

Dissociation Treatment of Condensing Systems. II

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effect of interaction of vibration and rotation may be taken into account by multiplying the weight of each vibrational state with the rotational sum of states. Thus weight factors $\bar{A}\sqrt{\bar{C}}$ will appear in Q where \bar{A} and \bar{C} are values of the moments of inertia averaged over the vibration. The other members of the series will also have moments of inertia different from the moment of inertia in the equilibrium position. Again assuming motion on straight lines for all atoms we find that in the 948-cm^{-1} level the moments of inertia are somewhat smaller, in the levels higher than 1610-cm^{-1} they may be greater than in equilibrium. As a rough approximation we shall multiply by the factor $A\sqrt{C}$ for all levels of the 948-cm^{-1} vibration, where A and C are the values in the equilibrium position. For the 1610-cm^{-1} level we still assume $\bar{C}=C$, but for \bar{A} we shall substitute the value $\frac{1}{2}C$ as would be obtained for a flat molecule. Thus the weight factor for the 1610-cm^{-1} level will be $\frac{1}{2}C\sqrt{C}=0.78A\sqrt{C}$. The terms showing the effect of

interaction of vibration and rotation are listed in column 10. The calculated values, given in column 11, include both the terms for centrifugal force and interaction of vibration and rotation. The differences between the observed and these final calculated values are given in column 12.

The remaining differences between experimental and calculated values fall far within experimental error. In fact the agreement is better than could have been expected from the approximate nature of our calculation. In particular the term arising from the interaction of vibration and rotation has been estimated in a very rough way. Its magnitude and perhaps even its sign is open to question. Comparison of experiment and theory shows, however, clearly that the presence of two minima in NH_3 has a considerable effect on specific heats. Measurements of the specific heats of ND_3 would be highly desirable since such measurements would furnish a further check on the theory of vibrations of the ammonia molecule.

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Dissociation Treatment of Condensing Systems. II*

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In a previous paper under the above title, in future referred to as Part I, it was shown how the theory of dissociating assemblies could be applied to an example containing only one component type of molecule which can form clusters of any size. The results were claimed as equivalent with those of Mayer (see reference 3, *a* and *b*). In a private communication Dr. Mayer has pointed out to the writer that this claim is only approximately correct, because the clusters were treated as of negligible size, excluded volumes being ignored. It is therefore necessary to regard Part I as giving a "perfect gas analogy" for the theory of the saturated vapor pressure curves at temperatures well below the critical value.

The present paper develops the more accurate theory by taking into account the excluded volumes and, besides the s - v - p curves, also presents a complete set of equations for the isothermals of the gas and vapor right through the critical temperature.

ASSUMPTIONS

AS in Part I,¹ it will be assumed that the interaction energy between any pair of molecules drops off discontinuously at a definite distance between centers. Each cluster will be assumed

approximately spherical in form. With a cluster of type s and a cluster of type r will be associated a similar distance σ_{rs} such that when their centers are separated by more than σ_{rs} , they are counted as separate clusters. This distance is assumed to depend only upon the numbers r and s in the following manner:

$$\sigma_{rs} = \frac{1}{2}(\sigma r^{\frac{1}{3}} + \sigma s^{\frac{1}{3}}). \quad (1)$$

* Contribution from the Physics Department, Yenching University.

¹ W. Band, "Dissociation Treatment of Condensing Systems," J. Chem. Phys. 7, 324 (1939).

The assumption that σ is independent of r and s is equivalent with the assumption that all clusters are packed with equal closeness.

The results given by Fowler,² §8.6, for a dissociating assembly whose molecules have finite size, which will be used here, are as follows: The partition function for a cluster of type s will be

$$f_s(T) = V(1 - \beta_s) \times (2\pi mskT)^{3/2} h^{-3} \exp(-W_s/kT), \quad (2)$$

where W_s is the mean energy per cluster to be treated in the same way as in Part I, Eq. (10); and where

$$\beta_s = (4\pi/3V) \sum_r N_r \sigma_{rs}^3 \quad (3)$$

with N_r as the number of clusters of type r . The law of mass action remains in the form

$$N_s/(N_1)^s = f_s(T)/\{f_1(T)\}^s. \quad (4)$$

The pressure exerted by the assembly is now, Fowler, Eq. (775),

$$PV = kT \sum_s N_s / (1 - \beta_s), \quad (5)$$

which equation is true only so long as all β_s are less than unity.

SATURATED VAPOR PRESSURE CURVES

In terms of the previous notation:

$$\mu_s = N_s/N, \quad \text{and} \quad \lambda = \sum_s' s\mu_s, \quad (6)$$

the law of mass action (4), using (2), becomes

$$\frac{\mu_s}{1 - \lambda} = s^{3/2} e^{-\chi/kT} \left\{ \frac{1 - \beta_s}{1 - \beta_1} \right\} \times \left[\frac{h^3 e^{-W/kT} (1 - \lambda)}{(2\pi mskT)^{3/2} V (1 - \beta_1)/N} \right]^{(s-1)}. \quad (7)$$

The condition for saturation is that the square bracket shall become unity:

$$V^*(1 - \beta_1^*)/N = \rho(1 - \lambda^*), \quad (8)$$

where

$$\rho = (2\pi mskT)^{-3/2} h^3 e^{-W/kT}. \quad (9)$$

Under this condition Eq. (7) gives

$$\mu_s^*/(1 - \lambda^*) = s^{3/2} e^{-\chi/kT} (1 - \beta_s^*)/(1 - \beta_1^*). \quad (10)$$

² Fowler, *Statistical Mechanics*, 2nd edition (Camb. Univ. Press, 1936).

From (6) and (10) we have

$$(1 - \lambda^*) = 1/(1 + \sigma^*), \quad (11)$$

where

$$\sigma^* = \sum_s' s^{5/2} e^{-\chi/kT} (1 - \beta_s^*)/(1 - \beta_1^*). \quad (12)$$

Then from (10) we derive

$$\mu_s^*/(1 - \beta_s^*) = s^{3/2} e^{-\chi/kT} / (1 + \sigma^*)(1 - \beta_1^*). \quad (13)$$

Since $\chi(1, T) = 0$, [see Part I, Eq. (12)], Eq. (5) now gives for the saturated vapor:

$$P^* V^* / NkT = (1 + \phi_0)/(1 + \sigma^*)(1 - \beta_1^*), \quad (14)$$

where

$$\phi_0 = \sum_s' s^{3/2} e^{-\chi/kT}. \quad (15)$$

The process of condensation will be complete when $\lambda = 1$, which, in (8), requires that $\beta_1 = 1$. The value of V for which this is true will be written as V_l , so that Eqs. (3) and (1) lead to

$$V_l = \beta_0(8 + \phi_3 + 3\phi_2 + 3\phi_1 + \phi_0)/(1 + \phi_3). \quad (16)$$

Here we have written

$$\phi_r = \sum_s' s^{(2r+9)/6} e^{-\chi/kT}, \quad (17)$$

$$\beta_0 = (2/3)\pi N\sigma^3 \quad (18)$$

and neglected the presence of the β_s in the expression (13) for $\mu_s = N_s/N$. This neglect is justifiable because V_l is of the nature of a small correction term itself. From (8) it now follows that

$$V^* - V_l = N\rho/(1 + \sigma^*).$$

When $\beta_s \ll 1$, all values of s , $\sigma^* \rightarrow \phi_3$, so that

$$V^* \rightarrow N\rho/(1 + \phi_3). \quad (19)$$

Writing

$$\phi = 8 + \phi_3 + 3\phi_2 + 3\phi_1 + \phi_0, \quad (20)$$

Eqs. (19) and (16) give

$$V^* - V_l = (N\rho - \beta_0\phi)/(1 + \phi_3). \quad (21)$$

This equation is strictly true only so long as $V^* \gg V_l$, but it is possible to extend it formally right up to the point where $V^* = V_l$, giving, formally, a critical temperature where

$$N\rho = \beta_0\phi. \quad (22)$$

Putting (21) into (14), the latter becomes

$$P^*(V^* - V_l)/NkT = (1 - \beta_0\phi/N\rho)(1 + \phi_0)/(1 + \phi_3) \quad (23)$$

which, again formally, can be used right up to the critical temperature given by (22).

The Eq. (22) determines a critical temperature in terms of the three physical parameters: the range of the molecular field, σ , the surface energy per molecule in a cluster, and the volume energy per molecule in a cluster. The volume V_l corresponds with the volume of the liquid phase, but does not pretend to be an accurate expression for it. Presumably the best way to apply the equations is to use $(V^* - V_l)$ as the observed volume change upon condensation, substitute it as such into (21) or (23), and adjust the parameters to give the best fit with the recorded variations with T and P .

EQUATIONS FOR IMPERFECT GAS

Write

$$\phi_{sr}^* = s^{(2r+9)/6} e^{-\chi/kT} (1 - \beta_s), \quad (24)$$

$$v = V/N, \quad (25)$$

$$Z = (\rho/v)(1 - \lambda)/(1 - \beta_1). \quad (26)$$

Eq. (7) becomes

$$\mu_s = \phi_{s0}^* (v/\rho) Z^s \quad (27)$$

and the first of conditions (6)[†] leads from this to

$$1 = (v/\rho)(1 - \beta_1)Z + \sum_s' \phi_{s3}^* Z^s (v/\rho) \quad (28)$$

or

$$(\rho/v) = Z(1 - \beta/v) + \sum_s' \phi_{s3}^* Z^s, \quad (29)$$

where

$$\beta = V_l/N. \quad (30)$$

Neglecting the factors $(1 - \beta_s)$ in the ϕ_{s3}^* terms beyond $s = 1$, the quantity Z can be expanded in a power series:

$$Z = a_1/v + a_2/v^2 + a_3/v^3 + \dots, \quad (31)$$

whose coefficients are determined by substitution in (29):

$$\begin{aligned} a_1 &= \rho, & a_2 &= \beta\rho - \phi_{23}\rho^2 \\ a_3 &= \rho\{\beta^2 - 3\beta\phi_{23} + \rho^2(2\phi_{23}^2 - \phi_{33})\}. \dagger \end{aligned} \quad (32)$$

Putting this approximation for Z into (27), and

[†] $\sum_s s\mu_s = 1$.

[‡] The asterisk omitted to indicate omission of $(1 - \beta_s)$ from ϕ_{sr}^* .

remembering the factor $(1 - \beta_s)$ in ϕ_{s0}^* , we obtain:

$$\begin{aligned} \sum_s' \mu_s / (1 - \beta_s) &= (\rho\phi_{20})/v \\ &+ \rho^2\phi_{20}\{2(\beta/\rho - \phi_{23}) + \phi_{30}\}/v^2 + \dots \end{aligned} \quad (33)$$

Also, from (26),

$$\begin{aligned} \mu_1 &= 1 - \lambda = (v/\rho)(1 - \beta/v)Z \\ &= 1 - (\rho\phi_{23})/v \\ &- \rho^2\{2\phi_{23}(\beta/\rho - \phi_{23}) + \phi_{33}\}/v^2 - \dots \end{aligned} \quad (34)$$

Finally, the pressure equation (5) can be written as

$$\begin{aligned} P(v - \beta) &= kT\{1 - \lambda + \mu(1 - \beta/v)\} \\ &= kT(1 - A/v - B/v^2 \dots), \end{aligned} \quad (35)$$

where, by comparison with (33) and (34), the coefficients are:

$$A = \rho(\phi_{23} - \phi_{20}), \quad (36)$$

$$\begin{aligned} B &= 2A(\beta - \rho\phi_{23}) + \rho\beta\phi_{20} + \rho^2(\phi_{33} - \phi_{30}). \\ \text{etc.} & \quad \text{etc.} \end{aligned} \quad (37)$$

For comparison with classical equations, it is sufficient to retain only the term in $1/v$, and write

$$P(V - V_l) = NkT - a/V, \quad (38)$$

where, referring to (24) and (9), (36) leads to

$$a = N^2 h^3 (\pi^3 m^3 k)^{-1} T^{-1} e^{-(W + \chi_2)/kT}. \quad (39)$$

The equation of Dieterici is equivalent to the form (38) with the value $a = a'T^{-1}$ (see Fowler, Eq. (825)) which makes an interesting comparison with (39). The order of magnitude of (39) is correct, and it depends upon T in a promising manner. Its extension down to temperatures below the critical value into the true vapor states is theoretically justifiable, because all orders of clustering have been accounted for. The only theoretical limitation is that the condensed phase shall not be present; the onset of this restriction is determined by the equations of the previous section.

PHENOMENA AT THE CRITICAL POINT

The presence of considerable proportions of very large clusters in the assembly under conditions close to the critical point, gives rise to a dependence upon gravitational potential which

up to now has been entirely neglected, both in the present work and in that of Mayer.³

At a point where the gravitational potential is gz , the partition function for a cluster of type s will have an extra factor $\exp(-msgz/kT)$. This factor will, through Eq. (7) affect the concentration of clusters of this type in the same ratio:

$$\mu_s(z) = \mu_s(0) \cdot \exp(-msgz/kT)$$

$$\text{and} \quad \partial \mu_s(z) / \partial z = -(msg/kT) \mu_s(z). \quad (40)$$

With m of order 10^{-23} there will be appreciable gradient of concentration per unit concentration only for clusters of type s of order 10^7 or larger. In an assembly containing a condensed phase, at a temperature well below the critical value, the mean concentrations are all very small except for small s , because even the liquid phase counts only for a single cluster. The transition from vapor to liquid is exceedingly sharp, and at no time are the concentrations of intermediate clusters appreciable. However as the temperature approaches the critical value, the transition becomes less sharp. At temperatures slightly below the critical value, under conditions which include the condensed phase, large clusters of type 10^7 or larger can be expected to occur in appreciable proportions. According to (40) there will then be an appreciable gradient of concentration among these clusters, physically observable as a blurring of the meniscus between the two phases.

This blurring of the meniscus while there still remains a difference in density between the two phases is well known, and has previously been interpreted by Harrison and Mayer⁴ in an essentially different manner from that suggested above. While ignoring the above affect of gravity in causing a "settling down" of larger clusters into the lower part of the container, Harrison and Mayer projected their saturated vapor equations up towards the critical temperature. They found that surface tension should disappear at a temperature somewhat below the critical tem-

perature derived by projecting the gas equations down to the latter point. Below the upper critical temperature the gas isotherms are parallel to the V axis for finite ranges.

However it should be pointed out that their partition functions were constructed on the assumption that all clusters are uniformly free to move about throughout the volume V of the whole assembly, when in fact the condensed phase, and all fairly large clusters, are effectively confined by the gravitational field to a comparatively small part of V . The equations developed on this assumption can therefore apply with precision only when there exists a negligible proportion of molecules in large clusters; their projection up to the critical point is not justified, and the results regarding the disappearance of surface tension would appear to be of doubtful validity.⁵

According to our present argument the usually observed critical temperature, at which the meniscus appears to vanish, is somewhat too low; the true critical point will be where the difference in density vanishes. The blurring of the meniscus could theoretically be made to occur simultaneously with the true critical conditions only by making the observations in an arrangement which neutralized the gravitational field.

CONCLUSIONS

The present work does not attempt to give an exact theory of the behavior of condensing systems, but claims only to reach similar precision, in the saturated vapor range, as did the Ursell theory in the imperfect gas range. It does, however, claim to give a more exact theory of the imperfect gas and the unsaturated vapor than the Ursell theory.

The theory of Ursell, considered as the basis for a van der Waals or Dieterici equation, has been extended down to critical temperature isothermals. This extension is merely formal in essence, because, as we now know, at these temperatures large clusters play a significant part, but were entirely omitted by the Ursell argument.

³ "Statistical Mechanics of Condensing Systems," (a) Part I, J. E. Mayer, J. Chem. Phys. 5, 67 (1937); (b) Part II, J. E. Mayer and P. G. Ackermann, *ibid.* 5, 74 (1937); (c) Part III, J. E. Mayer and S. F. Harrison, *ibid.* 6, 87 (1938).

⁴ S. F. Harrison and J. E. Mayer, "Statistical Mechanics of Condensing Systems, IV," J. Chem. Phys. 6, 100-104 (1938).

⁵ See also some remarks by Born and Fuchs, "Statistical Mechanics of Condensing Systems," Proc. Roy. Soc. 166A, 391-414 (1938).

The present equations permit a theoretically sound extension down below the critical temperature into the unsaturated vapor isothermals, so long as the volume is large compared with that of the liquid phase of the given assembly. It also permits an extension up to the critical temperature of the saturated vapor pressure curves, which is, however, merely a formal extension of equations which have been proved only under

the limitation that the condensed phase shall contain a negligible proportion of the molecules of the assembly.

These restrictions are inherent in the assumptions made at the beginning of the work, and there seems no way of removing them if the dissociation method is to retain its advantage of simplicity over that of the more completely rigorous treatment of Mayer.^{3a, b}

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Changes of Phase and Transformations of Higher Order in Monolayers

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The gaseous, liquid, mesomorphous and solid states in monolayers are defined and their close connection with the corresponding states in three dimensions rigorously established. This involves a new treatment of the two-dimensional liquid and of its transformation to the mesomorphous state. The properties of the three-dimensional vitreous state of fatty substances are shown to be particularly important in connection with the behavior of monolayers. The different critical and transformation temperatures are also defined and their significance explained. From this is derived a systematic classification of the different types of isotherms observed. By determining the variations of the compressibility, viscosity and apparent dipole moment with change of area, higher order transformations are detected in monolayers. These transformations occur at the same areas as those at which ordinary phase transformations occur at lower temperatures.

THE aim of this paper is to establish a general correlation between all the transformation phenomena observed in surface films and to show that they correspond closely to the transformations found with the same substances in bulk. This enables us to set up a rigorously defined nomenclature without the implication of any vaguely justified assumption. *Critical temperatures* and a *triple point* will be defined thus permitting us to arrange the different states in which a film can exist, when its temperature and pressure are fixed, in a systematic classification. For this purpose some new experimental data are included together with a new interpretation of some of the published experiments.†

Both from the theoretical and experimental point of view, transformations in two dimensions

are more readily studied than in three dimensions. In two dimensions, by relatively simple means, pressures which in three dimensions would correspond to some hundreds of atmospheres or alternatively to a few tenths of a millimeter of mercury can be attained. Likewise, molecular packing, molecular interaction, questions of order and disorder, are much simpler in a two-dimensional system than in a three-dimensional.

Besides the ordinary phase changes, transformations of a higher order are found in monolayers. These are detected by sharp discontinuities occurring simultaneously in three different physical properties: compressibility, apparent dipole moment and especially the surface viscosity. Accurate determination of variations in the compressibility and in the apparent dipole moment was made possible by the use of a method of automatic and continuous registration of both pressure and potential isotherms. A considerable improvement could thus be obtained

* Rockefeller Foundation Fellow 1938-39.

† References will be given only for typical experiments. For a general survey and bibliography see: E. K. Rideal, *Surface Chemistry* and N. K. Adam, *The Physics and Chemistry of Surfaces*.