke, Zeits. f. Physik **42,** 390 (1927).

"limits of error" in the table are not probable errors, and have proved in practice to be practically meaningless, as a comparison of old with recent values of i' obtained experimentally will show. On the whole the agreement shown in the table is excellent; and we may hope that in the future better experimental data will serve to verify even further the general correctness of the theory of the vapor pressure constants of diatomic vapors. We may also hope that future theoretical investigations will make it possible to account satisfactorily for the vapor pressure constants of polyatomic vapors.

CHAPTER IX

ENTROPIES AND CHEMICAL EQUILIBRIA

§9.1. Introduction

In order to find the difference between the entropies of a gram molecule of a substance in two different states of temperature and volume, it is necessary to use the relation

$$S_2 - S_1 = \int_1^2 \frac{C'}{T} dT \tag{9.1}$$

where S_2 is the entropy in state 2, S_1 the entropy in state 1, and C' is the specific heat per gram molecule measured as the substance is brought from state 1 to state 2 in some reversible fashion; being infinite in the proper fashion at the transition points encountered, so that a transition point at T' contributes Λ/T' to the integral. It is easy to refer the entropy of a gaseous or liquid state in this way to the entropy of the substance at some temperature T' when it is in the crystalline phase, and subjected merely to the pressure of its own vapor. It is now possible to refer the entropy of this state in turn to the entropy of a similar crystalline state at some lower temperature T''; the C' in Eq. (9.1) is now simply the usual $(C_p)_{\text{sol}}$, and as before it is infinite at transition points in the crystal, in the proper fashion. But if we try to find the difference between the entropy of the crystalline substance at some temperature T' and its entropy at the absolute zero itself by this equation, which then becomes

$$S_{T'} - S_0 = \int_0^{T'} \frac{(C_p)_{\text{sol}}}{T} dT \tag{9.101}$$

we are faced with the difficulty that experimental knowledge of $(C_p)_{\text{sol}}$ does not extend below a certain temperature T_0, which varies in practice from substance to substance but which is never smaller than about ½°K and which is usually about 10°K or even higher. T_0 can never be precisely the absolute zero, because the surroundings always radiate heat, during specific heat measurements. Thus we must necessarily always be ignorant of the specific heat of the substance at temperatures within a neighborhood of the absolute zero. The obvious procedure is to extrapolate the $(C_p)_{\text{sol}}$ found at temperatures above T_0 to the absolute zero, and then evaluate the integral, using the extrapolated value of $(C_p)_{\text{sol}}$ below T_0. Now if the crystal were simply a lattice of mass points, capable of oscillation, the specific heat at these low temperatures would be that given by a Debye analysis of the normal modes; C_v would vary at sufficiently small temperatures as T^3, and $C_p - C_v$ like $\alpha^2 T$ where α is the coefficient of thermal expansion. The extrapolation would be quite accurate and would furnish a definite accurate value for $S_{T'} - S_0$. But a crystal cannot be so regarded. Even if it is made up of a pure chemical element the existence of isotopes would cause certain distributions to have less energy than others, and at sufficiently low temperatures (which can safely be stated to be far below T_0) processes of diffusion would produce a contribution to the specific heat in addition to that due to the normal modes. By extrapolating, these contributions are neglected; and we must consider therefore that by extrapolating we are referring our entropy at T' to that of an "ideal" state of the crystal in which its normal modes are in their lowest quantum states, as in the case of the lattice of mass points at the absolute zero; but in which the isotopes are still mixed at random instead of being separated as one would expect them to be in the real crystal at the absolute zero, after sufficient lapse of time. If the crystal is made up of systems with internal degrees of freedom, they will in general have their very low quantum states still unresolved at T_0, in particular those depending on the orientation of nuclear spins; and thus by extrapolating the specific heat below T_0 we shall overlook their contributions to the total specific heat. Now it happens that in general the energies of the two lowest electronic states of atoms, and of the two lowest spherical oscillatory or rotational levels of molecules, are widely separated compared with kT_0, and that within these levels the component levels, ω_0 in number, corresponding to different nuclear configurations, and to spherical oscillatory wave functions with different symmetry properties in the case of oscillating molecules, have their energies very close together compared with kT_0. If the ω_0 different components of the "lowest" level have their energies sufficiently close together, then the specific heat of the crystal above T_0 can be shown to be the same, practically, as it would be if these energies were precisely equal. Accordingly, when we use Eq. (9.101) with an extrapolated $(C_p)_{\text{sol}}$, we are letting S_0 denote the entropy of an ideal state in which the molecules or atoms of the crystal have the statistical weights ω_0. Finally, since kT_0 will in general be large compared with the differences in energy caused by different distributions of para- and ortho-varieties among the lattice points of the crystal, if these varieties are present, our ideal state is one in which these varieties can mix in all fashions.

To sum up this discussion, when in applying thermodynamics we use Eq. (9.101) with experimental data in which $(C_p)_{\text{sol}}$ is extrapolated for temperatures lower than T_0, the S_0 refers not to the real entropy of the crystal at precisely the absolute zero, but to the entropy of the crystal when it is in an "ideal" state at the absolute zero; in which the normal modes are all in their lowest quantum states, in which the mixing of the isotopes and of the para- and ortho-varieties can occur in all fashions, and in which each molecule or atom of sort r can be represented by ${}_r\omega_0$ linearly independent wave functions (or more rigorously, that all of the P_r particles in a crystal of sort r could be represented together by $({}_r\omega_0)^{P_r}$ wave functions).

Before passing on to consider entropies further, we should observe that the symbols $(C_p)_{sol}$ in the integrals in the vapor pressure equations of previous chapters should be interpreted in accordance with the above discussion.

The conception of "ideal" states is a very useful one for calculating the changes of entropy which occur during chemical reactions. For physical chemists can evaluate the entropies of any states referred to the "ideal" states at the absolute zero; and we can readily evaluate the entropies of these "ideal" states at the absolute zero referred to a common standard, provided that we have sufficient knowledge of the way in which the crystals are constituted.

§9.11. Entropy in statistical mechanics

The entropy of any assembly can only be logically *defined* as a function S of the state of the assembly satisfying the differential form $(dQ=)dE+dW=TdS$, where dW is the external work done in any small reversible variation of the conditions of the assembly. The function S is naturally not unique, an additive constant which can be arbitrarily chosen being left unassigned, but this constant can always be so assigned[63] that

$$S = k \log C \qquad (9.11)$$

where C is the total number of accessible states of the assembly for the given value of its energy E; that is, the total number of linearly independent wave functions, having the proper symmetry, which can represent the assembly. This function $k\log C$ has in fact all the necessary properties.

With the help of (9.11) we can explain what we meant in Chapter IV by the calculated entropy of O_2 and NO gas "referred to a state which can be represented by only one independent wave function." Such a state would be one for which $C=1$, $S=0$ as defined by (9.11). If in these particular cases, neglecting nuclear spins, the "ideal solid state" at the absolute zero has $C=1$ then the calculated S for the gas should agree with the measured difference between the entropy of the gas, and the entropy of the solid extrapolated to the ideal state at the absolute zero. But if there is disagreement beyond the limits of experimental error then we must conclude, as we did for NO, that for the "ideal solid state" $C\neq 1$, even neglecting factors contributed to C by the nuclear spins. In that case of course we must have $C>1$, but that is just what we were led to conclude. The measured entropy corresponds to $k(\log C-\log C_0)$ where C_0 is the number of accessible states of the "ideal solid state" at the absolute zero.

If on the other hand the measured entropy could be so measured that, for example, we have always a true equilibrium with transitions between ortho- and para-states, and could be measured to such a low temperature that the ideal state corresponds to the state of absolutely lowest energy no matter how small the energy separations of the low group of states, then of course the measured entropy must be compared with $k(\log C-\log C_0')$

---

[63] Fowler, *Statistical Mechanics*, pp. 533, 534.

where C_0' is the number of accessible states corresponding to the absolutely lowest value of the energy. It will often be true that $C_0' < C_0$, but whether or no even in this case we have always $C_0' = 1$ is as yet entirely unknown: as the measurements which would make C_0' significant cannot conceivably be carried out the value of C_0' is not only unknown but unimportant.

In the same way if we wish to compare an observed entropy difference between any state of an assembly (a gaseous state at given temperature and pressure say) and the "ideal" solid state at the absolute zero, and it is thought necessary to take into account the nuclear spins and isotopic mixtures for computation of $k \log C$ in the gas phase, the contributions of these factors must always be included in $k \log C_0$ for the ideal state and the difference compared with observation. This comparison will be studied in detail in §9.7.

§9.2. The entropy of hydrogen at the absolute zero

Consider a gram molecule of crystalline hydrogen composed of $\frac{1}{4}N$ molecules of para-hydrogen and $\frac{3}{4}N$ molecules of ortho-hydrogen, in its "ideal" state at the absolute zero. N is Avogadro's number. In accordance with §3.1, the number of linearly independent wave functions which can represent the crystal is

$$C_0 = 1^{N/4} 9^{3N/4} N!/[(N/4)!(3N/4)!] \qquad (9.201)$$

since each molecule of para-hydrogen in the zero'th rotational level can be represented by one wave function, while each molecule of ortho-hydrogen in the first rotational level can be represented by 9 wave functions corresponding to the 3 possible eigenvalues of the z component of nuclear rotational angular momentum and to the 3 possible eigenvalues of the z component of nuclear spin angular momentum. By the use of Stirling's asymptotic formula for factorials we find, neglecting trivial terms, that

$$S_0 = k \log C_0 = \tfrac{3}{4} R \log 3 + R \log 4. \qquad (9.202)$$

It is possible, and perhaps worth while, to verify this value by a slightly different argument due to D. MacGillavry,[64] since it contains the terms

$$k \log \{N!/[(N/4)!(3N/4)!]\} = R[-\tfrac{1}{4}\log\tfrac{1}{4} - \tfrac{3}{4}\log\tfrac{3}{4}],$$

sometimes called the "paradox terms," due to mixing by diffusion of the two types of hydrogen. If one starts with hydrogen gas at a high temperature T the value of the entropy at this temperature is independent of whether ortho⇄para transitions can occur or not. We shall prove this in §9.7. The species exist at this temperature in any event in a true equilibrium ratio of 3 ortho-molecules to 1 para-molecule and the mixture must have a unique entropy. Now suppose that the gas is cooled down to the absolute zero by two different methods, and the entropy change observed on both routes; (a) as ordinary hydrogen with no ortho⇄para transitions, and (b) as ideal well-catalyzed hydrogen with abundant ortho⇄para transitions maintaining the

---

[64] D. MacGillavry, Phys. Rev. **36**, 1398 (1930).

true equilibrium ratio. On route (a) one arrives at the ordinary ideal state of hydrogen at the absolute zero for which S_0 should be given by (9.202) and on route (b) at a pure para-hydrogen crystal for which $S_0 = 0$. This entropy difference can be shown to correspond exactly to the difference of the entropy changes on routes (a) and (b).

It is interesting that in this case of hydrogen, due no doubt to the fact that the molecules rotate in the crystal, Simon, Mendelssohn and Ruhemann have found[65] anomalies in the specific heat below 11°K which correspond possibly to the separating out of the constituents of the mixed crystal, and perhaps also to the resolution of the 3 nuclear rotational levels with j equal to 1 in the case of ortho-hydrogen. Above 11°K the specific heat corresponds closely to a Debye function with Θ equal to 91°K. Accordingly we must take T_0 to be 11°K in the case of hydrogen, and in using in Eq. (9.101) the value of the entropy S_0 of the ideal state at the absolute zero given by (9.202), we must extrapolate $(C_p)_{sol}$ below 11°K by means of the Debye function with $\Theta = 91$°K. We must extrapolate in this same fashion, also, in evaluating the double integral in the vapor pressure equation for hydrogen on page 662.

Hydrogen may very well be unique in providing an instance of a diatomic molecule for which it is convenient to ignore the actual specific heat of the crystal, and start extrapolating, at temperatures higher than the lowest to which specific heat measurements extend. For in the case of oscillating molecules, the differences in energy corresponding to different nuclear configurations in the lowest oscillatory levels, or to oscillatory levels of different symmetry, can be shown by rough calculations to be probably of lower order than 0.01°K. We should not expect any separation of isotopes except at temperatures very much lower than this. We call the entropy of a crystalline substance in its "ideal" state at the absolute zero its "entropy at the absolute zero," for brevity.

§9.3. The general theory of entropies at the absolute zero, and of the changes of entropy which occur during reactions between crystals at the absolute zero

The generalization of the method of the last section is very simple. The number of linearly independent wave functions which can represent a gram molecule of crystal at the absolute zero, made up of different species r of the same chemical substance is

$$C_0 = N!\prod_r {}_r\omega_0^{D_rN}/\prod_r (D_rN)!$$

where D_r is the mole fraction of the r'th species. Hence in accordance with the previous discussions the entropy of this crystal at the absolute zero is given, except for trivial terms, by

$$S_0 = k \log C_0 = R \sum_r D_r \log ({}_r\omega_0/D_r). \tag{9.3}$$

We can apply the result (9.3) at once to the calculation of the changes in entropy which occur during chemical reactions between crystalline sub-

---

[65] Simon, Mendelssohn and Ruhemann, Naturwiss. **18**, 34 (1930).

stances in their ideal states at the absolute zero. Let the chemical equation describing the reaction be in the form

$$\sum_t q_t A_t = 0, \tag{9.301}$$

where the symbols A_t denote gram molecules of the pure chemical substances which take part in the reaction, and the q_t's denote the number of gram molecules of them which take part; being negative for those substances which disappear when the reaction occurs. Then when this reaction occurs at the absolute zero the change in entropy is

$$\Delta S_0 = \sum_t q_t S_0{}^t, \tag{9.31}$$

where $S_0{}^t$ is the entropy of a gram molecule of the t'th chemical substance at the absolute zero, calculated in accordance with the Eq. (9.3).

§9.4. The changes in entropy which occur during some simple reactions between crystalline substances at the absolute zero

All of the theory of the preceding sections of this chapter is general, and applies to crystals made up of any sorts of particles at all. Let us apply it to some of the substances considered in Chapter VIII, and let us start by considering the change of entropy in the reaction between crystals at the absolute zero described after (9.301) by $H_2+Cl_2-2HCl=0$. We have already calculated S_0 for hydrogen; to find S_0 for chlorine we make use of Table II of Chapter IV. The ground state of the free Cl_2 molecule is a $^1\Sigma$. We consider the five species of chlorine molecule considered in Chapter V, and we denote the spins of the Cl_{35} and Cl_{37} nuclei by n_1 and n_2, respectively. If we denote the gram atomic fractions of the isotopes of chlorine by A and by B respectively, we shall have very nearly $D_1+D_2=A^2$; $D_3=2AB$; $D_4+D_5=B^2$. For chlorine, therefore,

$$D_1 = \frac{n_1A^2}{2n_1+1}; \qquad D_2 = \frac{(n_1+1)A^2}{2n_1+1}; \quad D_3 = 2AB; \quad D_4 = \frac{n_2B^2}{2n_2+1};$$

$$D_5 = \frac{(n_2+1)B^2}{2n_2+1}; \qquad {}_1\omega_0 = n_1(2n_1+1); \quad {}_2\omega_0 = (n_1+1)(2n_1+1);$$

$${}_3\omega_0 = 2(2n_1+1)(2n_2+1); \quad {}_4\omega_0 = n_2(2n_2+1); \quad {}_5\omega_0 = (n_2+1)(2n_2+1).$$

Hence, if we use Eq. (9.3) we find after some reduction

$$S_0(Cl_2) = R\{2A \log[(2n_1+1)/A] + 2B\log[(2n_2+1)/B]\}.$$

Similarly, we find for hydrogen chloride, since the spin of a hydrogen nucleus is $\frac{1}{2}$,

$$S_0(HCl) = R\{A\log[2(2n_1+1)/A] + B\log[2(2n_2+1)/B]\}.$$

Hence, if we use the result for hydrogen given in Eq. (0.202), it follows from Eq. (9.31) that when the reaction $H_2+Cl_2-2HCl=0$ takes place at the absolute zero between the crystalline phases, the increase of entropy is

$$\Delta S_0 = S_0(H_2) + S_0(Cl_2) - 2S_0(HCl) = \tfrac{3}{4}R \log 3. \qquad (9.4)$$

It will be observed that this result is independent of the values of the nuclear spins of chlorine and of the ratio of the isotopes of chlorine, and in fact only differs from zero because of the extra factor $3^{3N/4}$ in (9.201) due to the orientations of the molecular angular momentum of the ortho-hydrogen molecules with $j=1$. This is in agreement with the observation made by Gibson and Heitler[66] that in certain gas reactions the limiting contributions made by nuclear spin to the entropy cancel in obtaining the entropy change which occurs during the reaction.

If we perform similar calculations *for any reactions between diatomic molecules all in* $^1\Sigma$ *states, in which all the molecules are oscillating about directions of equilibrium in the lattice near the absolute zero, we find that in all such cases*

$$\Delta S_0 = 0.$$

Wherever on the contrary we have to deal with extra weight factors in the lattice which do not arise from nuclear spins, but from electronic weight factors as in NO or rotational weight factors as in H_2 we are apt to find non-zero values of ΔS_0. Those so far identified are collected in Table V.

TABLE V. *Non-zero changes of entropy for some reactions occurring between crystalline phases at the absolute zero.*

Reaction	S_0
$H_2+Cl_2-2HCl=0$	$\frac{3}{4}R \log 3$
$H_2+Br_2-2HBr=0$	$\frac{3}{4}R \log 3$
$H_2+I_2 \quad -2HI \quad =0$	$\frac{3}{4} R\log 3$
$2NO-N_2 \quad -O_2 \quad =0$	$R \log 2$

If we know ΔS_0 and wish to find the change in entropy when the reaction proceeds at a higher temperature T, not necessarily between crystalline phases, we can find this change ΔS_T by the equation

$$\Delta S_T = \Delta S_0 + \sum_t q_t \int_0^T C_t' dT/T$$

where the C_t''s are the specific heats of the reacting substances A_t measured along reversible paths, becoming infinite in the proper fashion at the transition points, and extrapolated below the lowest temperatures at which measurements of specific heats $(C_p)_{sol}$ are performed on the crystals in the fashion usually followed by experimentalists; except for hydrogen, for which the extrapolation must proceed to 0°K from a temperature of 11°K or higher.

§9.5. The constant I in the equation for the equilibrium constant of a homogeneous gas reaction

Let us consider the homogeneous gas reaction $\Sigma_t q_t A_t = 0$. If K_p is the equilibrium constant in this reaction, then considerations of classical thermodynamics analogous to those used in Chapter I show that

---

[66] Gibson and Heitler, Zeits. f. Physik. **49**, 465 (1928).

$$\begin{aligned}\log K_p &= \log \Pi_t p_t^{q_t} \\ &= -\frac{(Q_p)_0}{RT} + \frac{1}{R}\sum_t (C_p{}^t)_0 \log T \\ &\quad + \int_0^T \frac{dT'}{RT'^2}\int_0^{T'} \sum_t q_t (C_p{}^t)_1 dT'' + I.\end{aligned} \tag{9.51}$$

In this equation q_t as before is the number of gram molecules of the t'th chemical substance reacting, with a negative sign for those that disappear when the reaction takes place, and p_t is the partial pressure of the t'th chemical substance. $(Q_p)_0$ 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 parts respectively of the specific heat at constant pressure of the t'th gaseous substance. I is a constant of integration which is not to be confused in this chapter with the use of the symbol I in previous chapters to denote moments of inertia.

One can show by taking the system through a Nernst cycle[67] that this constant I is related to the vapor pressure constants i_t of the vapors of the separate reacting substances by the equation

$$I = (1/R)\Delta S_0 + \sum_t q_t i_t \tag{9.52}$$

in which ΔS_0 is the change of entropy which occurs when the reaction proceeds between the crystalline phases at the absolute zero, as in §§9.3 and 9.4. It is usual to measure pressures in atmospheres, and to use common logarithms, in Eq. (9.51); if the new constant is denoted by I', then we should use instead of (9.52) the slightly different equation

$$I' = \frac{1}{R \log 10}\Delta S_0 + \sum_t q_t i_t'. \tag{9.53}$$

Eq. (9.52) provides a method of calculating I theoretically from a knowledge of the masses, moments of inertia and quantum states of the *gaseous* molecules concerned. The values of I found will be independent of the values which we have taken for the ω_0's, and will be far more certain to be correct therefore than either the calculated i's or the calculated S_0's. This independence is of course obvious when we approach the theory of the equilibrium constant from the statistical side, since then

$$K_p = \Pi_t (p_t)^{q_t} = \Pi_t\left(\frac{kTF(T)}{V}\right)^{q_t},$$

an equation which makes no reference to any solid phase. We shall not enter into this statistical theory here. To show this independence for diatomic gases with the material already at our disposal we observe that, if we use Eqs. (8.1), (8.15) and (9.3), Eq. (9.52) can be written in the form

---

[67] Fowler, reference 18, pp. 150, 151.

$$I = \sum_t q_t \sum_r D_r^t \log \frac{\Gamma_r^t G_r^t}{D_r^t}\,.$$

In this equation D_r^t is the mole fraction of the r'th species of the t 'th reacting substance, G_r^t is the G for this r'th species of the t'th substance (thus referring only to the gaseous molecules), and Γ_r^t is given by

$$\Gamma_r^t = 8\pi^2 A_r^t k^{7/2}(2\pi m_r^t)^{3/2}/h^5$$

where A_r^t is here the moment of inertia of the r'th species of molecules t, so that Γ_r^t depends upon the constants of the gaseous particles only. Thus if we calculate values of I' for *homogeneous* gas reactions involving diatomic gases by Eq. (9.53), using the calculated i's given in Table IV and the calculated ΔS_0's given in Table V, our results will depend only upon the constants of the gaseous molecules concerned, which are well known; and we shall in fact be able to investigate the accuracy of experimental determinations of I' by comparing the experimental values with our calculated values, since the former are more likely to be incorrect than the latter. Such a comparison can be made by the use of the second and third columns of Table VI, in which we have also considered two reactions involving monatomic vapors, reactions for which the ΔS_0's are obviously zero. Table VI contains also values of $\Delta S_0/(R \log 10)+\Sigma_t q_t i_t' = I''$ in which the i''s are the observed i''s taken from Table IV.

TABLE VI. *The constants I' of some homogeneous gas reactions.*

Reaction	I' Calculated	I' Observed[68]	I'' (See Text)
$H_2+Cl_2-2HCl=0$	-1.174	-1.12 ± 0.2	-0.86
$H_2+Br_2-2HBr=0$	-1.291	-1.25 ± 0.45	-1.21
$H_2+I_2-2HI=0$	-1.549	-1.51 ± 0.12	-1.54
$2NO-N_2-O_2=0$	1.310 High T	0.95 ± 0.3 High T	1.01 Low T
$2Cl-Cl_2=0$	1.53	1.40 ± 0.15	1.22
$2Br-Br_2=0$	1.26	1.41 ± 0.05	1.47

All the observed I''s in column 3 are in fairly good agreement with the calculated I''s in column 2 except for the reaction $2Br-Br_2=0$; but if we consider that the "limit of error" of 0.05 is probably flattering to the experiment then we must consider that the discrepancy could be still greater without furnishing us with any real cause for anxiety. The apparent excellence of the agreement of the number 1.01 in the 4th column with the figure in the 3rd column for the reaction $2NO-N_2-O_2=0$ is illusory; since the former refers to temperatures near to the boiling point of nitric oxide, for which Eucken measured the vapor pressure constant of NO; while the latter refers to temperatures in the neighborhood of 2400°K.

§9.6. Heterogeneous gas reactions

Eq. (9.51) is perfectly general, and applies to heterogeneous gas reactions as well as to homogeneous ones if *all* the partial pressures are taken into ac-

---

[68] Eucken, Phys. Zeits. 30, 818 (1929).

count in the equilibrium constant. However, it is usual to form a new constant K_p' for a heterogeneous gas reaction by omitting from the equilibrium constant K_p the partial pressures of those substances present, to any extent at all, in a condensed phase. Suppose that the substances $1, 2, \cdots r$ are present only as gases, but that condensed phases of the remaining substances $r+1, r+2. \cdots s$ are present (we must have $r \geqq 1$ if equilibrium is to be possible). Then we can at once combine Eqs. (1.1), (9.51) and (9.52) to obtain the equation for the new equilibrium constant of this heterogeneous reaction

$$\log K_p' = \log \prod_{t=1}^{r} p_t^{q_t} = -\frac{(Q_p)_0 - \sum_{r+1}^{s} q_t \Lambda_0^t}{RT} + \frac{1}{R} \sum_{1}^{r} q_t (C_p^t)_0 \log T$$
$$+ \int_0^T \frac{dT'}{RT'^2} \int_0^{T'} \left[\sum_{1}^{r} q_t (C_p^t)_1 + \sum_{r+1}^{s} q_t (C_p^t)_{\text{sol}} \right] dT'' + L$$

where $(C_p^t)_{\text{sol}}$ is the specific heat at constant pressure of the condensed phase of the t'th species, per gram molecule, and

$$L = \frac{\Delta S_0}{R} + \sum_{1}^{r} q_t i_t.$$

Thus to predict L the i's need only be known for those substances present entirely as gases; but we must also know, just as in the case of homogeneous gas reactions, the change in entropy ΔS_0 when the reaction takes place between the crystalline phases at the absolute zero. Since the writers have not been able to find ΔS_0 for any heterogeneous reaction whose constant L has been studied, they have not included any heterogeneous reaction in Table VI.

§9.7. The comparison of the observed and calculated entropies of gases

Suppose that we have a gram molecule of a pure gas at an absolute temperature T and occupying a volume V. There will be N molecules, and if the total energy of the gas is E, then the number of linearly independent wave functions capable of representing the gas will be given by

$$C = \left(\frac{1}{2\pi i}\right)^2 \int\int \frac{dx dz \Pi_t f(xz^{\epsilon_t})}{x^{N+1} z^{E+1}}$$

where the product is taken over all the energy levels ϵ_t of the molecules, with as many factors for any level as there are linearly independent wave functions to represent it. If the molecules obey the Einstein-Bose statistics, then $f(xz^{\epsilon_t}) = (1 - xz^{\epsilon_t})^{-1}$, while if the molecules obey the Fermi-Dirac statistics, then $f(xz^{\epsilon_t}) = 1 + xz^{\epsilon_t}$. Taking the entropy to be $S = k \log C$, we find that

$$S = k \sum_t \log f(\xi \theta^{\epsilon_t}) + \frac{E}{T} - R \log \xi, \tag{9.71}$$

where ξ and $\theta (= e^{-1/kT})$ as usual are given by the vanishing of the partial derivatives, with respect to x and z respectively, of the integrand of C. In accordance with the discussions of §§21.43 and 21.44 of Fowler's *Statistical Mechanics*, we may replace $\Sigma_t \log f(\xi\theta^{\epsilon_t})$ by

$$\xi F(\theta) = \xi \frac{(2\pi m)^{3/2} V f(\theta)}{h^3 (\log 1/\theta)^{3/2}},$$

where $f(\theta)$ is the partition function for internal motions of a gas molecule, with great accuracy for all gases at ordinary temperatures and concentrations. Since we have $N = \xi F(\theta)$ and $E = \xi\theta(\partial/\partial\theta) F(\theta) = N\theta(\partial/\partial\theta)\log F(\theta)$, we find therefore from (9.71) that

$$S = \frac{3}{2} R \log T + R \log V + \left[\frac{5}{2} R - R \log N + R \log \frac{(2\pi m k)^{3/2}}{h^3}\right] + R\left[\log f(\theta) + \frac{1}{kT}\frac{\theta f'(\theta)}{f(\theta)}\right].$$

If we set $m = Mm'$ where M is the molecular weight of the gas and m' is the mass of an atom of atomic weight 1, we find that if S is measured in calories per °C, then numerically

$$S = k \log C = (3/2)R \log T + R \log V + (3/2) R \log M - 11.06 + R\left[\log f(\theta) + \frac{1}{kT}\frac{\theta f'(\theta)}{f(\theta)}\right]. \tag{9.72}$$

The first four terms in the above expression for the entropy form merely the Sackur expression for the entropy of the gas when it is supposed to be made up of simple particles of molecular weight M without internal energy; the last term $R[\ ]$ gives the contribution to the entropy furnished by the internal energy of the particles. It may be written in the form

$$R\left[\log \sum_r \omega_r e^{-\epsilon_r/kT} + \frac{1}{kT} \frac{\sum_r \omega_r \epsilon_r e^{-\epsilon_r/kT}}{\sum_r \omega_r e^{-\epsilon_r/kT}}\right]$$

and can be evaluated either accurately from the spectroscopic energy levels, or less accurately but more expeditiously by such methods as those devised by Mulholland[69] and Sutherland[70] for diatomic molecules, or even by such still less accurate methods as those used in this article for approximating to the rotational partition functions of diatomic molecules. We do not need to be concerned here with the manner in which as a practical matter the last term of Eq. (9.72) is to be evaluated; the important thing is that it can be evaluated, and that it can be evaluated from a knowledge merely about those energy levels which are not large compared with kT. Before passing on to consider the case of mixed gases, we note that the inclusion of any constant factor g in all the terms of $f(\theta)$ may be avoided by using in the last term of Eq. (9.72) the $f(\theta)$ without that factor, and by adding $R \log g$ to the right-

---

[69] Mulholland, Proc. Camb. Phil. Soc. **24,** 280 (1928).

[70] Sutherland, Proc. Camb. Phil. Soc. **26,** 401 (1930).

hand member. In using Eq. (9.72) we must use the correct statistical weights for the energy levels of the molecules, or we shall not be calculating $k\log C$ correctly.

The occurrence of a pure gas in thermal experiments is perhaps rather exceptional; there will usually be present a mixture of isotopic varieties, or of varieties corresponding to non-combining groups of terms. Let us consider an assembly consisting of a gram molecule of mixed gases 1 and 2, with gram molecular fractions D_1 and D_2, respectively, molecular weights M_1 and M_2 respectively, and partition functions for the internal energies of the molecules $f_1(\theta)$ and $f_2(\theta)$, respectively. Corresponding to Eq. (9.71) we have now the equation

$$\begin{aligned} S = k\log C = k\sum_t \log f_1(\xi\theta^{\epsilon_t}) + k\sum_t \log f_2(\eta\theta^{\epsilon_t}) \\ + \frac{E}{T} - RD_1 \log \xi - RD_2 \log \eta \end{aligned} \tag{9.73}$$

where the first and second sums refer to the molecules of the first and second sorts, respectively, and where ξ and η correspond to the values of the selector variables x and y for the two sorts of molecules, respectively, for which the integrand of the complex integral is a minimum. We find by methods similar to those used in deriving Eq. (9.72) the equation

$$\begin{aligned} S = k\log C = (3/2)R\log T + R\log V + (3/2)R(D_1\log M_1 + D_2 \log M_2) - 11.06 \\ + D_1R\left[\log f_1(\theta) + \frac{1}{kT}\frac{\theta f_1'(\theta)}{f_1(\theta)}\right] + D_2R\left[\log f_2(\theta) + \frac{1}{kT}\frac{\theta f_2'(\theta)}{f_2(\theta)}\right] \\ - R(D_1 \log D_1 + D_2 \log D_2). \end{aligned} \tag{9.74}$$

This, it will be observed, is the sum of the entropies of the constituent gases, each occupying a volume V, given by Eq. (9.72), plus a term, the last term in Eq. (9.74), corresponding to the mixing of the gases. We may call the last term the entropy of mixing. We could have derived the same expression for the entropy of mixing by thermodynamical arguments instead of by statistical mechanics.

The generalization of Eq. (9.74) to mixtures of any number of gases is obvious; it is

$$\begin{aligned} S = k\log C = (3/2)R\log T + R\log V + (3/2)R\sum_r D_r \log M_r \\ - 11.06 + R\sum_r D_r\left[\log f_r(\theta) + \frac{1}{kT}\frac{\theta f_r'(\theta)}{f_r(\theta)}\right] \\ - R\sum_r D_r \log D_r. \end{aligned} \tag{9.75}$$

The varieties r may be different gases altogether, different isotopic varieties of the same gas, or non-combining varieties of the same isotopic gas. A simplification in Eq. (9.75) is possible in case some of the varieties, 1 and 2, say, are of the same isotopic nature and correspond merely to non-combining varieties, provided that the actual proportion D_1/D_2 between the gases is nearly the same as the long-time equilibrium proportion $f_1(\theta)/f_2(\theta)$ between the gases at the temperature T. These conditions are fulfilled for hydrogen at temperatures of 298°K and higher, and for most other gases at all temperatures above their boiling points. Since $D_1/D_2=f_1(\theta)/f_2(\theta)$, we may set $D_1+D_2=D_{1,2}$, and $f_1(\theta)+f_2(\theta)=f_{1,2}(\theta)$ and we have then at once that

$$\frac{3}{2} R \sum_{1,2} D_r \log M_r + R \sum_{1,2} D_r\left[\log f_r(\theta) + \frac{1}{kT}\,\frac{\theta f_r'(\theta)}{f_r(\theta)}\right] - R \sum_{1,2} D_r \log D_r$$

$$= \frac{3}{2} RD_{1,2} \log M_{1,2} + RD_{1,2}\left[\log f_{1,2}(\theta) + \frac{1}{kT}\,\frac{\theta f_{1,2}'(\theta)}{f_{1,2}(\theta)}\right] - RD_{1,2} \log D_{1,2}.$$

In using Eq. (9.75) to calculate entropies at ordinary temperatures we may therefore disregard the non-combining varieties, and treat them as constituting together a gas in which transitions occur freely between the ortho- and para-terms, provided that the actual proportions are nearly the long-time equilibrium proportions for that temperature. The entropy is then the same whether ortho⇄para transitions occur or not. This might have been expected, since the entropy of a gas is a function merely of its statistical state.

Eq. (9.75) will allow us to calculate the entropy $S=k \log C$ of any gas if we know the energies and the statistical weights of the levels which contribute significant terms to the sums; but to know the statistical weights of the levels calls for a knowledge of the values of the nuclear spins of the several nuclei. Further, as pointed out in §9.1, when we make *experimental* determinations of the entropies of a substance it is simplest to refer entropies to the ideal state of the crystalline phase at the absolute zero. Let us take the ideal crystalline state at the absolute zero as the state of zero entropy; and let us denote the entropy of our gas referred to this standard by S_m, so that

$$S_m = k \log C - S_0$$

where the S_0 is the S_0 of §9.3. Making use of Eqs. (9.3) and (9.75) we find for the entropy of the gas referred to the ideal solid state at the absolute zero the value

$$\begin{aligned} S_m &= k \log C - R \sum_r D_r \log \frac{{}_r\omega_0}{D_r} \\ &= (3/2)R \log T + R \log V + (3/2)R \sum_r D_r \log M_r - 11.06 \\ &\qquad + R \sum_r D_r\left[\log \frac{f_r(\theta)}{{}_r\omega_0} + \frac{1}{kT}\,\frac{\theta f_r'(\theta)}{f_r(\theta)}\right]. \end{aligned} \tag{9.76}$$

It will be seen at once by an examination of Eq. (9.76) that as long as we know the gram molecular fractions D_r of the constituents of our gas, and the values of $f_r(\theta)/{}_r\omega_0$, we can calculate the entropy of the gas referred to the ideal solid state at the absolute zero. We do not need to know the values of the nuclear spins to calculate $R\Sigma_r\, D_r[\ ]$. Further, this calculation[71] yields a value for the entropy in a form which we may compare at once with the results of experiments.

In the following table we compare the entropies calculated in accordance with Eq. (9.76) with the thermally measured entropies S_m', for gram molecules of a number of gases at atmospheric pressure and at temperatures T. In preparing this table we have made use of the measurements of Giauque and his fellow workers, and also of their calculations; the latter were based in all cases upon spectroscopically determined data for the internal energy levels of the molecules, and the partition functions were calculated by calculating the terms separately and adding them together. Small corrections should be applied to the calculated entropies S_m to take account of the deviations of the gases from the laws of ideal gases; these corrections calculated in accordance with Berthelot's equation are denoted by λ in the table, and are taken from the papers of Giauque and his co-workers. The values of ${}_r\omega_0$ used are those given in Table II of Chapter IV. The comparison is thus between $S_m+\lambda$ and S_m'. The state of zero entropy for this table is the ideal solid state at the absolute zero.

It will be seen that the numbers in the fifth and sixth columns agree closely with each other, verifying our values of ${}_r\omega_0$ given in Table II.

TABLE VII. *A comparison of the calculated and observed entropies of certain gases.*

Substance	T°K	S_m	λ	$S_m+\lambda=S_m'$ Calculated	S_m' Observed
NO (1)	121.36	43.06	−0.09	42.97	42.94
H_2 (2)	298.1	29.59	−0.13	29.46	29.61
O_2 (3)	90.13	40.68	−0.17	40.51	40.57
HCl (4)	188.07	41.45	−0.1	41.35	41.2
HBr (5)	206.38	44.92	−0.1	44.82	44.9
HI (6)	237.75	47.8	−0.1	47.7	47.8

AUTHORITIES

[1] Johnston and Giauque, J.A.C.S. **51**, 3194 (1929).
[2] Giauque, J.A.C.S. **52**, 4816 (1930).
[3] Giauque and Johnston, J.A.C.S. **51**, 2300 (1929).
[4] Giauque and Wiebe, J.A.C.S. **50**, 101 (1928).
[5] Giauque and Wiebe, J.A.C.S. **50**, 2193 (1928).
[6] Giauque and Wiebe, J.A.C.S. **51**, 1441 (1929).

§9.8. The Nernst Heat Theorem. General conclusions

We have nowhere in this article referred to the hypothesis commonly known as "Nernst's Heat Theorem," or the "Third Law of Thermodynamics." This hypothesis has of course played a great part in the develop-

---

[71] We are not following the procedure of Giauque and his co-workers exactly in comparing the observed and calculated entropies, because the comparison of the observed entropies referred to the ideal solid state at the absolute zero, with the entropies calculated in accordance with Eq. (9.76) is perhaps somewhat more consistent than the methods of comparison used by Giauque. Giauque includes the factors arising from the nuclear spins in his calculations for hydrogen, while he does not include them in the case of NO, HCl, HBr, and HI. Although Eq. (9.76) shows the neglecting of the spins to be justifiable, Giauque uses different states of zero entropy in his different calculations.

ment of the subject. It asserts that when reactions occur isothermally at temperature T between different pure crystalline substances, with a change of entropy ΔS, then

$$\lim_{T\to 0} \Delta S = 0.$$

(This is its most restricted form, to which alone we need pay attention. Other forms referring generally to condensed crystalline or amorphous or (ideally) liquid phases are now generally agreed to be invalid.) We have here examined numerous cases of such reactions theoretically and are forced to conclude that *if we extrapolate to the absolute zero from ordinary measurements and therefore refer to the ideal state, though*

$$\lim_{T\to 0} \Delta S = \Delta S_0 = 0$$

is very commonly true, yet it is not true in general that

$$\Delta S_0 = 0.$$

If on the other hand we could extrapolate to $T=0$ from measurements at such low temperatures that kT_0 is small compared with the finest of the energy separations of the very low states of the solid, then Nernst's Heat Theorem may or may not be true—we do not as yet know. But in no case will its truth ever be able to be investigated by direct thermal measurements in the foreseeable future, nor can it ever be used blindly in calculating changes of entropy during reactions at higher temperatures. The necessary kT_0 for the low limit of experimental measurement of specific heats lies far below the reach of any experimental refinements yet conceivable.

We reach therefore the rather ruthless conclusion that *Nernst's Heat Theorem strictly applied may or may not be true, but is always irrelevant and useless—applied to "ideal solid states" at the absolute zero which are physically useful concepts the theorem though often true is sometimes false, and failing in generality must be rejected altogether.* It is no disparagement to Nernst's great idea that it proves ultimately to be of limited generality. The part that it has played in stimulating a deeper understanding of all these constants, and its reaction on the development of the quantum theory itself cannot be overrated. But its usefulness is past and it should now be eliminated.

As another aspect of the same failure it is no longer possible to assert that the entropies of the ideal solid states of all substances can be assumed to be zero, nor is it even usually any longer convenient to do so, at least in a theoretical treatment. If we please we may of course assign the value zero to the entropy of the ideal solid state of any or all true elements, or if we prefer, of pure isotopes of pure elements. But even this will seldom be theoretically convenient. For the purpose of tabulating experimental results some conventional zero must always be chosen and the choice of zero for the entropy of the ideal solid state of any substance may then often be convenient. But its conventional character will no longer be so likely to be overlooked that any importance will be attached in future to the idea of *absolute entropy*, an idea which has caused much confusion and been of very little assistance in the development of the subject. The only natural choice of the entropy constant entitled to any claim to the character of absoluteness is obviously to define the entropy so that it is always $k\log C$. But now we must include nuclear spins and isotopic mixtures in evaluating C. Is it really certain that even by so doing we enumerate C with absolute finality?

One further point in conclusion. A determination of a vapor pressure as a function of temperature fixes the characteristics of the equilibrium of a two phase assembly. Any such equilibrium is determined when the free energies of the substance in its two phases are known, and these are known when the energy and entropy differences have been fully determined by observation of specific and latent heats. One may fairly assert therefore that it is a matter of indifference whether one studies the vapor pressure equation of a substance or the entropy difference of its two phases, both as a function of the temperature. It has become increasingly common of recent years, under the inspiration of G. N. Lewis, to study and report the entropies of the phases usually relative to an assumed zero value for the entropy of the ideal solid state at $T=0$. We have adopted this method here in only one section, and have followed on the whole the other method of vapor pressures mainly for historical reasons but also because it is hardly possible to improve on the simplicity of the theoretical vapor pressure equation and equation of dissociative equilibrium. But it should be clear that this does not imply any lack of sympathy with the newer presentation, which has much to recommend it practically, since the entropy is a far more generally useful quantity than the vapor pressure. It may well be that the study of vapor pressures will soon be almost entirely abandoned for a direct study of entropies. The questions that have exercised us in this article will reappear, superficially altered it is true, but in essential content the same.

APPENDIX I

CRYSTALS IN QUANTUM MECHANICS

§A1.1. Introduction

In several places in this article we have had to calculate the total number of linearly independent wave functions capable of representing a crystal. In Chapter II we considered a crystal made up of P atoms which could have various states of internal energy besides taking part in the normal modes of oscillation of the crystal as a whole. We made use of the partition function $[\kappa(z)]^P$ for the normal modes of the crystal. In Chapter III we considered a crystal made up of two sorts of molecules having the same masses but different states of internal energy, and we made use again of the function $\kappa(z)$. In Chapter V we considered crystals of chlorine composed of molecules of five sorts with three different but nearly equal masses. We made use again of the function $\kappa(z)$ for the normal modes. And in all of these cases we considered that a complete wave function for a crystal was a linear combination, with the proper symmetry properties, of functions of the form $\psi_m\psi_i$ to a first approximation, where ψ_m was a wave function representing a set of normal modes of the whole lattice, and ψ_i was a wave function representing a set of internal energy states for the particles which made up the lattice. We are not aware of the existence of any discussion of the wave functions of crystals to which we can refer the reader, in order to justify our procedure; and we accordingly shall proceed to discuss the wave functions of crystals in this appendix. We start for simplicity with a discussion of a linear "crystal" made up of three simple particles without internal energy.

§A1.2. A simple crystal

Let us consider a "crystal" made up of three particles of mass m, constrained to lie on a straight line AB, and whose potential energy function is

$$V = \tfrac{1}{2}b[(x_2 - x_1 - a)^2 + (x_3 - x_2 - a)^2]$$

for small values of $x_2 - x_1 - a$ and $x_3 - x_2 - a$. x_1, x_2 and x_3 are the abscissae of the particles, and we suppose that $x_1 < x_2 < x_3$. The quantity a is the lattice constant of our crystal. We have for the kinetic energy

$$T = \tfrac{1}{2}m(\dot{x}_1^2 + \dot{x}_2^2 + \dot{x}_3^2).$$

Let us take the center of mass of the set of particles to be at rest at the origin, so that $x_1 + x_2 + x_3 = 0$. We may do this because it amounts merely to neglecting the factor in the complete wave function which describes the motion of translation of the mass center; the problem is of course separable in the coordinates of the mass center and in the coordinates of the particles referred to the mass center. Then if we make the transformation to the normal coordinates q_1 and q_2 defined by

$$\left.\begin{aligned} q_1 &= \tfrac{1}{2}(6m)^{1/2}(x_1 + x_3) \\ q_2 &= \tfrac{1}{2}(2m)^{1/2}(x_1 - x_3 + 2a) \end{aligned}\right\}$$

we shall have

$$\begin{aligned} T &= \tfrac{1}{2}(\dot{q}_1^2 + \dot{q}_2^2) \\ V &= \tfrac{1}{2}\left(\frac{3b}{m} q_1^2 + \frac{b}{m} q_2^2\right). \end{aligned}$$

Since the Hamiltonian thus splits up into two parts, the complete wave function of the crystal will be

$$\Psi = \psi(q_1)\psi(q_2),$$

where the wave function $\psi(q_1)$ of the normal mode q_1 is a solution of the equation

$$\tfrac{1}{2}\left(\frac{3b}{m} q_1^2 - \frac{h^2}{4\pi^2}\frac{\partial^2}{\partial q_1^2}\right)\psi(q_1) = E_1\psi(q_1),$$

and the wave function $\psi(q_2)$ of the normal mode q_2 is a solution of the equation

$$\tfrac{1}{2}\left(\frac{b}{m} q_2^2 - \frac{h^2}{4\pi^2}\frac{\partial^2}{\partial q_2^2}\right)\psi(q_2) = E_2\psi(q_2).$$

The total energy is $E=E_1+E_2$.

The solutions of these equations, which are those for two linear harmonic oscillators, are well known. When the normal mode q_1 is in its n_1'th quantum state its energy E_1 is

$$E_1 = (n_1 + \tfrac{1}{2})\frac{h}{2\pi}\left(\frac{3b}{m}\right)^{1/2}$$

and its wave function is, except possibly for a constant factor,

$$\psi(q_1) = f_{n_1}(q_1)e^{-q_1^2/2a_1^2},$$

where

$$a_1^2 = h/[2\pi(3b/m)^{1/2}]$$

and $f_0(x)=1$, $f_1(x)=x$, $f_2(x)=x^2-a_1^2/2$, etc. Here n_1 can have the values 0, 1, 2, 3, 4, 5 $\cdots$ etc. Similarly, when the normal mode q_2 is in its n_2'th quantum state its energy is

$$E_2 = (n_2 + \tfrac{1}{2})(h/2\pi)(b/m)^{1/2}$$

and its wave function is, except for a constant factor,

$$\psi(q_2) = f_{n_2}(q_2)e^{-q_2^2/2a_2^2},$$

where

$$a_2^2 = h/[2\pi(b/m)^{1/2}].$$

If both modes are in the states $n=0$, then the crystal has a wave function given, except for a constant factor, by

$$\Psi = \exp\,[-\,(3m/4a_1^2)(x_1 + x_3)^2 - (m/4a_2^2)(x_1 - x_3 + 2a)^2]$$

and since this is only appreciably different from zero when the exponent vanishes or is nearly zero, we must have $x_1=-a$, $x_2=0$ and $x_3=a$ very nearly if the wave function is not to be extremely small. We observe that for this lowest quantum state there is only one linearly independent wave function for the "crystal". Suppose next, as another example, that $n_1=1$ and $n_2=0$. Then

$$\Psi = \tfrac{1}{2}(6m)^{1/2}(x_1 + x_3)\exp\left[-\frac{3m}{4a_1^2}(x_1 + x_3)^2 - \frac{m}{4a_2^2}(x_1 - x_3 + 2a)^2\right]$$

which will be appreciably different from zero only when

$$x_1 \sim -\,a + a_1(1/6m)^{1/2};\quad x_2 \sim -\,a_1(2/3m)^{1/2};\quad x_3 \sim a + a_1(1/6m)^{1/2}$$

or when

$$x_1 \sim -\,a - a_1(1/6m)^{1/2};\quad x_2 \sim a_1(2/3m)^{1/2};\qquad x_3 \sim a - a_1(1/6m)^{1/2}.$$

Considerations of this sort give us a fairly good mental picture of the nature of a set of normal modes of a crystal, in quantum mechanics.

§A1.3. A crystal composed of equivalent particles without internal motions. Its partition function

Let us now consider the more general case of a crystal made up of a set of similar massive particles, 1, 2, 3, $\cdots N$. Let us take a set of orthogonal axes OX, OY and OZ in space. Let the coordinates of the particles referred to this set of axes be $(x, y, z)_1$; $(x, y, z)_2$; $\cdots$. Due to the interactions of the particles with each other, there exists a potential function $V(x, y, z)$ for the set of particles, symmetrical in all of them because the particles are similar. Let us restrain particle 1 so that it lies at the origin, let us restrain particle 2 so that it lies on the OX axis, and let us restrain particle 3 so that it lies in the plane XOY. Then the potential function $V(0, 0, 0;\, x_2, 0, 0;\, x_3, y_3, 0;\, x_4, y_4, z_4, \cdots)$ will have minima; and the set of values of the coordinates corresponding to any of these minima will define the lattice points of a possible crystal of the original set of particles. The number of possible lattices will in general be finite if the set of particles is finite.

Let us fix our attention on one of these possible lattices; 0, 0, 0, q_4, 0, 0, q_7, q_8, 0, q_{10}, q_{11}, q_{12}, $\cdots$ (it is convenient to change the notation in this fashion). By Taylor's theorem, for sufficiently small displacements $\xi_s = q_{s'} - q_s$ of the particles from their lattice points q_s the potential function can be expressed in the form

$$V = \tfrac{1}{2}(b_{11}\xi_1^2 + b_{22}\xi_2^2 + \cdots + 2b_{12}\xi_1\xi_2 + \cdots + 2b_{3N-1,3N}\,\xi_{3N-1}\,\xi_{3N}) + \text{cubic terms} + \cdots \tag{A1.3}$$

and also, of course,

$$T = \tfrac{1}{2}m(\dot{\xi}_1^2 + \dot{\xi}_2^2 + \cdots + \dot{\xi}_{3N}^2).$$

We neglect the cubic terms in Eq. (A1.3), which can be taken care of later, if desired, by a perturbation method. It will always be possible to transform the coordinates ξ, by linear transformations, into normal coordinates[72] Q, linearly independent of each other, such that T and V will be in the forms

$$T = \tfrac{1}{2}(\dot{Q}_1^2 + \dot{Q}_2^2 + \cdots + \dot{Q}_{3N-6}^2)$$

$$V = \tfrac{1}{2}(\mu_1 Q_1^2 + \mu_2 Q_2^2 + \cdots + \mu_{3N-6} Q_{3N-6}^2)$$

where the μ's are constants. The number of independent Q's is $3N-6$ instead of $3N$ because of our requirement originally that $q_1 = q_2 = q_3 = q_5 = q_6 = q_9 = 0$. The Q's are of course linear functions $Q[(x, y, z)_1, (x, y, z)_2, \cdots]$ of the original spatial coordinates $(x, y, z)_i$ of the particles.

Let $a_r^2 = h/(2\pi\mu_r^{1/2})$. When the mode r is in the n'th quantum state, its energy is

$$E_r = (n + \tfrac{1}{2})(h/2\pi)\mu_r^{1/2}$$

where n can have the values 0, 1, 2, 3, 4, $\cdots$, and its wave function ψ_r is given by

---

[72] See Whittaker's *Analytical Dynamics*.

$$\psi_r[(x, y, z)_1, (x, y, z)_2, \cdots] = f_n(Q_r)e^{-Q_r^2/2a_r^2}.$$

Here $f_n(Q_r)$ is the Hermite polynomial of the n'th order, except for a constant factor. The total energy of the crystal is $E = \Sigma_r E_r$ and the total wave function is

$$\Psi[(x, y, z)_1, (x, y, z)_2, \cdots] = \Pi_r \psi_r$$

where the sum and product are taken over all the modes r. This wave function will not in general be symmetrical or antisymmetrical in the particles 1, 2, 3, $\cdots$ because we have thus far neglected symmetry considerations. The correct V function was symmetrical in all of the particles, but the approximate V function (A1.3) was not symmetrical. Actually, we can interchange any two particles in the crystal without obtaining a different crystal. Accordingly the correct wave function for the entire crystal is

$$\Psi' = \sum_P P\Psi[(x, y, z)_1, (x, y, z)_2, \cdots (x, y, z)_N] \cdot \qquad \text{(A1.35)}$$

where the summation is taken over all permutations P of the sets of coordinates $(x, y, z)_i$ within the function corresponding to all possible distributions of the N particles among the lattice points. In making the permutations the members of any set $(x, y, z)_i$ must of course be kept together. If the particles obey the Einstein-Bose statistics, then Ψ' must be symmetrical in all the particles, and all of the terms $P\Psi$ in Eq. (A1.35) must be given the same sign. If the particles obey the Fermi-Dirac statistics, then Ψ' must be antisymmetrical in all of the particles and the permutations $P\Psi$ must be given one sign when they are even and the opposite sign when they are odd. But in any case, whether or not we take account of symmetry considerations, there is one and only one linearly independent wave function corresponding to any particular assignment of quantum numbers $n_1, n_2, n_3, \cdots n_{3N-6}$ to the $3N-6$ normal modes 1, 2, 3, $\cdots 3N-6$, respectively.

It is now possible to construct, at least theoretically, the partition function $H(z)$ for this crystal, given by

$$H(z) = \sum_{n_1, n_2, n_3, \cdots} z^{E_{n_1, n_2, n_3, \cdots}}$$

where the sum is taken over all the possible choices of the set of n_r's. If the total energy of the crystal is E, then the number of linearly independent wave functions capable of representing the crystal is the coefficient of z^E in $H(z)$. For the evaluation of this sum in a simple case, the reader is referred to Chapter IV of Fowler's *Statistical Mechanics.* Whether or not, however, we are able to *calculate* this partition function $H(z)$ from purely theoretical considerations, we know that this function exists. For the number of linearly independent wave functions capable of representing the crystal when its energy is E is given by

$$C = \frac{1}{2\pi i}\int dz H(z)/z^{E+1} \qquad \text{(A1.36)}$$

and from the discussion in §21.41 of Fowler's *Statistical Mechanics* we find that the entropy of the crystal, except perhaps for an additive constant which may be arbitrarily chosen, is

$$S = k \log C = k \log H(\theta) + E/T. \tag{A1.37}$$

The function $H(z)/H(0)$ for positive real values of z, can therefore be found from the thermal properties of the crystal which can be observed experimentally. $H(z)$ will in general depend upon the volume of the crystal if the latter is isotropic and subject only to isotropic stress (hydrostatic pressure) and upon the components of stress if the crystal is anisotropic, as well as upon the temperature; but this need not concern us here. If the stresses are maintained constant, and if the entropy of the crystal is really an *extensive* property, then it follows from Eq. (A1.37) that $H(z)$ must be expressible in the form $[\kappa(z)]^N$, at least for large values of N, where $\kappa(z)$ is independent of N.

§A1.4. A pure crystal composed of similar systems possessing internal degrees of freedom. Its partition function

When we have actual physical systems making up the crystal, and not massive particles, we must take account of internal motions. Suppose that the systems composing the crystal are all the same. Then they can have different internal quantum states at the different lattice points. We denote the lattice points, which of course do not take part in any permutability relations, by $A_1, A_2, A_3, \cdots A_N$. Then instead of the unpermuted Ψ of the previous section we shall have for a wave function for the entire crystal

$$\Psi = \psi_{A_1}(\rho_1)\psi_{A_2}(\rho_2) \cdots \psi_{A_N}(\rho_N)\Pi_r\psi_r \tag{A1.40}$$

to the first approximation; where ρ_i denotes the coordinates describing the internal arrangement of the system i whose coordinates in space are $(x, y, z)_i$; and $\psi_{A_k}(\rho_i)$ is the wave function for internal motions of the particle i at the lattice point A^k. Accordingly, if we take account of the symmetry properties which the complete wave function of the crystal must have, we find for the complete wave function

$$\Psi' = \sum_P P\{\psi_{A_1}(\rho_1)\psi_{A_2}(\rho_2) \cdots \psi_{A_N}(\rho_N)\Pi_r\psi_r[(x, y, z)_1, (x, y, z)_2, \cdots (x, y, z)_N]\}, \tag{A1.41}$$

where the summation is over all the permutations P of the particles 1, 2, 3, $\cdots N$ as in the last section, with the same rule as to signs. In this process of permuting, the ρ_i's are of course to be permuted in the same manner for any term in the sum as the $(x, y, z)_i$'s are permuted in the same term. We should notice that in Eqs. (A1.40) and (A1.41) we have neglected the interactions between the normal modes of vibration of the crystal lattice and the internal quantum states of the systems making up the lattice. The existence of these interactions is of course necessary for the establishment of thermal equilibrium in the crystal, but we need not concern ouselves explicitly with them here, further than to notice that they exist.

It is obvious from the discussion of the last paragraph that corresponding to any assignment of the quantum numbers $n_1, n_2, \cdots$ of the normal modes of vibration of the crystal lattice, there exists one and only one linearly independent wave function capable of representing the entire crystal. It follows also that if the partition function for one of the similar systems in the crystal for internal motions is $f(z)$, and if as before $H(z)$ is the partition function for the entire crystal for normal modes of vibration, then the partition function for the entire energy of the crystal, taking account of the energy of the normal modes as well as of the internal energy of the systems, is

$$H(z)\,[f(z)]^N$$

and by the discussion of §A1.3 this is capable of being expressed in the form

$$[\kappa(z)f(z)]^N.$$

In obtaining this form we have neglected as we have said the interactions between the normal modes of vibration and the internal states of the systems; but it should be sufficiently accurate for our purposes when we make use of it, as in Chapter II for calculating vapor pressures.

§A1.5. A mixed crystal composed of particles without internal motions. Its partition function

Suppose that we have a crystal made up of N_1 particles of mass m_1 and N_2 particles of mass m_2, arranged in some definite manner among the N_1+N_2 lattice points of the crystal. Just as in the case of a crystal made up of particles of equal mass considered in §A1.3, there exists a set of normal modes of vibration of the crystal lattice, and any state of the set may be specified by the quantum numbers $n_1, n_2, n_3, \cdots$ There is as before only one linearly independent wave function for the crystal in this state, and the complete wave function will be a linear combination of terms obtained by permuting the N_1 particles of sort 1 among themselves and the N_2 particles of sort 2 among themselves, the signs of the terms being determined by the nature of the particles in the obvious fashion. The existence of all these terms corresponds to the fact that permutations of the sort specified above do not alter the crystal in any physically significant way. However, we have supposed that there was a definite set of lattice points in the crystal occupied by the particles 1, and a definite set occupied by the particles 2. If we interchange any of the particles 1 with particles 2, we shall obtain a different crystal. In general, there will be a different set of transformations to normal coordinates, the normal modes will be different functions of the coordinates of the particles, and the energy levels will be different, for each such crystal. The number of different crystals possible is $(N_1+N_2)!/(N_1!\,N_2!)$, if mixing can occur in all ways.[73] There will in general be a different partition function for each of these crystals, so that the partition function for a mixed crystal should in general be dependent upon the internal arrangement.

---

[73] See Chapter VII.

Let us denote the different arrangements by the numbers 1, 2, 3, $\cdots$ $(N_1+N_2)!/(N_1!\,N_2!)$. Let us denote the partition function for the whole crystal in the j'th arrangement by $H_j(z)$. If as we suppose all of the different arrangements are possible, then if we know merely the total energy of the crystal E, say, the number of linearly independent wave functions which can represent the crystal is the coefficient of z^E in

$$H^*(z) = \sum_j H_j(z)$$

where the summation is over all the $(N_1+N_2)!/(N_1!\,N_2!)$ values of j. $H^*(z)$ is therefore the partition function for the mixed crystal when all arrangements are possible, and will depend in general not only upon N_1+N_2, but also upon the ratio of N_1 to N_2. If only some arrangements are possible, then the partition function $H^*(z)$ in this case is obtained by summation over merely those values of j which correspond to possible arrangements.

The interesting case as far as applications are concerned in this article is that for which the masses of the particles are nearly the same, and for which mixing can occur in all fashions. If the masses were exactly the same, then all the $H_j(z)$'s would be the same and we should have

$$H^*(z) = (N_1 + N_2)!H(z)/(N_1!N_2!),$$

and hence

$$H^*(z) = (N_1 + N_2)![\kappa(z)]^{N_1+N_1}/(N_1!N_2!), \tag{A1.5}$$

from the considerations of §A1.3. Here $\kappa(z)$ is the same function as the $\kappa(z)$ for a pure crystal of either sort. If the masses are not exactly equal, but are only approximately equal, then we may expect Eq. (A1.5) to provide an approximate value for the partition function of the crystal.

Analogous considerations are applicable to the case of crystals made up of particles of more than two sorts.

§A1.6. A mixed crystal composed of systems with internal degrees of freedom. Its partition function

Suppose that we have a crystal made up of N_1 systems of mass m_1 and N_2 systems of mass m_2 arranged in some definite manner j among the lattice points of the crystal. Then corresponding to a specification of the quantum numbers $n_1, n_2, n_3, \cdots$ and to a specification of the wave function representing the system at each lattice point of the crystal, there corresponds one and only one wave function $\Psi j'$ of the whole crystal with the appropriate symmetry properties:

$$\Psi_j' = \sum_{P_1,P_2} P_1P_2\{[f_{A_1}(\rho_1)f_{A_2}(\rho_2)\cdots][\Pi_r\psi_r[(x,y,z)_1,(x,y,z)_2,\cdots]]\}. \tag{A1.60}$$

The permutations P_1 operate only on the coordinates of the systems of sort 1 in the first and second bracketted expressions in Eq. (A1.60); while the permutations P_2 operate only on the coordinates of systems of sort 2, in the first and second bracketted expressions. For any particular term, the permutations must of course operate on both bracketted expressions in the same manner. The signs of the $N_1!\ N_2!$ terms are to be determined from the consideration that whenever two particles of the same sort which obey the Einstein-Bose statistics are interchanged, the sign of a term is unaltered; while whenever two particles of the same sort which obey the Fermi-Dirac statistics are interchanged, the sign is changed.

If we neglect the interactions between the normal modes of vibration and the internal quantum states of the systems, then the partition function for the crystal when it is in the arrangement j is

$$H_j(z)\,[f_1(z)]^{N_1}[f_2(z)]^{N_2}$$

where the $H_j(z)$ is the same as the $H_j(z)$ of the last section, where $f_1(z)$ is the partition function for the internal energy of a system of sort 1, and $f_2(z)$ is the partition function for the internal energy of a system of sort 2. We are neglecting here to take account of the fact that the energy levels of a system of sort 1 may depend to some extent upon the types to which the neighboring systems belong and upon their energy states; the above form for the crystalline partition function will be only approximately correct. To take account of all the $(N_1+N_2)!/(N_1!\ N_2!)$ possible arrangements, we must sum the above expression over all values of j; and we then find for the complete crystalline partition function the value

$$H^*(z) = [f_1(z)]^{N_1}[f_2(z)]^{N_2}\sum_j H_j(z).$$

If mixing can occur in all ways then j takes on all the values from 1 to $(N_1+N_2)!/(N_1!\ N_2!)$; if the mixing can not occur in all ways then the sum is taken over those values of j which are possible. As in the previous section, if the masses of the systems are the same and if mixing can occur in all ways then we must have the sum in the above expression equal to

$$[(N_1+N_2)!/(N_1!N_2!)]\,[\kappa(z)]^{N_1+N_2}$$

where $\kappa(z)$ is the same function as the $\kappa(z)$ for a pure crystal of either sort, considered in §A1.3. Hence the crystalline partition function will be

$$H^*(z) = [(N_1+N_2)!/(N_1!N_2!)]\,[f_1(z)]^{N_1}[f_2(z)]^{N_2}[\kappa(z)]^{N_1+N_2}. \qquad \text{(A1.61)}$$

If the masses are only approximately equal then Eq. (A1.61) will be only approximately correct. The generalization for more than two sorts of systems is obvious.

An instance of the use of Eq. (A1.61) for two sets of systems with equal masses is provided by the case of hydrogen, made up of two varieties, considered in Chapter III. In Chapter V we made use of an expression of the same form as (A1.61), generalized to apply to the case where there were five sorts of systems and three different masses, for the crystalline partition function of chlorine.

APPENDIX II

THE ENUMERATION OF THE LINEARLY INDEPENDENT WAVE FUNCTIONS CAPABLE OF REPRESENTING ASSEMBLIES CONTAINING CRYSTALS

§A2.1. Introduction

It remains to give the mathematical justification of the steps by which we calculated the total number of linearly independent wave functions capable of representing our assemblies in Chapters II, III, V, and VII. A discussion of the legitimacy of our procedure in those chapters ought to be included in our article, because a rigorous treatment of assemblies containing crystals, along the lines of the discussions in the text, is nowhere available in print to our readers. We shall accordingly consider this matter in the remaining pages, referring whenever possible to theorems which are proved in Fowler's *Statistical Mechanics*.

§A2.2. The rigorous enumeration of the number of accessible states of assemblies containing crystals

In §2.2 we obtained the expression

$$C_N = \left(\frac{1}{2\pi i}\right)^2 \int\!\!\int \frac{dx dz \Pi_j (1 - xz^{\epsilon_j})^{-1} [\kappa(z)]^P}{x^{N+1} z^{E+1}} \tag{2.20}$$

for the number of linearly independent wave functions, symmetrical in all the atoms, capable of representing an assembly consisting of N atoms in the gas phase and P atoms in the crystal phase, when the total energy of the assembly is E. We wish to evaluate this integral by the method of steepest descents. We start by noticing that the integrand

$$\frac{\Pi_j (1 - xz^{\epsilon_j})^{-1} [\kappa(z)]^P}{x^N z^E}$$

is in the form of the integrand Φ of Eq. (339) of Fowler's *Statistical Mechanics* (except that ours is a double and not a triple summation). Therefore the lemma of §5.5 of Fowler's book applies: *For real positive values of x and z the function Φ has an absolute minimum at ξ, θ which is the unique solution of the equations*

$$\partial \Phi / \partial x = \partial \Phi / \partial z = 0$$

in the domain of convergence of Φ. If we write $\lambda = \log x$ and $\nu = \log z$, then we have

$$\frac{\partial^2 \Phi}{\partial \lambda^2} > 0 \text{ and } \begin{vmatrix} \dfrac{\partial^2 \Phi}{\partial \lambda^2}, & \dfrac{\partial^2 \Phi}{\partial \lambda \partial \nu} \\ \dfrac{\partial^2 \Phi}{\partial \lambda \partial \nu}, & \dfrac{\partial^2 \Phi}{\partial \nu^2} \end{vmatrix} > 0.$$

Consider the factor $\Pi_j(1-xz^{\epsilon_j})^{-1}$ in the numerator of the integrand Φ of Eq. (2.20). It is shown in Chapter XXI of Fowler's book that for any gas its logarithm $\Sigma_j\log(1-xz^{\epsilon_j})^{-1}$ always contains the volume V of the gas as a factor, whatever the values of x and z; provided only that Σ_j converges; and it does converge for the values of x and z which interest us. We may therefore set $\Sigma_j = V\Sigma_j'$ where Σ_j' is independent of V. Hence we can rewrite the integral (2.20) in the form

$$C_N = \left(\frac{1}{2\pi i}\right)^2 \iint \frac{dxdz}{xz} \frac{\exp\left\{V \sum_j{}' + P\log\kappa(z)\right\}}{x^N z^E}.$$

To determine ξ and θ we have the equations

$$V\xi\frac{\partial}{\partial\xi}\sum_j{}' = N \tag{A2.21}$$

and

$$V\theta\frac{\partial}{\partial\theta}\sum_j{}' + P\theta\frac{\partial}{\partial\theta}\log\kappa(\theta) = E. \tag{A2.22}$$

We observe that ξ and θ are *intensive* parameters. Their values are unaltered if V, N, E and P are made large in any fixed ratios. We are going to allow all of these quantities to become large in fixed ratios, and to indicate the dependence of P on V when we let V increase we may set $P = VP'$ where P' is a constant. We may assume that, when the circles of integration are made to pass through ξ, θ, this point provides the *unique* relevant maximum value of the modulus of the integrand on the contours of integration. To show that its neighborhood contributes the dominant part of the whole integral we write

$$x = \xi e^{i\alpha}, \quad z = \theta e^{i\beta}$$

and

$$V\sum_j{}' + VP'\log\kappa(z) = V\Psi(i\alpha, i\beta)$$

so that Ψ is independent of V. Then for small values of α and β the integrand takes the form

$$\frac{\exp\{V\Psi(0,0)\}}{\xi^N\theta^E}\exp\left[-\tfrac{1}{2}V\left\{\alpha^2\frac{\partial^2\Psi}{\partial i\alpha^2} + 2\alpha\beta\frac{\partial^2\Psi}{\partial i\partial i\beta} + \beta^2\frac{\partial^2\Psi}{\partial i\beta^2}\right\} + O(V\alpha^3) + O(V\alpha^4) + \cdots\right] \tag{A2.23}$$

in which the differential coefficients are to be evaluated at $\alpha = \beta = 0$. We have seen that this quadratic form is essentially positive. If V is large it follows by the arguments of §2.5 of Fowler's book that the variables α, β 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

$$\frac{2\pi}{V}\left\{ J\left(\frac{\dfrac{\partial\Psi}{\partial i\alpha},\quad \dfrac{\partial\Psi}{\partial i\beta}}{i\alpha \qquad i\beta}\right)_0 \right\}^{-1/2} \tag{A2.24}$$

The terms $O(V\alpha^3)$ vanish on integration. The terms $O(V\alpha^4)$ leave an error term $O(1/V)$. We have already shown in the lemma that $J_0 > 0$. We therefore find ultimately for C_N the asymptotic form

$$C_N = \frac{1}{2\pi V}\,\frac{\exp\{V\Psi(0,0)\}}{\xi^N \theta^E}\left[\{J_0\}^{-1/2} + O(1/V)\right] \tag{A2.25}$$

in which the error term involving the factor $O(1/V)$ becomes trivial as $V \to \infty$.

This establishes the result given in Eq. (2.211) of Chapter II of this article. To show that J_0 varies only slowly with N, we evaluate J_0 for simplicity for the case of small ξ which corresponds to the case of all gases under the conditions of temperature and pressure met with in practice, and for which, as indicated in §§21.43 and 21.44 of Fowler's *Statistical Mechanics*, $\Sigma_j \log\,(1 - xz^{\epsilon_j})^{-1} = xF(z)$ very nearly, where $F(z)$ is the partition function for a gas molecule. We then have

$$V\Psi = xF(z) + P\log\kappa(z)$$

and so

$$J_0 = \frac{1}{V^2}\left|\begin{matrix} \xi F(\theta)\,, & \xi\theta\dfrac{\partial F(\theta)}{\partial\theta} \\ \xi\theta\dfrac{\partial F(\theta)}{\partial\theta}\,, & \theta\dfrac{\partial}{\partial\theta}\left[\xi\theta\dfrac{\partial F(\theta)}{\partial\theta} + P\theta\dfrac{\partial}{\partial\theta}\log\kappa(\theta)\right] \end{matrix}\right|,$$

whence it follows that

$$J_0 = \frac{1}{V^2}NkT^2\frac{dE}{dT},$$

where dE/dT is the rate at which E increases as the temperature increases, when N is maintained constant. If we repeat the calculations of §2.2 in which we assumed that J_0 was a constant, but now use the above value for J_0 and thus take account of the dependence of J_0 upon N, we find that the changes in the arguments thereby introduced are trivial.

The generalization of the above arguments to apply to the case of hydrogen considered in Chapter III is obvious. We obtain Eq. (3.102) of Chapter III, and we find if we use the usual approximations $\Sigma_j \log\,(1 - xz^{\epsilon_j})^{-1} = xF(z)$, $\Sigma_k \log\,(1 - x'z^{\epsilon_k'})^{-1} = x'F'(z)$, that the Jacobian determinant J_0 in this equation is given by $J_0 = (1/V^3)NN'kT^2(dE/dT)$ where the derivative is taken for constant N and N'. Since J_0 varies only slowly with N and N', the arguments of §3.1 are valid. This same procedure can be used for establishing the results which we found in §7.2.

The generalization to cover the case of chlorine considered in Chapter V is likewise obvious. By a further elaboration of our former arguments we obtain in this case the expression

$$C(N_1, N_2, N_3, N_4, N_5)$$

$$= \frac{P!\Pi_1\Pi_2\Pi_3\Pi_4\Pi_5 \prod_1^5 [f_r(\theta)]^{P_r}\ [\kappa(\theta)]^P}{(2\pi V)^3 \prod_1^5 P_r!\ \theta^E \prod_1^5 \xi_r^{N_r}} \left[\{J_0\}^{-1/2} + O\left(\frac{1}{V}\right) \right]$$

where

$$J_0 = (1/V^6) N_1 N_2 N_3 N_4 N_5 k T^2 (dE/dT),$$

and hence the procedure in the text is correct in the case of chlorine also.

INDEX OF AUTHORS

INDEX OF SUBJECTS