The evaluation of Gibbs' phase-integral for imperfect gases. By H. D. URSELL, Trinity College. (Communicated by Mr R. H. FOWLER.)

Introduction.

Statistical mechanics is concerned primarily with what are known as "normal properties" of assemblies. The underlying idea is that of the generalised phase-space. The configuration of an assembly is determined (on classical mechanics) by a certain number of pairs of Hamiltonian canonical coordinates p, q, which are the coordinates of the phase-space referred to. Liouville's theorem leads us to take the element of volume $d\tau = \Pi \, dp \, dq$ as giving the correct element of *a priori* probability. Any isolated assembly is confined to a surface in the phase-space, for its energy at least is constant; when there are no other uniform integrals of the equations of motion, the actual probability of a given aggregate of states of the proper energy, i.e., of a given portion of the surface, varies as the volume, in the neighbourhood of points of this portion, included between two neighbouring surfaces of constant energies E, $E + dE$; it therefore varies as the integral of $(\partial E/\partial n)^{-1}$ taken over the portion. If I be the measure of the total phase-space available, interpreted in this way, and i that of the portion in which some particular condition is satisfied, then i/I is the probability of that condition being satisfied.

The importance of the idea lies in the fact that we can observe experimentally only a few functions of the canonical variables, and all points of the phase-space for which these have the same values are indistinguishable to us. We may therefore take any set of such measurable quantities as coordinates in a second space, and we can then calculate the probability of any given region in this space. A particular set of values of the measurables is said to be a normal property of the assembly if i/I has effectively the value unity for a region of negligible dimensions surrounding the point giving these values in the second space. Clearly a normal property must necessarily be an average property; moreover properties are only measurable when they are normal.

The present paper arose in a recalculation of such a ratio in a case in which the usual method seems unjustifiable. On the basis of Maxwell's law of velocity-distribution we can calculate the pressure of an ideal gas composed of point molecules, obtaining the usual law

$$p = nkT,$$

where n is the molecular density. In applying the same method to any other molecular model we are led at once into complications. Taking the usual picture of hard spherical molecules, of diameter D, and a hard elastic wall we find that the old formula applies provided that n denotes the molecular density at the boundary (strictly at a distance $\frac{1}{2}D$ from the boundary). Here n is the density at any particular point if $nIdv/N$ is the measure i of the available phase-space for which an assigned molecule has its centre in a small volume dv surrounding the point. This will not be the same when the point is at a distance $\frac{1}{2}D$ from the boundary as when it is in the interior of the gas.

The simplest way of obtaining a first approximation is perhaps as follows*. In the first place we may ignore the impulse coordinates, which give a factor in i or I quite independent of the other coordinates. Let V be the volume available for molecular centres; then by imagining the N molecules placed in position in the volume V in succession we find

$$I = V(V - \alpha)(V - 2\alpha) \ldots \ldots \{V - (N-1)\,\alpha\},$$

where α is eight times the volume of a molecule. Writing V' for $V - \frac{1}{2}\alpha$ we find in the same way

$$i = dv \,.\, V'(V' - \alpha)(V' - 2\alpha) \ldots \ldots \{V' - (N-2)\,\alpha\},$$

when dv is at the boundary. If it were in the interior we should have to put $V - \alpha$ for V'. Thus

$$\frac{nV}{N} = \frac{iV}{Idv} = \left(\frac{V'}{V-\alpha}\right)^N \prod_{r=1}^{N-1} \frac{(V + \frac{1}{2}\alpha - r\alpha)(V - \alpha)}{(V - r\alpha)(V - \frac{1}{2}\alpha)} = 1 + \frac{b}{V},$$

where $b = \frac{1}{2}N\alpha$, to the first order in b. Hence to the same order

$$pV = NkT\left(1 + \frac{b}{V}\right).$$

This method clearly leaves much to be desired on the score of rigour; moreover it is not easily susceptible of extension to closer approximations. Boltzmann (*loc. cit.*) obtains a second approximation by a similar direct calculation†; but his result is perhaps more safely based on the general method developed below.

§ 1. The phase-space available (considering only the positional coordinates) is that part of a $3N$-dimensional volume Ω (whose boundary is determined by that of the gas itself) for which no one of a set of conditions, in number $\frac{1}{2}N(N-1)$, of the form

$$(x_r - x_s)^2 + (y_r - y_s)^2 + (z_r - z_s)^2 \geqslant D^2 \ldots \ldots \ldots \ldots (1)$$

* Cf. Boltzmann, *Vorlesungen über Gastheorie*, II, § 61.
† Of the phase-integral, not of i, I separately.

is violated. Suppose we choose a set of k of these conditions, and calculate the volume of that part of Ω in which they are all violated; let Ω_k denote the sum of this quantity for all possible sets of conditions. Then

$$I = \Omega - \Omega_1 + \Omega_2 - \ldots\ldots + (-1)^r\,\Omega_r + \ldots \ \ldots\ldots(2).$$

For an element $d\tau$ of Ω in which s conditions are violated is counted $_sC_r$ times in $\Omega_r (r \leqslant s)$; and

$$\sum_{r=0}^{s} (-1)^r \cdot {}_sC_r = (1-1)^s = 0 \ \text{ if } s > 0$$
$$= 1 \qquad\qquad \text{if } s = 0.$$

Hence the sum on the right-hand side of (2) is precisely the volume of that portion of Ω in which $s = 0$. Jeans[*] adopts this method and finds

$$\Omega = V^N, \ \ \Omega_1 = \tfrac{1}{2}N(N-1)\cdot\tfrac{4}{3}\pi D^3 \cdot V^{N-1}.$$

Treating Ω_1 as a first order correction to Ω and calculating i similarly he deduces the value of p found above. He does not notice that Ω_1/Ω increases indefinitely with N, whatever the density, and that it is in fact very large for any observable mass of gas. It is a little surprising, but really might have been expected, that the terms in (2) should increase in absolute value at first; for the number of pairs of molecules engaged in a close encounter at any particular time is very large, so that s also will be very large for nearly the whole of Ω. There is therefore no alternative but to formulate the series (2) exactly, and then devise some means of summing it.

To illustrate the method we first suppose only one kind of molecule present, and that the r conditions violated in any term of Ω_r involve $2r$ different molecules. The number of ways of selecting r pairs of molecules is

$$\frac{N!}{2^r\,r!\,(N-2r)!},$$

hence $\qquad \Omega_r = \dfrac{N!}{2^r \cdot r!\,(N-2r)!}\,V^{N-r}(\tfrac{4}{3}\pi D^3)^r.$

Writing $-x$ for $\tfrac{2}{3}N\pi D^3/V$ (b in the usual notation) we find

$$I = V^N F(x) = V^N \sum_0 \frac{N!}{r!\,(N-2r)!}\,\frac{x^r}{N^r}.$$

If we also use y for $x^{-\frac{1}{2}}$, we have

$$N\frac{dF}{dx} = y^{2-N}\frac{d^2}{dy^2}(y^N F)$$
$$= N(N-1)F - 2(2N-3)\,x\frac{dF}{dx} + 4x^2\frac{d^2F}{dx^2}.$$

[*] *Dynamical Theory of Gases*, p. 158.

F is the solution of this equation which is regular at $x = 0$ and takes the value 1 there. Put $F = G^N$; then

$$\frac{1}{G}\frac{dG}{dx} = \left(1 - \frac{1}{N}\right) - \left(4 - \frac{6}{N}\right)\frac{x}{G}\frac{dG}{dx}$$

$$+ 4\left[\left(1 - \frac{1}{N}\right)\left(\frac{x}{G}\frac{dG}{dx}\right)^2 + \frac{x^2}{NG}\frac{d^2G}{dx^2}\right].$$

Now N is very large; hence we may write in place of the above

$$\frac{1}{G}\frac{dG}{dx} = 1 - \frac{4x}{G}\frac{dG}{dx} + 4\left(\frac{x}{G}\frac{dG}{dx}\right)^2,$$

or, if $g = \log G$, $$\frac{dg}{dx} = \left(1 - 2x\frac{dg}{dx}\right)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots(3).$$

This equation can be solved without difficulty in finite terms, though of course no physical importance attaches to any but the terms of the first order in x. We find

$$\frac{dg}{dx} = \frac{1 + 4x - \sqrt{(1 + 8x)}}{8x^2}$$

and $$g = \log\frac{1 + \sqrt{(1 + 8x)}}{2} - \frac{1 + 4x - \sqrt{(1 + 8x)}}{8x}.$$

If this were of general application the value of $-x$ or b could not exceed $\frac{1}{8}$; but this is not the case. We have of course

$$g = x + O\left(x^2\right);$$

hence Ng is large and negative, and $I = V^N e^{Ng}$ negligibly small compared with V^N.

§ 2. To evaluate I in general we must first expand each Ω_r. Consider a group of a molecules; their positions can be represented in a space of $3a$ dimensions. At any particular point of this space a certain set of conditions (1) are violated, and there is a whole region in which these same conditions are all broken. We can enumerate all the possible sets of conditions (1) such that each set binds the molecules it involves into a single connected group, the connecting links being the conditions (1). For any such set of conditions and the corresponding connected group of molecules there will be a symmetry number σ which is the number of per-mutations of the molecules among themselves which leave the set of conditions unaltered. In the $3a$-dimensional space there is a definite region in which these conditions (and possibly others as well) are violated; by permuting the molecules among themselves we get $(a\,!/\sigma)$ such regions, which may of course overlap. We now enumerate the *types* of such sets of conditions, and introduce the

following notation: in the rth type the number of conditions is p_r, and the number of molecules involved is a_r; we write ϵ_r for $(-1)^{p_r}$ and define a quantity ξ_r so that

$$\epsilon_r \xi_r V^{a_r} \sigma_r / N^{a_r-1}$$

is the volume of the region of a $3a_r$-dimensional space corresponding to the particular set of conditions of the rth type.

In accordance with the definition of Ω_k we now choose any k conditions (1) and calculate the volume of phase-space in which they are violated. Any such set resolves into a number of sets of the types defined above, the corresponding groups of molecules being mutually exclusive; let there be ν_r sets of the rth type, so that

$$k = \Sigma \nu_r p_r \quad\dots\dots\dots\dots\dots\dots\dots(4).$$

The number of sets of conditions for which the ν_r have assigned values is

$$\frac{N!}{(N - \Sigma a_r \nu_r)! \ \Pi(\nu_r! \ \sigma_r^{\nu_r})}.$$

Hence

$$\Omega_k = \Sigma \frac{N! \ V^{N - \Sigma a_r \nu_r}}{(N - \Sigma a_r \nu_r)! \ \Pi(\nu_r! \ \sigma_r^{\nu_r})} \ \Pi \left(\frac{\epsilon_r \xi_r V^{a_r} \sigma_r}{N^{a_r-1}}\right)^{\nu_r},$$

the summation being over all positive integral values of the ν_r satisfying (4). Thus

$$I = \Sigma(-1)^k \Omega_k = V^N \Sigma \frac{N! \ \Pi \xi_r^{\nu_r}}{(N - \Sigma a_r \nu_r)! \ \Pi \nu_r!} N^{\Sigma \nu_r - \Sigma a_r \nu_r} \ \dots(5),$$

the summation being over all positive integral ν_r. Clearly ξ_r is $O(b^{a_r-1})$ in the usual notation.

Write

$$F = F(\xi_r, y) = \Sigma \frac{(yN)^{N - \Sigma a_r \nu_r} \Pi (\xi_r N)^{\nu_r}}{(N - \Sigma a_r \nu_r)! \ \Pi \nu_r!} N! \ N^{-N}.$$

Then

$$\frac{1}{N} \frac{\partial F}{\partial \xi_r} = \left(\frac{1}{N} \frac{\partial}{\partial y}\right)^{a_r} F.$$

Moreover F is defined completely by these equations together with the conditions of being regular in the (ξ_r) at the origin and taking the value y^N there. Now if $a_r = a_s$, that is, if the number of molecules concerned in the rth and sth types of connected groups is the same, we have

$$\frac{\partial F}{\partial \xi_r} = \frac{\partial F}{\partial \xi_s},$$

and therefore F is a function of the sums $\Sigma \xi_{t (a_t = r)}$ only. Writing x_r for these we have

$$F = \Sigma \frac{(yN)^{N - \Sigma r \nu_r} \Pi (x_r N)^{\nu_r}}{(N - \Sigma r \nu_r)! \ \Pi \nu_r!} N! \ N^{-N},$$

and
$$\frac{1}{N}\frac{\partial F}{\partial x_r} = \left(\frac{1}{N}\frac{\partial}{\partial y}\right)^r F.$$

Put
$$y = e^z, \quad \delta = \Sigma r x_r \frac{\partial}{\partial x_r} ;$$

then
$$\left(\frac{\partial}{\partial z} + \delta\right)^k F = N^k F.$$

Also write
$$F = e^{Ng} ;$$

then

$$\frac{1}{N}\frac{\partial F}{\partial x_r} = \left(\frac{1}{N}e^{-z}\frac{\partial}{\partial z}\right)^r F$$

$$= e^{-rz}\left(\frac{1}{N}\frac{\partial}{\partial z} - \frac{r-1}{N}\right)\ldots\ldots\left(\frac{1}{N}\frac{\partial}{\partial z} - \frac{1}{N}\right)\left(\frac{1}{N}\frac{\partial}{\partial z}\right)F$$

$$= e^{-rz}\left(1 - \frac{r-1}{N} - \frac{\delta}{N}\right)\ldots\ldots\left(1 - \frac{1}{N} - \frac{\delta}{N}\right)\left(1 - \frac{\delta}{N}\right)F.$$

Now put $y = 1$ or $z = 0$; we find

$$\frac{1}{N}\frac{\partial F}{\partial x_r} = \left(1 - \frac{r-1}{N} - \frac{\delta}{N}\right)\ldots\ldots\left(1 - \frac{1}{N} - \frac{\delta}{N}\right)F(1 - \delta g)$$

$$= \left(1 - \frac{r-1}{N} - \frac{\delta}{N}\right)\ldots\ldots\left(1 - \frac{2}{N} - \frac{\delta}{N}\right)$$

$$\times F\left(1 - \frac{1}{N} - \delta g - \frac{\delta}{N}\right)(1 - \delta g)$$

$$= F\left(1 - \frac{r-1}{N} - \delta g - \frac{\delta}{N}\right)\ldots\ldots\left(1 - \frac{1}{N} - \delta g - \frac{\delta}{N}\right)(1 - \delta g).$$

Making $N \rightarrow \infty$ we get

$$\frac{\partial g}{\partial x_r} = (1 - \delta g)^r = h^r \quad \ldots\ldots\ldots\ldots\ldots\ldots(6),$$

where h is written for $(1 - \delta g)$. h satisfies the relation

$$h = 1 - \Sigma r x_r h^r \quad \ldots\ldots\ldots\ldots\ldots\ldots(7).$$

It is easily verified that subject to (7) the partial differential equations (6) are integrable. It is now clear how to evaluate g in series. We first solve (7) for h by successive approximations and then integrate the equations (6), putting $g = 0$ at the origin ($x_r = 0$). It is then given by

$$I = V^N e^{Ng}.$$

The method extends at once to a gas composed of several kinds of molecules. It is sufficient to consider a mixture of two kinds only, their numbers being N_a, N_b. We now define ξ_r so that the

volume of a $3(a_r + b_r)$-dimensional space corresponding to the rth kind of group (composed of a_r molecules of the first kind and b_r of the second kind) is

$$\epsilon_r \xi_r V^{a_r + b_r} \sigma_r / N_0^{a_r + b_r - 1}.$$

Here N_0 is supposed to be a number of the order of magnitude of N_a, N_b; there is some advantage in making it either an absolute constant, such as Loschmidt's number, or proportional to V. We now find

$$I = V^{N_a + N_b} F(\xi_r, 1, 1),$$

where

$$F(\xi_r, y, z)$$
$$= \Sigma \frac{y^{N_a - \Sigma a_r \nu_r} z^{N_b - \Sigma b_r \nu_r} \Pi \xi_r^{\nu_r}}{(N_a - \Sigma a_r \nu_r)! \, (N_b - \Sigma b_r \nu_r)! \, \Pi \nu_r!} N_0^{\Sigma \nu_r (a_r + b_r - 1)} N_a! \, N_b!,$$

and hence
$$\frac{1}{N_0} \frac{\partial F}{\partial \xi_r} = \left(\frac{1}{N_0} \frac{\partial}{\partial y}\right)^{a_r} \left(\frac{1}{N_0} \frac{\partial}{\partial y}\right)^{b_r} F.$$

We therefore put $\quad x_{r,s} = \Sigma \xi_t \, _{(a_t = r, \, b_t = s)}$

and making the same transformations as before we get finally

$$\frac{\partial g}{\partial x_{r,s}} = \left(\frac{N_a}{N_0} - \delta_a g\right)^r \left(\frac{N_b}{N_0} - \delta_b g\right)^s = h_a^r h_b^s \quad \ldots\ldots(8),$$

where
$$\left. \begin{aligned} h_a &= \nu_a - \delta_a g = \nu_a - \Sigma r x_{r,s} h_a^r h_b^s \\ h_b &= \nu_b - \delta_b g = \nu_b - \Sigma s x_{r,s} h_a^r h_b^s \end{aligned} \right\} \quad \ldots\ldots\ldots\ldots(9).$$

Here ν_a, ν_b, written for N_a/N_0, N_b/N_0 respectively, vary as the densities of the two components, and g vanishes at the origin $(x_{r,s} = 0)$. It should be noted that in (7) the summation begins at $r = 2$, and in (9) the terms $r = 1$, $s = 0$ and $r = 0$, $s = 1$ are absent from the summations. These terms are precisely the terms appearing on the left-hand sides of these equations, which take a more symmetrical form on transposition of the series; but the form in which they are written is that adapted to their actual use.

§ 3. We shall now calculate the first few terms in the expansion of g, remembering that x_r is $O(b^{r-1})$. For a pure gas we have

$$h = 1 - \Sigma r x_r h^r, \quad h^r = \partial g/\partial x_r.$$

We obtain successively

$$h = 1,$$
$$h = 1 - 2x_2,$$
$$h = 1 - 2x_2(1 - 4x_2) - 3x_3,$$

giving
$$g = x_2,$$
$$g = x_2 - 2x_2^2 + x_3,$$
$$g = x_2 + (x_3 - 2x_2^2) + (x_4 - 6x_2 x_3 + \tfrac{20}{3} x_2^3).$$

For a mixture we have

$$h_a = \nu_a - \Sigma r x_{r,s} h_a{}^r h_b{}^s,$$
$$h_b = \nu_b - \Sigma s x_{r,s} h_a{}^r h_b{}^s,$$

giving successively

$$h_a = \nu_a, \quad h_b = \nu_b,$$

$$h_a = \nu_a (1 - 2x_{2,0}\nu_a - x_{1,1}\nu_b), \quad h_b = \nu_b (1 - 2x_{0,2}\nu_b - x_{1,1}\nu_a),$$

$$h_a = \nu_a - 2x_{2,0}\nu_a{}^2 (1 - 4x_{2,0}\nu_a - 2x_{1,1}\nu_b)$$
$$- x_{1,1}\nu_a\nu_b \left[1 - 2x_{2,0}\nu_a - x_{1,1}(\nu_a + \nu_b) - 2x_{0,2}\nu_b\right]$$
$$- 3x_{3,0}\nu_a{}^3 - 2x_{2,1}\nu_a{}^2\nu_b - x_{1,2}\nu_a\nu_b{}^2,$$

with a corresponding formula for h_b. The terms in g of the first two orders are therefore

$$g = (\nu_a{}^2 x_{2,0} + \nu_a\nu_b x_{1,1} + \nu_b{}^2 x_{0,2})$$
$$+ \nu_a{}^3 (x_{3,0} - 2x_{2,0}{}^2) + \nu_a{}^2\nu_b (x_{2,1} - 2x_{2,0}x_{1,1} - \tfrac{1}{2}x_{1,1}{}^2)$$
$$+ \nu_a\nu_b{}^2 (x_{1,2} - 2x_{0,2}x_{1,1} - \tfrac{1}{2}x_{1,1}{}^2) + \nu_b{}^3 (x_{0,3} - 2x_{0,2}{}^2)\ldots(10).$$

I find for the coefficient of $\nu_a{}^3\nu_b$

$$x_{3,1} - (4x_{2,0} + x_{1,1}) x_{2,1} + \tfrac{1}{3}x_{1,1}{}^3 + 2x_{2,0}x_{1,1}{}^2 + 8x_{2,0}{}^2 x_{1,1},$$

and for that of $\nu_a{}^2\nu_b{}^2$

$$x_{2,2} - 2x_{2,1}(x_{0,2} + x_{1,1}) - 2x_{1,2}(x_{2,0} + x_{1,1})$$
$$+ (3x_{2,0} + 3x_{0,2} + x_{1,1}) x_{1,1}{}^2 + 4x_{2,0}x_{1,1}x_{0,2}.$$

That of $\nu_a\nu_b{}^3$ can be written down from symmetry, and those of $\nu_a{}^4$, $\nu_b{}^4$ from the result for a pure gas.

We shall now calculate x_2, x_3, $x_{2,0}$, etc., $x_{3,0}$, etc. for the case of hard spherical molecules. x_2 is a single ξ, and

$$p = 1, \quad \sigma = 2.$$

Hence
$$x_2 = -\frac{N}{2V^2} V \cdot \tfrac{4}{3}\pi D^3 = -\frac{\tfrac{2}{3}N\pi D^3}{V},$$

D being the diameter of a molecule. For a gaseous mixture we find

$$x_{2,0} = -\frac{\tfrac{2}{3}N_0\pi D_a{}^3}{V}, \quad x_{0,2} = -\frac{\tfrac{2}{3}N_0\pi D_b{}^3}{V},$$

$$x_{1,1} = -\frac{\tfrac{4}{3}N_0\pi D_{ab}{}^3}{V},$$

D_a, D_b being the respective diameters and D_{ab} the sum of the radii.

Again, x_3 is the sum of two different ξ's. For the first one

molecule overlaps two others, but these do not necessarily overlap one another. Hence $p = 2$, $\sigma = 2$, and

$$\frac{2\xi V^3}{N^2} = V\left(\tfrac{4}{3}\pi D^3\right)^2 \text{ or } \xi = 2x_2{}^2.$$

For the other ξ each pair of molecules overlap, and we have $p = 3$, $\sigma = 6$. When the first two have their centres at a distance $r < D$, the volume in which the centre of the third must lie is

$$2K(r) = 2\int_{\frac{1}{2}r}^{D} \pi(D^2 - x^2)\,dx = 2\pi\left(\tfrac{2}{3}D^3 - \tfrac{1}{2}D^2 r + \frac{r^3}{24}\right).$$

Hence
$$-\frac{6\xi V^3}{N^2} = V\int_0^D 4\pi r^2 \cdot 2K(r)\,dr,$$

or
$$\xi = -\frac{N^2}{6V^2}\cdot 8\pi^2 \int_0^D r^2\left(\tfrac{2}{3}D^3 - \tfrac{1}{2}D^2 r + \frac{r^3}{24}\right)dr$$

$$= -\frac{4\pi^2 N^2}{3V^2}D^6\left[\tfrac{2}{9} - \tfrac{1}{8} + \tfrac{1}{144}\right]$$

$$= -\frac{5\pi^2 N^2 D^6}{36V^2} = -\tfrac{5}{16}x_2{}^2.$$

Thus
$$x_3 = (2 - \tfrac{5}{16})x_2{}^2.$$

For a mixture we have of course

$$x_{3,0} = (2 - \tfrac{5}{16})x_{2,0}{}^2,$$

just as for a pure gas. $x_{2,1}$ is the sum of three terms. For the first one the b-molecule overlaps each of the a-molecules; we have $p = 2$, $\sigma = 2$, and

$$\xi = \tfrac{1}{2}x_{1,1}{}^2.$$

For the second term one of the a-molecules overlaps each of the others; hence $p = 2$, $\sigma = 1$, and

$$\xi = 2x_{2,0}x_{1,1}.$$

For the third term each pair of molecules overlap, and $p = 3$, $\sigma = 2$. When the a-centres are at distance $r < D_a$, that of the b-molecule must lie in a volume

$$2K(r) = 2\int_{\frac{1}{2}r}^{D_{ab}} \pi(D_{ab}{}^2 - x^2)\,dx.$$

Hence

$$\xi = -\frac{N_0{}^2}{2V^2}\int_0^{D_a} 4\pi r^2 \cdot 2K(r)\,dr$$

$$= -\frac{4\pi^2 N_0{}^2}{V^2}\int_0^{D_a} r^2\left(\tfrac{2}{3}D_{ab}{}^3 - \tfrac{1}{2}rD_{ab}{}^2 + \frac{r^3}{24}\right)dr$$

$$= -4\pi^2 N_0{}^2 V^{-2} D_a{}^3\left[\tfrac{2}{9}D_{ab}{}^3 - \tfrac{1}{8}D_a D_{ab}{}^2 + \tfrac{1}{144}D_a{}^3\right].$$

Inserting in the expansion for g we find that the second order terms expressed in terms of $x_{2,0}$, $x_{1,1}$, $x_{0,2}$ cancel out and we are left with

$$g = (\nu_a{}^2 x_{2,0} + \nu_a \nu_b x_{1,1} + \nu_b{}^2 x_{0,2}) - \tfrac{5}{16}(\nu_a{}^2 x_{2,0}{}^2 + \nu_b{}^2 x_{0,2}{}^2)$$
$$- 4\pi^2 N_0{}^2 D_a{}^3 V^{-2} \nu_a{}^2 \nu_b \left[\tfrac{2}{3} D_{ab}{}^3 - \tfrac{1}{8} D_{ab}{}^2 D_a + \tfrac{1}{144} D_a{}^3\right]$$
$$- 4\pi^2 N_0{}^2 D_b{}^3 V^{-2} \nu_a \nu_b{}^2 \left[\tfrac{2}{3} D_{ab}{}^3 - \tfrac{1}{8} D_{ab}{}^2 D_b + \tfrac{1}{144} D_b{}^3\right]\ldots(10').$$

§ 4. In the above, difficulties connected with the boundary have not been mentioned. As a matter of fact they take care of themselves if the numbers ξ_r, x_r, $x_{r,s}$ are evaluated strictly as defined. We may if we wish take them explicitly into account by writing $x_r + x_r{}'$ instead of x_r, where x_r is evaluated as above, neglecting the boundary, so that

$$x_r (V/N)^{r-1}$$

is a function only of r and the diameter D of a molecule, while $x_r{}'$ depends on the size and shape of the boundary. It would be effectively proportional to the area (S, say) of the latter, and we should have

$$x_r{}'/x_r = O(SD/V) = O(x_2/N)^{\frac{1}{3}} = O(b/N)^{\frac{1}{3}}.$$

Hence the effect of such considerations on the value of g is negligible. It is easily seen that the method of considering them described is equivalent to regarding the boundary as another kind of "molecule," of which only one is present. In the same way we can deal with the case in which a particular molecule is assigned a definite position; if the latter is in the interior of the gas we evidently have

$$x_r{}' = (r + 1)\, x_{r+1}/N.$$

In such a way we can calculate i and hence the pressure.

Unfortunately however the calculation is open to the same objections as the original one. For to find a ratio such as i/I accurately, say to order b^r, we need the value of g in each case correct to b^r/N; and this is precisely what we do not know.

It would presumably be possible to evade this difficulty by including in the differential equations the terms in N^{-1}, which would be linear in the differential coefficients of the second order; we could then obtain the terms in N^{-1} in g.

There is however another method of deducing the equation of state of an assembly from statistical theory, a method of extraordinary power. Due originally to Gibbs, its fundamental character has been emphasised in recent times by applications and extensions of it to quantised systems[*]. It will be remembered that the

* Darwin and Fowler, *Phil. Mag.*, vol. XLIV, and other papers.

definition of I was somewhat complex; in the method referred to there is introduced the "phase-integral"

$$H(\vartheta) = \int I(E)\,\vartheta^E\,dE = \int \vartheta^E\,d\tau \quad \ldots\ldots\ldots\ldots(11).$$

It is found that all the equilibrium properties of the assembly can be obtained from $H(\vartheta)$. In fact in the quantum theory case $H(\vartheta)$ is a power series (of a somewhat generalised kind) and it is natural to suppose that if we know it we can deduce $I(E)$. The phase-integral is dominated completely by the maximum of the integrand (in the first form given above); this occurs when

$$\frac{1}{I}\frac{dI}{dE} + \log \vartheta = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots(12).$$

This equation determines a value of the parameter ϑ which is characteristic of the state of the assembly when it has energy E; it may be shown that

$$\vartheta = e^{-1/kT}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13),$$

where T is the absolute temperature. If Y be a function satisfying certain conditions, fulfilled by all measurable quantities, its average value is given by

$$\overline{Y} = \frac{H_Y(\vartheta)}{H(\vartheta)} = \int Y\vartheta^E\,d\tau / \int \vartheta^E\,d\tau \quad \ldots\ldots\ldots\ldots(14),$$

with a proportional error of the order N^{-1}. In particular

$$E = \frac{H_E(\vartheta)}{H(\vartheta)} = \vartheta\,\frac{\partial}{\partial\vartheta} \log H(\vartheta)\ldots\ldots\ldots\ldots\ldots(15),$$

while if Y be the reaction $(-\partial E/\partial y)$ corresponding to any dynamically measurable coordinate y we have

$$\overline{Y} = -\frac{1}{\log \vartheta}\frac{\partial}{\partial y} \log H(\vartheta) \quad \ldots\ldots\ldots\ldots(16).$$

Hence the pressure is given by

$$p = kT\,\frac{\partial}{\partial V} \log H(\vartheta) \quad \ldots\ldots\ldots\ldots\ldots(17).$$

§ 5. Now our method of calculating I for a gas of impenetrable molecules extends at once to the evaluation of $H(\vartheta)$ for any gas. The impulse coordinates again give a factor in $H(\vartheta)$ entirely independent of the rest; for the remaining factor the integrand is ϑ^E, where E now represents the total potential energy of the assembly. This will be roughly a sum of terms corresponding to the various groups of molecules engaged at any time in a close encounter; we obtain successive approximations to the appropriate value of E and hence of ϑ^E at any point in the generalised space

by making the groups of molecules we regard as independent more and more all-inclusive. We find

$$H(\vartheta) = V^N e^{Ng} \qquad\qquad\dots\dots\dots\dots(18),$$

where in g the value of x_r is now such that $x_r V^r N^{1-r} r!$ is the integral taken over a $3r$-dimensional space of a quantity we may denote by $u_{(r)}$. For $r = 2$ it is

$$u_{(2)} = \vartheta^{E_{12}} - 1 = \vartheta_{(2)} - 1, \text{ say };$$

for $r = 3$, $u_{(3)} = \vartheta_{(3)} - \Sigma u_{(2)} - 1 = \vartheta_{(3)} - \Sigma\vartheta_{(2)} + 2.$

In general we must have

$$\vartheta_{(n)} = \Sigma \Pi u_{(i_r)} \dots\dots\dots\dots\dots\dots(19),$$

where the summation is taken over all possible divisions of the n molecules into distinct groups containing say $i_1, i_2, \dots i_s$ molecules respectively. If we fix our attention on a particular molecule, say the nth, we can sum all the terms in which the group containing this molecule is the same; this leads to

$$\vartheta_{(n)} = u_{(n)} + \Sigma u_{(n-1)}\vartheta_{(1)} + \Sigma u_{(n-2)}\vartheta_{(2)} + \dots \ \dots\dots(20),$$

where the u's refer to the various possible sub-groups which include the nth molecule, the ϑ's to the complementary sub-groups. $\vartheta_{(1)} = 1$ always. Now if we denote by

$$(i_1, i_2, \dots\dots i_s)$$

the coefficient of $\vartheta_{(i_1)}\vartheta_{(i_2)} \dots\dots \vartheta_{(i_s)}$ in $u_{(\Sigma i_r)}$, we get at once

$$0 = (i_1, i_2, \dots i_s) + (i_2, \dots i_s) + (i_1, i_3, \dots i_s) + \dots + (i_1, \dots i_{s-2}, i_s),$$

supposing the sth group to be the one containing the nth molecule. The above equation fails only when $s = 1$, when it is replaced by $1 = (n)$. Hence

$$(i_1, i_2, \dots\dots i_s) = (-1)^{s-1}(s-1)!$$

and so $u_{(n)} = \Sigma(-1)^{s-1}(s-1)!\ \vartheta_{(i_1)}\vartheta_{(i_2)}\vartheta_{(i_3)} \dots\dots \vartheta_{(i_s)} \dots(21),$

the summation being taken over every possible division of the n molecules into distinct sub-groups. For example,

$$u_{(4)} = \vartheta_{1234} - (\Sigma\vartheta_{123} + \Sigma\vartheta_{12}\vartheta_{34}) + 2\Sigma\vartheta_{12} - 6.$$

ϑ_{1234} now denotes $\vartheta^{E_{1234}}$, and E_{1234} the mutual potential energy of the four molecules, all others being supposed absent. We have omitted the factors $\vartheta_1, \vartheta_2, \vartheta_3, \vartheta_4$, which are all unity in the case considered so far.

When the gas is in a field of force, (21) still holds good, but we no longer have $\vartheta_{(1)} = 1$; moreover the first term of the series will not be V^N but V'^N, where

$$V' = \iiint \vartheta_{(1)}\ dx\,dy\,dz = \iiint \vartheta^E dx\,dy\,dz,$$

E being the potential energy of a single molecule in the field of force. It is therefore necessary to re-define x_r, using V' in place of V.

For a gaseous mixture we have a V_a and a V_b which are in general different; we find

$$H\left(\mathfrak{S}\right) = V_a{}^{N_a} V_b{}^{N_b} e^{N_0 g},$$

where, in g, $x_{r,s}$ is such that

$$x_{r,s} V_a{}^r V_b{}^s N_0{}^{1-s-r} r!\; s! = \int u_{(r+s)}\, d\tau_{r,s}.$$

The formal connection of the u's with the $\mathfrak{S}$'s, i.e. equation (21), is of course unaffected by distinctions between different kinds of molecules; but the $\mathfrak{S}$'s themselves will be affected by such distinctions. We can no longer say positively what the orders of x_r, $x_{r,s}$ must be; what we can say however is that in the simple case x_r varies as the $(r-1)$th power of the density, and that in the general case $x_{r,s}$ occurs in g with a coefficient $\nu_a{}^r \nu_b{}^s$.

To calculate the pressure we note that

$$V_a \propto V, \quad V_b \propto V,$$

and $$\log H\left(\mathfrak{S}\right) = \text{const.} + (N_a + N_b) \log V + N_0 g.$$

Also $$x_{r,s} \propto V^{r+s-1}.$$

Hence $$p = kT\left(\frac{N_a + N_b}{V} + N_0 \frac{\partial g}{\partial V}\right)$$

$$= N_0 kT\left[(\nu_a + \nu_b) + g'\right] V^{-1} \quad \ldots\ldots\ldots\ldots(22),$$

where g' is obtained from g by multiplying by $(r+s-1)$ the terms in $\nu_a{}^r \nu_b{}^s$. This formula applies of course in all cases; we have no need of the doubtful method of i/I.

In conclusion I would like to say how much this paper owes to the influence of Mr R. H. Fowler.