

(ii) It is noticeable that although the Beer-Lambert law holds only for monochromatic light, according to rigid optical theory, these experiments show that with not too wide a band it may still be applied. This would suggest that in the spectral region wherein we have worked the absorption of light by NO_2 is almost continuous, and that we can, without serious error, assume a mean value for ϵ .

On the Statistical Mechanics of Dilute and of Perfect Solutions.

By E. A. GUGGENHEIM, M.A., Gonville and Caius College, Cambridge.

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§ 1. *Introduction and Definitions.*—In a previous paper* the author discussed the laws of dilute and of perfect solutions. It was pointed out that the laws of dilute solutions take different forms according to the concentration scale used, these forms becoming identical only at infinite dilution. Of these various sets of laws that corresponding to the mole-fraction scale of concentration has in certain respects simpler properties than the others and is more symmetrical between solvent and solute. In particular only in this form is it possible for the laws of dilute solutions to hold at all concentrations, in which case they become the laws of perfect solutions.† It was shown how this set of laws of perfect solutions could be deduced by thermodynamic reasoning from certain assumptions about the additivity of energies and volumes on mixing, but these assumptions were not of a very simple form. Nor was any reason found why the laws of dilute solutions should take the particular form corresponding to the mole-fraction scale of concentration, except analogy with the laws of perfect solutions. In the present paper an attempt will be made to remedy this omission by considerations of statistical mechanics.

The method used will be that of partition functions described in Fowler's text-book.‡ This method is more elegant than Gibbs' method of the canonical ensemble, does not suffer from the logical inconsistencies of Boltzmann's

* E. A. Guggenheim, 'J. Physik Chem.,' vol. 34, p. 1751 (1930).

† Cf. Washburn, 'Z. Physik Chem.,' vol. 74, p. 537 (1910).

‡ "Statistical Mechanics" (1929).

method of "thermodynamic probability," and is more powerful than either of these.

To maintain so far as possible continuity with Fowler's treatment, the thermodynamic functions used will be the two characteristic functions Ψ and Φ of Planck. As it is more usual for chemists to use the Helmholtz free energy A and the Gibbs' free energy F , it is perhaps as well to define these various functions and give the exact relations between them. When any one of these has been evaluated, the others are, of course, obtainable by pure thermodynamics and any one of them is equally utilisable, though not necessarily equally convenient, with the others for the determination of an equilibrium.

Let E denote the energy, T the absolute temperature, S the entropy, p the pressure, V the volume of a whole system or a whole phase of a system, then we have the definitions

$$A = E - TS, \quad (1.1)$$

$$F = E - TS + pV = A + pV, \quad (1.2)$$

$$\Psi = S - E/T = -A/T, \quad (1.3)$$

$$\Phi = S - E/T - pV/T = -F/T. \quad (1.4)$$

Before commencing our treatment of solutions we shall discuss briefly the relationships between Ψ and Φ and their dependence on the pressure on the one hand for perfect gases and on the other hand for liquid phases, as an imperfect understanding of these relationships leads to confusion. For a perfect gas containing n molecules, whether all alike or not

$$pV = nkT, \quad (2)$$

where k is the gas constant, and so

$$\Phi = \Psi - nk. \quad (3)$$

For a liquid phase of given composition and temperature, on the other hand, the volume is related to the pressure by the formula

$$V = V^* \{1 - \kappa p\}, \quad (4)$$

where V^* is the value of V at very low, effectively zero, pressures and κ is the compressibility, which for all ordinary pressures may be assumed independent of p . The relation between Ψ and Φ therefore takes the form

$$\Phi = \Psi - \frac{V^* \cdot p}{T} \{1 - \kappa p\}. \quad (5)$$

Applying the well-known thermodynamic relation

$$V = \left(\frac{\partial F}{\partial p} \right)_T = -T \left(\frac{\partial \Phi}{\partial p} \right)_T \quad (6)$$

we obtain

$$V = -T \left(\frac{\partial \Psi}{\partial p} \right)_T + V^* \{1 - \kappa p\} - V^* \kappa p. \quad (7)$$

Comparing (7) with (4) we find

$$\left(\frac{\partial \Psi}{\partial p} \right)_T = - \frac{V^* \kappa p}{T}, \quad (8)$$

and after integrating

$$\Psi = \Psi^* - \frac{1}{2} \frac{V^* \kappa p^2}{T}, \quad (9)$$

where Ψ^* is the value of Ψ at zero pressure. Combining (5) and (9) we obtain finally

$$\Phi = \Psi^* - \frac{V^* \cdot p}{T} \{1 - \frac{1}{2} \kappa p\}. \quad (10)$$

From (9) we see that for an incompressible liquid Ψ like V is independent of p . In this case Φ is given by

$$\Phi = \Psi - \frac{V}{T} p, \quad (11)$$

where all the quantities on the right, except p itself, are independent of p . It is clear that for an incompressible liquid it is not possible to use V instead of p as an independent variable defining the state of the system. If the liquid is compressible it is indeed permissible to use V instead of p as an independent variable, but not at all convenient, as the formulæ would all become indefinite when $p \rightarrow 0$ instead of taking special simple forms.

§ 2. *The Statistical Formulation.*—The above considerations apply to a liquid phase of any composition, whether simple or a mixture. We shall therefore in our treatment of liquid phases take as independent variables the temperature, the pressure and the number of molecules of each species. For an assembly consisting of n_A molecules of A and n_B molecules of B, between which no chemical reactions are supposed to take place, the characteristic function Ψ is given by

$$\frac{\Psi}{k} = n_A \left\{ \log \frac{G_A}{n_A} + 1 \right\} + n_B \left\{ \log \frac{G_B}{n_B} + 1 \right\} + B(T, p). \quad (12)$$

Here k is the gas constant. G_A and G_B are the partition functions for the

kinetic energy and internal energy of the molecules A and B; the form of G_A and G_B need not concern us here; it suffices to mention that they depend on the temperature and possibly the pressure, but otherwise only on molecular properties such as mass, moments of inertia, vibration frequencies, etc., of the molecules. Finally $B(T, p)$ the partition function for the potential energy of the whole system is given by*

$$B(T, p) = \int \dots \int e^{-W/kT} (d\omega_A)^{n_A} (d\omega_B)^{n_B}. \quad (13)$$

Here W is the potential energy of the whole system, a function of the space co-ordinates of all the n_A molecules of A and n_B molecules of B. $(d\omega_A)^{n_A}$ is an abbreviation for the product of n_A elements of volume each corresponding to one particular A molecule; similarly $(d\omega_B)^{n_B}$. The multiple integral is to be evaluated over the whole of the $3(n_A + n_B)$ dimensional phase space. The whole problem reduces to the evaluation of $B(T, p)$.*

Fowler† does indeed devote a few paragraphs to dilute solutions, but the treatment there given is open to criticism. For a perfect gas $B(T, p)$ becomes simply $V^{n_A+n_B}$. For a dilute liquid solution of B in A (that is $n_B \ll n_A$), Fowler states that the solute molecules will contribute a factor V^{n_B} to $B(T, p)$, the remaining factor being independent of n_B . This argument seems to be due to a false analogy between dilute solutions and perfect gases, probably suggested by the popular but false analogy between osmotic pressure and gaseous pressure. To establish this point it is best to remind ourselves why $B(T, p)$ takes the form $V^{n_A+n_B}$ for a perfect gas. The explanation is simply that the volume V of a gas is determined entirely by that of its container and we can express this mathematically by setting

$$\begin{aligned} W &= 0 \text{ anywhere within the volume } V; \\ W &= \infty \text{ anywhere outside the volume } V. \end{aligned}$$

Integration then gives immediately

$$B(T, p) = V^{n_A+n_B}. \quad (14)$$

For a slightly imperfect gas the conditions are

$$\begin{aligned} W &\text{ is small anywhere within the volume } V; \\ W &= \infty \text{ anywhere outside the volume } V. \end{aligned}$$

* *Vide* Fowler, *loc. cit.*, p. 307.

† Fowler, *loc. cit.*, paragraphs 13.2 to 13.4.

Thus the integration over the whole of the phase space may still be replaced by integration over the hyper-volume $V^{n_A+n_B}$. This leads to the formulæ obtained by Fowler for imperfect gases.*

For a liquid, however, the conditions are entirely different. The volume V occupied by the liquid is not at all determined by a containing vessel but by the intermolecular forces. The size of the containing vessel will merely determine how many molecules will be present as vapour in equilibrium with the liquid; we may in any case assume that these are negligibly few compared with the molecules in the liquid phase. The behaviour of W for a single liquid is better described as follows. W has a pronounced minimum for certain, but not all, configurations in which all the n molecules are packed together in a volume V (the actual volume of the liquid). As shown by the large heat of evaporation of liquids (compared to kT) not near the critical point and their small compressibility, W will be much greater, effectively infinite, for all configurations in which the whole assembly occupies a volume appreciably greater or less than V . Since this minimum value of W will obviously be proportional to n the number of molecules in the assembly, we may write

$$W_{\min} = n \cdot w(T, p), \tag{15}$$

where $w(T, p)$ is independent of n . We thus obtain

$$B(T, p) = e^{-nw/kT} \int \dots \int (d\omega)^n, \tag{16}$$

where the integral has now to be evaluated over all configurations consistent with

$$W = nw. \tag{17}$$

We have now to estimate this hyper-volume of phase-space. It is fairly obvious that we need not take into consideration changes of configuration corresponding to a mere macroscopic alteration of shape or position of the liquid mass. There remain two types of change of configuration. Consider the molecules forming the liquid in one definite configuration satisfying the condition (17). Firstly, there are then obviously $n!$ configurations identically similar to this one except that the molecules have interchanged places. Secondly, in each of these configurations we may imagine a small compartment of volume v assigned to each molecule over which this molecule may move more or less

* Fowler, *loc. cit.*, e.g., formula (486).

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independently of the other molecules without appreciably disturbing the relation (17). Evaluation of the multiple integral then gives

$$B(T, p) = e^{-nw/kT} n! \nu^n. \quad (18)$$

This gives us for the characteristic function of a single liquid

$$\begin{aligned} \frac{\Psi}{k} &= n \left\{ \log \frac{G}{n} + 1 \right\} - \frac{nw}{kT} + n \{ \log n - 1 \} + n \log \nu, \\ &= n \left\{ \log G\nu - \frac{w}{kT} \right\}. \end{aligned} \quad (19)$$

As we do not know how w and ν depend on the temperature and pressure this leads nowhere for a single liquid. The argument is, however, readily extended to dilute solutions.

§ 3. *The Formulation for Dilute Solutions.*—If we define a solution of B in A as being ideally dilute when there are no long-range electrostatic forces between the molecules and n_B/n_A is so small that we may neglect its square, then of all relevant possible configurations the number of them in which two solute B molecules are within range of each other's field of force is negligible. In this case W will still have a pronounced minimum of the form

$$W_{\min} = n_A \cdot w_A(T, p) + n_B \cdot w_B(T, p), \quad (20)$$

where w_A and w_B are independent of the composition, for certain configurations in which the molecules are all collected in a space V . We then have

$$B(T, p) = e^{-\frac{n_A w_A + n_B w_B}{kT}} \int \dots \int (d\omega_A)^{n_A} (d\omega_B)^{n_B}, \quad (21)$$

the integral to be extended over all that part of the $3(n_A + n_B)$ dimensional phase space in which W has the value W_{\min} given by (20). The determination of this hyper-volume proceeds exactly as for a single liquid and leads to

$$B(T, p) = e^{-\frac{n_A w_A + n_B w_B}{kT}} (n_A + n_B)! \nu_A^{n_A} \nu_B^{n_B}, \quad (22)$$

and hence

$$\frac{\Psi}{k} = n_A \left\{ \log \frac{G_A \nu_A (n_A + n_B)}{n_A} - \frac{w_A}{kT} \right\} + n_B \left\{ \log \frac{G_B \nu_B (n_A + n_B)}{n_B} - \frac{w_B}{kT} \right\}. \quad (23)$$

In this formula ν , w , G may be functions of the pressure as well as the temperature. Let ν^* , w^* , G^* denote their respective values at very low (effectively

zero) pressures, these quantities being functions of the temperature only. The second characteristic function Φ is then according to (10) given by

$$\frac{\Phi}{k} = n_A \left\{ \log \frac{G_A^* v_A^* (n_A + n_B)}{n_A} - \frac{w_A^*}{kT} \right\} + n_B \left\{ \log \frac{G_B^* v_B^* (n_A + n_B)}{n_B} - \frac{w_B^*}{kT} \right\} - \frac{pV^*}{kT} \left\{ 1 - \frac{1}{2}\kappa p \right\}. \quad (24)$$

κ may be assumed independent of the pressure, but will generally vary with the temperature and composition of the solution. But since in an ideally dilute solution we may neglect the interaction between the solute molecules the volume V must be of the form

$$V = n_A v_A(T, p) + n_B v_B(T, p), \quad (25)$$

where v_A, v_B are independent of n_A, n_B , but depend on the pressure as well as the temperature. For equation (25) to hold at every pressure it is easily shown that κ must depend on the composition according to a relation of the form

$$\kappa = \frac{\kappa_A n_A v_A^* + \kappa_B n_B v_B^*}{n_A v_A^* + n_B v_B^*}, \quad (26)$$

where κ_A, κ_B are independent of the composition as well as of the pressure; κ_A in particular is the value of κ for the pure solvent. Substituting (26) into (24) we then obtain

$$\frac{\Phi}{k} = n_A \left\{ \log \frac{G_A^* v_A^* (n_A + n_B)}{n_A} - \frac{w_A^*}{kT} - \frac{p v_A^*}{kT} \left(1 - \frac{1}{2} \kappa_A p \right) \right\} + n_B \left\{ \log \frac{G_B^* v_B^* (n_A + n_B)}{n_B} - \frac{w_B^*}{kT} - \frac{p v_B^*}{kT} \left(1 - \frac{1}{2} \kappa_B p \right) \right\}. \quad (27)$$

Having now obtained formulæ for Ψ and Φ , it is straightforward thermodynamics to deduce all the laws of ideal dilute solutions. Thus for the equilibrium between two phases as regards A, we have to equate the chemical potential μ_A of A between the two phases; similarly for equilibrium as regards B, we have to equate the chemical potential μ_B of B in the two phases. The chemical potentials are defined by

$$\mu_A = \left(\frac{\partial A}{\partial n_A} \right)_{T, V, n_B} = \left(\frac{\partial F}{\partial n_A} \right)_{T, p, n_B} = -T \left(\frac{\partial \Psi}{\partial n_A} \right)_{T, V, n_B} = -T \left(\frac{\partial \Phi}{\partial n_A} \right)_{T, p, n_B}, \quad (28.1)$$

$$\mu_B = \left(\frac{\partial A}{\partial n_B} \right)_{T, V, n_A} = \left(\frac{\partial F}{\partial n_B} \right)_{T, p, n_A} = -T \left(\frac{\partial \Psi}{\partial n_B} \right)_{T, V, n_A} = -T \left(\frac{\partial \Phi}{\partial n_B} \right)_{T, p, n_A}. \quad (28.2)$$

Straightforward differentiation of (27) gives

$$\frac{\mu_A}{kT} = \log \frac{n_A}{G_A^* v_A^* (n_A + n_B)} + \frac{w_A^*}{kT} + \frac{pv_A^*}{kT} \left\{ 1 - \frac{1}{2} \kappa_A p \right\}, \quad (29.1)$$

$$\frac{\mu_B}{kT} = \log \frac{n_B}{G_B^* v_B^* (n_A + n_B)} + \frac{w_B^*}{kT} + \frac{pv_B^*}{kT} \left\{ 1 - \frac{1}{2} \kappa_B p \right\}. \quad (29.2)$$

For a mixture of the vapours of A and B, considered as perfect gases, we have on the other hand†

$$\frac{\Psi'}{k} = -\frac{A'}{kT} = n'_A \left\{ \log \frac{G'_A V'}{n'_A} + 1 \right\} + n'_B \left\{ \log \frac{G'_B V'}{n'_B} + 1 \right\}. \quad (30)$$

The functions referring particularly to the gaseous phase are denoted by dashed letters and the G' are functions of the temperature only. Combining (30) and (3) we have for Φ'

$$\begin{aligned} \frac{\Phi'}{k} &= -\frac{F'}{kT} = n'_A \log \frac{G'_A V'}{n'_A} + n'_B \log \frac{G'_B V'}{n'_B}, \\ &= n'_A \log \left(\frac{G'_A kT}{p'} \frac{n'_A + n'_B}{n'_A} \right) + n'_B \log \left(\frac{G'_B kT}{p'} \frac{n'_A + n'_B}{n'_B} \right). \end{aligned} \quad (31)$$

Differentiation of (30) at constant V or of (31) at constant p gives

$$\frac{\mu'_A}{kT} = \log \frac{n'_A}{G'_A V} = \log \left(\frac{p'}{G'_A kT} \frac{n'_A}{n'_A + n'_B} \right) = \log \frac{p'_A}{G'_A kT}, \quad (32.1)$$

$$\frac{\mu'_B}{kT} = \log \frac{n'_B}{G'_B V} = \log \left(\frac{p'}{G'_B kT} \frac{n'_B}{n'_A + n'_B} \right) = \log \frac{p'_B}{G'_B kT}, \quad (32.2)$$

where p'_A, p'_B are the partial vapour pressures defined by

$$p'_A = \frac{n'_A}{n'_A + n'_B} p', \quad (33.1)$$

$$p'_B = \frac{n'_B}{n'_A + n'_B} p'. \quad (33.2)$$

For equilibrium between liquid and vapour we have the conditions

$$\mu_A = \mu'_A, \quad (34.1)$$

$$\mu_B = \mu'_B. \quad (34.2)$$

These lead to

$$p'_A = \frac{n_A}{n_A + n_B} \frac{G'_A kT}{G_A^* v_A^*} \exp \left\{ \frac{w_A^*}{kT} + \frac{pv_A^*}{kT} \left(1 - \frac{1}{2} \kappa_A p \right) \right\}, \quad (35.1)$$

$$p'_B = \frac{n_B}{n_A + n_B} \frac{G'_B kT}{G_B^* v_B^*} \exp \left\{ \frac{w_B^*}{kT} + \frac{pv_B^*}{kT} \left(1 - \frac{1}{2} \kappa_B p \right) \right\}. \quad (35.2)$$

† Fowler, *loc. cit.*, e.g., formula (400) or (491).

So far the formulæ obtained have all been of a form symmetrical in A and B. This symmetry is, however, apparent only as it must be remembered that w_A^* , w_B^* , v_A^* , v_B^* , κ_A , κ_B are properties of a medium consisting essentially of A. Setting $n_B = 0$ in the formula for the vapour pressure of the solvent and comparing the equation so obtained with that for the solution we get

$$p'_A = p'^0_A \frac{n_A}{n_A + n_B}, \tag{36}$$

where p'^0_A is the vapour pressure of the pure solvent. This is Raoult's law on the mole-fraction scale. It is to be noted that p'_A and p'^0_A depend on the pressure p on the liquid as well as on the temperature. There is no corresponding simplification of the equation for the vapour pressure of the solute

We may write it in the more familiar form

$$p'_B = K \frac{n_B}{n_A + n_B}, \tag{37}$$

where K is independent of the composition. K, however, depends not only on the temperature but also on the pressure p of the solution according to the relation

$$\left(\frac{\partial \log K}{\partial p} \right)_T = \frac{v_B^*}{kT} (1 - \kappa_B p). \tag{38}$$

§ 4. *Osmotic Pressure.*—The osmotic pressure of a solution of B in A is the extra pressure that must be applied to the solution so that it may be in equilibrium as regards the solvent species A with the pure solvent at effectively zero pressure. If we denote this pressure by P we have as the condition of osmotic equilibrium

$$\mu_A(T, P, n_A, n_B) = \mu_A(T, 0, n_A, 0), \tag{39}$$

or according to (29.1)

$$\log \frac{n_A}{n_A + n_B} + \frac{P v_A^*}{kT} (1 - \frac{1}{2} \kappa_A P) = 0, \tag{40.1}$$

$$P (1 - \frac{1}{2} \kappa_A P) = \frac{kT}{v_A^*} \log \frac{n_A + n_B}{n_A}; \tag{40.2}$$

this is the correct form of the law of osmotic pressure on the mole-fraction scale.† Ignoring compressibility (40.2) simplifies to

$$P = \frac{kT}{v_A^*} \log \frac{n_A + n_B}{n_A}. \tag{41}$$

† *Vide Guggenheim, loc. cit., formula (4.3).*

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§ 5. *Errors in Fowler's Discussion.*—Fowler's proposed formula† for Ψ may be written in our notation

$$\Psi = n_A \psi_A \left(T, \frac{V}{n_A} \right) + n_B k \left\{ \log \frac{V G_B}{n_B} + 1 \right\}, \quad (42)$$

where G_B is a function of T only. According to the well-known thermodynamic relation

$$p = - \left(\frac{\partial \Psi}{\partial V} \right)_{T, n_A, n_B} = T \left(\frac{\partial \Psi}{\partial V} \right)_{T, n_A, n_B}, \quad (43)$$

equation (42) leads to the formula for the pressure,

$$p = T \left(\frac{\partial \psi_A}{\partial V/n_A} \right)_T + n_B \frac{kT}{V}, \quad (44)$$

which cannot be right, whatever value be assigned to

$$\left(\frac{\partial \psi_A}{\partial V/n_A} \right)_T.$$

According to our introductory discussion, Ψ is for an incompressible liquid a function of T, n_A, n_B only. Any formula for Ψ which contains V explicitly, apart from correction terms to take account of compressibility, will therefore lead to an impossible formula for p .

According to Fowler's treatment, formula (42) seemed to lead to a set of laws of dilute solutions not differing greatly from those obtained above. Careful investigation, however, shows that formula (42) does not in fact lead to Raoult's law even approximately. From (42) we deduce by differentiation

$$\frac{\mu_A}{T} = - \left(\frac{\partial \Psi}{\partial n_A} \right)_{T, V, n_B} = - \psi_A \left(\frac{V}{n_A} \right) + \left(\frac{\partial \psi}{\partial V/n_A} \right)_T \frac{V}{n_A}, \quad (45)$$

$$\frac{\mu_B}{T} = - \left(\frac{\partial \Psi}{\partial n_B} \right)_{T, V, n_A} = k \log \frac{n_B}{G_B V}, \quad (46)$$

Formula (46) is not unsatisfactory for treating equilibria involving the solute species B and leads to Henry's law in the form

$$p'_B = K_1 \frac{n_B}{V}, \quad (47)$$

where K_1 is independent of the composition. At infinite dilution this agrees with (37). Formula (45), on the other hand, if accurately applied to the

† Fowler, *loc. cit.*, formula (911).

equilibrium of the solvent species A leads to incorrect results. Combination of (45) with (32.1) gives for the partial vapour pressure of A in the solution

$$p'_A = G'_A kT \exp \left\{ -\frac{\psi_A(V/n_A)}{k} + \frac{V}{n_A k} \left(\frac{\partial \psi_A}{\partial V/n_A} \right) \right\}, \quad (48)$$

while for the partial vapour pressure of the pure solvent we have

$$p'^0_A = G'_A kT \exp \left\{ -\frac{\psi_A(V/n^0_A)}{k} + \frac{V}{n^0_A k} \left(\frac{\partial \psi_A}{\partial V/n^0_A} \right) \right\}, \quad (49)$$

where n^0_A/V denotes the value of n_A/V in the pure solvent. Combining (48) and (49) we find

$$\frac{p'_A}{p'^0_A} = \exp \left\{ \frac{\psi_A(V/n^0_A) - \psi_A(V/n_A)}{k} + \frac{V}{n_A k} \left(\frac{\partial \psi_A}{\partial V/n_A} \right) - \frac{V}{n^0_A k} \left(\frac{\partial \psi_A}{\partial V/n^0_A} \right) \right\}. \quad (50)$$

This leads nowhere without some assumption about the form of $\psi_A(V/n_A)$. To make (50) lead to a result approximating to Raoult's law, we have to assume that at given T and p

$$\frac{\psi_A(V/n_A)}{k} - \frac{V}{n_A k} \left(\frac{\partial \psi_A}{\partial V/n_A} \right) = \frac{\psi_A(V/n^0_A)}{k} - \frac{V}{n^0_A k} \left(\frac{\partial \psi_A}{\partial V/n^0_A} \right) + \frac{n_B}{n_A} + O\left(\frac{n_B}{n_A}\right)^2, \quad (51)$$

where $O(n_B/n_A)^2$ denotes terms of order $(n_B/n_A)^2$. This assumption leads to Raoult's law in the form

$$\frac{p'_A}{p'^0_A} = \exp \left\{ -\frac{n_B}{n_A} + O\left(\frac{n_B}{n_A}\right)^2 \right\}, \quad (52)$$

There is, however, no physical justification for (51) and, as already pointed out, neither this nor any other behaviour of ψ_A makes (44) physically possible. A similar criticism applies to the use of (45) for the derivation of a formula for the osmotic pressure. Actually (45) leads to

$$P \left(1 - \frac{1}{2} \kappa_A P \right) = \frac{kT}{v^*_A} \left\{ \frac{-\psi_A(V/n^0_A) + \psi_A(V/n_A)}{k} - \frac{V}{n_A k} \left(\frac{\partial \psi_A}{\partial V/n_A} \right) + \frac{V}{n^0_A k} \left(\frac{\partial \psi_A}{\partial V/n^0_A} \right) \right\}, \quad (53)$$

which transforms to an approximately correct formula only with the help of (51).†

† Professor Fowler has kindly informed me by a private communication that he agrees with the present method of treatment, and he recognises that the treatment given in his book is fallacious. He informs me further that the errors in his treatment were first pointed out to him by Professor J. D. van der Waals, junr., in a review of his book.

In conclusion, we will say a few words about perfect solutions. In the above deduction of the laws of dilute solution we had to assume that in the $(n_A + n_B)!$ permutations of the molecules amongst themselves the ones leading to configurations with two or more B molecules in contact were negligibly few. This assumption is no longer necessary if such configurations correspond to the same minimum value of the potential energy and the same volume occupied by the whole phase. In other words, it may be dispensed with if the fields of the A and B molecules are so similar that the "average free energy" of a B molecule (or A molecule) is the same whether it is surrounded by A molecules or B molecules. In such a case the above laws will hold for all concentrations. It is well known that such perfect solutions do in fact exist*, and for them it is only by using the mole-fraction scale of concentration that the observed laws can be expressed by simple formulæ.

I have much pleasure in thanking Professor Fowler for his kind and valuable criticism of this paper.

The Exchange of Energy between Gas Atoms and Solid Surfaces.
 II.—*The Temperature Variation of the Accommodation Coefficient of Helium.*

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In an earlier paper† it has been shown that, by paying careful attention to the removal of films of adsorbed gas, considerably lower values are found for the accommodation coefficient of helium with a tungsten surface than those ordinarily measured. These results for a clean surface, as opposed to those given by a surface covered with adsorbed films of unknown constitution and arrangement, must form one part of any theory of the interaction between gas atoms and a solid surface. The discovery by Stern of the phenomena of atomic reflection and diffraction shows that this theory must be treated from the point of view of wave mechanics.

* *Vide* Lewis and Randall, "Thermodynamics" (1923); and Hildebrand, "Solubility" (1924).

† Roberts, 'Proc. Roy. Soc.,' A, vol. 129, p. 146 (1930). References to earlier work will be found in this paper, which for convenience will be referred to as Paper I.