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Aan mijn Verloofde.

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CHAPTER I.

Introduction.

§ 1. PHASE TRANSITIONS.

In this introductory chapter we shall give a brief survey of the different kinds of problems which arise when one tries to obtain a molecular theory of the equation of state of gases and liquids.

First of all, one requires a theory that can explain the general qualitative features of the behaviour of gases and liquids. The most striking of these features is the existence of sharp phase transitions (condensation and evaporation). This means mathematically that the equation of state cannot be represented by one analytical function but consists of *several analytically different parts.* Since this property is common to all substances one would expect it to be possible to give a very general explanation demanding no exact knowledge of the interaction between molecules, since this is different for every substance.

The first attempt at such an explanation was the theory of VAN DER WAALS. In this theory the molecules of a substance are treated as mutually attracting elastic spheres. It is assumed that this attractive force (the "VAN DER WAALS force") acting between the molecules, is for each pair a function of the distance of separation only, and is independent of the velocities or of the positions of other molecules. These forces are therefore the same in every state of the substance. Forces of this kind are said to have the *property of additivity* because the total potential energy of a configuration is the sum of the potential energies of all the pairs.

Starting from these assumptions and using the methods of classical statistical mechanics one can show that for very small densities the equation of state for 1 mol of gas is given by

$$p+\frac{a}{V^2}=\frac{RT}{V}\left(1+\frac{b}{V}+\dots\right). \quad . \quad . \quad . \quad . \quad (1)$$

where p is the pressure, V the volume, T the absolute temperature,

R the gas constant and a and b are constants which are related respectively to the attraction forces and to the diameter of the molecules. This equation is quite arbitrarily extrapolated by VAN DER WAALS to the famous equation

$$\left(p+\frac{a}{V^2}\right)(V-b)=RT \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

which is claimed to be valid for all densities. This equation does *not* show the desired properties. In fact it represents a completely analytical connection between p, V and T. However, below a certain temperature T_c, the critical temperature, the isotherms are not monotonic functions, as they are for $T > T_c$, but consist of two parts where $(\partial p/\partial V)_T < 0$, connected by a part where $(\partial p/\partial V)_T > 0$. Now a state with $(\partial p/\partial V)_T > 0$ does not represent a state of stable equilibrium. In order to remove this unstable part one introduces as an experimentally known fact the states of coexistence of vapour and liquid, giving a line $p = \text{const.}$ which connects the two stable parts of the isotherm. These stable parts are then interpreted as the isotherms of the pure vapour and of the pure liquid. The value of the pressure of the two-phase system is determined by a thermodynamical consideration (MAXWELL rule).

It will be clear that this theory cannot be considered as a real molecular explanation of the transition phenomena but is rather a semi-phenomenological description.

Only very recently a new and, as may be hoped, more successful approach to a real theoretical explanation of the phase transition has been put forward by MAYER and his collaborators 1). The origin of MAYER's theory lies in a quite different line of development. Because of the fact that all efforts to derive a general exact equation of state had been unsuccessful, KAMERLINGH ONNES 2) proposed to represent the empirical data on the equation of state of gases by a development in inverse powers of the volume

$$pV=RT\left(1+\frac{B(T)}{V}+\frac{C(T)}{V^2}+\dots\right). \quad . \; . \; . \quad (3)$$

Here the first term gives the ideal gas law, which holds at large volume (small density), and the following terms represent the deviations from the ideal behaviour when the volume is diminished.

The quantities $B(T)$, $C(T)$, ... *) are called *second, third, ... virial coefficient* by KAMERLINGH ONNES **). For these coefficients it is possible to derive *exact expressions* in classical statistical mechanics, starting from the partition function (Zustands integral) introduced by GIBBS. These expressions were obtained from the first terms of a suitable expansion of this partition function. In order to justify this procedure URSELL [3]) has given a more detailed mathematical investigation of this development, which has been the starting point of MAYER's theory. He tries to show that the development (3) is only convergent when the density of the gas is smaller than a certain critical value, depending on temperature, and that when the gas is compressed further the theory gives automatically a pressure independent of the volume, corresponding to the coexistence of vapour and liquid. The isotherm of the pure liquid remains unexplained in this theory.

In the third chapter of this dissertation we shall give an account of MAYER's theory. There we shall show that it is possible to extend the considerations of URSELL and MAYER to quantum statistics and that there exists a close analogy between MAYER's theory and an older theory of EINSTEIN [4]) where a condensation phenomenon for an ideal BOSE gas was predicted. Furthermore we hope that from a mathematical standpoint this treatment will be more satisfactory than MAYER's original one.

The failure of this theory to explain the liquid isotherms may be due to the fact that it is, just as the VAN DER WAALS theory, an approximation from the "vapour side". Perhaps a treatment starting from the crystalline state would be better suited for this purpose. There have been many attempts in this direction, but without complete success.

§ 2. THE VAN DER WAALS FORCES.

For the qualitative theory sketched in the foregoing paragraph

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*) One sees immediately from (1) or (2) that in the VAN DER WAALS theory $B(T) = b - {}^{a}/_{RT}$.

**) In reality KAMERLINGH ONNES used a polynomial of six terms instead of an infinite series and gave the name virial coefficients to the coefficients of this polynomial, which are not the same as the coefficients of the infinite expansion. We shall, however, always mean the latter coefficients in speaking about virial coefficients.

an exact knowledge of the intermolecular forces is not necessary, but it is necessary if one wishes to find an exact quantitative expression for the equation of state. The determination of these forces however is not a problem in statistical mechanics but a quantum mechanical one and will not be treated in this dissertation. Moreover LONDON [5]) has recently given an excellent survey of its history and present situation so that we will give only a brief description.

Let us first consider the *attractive* forces. In the older pre-quantummechanical theories the intermolecular attraction was attributed to two causes. In polar substances there will be an interaction between the electric and magnetic dipoles (or higher poles) of the molecules. This interaction is called the *orientation effect* of KEESOM since it depends on the mutual orientation of the molecules. A priori there is an equal probability for a repulsive and an attractive interaction, but due to the BOLTZMANN factor the positions giving rise to an attraction will be preponderant. On the average therefore there will be an attraction which however decreases to zero with increasing temperature. This very unsatisfactory property of the orientation forces led DEBIJE to the consideration of a second effect which gives rise to an attraction independent of temperature. This is the so-called *induction effect*, which is due to the polarization of the molecules by the fields of force of neighbouring molecules.

There are two difficulties in these explanations:

1⁰. These forces are not additive but vary with varying states of the substance. For instance the polarization force almost disappears in a condensed state where each molecule is surrounded uniformly by its neighbours. This is contrary to all experimental evidence which shows that the intermolecular forces have always the same order of magnitude.

2⁰. For spherical symmetric molecules (like helium) there would be no attraction at all.

These difficulties are removed in the modern quantum mechanical theory of the VAN DER WAALS forces which is chiefly due to LONDON. Here the potential energy of two molecules at distance r is calculated by means of the perturbation calculus. The attraction appears then as a second order effect. This calculation can be interpreted as follows. One considers not only the interaction of the static multipoles of the molecules, but also the interaction of the rapidly varying multipoles corresponding to the possible transitions between the states of a molecule. This effect is called the *dispersion effect* because the characteristic quantities of these multipoles, the oscillator strengths, also occur in the dispersion formula. It is found that the interaction between dipoles gives rise to an attractive intermolecular potential which varies as the inverse sixth power of r. The consideration of higher poles leads to potentials which vary as the inverse of the eighth, tenth, etc. power of r. It is shown that all these forces have the property of additivity which was assumed in the VAN DER WAALS theory. Moreover it has been shown that even in most polar molecules they are preponderant over the statical orientation and induction effects.

When two molecules are brought close together their attraction is replaced by a very strong *repulsion*. The older theories did *not* explain it but symbolized the repulsion by treating the molecules as elastic spheres. In the new theory there are two reasons for a repulsion when the charge clouds of the molecules overlap:

1⁰. The electrostatic repulsion of the atomic nuclei which are then not completely screened by the electrons.

2⁰. The PAULI principle, which forces the electrons to move to higher states. For the potential of this repulsion one finds the approximate expression

$$C\,e^{-r/r_0}$$

where r_0 and C are two constants, characteristic of the molecule considered.

The approximate magnitude of the dipole-dipole interaction has been determined by LONDON for a number of substances by a semi-empirical method, using the experimental dispersion curve.

For the interaction of two helium atoms extensive calculations have been performed by several authors. SLATER [6]) and SLATER and KIRKWOOD [7]) have calculated the exponential repulsion and the dipole-dipole attraction. They find the potential

$$V(r) = \left(77\,e^{-4.6r} - \frac{0.149}{r^6}\right) 10^{-11}\,erg,\ r \text{ in } \mathring{A} \quad . \quad . \quad (4)$$

The dipole-quadrupole and quadrupole-quadrupole attraction have been calculated by MARGENAU[8]) and very recently by PAGE[9]). PAGE's expression for the attraction is

$$-\frac{0.149}{r^6}\left(1+\frac{1.75}{r^2}+\frac{3.99}{r^4}\right)10^{-11}\,erg\,.$$

§ 3. QUANTITATIVE RESULTS FOR THE EQUATION OF STATE.

The problem of finding an exact expression for the equation of state when the intermolecular forces are known has as yet not been solved. However, as we mentioned in § 1, in *classical* statistical mechanics one can give exact expressions for the virial coefficients, which are measurable quantities. In particular for the second virial coefficient one obtains in the case of central forces

$$B(T)=2\pi N\int_0^\infty dr\,r^2\left(1-e^{-V(r)/kT}\right)\ \frac{cm^3}{mol}. \quad . \quad . \quad . \quad (5)$$

where N is the number of molecules per mol, r the intermolecular distance in cm, $V(r)$ the intermolecular potential and k BOLTZMANN's constant. Two problems may be attacked by means of (5):

1. When one has a theoretical expression for $V(r)$ one can calculate $B(T)$ from (5) by a numerical or graphical integration. This gives the possibility of an experimental verification of the theoretical calculation of $V(r)$.

2. On the other hand, when $B(T)$ is known experimentally, eq. (5) gives an integral equation for $V(r)$. This fact has been extensively used by LENNARD–JONES[10]) for an empirical determination of the intermolecular forces. Because the integral equation (5) has not been explicity solved, LENNARD–JONES has assumed the following expression for $V(r)$:

$$V(r)=\frac{\lambda_n}{r^n}-\frac{\lambda_m}{r^m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Here the first term represents the repulsion and the second term the attraction. It is obviously necessary that $n > m$. LENNARD–JONES found that it is possible to represent the second virial coefficient of many substances by a suitable adaptation of the four arbitrary constants in (6). This fact already indicates that the values of

$B(T)$ in the regions of temperature used will not depend very sensitively on the exact form of $V(r)$, since the expression (6) will surely not represent exactly the actual intermolecular force. This is confirmed by the fact that a good agreement with experiment is obtained also by insertion of the SLATER–KIRKWOOD potential (4) into (5)[11].

The situation is quite different in the *quantum theory*. The expression for $B(T)$ which one obtains here (see Chapter IV, § 2) is not directly evaluable in terms of $V(r)$. Eq. (5) is the limit of this expression for high temperature. There are three reasons for deviations from (5) at lower temperatures:

1. Due to the wave character of the molecules they will not interact according to the laws of classical mechanics but *diffraction effects* will occur. These will be large when the DE BROGLIE wave length of the molecular motion is large, compared with the diameter of the molecules. This wave length is equal to $h/\sqrt{2mE}$, where h is PLANCK's constant, m the mass of the molecule and E its kinetic energy. The mean value of E is proportional to T and therefore the mean DE BROGLIE wave length is proportional to $1/\sqrt{mT}$. We see therefore that the diffraction effects will be large for light gases and low temperatures.
2. The classical BOLTZMANN *statistics* has to be replaced by the EINSTEIN–BOSE or the FERMI–DIRAC *statistics*. It will be shown in Chapter IV that this also gives deviations for light gases and low temperatures.
3. When the attraction between the molecules is strong enough, *discrete quantum states* of the relative motion of two molecules will exist or, in other words, loosely bound "polarization molecules" will be formed. This will have an effect on the second virial coefficient at low temperatures. Since this effect depends on the magnitude of the attractive forces, it may become important even for heavier gases.

The calculation of $B(T)$ with a known $V(r)$ turns out to be much more difficult than in the classical theory, and the solution of the inverse problem is almost impossible.

CHAPTER II.

The Partition Function.

§ 1. CLASSICAL AND QUANTUM THEORETICAL FORM OF THE PARTITION FUNCTION.

In our treatment of the equation of state we shall use throughout GIBBS' method of the canonical ensemble. We shall present this method directly in its quantum theoretical form.

Let the system whose thermodynamical properties one wishes to investigate have energy states E_i with weights G_i. A large number of independent, identical systems is called an *ensemble*. This ensemble is *canonical* when at the temperature T the relative numbers of systems in the different states are given by $G_i \, exp\,(-E_i/kT)$, where k is BOLTZMANN's constant. It is assumed then that the behaviour of the system in temperature equilibrium is given by the behaviour of the canonical ensemble in the sense that the mean value of a macroscopic quantity may be obtained by averaging this quantity over the ensemble, while the mean square fluctuation is given by the average of the square of the deviations from the mean value. From this assumption it can be proved that the HELMHOLTZ free energy,

$$\Psi = \varepsilon - T\,\eta$$

where ε is the energy and η the entropy, is obtained from the equation

$$e^{-\Psi/kT} = \sum_i G_i\, e^{-E_i/kT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The sum in (1), which is to be extended over all possible states, is called the *partition function* (Zustandssumme) of the system. An unessential arbitrariness is yet left in (1) because of the fact that the weights are only relatively defined numbers. This may be removed by any convention about their absolute value. It is usual to give to each non-degenerate state the weight unity. Then G denotes simply the multiplicity of the state E_i. With the determination of Ψ as a function of volume and temperature the problem of finding the equation of state is solved. Other quantities may be obtained immediately from Ψ by using simple thermodynamical formulae.

We shall now proceed to the classical analogue of (1). This will be done in two steps. Let the system consist of N identical molecules. Then the number of possible states is restricted by the symmetrical or by the antisymmetrical exclusion principle. These are the cases of EINSTEIN–BOSE (E. B.) or FERMI–DIRAC (F. D.) statistics. It will be often convenient, however, to consider systems for which all the states which are forbidden by one of the two exclusion principles exist. This case, which is of course purely academical, is called the case of BOLTZMANN statistics. For this case it is desirable to choose another convention for the absolute values of the weights, namely to give to each non-degenerate state the weight $1/N!$, so that

$$e^{-\Psi/kT} = \frac{1}{N!} \sum_i G_i \, e^{-E_i/kT} \quad \ldots\ldots \quad (2)$$

when G_i means again the multiplicity of the state E_i. With this convention the expressions (1) and (2) approach each other for high temperatures *).

The second step in the transition to classical statistical mechanics is to replace the sum in (2) by an integral over the phase space. For a monatomic gas we have then, since to each single quantum state corresponds a volume h^{3N} in phase space,

$$e^{-\Psi/kT} = \frac{1}{h^{3N} N!} \int \cdots \int d\mathbf{p}_1 \ldots d\mathbf{p}_N d\mathbf{r}_1 \ldots d\mathbf{r}_N e^{-H(\mathbf{p}_1, \ldots \mathbf{p}_N, \mathbf{r}_1, \ldots \mathbf{r}_N)/kT} \quad (3)$$

Here $\mathbf{r}_1, \ldots \mathbf{r}_N$ are the coordinates of the N particles, $\mathbf{p}_1, \ldots \mathbf{p}_N$ their momenta and $H(\mathbf{p}_1, \ldots \mathbf{p}_N, \mathbf{r}_1, \ldots \mathbf{r}_N)$ the HAMILTON function of the system. The integration has to be extended for the momenta over all values and for each $\mathbf{r}_k$ over the volume V of the vessel in which the system is enclosed. Since

$$H(\mathbf{p}_1, \ldots \mathbf{p}_N, \mathbf{r}_1, \ldots \mathbf{r}_N) = \frac{1}{2m} \sum_{k=1}^{N} p_k^2 + V(\mathbf{r}_1, \ldots \mathbf{r}_N)$$

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*) For the ideal gas this correspondence is shown in § 3 and for the non-ideal gas in § 4.

where m is the mass of a molecule and $V(\mathbf{r}_1, \ldots \mathbf{r}_N)$ the potential energy of the system, we can perform the integration over the momenta and find then

$$e^{-\Psi/kT} = \frac{1}{\lambda^{3N}} \frac{1}{N!} \int\limits_V \cdots \int\limits_V d\mathbf{r}_1 \ldots d\mathbf{r}_N \, e^{-V(\mathbf{r}_1, \ldots \mathbf{r}_N)/kT} \quad . \quad (4)$$

where

$$\lambda^2 = \frac{h^2}{2\pi m k T} \cdot \quad . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

The integrand $exp\,(-V/kT)$ represents the relative density of probability in configuration space for the canonical ensemble.

A function which plays the same role in the quantum theory can be easily found. Consider namely the expression

$$S(\mathbf{r}_1, \ldots \mathbf{r}_N) = \sum_i e^{-E_i/kT} \varphi_i^* (\mathbf{r}_1, \ldots \mathbf{r}_N) \varphi_i (\mathbf{r}_1, \ldots \mathbf{r}_N) \, . \quad . \quad (6)$$

where the summation has to be extended over all the normalised eigenfunctions φ_i *).
We have

$$e^{-\Psi/kT} = \int\limits_V \cdots \int\limits_V d\mathbf{r}_1 \ldots d\mathbf{r}_N \, S(\mathbf{r}_1, \ldots \mathbf{r}_N)$$

when the eigenfunctions φ_i are normalized according to

$$\int\limits_V \cdots \int\limits_V d\mathbf{r}_1 \ldots d\mathbf{r}_N \, \varphi_i^* \varphi_i = 1.$$

It is clear that the expression (6), which we shall call the SLATER *sum* [12]), represents the relative density in configuration space for the canonical ensemble, since $\varphi_i^* \varphi_i$ represents this density for each state. The strict analogue of the classical BOLTZMANN factor $exp\,(-V/kT)$ is the function

$$W(\mathbf{r}_1, \ldots \mathbf{r}_N) = \lambda^{3N} N! \, S(\mathbf{r}_1, \ldots \mathbf{r}_N) \quad . \ . \ . \ . \quad (7)$$

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*) Therefore to a state with weight G correspond G terms in the sum (6).

In the case of BOLTZMANN statistics we shall, in conformity with (2), define the SLATER sum by

$$S(\mathbf{r}_1, \ldots \mathbf{r}_N) = \frac{1}{N!} \sum_i e^{-E_i/kT} \varphi_i^* \varphi_i \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where now the eigenfunctions φ_i are no longer restricted by an exclusion principle.

§ 2. A TRANSFORMATION OF THE SLATER SUM.

The eigenvalues and eigenfunctions of the system and therefore also the SLATER sum are completely determined by its Hamiltonian operator $\mathcal{H}(\mathbf{p}_1, \ldots \mathbf{p}_N, \mathbf{r}_1, \ldots \mathbf{r}_N)$, where now $\mathbf{p}_k$ should be understood as the operator $h\partial/2\pi i\, \partial \mathbf{r}_k$ *).

It is possible to write the SLATER sum in a form which clearly demonstrates this fact.

By repeated application of $\mathcal{H}$ to the SCHRÖDINGER equation

$$\mathcal{H} \varphi_i = E_i \varphi_i$$

follows

$$\mathcal{H}^n \varphi_i = E_i^n \varphi_i.$$

Therefore

$$e^{-E_i/kT} \varphi_i = \left\{ \sum_{n=0}^{\infty} (-1)^n \frac{1}{n!\, k^n\, T^n} E_i^n \right\} \varphi_i = \left\{ \sum_{n=0}^{\infty} (-1)^n \frac{1}{n!\, k^n\, T^n} \mathcal{H}^n \right\} \varphi_i.$$

When we define **)

$$e^{-\mathcal{H}/kT} = \sum_{n=0}^{\infty} (-1)^n \frac{1}{n!\, k^n\, T^n} \mathcal{H}^n \quad . \quad . \quad . \quad . \quad . \quad (9)$$

then the SLATER sum may be written as

$$S(\mathbf{r}_1, \ldots \mathbf{r}_N) = \sum_i \varphi_i^* e^{-\mathcal{H}/kT} \varphi_i \quad . \quad . \quad . \quad . \quad . \quad (10)$$

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*) In the following the classical HAMILTON function will be written H, while the corresponding operator will be denoted by $\mathcal{H}$.

**) This definition should be used with some care. When f and g are non-commuting operators, for instance the parts of $\mathcal{H}$ corresponding to the kinetic and the potential energy, then

$$e^{f+g} = e^{g+f} \neq e^f e^g \neq e^g e^f.$$

The inequalities become equalities when f and g commute.

We shall now introduce a new complete orthogonal set of normalized functions $u_m(\mathbf{r}_1,\dots\mathbf{r}_N)$. Then each φ_i may be developed in terms of the u_m:

$$\varphi_i = \sum_m c_{im}\, u_m$$

and

$$S(\mathbf{r}_1,\dots\mathbf{r}_N) = \sum_i \sum_m \sum_l c^*_{im}\, c_{il}\, u^*_m\, e^{-\mathcal{H}/kT}\, u_l = \sum_m u^*_m\, e^{-\mathcal{H}/kT}\, u_m \quad . \qquad (11)$$

since

$$\sum_i c^*_{im}\, c_{il} = \delta_{ml}\,.$$

As the set u_m is quite arbitrary, (11) expresses the SLATER sum in the most general way.

§ 3. CONNECTION BETWEEN CLASSICAL AND QUANTUM THEORETICAL EXPRESSIONS. EXAMPLES [13]).

The SLATER sum has been defined as the analogue of the classical expression

$$S_c(\mathbf{r}_1,\dots\mathbf{r}_N) = \frac{1}{h^{3N}}\frac{1}{N!}\int\cdots\int d\mathbf{p}_1\dots d\mathbf{p}_N\, e^{-H/kT} = \frac{1}{\lambda^{3N}}\frac{1}{N!}e^{-V/kT} \quad (12)$$

One should therefore expect S_c to be the limit of S either for $h \to 0$ or for $T \to \infty$, for in the last case the high quantum states play the principal role. Before discussing this correspondence in general we shall illustrate it by some examples.

a. As the simplest system we choose a *single mass point* which may move freely on a line segment of length L. Then (12) becomes

$$S_c(x) = \frac{1}{h}\int\limits_{-\infty}^{\infty} dp\, e^{-p^2/2mkT} = \frac{1}{\lambda}$$

for $0 < x < L$, whereas $S_c(x) = 0$ for all other x.

In order to calculate the SLATER sum we observe that the normalized eigenfunctions are

$$\varphi_n = \left(\frac{2}{L}\right)^{1/2} \sin\frac{n\pi x}{L}, \quad n = 1, 2, \dots$$

and the eigenvalues

$$E_n = \frac{n^2 h^2}{8\,m\,L^2}.$$

Therefore

$$S(x) = \frac{2}{L} \sum_{n=1}^{\infty} e^{-n^2 h^2/8 m k T L^2} \sin^2 \frac{n \pi x}{L} \quad . \quad . \quad . \quad . \quad (13)$$

For large L the exponential factor changes slowly with n, while for x not in the neighbourhood of the boundaries the factor $\sin^2(n\pi x/L)$ changes rapidly. We therefore may replace the latter factor by its mean value ½ and replace the sum by an integral over n. This gives $S = S_c$. At the boundaries however the different terms are in phase and we must now replace the unchanged expression by an integral. This gives

$$S(x) = \frac{1}{\lambda}\left(1 - e^{-4\pi x^2/\lambda^2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

for small x and the same expression with $L - x$ instead of x at the other end of the segment *). We see therefore that $S(x)$ is equal to $S_c(x)$ except in regions of the order of magnitude λ at the ends of the segment, where it drops to zero. As $\lambda \rightarrow 0$ for $h \rightarrow 0$ or for $T \rightarrow \infty$ this shows clearly the correspondence mentioned above.

For a particle moving in a cubical box of more dimensions the SLATER sum is simply the product of (14) for each dimension.

b. Let us now consider a *linear harmonic oscillator* of frequency ν. The Hamiltonian is

$$H = \frac{p^2}{2m} + 2\pi^2 \nu^2 m\, x^2$$

and therefore

$$S_c(x) = \frac{1}{\lambda}\, e^{-\frac{\theta}{2} y^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

with

$$y = 2\pi x \sqrt{\frac{m \nu}{h}}$$

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*) For a more formal derivation of (14) see Note 1.

and

$$\theta = \frac{h\nu}{kT}.$$

In the quantum theory we have the eigenvalues

$$E_n = (n + \tfrac{1}{2})\, h\nu, \quad n = 0, 1, \dots$$

and the eigenfunctions

$$\varphi_n(x) = C_n\, e^{-\frac{y^2}{2}}\, H_n(y)$$

where $H_n\ (y)$ is the n^{th} Hermitian polynomial and

$$C_n = \left(\frac{4\pi^2\, n\nu}{h}\right)^{1/4} \frac{1}{(2^n\, n!\, \pi^{1/2})^{1/2}}.$$

Therefore the SLATER sum is

$$S(x) = \frac{\sqrt{2\theta}}{\lambda}\, e^{-\frac{1}{2}\theta - y^2} \sum_{n=0}^{\infty} e^{-n\theta}\, \frac{H_n^2(y)}{2^n\, n!}.$$

The summation, which can be performed exactly 14), gives

$$S(x) = \frac{1}{\lambda} \left(\frac{2\theta}{1 - e^{-2\theta}}\right)^{1/2} e^{-\frac{\theta}{2} - y^2 \tanh \frac{\theta}{2}} \quad . \quad . \quad . \quad . \quad (16)$$

which clearly goes over into (15) for $\theta \rightarrow 0$.

c. A simple example of a system of *several particles* is furnished by two mass points which move freely on a line segment of length L. Let x_1 and x_2 be the coordinates of the two particles. Then

$$S_c(x_1, x_2) = \frac{1}{2\lambda^2}.$$

In the quantum theory we shall treat the cases of BOLTZMANN, E. B. and F. D. statistics separately. In each case the eigenvalues are

$$E_{n_1 n_2} = \frac{(n_1^2 + n_2^2)\, h^2}{8\, m\, L^2}.$$

In BOLTZMANN statistics each state with $n_1 \neq n_2$ is degenerate, having the two eigenfunctions

$$\varphi^{(1)}_{n_1 n_2} = \frac{2}{L} \sin \frac{n_1 \pi x_1}{L} \sin \frac{n_2 \pi x_2}{L}$$

and

$$\varphi^{(2)}_{n_1 n_2} = \frac{2}{L} \sin \frac{n_2 \pi x_1}{L} \sin \frac{n_1 \pi x_2}{L}.$$

According to (8) we obtain in the same way as in case *a*

$$S_B = \frac{1}{2 \lambda^2} (1 - e^{-4 \pi x_1^2/\lambda^2}) (1 - e^{-4 \pi x_2^2/\lambda^2}) \quad . \quad . \quad . \quad (18)$$

which is again equal to S_c except when one of the particles is near a boundary of the segment *).

Now the exclusion principle removes the degeneracy by allowing only one definite linear combination of $\varphi^{(1)}_{n_1 n_2}$ and $\varphi^{(2)}_{n_1 n_2}$. In E. B. statistics this is the symmetrical combination $(\varphi^{(1)}_{n_1 n_2} + \varphi^{(2)}_{n_1 n_2})/\sqrt{2}$, in F. D. statistics the antisymmetrical combination $(\varphi^{(1)}_{n_1 n_2} - \varphi^{(2)}_{n_1 n_2})/\sqrt{2}$. The originally non-degenerate levels with $n_1 = n_2$ remain unaltered in E. B. statistics and disappear in the F. D. case. Therefore the SLATER sums are

$$\left. \begin{aligned} S_{\text{E.B.}}(x_1, x_2) = \frac{2}{L^2} \sum_{n_1 > n_2} e^{-(n_1^2 + n_2^2) h^2/8 m k T L^2} \left(\sin \frac{n_1 \pi x_1}{L} \sin \frac{n_2 \pi x_2}{L} + \right. \\ \left. + \sin \frac{n_2 \pi x_1}{L} \sin \frac{n_1 \pi x_2}{L} \right)^2 + \frac{4}{L^2} \sum_{n=1}^{\infty} e^{-n^2 h^2/4 m k T L^2} \sin^2 \frac{n \pi x_1}{L} \sin^2 \frac{n \pi x_2}{L} \end{aligned} \right\} \quad (19)$$

and

$$\left. \begin{aligned} S_{\text{F.D.}}(x_1, x_2) = \frac{2}{L^2} \sum_{n_1 > n_2} e^{-(n_1^2 + n_2^2) h^2/8 m k T L^2} \left(\sin \frac{n_1 \pi x_1}{L} \sin \frac{n_2 \pi x_2}{L} - \right. \\ \left. - \sin \frac{n_2 \pi x_1}{L} \sin \frac{n_1 \pi x_2}{L} \right)^2 \end{aligned} \right\} \quad (20)$$

---

*) Like (14) this expression holds for $x_1 < L/2$, $x_2 < L/2$, whereas in the other half of the segment we have to replace x_1 by $L - x_1$ and x_2 by $L - x_2$. The same will be the case in the expressions which will be given afterwards.

These expressions may be written as

$$\left.\begin{matrix} S_{\mathrm{E.B.}} \\ S_{\mathrm{F.D.}} \end{matrix}\right\} \begin{aligned} &= \frac{1}{L^2} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} e^{-(n_1^2+n_2^2)h^2/8mkTL^2} \left(\sin\frac{n_1 \pi x_1}{L} \sin\frac{n_2 \pi x_2}{L} \pm \right. \\ &\left. \pm \sin\frac{n_2 \pi x_1}{L} \sin\frac{n_1 \pi x_2}{L} \right)^2 = \\ &= \frac{2}{L^2} \left(\sum_{n=1}^{\infty} e^{-n^2h^2/8mkTL^2} \sin^2\frac{n\pi x_1}{L} \right) \left(\sum_{n=1}^{\infty} e^{-n^2h^2/8mkTL^2} \sin^2\frac{n\pi x_2}{L} \right) \pm \\ &\pm \frac{1}{2L^2} \left[\sum_{n=1}^{\infty} e^{-n^2h^2/8mkTL^2} \left\{ \cos\frac{n\pi}{L}(x_1 - x_2) - \cos\frac{n\pi}{L}(x_1 + x_2) \right\} \right]^2 \end{aligned} \quad (21)$$

Again replacing summation by integration we get

$$\left.\begin{matrix} S_{\mathrm{E.B.}} \\ S_{\mathrm{F.D.}} \end{matrix}\right\} = S_B \pm \frac{1}{2\lambda^2} \left(e^{-\frac{\pi}{\lambda^2}(x_1 - x_2)^2} - e^{-\frac{\pi}{\lambda^2}(x_1 + x_2)^2} \right)^2 \quad . \quad . \quad (22)$$

For the discussion of (22) we first remark that for $\lambda \rightarrow 0$ it goes over into S_c as we should expect. The term $exp\{-\pi(x_1 + x_2)^2/\lambda^2\}$ is less important since it has finite values only when both particles are at the boundary. The essential term is $exp\{-\pi(x_1 - x_2)^2/\lambda^2\}$ which causes a maximum in the E. B. case and a minimum in the F. D. case for $x_1 = x_2$. Therefore there is an *apparent attraction* between E. B. particles and an *apparent repulsion* between F. D. particles.

In an x_1, x_2 diagram (fig. 1) we have the following situation

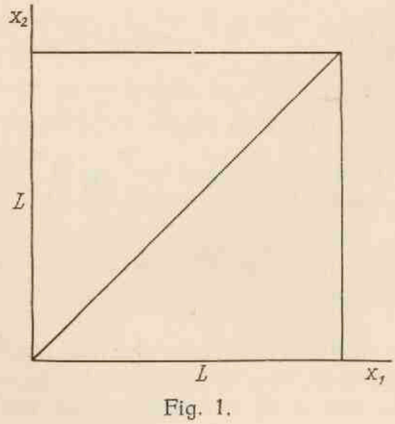

Fig. 1.

Almost everywhere S is equal to S_c. Deviations occur, however, along the sides, especially at the corners, and along the diagonal $x_1 = x_2$.

d. We turn next to the consideration of an *ideal gas*. The essential characteristics of such a gas are illustrated by the preceding example. Let the gas consist of N mass points of mass m, moving freely inside a cube of side L and let $\mathbf{r}_k\,(x_k, y_k, z_k)$ be the coordinates of the k^{th} particle. It is immediately seen that in the classical theory

$$S_c = \frac{1}{\lambda^{3N}} \frac{1}{N!} \cdot \qquad (23)$$

In the quantum theory the cases of BOLTZMANN, E. B. and F. D. statistics must again be discussed separately. For BOLTZMANN statistics one finds easily

$$S_B = \frac{1}{N!} \prod_{k=1}^{N} S(x_k)\, S(y_k)\, S(z_k)\,. \qquad (24)$$

where $S(x_k)$, $S(y_k)$, $S(z_k)$ are equal to the SLATER sum discussed in example *a*.

It is of interest here to discuss how the equation of state which follows from (24) differs from the ideal gas law.
We have

$$e^{-\Psi/kT} = \frac{1}{N!} \prod_{k=1}^{N} \int_0^L\!\!\int\!\!\int dx_k\, dy_k\, dz_k\, S(x_k)\, S(y_k)\, S(z_k).$$

For $S(x) = S_c(x) = 1/\lambda$ this gives

$$e^{-\Psi/kT} = \frac{1}{\lambda^{3N} N!} V^N$$

and therefore, using the formula

$$p = -\left(\frac{\partial \Psi}{\partial V}\right)_T$$

we obtain

$$p V = N k T, \qquad (25)$$

the ideal gas law.

For $S(x)$ as given by (14) we have

$$\int_0^L S(x)\,dx = 2\int_0^{L/2} S(x)\,dx = \frac{2}{\lambda}\int_0^{L/2}\left(1 - e^{-4\pi x^2/\lambda^2}\right)dx \cong$$

$$\simeq \frac{1}{\lambda}\left(L - 2\int_0^{\infty} e^{-4\pi x^2/\lambda^2}\,dx\right) = \frac{1}{\lambda}\left(L - \frac{\lambda}{2}\right).$$

Therefore

$$e^{-\Psi/kT} = \frac{1}{\lambda^{3N}}\,\frac{1}{N!}\left(L - \frac{\lambda}{2}\right)^{3N}$$

and

$$p = \frac{NkT}{V - \frac{\lambda}{2}V^{2/3}} = \frac{NkT}{V}\left(1 + V^{-1/3}\frac{\lambda}{2} + \dots\right). \quad . \quad (26)$$

This deviation from the ideal gas law is in all practical cases completely negligible. In helium, for instance, $\lambda = 0.755 \times 10^{-7}/\sqrt{T}$ cm and so for a volume of 1 cm^3 and a temperature even as low as 1° abs. the value of $V^{-1/3}\,\lambda/2$ is only 0.38×10^{-7}.

When we now turn to the E. B. and F. D. gases we may expect that the deviations from the ideal gas law due to the deviations of the SLATER sum from S_c at the boundaries of the vessel are again negligible and the only important deviations will be due to the deviations of S from S_c when some of the particles are near together, corresponding to the deviations along the diagonal in fig. 1. This is the reason why we shall not start from wave functions which fulfill the true boundary conditions but from the running waves

$$\left(\frac{1}{L}\right)^{3N/2} e^{\frac{2\pi i}{h}\sum_{k=1}^{N}(\mathbf{p}_k \cdot \mathbf{r}_k)}$$

with

$$\mathbf{p}_k = \frac{h\,\mathbf{k}_k}{L}$$

where $\mathbf{k}_k$ is a vector whose components can have all positive or negative integral values. The eigenvalues are then

$$\frac{1}{2m}\sum_{k=1}^{N} p_k^2.$$

In E. B. statistics we must take the symmetrical eigenfunction

$$\left(\frac{1}{L}\right)^{3N/2} \frac{1}{\sqrt{n_P}} \sum_{P}{}' e^{\frac{2\pi i}{h}\sum_{k=1}^{N}(\mathbf{p}_k\cdot\mathbf{r}_{Pk})}$$

where P is any permutation of the indices k, Pk is the index which replaces k after the application of P and the summation is to be extended over all *different* eigenfunctions $exp\ \{2\pi i \sum_{k=1}^{N}(\mathbf{p}_k.\mathbf{r}_{Pk})/h\}$. n_P is the number of these eigenfunctions. In F. D. statistics we have the antisymmetrical eigenfunction

$$\left(\frac{1}{L}\right)^{3N/2} \frac{1}{\sqrt{n_P}} \sum_{P}{}' \delta_P\, e^{\frac{2\pi i}{h}\sum_{k=1}^{N}(\mathbf{p}_k\cdot\mathbf{r}_{Pk})}$$

where δ_P is + i for an even and — 1 for an odd permutation.

In computing the SLATER sum we can eliminate, as in the transition from (19) and (20) to (21), the disagreeable factors n_P by summing for each particle independently over all values of the $\mathbf{k}_k$. The summation over the permutations has to be extended then over all the permutations and we have to divide the result by $N!$. Replacing the summation over $\mathbf{k}_k$ by an integration over $\mathbf{p}_k$ we obtain

$$\left.\begin{aligned}
S_{\text{E.B.}} &= \frac{1}{h^{3N}}\frac{1}{(N!)^2}\int\cdots\int d\mathbf{p}_1..d\mathbf{p}_N \sum_{P}\sum_{P'} e^{-\frac{2\pi i}{h}\sum_{k=1}^{N}(\mathbf{p}_k\cdot\mathbf{r}_{Pk})}\, e^{-\frac{1}{2mkT}\sum_{k=1}^{N}p^2{}_k}\, e^{\frac{2\pi i}{h}\sum_{k=1}^{N}(\mathbf{p}_k\cdot\mathbf{r}_{P'k})} = \\
&= \frac{1}{h^{3N}}\frac{1}{N!}\int\cdots\int d\mathbf{p}_1..d\mathbf{p}_N \sum_{P} e^{-\frac{2\pi i}{h}\sum_{k=1}^{N}(\mathbf{p}_k\cdot\mathbf{r}_{Pk})}\, e^{-\frac{1}{2mkT}\sum_{k=1}^{N}p^2{}_k}\, e^{\frac{2\pi i}{h}\sum_{k=1}^{N}(\mathbf{p}_k\cdot\mathbf{r}_k)} = \\
&= \frac{1}{\lambda^{3N}}\frac{1}{N!}\sum_{P} e^{-\frac{\pi}{\lambda^2}\sum_{k=1}^{N}|\mathbf{r}_k-\mathbf{r}_{Pk}|^2}
\end{aligned}\right\}\quad(27)$$

In the same way one obtains for F. D. statistics

$$S_{\mathrm{F.D.}} = \frac{1}{\lambda^{3N}} \frac{1}{N!} \sum_{P} \delta_P \, e^{-\frac{\pi}{\lambda^2} \sum_{k=1}^{N} |\mathbf{r}_k - \mathbf{r}_{Pk}|^2} \quad . \; . \; . \quad (28)$$

In these sums over all permutations the term corresponding to the identity gives S_B whereas the other terms represent the deviations arising from the exclusion principle.

For later use we shall write down for the case of E. B. statistics the function $W(\mathbf{r}_1, \ldots \mathbf{r}_N)$ which, according to (7) corresponds to the classical BOLTZMANN factor:

$$W_{\mathrm{E.B.}}(\mathbf{r}_1, \ldots \mathbf{r}_N) = \sum_{P} e^{-\frac{\pi}{\lambda^2} \sum_{k=1}^{N} |\mathbf{r}_k - \mathbf{r}_{Pk}|^2} \quad . \; . \; . \; . \quad (29)$$

It is clear that $W_{\mathrm{E.B.}} \to 1$ when all the particles are far away from each other, whereas $W_{\mathrm{E.B.}} > 1$ in all regions of configuration space where some particles are near together. This corresponds to the apparent attraction between the particles of an ideal E. B. gas, which was already mentioned in example *c*. One should point out that this attraction can *not* be represented by a potential which has the property of additivity.

We shall now calculate in first approximation for the ideal E. B. and F. D. gases the deviations from the ideal gas law. This first approximation is obtained by taking only those permutations into account which consist of the interchange of *two* particles. When we observe that there are $N(N-1)/2$ different simple interchanges we find

$$\left.\begin{matrix} e^{-\Psi_{\mathrm{E.B}}/kT} \\ e^{-\Psi_{\mathrm{F.D.}}/kT} \end{matrix}\right\} = \frac{1}{\lambda^{3N}} \frac{1}{N!} \left(V^N \pm \frac{N(N-1)}{2} V^{N-1} \lambda^3 \, 2^{-3/2} \right)$$

and therefore

$$\left.\begin{aligned} \left.\begin{matrix} p_{\mathrm{E.B.}} \\ p_{\mathrm{F.D.}} \end{matrix}\right\} &= \frac{NkT}{V} \mp \frac{N(N-1)}{V^2} \lambda^3 \, 2^{-5/2} + \ldots \cong \\ &\cong \frac{NkT}{V} \left\{ 1 \mp \frac{N}{16\,V} \left(\frac{h^2}{\pi m k T} \right)^{3/2} + \ldots \right\} \end{aligned}\right\} \quad . \; . \quad (30)$$

Eq. (30) contains the well known expressions for the second virial coefficients of an ideal E. B. and F. D. gas:

$$\left.\begin{matrix} B_{\text{E. B.}} \\ B_{\text{F. D.}} \end{matrix}\right\} = \mp \frac{N}{16} \left(\frac{h^2}{\pi m k T} \right)^{3/2} \quad . \; . \; . \; . \; . \; . \qquad (31)$$

Comparison of (26) and (30) shows clearly the difference in character of the deviations from the ideal gas law in the two cases. In (26) the deviation is independent of the density of the gas, in (30) it is proportional to it. The reason is that in the BOLTZMANN gas the deviation is caused by the interaction of each molecule with the walls of the vessel, giving, just as the main term, a contribution proportional to N. In the E. B. or F. D. case, however, the deviation is caused by the apparent interaction between pairs of molecules which gives a contribution proportional to the number of pairs or to N^2.

In Chapter III, §§ 4 and 5, a treatment of the equation of state of the ideal E. B. and F. D. gases will be given in which all the permutations in the expressions (27) and (28) are taken into account.

e. In the foregoing examples we have always treated the particles as simple mass points. It often occurs however that the molecules of a gas possess an intrinsic, constant *angular momentum*. We shall not investigate here the influence of the small magnetic forces which are associated with this spin, but only its influence on the weights and symmetry properties of the different states.

Consider *two* identical particles with an angular momentum $sh/2\pi$. This spin can have $2s + 1$ different directions in respect to a fixed axis, all with the same energy. In BOLTZMANN statistics, where the two spins can choose their directions independently, each state is $(2s + 1)^2$-fold degenerate and the partition function is simply multiplied with this factor. Here the spin has no influence on the thermodynamical properties of the system.

In E. B. and F. D. statistics on the contrary, the spin has a great influence. First consider E. B. statistics. Without spin only states occur whose wave functions are symmetrical in the coordinates. When the particles have a spin, however, the wave functions must be symmetrical in respect to a simultaneous interchange of the coordinates and of the spin directions, whereas the orbital wave functions need not be symmetrical. From the $(2s+1)^2$ different spin functions in BOLTZMANN statistics one can form $(s+1)(2s+1)$ symmetrical and $s(2s+1)$ antisymmetrical combinations. In order to make the complete wave function symmetrical the first ones have to be multiplied with symmetrical orbital wave functions, the others with antisymmetrical ones. Therefore in the SLATER sum the states with symmetrical orbital wave function will appear with weight $(s+1)(2s+1)$ and the states with antisymmetrical orbital wave function with weight $s(2s+1)$. In this way we get

$$S^{(s)}_{\text{E.B.}} = (s+1)(2s+1)\, S^{(0)}_{\text{E.B.}} + s(2s+1)\, S^{(0)}_{\text{F.D.}} \quad . \quad . \quad (32)$$

Here the upper index on S denotes the value of the spin.

In the same way one obtains for F. D. statistics

$$S^{(s)}_{\text{F.D.}} = (s+1)(2s+1)\, S^{(0)}_{\text{F.D.}} + s(2s+1)\, S^{(0)}_{\text{E.B.}} \quad . \quad . \quad (33)$$

We remark that, when s is large, $S^{(0)}_{\text{E.B.}}$ and $S^{(0)}_{\text{F.D.}}$ are mixed in almost equal proportions and we obtain practically the SLATER sum for BOLTZMANN statistics. One can express this by saying that the spin has the tendency to diminish the influence of the exclusion principle.

For systems of more than two particles the consideration of the spin becomes much more complicated. We remark only that the function $W(\mathbf{r}_1, \dots \mathbf{r}_N)$ has now to be defined by

$$W(\mathbf{r}_1, \dots \mathbf{r}_N) = \frac{\lambda^{3N} N!}{(2s+1)^N}\, S(\mathbf{r}_1, \dots \mathbf{r}_N).$$

§ 4. CONNECTION BETWEEN CLASSICAL AND QUANTUM THEORETICAL EXPRESSIONS. GENERAL THEORY.

The examples in the foregoing paragraph all showed a correspondence between the SLATER sum and the classical expression S_c in such a way that the first went over into the second when the parameter λ, which represents the DE BROGLIE wave length corresponding to a mean temperature motion, became small. For a general gas one should expect the particles to behave almost classically when their DE BROGLIE wave length is small compared with the distances in which their potential energy undergoes considerable changes. These latter distances are clearly of the order of magnitude of the dimension of the molecules, say d, where d is a sort of molecular diameter. We therefore expect a development of the form

$$S = S_c \left(1 + c_1 \frac{\lambda}{d} + c_2 \frac{\lambda^2}{d^2} + \dots\right) \quad . \quad . \quad . \quad . \quad (34)$$

Kirkwood 15) has investigated the connection between S and S_c for a non-ideal, monatomic E. B. or F. D. gas. We shall present his treatment only for the E. B. case; the F. D. case is completely analogous.

The theory is based on the general form (11) of the Slater sum. The Hamiltonian of the gas has the form

$$H(\mathbf{p}_1, \dots \mathbf{p}_N, \mathbf{r}_1, \dots \mathbf{r}_N) = \frac{1}{2m} \sum_{k=1}^{N} p_k^2 + V(\mathbf{r}_1, \dots \mathbf{r}_N).$$

Now a suitable choice for the set of wave functions u_m has to be made. In any case all the u_m must be symmetrical in the particles for otherwise the inverse of the transformation of the eigenfunctions of the gas into the u_m would not exist. We shall take the symmetrical combination of running waves which was used in example d of the foregoing paragraph. This means that the wall corrections will be neglected. For the Slater sum one now obtains (comp. eq. (27))

$$S = \frac{1}{h^{3N}} \frac{1}{N!} \int \cdots \int d\mathbf{p}_1 \dots d\mathbf{p}_N \sum_P e^{-\frac{2\pi i}{h} \sum_{k=1}^{N} (\mathbf{p}_k \cdot \mathbf{r}_{Pk})} e^{-\beta \mathcal{H}} e^{\frac{2\pi i}{h} \sum_{k=1}^{N} (\mathbf{p}_k \cdot \mathbf{r}_k)} \quad (35)$$

where

$$\beta = \frac{1}{kT}.$$

Consider now the function

$$F(\mathbf{p}_1, \dots \mathbf{p}_N, \mathbf{r}_1, \dots \mathbf{r}_N) = e^{-\beta \mathcal{H}} e^{\frac{2\pi i}{h} \sum_{k=1}^{N} (\mathbf{p}_k \cdot \mathbf{r}_k)} \quad . \quad . \quad (36)$$

By differentiating (36) with respect to β we see that F is a solution of the so-called Bloch equation 16)

$$\mathcal{H} F + \frac{\partial F}{\partial \beta} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

with the initial condition

$$(F)_{\beta=0} = e^{\frac{2\pi i}{h}\sum_{k=1}^{N}(\mathbf{p}_k\cdot\mathbf{r}_k)}.$$

If in (35), instead of the operator $\mathcal{H}$ we had written the classical Hamiltonian function H, we should have

$$S = \frac{1}{\lambda^{3N}N!}\, e^{-V/kT} \sum_{P} e^{-\frac{\pi}{\lambda^2}\sum_{k=1}^{N}|\mathbf{r}_k-\mathbf{r}_{Pk}|^2}$$

which differs from S_c only by the occurrence of the apparent intermolecular forces due to the E. B. statistics. For $V=0$ this is exact and the same as (27). When we therefore put

$$F = w\, e^{\frac{2\pi i}{h}\sum_{k=1}^{N}(\mathbf{p}_k\cdot\mathbf{r}_k)}\, e^{-\beta H} \quad . \; . \; . \; . \; . \quad (38)$$

then w represents the other quantum effects. Introducing (38) into (37) one finds for w the equation

$$\left.\begin{aligned} \frac{\partial w}{\partial \beta} &= \frac{ih}{2\pi m}\sum_{k=1}^{N}\{(\mathbf{p}_k\cdot\nabla_k w)-\beta w(\mathbf{p}_k\cdot\nabla_k V)\} + \\ &+ \frac{h^2}{8\pi^2 m}\sum_{k=1}^{N}\{\triangle_k w - 2\beta(\nabla_k w\cdot\nabla_k V) - \beta w\triangle_k V + \beta^2 w(\nabla_k V)^2\} \end{aligned}\right\} (39)$$

with

$$(w)_{\beta=0} = 1.$$

As we wish to see how S is approximated by S_c, it is appropriate to develop w in powers of h:

$$w = \sum_{n=0}^{\infty} h^n w_n. \quad . \; . \; . \; . \; . \; . \; . \; . \quad (40)$$

We introduce (40) into (39) and compare equal powers of h. This gives successively, after a simple integration,

$$\left.\begin{aligned}
w_0 &= 1 \\
w_1 &= -\frac{i\beta^2}{4\pi m}\sum_{k=1}^{N}(\mathbf{p}_k\cdot\nabla_k V) \\
w_2 &= -\frac{1}{8\pi^2 m}\left[\frac{\beta^2}{2}\sum_{k=1}^{N}\triangle_k V-\frac{\beta^3}{3}\left\{\sum_{k=1}^{N}(\nabla_k V)^2+\frac{1}{m}\left(\sum_{k=1}^{N}(\mathbf{p}_k\cdot\nabla_k)\right)^2 V\right\}+\right. \\
&\quad\left.+\frac{\beta^4}{4m}\left(\sum_{k=1}^{N}(\mathbf{p}_k\cdot\nabla_k V)\right)^2\right].
\end{aligned}\right\}\quad(41)$$

In this way all the w_n may be obtained in succession. When we now introduce this solution into (35) we find the following development for S:

$$\left.\begin{aligned}
S = S_c\sum_{P} e^{-\frac{\pi}{\lambda^2}\sum_{k=1}^{N}|\mathbf{r}_k-\mathbf{r}_{Pk}|^2}\Bigg\{1+\frac{1}{2kT}\sum_{k=1}^{N}(\mathbf{r}_k-\mathbf{r}_{Pk}\cdot\nabla_k V)-\\
-\frac{h^2}{48\pi^2 m k^2 T^2}\sum_{k=1}^{N}\left(\triangle_k V-\frac{1}{2kT}(\nabla_k V)^2\right)-\\
-\frac{1}{6kT}\left(\sum_{k=1}^{N}(\mathbf{r}_k-\mathbf{r}_{Pk}\cdot\nabla_k)\right)^2 V+\frac{1}{8k^2T^2}\left(\sum_{k=1}^{N}(\mathbf{r}_k-\mathbf{r}_{Pk}\cdot\nabla_k V)\right)^2+\ldots\Bigg\}
\end{aligned}\right\}\quad(42)$$

(It must be understood here that the operator ∇_k acts only on V).

In the case of BOLTZMANN statistics only the identical permutation should be taken into account. Then

$$S_B = S_c\left\{1-\frac{h^2}{48\pi^2 m k^2 T^2}\sum_{k=1}^{N}\left(\triangle_k V-\frac{1}{2kT}(\nabla_k V)^2\right)+\ldots\right\}. \quad (43)$$

This development has indeed the form (34) when we observe that the first derivatives of V play the role of $1/d$. The further terms of (43) will contain higher powers of h, higher derivatives and higher powers and products of the lower ones.

This method of obtaining successive approximations for S, starting from S_c, shows a great resemblance to the W. K. B. method of solving the SCHRÖDINGER equation. But the latter method is not directly applicable to our problem. In Chapter IV we shall however encounter a case where either KIRKWOOD's method or the W. K. B. method may be applied, both methods giving identical results.

The development (42) is of course only valid when the function V is differentiable any number of times. It will converge rapidly when $\lambda \nabla_k V/kT$, $\lambda^2 \triangle_k V/kT$, etc. are small compared with unity, that is to say, when V, measured in units kT, does not change much over the distance λ.

§ 5. THE PRODUCT PROPERTY.

In this paragraph a property of the SLATER sum will be discussed which is fundamental for the theory of the next Chapter.

Consider the function $W_N = W(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ as defined in (7) for gases of resp. 1, 2, ... N, ... particles in the same volume V. The W_N are symmetric functions of the arguments $\mathbf{r}_1, \ldots \mathbf{r}_N$. Furthermore $W_1 = 1$ for a monatomic gas without external forces *).

The product property may now be stated as follows. When we divide the particles into different groups containing α_1, α_2, ... particles, then for configurations where particles of different groups are so far away from each other that their interaction (including the apparent interaction due to E. B. or F. D. statistics) vanishes, we have

$$W_N = W_{\alpha_1} W_{\alpha_2} \ldots \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

This property is a consequence of the fact that in these configurations the Hamiltonian is separable into the sum of the Hamiltonians of the different groups. In the classical theory (44) follows immediately from this fact. In the quantum theory it is easiest to consider eq. (35) (or the analogue for F. D. statistics). For BOLTZMANN statistics, where only the identical permutation must be taken into account, our property is then again immediately clear. For E. B. and F. D. statistics observe that the integration over $\mathbf{p}_k$ leaves zero when the points $\mathbf{r}_k$ and $\mathbf{r}_{Pk}$ are far away from each other. Therefore only those permutations give a non-vanishing result where the k^{th} and the Pk^{th} particle are in the same group. But then the integrand of

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*) As follows from § 3, example a, this is true exactly in the classical theory and almost exactly in the quantum theory.

(35) may be written as a product of the analogous expressions for each group and therefore also the integral has the product property.

It should be stressed that for this proof it is *not* necessary to assume the additivity property of the intermolecular forces *). The function W_N has in general *not* the property that it can be split into factors, each containing only a pair of molecules, as is the case in the classical theory when the forces are additive.

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*) The range of the forces must of course be sufficiently short, so that a division into non-interacting groups is possible.

CHAPTER III.

The Theory of Condensation.

§ 1. THE PROBLEM.

In this chapter we shall investigate how far the qualitative features of the equation of state of gases and liquids may be understood by means of statistical mechanics. The main properties in which we are interested are illustrated by fig. 2 where two isotherms of a pure substance are drawn, one for a temperature above the critical temperature T_c and the other for a temperature below T_c. For large volumes (small densities) both curves are shaped according to the ideal gas law. It is clear theoretically that this should be so, because at small densities the interaction between the molecules may be neglected. For smaller volumes deviations from the ideal behaviour occur, due to the intermolecular forces. These deviations are quite different for the two temperatures. For $T > T_c$ the isotherm is always a smooth curve while for $T < T_c$ the curve consists of *three analytically different parts*, namely one representing the vapour, a

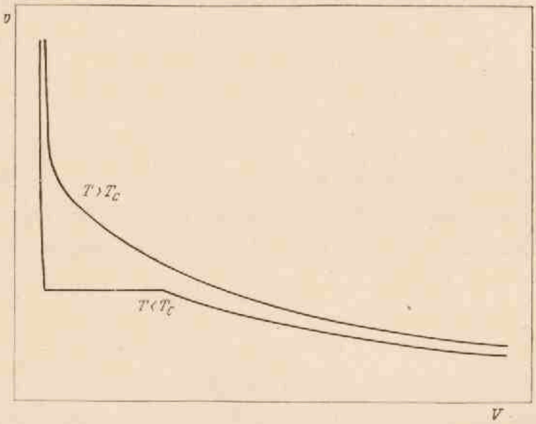

Fig. 2.

second horizontal part representing the saturated vapour in equilibrium with the liquid, and a third one representing the liquid.

The problem can now be stated as follows. Suppose one has N monatomic molecules of mass m in a vessel of volume V, then the free energy $\Psi(V, T)$ is determined by:

$$\left.\begin{aligned} e^{-\frac{\Psi}{kT}} &= \frac{1}{\lambda^{3N}} \frac{1}{N!} Q_N \\ Q_N &= \int_V \ldots \int_V d\mathbf{r}_1 \ldots d\mathbf{r}_N \, W(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) \end{aligned}\right\} \quad . \; . \quad (1)$$

where $W(\mathbf{r}_1, \ldots \mathbf{r}_N)$ and λ are defined by (II, 7) and (II, 5) and where the integral over each $\mathbf{r}_k$ has to be taken over the volume V. The pressure follows from Ψ according to:

$$p = -\left(\frac{\partial \Psi}{\partial V}\right)_T \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The question now is whether one can prove from (1) that at sufficiently low temperatures p as a function of V consists of three analytically different parts.

The following remarks may help to elucidate the problem.

a. As was already mentioned in the first chapter, the VAN DER WAALS theory does *not* give a solution of this problem, since here the real stable isotherm is not derived directly from the integral (1).

b. One might think perhaps that this stable isotherm *cannot* be derived from the integral (1) without further assumptions. One argues then that (1) gives the free energy for *one* homogeneous phase. One should make a separate calculation for the case when the system consists of *two* phases. For each volume one would obtain therefore two values for the free energy, corresponding to one or to two phases, and the real isotherm would be determined by the lowest value of the free energy. In our opinion this argument is *not* correct. The integral (1) contains all possible states of the system *) and the Ψ which one calculates from (1) will describe the most

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*) This point was especially emphasized by Prof. VAN DER WAALS Jr. in the discussion of MAYER's theory at the VAN DER WAALS centenary congress in Amsterdam.

probable state, which is the state of stable equilibrium. The real stable isotherm should therefore follow automatically from (1) without further assumptions.

c. On the other hand, from the mathematical standpoint, it is hard to imagine, how from (1) it can follow that Ψ (and therefore p) as a function of V consists of three analytically different parts. It seems to us that this is possible because we are really only interested in a *limit property* of Ψ. The problem has a physical sense only when N is very large. One may expect then that for a fixed specific volume

$$v = \frac{V}{N}$$

the free energy Ψ will become proportional to N. Or in other words, the limit

$$\psi(v, T) = Lim \frac{1}{N} \Psi(V, N, T) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

for $V \to \infty$, $N \to \infty$, $V/N = v$ fixed, will exist. Strictly speaking the property mentioned above has to be proved for ψ as function of v. It is not surprising that this function can consist of analytically different parts.

d. One may remark that the stable isotherm does not represent all states of the system which are realizable. There is for instance the well known phenomenon of supersaturation, which is represented by the continuation of the vapour part of the isotherm beyond the point of condensation. These states however are *not* states of stable equilibrium, except in vessels which are everywhere so narrow that capillary phenomena become of importance. Since we shall discuss the integral (1) only for the case that the vessel becomes large in all directions, it is clear that we shall *not* obtain the states corresponding to the supersaturated vapour.

§ 2. THE DEVELOPMENT OF URSELL.

URSELL ^{3}) has shown that it is possible to write the integral (1) as a polynomial of the N^{th} degree in the volume. His procedure was based on classical statistical mechanics but can easily be extended in order to include the quantum theory. One introduces a set of functions $U(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_l) = U_l$, which depend symmetrically on the coordinates of l molecules in the volume V. They are expressed in terms of the probabilities $W_1, W_2, \ldots W_l$ by means of the relations:

$$\left.\begin{aligned} &W(\mathbf{r}_1) = U(\mathbf{r}_1) = 1 \\ &W(\mathbf{r}_1, \mathbf{r}_2) = U(\mathbf{r}_1, \mathbf{r}_2) + U(\mathbf{r}_1)\, U(\mathbf{r}_2) \\ &W(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + U(\mathbf{r}_1, \mathbf{r}_2)\, U(\mathbf{r}_3) + \\ &+ U(\mathbf{r}_2, \mathbf{r}_3)\, U(\mathbf{r}_1) + U(\mathbf{r}_3, \mathbf{r}_1)\, U(\mathbf{r}_2) + U(\mathbf{r}_1)\, U(\mathbf{r}_2)\, U(\mathbf{r}_3) \end{aligned}\right\} \quad (4)$$

and so on. The general rule is the following. We divide the l particles which occur in W_l into a number of groups, and form the product of the functions U, which depend on the particles of these groups. Then W_l will be the sum of these products for all possible ways of division of the l particles. The U_l in terms of $W_1, W_2, \ldots W_l$ are uniquely defined by these relations. One finds for instance:

$$\left.\begin{aligned} U(\mathbf{r}_1, \mathbf{r}_2) &= W(\mathbf{r}_1, \mathbf{r}_2) - W(\mathbf{r}_1)\, W(\mathbf{r}_2) \\ U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= W(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - W(\mathbf{r}_1, \mathbf{r}_2)\, W(\mathbf{r}_3) - W(\mathbf{r}_2, \mathbf{r}_3)\, W(\mathbf{r}_1) - \\ &\quad - W(\mathbf{r}_3, \mathbf{r}_1)\, W(\mathbf{r}_2) + 2\, W(\mathbf{r}_1)\, W(\mathbf{r}_2)\, W(\mathbf{r}_3). \end{aligned}\right\} \quad (5)$$

The rule which expresses the U in the W, is the same as the rule which expresses the W in the U, except for a coefficient $(-1)^{k-1}\ (k-1)!$, when k is the number of groups into which the l particles are divided. This will be proved at the end of this paragraph.

The importance of the development (4) lies in the following fundamental property of the functions U_l. When we divide the l particles into different groups, containing $\beta_1, \beta_2, \ldots$ particles, then, for configurations where particles of different groups are so far away from each other that their interaction vanishes, we have $U_l = 0$. Less exactly one may say that U_l is different from zero only when all the particles are near each other *).

The proof of this theorem follows from the product property of the W_N which has been explained at the end of the second chapter.

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*) This does not mean, however, that each particle is interacting with all others, but only that all particles are linked together.

For U_3 for instance it can be verified immediately from the explicit expression (5). In this way one could give a general proof. It is simpler however to consider the configuration mentioned in the product property of W_N. Develop both sides of (II, 44) according to (4). The right hand side will then contain no U_l referring to particles of different groups. The sum of those terms on the left hand side, which contain U_l of this kind, must therefore be zero for this configuration. By applying this argument successively to W_2, W_3, etc., one shows by induction that each U_l of this kind must be zero, as the theorem requires.

A consequence of this theorem is that the integral of U_l over the coordinates of the l particles will become proportional to the volume V, when V is very large. To see this first perform the integration over the coordinates of $l-1$ particles, keeping the coordinates of the l^{th} particle fixed. Because of the fundamental property of U_l the result will be independent of the volume and independent of the position of the l^{th} particle, provided that V is sufficiently large and U_l approaches zero sufficiently fast when the $l-1$ particles are separated from the l^{th} particle. The integration over the coordinates of the l^{th} particle will then contribute a factor V to the integral. We shall write:

$$\int\limits_V \cdots \int\limits_V d\mathbf{r}_1 \ldots d\mathbf{r}_l \, U_l = V l! \, b_l \quad . \quad . \quad . \quad . \quad (6)$$

It will be clear now that by integrating the development (4) for W_N, one will obtain for Q_N a polynomial of degree N in V. The result can be written in the following form:

$$Q_N = N! \, \mathsf{S}' \prod_{l=1}^{N} \frac{(V b_l)^{m_l}}{m_l!} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The m_l are positive integers or zero. The summation sign means that one has to sum over all sets of values of the m_l, which fulfill the condition:

$$\sum_{l=1}^{N} l m_l = N \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

To prove this, consider a definite partition of N in m_1 groups of one particle, m_2 groups of two particles, and so on. The m_l will then clearly fulfill (8). To a definite set of values of m_l correspond many terms in the development (4), due to the different ways of distributing the N particles over the groups. All these terms will give the same result after integration, namely:

$$\prod_{l=1}^{N} (V l!\, b_l)^{m_l} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

The number of these terms will be:

$$N! \prod_{l=1}^{N} \frac{1}{(l!)^{m_l}\, m_l!} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

since the permutation of particles in one group and the permutation of groups of equal size will not give rise to new terms. By multiplying (9) and (10) and by summing over the m_l one obtains (7).

Sometimes it is useful to write URSELL's development (7) in a different form, namely

$$Q_N = N! \sum_{k=1}^{N} \frac{V^k}{k!} \mathsf{S}' \prod_{i=1}^{k} b_{\alpha} \quad . \; . \; . \; . \; . \; . \quad (11)$$

Here the α_i are positive non-zero integers and the round summation sign means that one has to sum over all sets of values of the α_i which fulfill the condition:

$$\sum_{i=1}^{k} \alpha_i = N \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

To prove (11), first consider the partition of N into the two groups α_1 and α_2. Then α_1 and α_2 fulfill (12) with $k=2$. To this partition corresponds again a number of terms in (4) which give the same result after integration, namely

$$V^2 \alpha_1!\, \alpha_2!\, b_{\alpha_1} b_{\alpha_2}.$$

The number of these terms will be

$$\frac{N!}{\alpha_1!\, \alpha_2!}$$

when $a_1 \neq a_2$ and

$$\frac{N!}{2!\,a_1!\,a_2!}$$

when $a_1 = a_2$.
In order to obtain the contribution to Q_N of all partitions of N into two groups we can sum over all integral values of a_1 and a_2 which fulfill the condition (12) when we observe that each partition with $a_1 \neq a_2$ will occur twice in this summation. The contribution of these partitions to Q_N is therefore

$$N!\frac{V^2}{2!}\,\mathbf{S}'\, b_{\alpha_1}\, b_{\alpha_2}.$$

The extension of this reasoning to partitions into more than two groups gives immediately (11).

Finally we shall show that Q_N can be expressed by means of the generating function

$$N!\,(e^{V\chi(t)}-1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where

$$\chi(t) = \sum_{l=1}^{\infty} b_l\, t^l. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

This means that Q_N is equal to the coefficient of t^N in the expansion of (13) in powers of t *).

For the proof of (13) we may start either from (7) or from (11). If we multiply each b_{α_i} in (11) by t^{α_i} then we may sum over all integral values of α_i independently and afterwards fulfill the condition (12) by taking the coefficient of t^N in the resulting expression. The generating function is therefore

$$N!\sum_{k=1}^{N}\frac{V^k}{k!}\Big(\sum_{\alpha_1=1}^{\infty}\cdots\sum_{\alpha_k=1}^{\infty} b_{\alpha_1}t^{\alpha_1}\cdots b_{\alpha_k}t^{\alpha_k}\Big) = N!\sum_{k=1}^{N}\frac{V^k}{k!}\Big(\sum_{l=1}^{\infty} b_l\, t^l\Big)^k.$$

The sum over k may be extended to infinity since the terms with

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*) The term -1 in (13) is unessential since $N \geqq 1$.

$k > N$ give rise only to powers of t higher than the N^{th} one. This gives immediately the expression (13).

From (13) we can find the expression of b_l in $Q_1, Q_2, \ldots Q_l$ and therefore the coefficients in the expansion (5). The expression of Q_N by means of (13) can be written as

$$\sum_{N=1}^{\infty} \frac{Q_N}{N!} t^N = e^{V\chi(t)} - 1 \; . \; . \; . \; . \; . \; . \; . \qquad (15)$$

which is equivalent to

$$V\chi(t) = \log\left(1 + \sum_{N=1}^{\infty} \frac{Q_N}{N!} t^N\right).$$

Therefore the generating function of $V\, b_l$ is

$$\log\left(1 + \sum_{N=1}^{\infty} \frac{Q_N}{N!} t^N\right).$$

One finds easily that this is equivalent to the following expression for $V\, b_l$, which is analogous to (11):

$$V b_l = \sum_{k=1}^{l} (-1)^{k-1} \frac{1}{k} \,\mathsf{S}' \prod_{i=1}^{k} \frac{Q_{\beta_i}}{\beta_i!} \; . \; . \; . \; . \; . \qquad (16)$$

where the round summation sign means that one has to sum over all sets of values of the β_i which fulfill the condition

$$\sum_{i=1}^{k} \beta_i = l \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (17)$$

Comparison of (16) and (11) leads immediately to the values of the coefficients mentioned after eq. (5).

§ 3. THE EQUATION OF STATE FOR THE VAPOUR PHASE.

MAYER has shown how to derive from the development of URSELL a general expression for the equation of state of the vapour phase. We shall give here essentially his first derivation which, although not rigorous, is very simple and gives the correct result. In § 6 an exact proof will be given.

Suppose that all b_l are positive, (which they probably are at sufficiently low temperatures), then for large N one may approximate the sum (7) by its largest term. To find the set of m_l which gives this maximum term, one proceeds in a way which is quite analogous to the usual derivation of the MAXWELL–BOLTZMANN distribution law in statistical mechanics. One then finds, using STIRLING's approximation for $m_l!$, that this maximizing set of m_l is given by:

$$\overline{m}_l = V b_l z^l \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (18)$$

where the parameter z has to be determined by the condition (8), so that

$$\frac{N}{V} = \frac{1}{v} = \sum_{l=1}^{\infty} l b_l z^l \; . \; . \; . \; . \; . \; . \; . \; . \quad (a)$$

By introducing this set of m_l one finds that $log\ Q_N$ is approximated by

$$log\ \overline{Q}_N = log\ N! - N\ log\ z + V \sum_{l=1}^{\infty} b_l z^l.$$

From (1) and (2) one obtains then for the pressure

$$p = kT \sum_{l=1}^{\infty} b_l z^l \; . \; . \; . \; . \; . \; . \; . \; . \quad (b)$$

In order to find an explicit expression for the equation of state, one has to eliminate z between the equations (a) and (b). BORN[17]) and MAYER have given a formal solution of this problem. Their result can be stated as follows *). Define a function

$$\varphi(\xi) = \sum_{\nu=1}^{\infty} \beta_\nu \xi^\nu$$

in such a way that $l^2 b_l$ is equal to the coefficient of ξ^{l-1} in the expansion of $exp\,(l\varphi(\xi))$. This gives the b_l expressed in terms of the β_ν. One can solve these equations successively for β_ν and thus express the β_ν uniquely in terms of the b_l. With the help of the

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*) For a simple proof see Note 2.

function $\varphi(\xi)$ the solution of eq. (a) can be written in the form

$$z = \frac{1}{v} e^{-\varphi\left(\frac{1}{v}\right)}.$$

By introducing this into (b) one obtains

$$p v = k T \left(1 - \sum_{\nu=1}^{\infty} \frac{\nu}{\nu + 1} \frac{\beta_\nu}{v^\nu}\right). \quad . \quad . \quad . \quad . \quad (19)$$

The expression of the β_ν in terms of the b_l gives then

$$\left. \begin{aligned} pV = NkT \bigg[1 - \frac{N b_2}{V} + \frac{N^2}{V^2}(-2 b_3 + 4 b_2^2) + \\ + \frac{N^3}{V^3}(-3 b_4 + 18 b_2 b_3 - 20 b_2^3) + \ldots \bigg]. \end{aligned} \right\} \quad . \quad (20)$$

This has the form of the expansion in virial coefficients (I, 3) with

$$B = -N b_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$C = N^2 (-2 b_3 + 4 b_2^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$D = N^3 (-3 b_4 + 18 b_2 b_3 - 20 b_2^3). \quad . \quad (23)$$

These expressions for the virial coefficients were already known in older theories and may be obtained directly from URSELL's expansion *).

All the other thermodynamical quantities can easily be expressed in terms of z and the b The following expressions are found:

Free energy

$$\Psi = -p V + N k T \log (\lambda^3 z) \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Thermodynamic potential

$$\zeta = \Psi + p V = N k T \log (\lambda^3 z) \quad . \quad . \quad . \quad . \quad . \quad (25)$$

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*) In reality one obtains in this way

$$B = -(N-1)\, b_2$$

$$C = 2\,(N-1)\,(2N-3)\, b_2{}^2 - 2\,(N-1)\,(N-2)\, b_3$$

which coincides with (21) and (22) for large N.

Entropy

$$\eta=-\left(\frac{\partial\Psi}{\partial T}\right)_V=\frac{pV}{T}+\tfrac{3}{2}Nk-Nk\log(\lambda^3 z)+kTV\sum_{l=1}^{\infty}\frac{db_l}{dT}z^l \quad . \quad (26)$$

Energy

$$\varepsilon=\Psi+T\eta=\tfrac{3}{2}NkT+kT^2V\sum_{l=1}^{\infty}\frac{db_l}{dT}z^l \quad . \quad . \quad . \quad (27)$$

Specific heat at constant volume

$$\left.\begin{aligned}c_V=T\left(\frac{\partial\eta}{\partial T}\right)_V&=\tfrac{3}{2}Nk+2kTV\sum_{l=1}^{\infty}\frac{db_l}{dT}z^l+\\&+kT^2V\sum_{l=1}^{\infty}\frac{d^2b_l}{dT^2}z^l-kT^2V\frac{\left(\sum_{l=1}^{\infty}l\frac{db_l}{dT}z^l\right)^2}{\sum_{l=1}^{\infty}l^2b_lz^l}\end{aligned}\right\} . \quad (28)$$

Compressibility

$$-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T=\frac{1}{kT}\frac{\sum_{l=1}^{\infty}l^2b_lz^l}{\left(\sum_{l=1}^{\infty}l\,b_lz^l\right)^2} \quad . \quad . \quad . \quad . \quad (29)$$

The eq. (25) shows the thermodynamic meaning of the parameter z.

§ 4. THE IDEAL EINSTEIN–BOSE GAS.

The equations (a) and (b) show a remarkable analogy to the equation of state of an ideal E. B. gas as given by EINSTEIN 4). He obtained:

$$\frac{N}{V}=\frac{1}{v}=\frac{1}{\lambda^3}\sum_{l=1}^{\infty}\frac{A^l}{l^{3/2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a_1)$$

$$p=\frac{kT}{\lambda^3}\sum_{l=1}^{\infty}\frac{A^l}{l^{5/2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b_1)$$

from which again the equation of state results by elimination of A.

Eqs. (a) and (b) become identical with (a_1) and (b_1) by putting

$$z = \frac{A}{\lambda^3}; \quad b_l = \frac{\lambda^{3(l-1)}}{l^{5/2}}. \quad \ldots \ldots \quad (30)$$

This analogy is especially of interest, since EINSTEIN has shown that the equations (a_1) and (b_1) give rise to a condensation phenomenon. Furthermore the case of the ideal E. B. gas furnishes an example where the b_l, which are characteristic for the behaviour of a real gas, can be determined explicitly.

The equations (a_1) and (b_1) were derived by EINSTEIN from the E. B. velocity distribution law. According to this law the number of particles with velocity components between ξ and $\xi + d\xi$, η and $\eta + d\eta$, ζ and $\zeta + d\zeta$ is

$$\frac{V m^3}{h^3} \frac{d\xi \, d\eta \, d\zeta}{\frac{1}{A} e^{\frac{E}{kT}} - 1}$$

where

$$E = \frac{m}{2} (\xi^2 + \eta^2 + \zeta^2).$$

In this form of the distribution law the quantization of the translational motion is neglected. The parameter A is determined by the condition

$$N = \frac{V m^3}{h^3} \iiint\limits_{-\infty}^{\infty} \frac{d\xi \, d\eta \, d\zeta}{\frac{1}{A} e^{\frac{E}{kT}} - 1} \quad \ldots \ldots \quad (31)$$

and the total energy is

$$\varepsilon = \frac{V m^3}{h^3} \frac{m}{2} \iiint\limits_{-\infty}^{\infty} \frac{(\xi^2 + \eta^2 + \zeta^2) \, d\xi \, d\eta \, d\zeta}{\frac{1}{A} e^{\frac{E}{kT}} - 1}. \quad \ldots \quad (32)$$

From the last equation the pressure may be obtained by using the virial theorem

$$p V = \tfrac{2}{3} \varepsilon.$$

The equations (a_1) and (b_1) are then obtained by developing the integrands of (31) and (32) in powers of $A \; exp \; (-E/kT)$, which is possible for $A < 1$, and by integrating term by term.

An alternative derivation of Eqs. (a_1) and (b_1) will show more clearly the origin of their analogy with (a) and (b). In chapter II we have found the expression (II, 29) for the function W_N of an ideal E. B. gas:

$$W_N = \sum_P e^{-\frac{\pi}{\lambda^2} \sum_{0=1}^{N} |\mathbf{r}_k - \mathbf{r}_{Pk}|^2} \quad . \; . \; . \; . \; . \; . \; . \quad (33)$$

The integral Q_N can now be written in the same form as URSELL's development (7). Observe namely that by integrating one term of (33), corresponding to a definite permutation P, over $d\mathbf{r}_1 \ldots d\mathbf{r}_N$ one obtains a power of V which is equal to the number of cycles into which this permutation can be decomposed. The sum (33) is therefore analogous to the development (4) of W_N in the U_l. Suppose that the permutation P can be decomposed into m_1 cycles of one particle, m_2 cycles of two particles and so on. The m_l will then again fulfill the condition (8). To a definite set of values of m_l there will correspond many terms in (33), each of which gives the same contribution to the integral Q_N. The number of these terms will be

$$N! \prod_{l=1}^{N} \frac{1}{l^{m_l} m_l!} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (34)$$

This is different from (10) because only the l cyclic permutations of the particles in one cycle will not give rise to new terms. To obtain Q_N in exactly the same form as in (7) we must write $V \, l \, b_l$ for the integral over the coordinates of the particles of a cycle of length l. Therefore:

$$V \, l \, b_l = \int\limits_V \ldots \int\limits_V d\mathbf{r}_1 \ldots . \, d\mathbf{r}_l \, e^{-\frac{\pi}{\lambda^2}(r^2_{12} + r^2_{23} + \ldots + r^2_{l1})} \quad . \; . \quad (35)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The contribution of a term of (33) corresponding to a definite set of values of m_l will then be

$$\prod_{l=1}^{N} (V \, l \, b_l)^{m_l} . \quad . \; . \; . \; . \; . \; . \; . \; . \quad (36)$$

By multiplying (34) and (36), and by summing over the m_l one again obtains (7).

The integral (35) can be performed straightforwardly *). One finds then for b_l the result (30) and we have already seen that with this value of b_l the equations (a) and (b) of MAYER become the equations (a_1) and (b_1) of EINSTEIN.

§ 5. THE CONDENSATION PHENOMENON.

The reasoning by which EINSTEIN derived the condensation phenomenon for an ideal E.B. gas from Eqs. (a_1) and (b_1) is as follows. For small values of the density the corresponding value of A will be small. By increasing the density A will increase monotonically. This goes on until for a finite value of the density, A reaches the value one. Then:

$$\frac{N}{V}=\frac{1}{v_c}=\frac{1}{\lambda^3}\sum_{l=1}^{\infty}\frac{1}{l^{3/2}}=\frac{2.61}{\lambda^3}\,. \quad . \quad . \quad . \quad . \quad (37)$$

$$p=p_s=\frac{kT}{\lambda^3}\sum_{l=1}^{\infty}\frac{1}{l^{5/2}}=1.34\,\frac{kT}{\lambda^3} \quad . \quad . \quad . \quad . \quad (38)$$

For $A > 1$ the series (a_1) and (b_1) diverge. According to EINSTEIN $1/v_c$ is the maximum density which can be reached. By further compression of the gas, the superfluous particles will "condense" into the state of zero energy and will not contribute to the pressure nor to the density so that the pressure will remain p_s. We have therefore indeed a kind of condensation phenomenon, which has however some uncommon features, for instance:

a. The volume of the condensed phase is zero.

b. There does not exist a critical temperature.

In order to get a closer idea of this condensation phenomenon we shall give the expressions for some of the thermodynamic quantities in the vapour phase and in the region of equilibrium

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*) See Note 3. The same integral occurs in a paper of KRAMERS [18]) on ferromagnetism.

between vapour and "liquid". In the vapour phase we have

$$\Psi = -pV + NkT \log A \quad ; \quad \zeta = NkT \log A$$

$$\eta = \frac{5}{2}\frac{pV}{T} - Nk \log A \quad ; \quad \varepsilon = \frac{3}{2}pV$$

$$c_V = \frac{15}{4}\frac{pV}{T} - \frac{9}{4}Nk\frac{\sum\limits_{l=1}^{\infty}\frac{A^l}{l^{3/2}}}{\sum\limits_{l=1}^{\infty}\frac{A^l}{l^{1/2}}} \; ; \; \left(\frac{\partial p}{\partial V}\right)_T = -\frac{kT}{\lambda^3 V}\frac{\left(\sum\limits_{l=1}^{\infty}\frac{A^l}{l^{3/2}}\right)^2}{\sum\limits_{l=1}^{\infty}\frac{A^l}{l^{1/2}}}$$

and in the two phase system

$$\Psi = -p_s V \; ; \; \zeta = 0$$

$$\eta = \frac{5}{2}\frac{p_s V}{T} \; ; \; \varepsilon = \frac{3}{2}p_s V$$

$$c_V = \frac{15}{4}\frac{p_s V}{T} \; ; \; \left(\frac{\partial p_s}{\partial V}\right)_T = 0.$$

The differences between the values of the thermodynamical quantities for the two phases are obtained from the last group of formulae by putting $V = V_c$ and $V = 0$ respectively. We see that ζ is equal for both phases, which is the thermodynamical requirement for each phase transition. Furthermore this phase transition is one of the first kind since the volume and the entropy are different for the two phases, the differences being V_c and $5 p_s V_c / 2T$ respectively. From (38) follows

$$\frac{dp_s}{dT} = \frac{5}{2}\frac{p_s}{T} = \frac{\triangle \eta}{\triangle V}$$

which is CLAPEYRON's equation. On the other hand we remark two other points in which this phase transition differs from the condensation of a real gas, namely

c. $(\partial p / \partial V)_T$ has no discontinuity for $V = V_c$.

d. C_V has no discontinuity for $V = V_c$ *).

---

*) The continuity of C_V has been remarked by LONDON [19]). His conclusion however, that this would mean that we have to do here with a phase transition of the third kind, seems to us incorrect when one uses the term in the sense given by EHRENFEST [20]).

This follows from the fact that $\sum_{l=1}^{\infty} 1/l^{1/2}$ diverges. In fig. 3 we have drawn some isotherms of the ideal E. B. gas, according to (a_1), (b_1) and (38).

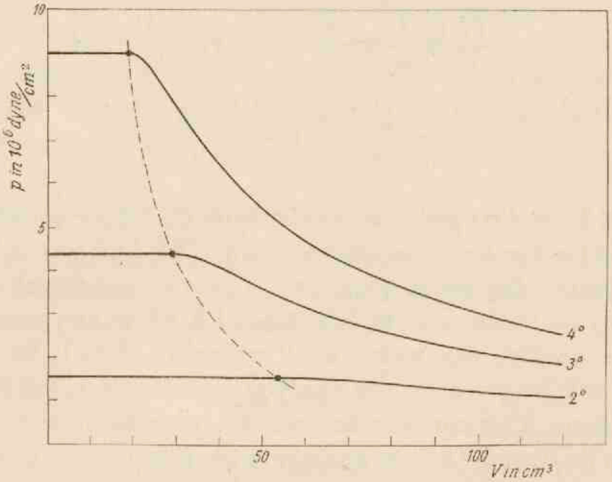

Fig. 3. Isotherms of the ideal EINSTEIN–BOSE gas.

The reasoning by which MAYER first derived the condensation phenomenon for a real gas is quite analogous to the argument of EINSTEIN. It can be expressed as follows. Suppose that the series (*a*) and (*b*) have a certain finite convergence radius $\bar{z}$, and that they are still convergent for $z = \bar{z}$ *).

When in addition the b_l are positive, then by increasing the density the corresponding value of z will increase monotonically till the maximum value $z = \bar{z}$ is reached. For higher densities the series (*a*) and (*b*) cease to have significance. Using a physical interpretation of the equations, MAYER tries to show that by further compression of the vapour condensation will occur, while the pressure remains constant and equal to the value

$$p_s = kT \sum_{l=1}^{\infty} b_l \bar{z}^l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

---

*) In fact, MAYER tries to prove that for large l the b_l become asymptotically equal to $b_0^{l-1}/l^{5/2}$, which would make the analogy with the ideal E. B. gas still closer. This result of MAYER seems to us incorrect (see § 7); it does not affect however his explanation of the condensation phenomenon.

These explanations of the condensation phenomenon are certainly not yet complete. An instructive example is furnished by the ideal FERMI–DIRAC gas. One shows easily that for this case the equation of state is determined by

$$\frac{N}{V} = \frac{1}{v} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} (-1)^{l-1} \frac{A^l}{l^{3/2}} \quad . \; . \; . \; . \; . \quad (a_2)$$

$$p = \frac{kT}{\lambda^3} \sum_{l=1}^{\infty} (-1)^{l-1} \frac{A^l}{l^{5/2}} \quad . \; . \; . \; . \; . \; . \quad (b_2)$$

when $A \leqq 1$. At first sight one might think that these equations will also predict a condensation phenomenon. This however is *not* correct. Although the series (a_2) and (b_2) are convergent only for $A \leqq 1$, they represent analytic functions of A, which can be continued along the positive real axis for all values of $A > 1$, so that the pressure will be given by *one* analytic function of v for all values of the volume. This can also be seen directly when one derives the equations (a_2) and (b_2) in analogy with EINSTEIN's derivation of (a_1) and (b_1). The formulae for N and ε are obtained from (31) and (32) by replacing the -1 by $+1$ in the denominator. These integrals, in contrast with (31) and (32), are convergent for all positive values of A. Only for $A \leqq 1$ they give rise to the series (a_2) and (b_2). This is in contrast to the case of the ideal E. B. gas, where the point $A = 1$ is a *singular* point of the functions (a_1) and (b_1). It can be shown (see § 6) that for the real gas also an essential condition for condensation is that the functions (a) and (b) have a singularity on the positive real axis of z.

Another objection against the reasoning of EINSTEIN has been raised by UHLENBECK[21]). The Eqs. (a_1) and (b_1) are derived namely by neglecting the quantization of the translational motion of the molecules. Instead of the integrals (31) and (32) one should write sums over all the possible discrete states. In the alternative derivation this corresponds to the neglect of the influence of the walls of the vessel in the calculation of b_l. This neglect is justified for small values of A, but it becomes dangerous in the neighbourhood or $A = 1$. In fact, when we regard the sum which should be used instead of the integral (31), we see that the term for the lowest state (which may always be taken as the zero for the energy scale) becomes infinite for $A = 1$ and therefore the number of particles does not remain finite when A approaches 1, so that the above reasoning fails. It remains true however that for densities larger than $1/v_c$ the isotherm will be almost horizontal, and that this will be more pronounced the larger the volume is. Only in the limit $V \to \infty$ will the isotherm consist of two different parts. When we always understand the condensation phenomenon in the sense of such a limit property (comp. remark *c* of § 1) then this objection therefore loses its validity.

§ 6. THE RIGOROUS TREATMENT.

We shall start from URSELL's development, but instead of making the approximations of § 3, we shall now determine strictly for $N \to \infty$, $V \to \infty$, $V/N = v$ finite

$$Lim \left(\frac{Q_N}{N!}\right)^{1/N} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

which according to (1) and (3) is equal to $\lambda^3 exp(-\psi/kT)$ *). Using CAUCHY's theorem of residues the expression of URSELL's development by means of the generating function (13) can be written in the form

$$\frac{Q_N}{N!} = \frac{1}{2\pi i} \oint \frac{dt}{t^{N+1}} e^{Nv\chi(t)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

where the integral has to be taken around the origin of the complex t-plane, excluding the singularities of $\chi(t)$. The function $\chi(t)$ is the fundamental function of the problem.

The first method which presents itself for treating the integral (41) is the method of steepest descents **). We have found another method, however, more appropriate for the discussion of the limit (40).

---

*) The Q_N are of course all *positive*, since they are integrals over the probabilities W_N.

**) In a paper by KRAMERS [18]) on ferromagnetism occurs an integral which is identical with (41) for the case of the ideal E. B. gas, and which has been treated by him with the method of steepest descents. KRAMERS was the first to show that for this case at least the limit (40) as a function of v consists of two analytically different parts.

Consider the power series

$$F(x) = \sum_{N=1}^{\infty} \frac{Q_N}{N!} x^N. \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

where the different Q_N have to be taken for the *same* value of $V/N = v$ *). According to the well known theorem of CAUCHY the limit (40) is now just equal to the inverse of the radius of convergence R of $F(x)$. On the other hand the series (42) defines an *analytic* function of x, and we can therefore find the convergence radius R by determining the singularity of this function which is nearest to the origin.

Another expression of $F(x)$ can be found as follows. Introduce (41) into (42); then the summation and integration can be interchanged when x is so small that on the whole contour

$$|x\xi(t)| < 1$$

where:

$$\xi(t) = \frac{e^{v\chi(t)}}{t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

It is always possible to find such an x because $|\xi(t)|$ is bounded on the contour. The summation of the geometric series gives then

$$F(x) = \frac{1}{2\pi i} \oint \frac{dt}{t} \frac{x\xi(t)}{1 - x\xi(t)} \quad . \quad . \quad . \quad . \quad . \quad (44)$$

The integral can be calculated by means of the theorem of residues. The only poles of the integrand within the contour are $t = 0$ and the zeros of the function $1 - x\xi(t)$. For sufficiently small x this function has only one simple zeropoint. One sees this from CAUCHY's integral. The excess of the number of zeros over the number of poles of $1 - x\xi(t)$ within the contour is given by

$$n - p = -\frac{x}{2\pi i} \oint \frac{\xi'(t)}{1 - x\xi(t)} dt.$$

---

*) The series (42) is completely different from the series (15) where all Q_N were taken for the same value of V.

The integral has always a certain finite value, so that $n-p$ can be made as small as one pleases by taking x small enough. Therefore $n-p$ must be zero, since it can assume integral values only. Now $1-x\xi(t)$ has one simple pole within the contour, namely $t=0$, and therefore also one simple zero, say at $t=t_0$. The evaluation of (44) by means of the theorem of residues gives then

$$F(x)=\frac{v\,t_0\,\chi'(t_0)}{1-v\,t_0\,\chi'(t_0)} \quad . \; . \; . \; . \; . \; . \; . \quad (45)$$

where:

$$1-x\,\xi(t_0)=0 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (46)$$

If we start from the origin and move along a definite path in the x-plane, the equation (46) will determine t_0 as an analytic function of x. Along the corresponding path in the t_0-plane *) $\chi'(t_0)$ will be again an analytic function of t_0 and therefore of x. In this way (45) defines an analytic function of x, which for small x coincides with the power series (42), and which therefore represents its analytical continuation.

We have now to determine the singularity of $F(x)$ which is nearest to the origin. One needs to consider only real positive values of x, because of the fact that the series (42) has real and positive coefficients, so that the real positive point on its circle of convergence will be a singularity of $F(x)$ [22]. One sees from (45) and (46) that the *possible* singularities of $F(x)$ are the values of x which correspond to the zeros of the denominator $1-v\,t_0\chi'(t_0)$ and which correspond to the singularities of $\chi(t_0)$. Whether these values of x are actually singularities of $F(x)$ and which of them is nearest to the origin depends on the properties of the function $\chi(t_0)$ and on the value of v. We know that for small values of t_0, $\chi(t_0)\simeq t_0$. We shall assume further:

a. $\chi(t_0)$ has a *finite* radius of convergence equal to r.

b. $\chi(t_0)$ has a singularity $\bar{z}$ on the real positive axis; $\bar{z}$ may be greater than or equal to r. The latter case will occur for instance when all the b_l are positive.

c. $\chi(\bar{z})$ and $\chi'(\bar{z})$ are finite; the point z will therefore be a branch point of $\chi(t_0)$.

---

*) Which also starts from the origin, since $t_0=0$ for $x=0$.

d. The inverse function of $\chi(t_0)$ is singular at the point corresponding to $t_0 = \bar{z}$.

e. $t_0 \chi'(t_0)$ is monotonically increasing on the real axis between $t_0 = 0$ and $t_0 = \bar{z}$ *); this will again be the case when the b_l are positive.

To find the singularities of $F(x)$ we shall start from the origin and move along the real positive axis in the x-plane. When v is large enough one sees that the first singularity of $F(x)$ which one meets will be determined by the zeropoint of the denominator in (45). Let us call this zeropoint $t_0 = z$, so that

$$v z \chi'(z) = 1 \quad \ldots\ldots\ldots \quad (47)$$

The corresponding value of x, and therefore the radius of convergence R, according to (46) will be

$$R = z e^{-v\chi(z)}$$

This is therefore the inverse of the limit (40), from which one immediately obtains the expression for the pressure

$$p = kT\chi(z) \, . \quad \ldots\ldots\ldots \quad (48)$$

The equations (47) and (48) are identical with the Eqs. (*a*) and (*b*), which are now therefore rigorously proved when v is large enough. It should be pointed out that for this proof *none* of the assumptions *a*—e are necessary. Because of assumption e **) the equations (47) and (48) will remain valid until

$$v = v_c = \frac{1}{\bar{z}\chi'(\bar{z})} \quad \ldots\ldots\ldots \quad (49)$$

In the case that $\bar{z} > r$, and for values of z between r and $\bar{z}$, the equations (47) and (48) are no longer identical with the series (*a*) and (*b*), but represent their analytical continuations. For all these values of v the pressure remains a smooth function of the volume.

Because of assumption c, v_c has a finite value. Suppose now that v

---

*) One must also exclude the possibility that $t_0\chi'(t_0)$ has a horizontal inflexion point in this region.

**) When this assumption is not fulfilled, so that $t_0\chi'(t_0)$ has at least one maximum (say at $t_0 = \bar{t}$), then for a value of v corresponding to $z = \bar{t}$, $(\partial p/\partial v)_T$ becomes infinite (comp. eq. (29)). This has been pointed out by BORN and FUCHS[23]). It gives the *physical* reason for the assumption e.

is smaller than v_c. When we again move along the real positive x-axis, we shall reach the point corresponding to $t_0 = \bar{z}$ before meeting a zero of the denominator of (45). Because of assumption *d* this value of x will be a singularity of $F(x)$. In this case therefore

$$R = \bar{z}\, e^{-v\chi(\bar{z})}$$

This corresponds to the *constant* pressure:

$$p = p_s = k\,T\,\chi(\bar{z}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

When $\bar{z} = r$ this is identical with equation (39) of MAYER. The pressure as a function of v consists therefore of two analytically different parts, namely the curve represented by (47) and (48) for $v > v_c$ and the horizontal line (50) for $v < v_c$.

§ 7. FURTHER REMARKS.

1⁰. In § 3 we have introduced the quantities β_ν in a formal way in order to perform the elimination of z between the equations (a) and (b). MAYER and BORN were led to these quantities by the consideration of the integrals defining the b_l in the case of classical statistical mechanics. They showed that these integrals can be split up into the sums of products of certain "irreducible" integrals, which are immediately related to the β_ν We have *not* been able to generalize this physical interpretation of the β_ν for the quantum theory.

2⁰. MAYER and BORN have tried to derive from the expression of the b_l in terms of the β_ν certain general properties of the characteristic function $\chi(z)$. In particular MAYER has tried to make plausible that in a certain region of temperatures below the critical temperature, b_l behaves asymptotically for large l as

$$b_l \cong \frac{b_0^{l-1}}{l^{5/2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (51)$$

One would obtain this by writing the expression of b_l in terms of the β_ν in the form

$$l^2\, b_l = \frac{1}{2\pi i} \oint d\xi\, \frac{e^{l\varphi(\xi)}}{\xi^l} \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

and applying the method of steepest descents to this integral. A consequence of (51) is that $(\partial p/\partial v)_T$ becomes zero at the condensation point $v = v_c$, just as in the case of the ideal E. B. gas.

These considerations seem to us very doubtful, since they are based *only* on the formal expression (52) for the b_l. The physical interpretation of the β_ν is nowhere used. Since the quantities β_ν can be defined uniquely by means of (52) for *each arbitrary* set of quantities b_l, this would mean that each infinite set would behave asymptotically like (51). This is of course nonsense. It is clear that one can hope to make a further advance only by going back to the physical meaning of the b_l or the β_ν. In particular it seems to us impossible to say anything in general about the behaviour of $(\partial p/\partial v)_T$ near the condensation point. This will depend on the series

$$\sum_{l=1}^{\infty} l^2 \, b_l \, \bar{z}^l$$

which may be divergent or convergent. In the first case $(\partial p/\partial v)_T$ will be zero for $v = v_c$ while in the latter case it will have a finite value.

3⁰. From the further investigation of the integrals representing b_l must follow especially the properties *a*—*e* (§ 6) of $\chi(z)$, which are necessary to explain the condensation phenomenon. An *essential difficulty* seems to us to lie in the fact that even with the assumptions *a*—*e* of $\chi(z)$ it is impossible to obtain the *third* part of the isotherm, corresponding to the liquid state. The reason is that for all $v < v_c$ the singularity of $F(x)$ which is nearest to the origin, is determined by the singularity $\bar{z}$ of $\chi(z)$, which is independent of v. Therefore the isotherm will remain horizontal for all $v < v_c$.

It is clear that the origin of this difficulty has to be found in the neglect of the dependence of the b_l on the volume V. It is true of course that for every finite l the quantity b_l has a definite limit for $V \to \infty$. We have assumed however more than this, since the properties of $\chi(z)$ depend on the behaviour of b_l for large l. There is clearly a double limiting process involved and it may be that the solution of the difficulty will be found by a more correct treatment of these limits.

CHAPTER IV.

The second virial coefficient of a monatomic gas.

§ 1. INTRODUCTION.

The foregoing chapter was chiefly devoted to an explanation of the qualitative features of the equation of state. However we have also shown that the isotherms in the gaseous state are exactly given by the development of KAMERLINGH ONNES and we have obtained expressions for the virial coefficients in terms of the integrals b_l, such that the n^{th} virial coefficient contains the b_l up to $l = n$. This gives us the possibility of treating the last problem mentioned in the first chapter, namely the investigation of the intermolecular forces from the equation of state. For, in order to calculate the n^{th} virial coefficient, we do not have to consider the whole gas but only systems of at most n particles. If this calculation in terms of a certain assumed intermolecular potential is possible, comparison with experiment can decide whether the assumed potential is a good approximation. For this purpose the second virial coefficient is best suited, because its calculation is simplest and the most reliable experimental data are obtained for this coefficient. Many investigations have been performed on these lines, most starting from the classical expression for the second virial coefficient. It will be our principal purpose to investigate the influence of the quantum theory. According to the general considerations of the second chapter, this influence will be largest for low temperatures.

§ 2. THE GENERAL EXPRESSION FOR THE SECOND VIRIAL COEFFICIENT.

In chapter III, eq. (21) we found that the second virial coefficient was equal to

$$B = -N b_2$$

where

$$b_2 = \frac{1}{2V} \int\limits_V \int\limits_V d\mathbf{r}_1 \, d\mathbf{r}_2 \, U(\mathbf{r}_1, \mathbf{r}_2) =$$

$$= \frac{1}{2V} \int\limits_V \int\limits_V d\mathbf{r}_1 \, d\mathbf{r}_2 \, \{ W(\mathbf{r}_1, \mathbf{r}_2) - W(\mathbf{r}_1) \, W(\mathbf{r}_2) \} .$$

Therefore the *classical* expression is

$$B_c = \frac{N}{2V} \int\int d\mathbf{r}_1 \, d\mathbf{r}_2 \, (1 - e^{-V(r)/kT})$$

where $V(r)$ is the potential energy of two particles at distance r. We now introduce the coordinates of the centre of gravity and the relative coordinates of the two particles. Integration over the first gives a factor V. For the relative motion we introduce polar coordinates. Then the angular integration may be performed and we get the well known expression

$$B_c = 2\pi N \int\limits_0^\infty dr \, r^2 (1 - e^{-V(r)/kT}) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This expression has the great advantage that it can always be evaluated, at least numerically, when the potential $V(r)$ is known. This is not the case with the *quantum theoretical* expression which will be derived now.

For particles with no spin we have (comp. (II, 7))

$$B = - \frac{N \lambda^6}{2V} \int\int d\mathbf{r}_1 \, d\mathbf{r}_2 \, \{ 2S(\mathbf{r}_1, \mathbf{r}_2) - S(\mathbf{r}_1) \, S(\mathbf{r}_2) \} \quad . \quad . \quad (2)$$

The integral $\int\int d\mathbf{r}_1 \, d\mathbf{r}_2 \, S(\mathbf{r}_1, \mathbf{r}_2)$ is equal to the partition function of a two particle system, whereas the integral $\int\int d\mathbf{r}_1 \, d\mathbf{r}_2 \, S(\mathbf{r}_1) \, S(\mathbf{r}_2)$ can be written as two times the partition function of an ideal BOLTZMANN gas of two particles. Let us first consider the BOLTZMANN gas. Then (comp. (II, 2))

$$B_B = \frac{N \lambda^6}{2V} \sum_i (G_i^{(0)} e^{-E_i^{(0)}/kT} - G_i \, e^{-E_i/kT}) \quad . \quad . \quad . \quad (3)$$

where the first term refers to a system of two noninteracting particles. Both terms can be written as the product of two partition functions, the first referring to the translation of the centre of gravity, the second to the relative motion. The first factor for both terms is equal to $2^{3/2}V/\lambda^3$ (the factor $2^{3/2}$ arises from the fact that the mass of the whole system is $2m$) and therefore

$$B_B = 2^{1/2} N \lambda^3 \sum_i \left(G_i^{(0)} e^{-E_i^{(0)}/kT} - G_i e^{-E_i/kT}\right)$$

where now the partition functions refer to the relative motion only. We shall introduce polar coordinates r, ϑ, φ and group the states according to the radial, azimuthal and magnetic quantum numbers, n, l, m. The states which differ only in m have the same energy, so that each state has a $(2l+1)$-fold degeneracy. Therefore

$$B_B = 2^{1/2} N \lambda^3 \sum_{l=0}^{\infty} (2l+1) \sum_n \left(e^{-E_{nl}^{(0)}/kT} - e^{-E_{nl}/kT}\right) \quad . \quad . \quad (4)$$

The quantities E_{nl} and $E_{nl}^{(0)}$ are the eigenvalues of the radial wave equations

$$v_{nl}'' + \frac{4\pi^2 m}{h^2} \left\{E_{nl} - V(r)\right\} v_{nl} - \frac{l(l+1)}{r^2} v_{nl} = 0 \quad . \quad . \quad (5)$$

and

$$v_{nl}^{(0)''} + \frac{4\pi^2 m}{h^2} E_{nl}^{(0)} v_{nl}^{(0)} - \frac{l(l+1)}{r^2} v_{nl}^{(0)} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where v_{nl}/r and $v_{nl}^{(0)}/r$ are the radial parts of the wave functions. In addition to these equations there is a boundary condition for the wave functions, because the particles are enclosed in a finite vessel. Since the final result for the virial coefficient is always obtained as a limit for infinite volume we may choose the boundary condition arbitrarily, if only it is the same for (5) and (6). As the simplest choice we shall assume the v_{nl} and $v_{nl}^{(0)}$ are zero for $r = R$, where R is large compared with the range of $V(r)$. Without such a condition the spectrum of (6) is entirely continuous. But the boundary condition at $r = R$ will make of this a finely spaced discrete spectrum. On the other hand, eq. (5) may have some discrete eigenvalues when $V(r)$ has a strong enough attractive part, corresponding to the formation of "polarization molecules", but the largest part of its spectrum will be continuous. With the condition at $r = R$ this part will also be discrete *). It will be clear that this discrete spectrum is completely determined by the values of the wave function for *large* r.

The unnormalized solution of (6) which behaves regularly for $r = 0$ is

$$v_{nl}^{(0)}(r) = \sqrt{r}\, J_{l+1/2}(k_{nl}^{(0)}\, r).$$

Here

$$k_{nl}^{(0)} = \frac{2\pi \sqrt{m E_{nl}^{(0)}}}{h} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

For large r this solution is proportional to

$$\sin\left(k_{nl}^{(0)}\, r - \frac{l\pi}{2}\right)$$

and therefore the $k_{nl}^{(0)}$ are determined by

$$k_{nl}^{(0)}\, R - \frac{l\pi}{2} = n\pi \quad . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

Eq. (5) is for large r identical with (6). Its solution for large r is therefore a linear combination of the two fundamental solutions of (6) or, asymptotically, of $\sin\left(k_{nl} r - \frac{l\pi}{2}\right)$ and $\cos\left(k_{nl} r - \frac{l\pi}{2}\right)$. This can also be written as

$$v_{nl} \backsim \sin\left\{k_{nl}\, r - \frac{l\pi}{2} + \eta_l(n)\right\} \quad . \; . \; . \; . \; . \; . \quad (9)$$

The quantity $\eta_l(n)$ represents the *phase shift* of the wave v_{nl} compared with the free wave $v_{nl}^{(0)}$. It is determined by the condition that v_{nl} becomes zero at least as r for $r = 0$. The "continuous" eigenvalues of (5) are determined by

$$k_{nl}\, R - \frac{l\pi}{2} + \eta_l(n) = n\pi. \quad . \; . \; . \; . \; . \; . \quad (10)$$

---

*) For convenience we shall refer to this set as to the "continuous" spectrum in contradistinction to the original discrete states which are not affected by the boundary condition.

Now we can transform (4) by changing the summation over the "continuous" part of n by an integration. Observing that, because of (8) and (10), in the first term of (4)

$$dn = \frac{R}{\pi}\, dk$$

and in the second

$$dn = \frac{R}{\pi}\, dk + \frac{1}{\pi}\, \frac{d\eta_l(k)}{dk}\, dk$$

we find

$$B_B = \sum_{l=0}^{\infty} (2l+1)\, B_l \quad . \; . \; . \; . \; . \; . \; . \quad (11)$$

with

$$\left.\begin{aligned} B_l &= B_{l,\,discr.} + B_{l,\,cont.} \\ B_{l,\,discr.} &= -\, 2^{1/2}\, N\, \lambda^3 \sum_n e^{-E_{n\,l}/kT} \\ B_{l,\,cont.} &= -\, \frac{2^{1/2}\, N\, \lambda^3}{\pi} \int_0^{\infty} dk\, \frac{d\eta_l(k)}{dk}\, e^{-k^2/k_0^2} \end{aligned}\right\} \quad . \; . \; . \quad (12)$$

and

$$k_0^2 = \frac{4\pi^2\, m\, k\, T}{h^2} = \frac{2\pi}{\lambda^2} \quad . \; . \; . \; . \; . \; . \; . \quad (13)$$

The negative quantities E_{nl} are the discrete eigenvalues of (5).

We shall now consider the E. B. gas. Instead of (3) we have now

$$B_{\mathrm{E.B.}} = \frac{N\lambda^6}{2V} \sum_i \left(G_i^{(0)}\, e^{-E_i^{(0)}/kT} - 2\, G_i\, e^{-E_i/kT}\right). \quad . \; . \; . \quad (14)$$

The first term is the same as in (3), but the second is different. The separation into translational and relative motion is the same as before. In the summation over the different states of relative motion we must take only those states into account whose eigenfunctions are symmetrical in the two particles. Now interchange of the particles means replacement of φ by $\varphi + \pi$ and of ϑ by $\pi - \vartheta$. As is well known, the angular part of the wave function remains unchanged under this substitution for even l, whereas it changes its sign for odd l. Instead of (4) we get therefore

$$B_{\text{E.B.}} = 2^{1/2} N \lambda^3 \left\{ \sum_{l=0}^{\infty} (2l+1) \sum_n e^{-E^{(0)}_{nl}/kT} - \right. \\ \left. - 2 \sum_{l\ \mathit{even}} (2l+1) \sum_n e^{-E_{nl}/kT} \right\} \quad . \ . \quad (15)$$

If the gas, for which we want to calculate B, were an *ideal* E. B. gas, then we should have to replace the E_{nl} in the second sum of (15) by $E^{(0)}_{nl}$. But in this case we already know the expression for B (Ch. II, eq. (31)). Therefore (15) may be written as

$$B_{\text{E.B.}} = -\frac{N\lambda^3}{2^{5/2}} + 2^{3/2} N \lambda^3 \sum_{l\ \mathit{even}} (2l+1) \sum_n \left(e^{-E^{(0)}_{nl}/kT} - e^{-E_{nl}/kT}\right).$$

We can now proceed in the same way as for the BOLTZMANN gas and find

$$B_{\text{E.B.}} = -\frac{N\lambda^3}{2^{5/2}} + 2 \sum_{l\ \mathit{even}} (2l+1) B_l \quad . \ . \ . \ . \quad (16)$$

where B_l is again given by (12).

For F. D. statistics one obtains in the same way

$$B_{\text{F.D.}} = \frac{N\lambda^3}{2^{5/2}} + 2 \sum_{l\ \mathit{odd}} (2l+1) B_l \quad . \ . \ . \ . \ . \quad (17)$$

The general formulae (11), (12), (16) and (17) for the second virial coefficient have been found by UHLENBECK and BETH 24). The expression (12) for $B_{l,\,cont.}$ was obtained independently by GROPPER 25).

We may generalize these expressions to include the case where the particles possess an angular momentum $s h/2\pi$. In BOLTZMANN statistics, as we have seen in Ch. II, the spin has no influence. For E. B. and F. D. statistics we obtain easily from the considerations in Ch. II, § 3, example e

$$B^{(s)}_{\text{E.B.}} = \frac{s+1}{2s+1} B^{(0)}_{\text{E.B.}} + \frac{s}{2s+1} B^{(0)}_{\text{F.D.}} . \quad . \ . \ . \quad (18)$$

$$B^{(s)}_{\text{F.D.}} = \frac{s+1}{2s+1} B^{(0)}_{\text{F.D.}} + \frac{s}{2s+1} B^{(0)}_{\text{E.B.}} . \quad . \ . \ . \quad (19)$$

where $B^{(0)}_{\text{E.B.}}$ and $B^{(0)}_{\text{F.D.}}$ are the expressions (16) and (17). For large s both (18) and (19) reduce to B_B.

The expressions (16) and (17) for B consist of three parts which each have a definite physical meaning. The first term represents the effect of the apparent attraction in an E. B. gas or of the apparent repulsion in a F. D. gas. In the second term the part containing $B_{l,\,discr.}$ shows how the pressure is lowered by the diminishing of the number of independently moving particles, due to the formation of polarization molecules. It is in fact possible to derive this term directly according to this interpretation by means of the formulae for dissociative equilibrium. The part in the second term which contains $B_{l,\,cont.}$ represents the effect of the collisions between the molecules. As we have seen, it depends only on the asymptotic behaviour of the wave functions of the relative motion of two particles, represented by the phase shifts $\eta_l(k)$.

The calculation of B consists therefore in the calculation of the discrete eigenvalues E_{nl} and of the phase shifts $\eta_l(k)$. These latter quantities also play a fundamental role in the theory of atomic collisions, and it is in connection with this theory that the existing calculations on the $\eta_l(k)$ are performed. For this reason we shall give in the following paragraph the fundamental formulae of the collision theory, together with the formulae for the transport phenomena in gases, which are closely related to them.

§ 3. COLLISION THEORY AND TRANSPORT PHENOMENA.

When a beam of particles, moving with a velocity v, falls on a particle at rest, many of them will be deflected in different directions. Suppose the density of the beam to be such that an area of 1 cm^2 perpendicular to the beam is traversed by one particle per second. We shall call $I(\vartheta)\,d\omega$ the number of particles which is scattered per second into a solid angle $d\omega$ in a direction which makes an angle ϑ with the original beam. The number of particles scattered between ϑ and $\vartheta + d\vartheta$ will be called the differential cross-section

$$d\sigma = 2\pi\, I(\vartheta) \sin\vartheta\, d\vartheta \quad \ldots\ldots \quad (20)$$

The total number of particles scattered per second is the total cross-section

$$\sigma = 2\pi \int_0^\pi I(\vartheta) \sin\vartheta\, d\vartheta \quad \ldots\ldots \quad (21)$$

The problem of collision theory is to calculate $I(\vartheta)$ and σ as functions of the velocity when the potential between the interacting particles is known.

We shall suppose that the scattering and scattered particles have the same mass m but are nevertheless distinguishable for the moment *). The expression for the differential cross-section will be given for the system where the centre of gravity of the two interacting particles is at rest. In this system, which is moving with a velocity $v/2$, the two particles move before and after the collision with the equal and opposite velocity $v/2$. The angle of scattering in this system, θ, is twice the corresponding angle ϑ in the original system, as may be seen from a simple geometrical consideration. Hence the results obtained for the differential cross-section in the moving system can be transformed to the original one. The total cross-section is of course the same in the two systems. In the original system the angle between the directions of the two particles after collision is 90°.

For $I(\theta)$ one obtains the result [26])

$$I(\theta) = \frac{1}{4k^2} \left| \sum_{l=0}^{\infty} (2l+1)\left(1 - e^{2i\eta_l(k)}\right) P_l(\cos\theta) \right|^2 \quad . \quad . \quad (22)$$

where

$$k = \frac{\pi m v}{h} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

$P_l(\cos\theta)$ are the LEGENDRE polynomials and $\eta_l(k)$ is the phase shift in the radial part of the wave function of the relative motion of the two particles, as defined in eq. (9). From (22) one obtains for the total cross-section

$$\sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \eta_l(k) \quad . \quad . \quad . \quad . \quad . \quad (24)$$

We shall now give the formulae for the case when the exclusion principle is taken into account. Because the two interacting particles are indistinguishable the cross-sections will now refer to the pro-

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*) This corresponds to the case of BOLTZMANN statistics in statistical mechanics.

bability of finding a scattered particle, and it will not be possible to conclude whether this particle is the incident particle or the one originally at rest. For particles without spin one obtains

$$I_{\text{E.B.}}(\theta) = \frac{1}{k^2} \left| \sum_{l\ even} (2l+1)\left(1 - e^{2i\eta_l(k)}\right) P_l(\cos\theta) \right|^2 \quad . \quad . \quad (25)$$

$$I_{\text{F.D.}}(\theta) = \frac{1}{k^2} \left| \sum_{l\ odd} (2l+1)\left(1 - e^{2i\eta_l(k)}\right) P_l(\cos\theta) \right|^2 . \quad . \quad (26)$$

$$\sigma_{\text{E.B.}} = \frac{16\pi}{k^2} \sum_{l\ even} (2l+1)\, sin^2\, \eta_l(k) \quad . \quad . \quad . \quad . \quad (27)$$

$$\sigma_{\text{F.D.}} = \frac{16\pi}{k^2} \sum_{l\ odd} (2l+1)\, sin^2\, \eta_l(k) \quad . \quad . \quad . \quad . \quad (28)$$

For particles with spin s, one has (if the spin directions of both particles are isotropically distributed)

$$I^{(s)}_{\text{E.B.}}(\theta) = \frac{s+1}{2s+1} I^{(0)}_{\text{E.B.}}(\theta) + \frac{s}{2s+1} I^{(0)}_{\text{F.D.}}(\theta). \quad . \quad . \quad (29)$$

$$I^{(s)}_{\text{F.D.}}(\theta) = \frac{s+1}{2s+1} I^{(0)}_{\text{F.D.}}(\theta) + \frac{s}{2s+1} I^{(0)}_{\text{E.B.}}(\theta) . \quad . \quad . \quad (30)$$

and analogous expressions for the total cross-sections.

The values of the transport quantities in gases can be expressed in terms of the collision cross-sections [27]). One finds in first approximation for the coefficient of viscosity in E. B. and F. D. statistics

$$\eta = \frac{10\sqrt{2}\,\pi^4 h}{\lambda^9} \frac{1}{\int\limits_0^\infty dk\, k^7\, e^{-k^2/k_0^2}\, \sigma_T(k)} . \quad . \quad . \quad . \quad (31)$$

and for the coefficient of heat conduction

$$\mu = \tfrac{5}{2}\, c_V\, \eta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

Here c_V is the specific heat per gram of the ideal gas, $3k/2m$, k_0 is defined by (13) and $\sigma_T(k)$ is the so-called transport cross-section

$$\sigma_T(k) = 2\pi \int_0^\pi I(\theta) \sin^3\theta \, d\theta \, . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

with $I(\theta)$ given by (25) or (26).

From these results we see that in the theory of collisions and of transport phenomena the problem is the same as in the theory of the second virial coefficient, namely the calculation of the phase shifts $\eta_l(k)$. It is therefore possible in principle to correlate the experimental data on the second virial coefficient with the results of collision experiments and with the measurements on viscosity and heat conduction.

§ 4. QUALITATIVE REMARKS ABOUT THE PHASE SHIFTS.

For a general potential $V(r)$ it is not possible to give an exact analytical expression for the quantities $\eta_l(k)$ and we have to make use of numerical or graphical calculations or of approximation methods. First we shall try to get a general idea about the shape of η_l as a function of k. This function was defined as the difference in phase between the asymptotic solutions of the one dimensional SCHRÖDINGER equation

$$v_l''(k,r) + \frac{4\pi^2 m}{h^2} \{E - Q(r)\} \, v_l(k,r) = 0, \quad \frac{4\pi^2 mE}{h^2} = k^2 \, . \quad (34)$$

with

$$Q(r) = V(r) + \frac{h^2}{4\pi^2 m} \frac{l(l+1)}{r^2} \quad . \quad . \quad . \quad . \quad . \quad (35)$$

and of (34) with

$$Q(r) = \frac{h^2}{4\pi^2 m} \frac{l(l+1)}{r^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

both solutions being determined by the condition that they become zero at least as r for $r \rightarrow 0$. Because η_l is a term in the phase of the wave function, and the sign of the wave function is arbitrary, one may always add an arbitrary multiple of π to its value. Of course this arbitrariness has no influence on the expressions for the second virial coefficient and for the collision cross-sections. Therefore this arbitrary constant may be fixed in any convenient way. We shall do it always in such a manner that η_l becomes a continuous function of k. When the potential $V(r)$ is finite everywhere it is possible for instance to fix η_l in such a way that it approaches zero for k large, because then the disturbance of the wave function by the field of force becomes small.

Before we examine a $V(r)$ of the type which actually occurs between two molecules it will be useful to give the values of η_l when the molecules are considered as noninteracting elastic spheres of diameter ϱ. In this case η_l can be calculated exactly. The potential is now

$$V(r) = \infty, \quad r < \varrho$$

$$V(r) = 0\,, \quad r > \varrho$$

The solution of (34) will be that linear combination of the two fundamental solutions of this equation for $V(r) = 0$ which is determined by the condition of being zero for $r = \varrho$. The fundamental solutions are

$$\sqrt{r}\, J_{l+{}^1\!/_2}(kr) \quad \text{and} \quad \sqrt{r}\, J_{-l-{}^1\!/_2}(kr)$$

and therefore the required linear combination is

$$\sqrt{r}\, \{J_{-l-{}^1\!/_2}(k\varrho)\, J_{l+{}^1\!/_2}(kr) - J_{l+{}^1\!/_2}(k\varrho)\, J_{-l-{}^1\!/_2}(kr)\}$$

From the asymptotic expressions for the BESSEL functions follows

$$\tan \eta_l(k) = (-1)^{l+1} \frac{J_{l+{}^1\!/_2}(k\varrho)}{J_{-l-{}^1\!/_2}(k\varrho)} \quad \ldots\ldots \quad (37)$$

which for large k becomes asymptotically

$$\tan \eta_l(k) = \begin{cases} -\tan(k\varrho), & l \text{ even} \\ \cot(k\varrho), & l \text{ odd} \end{cases} \quad \ldots\ldots \quad (38)$$

so that one can take for instance

$$\eta_l(k) = \begin{cases} -k\varrho, & l \text{ even} \\ \dfrac{\pi}{2} - k\varrho, & l \text{ odd} \end{cases} \quad \ldots\ldots \quad (39)$$

for k large.

The actual potential $V(r)$ consists of a strong repulsion when r is small which for larger r goes over into a short ranged attraction. The effective potential in equation (34) is for $l \neq 0$ the sum of this $V(r)$ and of the potential of the centrifugal force. This effective potential has therefore the shape of fig. 4. We can now find the behaviour of $\eta_l(k)$ when k is very large or very small. Consider first the case $l \neq 0$. When k is very small the wave function will be negligibly small in the region where $V(r)$ is large, because the centrifugal repulsion acts like a potential barrier. The wave function is therefore practically undisturbed by $V(r)$ and with a suitable choice of the arbitrary constant it becomes zero for $k = 0$. In fact we shall show in the next paragraph that $\eta_l(k)$ behaves as the $(2l+1)^{\text{th}}$ power of k for small k. When k is somewhat larger the wave function will be perturbed by the attractive part of $V(r)$. This will make η_l positive because in regions where $V(r)$ is negative the wave function oscillates more rapidly than the corresponding wave function for $V(r) = 0$, which means an increase of the phase. When

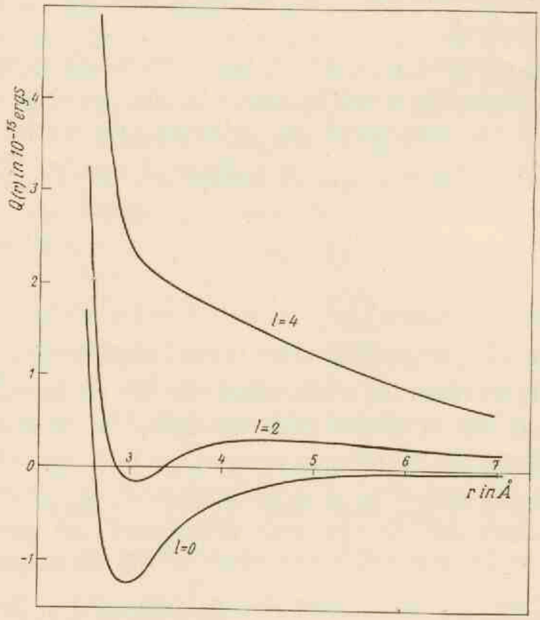

Fig. 4. The function $Q(r)$ for the SLATER–KIRKWOOD potential.

k becomes so large that the wave function has considerable values in the region where $V(r)$ is positive, η_l will begin to decrease and finally becomes negative. For very large k *) the η_l will be entirely determined by the repulsion and behave approximately as the $\eta_l(k)$ of an elastic sphere of diameter r_0, where r_0 is the classical distance of closest approach.

For $l = 0$ the behaviour for large k is the same, whereas the discussion for small k is a little more complicated. One can show however in a way indicated by FERMI [28]) that $\eta_l(k)$ behaves like k for small k, in conformity with the result for $l \neq 0$. The asymptotic solution of the wave equation for $l = 0$

$$v_0(k, r) = A \sin \{kr + \eta_0(k)\}$$

must for small k go over into the asymptotic solution for $k = 0$, which is clearly

$$v_0(0, r) = b(a + r).$$

This gives the two equations for small k

$$A k \cos \eta_0(k) = b$$

$$A \sin \eta_0(k) = a b$$

and therefore

$$\tan \eta_0(k) = a k \quad . \; . \; . \; . \; . \; . \; . \; . \quad (40)$$

or

$$\eta_0(k) = a k \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (41)$$

It will be of interest for later discussion to investigate the case where the potential field possesses a discrete or virtual level close to zero. For simplicity we shall assume $V(r) = 0$ for $r > r_1$. Consider first the (exceptional) case where this level lies just at energy zero. In this case the wave function for $k = 0$ outside the field of force is a constant or, in other words, the tangent of the wave function is horizontal at $r = r_1$. Now eq. (41) breaks down and has to be replaced by $\eta_0(k) = \pi/2$ for small k. When the attraction is a little stronger so that there exists a discrete level close

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*) That means here that the energy is large compared with the attractive part of $V(r)$. It must not be so large that the molecules can be excited for then their description as simple centres of forces becomes invalid.

to zero, then the wave function for $k = 0$ will be a little more curved and will have a small negative derivative (taking the wave function itself as positive) at $r = r_1$. This means that a is large and negative. Because of (41) $\eta_0(k)$ will therefore decrease very rapidly with increasing k till it reaches the value $-\pi/2$ *). On the other hand, when the attraction is a little less, there will be a virtual level and a will be large and positive. One can easily see that in both cases the value $\pm\pi/2$ of η_0 will be reached for an energy of the order of the energy of the virtual level or of the absolute value of the energy of the discrete level. For a virtual level one can see this as follows. The level is defined as the energy corresponding to the minimum ratio of the amplitudes of the wave function outside and inside the field of force. This is obviously the case when the wave function has a horizontal tangent at $r = r_1$. But then the wave function outside has the form

$$A \cos (k r - k r_1) = A \sin (k r - k r_1 + \pi/2)$$

so that the phase, because of the smallness of kr_1, is practically equal to $\pi/2$. When there is a discrete level of energy $-h^2 k_1{}^2/4\pi^2 m$, its wave function will be $A \exp(-k_1 r)$ for $r > r_1$. The wave function for $k = 0$ will have practically the same derivative $-k_1 A \exp(-k_1 r_1)$ for $r = r_1$, so that $a = -r_1 - 1/k_1 \cong -1/k_1$, which means that $\eta_0(k)$ is of the order unity for $k \cong k_1$.

§ 5. BORN'S APPROXIMATION.

After this qualitative discussion we shall try to calculate the $\eta_l(k)$ by approximation methods and shall use the results to calculate the second virial coefficient. There are two standard methods available, namely that of BORN [29]) and that of WENTZEL, KRAMERS and BRILLOUIN (W. K. B. method) [30]).

The approximation of BORN consists in treating the potential $V(r)$ as a small perturbation in equation (34). We may expect that

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*) If one prefers to have $\eta_0(k)$ for $k \neq 0$ change continuously with varying field of force one has to put $\eta_0(0) = \pi$ instead of $\eta_0(0) = 0$ when there is *one* discrete level, or, more generally, $\eta_0(0) = n\pi$ when there are n discrete levels with $l = 0$. Analogously one has to take $\eta_l(0)$ as many times π as there are discrete levels with azimuthal quantum number l. For a $V(r)$ which is finite everywhere this choice of $\eta_l(0)$ will give obviously $\eta_l(k) = 0$ for $k \rightarrow \infty$.

this method will yield reliable results when $V(r)$ is small compared with the total energy in those regions where the solution of the unperturbed equation has considerable values. As we saw in the foregoing paragraph, this condition is only fulfilled for $l \neq 0$ and small k. A calculation of the second virial coefficient by using BORN's method throughout can therefore not be expected to yield good results. We can however make the following, rather academic, statement. *Suppose that $V(r)$ is small for all r* (contrary to the actually existing potential fields), then for high temperatures the energies of the particles will be large compared with $V(r)$, and we may apply BORN's approximation. But for high temperatures the classical theory is valid, so that we can expect that the results obtained with BORN's approximation will be the same as those obtained with the classical formula (1) when one introduces the approximation corresponding to $V(r) \ll kT$. This statement is confirmed by the calculation.

The well known formula for $\eta_l(k)$ which results from BORN's approximation is

$$\eta_l(k) = -\frac{2\pi^3 m}{h^2}\int\limits_0^\infty dr\, r\, V(r)\, J^2_{l+1/2}(kr). \quad . \quad . \quad . \qquad (42)$$

This will be introduced in eq. (11) for the second virial coefficient in BOLTZMANN statistics, where we may neglect the contribution from the discrete states. This gives

$$\left.\begin{aligned}
B_B &= -\frac{2^{1/2} N \lambda^3}{\pi} \sum_{l=0}^{\infty} (2l+1) \int\limits_0^\infty dk\, \frac{d\eta_l(k)}{dk}\, e^{-k^2/k_0^2} = \\
&= -\frac{2^{3/2} N \lambda^3}{\pi k_0^2} \sum_{l=0}^{\infty} (2l+1) \int\limits_0^\infty dk\, k\, \eta_l(k)\, e^{-k^2/k_0^2} = \\
&= \frac{2^{1/2} N \lambda^3}{kT} \int\limits_0^\infty dr\, r\, V(r) \int\limits_0^\infty dk\, k\, e^{-k^2/k_0^2} \sum_{l=0}^{\infty} (2l+1)\, J^2_{l+1/2}(kr) = \\
&= \frac{2^{3/2} N \lambda^3}{\pi k T} \int\limits_0^\infty dr\, r^2\, V(r) \int\limits_0^\infty dk\, k^2\, e^{-k^2/k_0^2} = \frac{2\pi N}{kT} \int\limits_0^\infty dr\, r^2\, V(r).
\end{aligned}\right\} \qquad (43)$$

Here we have used the well known formula

$$\sum_{l=0}^{\infty} (2l+1) J^2_{l+1/2}(x) = \frac{2x}{\pi}.$$

The formula (43) for B_B follows indeed from (1) by expanding the exponential. The introduction of (42) into the Eqs. (16) and (17) for B in E. B. and F. D. statistics also gives rise to closed expressions. One finds

$$B_{\text{E.B.}} = -\frac{N\lambda^3}{2^{5/2}} + \frac{2\pi N}{kT}\int_0^{\infty} dr\, r^2\, V(r)\,(1 + e^{-4r^2k_0^2}). \quad . \quad (44)$$

$$B_{\text{F.D.}} = \frac{N\lambda^3}{2^{5/2}} + \frac{2\pi N}{kT}\int_0^{\infty} dr\, r^2\, V(r)\,(1 - e^{-4r^2k_0^2}) \quad . \quad . \quad (45)$$

For their derivation one has to use the formulae 31)

$$\sum_{l\ even} (2l+1) J^2_{l+1/2}(x) = \frac{1}{\pi}\left(x + \frac{\sin 2x}{2}\right)$$

$$\sum_{l\ odd} (2l+1) J^2_{l+1/2}(x) = \frac{1}{\pi}\left(x - \frac{\sin 2x}{2}\right).$$

Finally we shall show that the behaviour of $\eta_l(k)$ for $l \neq 0$ and small k, as stated in the foregoing paragraph, follows from BORN's approximation, which is valid in this case. Consider that in (42) not only k, but also kr can be considered as small because, due to the rapid decrease of $V(r)$, large values of r do not contribute to the integral. We may therefore insert the series expansion for the BESSEL function by means of which we obtain an expansion of $\eta_l(k)$ in odd powers of k, starting with the $(2l+1)^{\text{th}}$ power.

§ 6. THE W. K. B. METHOD, FIRST APPROXIMATION.

In the second chapter we have shown the connection between the classical and the quantum theoretical expressions for the partition function. In particular we have seen that the two expressions become identical in the limit of high temperatures. By means of the method of KIRKWOOD it was possible to approximate the quantum theoretical partition function successively, starting from the classical partition function. This method can be applied directly[31]) to an approximate calculation of the deviations of the second virial coefficient from its classical values. These calculations will be performed in §§ 8 and 9. In this and the following paragraph we shall show that the same result can also be obtained by applying the W. K. B. method to the calculation of the $\eta_l(k)$.

We start from the radial wave equation (34) and shall write for its solution

$$v_l = e^{\frac{2\pi i}{h} G_l} \quad \ldots\ldots\ldots \quad (46)$$

G_l will be developed into the series

$$G_l = G_l^{(0)} + \frac{h}{2\pi i} G_l^{(1)} + \left(\frac{h}{2\pi i}\right)^2 G_l^{(2)} + \ldots\ldots \quad (47)$$

By substitution of (46) and (47) in (34) and comparing equal powers of h *), the terms of (47) can be obtained successively by simple integrations. In this way one obtains the two independent solutions

$$\left.\begin{aligned} v_l = \frac{1}{(E-Q)^{1/4}} exp \Bigg[\frac{2\pi i}{h} \int^r dr \sqrt{m(E-Q)} - \\ - \frac{1}{32\sqrt{m}} \frac{h}{2\pi i} \int^r dr \frac{4Q''(E-Q) + 5Q'^2}{(E-Q)^{5/2}} + \ldots \Bigg] \\ \text{and} \qquad\qquad\qquad\qquad\qquad\qquad \\ v_l = \frac{1}{(E-Q)^{1/4}} exp \Bigg[-\frac{2\pi i}{h} \int^r dr \sqrt{m(E-Q)} + \\ + \frac{1}{32\sqrt{m}} \frac{h}{2\pi i} \int^r dr \frac{4Q''(E-Q) + 5Q'^2}{(E-Q)^{5/2}} + \ldots \Bigg] \end{aligned}\right\} . \quad (48)$$

where the lower limit of the integration is arbitrary.

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*) In order to get a good approximation to classical mechanics, one has to disregard in this comparison the fact that $Q(r)$ contains PLANCK's constant, since $Q(r)$ must be considered as a classical quantity, namely the sum of the potential energy and the energy of the centrifugal force.

The conditions of validity for this approximation will be discussed later on. Here we remark only that (48) is certainly invalid when $Q(r) = E$. When there are several regions of r, separated by points where $Q(r) = E$ (the limit points of the classical motion), then the problem arises how to determine the linear combinations of the two solutions (48) (now with fixed integration constants) in the different regions in order that the W. K. B. solution in these regions may approximate the same exact wave function. This problem has been solved by KRAMERS. When in this way the W. K. B. solution is determined, it is easy to find the value of $\eta_l(k)$. We shall develop $\eta_l(k)$ according to

$$\eta_l(k) = \eta_l^{(1)}(k) + \eta_l^{(2)}(k) + \dots \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

where the successive terms arise from the successive terms in the exponent of (48). In this paragraph we shall be concerned with the first approximation only.

As may be seen from fig. 4 there can exist one or three limit points of the classical motion (except for special values of E where there are two). Consider first the case where there is one such point which will be called $r_0(k)$. We have now to determine the W. K. B. solution for $r > r_0$ which approximates the exact solution which becomes zero at the origin. From KRAMERS' connection formulae one finds for this solution

$$\left.\begin{array}{c} v_l = \dfrac{1}{\{E - Q(r)\}^{1/4}} \cos\left(-\dfrac{\pi}{4} + \displaystyle\int_{r_0}^{r} \sqrt{k^2 - f(r)}\, dr\right) \\ f(r) = \dfrac{4\pi^2 m}{h^2} Q(r); \quad k^2 - f(r_0) = 0 \end{array}\right\} . \quad (50)$$

For large r this is asymptotically

$$v_l \backsim \cos\left(kr - kr_0 - \frac{\pi}{4} + \int_{r_0}^{\infty} (\sqrt{k^2 - f(r)} - k)\, dr\right) \quad . \quad (51)$$

In order to obtain $\eta_l(k)$ this must be compared with the free particle wave function. It is more consistent to make the comparison with the W. K. B. solution for the free particle rather than with the exact function *). The W. K. B. solution for the free particle is found from (51) by inserting $f(r) = l(l+1)/r^2$ and performing the integration. The result is

$$v_{l,\,free} \backsim \cos\left(kr - \frac{\pi}{4} - \frac{\pi}{2}\sqrt{l(l+1)}\right)$$

and therefore we find for the first W. K. B. approximation of $\eta_l(k)$

$$\eta_l^{(1)}(k) = \frac{\pi}{2}\sqrt{l(l+1)} - kr_0 + \int_{r_0}^{\infty}\left(\sqrt{k^2 - f(r)} - k\right) dr \quad . \quad (52)$$

and

$$\frac{d\eta_l^{(1)}(k)}{dk} = -r_0 + \int_{r_0}^{\infty}\left(\frac{k}{\sqrt{k^2 - f(r)}} - 1\right) dr \,. \quad . \quad . \quad (53)$$

When there are three limit points of the classical motion, $r_1 < r_2 < r_3$, one obtains

$$\frac{d\eta_l^{(1)}(k)}{dk} = -r_3 + \int_{r_3}^{\infty}\left(\frac{k}{\sqrt{k^2 - f(r)}} - 1\right) dr + \int_{r_1}^{r_2} \frac{k}{\sqrt{k^2 - f(r)}}\, dr \quad (54)$$

The following theorem can now be proved. Let there be for fixed l so many discrete levels E_{nl} that the sum over n in the formula for the second virial coefficient may be replaced by an integral. Then, using the first W. K. B. approximation for the calculation of E_{nl} and $\eta_l(k)$, we obtain

$$B_l^{(1)} = -N\lambda^2 \int_0^{\infty} dr\, e^{-l(l+1)/k_0^2 r^2}\left(e^{-V(r)/kT} - 1\right) \quad . \quad . \quad (55)$$

We shall prove (55) first in the case where l is so large that $f(r)$ is monotonic for all r. In this case no discrete levels are present, so that $B_l = B_{l,\,cont.}$. By introducing (53) in (12) one gets

$$B_l^{(1)} = -\frac{2^{1/2} N\lambda^3}{\pi}\int_0^{\infty} dk\, e^{-k^2/k_0^2}\left\{-r_0(k) + \int_{r_0}^{\infty}\left(\frac{k}{\sqrt{k^2 - f(r)}} - 1\right) dr\right\} \quad (56)$$

---

*) For the calculation of $d\eta_l/dk$ the use of the exact and of the W. K. B. solution for the free particle give the same result.

This integral has to be transformed in such a manner that the integration over k can be performed. When we do this *) we obtain

$$\left.\begin{aligned} B_l^{(1)} = -\frac{2^{1/2} N \lambda^3}{\pi} \Bigg[& \frac{\pi}{2}\sqrt{l(l+1)} + \\ & + \int_0^\infty dr \left(-\frac{k_0 \sqrt{\pi}}{2} + \tfrac{1}{2} \int_{f(r)}^\infty dx \, \frac{e^{-x/k_0^2}}{\sqrt{x - f(r)}} \right) \Bigg], \quad x = k^2 \end{aligned}\right\} . \tag{57}$$

Now the integration over x can be easily performed by taking $x - f(r)$ as a new integration variable. The result is

$$B_l^{(1)} = -\frac{2^{1/2} N \lambda^3}{\pi} \left[\frac{\pi}{2}\sqrt{l(l+1)} + \frac{k_0\sqrt{\pi}}{2} \int_0^\infty dr \left(e^{-f(r)/k_0^2} - 1 \right) \right]$$

which reduces to (55) by observing that

$$\frac{\pi}{2}\sqrt{l(l+1)} = \frac{k_0\sqrt{\pi}}{2} \int_0^\infty dr \left(1 - e^{-l(l+1)/k_0^2 r^2} \right).$$

We may now consider the case that $f(r)$ is not monotonic but still always positive. In this case also there are no discrete states. But now in a certain region of values of k there are three limit points of the classical motion and there we have to apply eq. (54) instead of (53). A calculation similar to the foregoing confirms (55) for this case too.

When there are regions where $f(r)$ is negative, there may be discrete states. Now $B_{l,\,conf.}^{(1)}$ is not given by the right hand side of (55). We shall give the calculation for $l = 0$ only. The case $l \neq 0$ is quite analogous. Again the integral (56) has to be calculated, but now $f(r) = 4\pi^2 m\, V(r)/h^2$. Instead of (57) one finds

$$\left.\begin{aligned} B_{0,\,conf.}^{(1)} = -\frac{2^{1/2} N \lambda^3}{\pi} \Bigg[& \int_0^\infty dr \left(-\frac{k_0\sqrt{\pi}}{2} + \tfrac{1}{2} \int_{f(r)}^\infty dx \, \frac{e^{-x/k_0^2}}{\sqrt{x - f(r)}} - \right. \\ & \left. - \tfrac{1}{2} \int_{r_0(0)}^\infty dr \int_{f(r)}^0 dx \, \frac{e^{-x/k_0^2}}{\sqrt{x - f(r)}} \right] . \end{aligned}\right\} \tag{58}$$

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*) See Note 4.

We shall now add the contribution from the discrete states which, after replacement of the summation by an integration, can be written as

$$B_{0,\,discr.} = -\,2^{1/2} N \lambda^3 \int\limits_{V_{min}}^{0} dE \, \frac{dn}{dE} \, e^{-E/kT}. \quad . \quad . \quad . \qquad (59)$$

where V_{min} is the minimum value of $V(r)$. The energies $E_{no}^{(1)}$ are, according to the W. K. B. method, given by

$$2 \int\limits_{r_a}^{r_b} \sqrt{m \left\{ E_{no}^{(1)} - V(r) \right\}} \, dr = (n + \tfrac{1}{2}) \, h \quad . \quad . \quad . \quad . \qquad (60)$$

where r_a and r_b are the two limit points of the classical motion. Therefore

$$\frac{dn}{dE} = \frac{1}{h} \int\limits_{r_a}^{r_b} \sqrt{\frac{m}{E - V(r)}} \, dr. \quad . \quad . \quad . \quad . \quad . \qquad (61)$$

Introducing (61) into (59) and substituting $E = h^2 x / 4 \pi^2 m$ (x is here negative), we find

$$\left. \begin{aligned} B_{0,\,discr.}^{(1)} &= -\frac{2^{1/2} N \lambda^3}{2\pi} \int\limits_{f_{min}}^{0} dx \, e^{-x/k_0^2} \int\limits_{r_a}^{r_b} dr \, \frac{1}{\sqrt{x - f(r)}} = \\ &= -\frac{2^{1/2} N \lambda^3}{2\pi} \int\limits_{r_0(0)}^{\infty} dr \int\limits_{f(r)}^{0} dx \, \frac{e^{-x/k_0^2}}{\sqrt{x - f(r)}} \end{aligned} \right\} . \qquad (62)$$

Adding (58) and (62) we obtain

$$B_0^{(1)} = -\,N \lambda^2 \int\limits_{0}^{\infty} dr \left(e^{-V(r)/kT} - 1 \right)$$

in accordance with (55).

By means of (55) one can derive the first W. K. B. approximation for the second virial coefficient. In BOLTZMANN statistics the result is

$$\left.\begin{aligned} B_B^{(1)} &= \sum_{l=0}^{\infty} (2l+1) B_l^{(1)} = \\ &= -N\lambda^3 \int_0^{\infty} dr \left(e^{-V(r)/kT} - 1\right) \sum_{l=0}^{\infty} (2l+1)\, e^{-l(l+1)/k_0^2 r^2} \end{aligned}\right\} . \qquad (63)$$

when we interchange summation and integration. For E. B. and F. D. statistics we have to sum over even, and over odd, values of l respectively and to multiply by a factor two. The sum

$$\sum_{l=0}^{\infty} (2l+1)\, e^{-l(l+1)/k_0^2 r^2}$$

cannot be calculated exactly. However, MULHOLLAND [32]) has given the following asymptotic expansion for this sum, which furnishes an approximation for high temperatures,

$$\left.\begin{aligned} \sum_{l=0}^{\infty} (2l+1)\, e^{-l(l+1)/k_0^2 r^2} \backsim e^{1/4 k_0^2 r^2} \Big[& {k_0}^2 r^2 + a_0 + \frac{a_1}{{k_0}^2 r^2} + \ldots + \\ & + \frac{a_k}{k!} \frac{1}{({k_0}^2 r^2)^k} + \ldots \Big] = {k_0}^2 r^2 + \frac{1}{3} + \frac{1}{15} \frac{1}{{k_0}^2 r^2} + \ldots \end{aligned}\right\} \qquad (64)$$

where

$$a_n = (-1)^n \frac{1}{n+1} B_{2n+2} \left(1 - 2^{-2n-1}\right)$$

and the Bernoullian numbers B_n are defined as the coefficients of $x^n/n!$ in the expansion of $x/(e^x - 1)$. The same expansion is obtained for twice the sum over even or odd l. By inserting the first term of this expansion in (63) one obtains the classical expression (1). It is premature to introduce here the second term of MULHOLLAND's expansion in order to obtain the first deviation from the classical formula, since the second approximation of the W. K. B. method will give a contribution of the same order of magnitude.

§ 7. THE W. K. B. METHOD, SECOND APPROXIMATION.

It follows from the W. K. B. solution (48) that in the case of a monotonic $f(r)$ the second term in the approximation of $\eta_l(k)$ is

$$\eta_l^{(2)}(k) = -\frac{1}{32}\int_{r_0}^{\infty} dr \frac{4f''(k^2-f)+5f'^2}{(k^2-f)^{5/2}} \quad . \; . \; (65)$$

The difficulty is that this integral diverges. An examination of the derivation of KRAMERS' connection formulae shows however that the integral (65) has to be interpreted as the half of a complex integral in the r-plane, taken along the contour of fig. 5. HADAMARD [33]) has shown that this can be written in real form as the "principal part" of (65). This means one must integrate (65) partially so many times that the resulting integral becomes convergent while the infinite terms of the integrated parts have to be dropped. By using HADAMARD's symbol for this principal part we find after a partial integration that one can write for the second approximation to $\eta_l(k)$ *)

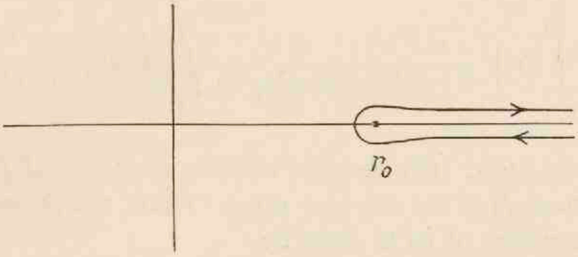

Fig. 5.

$$\eta_l^{(2)}(k) = -\frac{1}{32}\Big/\overline{\int_{r_0}^{\infty} dr \frac{f'^2}{(k^2-f)^{5/2}}} \quad . \; . \; . \; . \; (66)$$

and

$$\frac{d\eta_l^{(2)}(k)}{dk} = \frac{5k}{32}\Big/\overline{\int_{r_0}^{\infty} dr \frac{f'^2}{(k^2-f)^{7/2}}} \quad . \; . \; . \; . \; (67)$$

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*) Insertion of $f(r) = l(l+1)/r^2$ in (66) gives, as shown in Note 5, $\eta_l^{(2)}(k) = -\pi/16\sqrt{l(l+1)}$. It is therefore more consistent to substract this value from the expression (66). This has of course no influence on the value of $d\eta_l^{(2)}/dk$.

The energies of the discrete states are in second approximation given by

$$2\int_{r_a}^{r_b} dr\, \sqrt{m\,(E_{nl}-Q)} + \frac{h^2}{64\pi^2\sqrt{m}} \sqrt{\int_{r_a}^{r_b} dr\, \frac{Q'^2}{(E_{nl}-Q)^{5/2}}} = (n+\tfrac{1}{2})\,h$$

and therefore

$$\frac{dn}{dE} = \int_{r_a}^{r_b} dr\, \sqrt{\frac{m}{E-Q}} - \frac{5\,h^2}{128\,\pi^2\sqrt{m}} \sqrt{\int_{r_a}^{r_b} dr\, \frac{Q'^2}{(E-Q)^{7/2}}}\,. \qquad (68)$$

By means of (67), (68) and the obvious extension of (67) for a non-monotonic $f(r)$ we can now prove *) that the second term in the approximation of B_l is given by

$$B_l^{(2)} = \frac{N\lambda^8}{24\pi^3} \int_0^\infty dr\, e^{-l(l+1)/k_0^2 r^2} \left\{ e^{-V/kT} \left(\frac{4\pi^4 m^2}{h^4} V'^2 - \frac{4\pi^2 m\, l(l+1)\, V'}{h^2 r^3} + \frac{l^2 (l+1)^2}{r^6} \right) - \frac{l^2 (l+1)^2}{r^6} \right\}\Bigg). \qquad (69)$$

This has to be introduced in the formulae for the second virial coefficient. For the sums over l which now occur we can give asymptotic expressions for high temperature by differentiating (64) with respect to $1/k_0^2 r^2$. In this way we obtain

$$\sum_{l=0}^{\infty} l\,(l+1)\,(2\,l+1)\, e^{-l(l+1)/k_0^2 r^2} \backsim k_0^4\, r^4$$

$$\sum_{l=0}^{\infty} l^2\,(l+1)^2\,(2\,l+1)\, e^{-l(l+1)/k_0^2 r^2} \backsim 2\,k_0^6\, r^6.$$

By introducing these expressions one finds for the contribution of

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*) See Note 5.

the second W. K. B. approximation to the second virial coefficient

$$\tfrac{2}{3} N\lambda^2 \int_0^\infty dr\,(e^{-V/kT} - 1) + \frac{N\lambda^2}{12 k^2 T^2} \int_0^\infty dr\, r^2\, e^{-V/kT}\, V'^2 - $$

$$- \frac{N\lambda^2}{3kT} \int_0^\infty dr\, r\, e^{-V/kT}\, V'.$$

We have to add here the result which is obtained by introducing the second term of (64) in (63):

$$- \frac{N\lambda^2}{3} \int_0^\infty dr\,(e^{-V/kT} - 1).$$

Therefore

$$B^{(2)} = \frac{N\lambda^2}{3} \int_0^\infty dr\,(e^{-V/kT} - 1) + \frac{N\lambda^2}{12 k^2 T^2} \int_0^\infty dr\, e^{-V/kT}\, V'^2 - $$

$$- \frac{N\lambda^2}{3kT} \int_0^\infty dr\, r\, e^{-V/kT}\, V'.$$

By partial integration of the first term we see that the first and the last term cancel. Therefore, finally

$$B^{(2)} = \frac{N\lambda^2}{12 k^2 T^2} \int_0^\infty dr\, r^2\, e^{-V/kT}\, V'^2 \quad . \quad . \quad . \quad . \quad (70)$$

§ 8. APPROXIMATION OF B_l BY MEANS OF KIRKWOOD'S METHOD.

The results of the last two paragraphs can be obtained with much less labour by applying the method of KIRKWOOD to the SLATER sum of the relative motion of two particles. We have nevertheless thought it worth while to give the calculation with the W. K. B. method because the W. K. B. expressions for $\eta_l(k)$ may be of some use for practical calculations and because this method shows more explicitly the contribution of the discrete levels, which in the method of KIRKWOOD is completely obscured.

In order to find the development for B_l we have to apply KIRKWOOD's method to the partition function of the relative motion of two particles after separation of the angular coordinates. We start therefore from eq. (4) which we shall write as

$$B_B = \sum_{l=0}^{\infty} (2l+1)\, B_l = 2^{1/2} N \lambda^3 \sum_{l=0}^{\infty} (2l+1) \int_0^{\infty} dr \{S_{l,\mathrm{free}}(r) - S_l(r)\} \quad (71)$$

so that

$$\int_0^{\infty} dr\, S_l(r) = \sum_n e^{-E_{nl}/kT}.$$

Then

$$S_l(r) = \sum_n e^{-E_{nl}/kT}\, v_{nl}^*(r)\, v_{nl}(r) = \sum_n v_{nl}^*\, e^{-\beta \mathcal{H}}\, v_{nl}$$

with

$$\mathcal{H} = -\frac{h^2}{4\pi^2 m} \frac{d^2}{dr^2} + Q(r);\ \beta = \frac{1}{kT}$$

and $Q(r)$ as given by (35). The v_{nl} are normalized according to

$$\int_0^{R} dr\, v_{nl}^*(r)\, v_{nl}(r) = 1.$$

Instead of the complete set v_{nl} we shall introduce the set

$$\frac{1}{\sqrt{R}} e^{\frac{2\pi i}{h} p_n r}$$

with

$$p_n = \pm \frac{nh}{R}.$$

As was already remarked in chapter II the fact that this set does not satisfy the boundary conditions is not important. We have now

$$S_l(r) = \frac{1}{h} \int_{-\infty}^{\infty} dp\, e^{-\frac{2\pi i}{h} pr}\, e^{-\beta \mathcal{H}}\, e^{\frac{2\pi i}{h} pr}. \quad . \quad . \quad . \quad (72)$$

We can follow the scheme of Ch. II, § 4, where now

$$F = e^{-\beta \mathcal{H}}\, e^{\frac{2\pi i}{h} p r} = w\, e^{\frac{2\pi i}{h} p r}\, e^{-\beta \mathcal{H}} .$$

The equation for w is

$$\frac{\partial w}{\partial \beta} = \frac{i h p}{\pi m}\left(\frac{\partial w}{\partial r} - \beta \frac{dQ}{dr} w\right) + \frac{h^2}{4\pi^2 m}\left\{\frac{\partial^2 w}{\partial r^2} - 2\beta \frac{dQ}{dr}\frac{\partial w}{\partial r} - \right.$$
$$\left. - \beta w \frac{d^2 Q}{dr^2} + \beta^2 w \left(\frac{dQ}{dr}\right)^2\right\} \quad ; \quad (w)_{\beta=0} = 1$$

with the solution

$$\left.\begin{aligned} w_0 &= 1 \\ w_1 &= -\frac{i}{2\pi m}\beta^2 p \frac{dQ}{dr} \\ w_2 &= -\frac{\beta^2}{8\pi^2 m}\frac{d^2 Q}{dr} + \beta^3 \left\{\frac{p^2}{6\pi^2 m^2}\frac{d^2 Q}{dr^2} + \frac{1}{12\pi^2 m}\left(\frac{dQ}{dr}\right)^2\right\} - \\ &\quad - \frac{\beta^4 p^2}{8\pi^2 m^2}\left(\frac{dQ}{dr}\right)^2 \\ &\cdots\cdots\cdots\cdots\cdots\cdots \end{aligned}\right\} \quad (73)$$

Now developing S_l according to

$$S_l(r) = \sum_{n=0}^{\infty} S_l^{(n)}(r) \quad . \; . \; . \; . \; . \; . \; . \quad (74)$$

we obtain, by introducing the solution (73) into (72) and performing the integration over p

$$\left.\begin{aligned} S_l^{(0)}(r) &= \frac{1}{\lambda\sqrt{2}}\, e^{-Q/kT} \\ S_l^{(1)}(r) &= 0 \\ S_l^{(2)}(r) &= \frac{\lambda}{12\sqrt{2}\,\pi k T}\, e^{-Q/kT}\left\{-\frac{d^2 Q}{dr^2} + \frac{1}{2kT}\left(\frac{dQ}{dr}\right)^2\right\}. \\ &\cdots\cdots\cdots\cdots\cdots\cdots \end{aligned}\right\} \quad (75)$$

The corresponding functions for the free particles are obtained by putting $Q(r) = h^2 l(l+1)/4\pi^2 m r^2$ in these formulae. The terms in the development of B_l which corresponds to (74) are obtained by introducing the solution (75) and the corresponding solution for free particles into (71). In this way one easily finds that $B_l^{(0)}$ is given by the expression (55), $B_l^{(1)} = 0$, while $B_l^{(2)}$ becomes after a partial integration identical with (69).

§ 9. APPROXIMATION OF B BY MEANS OF KIRKWOOD'S METHOD.

We have already seen that an expansion for B can be obtained by introducing the expression for B_l into the formulae for B and using the asymptotic expansion (64) of MULHOLLAND for the summation over l. The resulting expansion for B can however be obtained directly by applying KIRKWOOD's method to the partition function of two particles without separation of the angular coordinates [31]). This procedure has the advantage that now one can also give the expansion for E. B. and F. D. statistics. This was not possible by starting from B_l because of the fact that the expansion of MULHOLLAND remains unaltered for the sums over even or odd l which occur in these statistics.

Since we have already obtained in Ch. II the general expansion of the SLATER sum for a gas of N particles, we shall start from the expression for B before the separation of the motion of the centre of gravity, *i.e.* from eq. (2). Here we shall introduce eq. (II, 42) and then introduce relative coordinates in the integral.

Let us first consider for simplicity the case of BOLTZMANN statistics. Then, from (2) and (II, 43)

$$B_B = \frac{N}{2V} \int\limits_V \int\limits_V d\mathbf{r}_1 \, d\mathbf{r}_2 \left[1 - e^{-V/kT} \left\{ 1 - \frac{\lambda^2}{24 \pi k T} \sum_{i=1,2} \left(\triangle_i V - \frac{1}{2kT} (\nabla_i V)^2 \right) + \ldots \right\} \right].$$

When we now introduce the variables $\mathbf{r}_1, \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, instead of $\mathbf{r}_1$, $\mathbf{r}_2$, and make use of the fact that V depends only on r so that

$$\triangle_1 V = \triangle_2 V = \triangle V = \frac{d^2 V}{dr^2} + \frac{2}{r} \frac{dV}{dr}$$

$$(\nabla_1 V)^2 = (\nabla_2 V)^2 = (\nabla V)^2 = \left(\frac{dV}{dr} \right)^2,$$

then, after a partial integration

$$B_B = 2\pi N \int_0^\infty dr\, r^2 \left[1 - e^{-V/kT} \left\{ 1 - \frac{\lambda^2}{24\pi k^2 T^2} V'^2 + \ldots \right\} \right]. \quad (76)$$

which indeed deviates from the classical expression by the term (70) *).

For E. B. statistics we obtain from (2) and (II, 42)

$$\begin{aligned} B_{\mathrm{E.B}} = \frac{N}{2} \int d\mathbf{r} \Big[& 1 - e^{-V/kT} (1 + e^{-2\pi r^2/\lambda^2}) \Big\{ 1 - \\ & - \frac{\lambda^2}{12\pi k T} \left(\triangle V - \frac{1}{2kT} (\nabla V)^2 \right) + \ldots \Big\} - \\ & - e^{-V/kT} e^{-2\pi r^2/\lambda^2} \Big\{ \frac{1}{kT} (\mathbf{r} \cdot \nabla V) - \\ & - \frac{2}{3kT} (\mathbf{r} \cdot \nabla)^2 V + \frac{1}{2k^2 T^2} (\mathbf{r} \cdot \nabla V)^2 + \ldots \Big\} \Big]. \end{aligned}$$

With

$$(\mathbf{r} \cdot \nabla V) = r \frac{dV}{dr}; \quad (\mathbf{r} \cdot \nabla)^2 V = r^2 \frac{d^2 V}{dr^2}$$

this becomes after a partial integration

$$\left. \begin{aligned} B_{\mathrm{E.B.}} = 2\pi N \int_0^\infty dr\, r^2 \Big[& 1 - e^{-V/kT} (1 + e^{-2\pi r^2/\lambda^2}) \left(1 - \frac{\lambda^2}{24\pi k^2 T^2} V'^2 \right) - \\ & - e^{-V/kT} e^{-2\pi r^2/\lambda^2} \left(\frac{2}{3kT} V' - \frac{2}{3kT} r^2 V'' + \frac{1}{2k^2 T^2} r^2 V'^2 \right) \Big] \end{aligned} \right\} (77)$$

§ 10. REMARKS ON THE ACTUAL CALCULATION OF B.

a. The validity of the approximations used. We must investigate now how far the methods represented in the foregoing paragraphs are suited to a practical calculation of the second virial coefficient

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*) In the paper of UHLENBECK and BETH 31) the next term has been calculated.

when the intermolecular potential is known. We have already seen that for potentials actually occurring the BORN approximation cannot be used throughout. It can be used only for the calculation of $\eta_l(k)$ when $l \neq 0$ and k is small.

For the W. K. B. method and the equivalent method of KIRKWOOD the condition of validity was given in chapter II. The change over a distance λ of the potential, measured in units kT, must be small at least for values of r where $V(r)/kT$ is not large. In order to check this condition we must know the function $V(r)$. For that we refer to the quantum mechanical calculations mentioned in the first chapter. The theoretical potential which has been discussed most in connection with the second virial coefficient and the transport phenomena is that of SLATER and KIRKWOOD for helium, eq. (I, 4). This potential, when inserted into the classical formula (1) for B, gives a good representation of the experimental values [11]). We shall see however that one cannot attach much significance to this correspondence. From (I, 4) we find that for $r = 2.6$ Å, where $V(r) = 0$

$$\frac{\lambda}{kT}\frac{dV}{dr} = \frac{528}{T^{3/2}}$$

so that we may expect the W. K. B. method or the method of KIRKWOOD to give a good approximation only for $T > 70°$ K. For lower temperatures it is therefore certainly not permitted to use the classical expression for B and the agreement with experiment has to be considered as accidental. On the other hand, for $T = 70°$ we have $kT = 96 \times 10^{-16}$ erg, whereas the minimum of $V(r)$ is -12.6×10^{-16} erg. For $T > 70°$ therefore inaccuracy in the *attractive* part of $V(r)$ will not have much influence on the resulting value of B. We can conclude only that the SLATER–KIRKWOOD potential gives a good value for the atomic diameter of helium.

In order to get an idea of the order of magnitude of the different terms in (77) we have calculated some of them for the SLATER–KIRKWOOD potential for a temperature of 10° K. One finds for instance for one mol of gas

$$2\pi N \int_0^\infty dr\, r^2 \left(1 - e^{-V/kT}\right) = -48.7 \text{ cm}^3$$

$$-2\pi N \int_0^\infty dr\, r^2\, e^{-V/kT}\, e^{-2\pi r^2/\lambda^2} = -\,0.0536 \text{ cm}^3$$

$$2\pi N \frac{\lambda^2}{24\pi k^2 T^2} \int_0^\infty dr\, r^2\, e^{-V/kT}\, V'^2 = 540 \text{ cm}^3.$$

We see therefore that, while the deviation due to E. B. statistics is small, the other quantum correction is much larger than the classical value itself.

b. Behaviour of B at very low temperatures. According to the classical formula (1), B will go exponentially to $-\infty$ when $T \rightarrow 0$ for every potential field $V(r)$ which is somewhere negative. In the quantum theory the situation is not so simple. We shall take T so small that in eq. (16) we have to consider only the contribution of $l = 0$. We can make an estimate for which temperatures this is permitted. For $l = 2$ the function $f(r)$ for the SLATER–KIRKWOOD potential has a maximum of 0.189 Å^{-2} for $r = 4.6$ Å. When therefore $k_0^2 < 0.189$ Å^{-2} the value of $B_{2,\,cont.}$ and all $B_{l,\,cont.}$ with $l > 2$ will be small. This value of k_0^2 corresponds to a temperature of 2.28° K so that our discussion strictly speaking will be valid only for temperatures from about 2° downwards. In this region we have therefore, since helium is an E. B. gas

$$B = -\frac{N\lambda^3}{2^{5/2}} - 2^{3/2} N \lambda^3 \sum_n e^{-E_{n0}/kT} + 2 B_{0,\,cont.} \quad . \quad . \quad (78)$$

We now have to discuss four different cases.

1. Let there be no discrete levels and let the energies of all virtual levels be large compared with kT. Then in the calculation of $B_{0,\,cont.}$ we can, according to the considerations at the end of § 4 and because k_0^2 is small, replace $d\eta_0/dk$ by the constant a. Therefore

$$B = -\frac{N\lambda^3}{2^{5/2}} - 2N\lambda^2 a.$$

Inserting the numerical values for helium one finds, for one mol

$$B = -\frac{69.5}{T^{3/2}} - \frac{91.6\, a}{T} \text{ cm}^3 \quad ; \quad a \text{ in Å units} \quad . \quad . \quad (79)$$

Eq. (79) represents the beginning of an expansion which can be obtained by inserting in the general eq. (16) for $d\eta_l/dk$ its expansion in powers of k, which contains even powers only. The expansion obtained has therefore the form

$$B = -\frac{\beta_0}{T^{3/2}} - \frac{\beta_1}{T} + \beta_2 + \beta_3 T + \beta_4 T^2 + \dots \quad . \quad . \quad (80)$$

Here the first term, the second virial coefficient of an ideal E. B. gas, is known. The second term depends on the value of *a*. The absolute value of *a* could in principle be determined experimentally from the cross-section for slow collisions between two helium atoms which, according to (27) is equal to $16\pi a^2$, or from the values of the coefficients of viscosity and of heat conduction at very low temperatures, according to (31) and (32). The existing experimental material is however not sufficient for this determination.

2. In the case when there are discrete levels whose energies in absolute value are $\rangle\rangle\, kT$, and also the energies of the virtual levels are $\rangle\rangle\, kT$, we have only to add their contribution to the expression for B in the foregoing case. Therefore, in addition to the expansion (80), we have one or more terms which go to $-\infty$ as $-exp\,(c/T)/T^{3/2}$ for $T \to 0$.

3. Let there now be no discrete levels but one virtual level with energy $\langle\langle\, kT$. As we saw in § 4, $\eta_0(k)$ will now *increase* rapidly from zero to $\pi/2$ in an interval where $exp\,(-k^2/k_0{}^2)$ is practically constant and then change more slowly. The integral in the expression (12) for $B_{0,\,cont.}$ will therefore be practically equal to this increase of $\eta_0(k)$, or to $\pi/2$. Therefore

$$B \cong -\frac{N\lambda^3}{2^{5/2}} - 2^{1/2} N\lambda^3 = -9\,\frac{N\lambda^3}{2^{5/2}} = -\frac{625.5}{T^{3/2}}\,\text{cm}^3. \quad . \quad (81)$$

In order to calculate the next approximation, which depends on the ratio of the energy of the virtual level to kT, one would have to know more precisely the shape of $\eta_0(k)$.

4. When there is a discrete level whose energy in absolute value is $\langle\langle\, kT$ and the energies of all virtual levels are $\rangle\rangle\, kT$, then $\eta_0(k)$ will *decrease* rapidly from 0 to $-\pi/2$ (or from π to $\pi/2$). Therefore $B_{0,\,cont.}$ will be the negative of the $B_{0,\,cont.}$ in case 3. In the contribution from the discrete level we can replace the exponential

by unity and we then find that B is again given by (81). It is therefore not possible by using this first approximation to decide experimentally between the cases 3 and 4.

The theoretical calculations of the VAN DER WAALS forces for helium (see Ch. I, § 2) all exclude the cases 1 and 2. The expressions of SLATER and KIRKWOOD, MARGENAU, and PAGE all predict the existence of a discrete level of about 0.5×10^{-16} erg, corresponding to a temperature of some tenths of a degree. On the other hand the attraction deduced by LONDON from the dispersion curve of helium is smaller and probably gives rise to a virtual level close to zero.

The experimental values of B for helium are also decidedly in favour of case 3 or 4, *i.e.* they make it probable that there exists a discrete or virtual level close to zero. If this were not the case, B would be determined by (79)*) with $a \langle\langle \lambda$ for sufficiently low temperatures. Let us take for instance $a = 1$ Å. Then for $T = 3°$ we get $B = -43.9\ \mathrm{cm}^3/\mathrm{mol}$, whereas from (81) one would obtain $B = -120.3$. The experimental values of KEESOM and KRAAK [34]) are -117.2; -96.5; -74.7 for $T = 2.58°$; $3.09°$; $4.22°$. It is clear that these values agree better with (81) than with (79).

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*) The case of a large discrete level can safely be ruled out.

NOTES.

1.

Calculation of the Slater sum for a onedimensional free particle.

A formal derivation of eq. (II, 20) is obtained by applying POISSON's summation formula [35]) to (II, 19), which gives

$$S(x)=\frac{1}{\lambda}\sum_{\nu=-\infty}^{\infty} e^{-4\pi L^2\nu^2/\lambda^2}-\frac{1}{\lambda}\sum_{\nu=-\infty}^{\infty} e^{-4\pi L^2\left(\nu+\frac{x}{L}\right)^2/\lambda^2}$$

This formula shows directly that $S(x)=S(L-x)$ and that (II, 20) is the first approximation of (II, 19) for small λ/L.

2.

Elimination of z between the equations (III, a) and (III, b).

The problem is the following: When the equations

$$x=\frac{1}{v}=\sum_{l=1}^{\infty} l\, b_l\, z^l \quad . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

and

$$y=\frac{p}{kT}=\sum_{l=1}^{\infty} b_l\, z^l \quad . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

are given, to find the function $y(x)$ in the form of a power series. This problem can be solved by using the following theorem, which is a simple specialization of the theorem of LAGRANGE [36]):

When $f(\xi)$ is analytic within and on a contour C which surrounds the origin, and the value of z is so chosen that on C

$$|z\, f(\xi)|<|\xi| \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$

then the equation

$$x=z\, f(x) \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

has one solution within C, namely

$$x = \sum_{n=1}^{\infty} \frac{z^n}{n!} \left[\frac{d^{n-1}}{d\xi^{n-1}} f^n(\xi) \right]_{\xi=0} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Conversely, when (5) is given, the expression of z in x is, for values of z which fulfil (3), given by (4).

Now (1) can be put in the form (5) by introducing a function $\varphi(\xi)$ in such a way that $l_2 b_l$ is the coefficient of ξ^{l-1} in the expansion of $exp\,(l\varphi(\xi))$, or

$$l^2 b_l = \frac{1}{(l-1)!} \left[\frac{d^{l-1}}{d\xi^{l-1}} e^{l\varphi(\xi)} \right]_{\xi=0} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Introducing (6) into (1) we find

$$x = \sum_{l=1}^{\infty} \frac{z^l}{l!} \left[\frac{d^{l-1}}{d\xi^{l-1}} e^{l\varphi(\xi)} \right]_{\xi=0} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

from which, by comparison with (5) and (4) follows

$$z = x\, e^{-\varphi(x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Introducing this in (2), we find

$$y = \int_0^z \frac{x}{z} dz = \int_0^x e^{\varphi(x)} d\left(x\, e^{-\varphi(x)}\right) = x - \int_0^x x\, \varphi'(x)\, dx \,. \quad . \quad (9)$$

which is identical with equation (III, 19) of the text.

3.

Calculation of b_l for the ideal E. B. gas.

We must calculate the following integral

$$I = \int \dots \int d\mathbf{r}_2\, d\mathbf{r}_3 \dots d\mathbf{r}_l\, e^{-\frac{\pi}{\lambda^2}(r^2_{12} + r^2_{23} + \dots + r^2_{l1})} \quad . \quad . \quad (1)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and the integral has to be extended over all possible values of the variables. Consider first the integral

$$J = \int d\mathbf{r}_2\, e^{-\alpha r^2_{12} - \beta r^2_{23}} . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Take the coordinates of the first particle as origin and the direction from the first to the second particle as x-direction, then

$$\left.\begin{aligned} J = \iiint\limits_{-\infty}^{\infty} dx_2\, dy_2\, dz_2\, e^{-\alpha x_2^2 - \beta(r_{13} - x_2)^2 - (\alpha+\beta)(y_2^2 + z_2^2)} = \\ = \left(\frac{\pi}{\alpha+\beta}\right)^{3/2} e^{-\frac{\alpha\beta}{\alpha+\beta} r^2_{13}} \end{aligned}\right\} . \quad (3)$$

Now we can calculate I by successively integrating over r_2, r_3, etc., always using (3). In this way we obtain

$$\left.\begin{aligned} I = \lambda^{3(l-2)} \left(\frac{1}{2} \cdot \frac{2}{3} \cdots \frac{l-2}{l-1}\right) \int d\mathbf{r}_l\, e^{-\frac{\pi}{\lambda^2} \frac{l}{l-1} r^2_{1\,l}} = \\ = \lambda^{3(l-1)} \left(\frac{1}{2} \cdot \frac{2}{3} \cdots \frac{l-1}{l}\right)^{3/2} = \frac{\lambda^{3(l-1)}}{l^{3/2}} \end{aligned}\right\} . \quad (4)$$

which is the result used in the text.

4.

Calculation of $B_{l,\,cont.}$ in the first W. K. B. approximation.

a. First let $f(r)$ be monotonic, then

$$\left.\begin{aligned} B^{(1)}_{l,\,cont.} = B^{(1)}_l = -\frac{2^{1/2} N \lambda^3}{\pi} I \\ I = \int\limits_0^{\infty} dk\, e^{-k^2/k_0^2} \left\{ -r_0(k) + \int\limits_{r_0}^{\infty} dr \left(\frac{k}{\sqrt{k^2 - f(r)}} - 1\right)\right\} \end{aligned}\right\} . \quad (1)$$

where $r_0(k)$ is the root of

$$k^2 - f(r) = 0.$$

It is not permissible simply to interchange the integrations over r and k. One has instead to proceed in the following way. Fix a value R of r which is so large that $f(r)$ is practically equal to $l(l+1)/r^2$ for $r > R$, or

$$k(r) = \sqrt{f(r)} = \frac{\sqrt{l(l+1)}}{r},\ r > R.$$

By doing this we have divided the integration region into three

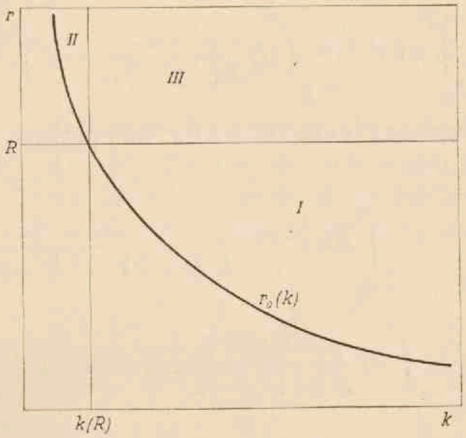

Fig. 6.

parts (fig. 6). We shall calculate the integrals over these parts separately in the limit $R \to \infty$. The contribution of part I is

$$\left.\begin{aligned} &\int_{k(R)}^{\infty} dk\, e^{-k^2/k_0^2} \left(-R + \int_{r_0}^{R} dr \frac{k}{\sqrt{k^2 - f(r)}} \right) \cong \\ &\cong \sqrt{l(l+1)} - \frac{R k_0 \sqrt{\pi}}{2} + \frac{1}{2} \int_0^R dr \int_{f(r)}^{\infty} dx \frac{e^{-x/k_0^2}}{\sqrt{x - f(r)}} \to \\ &\to \sqrt{l(l+1)} + \frac{1}{2} \int_0^{\infty} dr \left(-k_0 \sqrt{\pi} + \int_{f(r)}^{\infty} dx \frac{e^{-x/k_0^2}}{\sqrt{x - f(r)}} \right) \end{aligned}\right\} \quad (2)$$

where $x = k^2$. The contribution of part II is

$$\int_0^{k(R)} dk\, e^{-k^2/k_0^2} \left\{ -r_0 + \int_{r_0}^{\infty} dr \left(\frac{k}{\sqrt{k^2 - f(r)}} - 1 \right) \right).$$

Now r_0 is so large for $k < k(R)$ that we may replace $f(r)$ by

$l(l+1)/r^2$. The integral over r is just r_0 so that the contribution of this part vanishes *). Finally, the integral over part III is

$$\int_{k(R)}^{\infty} dk\, e^{-k^2/k_0^2} \int_{R}^{\infty} dr \left(\frac{k}{\sqrt{k^2 - f(r)}} - 1 \right).$$

We can again replace $f(r)$ by $l(l+1)/r^2$ and perform the integration over r. We get then

$$\left.\begin{aligned} &\int_{k(R)}^{\infty} dk\, e^{-k^2/k_0^2} \frac{l(l+1)}{k^2 R + k\sqrt{k^2 R^2 - l(l+1)}} = \\ &= \sqrt{l(l+1)} \int_{1}^{\infty} dt\, \frac{e^{-l(l+1)t^2/k_0^2 R^2}}{t^2 + t\sqrt{t^2-1}} \rightarrow \sqrt{l(l+1)} \left(\frac{\pi}{2} - 1 \right). \end{aligned}\right\} \quad (3)$$

Adding (2) and (3) we obtain eq. (57) of the text.

b. For $l = 0$ the calculation is simpler. We may perform the integration over r to a large value R and then let R go to infinity. A calculation, similar to the derivation of (2) gives

$$I = \underset{R \rightarrow \infty}{Lim} \left[-\frac{R k_0 \sqrt{\pi}}{2} + \frac{1}{2} \int_{0}^{r_0(0)} dr \int_{f(r)}^{\infty} dx\, \frac{e^{-x/k_0^2}}{\sqrt{x - f(r)}} + \right.$$
$$\left. + \frac{1}{2} \int_{r_0(0)}^{R} dr \int_{0}^{\infty} dx\, \frac{e^{-x/k_0^2}}{\sqrt{x - f(r)}} \right].$$

This is identical with eq. (58) of the text.

5.

Calculation of $B_{l,\,cont.}$ in the second W. K. B. approximation.

Before calculating $B^{(2)}_{l,\,cont.}$ we shall compute $\eta_l^{(2)}(k)$ according to eq. (66) of the text for the case of a free particle. We have then

$$\eta_l^{(2)}(k) = -\frac{l^2(l+1)^2}{8} \Bigg/ \overline{\int_{\sqrt{l(l+1)}/k}^{\infty} dr\, \frac{1}{r^6 \left(k^2 - \frac{l(l+1)}{r^2} \right)^{5/2}}}. \quad (1)$$

---

*) This result is obvious since $d\eta_l^{(1)}/dk$ vanishes for a free particle.

Putting $l(l+1)/r^2 = t^2$ one obtains

$$\eta_l^{(2)}(k) = -\frac{1}{8\sqrt{l(l+1)}} \Big/\overline{\int_0^k dt \frac{t^4}{(k^2-t^2)^{5/2}}} \quad . \quad . \quad . \quad (2)$$

According to the definition of the principal value of an integral we must integrate (2) partially till the resulting integral becomes convergent and drop the infinite parts of the integrated terms. We obtain then, because the finite parts of the integrated terms are all zero

$$\eta_l^{(2)}(k) = -\frac{1}{8\sqrt{l(l+1)}} \int_0^k \frac{dt}{\sqrt{k^2-t^2}} = -\frac{\pi}{16\sqrt{l(l+1)}} \qquad (3)$$

as stated in the footnote of p. 73.

We shall now calculate $B_{l,\,cont.}^{(2)}$ for the case of a monotonic $f(r)$. Then

$$\left.\begin{aligned} B_{l,\,cont.}^{(2)} &= B_l^{(2)} = -\frac{2^{1/2}.\,5\,N\lambda^3}{32\pi}\,I \\ I &= \int_0^\infty dk\,k\,e^{-k^2/k_0^2} \Big/\overline{\int_{r_0}^\infty dr \frac{f'^2}{(k^2-f)^{7/2}}} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (4)$$

We shall again divide the integration region into three parts as in the foregoing note, so that

$$I = I_I + I_{II} + I_{III}$$

with

$$I_I = \int_{k(R)}^\infty dk\,k\,e^{-k^2/k_0^2} \Big/\overline{\int_{r_0}^R dr \frac{f'^2}{(k^2-f)^{7/2}}}$$

$$I_{II} = \int_0^{k(R)} dk\,k\,e^{-k^2/k_0^2} \Big/\overline{\int_{r_0}^\infty dr \frac{f'^2}{(k^2-f)^{7/2}}}$$

$$I_{III} = \int_{k(R)}^\infty dk\,k\,e^{-k^2/k_0^2} \int_R^\infty dr \frac{f'^2}{(k^2-f)^{7/2}}.$$

First we remark that I_{II} is zero. For here we may replace $f(r)$ by $l(l+1)/r^2$ and therefore the integral over r is proportional to $d\eta_l^{(2)}/dk$ for a free particle which, according to (3), is zero. By successive partial integration and by dropping the infinite terms we can write I_I in the form

$$\left.\begin{aligned} I_I = \int\limits_{k(R)}^{\infty} dk\, k\, e^{-k^2/k_0^2} \Bigg[& \frac{2}{5} \frac{f'(R)}{\{k^2 - f(R)\}^{5/2}} - \frac{4}{15} \frac{f''(R)}{f'(R)\{k^2 - f(R)\}^{3/2}} + \\ & + \frac{8}{15} \left(\frac{f'''(R)}{f'(R)^2} - \frac{f''(R)^2}{f'(R)^3} \right) \frac{1}{\{k^2 - f(R)\}^{1/2}} - \\ & - \frac{8}{15} \int\limits_{r_0}^{R} \frac{dr}{(k^2 - f)^{1/2}} \left(\frac{f''''}{f'^2} - \frac{4 f''' f''}{f'^3} - \frac{3 f''^3}{f'^4} \right) \Bigg] \end{aligned} \right\} . \qquad (5)$$

Here the first two terms would give infinite results. They can however be compensated by I_{III} which after two partial integrations can be brought into the form

$$\left.\begin{aligned} I_{III} = \int\limits_{k(R)}^{\infty} dk\, k\, e^{-k^2/k_0^2} \Bigg[& - \frac{2}{5} \frac{f'(R)}{\{k^2 - f(R)\}^{5/2}} + \frac{4}{15} \frac{f''(R)}{f'(R)\{k^2 - f(R)\}^{3/2}} + \\ & + \frac{4}{15} \int\limits_{R}^{\infty} \frac{dr}{(k^2 - f)^{3/2}} \left(\frac{f'''}{f'} - \frac{f''^2}{f'^2} \right) \Bigg] \end{aligned} \right\} \qquad (6)$$

By adding I_I and I_{III} and substituting $l(l+1)/r^2$ for $f(r)$ when $r \geqq R$ we obtain

$$\left.\begin{aligned} I = I_I + I_{III} = \int\limits_{\sqrt{l(l+1)}/R}^{\infty} dk\, k\, e^{-k^2/k_0^2} \Bigg[& - \frac{4R}{5\, l(l+1)} \frac{1}{\sqrt{k^2 - l(l+1)/R^2}} + \\ & + \frac{4}{5} \int\limits_{R}^{\infty} \frac{dr}{r^2} \frac{1}{\{k^2 - l(l+1)/r^2)^{3/2}} - \\ - \frac{8}{15} \int\limits_{r_0}^{R} \frac{dr}{(k^2 - f)^{1/2}} & \left(\frac{f''''}{f'^2} - \frac{4 f''' f''}{f'^3} - \frac{3 f''^3}{f'^4} \right) \Bigg] = A + B + C \end{aligned} \right\} \qquad (7)$$

For the first term of (7) one finds easily

$$A = -\frac{2k_0 R\sqrt{\pi}}{5\,l(l+1)}\, e^{-l(l+1)/k_0^2R^2} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

On carrying through the integration over r the second term becomes

$$B = \frac{4}{5R} \int\limits_{\sqrt{l(l+1)}/R}^{\infty} \frac{dk}{k}\, \frac{e^{-k^2/k_0^2}}{\{k^2 - l(l+1)/R^2\}^{1/2}}$$

In order to calculate this we differentiate with respect to k_0:

$$\left.\begin{aligned} \frac{dB}{dk_0} &= \frac{8}{5Rk_0^3} \int\limits_{\sqrt{l(l+1)}/R}^{\infty} dk\,k\, \frac{e^{-k^2/k_0^2}}{\{k^2 - l(l+1)/R^2\}^{1/2}} = \frac{4\sqrt{\pi}}{5Rk_0^2}\, e^{-l(l+1)/k_0^2R^2} \\ B &= \frac{4\sqrt{\pi}}{5R} \int\limits_0^{k_0} \frac{dx}{x^2}\, e^{-l(l+1)/x^2R^2} \rightarrow \frac{2\pi}{5\sqrt{l(l+1)}} \end{aligned}\right\} (9)$$

In the last term of (7) we may interchange the integrations and obtain then, after performing the integration over k

$$C = -\frac{4k_0\sqrt{\pi}}{15} \int\limits_0^R dr\, e^{-f/k_0^2} \left(\frac{f''''}{f'^2} - \frac{4f'''f''}{f'^3} - \frac{3f''^3}{f'^4} \right).$$

By partial integration this becomes

$$C = \frac{2k_0R\sqrt{\pi}}{5l(l+1)}\, e^{-.\,(l+1)/k_0^2R^2} - \frac{4\sqrt{\pi}}{15k_0} \int\limits_0^{\infty} dr\, e^{-f/k_0^2} \left(\frac{f'''}{f'} - \frac{f''^2}{f'^2} \right). \quad (10)$$

Addition of (8), (9) and (10) gives

$$I = \frac{2\pi}{5\sqrt{l(l+1)}} - \frac{4\sqrt{\pi}}{15k_0} \int\limits_0^{\infty} dr\, e^{-f/k_0^2} \left(\frac{f'''}{f'} - \frac{f''^2}{f'^2} \right).$$

By partial integration of the first term of the integral this can be written as

$$I=\frac{2\pi}{5\sqrt{l(l+1)}}-\frac{4\sqrt{\pi}}{15k_0^5}\int_0^\infty dr\, e^{-f/k_0^2} f'^2 . \quad . \quad . \qquad (11)$$

From (4) and (11) we immediately obtain eq. (69) of the text by inserting the expression (35), (50) for $f(r)$ and by replacing the first term of (11) by the negative of the second term with $f(r)=l(l+1)/r^2$.

We shall not give here the calculation for a non-monotonic $f(r)$ since it presents no special difficulties.

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REFERENCES.

1) J. E. MAYER, Journ. chem. Phys. **5**, 67, 1937.
J. E. MAYER and PH. G. ACKERMANN, ibid., **5**, 74, 1937.
J. E. MAYER and S. F. HARRISON, ibid., **6**, 87, 1938.
S. F. HARRISON and J. E. MAYER, ibid., **6**, 101, 1938.
2) H. KAMERLINGH ONNES, Comm. Leiden, Nos. 71, 74, 1901.
3) URSELL, Proc. Cambr. phil. Soc. **23**, 685, 1927. Comp. also R. H. FOWLER, Statistical Mechanics, Ch. 8.
4) A. EINSTEIN, Berl. Ber. 1924, p. 261; 1925, p. 3.
5) F. LONDON, Trans. Faraday Soc. **33**, 8, 1937. Here the older litterature on VAN DER WAALS forces will be found.
6) J. C. SLATER, Phys. Rev. **32**, 349, 1928.
7) J. C. SLATER and J. G. KIRKWOOD, Phys. Rev. **37**, 682, 1931.
8) H. MARGENAU, Phys. Rev. **38**, 747, 1931.
9) C. H. PAGE, Phys. Rev. **53**, 426, 1938.
10) Comp. R. H. FOWLER, Statistical Mechanics, Ch. 10.
11) J. G. KIRKWOOD and F. G. KEYES, Phys. Rev. **37**, 832, 1931.
12) J. C. SLATER, Phys. Rev. **38**, 237, 1931.
13) Comp. G. E. UHLENBECK and L. GROPPER, Phys. Rev. **41**, 79, 1932; G. E. UHLENBECK, J. Math. Phys. **14**, 10, 1935.
14) G. E. UHLENBECK and L. S. ORNSTEIN, Phys. Rev. **36**, 823, 1930.
15) J. G. KIRKWOOD, Phys. Rev. **44**, 31, 1933.
16) F. BLOCH, Z. Phys. **74**, 295, 1932.
17) M. BORN, Physica **4**, 1034, 1937.
18) H. A. KRAMERS, Leiden Comm., Suppl. N⁰. 83, 1936.
19) F. LONDON, Nature **141**, 643, 1938.
20) P. EHRENFEST, Comm. Leiden, Suppl. N⁰. 75 *b*, 1933.
21) G. E. UHLENBECK, Dissertation Leiden, 1927, p. 69.
22) Comp. J. HADAMARD, La série de Taylor et son prolongement analytique, Paris 1901, p. 20 (or 2nd ed. p. 41).
23) M. BORN and K. FUCHS, Proc. roy. Soc. London, in press.
24) E. BETH and G. E. UHLENBECK, Physica **4**, 915, 1937.
25) L. GROPPER, Phys. Rev. **51**, 1108, 1937.
26) Comp. N. F. MOTT and H. S. W. MASSEY, The theory of atomic collisions, Chs. 2 and 5.
27) H. S. W. MASSEY and C. B. O. MOHR, Proc. roy. Soc. London, **141**, 434, 1933; E. A. UEHLING, Phys. Rev. **46**, 917, 1934.
28) E. FERMI a.o., Proc. roy. Soc. London, **149**, 522, 1935.
29) Comp. ref. 26, Ch. 2, § 2.
30) Comp. for instance J. L. DUNHAM, Phys. Rev. **41**, 713, 1932.

31) G. E. Uhlenbeck and E. Beth, Physica **3**, 729, 1936.
32) H. P. Mulholland, Proc. Cambr. phil. Soc. **24**, 280, 1928.
33) J. Hadamard, Le problème de Cauchy, Paris 1932, p. 184.
34) W. H. Keesom and H. H. Kraak, Comm. Leiden, N⁰. 234 e, 1934.
35) Comp. R. Courant and D. Hilbert, Methoden der mathematischen Physik, I, 2nd ed. p. 64.
36) Comp. E. T. Whittaker and G. N. Watson, Modern Analysis, 4th ed., p. 132.

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STELLINGEN

I.

De wijze, waarop MAYER en HARRISON de volume-afhankelijkheid der grootheden b_l behandelen, is onjuist.

J. E. MAYER en S. F. HARRISON, Journ. Chem. Phys. **6**, 87, 1938.

II.

De overeenstemming van de door VAN ITTERBEEK en KEESOM gemeten waarden voor de viscositeitscoëfficiënt van helium met de door UEHLING theoretisch berekende, kan niet als een experimentele bevestiging van de quantumtheorie der viscositeit beschouwd worden.

A. VAN ITTERBEEK en W. H. KEESOM, Physica, **5**, 257, 1938.

III.

Het feit, dat op grond van de door FERMI gegeven theorie der straling berekende kernkrachten veel te zwak zijn, is geen beslissend argument tegen de samenhang van de kernkrachten met de β-radioactiviteit.

IV.

De wijze, waarop FRÖHLICH, HEITLER en KEMMER de krachten tussen protonen en neutronen en de magnetische momenten van deze deeltjes berekenen, is niet consequent.

H. FRÖHLICH, W. HEITLER en N. KEMMER, Proc. Roy. Soc. London, **166**, 154, 1938.

V.

De wijze, waarop VAN LAAR de vergelijking $d\varepsilon = c_V dT + ldV$ integreert, is nodeloos omslachtig.

J. J. VAN LAAR, Chemisch Weekblad, **35**, 351, 1938.

VI.

De door UHLENBECK en BETH gegeven sommatieformules zijn een direct gevolg van de formule van CLEBSCH.

Dissertatie, blz. 66; G. N. WATSON, Theory of BESSEL Functions, blz. 363.

VII.

Uit de bepaling van de levensduren en van de verhouding der activiteiten van twee isomere β-radioactieve atoomkernen kan een bovenste grens worden afgeleid voor de waarschijnlijkheid van de overgang tussen deze kernen.

VIII.

De bepaling van de bovenste grens van een continu β-spectrum met behulp van absorptiemetingen geeft geen betrouwbare resultaten.

E. E. WIDDOWSON en F. C. CHAMPION, Proc. Phys. Soc. **50**, 185, 1938.

IX.

De metingen van ALICHANIAN en zijn medewerkers over de vorm van het β-spectrum van $Ra\,E$ en $Th\,C$ rechtvaardigen niet de door deze onderzoekers getrokken conclusie omtrent een van nul verschillende massa van het neutrino.

A. I. ALICHANIAN, A. I. ALICHANOW, B. S. DŽELEPOW en S. J. NIKITIN, Phys. Rev. **53**, 766 en 767, 1938.

X.

Bij geschikte ontladingen in moleculaire gassen kan men uit de optische bepaling van de rotatie-energieverdeling van het molecuul en van het molecuulion besluiten of de ionen hoofdzakelijk in aangeslagen dan wel in de grondtoestand gevormd worden.