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Dissociation Treatment of Condensing Systems*

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INTRODUCTION

FOWLER¹ pointed out that imperfect gas theory can be treated as a problem in dissociation, but expressed a doubt as to whether this method would work out so conveniently as did Ursell's at fairly high concentrations. However the success of Mayer's² work using the existence of a most probable type of clustering dependent upon temperature, suggests that the dissociation method might be more effective than at first appeared. Mayer's general results in fact can be derived almost immediately from the theory of dissociating assemblies, thus avoiding much of his preliminary argument. Fowler's general method³ for gaseous assemblies with any number of components and any number of reactions is at once applicable to a gas of *one* component and any number of reactions—clustering processes or collisions. The dissociating molecule of type s is now a cluster of s atoms. Fowler's Eqs. (479) and (484), giving the law of mass action and the external pressure exerted by the gas, are, with classical partition functions, almost obviously identical with Mayer's Eqs. (43) and (37) when recast into the notation there used. The dissociation treatment moreover leads to a much more tractable method of attacking actual cases than that used by Mayer and Ackermann.⁴

DISSOCIATION THEORY

Consider a classical assembly of molecules forming an imperfect gas. The field of force around any molecule will be supposed to be confined within a small volume τ . A cluster of type 2 will be counted as formed whenever two molecules approach each other so closely (i.e., collide) so that the center of either is within the τ of the

other. The cluster will be counted as dissociating when the molecules move out of such a range. A cluster of type s is such that every one of the s molecules is linked to every other of them at least indirectly by such interacting pairs. A free molecule will, merely for convenience in notation, be called a cluster of type 1.

Any cluster of given type can change its pattern, and hence its internal energy, in a theoretically enumerable number of ways. The total interaction energy with a cluster of type s may, theoretically, be averaged over these different patterns, and this average may be used in constructing classical partition functions for this type of cluster as one dissociating constituent in the assembly.

The assembly is to be treated as perfect, in the sense that any interaction potential between the clusters is already taken care of in the processes of association and dissociation. Even free molecules do not interact as such, because the occurrence of such interaction is merely counted as the appearance of a new cluster of higher type.

Let N be the total number of molecules in the assembly, N_s be the number of clusters of type s in any particular example of the assembly. Then

$$N = \sum s N_s. \quad (1)$$

Write $f_s(T)$ for the partition function of the cluster of type s , then Fowler's Eq. (479) immediately reduces to the following set of relations between the averages of N_s :

$$\bar{N}_s / (\bar{N}_1)^s = f_s(T) / [f_1(T)]^s. \quad (2)$$

Also Fowler's Eq. (484) reduces to the following expression for the external pressure exerted on the gas:

$$PV = kT \sum \bar{N}_s. \quad (3)$$

Introducing Mayer's notation²

$$\begin{aligned} \mu_s &= N_s / N, & \mu &= \sum' \mu_s \\ \lambda &= (N - N_1) / N = \sum' s \mu_s, \end{aligned} \quad (4)$$

where \sum' means sum from $s=2$; the law of mass

* Contribution from the Physics Department, Yenching University.

¹ R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, 1936), §9.6.

² J. E. Mayer, *J. Chem. Phys.* **5**, 67-74 (1937).

³ Reference 1, §5.3.

⁴ J. E. Mayer and P. G. Ackermann, *J. Chem. Phys.* **5**, 74-83 (1937).

action becomes

$$\bar{\mu}_s/(1-\bar{\lambda})^s = N^{(s-1)} f_s(T)/[f_1(T)]^s. \quad (5)$$

From (4) we can also write this as

$$\bar{\lambda}/(1-\bar{\lambda}) = \sum' s N^{(s-1)} (1-\bar{\lambda})^{(s-1)} \times f_s(T)/[f_1(T)]^s. \quad (6)$$

If from this point on, no further use is made of the idea of clusters, the result (6) reduces to precisely the same as Mayer's. For in this case the partition function for the cluster of type s is merely that for an assembly of s atoms possessing interaction energy:

$$f_s(T) = V(2\pi mkT)^{(3s/2)} h^{(-3s)} b(s, T), \quad (7)$$

where

$$b(s, T) = \frac{1}{s!} \int \cdots \cdots \cdots \int_{\text{cluster}} \exp(-W_s/kT) dq_1 \times \cdots \times dq_{3(s-1)}. \quad (8)$$

Here W_s is the total interaction energy of the cluster, and the integrals have to be taken only over those regions in phase coordinate space in which the cluster remains a cluster of the given type s . By the trick of substituting $[\exp(-W_s/kT) - 1]$ for $\exp(-W_s/kT)$ these integrations can be extended over the whole space, provided the volume of the cluster itself is neglected; substituting (7) and (8) into (6) Mayer's Eq. (43) is at once produced. This shows that Mayer's result follows as a special case of dissociation theory; our Eq. (6) will permit use of other than classical partition functions, in a manner which could not have been assumed from the arguments employed in Mayer's work.

CONDENSATION AS A CLUSTERING PROCESS

If at the point, Eq. (6), the physical meaning of a cluster is made use of, considerable simplification of the ensuing computations is effected; greater physical insight is also gained by this method of attack.

In the previous method, call it the pure collision method, the kinetic and potential energies are treated separately. While rigorously correct, this separation is responsible for the neglect of an

important distinction between binary and higher order collisions. During an elastic collision between two atoms there is necessarily produced kinetic energy equal and opposite to any decrease in potential energy of interaction, and no stable cluster can be formed. All imperfect gas theory, prior to Mayer's work, appears to assume that higher order collisions are of the same kind but of negligible frequency, and hence omits them from the analysis. But, as soon as the possibility of ternary collisions is admitted, actually stable clusters of type two are possible of a lifetime almost indefinitely long compared with the duration of a simple binary collision. Their effect is therefore very much greater than their frequency of formation would suggest, and it is definitely wrong to suppose that they can be neglected in comparison with elastic binary collisions. In fact their presence is accounted for in the pure collision method, because all kinetic energies are associated with every potential energy; but the method conceals their presence by a mathematical trick.

In fact with a Maxwell distribution over kinetic energies the more stable clusters are the more probable, and a good approximation to the truth would be secured by assuming that pure binary collisions are in fact of negligible importance compared with stable binary clusters. This is exactly the opposite of the assumption that comes most easily from a pure collision point of view.

The condensed phase of the assembly is now to be regarded as that condition in which the whole assembly is in one single cluster, $N_s = 1$, $s = N$. The latent heat of the phase change is to be identified with the energy which must be removed in order to reduce to a stable cluster what would otherwise be a mere transitory collision involving the whole assembly. This energy removal cannot consistently be supposed to take place only at the formation of the final grand cluster; it is a general feature of clusters of all types, and occurs continually as clustering progresses, e.g. during a decrease in the volume of a vapor. It is merely because there is, as shown by Mayer, a critical molecular volume at which clustering rapidly becomes important, that latent heat also appears to be removed only

at one definite temperature. From this point of view the heat loss during the Joule-Thomson porous plug experiment gives the latent heat curve at temperatures above boiling point.

SATURATED VAPOR EQUATIONS

Considering a cluster of type s simply as a single "molecule" or system of mass ms , its partition function will be, instead of (7):

$$f_s(T) = V(2\pi mskT)^{(3/2)}h^{-3} \exp(-\bar{W}_s/kT), \quad (9)$$

where \bar{W}_s is the mean internal energy of such clusters. This must include all negative energy of interaction between the a atoms, and all "internal" kinetic energy. The latter will be assumed proportional to $(s-1)$, will actually have the mean value $3/2kT(s-1)$ for a Maxwellian distribution. The interaction energy will also be nearly proportional to $(s-1)$, but there will be a correction term due to surface energy which will increase less rapidly than s . Therefore write:

$$\bar{W}_s = W(s-1) + \chi(s, T), \quad (10)$$

where

$$\chi(s, T) \ll W(s-1), \text{ large } s. \quad (11)$$

Also from the physical meaning of \bar{W}_s it is necessarily true that

$$\chi(1, T) = 0. \quad (12)$$

Using these results in (9) for the partition function, the equation of mass action (6) becomes:

$$\frac{\bar{\lambda}}{1-\bar{\lambda}} = \sum' s^{5/2} e^{-\chi/kT} \left\{ \frac{h^3 e^{-W/kT} (1-\bar{\lambda})}{(2\pi mskT)^{3/2} V/N} \right\}^{(s-1)} \quad (13)$$

As in Mayer's work, there will be a critical value $\bar{\lambda}_c$ of $\bar{\lambda}$ when

$$V_c/N = h^3 (2\pi mskT)^{-3/2} (1-\bar{\lambda}_c) e^{-W/kT}, \quad (14)$$

where

$$\bar{\lambda}_c/(1-\bar{\lambda}_c) = \sigma = \sum' s^{5/2} e^{-\chi/kT}. \quad (15)$$

Similarly, from (5) the critical value $\bar{\mu}_c$ of $\bar{\mu}$ can be derived:

$$\bar{\mu}_c/(1-\bar{\lambda}_c) = \phi = \sum' s^{3/2} e^{-\chi/kT}. \quad (16)$$

Using (4) at the saturation point given by (14), (15) and (16), we have the equations for the saturated vapor in the form:

$$P_c V_c = NkT(1+\phi)/(1+\sigma). \quad (17)$$

It is remarkable that this $P-V$ curve depends through the sums (15) and (16) only upon the *surface* energy of the clusters.

The essential advantage of this method of attack over that of Mayer and Ackermann⁴ is that the computational difficulties are resolved into two separate problems. In the first problem, outlined above, it is proposed to obtain, from the properties of saturated vapor, information on surface energies of clusters of vapor molecules. In the second problem this information would be used in a study of molecular force fields.

A rough check on the properties of water vapor has shown the orders of magnitude correct. The detailed analysis is now being attempted.

The writer wishes to thank Professor R. H. Fowler for introducing him to this subject.