

# ON EQUATION OF STATE OF REAL GASES.

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## I. INTRODUCTION.

In several previous papers [Dutta, I, (1947), II, (1948), III and IV, (1951)], by applying a new statistical method of calculation, the general behaviour of real gases have been investigated. As in the usual treatment the peculiarities of a real gas as distinguished from the ideal gas have been attributed to the finite volume of the molecules and to the effects of fields of forces, e.g., of cohesion, etc. A distribution function has been constructed by considering the distributions of the representative points of the molecules in the configurational and momenta spaces separately. In the configurational space a concept of exclusion has been introduced by assuming this space to be made up of cells (of exclusion) each of volume  $b$  which can remain either vacant or be filled by one molecule only. This yields the partial thermodynamic probability corresponding to the configurational space. The momenta space is similarly divided to cells, each of volume  $\frac{h^3}{b}$ , and the corresponding partial thermo-

dynamic probability has been written down in the usual way. The product of these two partial thermodynamic probabilities is taken as the thermodynamic probability of the assembly constituting the real gas under study.

In the present paper the Planck-Saha-Bose equation of state has been worked out for Van der Waal's fields of forces. The result has been made more accurate by taking into consideration the overlapping of the volumes of exclusion by a method similar to Boltzmann's. Further improvement has been sought to be introduced by following a somewhat more rigorous method of calculation. The results of the usual theory are obtained similar in form but with slightly altered coefficient.

## 2. DESCRIPTION OF THE ASSEMBLY.

The assembly under consideration consists of  $N$  non-dissociating and non-associating molecules, each commanding a volume of exclusion of magnitude ' $b$ '. The assembly is enclosed within a volume  $V$ .

Now, the effect of cohesion between molecules manifests itself as the formation of a very thin surface layer of potential energy slightly greater than that of the interior. Let the interior be of volume  $V_1$ , and of potential energy  $w_1$ , and the surface layer of volume  $V_2$ , and of potential energy  $w_2$ . Now  $V_2 \ll V_1$ ,  $w_1 < w_2$ .

After this, the layer will be divided into cells of volume ' $b$ ' as usual. It is assumed that  $b \ll V_1, V_2$ . Let  $N_1, N_2$  be numbers of molecules in the interior, and in the surface-layer respectively in any complexion. Let  $a_i$  represent the number of molecules with energy  $\epsilon_i$ .

## 3. CALCULATIONS.

It has been shown that, by following the arguments set forth in section 1, the thermodynamic probability of an assembly constituting a real gas can be written as

$$W = \frac{\left(\frac{V_1}{b}\right)! \left(\frac{V_2}{b}\right)! \dots N!}{N_1! \left(\frac{V_1}{b} - N_1\right)! N_2! \left(\frac{V_2}{b} - N_2\right)! \dots \pi a_i!} \quad (1)$$

As shown in a previous paper, (Dutta, II, 1948), we have the following:

$$\left. \begin{aligned} N_1 &= \frac{V_1}{b} e^{-\nu - \frac{w_1}{kT}}, \\ N_2 &= \frac{V_2}{b} e^{-\nu - \frac{w_2}{kT}}, \\ a_i &= e^{-\lambda - \frac{\epsilon_i}{kT}}, \end{aligned} \right\} \dots \dots \dots \dots \dots \dots \dots \quad (2)$$

where

$$\left. \begin{aligned} \lambda &= \log \left\{ \frac{1}{N} \frac{b}{h^3} (2\pi m kT)^{\frac{3}{2}} \right\} \\ \nu &= \log \left\{ \frac{V_1 e^{-\frac{w_1}{kT}} + V_2 e^{-\frac{w_2}{kT}}}{Nb} \right\} \end{aligned} \right\} \dots \dots \dots \dots \dots \dots \dots \quad (3)$$

As in the same paper, the following expressions for important thermodynamic functions are also easily obtained.

$$\begin{aligned} S &= K \left[ - \left(\frac{V_1}{b}\right) \left(1 - \frac{N b e^{-\frac{w_1}{kT}}}{V_1 e^{-\frac{w_1}{kT}} + V_2 e^{-\frac{w_2}{kT}}}\right) \log \left(1 - \frac{N b e^{-\frac{w_1}{kT}}}{V_1 e^{-\frac{w_1}{kT}} + V_2 e^{-\frac{w_2}{kT}}}\right) \right. \\ &\quad - \left(\frac{V_2}{b}\right) \left(1 - \frac{N b e^{-\frac{w_2}{kT}}}{V_1 e^{-\frac{w_1}{kT}} + V_2 e^{-\frac{w_2}{kT}}}\right) \log \left(1 - \frac{N b e^{-\frac{w_2}{kT}}}{V_1 e^{-\frac{w_1}{kT}} + V_2 e^{-\frac{w_2}{kT}}}\right) \\ &\quad \left. + N \lambda + N \nu + \frac{E}{kT} + N \log N \right] \dots \dots \dots \dots \dots \quad (4) \end{aligned}$$

and,

$$\begin{aligned} \psi &= K \left[ - \left(\frac{V - V_2}{b}\right) \left\{ 1 - \frac{N b}{V - V_2 (1 - e^{-\frac{w}{kT}})} \right\} \log \left\{ 1 - \frac{N b}{V - V_2 (1 - e^{-\frac{w}{kT}})} \right\} \right. \\ &\quad - \left(\frac{V_2}{b}\right) \left\{ 1 - \frac{N b e^{-\frac{w}{kT}}}{V - V_2 (1 - e^{-\frac{w}{kT}})} \right\} \log \left\{ 1 - \frac{N b e^{-\frac{w}{kT}}}{V - V_2 (1 - e^{-\frac{w}{kT}})} \right\} \\ &\quad + N \log \left\{ 1 + \frac{V_2}{V} (1 - e^{-\frac{w}{kT}}) \right\} \\ &\quad \left. - N \frac{w_1}{kT} + N \log \left\{ \frac{1}{N} \frac{(2\pi m kT)^{\frac{3}{2}}}{h^3} \right\} \right] \dots \dots \dots \dots \dots \quad (5) \end{aligned}$$

where

$$w = w_2 - w_1. \quad \dots \quad (6)$$

Now, if the field be assumed to be weak and short-ranged (which is generally taken to be true for Van der Waal's field), then  $\frac{V_2}{V}$  and  $w$  are small. So the expressions for thermodynamic functions can be expanded in a power series of  $\frac{V_2}{V}$  and  $(1 - e^{-\frac{w}{kT}})$ , and terms involving powers of  $\frac{V_2}{V}$  and  $(1 - e^{-\frac{w}{kT}})$  higher than the first may be neglected.

Then,

$$\psi = K \left[ -\left(\frac{V}{b}\right) \left(1 - \frac{Nb}{V}\right) \log \left(1 - \frac{Nb}{V}\right) + N \log V + N \frac{V_2}{V} \left(1 - e^{-\frac{w}{kT}}\right) - N \frac{w_1}{kT} + N \log \left\{ \frac{1}{N} \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \right\} \right] \quad \dots \quad (7)$$

Now, from the well-known thermodynamic relation,

$$p = T \left( \frac{\partial \psi}{\partial V} \right)_T$$

we have

$$p = NkT \left[ -\frac{1}{Nb} \log \left(1 - \frac{Nb}{V}\right) - \frac{1}{V} \left\{ \left( \frac{\partial V_2}{\partial V} \right)_T - \frac{V_2}{V} \right\} \left(1 - e^{-\frac{w}{kT}}\right) - \frac{V_2}{V} e^{-\frac{w}{kT}} \frac{1}{kT} \left( \frac{\partial w}{\partial V} \right)_T - \frac{1}{kT} \left( \frac{\partial w_1}{\partial V} \right)_T \right] \quad \dots \quad (8)$$

or

$$p + \frac{\alpha}{V^2} = -\frac{kT}{b} \log \left(1 - \frac{Nb}{V}\right) \quad \dots \quad (8a)$$

where,

$$\alpha = NkT \left[ \left\{ V \left( \frac{\partial V_2}{\partial V} \right)_T - V_2 \right\} \left(1 - e^{-\frac{w}{kT}}\right) + \frac{V_2}{kT} e^{-\frac{w}{kT}} V \left( \frac{\partial w}{\partial V} \right)_T + \frac{1}{kT} \left( \frac{\partial w_1}{\partial V} \right)_T \right] \quad \dots \quad (9)$$

It should be noted that the expression for  $\alpha$ , obtained here, is same as that for  $\alpha$  in a previous paper (Dutta, II, 1948), and it is shown there that  $\alpha$  is proportional to  $N^2$ . So,  $\frac{\alpha}{V^2}$  is the usual Van der Waal's correction for pressure. The equation (8a) is the Planck-Saha-Bose equation of state for real gas (Planck, 1908; Saha and Bose, 1918).

#### 4. A MORE ACCURATE SPECIFICATION OF $b$ .

Now, ' $b$ ', the volume of exclusion of each molecule means the volume which the centre of any molecule commands exclusively of any other. In papers referred to the above  $b$  has been taken to be independent of the volume and the temperature and ultimately taken to be equal to the volume of a sphere about the centre of a molecule with a radius equal to the diameter of a molecule. This sphere will be

referred as the covering sphere (Deckungssphären) of a molecule. But a little reflection will show that it is only a very rough approximation of the reality. It is a fact that the centre of a molecule of finite dimension cannot come within the covering sphere of the other, but it can come to such a close position that it is on the surface of a covering sphere of the other. Now, when the centre of one molecule comes sufficiently near to the surface of the covering sphere of the other, portions of their covering spheres will overlap. So, 'b', which represents the average volume of covering sphere of one molecule left exclusively for it, cannot be equal to that of the covering sphere. If the volume of the covering sphere be denoted by  $b_0$  then  $b$  the average value exclusively commanded by each molecule may plausibly be written as

$$b = b_0 \left\{ 1 - f \left( \frac{N}{V}, T, b_0 \right) \right\} \dots \dots \dots (10)$$

Obviously, the volume of each cell of configurational space in present calculations of previous sections should be taken as this  $b$ .

It will be assumed that the function  $f$  can approximately be represented as  $\frac{Nb_0}{V} \gamma$ , so that the above relation may be approximately replaced by

$$b = b_0 \left( 1 - \gamma \frac{Nb_0}{V} \right) \dots \dots \dots (11)$$

Here,  $\gamma$  has been introduced for taking into account the two factors, i.e. that the portion of the volume  $V$ , really occupied by matter is not  $Nb_0$ , but something less than this, and secondly, that some portions of this cannot really be occupied due to the geometry of shape playing a rôle in packing.

#### 5. CALCULATIONS WITH 'b'.

Now, for simplicity, we shall first consider the case in which the field is absent. The exclusion to the cases of Van der Waal's field of force or of the like appears to be easy and straightforward. Then, in absence of any field of force, it yields

$$\begin{aligned} \psi &= k \left[ - \left( \frac{V}{b} \right) \left( 1 - \frac{Nb}{V} \right) \log \left( 1 - \frac{Nb}{V} \right) + N \log V + N \log \left\{ \frac{1}{N} \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \right\} \right] \\ &= Nk \left[ \log V - \frac{1}{2} \left( \frac{Nb}{V} \right) - \frac{1}{6} \left( \frac{Nb}{V} \right)^2 - \frac{1}{12} \left( \frac{Nb}{V} \right)^3 - \dots \right. \\ &\quad \left. + \log \left\{ \frac{1}{N} \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \right\} \right] \dots \dots \dots (12) \end{aligned}$$

Retaining up to  $\left( \frac{Nb_0}{V} \right)^2$  we have,

$$\psi = Nk \left[ \log V - \frac{1}{2} \frac{Nb_0}{V} - \frac{1-3\gamma}{6} \left( \frac{Nb_0}{V} \right)^2 + 1 + \log \left\{ \frac{1}{N} \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \right\} \right] \dots (13)$$

and

$$\begin{aligned} p &= T \left( \frac{\partial \psi}{\partial V} \right)_T \\ &= \frac{NkT}{V} \left[ 1 + \frac{(\frac{1}{2}Nb_0)}{V} + 4 \frac{1-3\gamma}{3} \frac{(\frac{1}{2}Nb_0)^2}{V^2} \right] \dots \dots (14) \end{aligned}$$

6. EVALUATION OF  $\gamma$ .

To be convinced of the potentiality of the present method,  $\gamma$  has been at first calculated on using the method referred above, and on following the basic Boltzmann's ideas of overlapping of covering spheres. (Boltzmann, 1923.) Of course, slight modifications are introduced to fit it with the formalism of the present scheme. The calculation yields the same value for the second virial coefficient as obtained by Boltzmann. A close scrutiny of the method shows that the method is open to serious objection. In a later section, we have given a new method for calculation of  $\gamma$ , which, though approximate, is free from objectionable features just mentioned.

To evaluate  $\gamma$  up to first approximation, it will be assumed that the assembly is of such a density that the frequencies of encounters (better, overlapping) of higher order than the second is negligibly small, and their contributions will be neglected here. Only, simultaneously overlapping of covering spheres of a pair of molecule will be considered here. The extension of present discussions of those cases where simultaneous overlapping of covering spheres of higher order appears to be straightforward and will be developed hereafter.

Evidently, there will be an overlapping of covering spheres where the distance between the centres of any two molecules is less than the diameter  $2d$ , where  $d$  represents the diameter of a molecule. Let the attention be focussed upon the centre of a particular molecule, and let the centre of any other molecule come to a distance  $x$  from that of the molecule, where  $d < x < 2d$ . Now the portion of the volume of any of the covering spheres which is left exclusively to the molecule under consideration is the volume of the larger segment of the covering sphere cut up by the common plane-section while the remaining smaller segment is to be taken as the volume lost due to overlapping. The portion of the volume of the covering sphere of the molecule under consideration, overlapped by other, can be written after Boltzmann, as

$$K_n = \pi \int_{\frac{x}{2}}^d (d^2 - y^2) dy = \pi \left( \frac{2d^3}{3} - \frac{d^2x}{2} + \frac{x^3}{4} \right) \dots \dots \dots (15)$$

Then, the frequency of overlapping under the conditions that the centre of one molecule is at distance  $(x, x+dx)$  from the other may be taken as

$$p_x = \frac{4\pi x^2 dx}{V} \cdot n \dots \dots \dots (16)$$

Let us assume that with the centre of the colliding molecule lying within distance  $(x, x+dx)$  from the centre of found molecules it is geometrically possible for only  $n$  molecules to participate in overlapping with a given single molecule. We shall leave to  $n$  the theoretical possibility of varying from 0 to  $N$ .

The frequency of overlapping in all layers between  $x$  and  $x+dx$  round all molecules is then

$$dn_x = \frac{4\pi x^2 dx}{V} n \cdot \frac{n}{2} \dots \dots \dots (17)$$

since in pairing each molecule is counted twice.

So, the expected value of volume overlapped in the covering spheres of pair of molecules, (when  $n$  molecules are participating or having tendency of overlapping), is

$$\begin{aligned} Z_n &= \int 2K_x dn_x = \frac{1}{2} \frac{\pi^2 n^2}{V} \int_d^{2d} 2 \left( \frac{8d^3}{3} - 2d^2x + \frac{x^3}{3} \right) x^2 dx \\ &= \frac{17}{16} \frac{n^2 b_0^2}{V} = 2n^2 b' \dots \dots \dots (18) \end{aligned}$$

where

$$b' = \frac{17 b_0^2}{32 V} \quad \dots \quad \dots \quad \dots \quad \dots \quad (19)$$

Now, in different complexions, different numbers of molecules will participate or will have tendency to participate in overlapping. In different complexions, the number of pair of molecules participating or having tendency to participate varies from 1 to  $\frac{N}{2}$ . So, to calculate the required value of  $\gamma$  average should be taken amongst all those cases.

Then, average volume, lost in overlapping, per pair, is

$$\bar{Z} = \frac{\sum_1^{\frac{N}{2}} n^2 \cdot 2b'}{\sum_1^{\frac{N}{2}} n} = \frac{\frac{1}{3} \left(\frac{N}{2}\right)^3 \cdot 2b'}{\frac{1}{2} \left(\frac{N}{2}\right)^2} = \frac{1}{3} N \cdot 2b' \text{ (approximately)} \quad \dots \quad \dots \quad (20)$$

Then, average volume, lost in overlapping, per individual, is

$$\gamma \frac{N b_0^2}{V} = \frac{1}{2} \cdot \frac{1}{3} \cdot N \cdot 2b' = \frac{1}{3} \cdot \frac{17 N b_0^2}{32 V} \quad \dots \quad \dots \quad \dots \quad (21)$$

$$\therefore \gamma = \frac{1}{3} \cdot \frac{17}{32} = \frac{17}{96} \quad \dots \quad \dots \quad \dots \quad \dots \quad (22)$$

Then, from equation (13) and (14), it follows that

$$\psi = Nk \left[ \log V - \frac{\frac{1}{2} N b_0}{V} - \frac{5}{16} \frac{(\frac{1}{2} N b_0)^2}{V^2} + 1 + \log \left\{ \frac{1}{N} \frac{(2\pi m k T)^{\frac{3}{2}}}{h^3} \right\} \right] \quad \dots \quad \dots \quad (23)$$

and

$$\begin{aligned} p &= \frac{NkT}{V} \left[ 1 + \frac{\frac{1}{2} N b_0}{V} + \frac{5}{8} \frac{(\frac{1}{2} N b_0)^2}{V^2} \right] \\ &= \frac{NkT}{V} \left[ 1 + \frac{\beta}{V} + \frac{5}{8} \frac{\beta^2}{V^2} \right] \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (24) \end{aligned}$$

This equation is same as that which Boltzmann (1923), and others obtained by different methods.

Now, in presence of Van der Waal's field of force, proceeding as in above from equations (7), (8) and (8a), this equation becomes

$$p + \frac{\alpha}{V^2} = \frac{NkT}{V} \left[ 1 + \frac{\beta}{V} + \frac{5}{8} \frac{\beta^2}{V^2} \right] \quad \dots \quad \dots \quad \dots \quad (25)$$

*Comparison of the method, developed above with the method of Boltzmann.*

Before proceeding further, it appears to be necessary and, also, illuminating to analyse the method, developed above, and one of the other well-known methods, which is due to Boltzmann, for considering the effect of overlapping of covering spheres, and to be convinced of similarity and difference between them. To calculate the effect of volume exclusion for covering spheres and of their overlapping, Boltzmann constructed the expression for thermodynamic probability on starting

from the supposition that the volume is initially empty and is then filled by introducing molecules one by one. According to him, the contribution to the expression of the thermodynamic probability by the first molecule entering in the volume is taken to be a factor  $V$ , that by the second is taken as  $V-b_0$ , that by the third as  $V-2b_0+Z_2$ , that of the fourth is  $V-3b_0+Z_3$  and so on, where  $Z_n$  has interpretations similar to (18) above. The product of all these factors is taken as the correction for the effect of the volume exclusion together with the overlapping of covering spheres of molecules.

But, this supposition of the introducing molecules one by one in the volume considered is very artificial, and is not consistent with the formalism of the usual method of Planck and Lorentz based on Boltzmann hypothesis. Now, if the formalism of the usual statistical methods, based on Boltzmann hypothesis, is strictly adhered to then what Boltzmann has done will appear to be equivalent to taking respective consideration of the overlapping of covering spheres of one molecule by no molecule, by one molecule only, by two only and so on. Moreover, as the effects of overlapping by no molecule, by one only, by two only, and so on, are taken to be involved equally in calculations, so the occurrences of overlapping of covering spheres of one molecule by no molecule, by one only by two only, and so on, as it appears, are tacitly assumed to be equally frequent. Now, the method, developed in previous article, are based on these two hypothesis and so is equivalent to that of Boltzmann in principles, and yields same results as it is to be expected.

*Criticism of the above and suggestion of a new scheme of calculation.*

The methods, developed and discussed in the above, appear to be open mainly to two objections. Firstly, in those methods, overlapping of covering sphere of one molecule by molecules where  $n$  is different from  $N$ , and varies from 0 to  $N$ , has been considered. A little reflection will show that this way of approach is very artificial. As the total number of molecules in volume is always  $N$ , and as there are random distributions amongst them in different complexions, so there is no justification for taking  $n$ , the number of molecules participating or having tendency to participate in overlapping, different from  $N-1$  or  $N$  as  $1 \ll N$ . So, the frequency (or, better probability) of the layer between  $x$  and  $x+dx$  about the centre of a particular molecule, being occupied, should be taken as

$$dn_x = \frac{4\pi x^2 dx}{V} \cdot N. \quad \dots \dots \dots (26)$$

and, so, the expected value of volume overlapped from the covering sphere of that molecule is to be taken as

$$\begin{aligned} Z_N &= \frac{\pi^2 N}{V} \int_a^{2d} \left( \frac{8d^3}{3} - 2d^2x + \frac{x^3}{6} \right) x^2 dx \\ &= \frac{17 N b_0^2}{16 V} = 2b'' \quad \dots \dots \dots (27) \end{aligned}$$

where

$$b'' = \frac{17 N_0 b_0^2}{32 V}. \quad \dots \dots \dots (28)$$

Secondly, in averaging process of  $\bar{Z}$  in the above, considerable contribution has been taken even for very improbable occurrences. This is highly objectionable. In this connection it is to be remembered that, in some complexions, there will be no overlapping, in some complexions, there will be overlapping amongst one pair only, in some amongst two only, etc., but the frequencies of occurrence of the complexions

of different types are different, as will be clear from the discussions given below. So proper considerations should be taken for this fact, and the average taking in (20) should be a weighted average. For this, the probability (or frequency) of occurrences of complexions with no overlapping, those with one pair only, etc., should be calculated first.

In forming some ideas about these probabilities of frequencies, as usual, the *a priori* probability of any particle to occur in a volume  $\Delta V$  will be taken as  $\frac{\Delta V}{V}$ .

So, *a priori* probability of the centre of any molecule occurring within a cell in the configurational space is to be taken as  $b/V$ . The volume of a sphere with radius equal to the diameter of the covering sphere is  $8b$ . There is no overlapping of covering spheres of a particular molecule, if centre of no other molecule come within a distance  $d$  and  $2d$  from the centre of the particular molecule. In the present formalism of distribution of representative points of molecules in cells of configurational space this fact can be roughly expressed as there is no overlapping of covering sphere of a particular molecule, if 7 cells, contiguous to cell occupied by the representative point of each molecule, remain vacant. For this calculation, no distinction (which is expected to give higher order terms) will be made between  $b$  and  $b_0$ . Thus, the number of arrangements in configurational space, without any overlapping of covering sphere is

$$\frac{V}{b} \left( \frac{V-8b}{b} \right) \dots \left( \frac{V-\overline{N-1}8b}{b} \right) = \frac{8^N \left( \frac{V}{8b} \right)!}{N! \left( \frac{V}{8b} - N \right)!}$$

As molecules are perfectly similar such that permutations amongst themselves will give no new arrangement, so the number of complexions is

$$\frac{8^N \left( \frac{V}{8b} \right)!}{N! \left( \frac{V}{8b} - N \right)!}$$

So, the probability of occurrences of no overlapping is

$$\begin{aligned} \frac{\left( \frac{V}{8b} \right)! 8^N}{N! \left( \frac{V}{8b} - N \right)!} \cdot \left( \frac{b}{V} \right)^N &\cong \frac{\left( \frac{V}{8b} \right)^{\frac{V}{8b}} \cdot 8^N}{N^N \left( \frac{V}{8b} - N \right)^{\frac{V}{8b} - N}} \left( \frac{b}{V} \right)^N \\ &= \frac{1}{N^N \left( 1 - N \cdot \frac{8b}{V} \right)^{\frac{V}{8b} - N}} \cong \frac{1}{N^N} \quad \dots (20) \end{aligned}$$

Now, to calculate the number of complexions in which there is overlapping amongst one pair of molecules only,  $(N-1)$  representative points of  $(N-1)$  molecules are distributed in such a way that 7 contiguous cells about each cell occupied by any one of  $(N-1)$  representative points are vacant. The number of way, in which this is possible, is

$$\frac{V}{b} \left( \frac{V-8b}{b} \right) \left( \frac{V-2 \cdot 8b}{b} \right) \dots \left( \frac{V-\overline{N-2} \cdot 8b}{b} \right) = \frac{8^{N-1} \cdot \left( \frac{V}{8b} \right)!}{\left( \frac{V}{8b} - N - 1 \right)!}$$



Now, the remaining representative point is to be imagined to be coupled with one of the  $(N-1)$  representative points, considered above, in such a way, that it occupies one of the 7 cells, contiguous to one of the cells occupied by one so that the total number of arrangement becomes

$$\frac{7 \cdot \left(\frac{V}{8b}\right)! \cdot 8^{N-1}}{\left(\frac{V}{8b} - N + 1\right)!}$$

Now, as the permutation of representative points amongst themselves will cause no difference, so the number of complexions will be

$$\frac{7 \cdot \left(\frac{V}{8b}\right)! \cdot 8^{N-1}}{N! \left(\frac{V}{8b} - N + 1\right)!}$$

So, the probability of occurrences of complexions having overlapping is

$$\begin{aligned} \frac{7 \cdot 8^{N-1} \cdot \left(\frac{V}{8b}\right)!}{N! \left(\frac{V}{8b} - N + 1\right)!} \left(\frac{b}{V}\right)^{N-1} \cdot \left(\frac{b}{8b}\right) &= \frac{7}{8^2} \cdot \frac{1}{N^N} \cdot \frac{1}{\left(1 - \frac{N-1}{V} \cdot 8b\right)^{\frac{V}{8b} - N + 1}} \\ &\approx \frac{1}{N^N} \cdot \frac{7}{64} \cdot \dots \dots \dots \dots \quad (30) \end{aligned}$$

Similarly, the probability of occurrences of those complexions having overlapping amongst  $r$  pair only is

$$\frac{7^r 8^{N-r} \left(\frac{V}{8b}\right)!}{N! \left(\frac{V}{8b} - N + r\right)!} \cdot \left(\frac{b}{V}\right)^{N-r} \left(\frac{b}{8b}\right)^r \approx \left(\frac{7}{64}\right)^r \frac{1}{N^N} \cdot \dots \dots \quad (31)$$

So, the average value of volume lost from covering spheres of each pair of molecules due to overlapping is

$$\begin{aligned} \bar{Z} &= \frac{\sum_{r=0}^N \frac{1}{N^N} \left\{ \left(\frac{7}{64}\right)^r \cdot 4r \cdot b^r \right\}}{\sum_{r=0}^N \frac{1}{N^N} \left(\frac{7}{64}\right)^r} \\ &= \frac{\sum_{r=0}^{\infty} r \left(\frac{7}{64}\right)^r}{\sum_{r=0}^{\infty} \left(\frac{7}{64}\right)^r} 4b^r \end{aligned}$$

$$\begin{aligned} & \frac{\frac{7}{64} \frac{1}{\left(1 - \frac{7}{64}\right)^2}}{\frac{1}{1 - \frac{7}{64}}} \cdot 4b'' \\ & = \frac{7}{64} \cdot \frac{64}{57} \cdot 4b'' = \frac{28}{57} b''. \quad \dots \quad \dots \quad \dots \quad \dots \quad (32) \end{aligned}$$

So, the average value of volume lost from covering spheres due to overlapping per molecule is

$$\frac{14}{57} b''. \quad \dots \quad \dots \quad \dots \quad \dots \quad (33)$$

$$\therefore b = b_0 - \frac{14}{57} b'' = b_0 \left( 1 - \frac{14}{57} \cdot \frac{17 N b_0}{32 V} \right)$$

and so,

$$\gamma = \frac{14}{57} \cdot \frac{17}{32} \quad \dots \quad \dots \quad \dots \quad \dots \quad (34)$$

Then,

$$\begin{aligned} p &= \frac{NKT}{V} \left[ 1 + \frac{\frac{1}{2} N b_0}{V} + \frac{5}{8} \left( 1 + \frac{17}{57} \right) \frac{\left( \frac{1}{2} N b_0 \right)^2}{V^2} \right] \\ &= \frac{NKT}{V} \left[ 1 + \frac{\beta}{V} + \frac{5}{8} \left( 1 + \frac{17}{57} \right) \frac{\beta^2}{V^2} \right]. \quad \dots \quad \dots \quad \dots \quad (35) \end{aligned}$$

In presence of Van der Waal's field of force this becomes

$$p + \frac{\alpha}{V^2} = \frac{NKT}{V} \left[ 1 + \frac{\beta}{V} + \frac{5}{8} \left( 1 + \frac{17}{57} \right) \frac{\beta^2}{V^2} \right]. \quad \dots \quad \dots \quad \dots \quad (36)$$

The second virial coefficient (i.e. coefficient of  $\frac{\beta^2}{V^2}$ ) as obtained here, differs from the usually accepted value by 30% only.

#### CONCLUSION.

The value of virial coefficient obtained by Boltzmann and others, which is believed to be correct is  $\frac{5}{8}$ . The calculation in section 8, which takes account of frequency of occurrence is expected to yield a value, somewhat more accurate than that obtained by Boltzmann. However, the present line of thought at least indicates that calculations improving the hitherto accepted result,  $\frac{5}{8}$ , are possible. Anyway, detailed information from properly designed experiments, together with a thorough and minute revision of the usual arguments probably in the light of the discussion made in the paper, is expected to throw more light on this subject.

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## SUMMARY.

The present paper is divided mainly into two parts. In the first part, the Planck-Saha-Bose Equation of State, which will be taken as basis for deducing more accurate equations of state in later development, has been obtained by the statistical method, developed by the author in some of his previous papers. In the second part, on taking the overlapping of the Deckungsphären into consideration by the above method after suitable modifications, the usually accepted value of the second virial coefficient of the equation of state has been obtained. After this, the relation (or better equivalence) between this method and that of Boltzmann has been discussed, and some of the unsatisfactory features, common in both the methods, have been pointed out. Finally a modified method, which is free from the above mentioned unsatisfactory features up to some extent, has been suggested, and a value of the second virial coefficient obtained by rough calculations from this method is, of course, found to deviate from the accepted value by about 30%. But from the theoretical discussions, put forward in the paper, the value obtained here, appears to be more reliable, and is expected to be verified when more accurately designed experiments will be performed.

## REFERENCES.

- Boltzmann, L. (1923). Vorlesungen über Gas-Theorie, 165-76.  
Dutta, M. (1947). Imperfect Gases after Fermi's Model, I. *Proc. Nat. Inst. Sci. Ind.*, **13**, 247.  
————— (1948). Imperfect Gases after Fermi's Model, II. *Ibid.*, **14**, 163.  
————— (1951). Imperfect Gases after Fermi's Model, III. *Ibid.*, **17**, 27.  
————— (1951). Imperfect Gases after Fermi's Model, IV. *Ibid.*, **17**, 445.  
Planck, M. (1908). Über der Kanonische Zustandgleichung Einatomiger Gase. *Sitz. u. Ber. Kgl. Preuss Akad.*, p. 633.  
Saha, M. N. and Basu, S. N. (1918). On the Influence of Finite volume of Molecules on the Equation of State. *Phil. Mag.*, **16**, 199.