

A QUASI-LATTICE THEORY OF REAL GASES AND OF STRONG ELECTROLYTES IN SOLUTIONS¹

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INTRODUCTION.

In usual theories of specific heats and the like for crystalline bodies, atoms (or ions) are generally assumed to vibrate, in a regular manner, about their equilibrium positions which form a regular three-dimensional lattice. But, this simple picture has not been found suitable for explaining other group of phenomena like the evaporation of a crystal, the dissolution of a crystal in liquid media, the mutual diffusion of crystalline bodies, etc. For explaining these phenomena, Frenkel and others (Frenkel, 1946) have proposed a modified picture for the structure of crystalline bodies. In this modified picture, atoms (or ions) do not, by themselves, form a regular lattice, but even then a regular lattice may be considered as formed by atoms (or ions) together with the vacant sites (caused by the evaporation or the displacement of atoms or ions), which are generally referred to as the 'holes', and are to be counted as some sort of physical entities entering into calculations like the atoms (or ions) themselves. Thus the crystalline bodies are looked upon as some sort of binary alloys of atoms (or ions) and 'holes'. As in alloys, the ratio of the number of atoms (or ions) and 'holes' is taken to be capable of all possible variations. Of course, the number of holes in the system is generally taken to increase with the temperature.

Lennard-Jones and Devonshire (1937) have investigated important thermodynamic behaviours of normal liquids, viz., coefficients of thermal expansion, the heat of fusion, etc., from a picture for the structure of normal liquid, similar to that delineated above. According to them, the structure of normal liquids may be looked upon as a sort of alloy of atoms and 'holes' and the essential difference of the picture for normal liquids from that of solid is that in solids there is a long-distance order (in arrangements) but in the liquids the long-distance order disappears and only short-distance order is conspicuous.

In the present paper, it will be shown that the usual expressions for thermodynamic functions of real gases and useful formulae for distributions of ions of strong electrolytes in solutions can be obtained from similar pictures for their structures. Here, real gases and ions of strong electrolytes in solutions will be looked upon as sorts of alloys of molecules (atoms or ions) and 'holes' extended over the entire volume of the enclosure or of the solutions. The number of lattice-points in volume V will be taken as V/b , where b is different for different molecules (atoms or ions) due to the existence of an (average) minimum approach, either for the finite dimension of molecules or for the mutual repulsive interaction amongst molecules (atoms or ions) or for some other similar reasons. Of these V/b lattice-

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points, N are to be taken as occupied by N molecules (atoms or ions), and the rest, $V/b - N$, are occupied by the 'holes'. Along with Lennard-Jones and Devonshire, the interchanges of the mutual positions in the lattice are to be taken as frequent (of course, in the present case, they are more frequent than in case of liquids). The total number of possible arrangements of molecules (atoms or ions) and holes will be termed as the configurational thermodynamic probability (corresponding to the configurational entropy). The total thermodynamic probability will be taken as the product of the usual expression for thermodynamic probability (calculated after Planck and Lorentz but for distributions with respect to kinetic energy only and referred here as momental thermodynamic probability) and the expression of the configurational thermodynamic probability. In this way, the full information about the deviation from ideal gases (in case of real gases) and from ideal solutions (in case of solutions of strong electrolytes) which can be attributed to the existence of an (average) minimum approach can be obtained simply and directly.

To fit the usual concept of randomness (of gas-theories) with the present theory, one is to remember the important remarks (of course, originally made for real metallic alloys) of Bethe (1935). The arrangements, having large number of realisations, are expected to be of most frequent occurrences, in spite of its higher energy, causing the disappearance of correlations of distant atoms. In the present case (which is really an extreme case where the binding energy is very small), the disappearance of the correlations of atoms (distant and near) is quite natural and is to be interpreted as the usual randomness in gases. In these cases, according to Bethe, the number of possible realisation of arrangements of atoms (i.e., the configurational thermodynamic probability) is more important than the energies of arrangements.

Now, apart from the existence of an average minimum approach of the molecules, the other factor, to which the characteristic behaviour of real gases is generally attributed, is the effect of the field of forces, external or due to mutual interactions amongst molecules themselves or amongst the molecules and the boundary walls. To extend the present treatment, proposed above, to these cases, a simple restriction to be imposed on the nature of fields of forces is that the field of force will have, at least, in average a potential, the gradient of which can be supposed to be so small that any change of forces within a distance of molecular dimension can be neglected. Thus, the space within the enclosure of volume V can be divided into layers of constant potential energies (at least, in average), and the portions of the system, under consideration, in different potential-energy layers will be looked upon as different alloys of molecules and holes, of similar lattice-pattern, which are in phase equilibrium with one another. Here, it is to be admitted that the division of the configurational space into layers of constant potential energies (in average) is subject to some theoretical objections, as the potential energy may depend on the instantaneous distributions of particles. In case of external field or in case of slowly varying long-ranged forces or the like this division of the potential energy layers is quite permissible. But in case of other fields of forces, mainly due to mutual interactions amongst the molecules themselves, the validity of division of the configurational space is not above criticisms. In support of the procedure, proposed above, it can be added that similar ideas of existence of layers of some (average) constant potential energies *ab initio* is common amongst other successful statistical theories of real gases, specially in the presence of long-ranged forces (Fowler, 1936).

As it is well known, the Vant Hoff's law of osmotic pressure for ideal solution is generally explained from an ideal gas-like structure for the solutes in ideal solutions. The deviations of the osmotic and the allied properties of real solutions are generally explained in a way similar to that used for explaining the deviations of properties of real gases from those of ideal gases. So in the present paper, the ions of strong electrolytes in solutions have been treated similarly, as a system of alloys of ions and holes under a long-ranged field due to Coulomb's interactions

between ions and the laws ¹ for distribution of ions in the solutions, similar to those empirical laws which Bagchi (1950) has shown to yield a better agreement of the theoretical and the experimental values for activity coefficients, have been obtained.

SEC. A. GAS OF MOLECULES OF FINITE DIMENSIONS.

To have a clear understanding of the method, the simplest type will be considered first. The real gas of the simplest type is the gas which is composed of molecules of finite dimensions (or of molecules, under such a field of force that the effect can be accounted for from the assumption of the existence of an average minimum approach), and in which the effect of other field of forces (internal or external) on the thermodynamic behaviour of the system is insignificant and so can be neglected.

For this, let us consider an enclosure of volume V , containing N molecules, each of which is supposed to possess a volume of exclusion, b . It is assumed that there is no association or dissociation amongst the molecules in the assembly.

As already proposed, the system will be assumed to be composed of N molecules and $\frac{V}{b} - N$ 'holes' distributed amongst $\frac{V}{b}$ lattice-points. Then, the configurational thermodynamic probability is

$$\frac{\left(\frac{V}{b}\right)!}{N! \left(\frac{V}{b} - N\right)!} \dots \dots \dots (1)$$

The momental thermodynamic probability, calculated after Planck-Lorentz, is,

$$\frac{N!}{\prod_i a_i!}, \dots \dots \dots (2)$$

where a_i is the number of molecules having the kinetic-energy ϵ_i .

Then, the total thermodynamic probability is

$$\frac{\left(\frac{V}{b}\right)!}{\left(\frac{V}{b} - N\right)! \prod_i a_i!} \dots \dots \dots (3)$$

This expression for thermodynamic probability is the same as that obtained previously in a paper (Dutta, 1946), and, so, the usual expression for thermodynamic functions for real gases of the type considered here are to be obtained by the method based on Boltzmann principle as in the paper (*loc. cit.*). These expressions are

$$a_i = e^{\frac{\lambda - \epsilon_i}{kT}}, \dots \dots \dots (4)$$

$$E = \frac{3}{2} N kT, \dots \dots \dots (5)$$

¹ Recently, Eigen and Wicke, in a note (Die Naturwissenschaften, Vol. 38, p. 445), have obtained good fit for activity coefficients from a distribution formula which they have claimed as new, but which is only a special form of the present laws as shown by the author (in Die Naturwissenschaften, Vol. 39, p. 108).

$$S = Nk \left[\frac{3}{2} + \log V + \frac{3}{2} \log T + \log \left\{ \frac{b}{h^3} (2\pi mk)^{\frac{3}{2}} \right\} - \log N - \frac{V}{Nb} \left(1 - \frac{Nb}{V} \right) \log \left(1 - \frac{Nb}{V} \right) \right], \quad \dots \quad (6)$$

$$\Psi = S - \frac{E}{T} = \left[\log V + \frac{3}{2} \log T + \log \left\{ \frac{b}{h^3} (2\pi mk)^{\frac{3}{2}} \right\} - \log N - \frac{V}{Nb} \left(1 - \frac{Nb}{V} \right) \log \left(1 - \frac{Nb}{V} \right) \right], \quad (7)$$

$$p = - \frac{kT}{b} \log \left(1 - \frac{Nb}{V} \right). \quad \dots \quad (8)$$

This is the Planck-Saha-Bose Equation of state for real gases when the effect of the field can be ignored.

In the limiting case, $\frac{Nb}{V} \rightarrow 0$, the above expressions become:

$$S = Nk \left[\frac{3}{2} + \frac{3}{2} \log T + \log \left\{ \frac{1}{N} \frac{(2\pi mk)^{\frac{3}{2}}}{h^3} \right\} \right], \quad \dots \quad (9)$$

and

$$p = \frac{NkT}{V}. \quad \dots \quad (10)$$

These are the usual expressions for ideal gases. Up to the first approximation, these become:

$$S = Nk \left[\frac{5}{2} + \frac{3}{2} \log T + \log V - \frac{1}{2} \frac{Nb}{V} + \log \left\{ \frac{(2\pi mk)^{\frac{3}{2}}}{h^3} \right\} \right], \quad \dots \quad (11)$$

and

$$p = \frac{NkT}{V} \left[1 + \frac{1}{2} \frac{Nb}{V} \right] = \frac{NkT}{V - \beta}, \quad \dots \quad (12)$$

where

$$\beta = \frac{1}{2} Nb. \quad \dots \quad (13)$$

SEC. B. VAN DER WAAL'S GAS.

Before proceeding with general discussion of real gases under any field of forces, we shall consider the gas under Van der Waal's field of forces. In this case, the forces between the molecules, the effects of which have not been considered along with the repulsive forces considered in the above section, are taken to be short-ranged forces of attraction depending on their mutual distances. So, about every molecule, there is a sphere of action of molecular interaction such that only those molecules which came within this sphere will produce any significant influence on the molecule under consideration. Thus, in the interior of the gas, it can be taken that there is a symmetrical molecular distribution within a sphere of action of molecular interaction such that the resultant force of attraction on the molecule at the centre is zero, and thus molecules in the interior will have a constant potential energy. For molecules in the surface layer, due to the intersections of the sphere of action

of attraction by the boundary-walls, the distribution of molecules within the sphere of action about the molecule under consideration is not spherically symmetrical, and so, the resultant force on the molecule is not zero. Thus, the potential energies of molecules in the surface-layer will be different from those in the interior. Of course, there will be a variation of potential energies within the surface-layer; but for the sake of simplicity of calculation, we shall neglect the variation. We shall assume that the potential energies of molecules in the surface-layer is, at least in average, the same in the layer and is different from that of the interior.

As proposed in the introduction, we shall suppose that the system under consideration is composed of two alloys of molecules and holes, one occupies the interior and the other, the surface layer and they are in phase-equilibrium.

Let V_1, V_2 be the volumes of the interior and the surface-layer containing, at any instant, N_1, N_2 molecules of potential energies, w_1, w_2 respectively. Then, the thermodynamic probability becomes (according to the suggestions stated above)

$$W = \Pi \frac{\left(\frac{V_i}{b}\right)!}{\left(\frac{V_i}{b} - N_i\right)! \Pi a_{i1}!}, \quad (i = 1, 2), \quad \dots \quad (14)$$

where a_{11} and a_{21} are numbers of molecules in the interior and in the surface layer with kinetic energies ϵ_1 .

From this, the expressions for usual thermodynamic functions and for microscopic distributions can be simply obtained, by the method based on Boltzmann's principle as

$$\frac{a_{i1}}{\frac{V_i}{b} - N_i} = e^{-\lambda' - \frac{\epsilon_1 + w_i}{kT}}, \quad \dots \quad (15)$$

$$N_i = \frac{V_i}{b} \cdot \frac{1}{e^{\lambda' + \frac{w_i}{kT}} + 1}, \quad \dots \quad (16)$$

$$a_i = a_{11} + a_{21} = e^{-\lambda - \frac{\epsilon_1}{kT}}, \quad \dots \quad (17)$$

and

$$\begin{aligned} \Psi = k \left[-\left(\frac{V - V_2}{b}\right) \left\{ 1 - \frac{Nb}{V - V_2} \frac{1}{\left(1 - e^{-\frac{w}{kT}}\right)} \right\} \log \left\{ 1 - \frac{Nb}{V - V_2} \frac{1}{\left(1 - e^{-\frac{w}{kT}}\right)} \right\} \right. \\ \left. - \frac{V_2}{b} \left\{ 1 - \frac{Nb e^{-\frac{w}{kT}}}{V - V_2 \left(1 - e^{-\frac{w}{kT}}\right)} \right\} \log \left\{ 1 - \frac{Nb e^{-\frac{w}{kT}}}{V - V_2 \left(1 - e^{-\frac{w}{kT}}\right)} \right\} \right. \\ \left. + N \log V + N \log \left\{ 1 + \frac{V_2}{V} \left(1 - e^{-\frac{w}{kT}}\right) \right\} - N \frac{w_1}{kT} + N \log \left\{ \frac{1}{N} \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \right\} \right] \dots \quad (18) \end{aligned}$$

where

$$w = w_2 - w_1 \quad \dots \quad (19)$$

Now, as in the paper (Dutta, 1948), when the field is weak and short-ranged (which is generally taken to be the case for Van der Waal's field), $\frac{V_2}{V}$ and $\frac{w}{kT}$ are small. So the expression for Ψ can be expanded in powers of $\frac{V_2}{V}$ and $(1 - e^{-\frac{w}{kT}})$ and terms containing second and higher powers of $\frac{V_2}{V}$ and $(1 - e^{-\frac{w}{kT}})$ can be neglected. Then we have

$$\Psi = k \left[-\left(\frac{V}{b}\right) \left(1 - \frac{Nb}{V}\right) \log \left(1 - \frac{Nb}{V}\right) + N \log V + N \frac{V_2}{V} \left(1 - e^{-\frac{w}{kT}}\right) - N \frac{w_1}{kT} + N \log \left\{ \frac{1}{N} \frac{(2\pi m k T)^{\frac{3}{2}}}{h^3} \right\} \right]. \quad (20)$$

Then,

$$p = T \left(\frac{\partial \Psi}{\partial V} \right)_T \\ = NkT \left[-\frac{1}{Nb} \log \left(1 - \frac{Nb}{V}\right) - \frac{1}{V} \left\{ \left(\frac{\partial V_2}{\partial V} \right)_T - \frac{V_2}{V} \right\} \left(1 - e^{-\frac{w}{kT}}\right) - \frac{V_2}{V} e^{-\frac{w}{kT}} \frac{1}{kT} \left(\frac{\partial w}{\partial V} \right)_T - \frac{1}{kT} \left(\frac{\partial w_2}{\partial V} \right)_T \right], \dots \quad (21)$$

or

$$p + \frac{\alpha}{V^2} = -\frac{kT}{b} \log \left(1 - \frac{Nb}{V}\right), \quad \dots \quad (22)$$

where

$$\alpha = NkT \left[\left\{ V \left(\frac{\partial V_2}{\partial V} \right)_T - V_2 \right\} \left(1 - e^{-\frac{w}{kT}}\right) + \frac{V_2}{kT} e^{-\frac{w}{kT}} \cdot V \cdot \left(\frac{\partial w}{\partial V} \right)_T + \frac{V_2}{kT} \left(\frac{\partial w_1}{\partial V} \right)_T \right] \dots \quad (23)$$

The equation (21) is the Planck-Saha-Bose equation of state for Van der Waal's gas (Mazumdar, 1929). Now, if the expressions (20) and (21) are expanded in powers of $\left(\frac{Nb}{V}\right)$ and if $\left(\frac{Nb}{V}\right)^2$ and higher powers are neglected, then we have

$$\Psi = Nk \left[\frac{3}{2} \log T + \log V - \frac{1}{2} \frac{Nb}{V} - \frac{V_2}{V} \left(1 - e^{-\frac{w}{kT}}\right) + 1 - \log N - \frac{w_1}{kT} + \log \left\{ \frac{(2\pi m k)^{\frac{3}{2}}}{h^3} \right\} \right], \dots \quad (24)$$

and

$$p + \frac{\alpha}{V^2} = \frac{NkT}{V} \left[1 + \frac{1}{2} \frac{Nb}{V} \right] = \frac{NkT}{V - \beta}, \quad \dots \quad (25)$$

Evidently, β ($= \frac{1}{2}Nb$) is independent of T and V , and α is a function of T , V . Now, as in the paper (Dutta, II, 1948), when suitable assumption for the field is introduced, α can be shown to be independent of T and V up to the first approximation. Then, the equation (24) is the usual form of Van der Waal's equation of State for real gas.

SEC. C. CALCULATIONS OF HIGHER VIRIAL COEFFICIENTS IN THE EQUATIONS OF STATES.

When more accurate expressions for the equations of state for real gases are required, then after starting from the equation (20), the higher virial coefficients of the equations of states can be calculated from considerations of the overlapping of the 'Deckung-sphären', by a method similar to that developed in one of the previous papers (Dutta, 1952) of the author.

SEC. D. REAL GASES OF GENERAL TYPE.

Now, we shall extend our discussions to the case of real gases under a field of force of general types (of course, subject to the restrictions mentioned in the introduction). As suggested in the introduction, the space within the volume is taken to be divided into layers of volumes $V_1, V_2, \dots, V_i, \dots$ at any instant, containing $N_1, N_2, \dots, N_i, \dots$ molecules with potential energies $w_1, w_2, \dots, w_i, \dots$ respectively. The system, under considerations, will be considered as composed of simpler constituent systems, (similar to that considered in the section A), occupying the volumes $V_1, V_2, \dots, V_i, \dots$ and these simpler systems are taken to be in phase-equilibrium. Then, the thermodynamic probability for the constituent system in the i -th layer is

$$\frac{\left(\frac{V_i}{b}\right)!}{\left(\frac{V_i}{b} - N_i\right)! \Pi_i a_{ii}!}, \dots \dots \dots (26)$$

where a_{ii} is the number of molecules in the i -th layer and with the kinetic energy ϵ_i .

Then, the total thermodynamic probability for the entire system, under considerations, is

$$W = \Pi_i \frac{\left(\frac{V_i}{b}\right)!}{\left(\frac{V_i}{b} - N_i\right)! \Pi_i a_{ii}!} \dots \dots \dots (27)$$

This expression (26) for the thermodynamic probability is same as that obtained previously in one of the papers (Dutta, 1951), and so, the expression for usual thermodynamic functions can be obtained by the method, based on Boltzmann's principle, as shown in the paper (*loc. cit.*). The equation of state, obtained in this case, is

$$p(V - \beta') = NkT e^{-\frac{\alpha'}{NkTV}}, \dots \dots \dots (28)$$

where β' , α' in general are functions of temperature and volume. When suitable assumptions about the nature of the field are introduced, then β' reduces to β , and α' can be shown to have the form as required in the equation of states of Dieterici.

SEC. E. MIXTURE OF REAL GASES OF THE SIMPLEST TYPE.

In order to consider the mixture of real gases of the simplest type (similar to those considered in section A), it will be assumed that there are two mutually interpenetrating lattices of lattice-points $\frac{V}{b_1}$ and $\frac{V}{b_2}$ as possible sites for molecules of type (1) and (2) respectively, where b_1, b_2 are the volumes of exclusions of molecules of type (1) and (2) amongst their own type. Now, along with b_1, b_2 , another quantity b_{12} will be introduced to represent the volume of exclusion of one type with respect to the other. Then $\frac{V-N_1b_{12}}{b_2}$ will be taken as number of lattice-points available for distributing molecules of type (2) when molecules of type (1) are already distributed. Similarly, $\frac{V-N_2b_{12}}{b_1}$ are the same for molecules of type (1) when molecules of type (2) have already been distributed.

Then, the thermodynamic probability for the system under consideration, (when the effect of the fields of forces other than the effect of which can be accounted for from the assumption of an average minimum approach can be ignored), is to be written as

$$W_{12} = \frac{\left(\frac{V}{b_1}\right)!}{\left(\frac{V}{b_1} - N_1\right)! \prod_i a_i!} \cdot \frac{\left(\frac{V - N_1 b_{12}}{b_2}\right)!}{\left(\frac{V - N_1 b_{12}}{b_2} - N_2\right)! \prod_i c_i!}, \dots \dots (29)$$

where a_i and c_i are the number of molecules of types (1) and (2) with kinetic energies ϵ_i and η_i respectively.

Here, it is to be noted that the expression (28) is not symmetrical with respect to N_1, N_2, b_1, b_2 characteristic quantities for molecules of types (1) and (2). This is due to the fact that in writing the expression (28), the molecules of type (1) are taken to be distributed first and the others, after that what type of molecules has occupied the volume is not generally known. Moreover, in an equilibrium theory, this fact appears to be of no interest. This selection of molecules of one type, as distributed earlier than the other, is artificial one and has been introduced only for convenience of calculations. On the other hand, from physical considerations, it is expected that the expression for thermodynamic probability should be symmetrical. To symmetricise this expression, we shall take

$$\log W = \frac{1}{2} (\log W_{12} + \log W_{21}), \dots \dots (30)$$

where W_{21} is the thermodynamic probability calculated assuming the molecules of type (2) to be distributed earlier than those of type (1).

The expression for $\log W$, obtained here, is same as that of a previous paper (Dutta, IV, part I, 1951), and so, as in the paper, the expressions for usual thermodynamic functions can be obtained by the method based on Boltzmann principle. The equation of states, obtained in this case, is

$$p = \frac{NkT}{V} \cdot \frac{1}{2} \cdot \left[-\frac{V}{Nb_1} \left\{ \log \left(1 - \frac{c_1 N b_1}{V} \right) + \log \left(1 - \frac{c_1 N b_1}{V - c_2 N b_{12}} \right) \right\} \right. \\ \left. - \frac{V}{N b_2} \left\{ \log \left(1 - \frac{c_2 N b_2}{V} \right) + \log \left(1 - c_2 \frac{N b_2}{V - C_1 N b_{12}} \right) \right\} \right], \dots (31)$$

where

$$c_1 = \frac{N_1}{N}, \quad c_2 = \frac{N_2}{N}, \quad N = N_1 + N_2. \quad \dots \quad (32)$$

This is the form of Planck-Saha-Bose equation of states for mixture of real gases of simplest type.

$$\text{From gases, } \frac{V}{N_1 b} \text{ and } \frac{V}{N_2 b} \gg 1, \quad \dots \quad (33)$$

so that up to the zeroth approximation, we have

$$p = \frac{NkT}{V}, \quad \dots \quad (34)$$

and up to the first approximation, we have

$$\begin{aligned} p &= \frac{NkT}{V} \left[1 + c_1^2 \cdot \frac{1}{2} \frac{Nb_1}{V} + 2c_1 c_2 \cdot \frac{1}{2} \frac{Nb_{12}}{V} + c_2^2 \cdot \frac{1}{2} \frac{Nb_2}{V} \right] \\ &= \frac{NkT}{V} \left[1 + \frac{c_1^2 \beta_1 + 2c_1 c_2 \beta_{12} + c_2^2 \beta_2}{V} \right] \\ &= \frac{NkT}{V} \left[1 + \frac{\beta}{V} \right] = \frac{NkT}{V - \beta}. \quad \dots \quad (35) \end{aligned}$$

This is the usual equation of state for gases of finite dimension, and β has the same form as suggested by Lorentz (1927).

SEC. F. MIXTURE OF VAN DER WAAL'S GASES.

In this case, as in the case of simple Van der Waal's gas, the system, under considerations, will be taken as composed of two simpler constituent systems (of the type considered in the preceding section), one occupying the interior and the other the surface-layers. Then, the thermodynamic probability will be obtained as

$$\log W = \frac{1}{2} (\log W_{12} + \log W_{21}), \quad \dots \quad (36)$$

where

$$\begin{aligned} W_{12} &= \prod_i \frac{\left(\frac{V_i}{b_1}\right)! \cdot \left(\frac{V_i - N_{1i} b_{12}}{b_2}\right)!}{\left(\frac{V_i - N_{1i}}{b_1}\right)! \prod_i a_{1i}! \left(\frac{V_i - N_{1i} b_{12} - N_{2i}}{b_2}\right)! \prod_i c_{1i}!}, \\ &\quad (i = 1, 2). \quad \dots \quad (37) \end{aligned}$$

In the above, N_{11} and N_{21} are number of molecules of types (1) and (2) respectively in the interior; N_{12} and N_{22} are those in the surface-layers, a_{1i} and c_{1i} are the number of molecules of both types in the interior and with kinetic energies ϵ_i and η_i respectively; and a_{2i} and c_{2i} are the similar quantities in the surface-layers.

Here, $\log W$ has the same expression as that obtained in a previous paper (Dutta, IV, part 2, 1951) and so, as in that paper, the expression for usual thermo-

dynamic functions can be obtained by the method, based on Boltzmann's principle. The equation of states, obtained up to the first approximation, is

$$p + \frac{\alpha}{\bar{V}^2} = \frac{NkT}{\bar{V} - \beta}, \quad \dots \quad \dots \quad (38)$$

where

$$\beta = c_1^2 \beta_1 + 2c_1 c_2 \beta_{12} + c_2^2 \beta_2, \quad \dots \quad \dots \quad (39)$$

and

$$\alpha = c_1^2 \alpha_1 + 2c_1 c_2 \alpha_{12} + c_2^2 \alpha_2. \quad \dots \quad \dots \quad (40)$$

This is the Van der Waal equation of states for mixture of real gases as suggested by Lorentz (1927).

SEC. G. MIXTURE OF REAL GASES OF GENERAL TYPES.

Our present discussion can be directly and straightforwardly extended to the case of the mixture of real gases under any field of forces (of course, subject to the restrictions mentioned in the introduction). Here, the system, under consideration, will be taken as composed of a number of simpler constituent systems (of the type, discussed in section E) occupying different potential-energy layers. After introducing suitable symbols similar to those in the sections D and F, the thermodynamic probability can be written as

$$\log W = \frac{1}{2} (\log W_{12} + \log W_{21}), \quad \dots \quad \dots \quad (41)$$

where

$$W_{12} = \prod_i \frac{\left(\frac{V_i}{b_1}\right)!}{\left(\frac{V_i}{b_1} - N_{1i}\right)! \prod_i a_{ii}!} \cdot \frac{\left(\frac{V_i - N_{1i} b_{12}}{b_2}\right)!}{\left(\frac{V_i - N_{1i} b_{12}}{b_2} - N_{2i}\right)! \prod_i c_{ii}!} \quad \dots \quad (42)$$

The expression (40) for the thermodynamic probability is the same as that obtained in the paper (Dutta, IV, part 3, 1951), and so, the expressions for usual thermodynamic functions can be obtained by the method based on Boltzmann's principle, as shown in that paper (*loc. cit.*). The equation of states, as shown there after proper simplifications and assumptions can be put in the form,

$$p = NkT \left\{ c_1 \frac{e^{-\frac{\alpha_1}{NkT\bar{V}}}}{\bar{V} - \gamma_1} + c_2 \frac{e^{-\frac{\alpha_2}{NkT\bar{V}}}}{\bar{V} - \gamma_2} \right\} \dots \quad \dots \quad (43)$$

This is to be regarded as the Dieterici's equation of states for mixture of real gases.

SEC. H. DISTRIBUTION OF IONS OF STRONG ELECTROLYTES IN SOLUTIONS.

Bagchi (1950) has shown that a better and closer fit between the theoretical and the experimental values of the activity-coefficients is obtained, if in the Debye-Hückel theory of strong electrolytes in solutions a new distribution formula is taken in place of that of Boltzmann. The distribution formula assumed by Bagchi is

$$n_+ = \frac{N}{B_+ \exp\left(\frac{\epsilon + \psi}{kT}\right) + 1}, \quad \dots \quad \dots \quad (44)$$

$$n_- = \frac{N}{B_- \exp\left(\frac{\epsilon_- \psi}{kT}\right) + 1}, \quad \dots \quad (45)$$

where n_+ and n_- are concentrations of positive and negative ions of charges ϵ_+ and ϵ_- respectively, where ψ is the electric potential, K is the Boltzmann's constant, T the absolute temperature, and N the total number of ions per unit volume of solution; B_+ and B_- are some suitable constants.

To consider the distributions of ions in solutions, it is to be remembered that in nature, the common electrolytes in the solid-phase exist as crystals. Now, as in the Debye-Hückel theory (Hückel, 1924), if we assume that by introduction of dielectric constants in the calculations of the electric field of the ions, the effect of the solvent can be accounted for, then the dissolution of the crystals of strong electrolytes in solvents may be worked upon as the slowly filling up of the intermediate space within the lattice by a dielectric medium. Now the binding forces between the molecules in a lattice tend to establish an order and the kinetic motions of the molecules try to produce disorder. Now, for the filling up of the intermediate space in a crystal by dielectric medium the binding force will diminish whereas the kinetic motions remain unaltered. As a consequence, the crystal will begin to be distorted and ultimately will appear to be of the type of distorted crystal discussed by Frenkel (1942), i.e., to be a sort of alloys of molecules and holes. Thus, the method, developed above, can be applied for treating the behaviour of ions of strong electrolytes in solutions.

Let $V_1, V_2, \dots, V_i, \dots$ be volumes of potential layers of potentials, $\psi_1, \psi_2, \dots, \psi_i, \dots$ respectively in average. Let, at any instant, $N_1^+, N_2^+, \dots, N_i^+, \dots$ and $N_1^-, N_2^-, \dots, N_i^-, \dots$ be the numbers of positive and negative ions in layers of volumes $V_1, V_2, \dots, V_i, \dots$ respectively. As in previous cases, the entire system will be taken to be composed of simpler constituent systems, occupying different potential layers. Then, as in (39) and (40), the thermodynamic probability will be written as

$$\log W = \frac{1}{2} (\log W_{+-} + \log W_{-+}), \quad \dots \quad (46)$$

where

$$W_{+-} = \prod_i \frac{\left(\frac{V_i}{b_+}\right)! \left(\frac{V_i - N_i^+ b_{+-}}{b_-}\right)}{\left(\frac{V_i}{b_+} - N_i^+\right)! \prod_i \Pi a_{+i}! \left(\frac{V_i + N_i^+ - b_{+-}}{b_-} - N_i^-\right)! \prod_i \Pi a_{-i}!}, \quad \dots \quad (47)$$

and similar expression is for W_{-+} .

Then, by calculations, similar to those in one of the previous papers (Dutta and Bagchi, 1950), one obtains, for concentrations corresponding to potential ψ_i ,

$$n_i^+ = \frac{\frac{1}{b_+}}{B_+ e^{\frac{\epsilon_+ \psi_i}{kT}} + 1} \quad \dots \quad (48)$$

$$n_i^- = \frac{\frac{1}{b_-}}{B_- e^{\frac{\epsilon_- \psi_i}{kT}} + 1} \quad \dots \quad (49)$$

$\frac{1}{b_+}$ and $\frac{1}{b_-}$ are numbers of lattice points per unit volume of the solution. Bagchi

in his papers, written earlier than the paper referred to above, has taken empirically and for simplicity of calculations

$$\frac{1}{b_+} = \frac{1}{b_-} = N = \text{total number of ions present per unit volume (48).}$$

CONCLUSION.

In microscopic theory of matter, we usually consider two types of problems, viz., one, of the crystals and the like, is of perfect order, and the other, of gases and the like, is of perfect randomness. The transitions from states of perfect order to perfect disorder are not yet clearly visualised in the microscopic theories, up till now. The quasi-lattice-theory for real gases and for ions of strong electrolytes in solution, as developed in the present paper, along with that for solid of Frenkel and others and with that for liquid of Lennard-Jones and others, shows the possibility of divisions of an unified picture for the structure of matter in different phases.

SUMMARY.

In the present paper, a quasi-lattice theory, similar to the theory of solids developed by Frenkel and others, and to that of liquid by Lennard-Jones and Devonshire, has been developed for real gases and ions of strong-electrolytes in solutions. In the present theory, the systems of real gases and ions of strong electrolytes in solutions are taken as sorts of alloys of the molecules (atoms or ions) and the holes. From this picture and by the method of Planck and Lorentz based on Boltzmann's principle, expressions for usual thermodynamic functions and laws of microscopic distributions have been deduced.

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