

ON A TREATMENT OF IMPERFECT GAS AFTER FERMI'S MODEL

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(Received December 12, 1946 ; read April 4, 1947)

ABSTRACT.

In this paper, a statistical theory of imperfect gases has been developed by application of a principle analogous to Pauli's Exclusion Principle and method of Fermi. The equation of state as given by Saha and Bose has been deduced. Further, Van der Waal's equation up to first approximation has been obtained by accounting for the boundary effect and cohesion by equivalent increase in total volume.

I. INTRODUCTION.

The method of counting the total number of thermodynamic complexions of a set of particles in phase-space, and then, of introduction of entropy, after Planck, by application of Boltzmann's principle is the simplest and finest of all the methods, used in the statistical theories of thermodynamics. This method is not only successful in explaining the behaviour of the ideal gas completely but is also equally successful in quantum statistics. Few attempts have, however, to our knowledge, been so far made to extend this method to the theory of an imperfect gas, or to that of a liquid. The present work represents an endeavour to apply this method to the theory of an imperfect gas. We have here obtained for an imperfect gas a new equation of state from which the equation of state of an ideal gas as well as that of Van der Waal's gas follows by suitable approximation. We start with the accepted view that the physical behaviour of an imperfect gas is attributable to two factors, namely, the finite size of the molecules, and the forces of molecular cohesion. We propose, accordingly, to develop our theory in two stages, in the first of which account is taken of the finite size of the molecules, and in the second, of the cohesive forces.

In the present method, the only dynamical property of particle, which plays an important rôle in distribution, is its energy. Now in the case of an imperfect gas, the total energy is separable into kinetic energy (depending on momenta only) and potential energy (depending on configurational co-ordinates only). (Fowler 1936.) As the distribution of the particles is random with respect to kinetic energy and potential energy separately (we mean thereby that the positional and the momenta co-ordinates of the particles are unconnected), the positional and the momentum space can be considered separately with much convenience. The product of the thermodynamic probabilities corresponding to the two spaces will evidently give the total thermodynamic probability.

2. EFFECT OF FINITE DIMENSION OF MOLECULES.

We consider an assembly of N molecules, in an enclosure of volume V , each of which is supposed to possess a rigid volume b of exclusion. There is no association or dissociation in the assembly.

Now, the total volume V is divided into space-cells of volume b , the number of such cells is then V/b and is evidently a large number, b being small. Then, the effect of volume of exclusion can be stated as, a cell of the physical space cannot

contain more than one particle. The cell may be vacant or occupied by only one particle.

Then, the total number of ways in which N molecules may be distributed amongst the (V/b) cells is

$$\frac{(V/b)!}{N!(V/b-N)!}$$

Turning now to the consideration of the distribution of N molecules in momenta space, we remark that the volume of a cell in phase-space being h^3 , the volume of a cell in momenta space is to be taken as h^3/b , since the volume of a cell in the physical space is, by hypothesis, b . As the energy of a molecule is given by

$$\epsilon = \frac{1}{2m} (p_1^2 + p_2^2 + p_3^2),$$

so the number of cells h^3/b in the microcanonical layer

$$(\epsilon_r, \epsilon_r + d\epsilon) = \frac{b}{h^3} \cdot 2\pi (2m)^{\frac{3}{2}} \epsilon_r^{-\frac{1}{2}} d\epsilon.$$

Now, if a_r denotes number of molecules in the layer $(\epsilon_r, \epsilon_r + d\epsilon)$ then the number of ways, in which molecules may be distributed, is

$$\frac{N!}{a_1! a_2! \dots a_r! \dots}$$

where $\sum a_r = N, \quad \sum a_r \epsilon_r = E.$

Then the thermodynamic probability is

$$W = \frac{(V/b)!}{(V/b-N)! N!} \cdot \frac{N!}{a_1! a_2! \dots a_r! \dots}$$

To get the entropy, this expression is to be maximised, subject to above-mentioned restrictions.

This gives

$$a_r = e^{-\lambda - \mu \epsilon_r},$$

where λ, μ are, as usual, undetermined constants

and $S = k [V/b \log V/b - (V/b-N) \log (V/b-N) + N\lambda + \mu E].$

Now,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_V = k\mu, \quad \therefore \mu = \frac{1}{kT}$$

and

$$N = \sum a_r = \sum_r e^{-\lambda - \epsilon_r/kT} = e^{-\lambda} \iiint_{-\infty}^{\infty} e^{-(p_1^2 + p_2^2 + p_3^2)/2mkT} \cdot \frac{dp_1 dp_2 dp_3}{h^3/b}$$

or

$$\lambda = \log \left\{ \frac{b}{N h^3} (2\pi m kT)^{\frac{3}{2}} \right\},$$

and

$$E = \sum_r a_r \epsilon_r = e^{-\lambda} \int \int \int_{-\infty}^{\infty} \frac{1}{2m} (p_1^2 + p_2^2 + p_3^2) e^{-(p_1^2 + p_2^2 + p_3^2)/2mkT} \frac{dp_1 dp_2 dp_3}{h^3/b}$$

$$= \frac{3}{2} NkT.$$

Then, finally,

$$S = k \left[\frac{V}{b} \log \frac{V}{b} - \left(\frac{V}{b} - N \right) \log \left(\frac{V}{b} - N \right) + \frac{3}{2} N + \frac{3}{2} N \log T - N \log N + N \log \left\{ \frac{b}{h^3} (2\pi mk)^{\frac{3}{2}} \right\} \right],$$

and

$$\Psi = S - \frac{E}{T}$$

$$= k \left[\frac{V}{b} \log \frac{V}{b} - \left(\frac{V}{b} - N \right) \log \left(\frac{V}{b} - N \right) + \frac{3}{2} N \log T - N \log N + N \log \left\{ \frac{b}{h^3} (2\pi mk)^{\frac{3}{2}} \right\} \right].$$

Then as usual (Saha and Bose Equation),

$$p = T \left(\frac{\partial \Psi}{\partial V} \right)_T = - \frac{kT}{b} \log \left(1 - \frac{Nb}{V} \right).$$

In the limiting case, $\frac{Nb}{V} \rightarrow 0$, the equations give expressions for ideal gas as

$$S = kN \left[\frac{5}{2} + \frac{3}{2} \log T + \log \left\{ \frac{V}{N} \frac{(2\pi mk)^{\frac{3}{2}}}{h^3} \right\} \right], \quad p = \frac{kNT}{V}.$$

Up to 1st approximation, these give,

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

and

$$p = \frac{kNT}{V} \left(1 + \frac{1}{2} \frac{Nb}{V} \right).$$

These are the expressions for entropy and pressure of a Van der Waals' gas, when cohesive force is ignored, and only, the correction for the finite size of the molecules is made.

3. CORRECTION FOR COHESIVE FORCES.

The cohesive forces are assumed here to be of Van der Waals' type, i.e., they are short-ranged isotropic forces of attraction. The effect of the cohesive forces may, therefore, be described as amounting to the production of a molecular density

in the interior of the enclosure slightly greater than that in the thin surface layer (parallel to the walls of enclosure). Were the cohesive forces removed, and replaced by a uniform field such that the potential energy of every particle is the same as that in the surface layer, then the volume requirement of the N molecules under the same pressure and at the same temperature will be slightly greater than V . Writing a for the small additional volume, we may say that an actual volume V with the forces of cohesion becomes equivalent, under the same conditions of temperature and pressure, to a volume $(V+a)$ without forces of cohesion. Full account of the forces of cohesion may, on this view be taken, if the actual volume V is replaced by $(V+a)$ in the above thermodynamic expressions. So, the thermodynamic expressions can be written as

$$S = k \left[\frac{V+a}{b} \log \frac{V+a}{b} - \left(\frac{V+a}{b} - N \right) \log \left(\frac{V+a}{b} - N \right) + N \log \left\{ \frac{b}{N h^3} (2\pi m k T)^{\frac{3}{2}} \right\} + \frac{E}{kT} \right],$$

$$\Psi = S - \frac{E}{T} = k \left[\frac{V+a}{b} \log \frac{V+a}{b} - \left(\frac{V+a}{b} - N \right) \log \left(\frac{V+a}{b} - N \right) + \frac{3}{2} N \log T - N \log N + N \log \left\{ \frac{b}{h^3} (\pi m k)^{\frac{3}{2}} \right\} \right],$$

and

$$p = T \left(\frac{\partial \Psi}{\partial V} \right)_T = \frac{kT}{b} \log \left(1 - \frac{Nb}{V+a} \right) \left\{ 1 + \left(\frac{\partial a}{\partial V} \right)_T \right\}.$$

4. APPROXIMATE EVALUATION OF a AND p .

Let n_i , n_s be number densities, and, w_i , w_s be potential energies of particles in the interior of the enclosure and in the surface layer respectively, where $n_s < n_i$. Let V_s be volume of the surface layer.

Then,

$$(V+a)n_s = (V-V_s)n_i + V_s n_s.$$

Therefore

$$a = \frac{(V-V_s)(n_i-n_s)}{n_s}.$$

Assuming density law for gas, we have

$$n_i \propto e^{-\frac{w_i}{kT}}, \quad n_s \propto e^{-\frac{w_s}{kT}}$$

and so

$$w_i < w_s.$$

Therefore

$$a = (V-V_s) \left(e^{\frac{w}{kT}} - 1 \right),$$

where

$$w = w_s - w_i > 0.$$

Therefore

$$a = (V-V_s) \frac{w}{kT}, \quad (\text{approximately}).$$

Now, in the assembly of Van der Waals' gas,

$$V_s \simeq At,$$

where A is the area, and t the thickness of layer less than the radius of the sphere of influence of Van der Waals' force which is generally very small. Therefore

$$V_s \ll V.$$

Up to 1st approximation,

$$a = \frac{Vw}{kT}.$$

Now, it is easy to see that

$$w = \frac{N}{V} c,$$

where c only depends upon mass of molecule and nature of the force.

Up to this approximation,

$$\left(\frac{\partial a}{\partial V}\right)_T = 0.$$

Then

$$\begin{aligned} p &= -\frac{kT}{b} \log \left(1 - \frac{Nb}{V+a}\right) \\ &= \frac{NkT}{V} \left[1 + \frac{\frac{1}{2}Nb}{V} - \frac{a}{V}\right], \text{ correct up to 1st approximation.} \end{aligned}$$

or

$$p + \frac{\alpha}{V^2} = \frac{NkT}{V-\beta},$$

where

$$\alpha = NkT a = N^2 c,$$

where c and hence α is independent of volume and temperature. This is the Van der Waals' equation.

The following point may be noted in connection with the above process. The difference of energies of the assembly of N molecules enclosed in a volume V under cohesive force and of the assembly of the same particles in a volume $(V+a)$ under no cohesive force and under uniform field is

$$-Nw.$$

On the other hand, the change of energy due to change of volume under constant pressure is

$$\int_V^{V+a} p dV = p a = \frac{NkT}{V} \cdot \frac{Vw}{kT} = Nw.$$

Thus, in the change as pictured here the total energy remains unchanged. The original and the altered assemblies have both the same N and E values.

5. CONCLUSION.

This present paper is different from the previous discussions on this topic mainly on two points, (i) division of the physical space of particles into cells of volume

equal to the volume of exclusion, (ii) consideration of the effect of cohesion as a correction in volume only.

So far as the first idea is concerned, it is only a new way of looking at the effect of rigid volume of exclusion. This idea makes the treatment of volume of exclusion so easy that it is likely it will prove very suitable in simplifying the theories of imperfect Gases and Liquids.

So far as the second idea is concerned, it may be added that, the increase of volume due to boundary effect can also be easily and clearly visualised according to modern picture of boundary effect. According to Millikan (1923) in the light of various experiments done by them, during the collisions with the boundary, the particles are adsorbed by the surface, and, then, re-emitted with random velocities. This in a way may be looked upon as increasing the effective volume of the assembly of the particles pictured in this paper. As the number of molecules adsorbed is proportional to number density, so, the constant a is proportional to N . But, as the idea is not yet fully developed in this line, a correct expression of the boundary effect cannot be obtained at this stage.

The writer takes this opportunity to express his gratitude and thanks to Dr. S. C. Kar, Prof. N. R. Sen and Prof. S. N. Bose for helpful discussions and keen interest.

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