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## On the Behavior of Pure Substances Near the Critical Point

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It has been suggested several times that the phenomena of condensation could be understood by considering the vapor as a system in which molecules are associating into clusters, these obeying the ordinary laws of equilibrium. One can also consider the liquid as a system in which bubbles of vapor are forming. The present paper attempts to apply these ideas to phenomena occurring in the neighborhood of the critical point. Only thermodynamic methods are used, in conjunction with some general assumptions concerning the properties of the molecules involved. Some aspects of the surface tension of the liquid near the critical point have been considered in some detail. The highest temperature  $T_m$  at which a meniscus can exist is assumed to be the temperature at which the surface

tension vanishes at the same time that the condition for equilibrium between liquid and vapor phases is fulfilled. It is concluded that the pressure-volume isotherm at  $T_m$  has a finite horizontal region, corresponding to the squeezing out of surface when the surface tension is zero. The slope of the isotherm at  $T_m$  in the vapor region outside the horizontal portion is closely related to the slope in the liquid region just to the other side of the horizontal part; these slopes approach zero as the flat part is approached. Above  $T_m$  there is still a process which may be called condensation, but no horizontal part to the isotherms. This is in contradiction to conclusions reached by Mayer and Harrison on the basis of their statistical theory of condensation, but is apparently not in real contradiction to the theory.

### 1. INTRODUCTION

OVER a considerable period of years data have been accumulating which indicate that the phenomena occurring in the neighborhood of the critical point of a pure substance are more complicated than expected from the simple van der Waals theory. This theory would lead one to expect a roughly parabolic shape for the coexistence curve in a pressure-volume diagram, which encloses those sections of the isotherms over which a distinct meniscus can be observed. There is, however, much evidence that this curve actually has a finite horizontal (constant-pressure) portion at the top, instead of being rounded.<sup>2</sup> Some experiments also indicate a tendency for layers of different density to persist at temperatures above that at which the meniscus disappears.<sup>3</sup> Hein stated that, after raising the temperature to obtain density equalization, these density differences would reappear on cooling, though the temperature remained above the critical temperature, which might lead one to

believe that they represented equilibrium states. However, Maass and his co-workers said this would not occur, and there is plenty of evidence that complete equilibrium is not attained under these conditions. More recent evidence<sup>4</sup> indicates that a single completely homogeneous phase is obtained either by shaking or by long standing.

It was suggested by Mayer and Harrison,<sup>5</sup> as a result of a statistical mechanical theory of condensation, that the pressure-volume isotherms continue to have a horizontal portion at temperatures slightly above the temperature  $T_m$  at which the meniscus disappears, and that the true critical temperature is the temperature above which such a horizontal region does not occur. According to the theory, the isotherms in this region close to the critical temperature should differ from those below the temperature at which the meniscus disappears, in that there should be no break in the slope of the curve as the horizontal portions are approached.

The best experimental data on these properties of the isotherms are not entirely unequivocal. McIntosh, Dacey, and Maass<sup>6</sup> obtained isotherms for ethylene, and the curves which they fitted to their experimental points showed horizontal

<sup>1</sup> On leave 1946-47 at the Clinton Laboratories, Oak Ridge, Tennessee.

<sup>2</sup> See, e.g., E. Schröder, *Zeits. f. physik. Chemie* **A129**, 79 (1927); **A140**, 241, 379 (1929); S. G. Mason, S. N. Naldrett, and O. Maass, *Can. J. Research* **B18**, 103 (1940); S. N. Naldrett and O. Maass, *ibid.* **B18**, 118 (1940).

<sup>3</sup> See, e.g., P. Hein, *Zeits. f. physik. Chemie* **86**, 385 (1914); J. S. Tapp, E. W. R. Steacie, and O. Maass, *Can. J. Research* **9**, 217 (1933); C. A. Winkler and O. Maass, *ibid.* **9**, 613 (1933). For reviews see A. L. Clark, *Chem. Rev.* **23**, 1 (1938); O. Maass, *ibid.* **23**, 17 (1938).

<sup>4</sup> Page 120 of article by Naldrett and Maass, Reference 2.

<sup>5</sup> J. E. Mayer and S. F. Harrison, *J. Chem. Phys.* **6**, 87, 101 (1938).

<sup>6</sup> R. L. McIntosh, J. R. Dacey, and O. Maass, *Can. J. Research* **B17**, 206, 241 (1939).

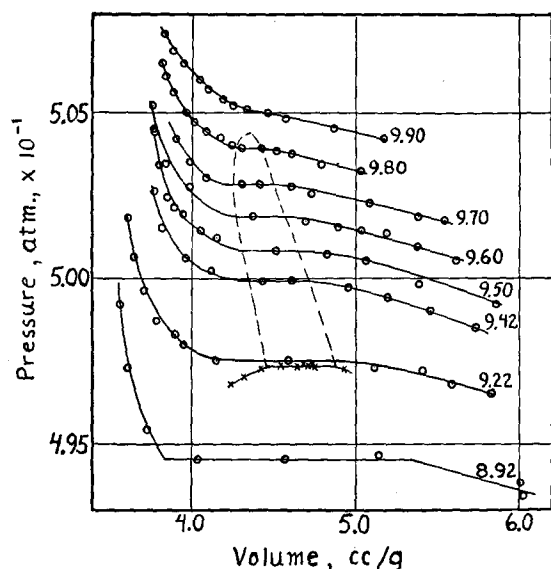


FIG. 1. Isotherms for ethylene, at temperatures indicated on curves, assuming horizontal portions above  $T_m$ , as enclosed by the broken line. The crosses are from data of Naldrett and Maass obtained by finding the temperature at which the meniscus disappeared at a fixed specific volume. These have been placed on the pressure-volume diagram by interpolation.

sections. A sudden change of slope was shown at the ends of the horizontal portions. The data, however, do not necessarily demand a sudden change in slope nor even, for that matter, a horizontal portion in the isotherms. In Figs. 1 and 2, we have replotted the data of McIntosh, Dacey, and Maass. In Fig. 1 we have drawn in a set of isotherms showing horizontal sections but no abrupt changes in slope. In Fig. 2 we have drawn in a set of isotherms showing no horizontal sections. Either one of these sets of curves agrees with the experimental results within the limits of experimental error. It is true that the positions of the points on a number of the isotherms seem to indicate a decrease in slope near the critical volume, though it is within the experimental error. On the other hand, as noted before, Naldrett and Maass<sup>4</sup> made the observation that a system, slightly above the temperature at which a meniscus can be observed but still showing layers of different density, finally settles down to a completely homogeneous state. This shows that the two layers, which presumably represent points along the "horizontal" portion of the isotherm, have different free energies; hence the isotherm cannot be exactly horizontal.

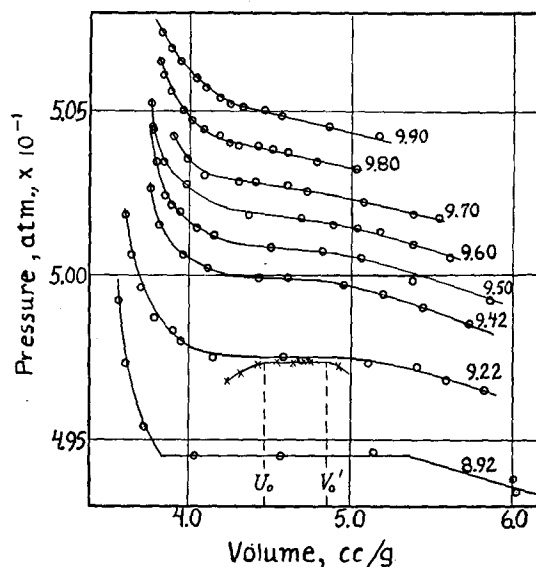


FIG. 2. Isotherms for ethylene, at temperatures indicated on curves, assuming no horizontal portions above  $T_m$ . For significance of the crosses see Fig. 1. For  $U_0$  and  $V_0'$  see Section 5.

It may be mentioned that the isotherms for carbon dioxide, obtained by Michels, Blaisse, and Michels,<sup>7</sup> showed a slope distinctly different from zero only  $0.15^\circ$  above the critical temperature. The pressure measurements were exceedingly accurate, but the non-zero slope was attributed by Mayer and Streeter<sup>8</sup> to small traces of impurities. It is, of course, exceedingly difficult to be sure that the last traces of impurities have been eliminated. By obtaining samples of materials from different sources and purifying by different methods, it might be possible to show by the reproducibility of the data that the impurities have been reduced to a point where they make no further difference. Such a procedure has not as yet been carried out, but Michels, Blaisse, and Michels considered the purity of their material to be adequately confirmed by the fact that the isotherms below the critical point appear to be exactly horizontal. It is, indeed, not obvious that impurities should have more effect just above the critical temperature than just below it.

Mayer and Harrison's theory is highly mathe-

<sup>7</sup> A. Michels, B. Blaisse, and C. Michels, *Proc. Roy. Soc. A* **160**, 358 (1937). These authors did not observe the meniscus, but their results appear to indicate that the horizontal portion of the isotherm at  $T_m$  is of finite length.

<sup>8</sup> J. E. Mayer and S. F. Streeter, *J. Chem. Phys.* **7**, 1019 (1939).

matical, and the results depend upon assumptions regarding the behavior of certain integrals. These are exceedingly difficult to evaluate because, near the critical point the integrands have large numbers of positive and negative parts, which nearly cancel each other. Further, there are limitations on the range of validity of the theory, which will be discussed later. Under these circumstances it would be an advantage if the phenomena could be considered from a somewhat more pictorial point of view. It will be the purpose of this paper to present such a pictorial theory and to see to what extent the experimental results may be understood on such a basis. The method it is proposed to use is that of associating molecules. Some of the advantages of this method were pointed out by Band,<sup>9</sup> and a somewhat similar treatment was also given by Frenkel.<sup>10</sup> However, in the theory developed by Band the situation near the critical point is not very clear, and Frenkel did not attempt an application in this region. The critical phenomena will receive our particular attention. Actually our procedure will follow more closely one suggested earlier by N. and E. Rashevsky<sup>11</sup> in considering the phenomena exhibited by emulsions. This method is almost entirely thermodynamic, and no formidable mathematical formalism is required.

The work of Mayer and Harrison is based upon the theory of clusters first introduced by Ursell.<sup>12</sup> In this theory a cluster is a mathematical abstraction, which has some resemblance to, but is not identical with, an aggregation of molecules in the usual physical sense. In this paper, we shall deal with real physical clusters of molecules, and since there seems to be no other word which is as descriptive, we shall use the term "cluster" in this sense, occasionally using "aggregation" and "droplet" as synonyms. When we have occasion to refer to a cluster in the sense of Mayer or Ursell, we shall use a modifying term, as "mathematical cluster" or "abstract cluster."

<sup>9</sup> W. Band, J. Chem. Phys. **7**, 324, 927 (1939); T. P. Tseng, S. K. Feng, C. Cheng, and W. Band, *ibid.* **8**, 20 (1940); C. Cheng, T. P. Tseng, S. K. Feng, and W. Band, *ibid.* **9**, 123 (1941).

<sup>10</sup> J. Frenkel, J. Chem. Phys. **7**, 200, 538 (1939).

<sup>11</sup> N. Rashevsky and E. Rashevsky, Zeits. f. Physik **46**, 300 (1927).

<sup>12</sup> H. D. Ursell, Proc. Camb. Phil. Soc. **23**, 685 (1927); J. E. Mayer, J. Chem. Phys. **5**, 67 (1937).

## 2. ASSOCIATION THEORY OF CONDENSATION

Let us consider one mole of gas in volume  $V$  to consist of  $n_1$  single molecules,  $n_2$  pairs of molecules held together by cohesive forces (in simple cases van der Waals forces),  $n_3$  triplets,  $\dots$ ,  $n_s$  clusters of  $s$  molecules each,  $\dots$ , all in equilibrium with each other. Then

$$\sum_s s n_s = N \quad (1)$$

where  $N$  is Avogadro's number. We let the corresponding concentrations ( $n_1/V$ ,  $n_2/V$ ,  $n_3/V$ ,  $\dots$ ,  $n_s/V$ ,  $\dots$ ) be designated as  $c_1$ ,  $c_2$ ,  $c_3$ ,  $\dots$ ,  $c_s$ ,  $\dots$  and the respective chemical potentials (referring to single clusters, rather than to moles of clusters) be denoted by  $\mu_1$ ,  $\mu_2$ ,  $\mu_3$ ,  $\dots$ ,  $\mu_s$ ,  $\dots$ . Then, if the gas is sufficiently dilute so that the perfect gas laws may be considered valid

$$\mu_s = s\phi_s + kT \ln c_s, \quad (2)$$

where  $s\phi_s$  is the value of  $\mu_s$  when  $c_s = 1$ . In particular, of course,  $\phi_1$  is the value of  $\mu_1$  when  $c_1 = 1$ . To get an expression for  $\phi_s$  we can consider the reaction

$s$  single molecules ( $c_1 = 1$ )  $\rightarrow$   
cluster of  $s$  molecules ( $c_s = 1$ )

and define a quantity  $\beta$  by the equation

$$\beta = \phi_s - \phi_1. \quad (3)$$

$\beta$ , then, is the free energy of condensation, per molecule, of single molecules at unit concentration to form a very large drop. The total free energy of the reactants in the reaction being considered is  $s\phi_1$  and that of the products is  $s\phi_s$ . The reaction involved the condensation of  $s-1$  molecules on one molecule, and the free energy would be  $\beta(s-1)$ , except for surface effects, which would be expected to add a term of the form  $\gamma s^{\frac{1}{3}}$ . The constant  $\gamma$  is related to, but not exactly equal to the surface tension, and the number of molecules at the surface of the cluster will be in general proportional to  $s^{\frac{1}{3}}$ . Still a further correction term, which we shall call  $\epsilon_s$ , will be needed to take care of the fact that this proportionality with  $s^{\frac{1}{3}}$  will not hold for very small droplets. We thus get

$$s\phi_s = s\phi_1 + \beta(s-1) + \gamma s^{\frac{1}{3}} + \epsilon_s. \quad (4)$$

Substituting  $s = 1$ , since  $\phi_s$  is then equal to  $\phi_1$ , we see that

$$\epsilon_1 = -\gamma. \quad (5)$$

On the other hand,

$$\lim_{s \rightarrow \infty} \epsilon_s = 0. \quad (5a)$$

$\phi_1$ ,  $\beta$ ,  $\gamma$ , and  $\epsilon_s$  will, of course, depend on the temperature.

The condition of equilibrium is that the total free energy  $F$  of the system should be a minimum. Hence

$$\delta F = \sum_s \mu_s \delta n_s = 0 \quad (6)$$

subject to the condition which follows from Eq. (1) that

$$\sum_s s \delta n_s = 0. \quad (7)$$

From Eqs. (6) and (7) we obtain

$$\mu_s + \alpha' s = 0 \quad (8)$$

where  $\alpha'$  is a Lagrange multiplier. With Eqs. (2) and (4) this gives

$$c_s = \exp(\beta - \alpha s - \gamma s^{\frac{2}{3}} - \epsilon_s) / kT \quad (9)$$

where  $\alpha = \phi_1 + \beta + \alpha'$ . In particular, remembering Eq. (5)

$$c_1 = e^{(\beta - \alpha) / kT}, \quad (10)$$

$\alpha$  is determined by Eq. (1), or it may be considered to be determined by Eq. (10), all the other  $c_s$  being determined in terms of  $c_1$ .

Let us now consider the gas, starting from a highly expanded state, to be gradually compressed. Before compression, with  $V$  very large,  $c_1$  will be very small. The quantities  $\beta$  and  $\gamma$  are fixed, so in order for Eq. (10) to hold it will be necessary for  $\alpha$  to be large and positive. As  $V$  decreases, all  $c_s$  and, in particular,  $c_1$  will increase; this means that  $\alpha$  must decrease. Eventually  $\alpha$  will become zero. If  $\alpha$  becomes negative, the terms of Eq. (9) will ultimately increase with  $s$ , and as  $s$  increases indefinitely become infinite. It is thus seen that when  $\alpha$  becomes zero, this is the signal for condensation; condensation saves  $\alpha$  from becoming negative, and it can remain zero for the gas phase as the amount of the gas phase decreases. It will be observed that even when  $\alpha$  becomes zero  $c_s$  will decrease fairly rapidly with  $s$  if  $\gamma$  is of reasonable magnitude because of the  $\gamma s^{\frac{2}{3}}$  term,  $\epsilon_s$  being only a correction term. The divergence of the series of  $c_s$  values, therefore, occurs suddenly as long as  $\gamma$  itself is positive. At

the point of condensation we have

$$c_1 = e^{\beta / kT} \quad (11)$$

which, in view of the interpretation of  $\beta$  as the free energy of condensation of single molecules, is obviously the correct relationship. In fact, this is practically a truism; the interest of the method is in dealing with the phenomena near the critical point.

$\alpha$  may be interpreted as the difference in molecular free energy between the liquid and the vapor. We may build up the vapor, at constant temperature and pressure, by small additions of single unassociated molecules. Between the small additions we allow equilibrium between clusters to be reestablished; since we never depart appreciably from equilibrium the reestablishment of equilibrium takes place with no free energy change. Hence we may write for the free energy of the entire vapor

$$\begin{aligned} F &= N\mu_1 = N\phi_1 + NkT \ln c_1, \\ &= N\phi_1 + N(\beta - \alpha), \\ &= N\phi_\infty - N\alpha. \end{aligned} \quad (12)$$

From Eq. (12) we may obtain another useful relationship. We recall from thermodynamics that

$$(\partial F / \partial p)_T = V. \quad (13)$$

We may also write

$$N(\partial \phi_\infty / \partial p)_T = U, \quad (14)$$

where  $U = Nu$  is the molal volume of the condensed phase. Equation (14) follows because  $N\phi_\infty$  is the free energy of the condensed phase. From Eq. (12), then, we obtain

$$N(\partial \alpha / \partial p)_T = U - V. \quad (15)$$

### 3. EFFECT OF GAS IMPERFECTIONS

We have noted that the parameters  $\phi_1$ ,  $\beta$ , and  $\epsilon_s$  will depend on temperature. If we could treat the mixture of clusters of different sizes as though it were a mixture of various species of ideal gases, these quantities would be independent of pressure. Actually they will become dependent on pressure when the pressure becomes high, because of gas imperfections. Gas imperfections will also affect the validity of Eq. (2).

Our considerations will be based on the assumption that even at densities around the

critical density it is possible to distinguish a cluster from its surroundings. However, under these circumstances even the single molecules will be close enough together so that they will exert forces on each other, as well as on the larger clusters. In general, inter-cluster forces will affect the free energy of all the clusters.

The effect of the volume occupied by the molecules themselves may be taken into account by assuming that the  $c_s$  represent the concentrations in a free volume rather than in the total volume. The free volume will not necessarily be the same for all size clusters.

In order to formulate these ideas more precisely we recall that

$$\mu_s = \bar{E}_s + p\bar{V}_s - T\bar{S}_s^* \quad (16)$$

where  $\bar{E}_s$ ,  $\bar{V}_s$ , and  $\bar{S}_s$  are the partial molecular energy, volume, and entropy for the clusters with  $s$  molecules. In an ideal system we would always have  $\bar{E}_s = E_s^0$ ,  $p\bar{V}_s = kT$ , and  $\bar{S}_s = s_s^0 - k \ln c_s$ . To take account of the gas imperfections we shall write

$$\bar{E}_s + p\bar{V}_s = E_s^0 + kT + s\eta_s \quad (17)$$

where  $s\eta_s$  is the energy caused by inter-cluster forces, together with a small correction arising from the deviation of  $p\bar{V}_s$  from  $kT$ . On the other hand, we shall continue to write

$$\bar{S}_s = s_s^0 - k \ln c_s, \quad (18)$$

this equation defining the  $c_s$  and thus the free volumes. We thus obtain

$$\mu_s = s\phi_s^* + s\eta_s + kT \ln c_s \quad (19)$$

where  $\phi_s^*$  is a true constant given by

$$s\phi_s^* = E_s^0 + kT - Ts_s^0. \quad (20)$$

$\phi_s$  is given by

$$\phi_s = \phi_s^* + \eta_s. \quad (21)$$

Since the inter-cluster forces become relatively unimportant for large clusters, we may write

$$\eta_\infty = 0. \quad (22)$$

$\beta$  is still given by Eq. (3) though it is no longer constant, since  $\phi_1$  will depend on pressure, as will all the  $\phi_s$ .

\* Here we treat a cluster of  $s$  molecules as though it were one large molecule. The superscript zeros just below refer to standard states of unit concentration of clusters which form a hypothetical ideal gas mixture.

Taking note only of the changes in the properties of the quantities involved in them, we may use all the equations of Section 2 unaltered.  $\beta$  and  $\gamma$ , though dependent on pressure, can be considered independent of the index  $s$ , all discrepancies being taken care of by  $\epsilon_s$ .

The free volumes, as noted, may depend on  $s$ . In fact, it may readily be seen that the free volumes for large clusters will be smaller than those for small clusters. When the large aggregations are pushed so close together that their edges touch, so that their free volume has essentially vanished, there will still be room in the interstices for the single molecules and smaller clusters. We shall assume for the sake of qualitative considerations that the free volume under any circumstances approaches a limiting value for large  $s$ .

It should also be borne in mind that the free lengths which are considered here (and whose cubes will give the free volumes) are small compared to the mean distance through which molecules are free to move in the field of their neighbors. Since the picture we are presenting requires that clusters be distinguishable, the free length can extend no farther than it is possible for a molecule or cluster to move without becoming part of another cluster. Thus a single molecule must be farther from any of its neighbors than the molecules within a cluster, but this distance does not represent a particularly large free length.

#### 4. THE SURFACE TENSION NEAR THE CRITICAL POINT

Something about the dependence of  $\gamma$  on the pressure may be learned from a thermodynamic relationship. First we may note, as shown in Appendix I, that (assuming spherical clusters)  $0.23\gamma$  may be taken as the actual surface tension expressed as energy per surface molecule. We may then write<sup>13</sup>

$$0.23(\partial\gamma/\partial p)_T = \Delta u_\sigma \quad (23)$$

where  $\Delta u_\sigma$  is the excess volume required by a molecule at the surface above that required by a molecule inside a cluster or inside the liquid. Since the molecules at the surface are less strongly bound than those inside, they should have greater

<sup>13</sup> G. N. Lewis and M. Randall, *Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1923), p. 248.

freedom of motion normal to the surface and should be less closely packed.<sup>14</sup> Both of these effects would tend to make  $\Delta u_\sigma$  positive, and  $\gamma$  will increase with increasing pressure. We may expect  $\Delta u_\sigma$  to be of the order of magnitude of, but probably less than,  $u$ .

The surface tension is small in the neighborhood of the critical temperature. The temperature at which the surface tension is zero when liquid is in equilibrium with vapor we shall call  $T_m$ . This is, we assume, the highest temperature at which a meniscus can be observed. The pressure at  $T_m$  at which liquid and vapor are in equilibrium we shall call  $p_m$ .

We may obtain an approximate relation between  $T_m$  and the value of  $\beta$  at  $T_m$  and under the pressure  $p_m$ . This results from forming an estimate of the surface tension,  $0.23\gamma$ , and setting it equal to zero. We may write  $0.23\gamma = \Delta E_\sigma + p\Delta u_\sigma - T\Delta s_\sigma$ , where  $\Delta E_\sigma$  is the excess of energy and  $\Delta s_\sigma$  is the excess of entropy per molecule at the surface. Setting this equal to zero, we have

$$\Delta E_\sigma + p_m \Delta u_\sigma - T_m \Delta s_\sigma = 0. \quad (24)$$

We shall now attempt rough estimates of  $\Delta s_\sigma$  and  $\Delta E_\sigma$ . When a molecule comes to the surface, its translational entropy increases because of the lack of constraint on the side away from the liquid. We might expect the force caused by a given displacement normal to the surface to be about halved, which would mean that the average vibration frequency would be lowered by a factor of 2<sup>1</sup>. The corresponding increase in entropy would be  $\frac{1}{2}k \ln 2$ . Since the vibrations parallel to the surface would be somewhat affected, too, and since the density at the surface is less than in the interior of the liquid, it will, perhaps, be a fair estimate to say that the entropy increases by  $k \ln 2$ . The energy increase,  $\Delta E_\sigma$ , might be expected to be of the order of  $\frac{1}{4}\Delta E_v$ , where  $\Delta E_v$  is the energy of vaporization per molecule, because a molecule at the surface has about three-fourths as many nearest neighbors as one in the interior of the liquid, so the vaporization process might be said to have proceeded to an extent of about one-fourth. However, because of the lower density at the surface, the transfer of a molecule to the

surface is equivalent to a greater fraction of the vaporization than this. It seems about right<sup>15</sup> to set  $\Delta E_\sigma = 0.4\Delta E_v$ . This is not based on data near the critical point, but it should not cause much error to use it.

The molecule which enters the surface will be under the influence of vapor molecules outside the surface to about the same extent as a single molecule is under the influence of forces arising from neighboring molecules and clusters. Therefore, it is reasonable to set for the  $\Delta E_v$  under these circumstances

$$\Delta E_v = \bar{E}_1 - E_\infty$$

where  $E_\infty$  is the energy per molecule of a large cluster. Using Eq. (17) with  $s=1$

$$\Delta E_v = E_1^0 + kT + \eta_1 - p\bar{v}_1 - E_\infty. \quad (25)$$

Now

$$\begin{aligned} \beta &= \phi_\infty - \phi_1 \\ &= \phi_\infty - \phi_1^* - \eta_1. \end{aligned}$$

Since  $\phi_\infty$  is a free energy term we may write

$$\phi_\infty = E_\infty + pu - Ts_\infty.$$

Also

$$\phi_1^* = E_1^0 + kT - Ts_1^0.$$

Therefore, if we set  $\Delta s_v^0 = s_1^0 - s_\infty$

$$\begin{aligned} \beta &= E_\infty - E_1^0 - \eta_1 + pu - kT + T\Delta s_v^0 \\ &= -\Delta E_v + pu - p\bar{v}_1 + T\Delta s_v^0. \end{aligned} \quad (26)$$

From its definition, we can set  $\Delta s_v^0$  equal to  $k \ln(1/u_f)$ , where  $u_f$  is the free volume per molecule in the condensed phase, that is, in a large cluster.  $u_f$  may be estimated in terms of  $u$ , the actual volume per molecule of the condensed phase near the critical point.

As has been pointed out by Eyring and Hirschfelder,<sup>16</sup> the free volume of a liquid is best calculated as the cube of a free length, and the free length may be assumed in first approximation to increase at the same rate as the linear expansion. Thus if we let  $l_f$  be the free length near the critical point we may say that  $u^{1/3} - l_f$  is roughly the length which is not free, and we may identify  $u^{1/3} - l_f$  with the cube root of the volume at the melting point. The ratio of the volume at

<sup>14</sup> Compare H. Eyring, J. Walter, and A. E. Stearn in *Surface Chemistry* (edited by F. R. Moulton, A. A. A. S., 1943), p. 88.

<sup>15</sup> W. D. Harkins, *Zeits. f. physik. Chemie* **A139**, 647 (1928) (see especially p. 665).

<sup>16</sup> H. Eyring and J. O. Hirschfelder, *J. Phys. Chem.* **41**, 249 (1937).

the critical point to that at the melting point is, therefore,  $u/(u^3-l_f)^3$ , and this is known to be about 3. This gives  $l_f=0.306u^3$  or  $u_f=l_f^3=0.03u$ . Hence  $\Delta s_v^0 \sim -k \ln(0.03u)$ . The effect of communal entropy is neglected in this rough calculation.

We set this value of  $\Delta s_v^0$  in Eq. (26), solve for  $\Delta E_v$ , set  $\Delta E_v=0.4\Delta E_v$  in Eq. (24), and insert also in Eq. (24) our estimated value of  $\Delta s_v$ . This gives at  $T=T_m$  and  $p=p_m$

$$\beta = -kT_m \ln(0.17u) + p_mu - p_m\bar{v}_1 + 2.5p_m\Delta u_\sigma. \quad (27)$$

As noted above,  $\Delta u_\sigma$  will be of the order of  $u$ .  $p_mu$  will be considerably less than  $kT$ ; since the single molecules feel the attractive forces less than the molecules within a large cluster,  $p_m\bar{v}_1$  should be larger than  $p_mu$ , but it cannot be as great as  $kT$ . Therefore, the last three terms in Eq. (27) may be reasonably neglected in the applications we shall make, and we shall use

$$\beta \sim -kT_m \ln(0.17u). \quad (28)$$

The estimates of  $\Delta s_v$  and  $\Delta u_\sigma$ , which we have made in the above discussion, can be checked roughly from experimental data.  $\Delta s_v$  is equal to  $-(\partial\gamma_\sigma/\partial T)_p$  where  $\gamma_\sigma \sim 0.23\gamma$  is the free energy per molecule at the surface.  $(\partial\gamma_\sigma/\partial T)_p$  is closely related to the Eötvös constant, which is equal to  $-d(U^3\gamma_0)/dT$  where  $\gamma_0$  is the ordinary surface tension and  $U$  is the molal volume of the liquid. If we transform this to  $d(u^3\gamma_0)/dT$ , the quantity obtained will be almost the same as  $(\partial\gamma_\sigma/\partial T)_p$ , since  $u^3$  is roughly the area occupied by a molecule. The Eötvös constant is usually of the order of 2 erg mole<sup>-3</sup> deg.<sup>-1</sup>, which makes  $d(u^3\gamma_0)/dT$  about  $-2.8 \times 10^{-16}$  erg molecule<sup>-3</sup> deg.<sup>-1</sup>. Comparing this with the value of the Boltzmann constant,  $k=1.37 \times 10^{-16}$  erg deg.<sup>-1</sup>, we see that our estimate of  $\Delta s_v$  as  $k \ln 2$  is of the right order of magnitude.

Turning now to  $\Delta u_\sigma$ , we may estimate this quantity if we are willing to admit that a change of volume at the surface has the same effect on the entropy as a change of volume in general. We then set  $\Delta s_v/\Delta u_\sigma = (\partial S/\partial U)_T$ . Since  $(\partial S/\partial U)_T = (\partial p/\partial T)_u$ , it may be estimated from Fig. 1 or 2 to be slightly over 1 atmos. per deg. for liquid ethylene. Taking  $\Delta s_v$  as  $k \ln 2$ , we find  $\Delta u_\sigma$  to be about  $10^{-22}$  cc per molecule, which is obviously of the same order of magnitude as  $u$ .

Measurements of the surface tensions of methyl ether and of propylene have been carried close to the critical temperature,  $T_c$  (which may or may not be identical with our  $T_m$ ), by Winkler and Maass.<sup>17</sup> They found that the surface tension was not a linear function of  $T_c - T$ , but that the slope of the curve, surface tension *vs.* temperature, became considerably smaller near the critical point. The values seemed to follow either the rule suggested by Ferguson<sup>18</sup> (specializing an equation of van der Waals) that the surface tension should be proportional to  $(T_c - T)^{6/5}$  or that suggested by Katayama<sup>18</sup> that it should be proportional to  $(T_c - T)(U^{-1} - V^{-1})^{1/2}$ . Ferguson's formula would lead to a slope which is zero, though only weakly, at  $T_c$ , while Katayama's formula would still give a finite slope if  $T_c$  is the same as  $T_m$ , since the molal volume of the liquid,  $U$ , and of the vapor,  $V$ , are not equal at this point. It is difficult to give a suggestion as to the exact significance of these formulas;<sup>19</sup> however, there are at least two factors which would contribute to a decrease in the slope of the surface tension *vs.* temperature curve near the critical point.

In the first place, the surface tension which is being measured is the surface tension between the saturated liquid and its vapor. We must write

$$\begin{aligned} d\gamma_\sigma/dT &= (\partial\gamma_\sigma/\partial T)_p + (\partial\gamma_\sigma/\partial p)_T dp/dT \\ &= -\Delta s_v + \Delta u_\sigma dp/dT. \end{aligned} \quad (29)$$

Since  $dp/dT$  near the critical point is of the same order of magnitude as  $(\partial p/\partial T)_v$ , and this is roughly equal to  $\Delta s_v/\Delta u_\sigma$ , it is seen that the two terms in Eq. (29) will be of the same order of magnitude, and since they are of opposite sign,  $d\gamma_\sigma/dT$  should be smaller near the critical point than it would be far removed from it where  $dp/dT$  is very small.

Furthermore, near the critical point the vapor is full of droplets, and the liquid will also be full

<sup>17</sup> C. A. Winkler and O. Maass, *Can. J. Research* **9**, 65 (1933).

<sup>18</sup> See N. K. Adam, *The Physics and Chemistry of Surfaces* (Oxford University Press, New York, 1941), third edition, pp. 165.

<sup>19</sup> R. H. Fowler, *Proc. Roy. Soc. A* **159**, 229 (1937); R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (The Cambridge University Press, New York, 1939), pp. 445, have discussed these formulas and their application in the neighborhood of the critical point. This discussion, however, is based upon the assumptions that the co-existence curve has the rounded top of the van der Waals theory and that the density of the liquid remains constant to the surface.



of bubbles. This means that an increase in the extent of the boundary between the two phases is greater than the actual increase in the true surface. This can be visualized by considering what happens when one slices a piece of Swiss cheese. If a cut made through the liquid intersects some bubbles, an increase in true surface area will only result from the part which does not go through the bubbles. This will result in an apparently lower surface energy in this temperature region, hence a flatter approach to  $\gamma_s = 0$ .

None of these considerations indicate that  $\gamma$  will not go through zero and become negative. A negative surface tension cannot be observed but is important for our considerations.

As soon as the surface tension vanishes, there will be a tendency for the formerly nearly spherical droplets to spread out in such forms as to have the greatest possible surface, such as sheets or filaments. The question as to whether a filament will be more stable than a flat surface is a fairly complicated one, however. The molecules in a filament have considerably more freedom of motion than those on a surface, but they also have fewer neighbors. It is, therefore, difficult to say whether the entropy term should be expected to overtake the energy term at a higher or lower temperature than for the flat surface. However, if a filament became stable at a temperature lower than that at which the surface tension of a flat surface vanished, we might expect the system to tend at this temperature suddenly to go over to filaments, causing what would appear to be a sudden drop to a state of zero surface tension. This certainly does not seem to be the case.

The considerations for wide-spread disks with sharp edges should be qualitatively the same as for filaments. However, it is possible to have flat disks with bulges around the edge, thus avoiding sharp corners. Furthermore it is quite possible that filaments become stable only slightly above the temperature at which the surface tension for flat surfaces vanishes. In any event filaments and disks are wasteful of space. It may, therefore, be expected that they will be suppressed when the system is fairly highly compressed.

Even if filaments and thin films are avoided, it does appear that as soon as the surface tension

becomes negative there will be a tendency for the proliferation of surfaces in the form of bulges and protuberances. The surface of a cluster will probably be practically proportional to its volume; since the  $s^3$  term in Eq. (4) will thus be replaced by a term proportional, or nearly proportional, to  $s$ , the effect of surface tension will largely disappear. However, the larger the cluster the greater will be the number of possible configurations it may take on account of folding and distortion of the surface. This may be expected to introduce a term of the form  $s^a$ , where  $a$  is a fairly small number, into the partition function for the cluster, and hence a term  $NkTa \ln s$  into the free energy expression. Some of these considerations have been mentioned by Mayer and Streeter.<sup>8</sup>

It may be noted that since  $\gamma$  decreases with decreasing pressure, the effects of negative surface tension will already appear at  $T = T_m$  on the vapor side of the isotherm where  $p < p_m$ . But even the system of bulges and protuberances will be wasteful of space, certainly of free space, and so as  $p$  approaches  $p_m$  this particular effect of negative surface will be suppressed, both because there is less space and because the surface tension becomes less negative.

## 5. THE PHENOMENA AT TEMPERATURE $T_m$

On the basis of the discussion of the preceding sections, we shall now attempt a description of the phenomena which take place in the neighborhood of the critical point. We have seen (just preceding Eq. (11)) that, when  $\gamma$  is positive, very large clusters suddenly come into equilibrium when  $\alpha$  vanishes, and we interpret this as the normal type of condensation. However, at  $T_m$ , where  $\gamma$  becomes zero, the large droplets may come in gradually, and the process  $\alpha \rightarrow 0$  needs reinterpretation. For large value of  $s$ , Eq. (9) becomes

$$\begin{aligned} c_s &= e^{(\beta - \alpha s)/kT_m} \\ &\approx c_1 e^{-\alpha(s-1)/kT_m}, \end{aligned} \quad (30)$$

We shall for the moment neglect the free energy term  $NkTa \ln s$  mentioned at the end of the preceding section.

We shall assume that the free volume approaches a definite value  $V_f$  for large  $s$ . Then,

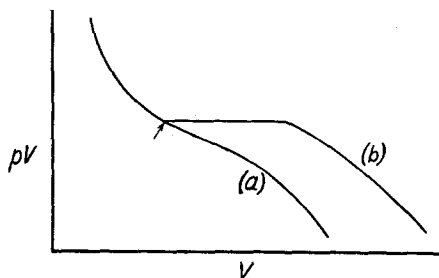


FIG. 3.

if  $\alpha$  is sufficiently small so that most of the molecules are contained in large clusters we may define a total net concentration  $C = N/V_f$ , and write

$$C \cong \sum_s s c_s. \quad (31)$$

Using Eq. (30)

$$C = e^{\beta/kT_m} (1 - e^{-\alpha/kT_m})^{-2} e^{-\alpha/kT_m}. \quad (32)$$

If  $\alpha/kT_m$  is very small, this becomes approximately

$$C = e^{\beta/kT_m} (kT_m/\alpha)^2 \quad (33)$$

which, solved for  $\alpha$ , gives

$$\alpha = kT_m (e^{\beta/kT_m}/C)^{1/2}. \quad (34)$$

As  $\alpha \rightarrow 0$ , the system approaches a state in which  $e^{\beta/kT_m} = c_1$  is vanishingly small compared to  $C$ . This can only happen if  $V_f$  approaches zero. Since  $V_f$  is a free volume, it is possible for this situation to occur while the total volume  $V$  is still finite. There will be a volume, which we shall call  $V_0'$ , so small that large clusters can no longer move independently, and at this point  $V_f$  is zero. When the system is compressed to still lower values of  $V$ , the large aggregation itself is being compressed. As we have remarked above, this large aggregation will contain many internal surfaces. If the surface tension is zero (i.e., at temperature  $T_m$ ), there will be no resistance to the further change in volume and hence no free energy, or pressure, change until these surfaces are squeezed out.

Another expression for the quantity  $C = N/V_f$  may be obtained directly from the determination of  $V_f$  as a function of  $V$ . This problem is very similar to the one previously discussed, which led to Eq. (27).  $V_f^{1/3}$  may be taken as the free

length, which may be set equal to  $V^{1/3} - V'^{1/3}$ , where  $V'$  is the volume which would be occupied if the system were compressed, without change in the density or total amount of material in the large clusters, until the free volume just vanished. If the large clusters neither evaporated nor accumulated material and were incompressible,  $V'$  would be equal to  $V_0'$ . Actually  $V'$  is a function of  $V$  and approaches  $V_0'$  as  $V$  approaches  $V_0'$ .

From the identity,

$$x - y = (x^{1/3} - y^{1/3})(x^{2/3} + x^{1/3}y^{1/3} + y^{2/3}),$$

we may write, if  $V - V'$  is small compared to  $V$ ,

$$V_f^{1/3} = (V - V')/3V'^{2/3}. \quad (35)$$

Hence

$$C = 27NV'^2(V - V')^{-3}. \quad (36)$$

From Eq. (34) then,

$$\alpha = kT_m e^{\beta/2kT_m} (V - V')^{1/3} / (27N)^{1/3} V'^{2/3}. \quad (37)$$

If we neglect the variation of  $\beta$ , we may use Eq. (28) to get a rough evaluation. This gives

$$\alpha/kT_m \sim 0.5(V - V')^{1/3}/V_0'^{2/3}. \quad (38)$$

In this we have set  $V' = U = V_0'$  in the denominator.

The above equations are all predicated on the assumption that  $\gamma$  is zero and remains zero. Actually, as we have noted before,  $\gamma$  will depend on the volume; but for  $V > V_0'$  the value of  $\gamma$  will only decrease below zero, so the system will still act as though it had zero surface tension, as far as Eq. (30) and the quantities based on it are concerned; that is, the effect of  $\gamma$  may be included in  $\alpha$ .

Equation (15) may be used to find the rate at which  $\alpha$  changes as the volume is increased beyond  $V_0'$ . For a small range of such volumes  $U - V$  will not vary too much and may be set equal to  $U_0 - V_0'$ , where  $U_0$  is the value of  $U$  when  $V = V_0'$ . At the critical point for ethylene we see from Fig. 2 that  $V_0' - U_0$  is about  $0.1V_0$ . An increase in volume until  $V - V_0'$  is about  $0.2V_0'$  lowers the pressure by 0.1 atmos., and from Eq. (15), using  $V - U = 0.1U \sim 0.1 \times 4$  cc/g, we find that  $\alpha/kT$  changes from zero to about  $0.5 \times 10^{-4}$ . A rough evaluation of  $V - V'$  may

then be made from Eq. (38), and we estimate<sup>20</sup> that when  $V - V_0'$  is about  $0.2V_0'$  then  $V - V'$  is about  $0.002V_0'$ .

Since the change in  $V - V'$  is so much less than  $V - V_0'$ , it appears that over this range  $dV' \cong dV$ . It would seem that over as great a range in  $V - V_0'$  as this, the effect could only be ascribed to expansion of the large clusters as the pressure is decreased, so that they continue almost to fill the space available. This would be further aided as  $\gamma$  became negative, by the tendency of the large clusters to take shapes which have a large surface. Just at  $V = V_0'$  the large clusters resemble the liquid phase; the large clusters themselves will contain bubbles of gas, as the liquid itself must. The expansion of the liquid is a combination of the expansibility (inverse of compressibility) of true liquid and the bubbles contained in it; and it appears that the expansibility of the vapor is the combined expansibility of the gas substance and the droplets contained therein, the droplets in turn containing gas within themselves, and so on. If, however, rather than considering the clusters and bubbles, which are complex entities, we should desire to fix our attention on what we might call "true" liquid (liquid without bubbles) and "true" vapor (the part composed of single molecules and small clusters), then we could not exclude the possibility that the expansibility of liquid and vapor are caused by changes in the relative amounts of "true" liquid and "true" vapor. We cannot eliminate this possibility because our equations deal only in free volumes, and we cannot estimate very exactly what the actual molecular density of true vapor may be. In any event, since there is no discontinuity at the point where  $\gamma = 0$  and  $\alpha = 0$ , it seems natural, though perhaps still a little speculative, to set the coefficient of compressibility of the large

<sup>20</sup> The estimate of  $V - V'$  is based, it will be recalled, upon the assumption that the free energy term  $NkTa \ln s$  mentioned at the end of Section 4 could be neglected; that is, we assume  $a = 0$ . If  $a$  were 1, then Eq. (33) would be replaced by  $C = 2e^{\beta/kT_m}(kT_m/\alpha)^3$ . The final result would be that when  $V - U = 0.2U$  and  $\alpha/kT$  is about  $10^{-4}$ , we would get a very much smaller value for  $V - V'$ . Our conclusions, then, would hold *a fortiori*, and this would be true for any value of  $a > 0$ . There seems to be no reason to suppose that  $a$  would be less than zero. We may also remark that (as can be readily seen from the calculations in Section 6) the value of  $\gamma$  remains so small that it would not change our conclusions even if the  $s^{\frac{1}{2}}$  term remained in the expression for the free energy.

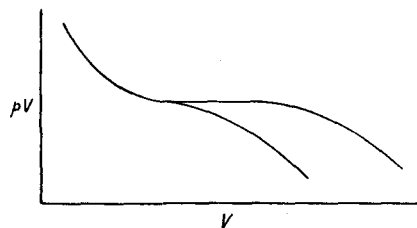


FIG. 4.

clusters in the vapor phase at  $V = V_0'$  equal to the coefficient of compressibility of liquid at  $U = U_0$ , or  $V_0'^{-1}(\partial V'/\partial P)_T = U_0^{-1}(\partial U/\partial p)_T$ , which gives, at  $V = V_0'$

$$(\partial V/\partial p)_T \cong (V_0'/U_0)(\partial U/\partial p)_T. \quad (39)$$

In other words, the slope of the isotherm to the right of the horizontal portion at  $T_m$  is determined by, and is approximately equal to, the slope on the left. If these ideas are correct, the situation may be illustrated graphically as shown in Fig. 3. Suppose that, if we could have a liquid which did not vaporize, it would follow an isotherm of the form illustrated in Fig. 3(a). It is in equilibrium with vapor at the point indicated by the arrow. Just at  $T_m$ , this point coincides with the condition of zero surface tension. The curve splits apart, so to speak, at this pressure and, as shown in Fig. 3(b), the section at lower pressures is simply transferred to large volumes, only slightly distorted. The amount of distortion will increase, of course, at larger volumes.

However, if this much is correct we can draw a further conclusion. Since  $\beta$  will certainly not vary rapidly at  $V = V_0'$ , we may use Eq. (38) to find  $(\partial \alpha/\partial V)_T$ :

$$(\partial \alpha/\partial V)_T \cong 0.75(V - V')^{\frac{1}{2}} V_0'^{-\frac{1}{2}} (1 - dV'/dV).$$

Combining this with Eq. (15) we obtain

$$(\partial p/\partial V)_T \cong 0.75N(V - V')^{\frac{1}{2}} V_0'^{-\frac{1}{2}} \times (U - V)^{-1} (1 - dV'/dV). \quad (40)$$

This will vanish at  $V = V_0'$ , since  $(V - V')^{\frac{1}{2}}$  then becomes zero. This, in itself, would not be of great importance, since it vanishes to a low order; and it can be readily shown that if  $V'$  were constant the value of  $(\partial p/\partial V)_T$  would actually become quite large when  $V$  was only slightly greater than  $V_0'$ . However, since  $V'$  does in-

crease with  $V$ , the value of  $(\partial p/\partial V)_T$  does not increase nearly this rapidly, and, if  $dV'/dV$  does actually approach 1 as  $V \rightarrow V'_0$ , then we see that  $(\partial p/\partial V)_T$  becomes zero to a higher order. We may thus expect Fig. 3 to be replaced by Fig. 4, and the curve at  $T_m$  will be quite smooth.<sup>21</sup> This is indeed indicated by Fig. 2.

In the calculations of this section we have assumed that the free volume of a large cluster is not affected by the presence of the small clusters. In other words, we assume, for example, that the reaction, 2 clusters ( $s=2000$ )  $\rightleftharpoons$  1 cluster ( $s=4000$ ), comes to the same equilibrium as if the space occupied by the small clusters were empty. This will be true if the large clusters can move around throughout the space without thereby affecting the freedom of motion of the small clusters. This should be approximately the case, because the small clusters do not form a very densely packed molecular system. Even though the free volumes of individual cluster sizes may be very small, as indicated at the end of Section 3, it is rather the actual spacing of the individual molecules of the small clusters which is important here. For, if a certain amount of association or dissociation among the small clusters is forced by motion of the large clusters, this may still take place without appreciably affecting the total free energy of all the molecules in the small clusters, since all sizes of cluster are in equilibrium with each other. Any residual effect on the collective free energy of the small clusters caused by the occurrence of association or dissociation among the large clusters is probably proportional to the surface of the large clusters, and is properly taken into account in the surface tension term.

## 6. THEORY OF EVAPORATION

Frenkel<sup>10</sup> has pointed out that a general theory of heterophase fluctuations can be adapted to the formation of bubbles in a liquid, as well as to the formation of droplets in a vapor. So we may expect to be able to develop a theory of evaporation, complementary to the theory of condensation, in which evaporation will be preceded by the appearance of bubbles in the liquid.

<sup>21</sup> The free energy term  $NkTa \ln s$  mentioned at the end of Section 4 could conceivably upset this conclusion. If  $a$  were equal to 1, for example,  $\alpha$  would be proportional to  $V - V'$  instead of  $(V - V')^{\frac{1}{3}}$ , and  $(\partial \alpha/\partial V)_T$  would be proportional to  $1 - dV'/dV$  instead of  $(V - V')^{\frac{1}{3}}(1 - dV'/dV)$ . If, however,  $dV'/dV$  approaches 1 at  $V = V'_0$ , as would seem even more probable if  $a$  were greater than zero, the conclusion would still hold. Were  $a$  greater than 1, it would be necessary for  $1 - dV'/dV$  to approach zero, in order to avoid an infinity. However, if the droplets nearly fill the volume, it seems unlikely that the many configurations of the large droplets, which would result in the term  $NkTa \ln s$ , could be realized on account of the interference of their neighbors. I, therefore, believe that the discussion based on Eq. (40) gives the best account of the true situation.

Since the same liquid and vapor are involved in the two cases, there will be a relationship between the parameters, and on this account it seems worth while to develop the bubble theory of evaporation in some detail.

The bubbles are in some respects similar to the "holes" in liquids which have been considered before,<sup>22</sup> but are not the same thing since they are defined by the number,  $t$ , of gas molecules contained within the bubble. Such bubbles will appear in appreciable numbers, for reasons we shall see, only very close to the critical point; the "holes" which are usually discussed may be a real property of a liquid, and any contribution they may make to the molecular free energy, in addition to the effect of the bubbles, is included in the quantity we have called  $\phi_\infty$ . Both the holes and the bubbles lower  $\phi_\infty$  from the value it would have if they did not exist—otherwise neither holes nor bubbles could occur. The bubbles affect  $\phi_\infty$  simply by lowering the mole fraction of true liquid in the mixture.

The molecular free energy of a gas bubble consisting of an infinite number of molecules is given by  $\phi_\infty - \alpha$ . This follows from Eq. (12) since an infinitely large bubble is nothing but a vapor phase. We assume that the relation continues to hold for finite bubbles, where the liquid is the stable phase and  $\alpha$  is negative; in fact, the negative values of  $\alpha$  may be considered to be defined in this way.

The chemical potential  $\mu_t$  of a gas bubble containing  $t$  molecules will have a term  $t(\phi_\infty - \alpha)$ . There will also be a contribution from a surface term proportional to  $t^{\frac{1}{3}}$ . However, the molecules at the surface will actually be supplied by the liquid rather than the vapor. If we are to express this term in terms of the quantity  $\gamma$  which we have previously defined, we must multiply  $t$  by the ratio of the density of the liquid,  $1/u = N/U$ , to the density of the gas,  $1/v = N/V$ . The term is, therefore,  $\gamma(tv/u)^{\frac{1}{3}}$ . To this we must add a correction term  $\epsilon_t$  for small bubbles. Finally, there will be a term arising from the mobility of the bubble. This may be obtained if we fix our attention on a single arbitrarily chosen molecule in the bubble, assuming that it can

<sup>22</sup> See S. Glasstone, K. J. Laidler, and H. Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), p. 477.

wander at will through its portion of the volume of the liquid, namely  $c_i^{-1}$ , in addition to its space within the bubble, namely, its free volume  $v_f'$ . If  $c_i$  is defined as the proper kind of effective concentration, we may say that the free volume of the selected molecule is  $c_i^{-1} + v_f'$ . The other molecules in the bubble, being constrained to move with the chosen molecule, have only the free volume  $v_f'$ . The fact that the chosen molecule has the free volume  $c_i^{-1} + v_f'$  instead of  $v_f'$  means that we must add to the chemical potential a term  $-kT \ln[(c_i^{-1} + v_f')/v_f']$ . Summarizing

$$\mu_i = t\phi_\infty - t\alpha + \gamma(tv/u)^{1/3} + \epsilon_i - kT \ln[(c_i^{-1} + v_f')/v_f']. \quad (41)$$

The total change in free energy produced by an arbitrary variation of the numbers of bubbles  $n_i$  will be given by

$$\delta F = \sum_i \mu_i \delta n_i - \phi_\infty \delta N_0$$

where  $N_0$  is the total number of molecules in bubbles and  $-\delta N_0$ , therefore, is the change in the total number of molecules not in bubbles. Obviously

$$\delta N_0 = \sum_i t \delta n_i.$$

Setting this into the expression for  $\delta F$  and setting it equal to zero, we obtain

$$\sum_i \delta n_i (\mu_i - t\phi_\infty) = 0.$$

Since there is now no restriction on the  $\delta n_i$ 's, we may set the coefficient of each one equal to zero. This gives

$$v_f'/(c_i^{-1} + v_f') = \exp[t\alpha - \gamma(tv/u)^{1/3} - \epsilon_i]/kT \quad (42)$$

as the equation which determines  $c_i$ .

The quantity on the left-hand side of Eq. (42) obviously cannot become greater than 1. As long as  $\alpha$  is negative and  $\gamma$  is positive (since  $\epsilon_i$  is a correction to the term  $\gamma(tv/u)^{1/3}$  which cannot change its sign), the right-hand side is less than 1. This is true even if  $\alpha=0$ , but as soon as  $\alpha$  becomes positive the terms with large  $t$  become greater than 1 and, in fact, the expression diverges. The pressure at which  $\alpha$  becomes positive is, therefore, the vapor pressure, in agreement with conclusions reached from the study of the condensation process.

It is of interest to note that, if  $\gamma$  is appreciable

and  $v/u$  large, the exponential quantities on the right-hand side of Eq. (42) are very small even when  $\alpha=0$ . This means that  $c_i$  must be very small; in other words, except close to the critical point, where  $\gamma$  is small and  $v/u$  near 1, there will be practically no bubbles.

At  $T=T_m$  the two quantities  $\gamma$  and  $\alpha$  are zero together when the volume of the liquid  $U$  is equal to  $U_0$ , the value at the low volume end of the flat part of the isotherm; but for  $U < U_0$ , the terms in  $\alpha$  and  $\gamma$  are of the same sign since  $\alpha$  is less than 0 and  $\gamma$  greater than zero. As  $U \rightarrow U_0$  and  $p \rightarrow p_m$ , therefore, the right-hand side of Eq. (42) increases, and the expressions for all values of  $t$  approach 1 simultaneously. We thus get a gradual approach to a condition of big bubbles, that is, a foam.

Let us now consider the situation when the liquid has been compressed to 0.1 atmos. above  $p_m$ . The rate of change of  $\alpha$  will be about the same as on expansion of the gas phase;  $\alpha$  will go to about  $-0.5 \times 10^{-4}$ . By comparing Eqs. (23) and (15) we see that the change of  $\gamma$  will be about 50 times as great as that of  $\alpha$ ;  $\gamma/kT$  will become about  $3 \times 10^{-3}$ . If the terms other than  $t\alpha$  are negligible in the exponent of Eq. (42), and provided that  $v_f'$  is small enough, the maximum value of  $tc_i$  occurs at  $t=t_{\max} = |kT_m/\alpha|$ , or, about 3, indicating that the surface tension will have a large but not an overwhelming effect, and the effect will be smaller the less the amount of the compression above  $p_m$ . For the purpose of evaluating  $c_i$ , a correction to the approximate equation

$$v_f'/(c_i^{-1} + v_f') = e^{t\alpha/kT_m}$$

could be made by multiplying the right-hand side by  $e^{-\gamma(t_{\max}v/u)^{1/3}/kT_m}$ . This would give us an expression from which  $c_i$  could be found, provided  $v_f'$  were known. Actually we shall be content with an inequality, and since  $c_i = 1/c_i^{-1} > 1/(c_i^{-1} + v_f')$  we write

$$c_i > v_f'^{-1} e^{t\alpha/kT_m} e^{-\gamma(t_{\max}v/u)^{1/3}/kT_m}. \quad (43)$$

We shall now consider a quantity  $C_0$ , analogous to the quantity  $C$  of Section 5.  $C_0$  is defined as the number of molecules in bubbles per unit free volume for the motion of bubbles in the liquid. It may be approximately obtained as

$\int_0^\infty t c_i dt$ . Therefore, from Eq. (43), since  $\alpha < 0$ ,

$$C_0 > v_f'^{-1} e^{-\gamma(t_{\max} v/u)^{1/2}/kT_m} (kT_m/\alpha)^2. \quad (44)$$

By reasoning similar to that which resulted in Eq. (36), we may write

$$C_0 = \frac{27N_0(fN_0v)^2}{(U-fN_0v)^3}. \quad (45)$$

Here  $N_0v$  is the total volume of the bubbles, and  $fN_0v$  is the total volume of the liquid at which the free volume  $U_f$  of the bubbles would vanish, assuming  $N_0$  and  $v$  constant.  $f$  will be slightly greater than 1, since it is only necessary that the bubbles touch in order for  $U_f$  to vanish. It will be recognized that use of Eq. (45) may not be entirely consistent with our definition of  $C_0$  in terms of effective concentrations  $c_i$  which are set up so that the sum  $c_i^{-1} + v_f'$  gives the effective free volume of a chosen molecule in a bubble. If we use Eq. (45), it might, for example, be supposed that it would be better to add free lengths, using  $(c_i^{-1} + v_f'^{1/2})^3$  instead of  $c_i^{-1} + v_f'$  in Eq. (41); but changes of this sort would still allow us to insert Eq. (45) into the inequality (44).

We may write for the total volume of the liquid, including the bubbles,

$$U = (N - N_0)u' + N_0v \quad (46)$$

where  $u'$  is the molecular volume of the liquid aside from the bubbles. The denominator of Eq. (45) becomes  $Nu' - N_0(fv - v + u')$ . This is zero when  $U = U_0$ . Suppose at some smaller value of  $U$  the value of  $N_0$  has become  $N_0 + \delta N_0$ . If  $v$  and  $u'$  do not change, the denominator becomes  $\delta N_0(fv - v + u')$ . Therefore, Eq. (45) becomes

$$C_0 = \frac{27f^2N_0^3v^3}{v(fv - v + u')^3(\delta N_0)^3} \quad (47)$$

and using (44) we obtain

$$\left(\frac{\delta N_0}{N_0}\right)^3 < 27e^{\gamma(t_{\max} v/u)^{1/2}/kT_m} \times \frac{v_f'}{v} \frac{f^2v^3}{(fv - v + u')^3} \left(\frac{\alpha}{kT_m}\right)^2. \quad (48)$$

Since  $v \sim u'$  and  $f \sim 1$ , and since  $v_f'$  will be smaller

than  $v$ , we may write

$$\delta N_0/N_0 < 3e^{\gamma(t_{\max} v/u)^{1/2}/kT_m} |\alpha/kT_m|^{1/2}. \quad (49)$$

For the case we have considered, namely  $p - p_m = 0.1$  atmos., we find that this gives  $\delta N_0/N_0 < 0.01$ . It is clear that this will be insufficient to account for the decrease in volume caused by an increase in pressure of 0.1 atmos. For smaller values of  $p - p_m$  the discrepancy would be still greater. In this calculation we have neglected changes in  $u'$  and  $v$ . The result shows that this is not permissible, and we see that the high compressibility of the liquid is a result of the intrinsic compressibility of the true liquid part and of the bubbles, but is not to be ascribed merely to the squeezing out of the bubbles. In this respect the liquid phase is very similar to the vapor phase.

We are now in a position to consider a little more closely the nature of the process by which the surface is decreased as the spongy mass of liquid and vapor is squeezed from molecular density  $1/v_0'$  to molecular density  $1/u_0$  across the flat part of the isotherm at  $T_m$ . As we approach the density  $1/v_0'$  from the low density side we have droplets of average density approximately  $1/u_0$  dispersed in a medium consisting of single molecules and smaller droplets which is of considerably lower density. The droplets or clusters themselves consist of material of higher density in which bubbles are dispersed; in fact, in view of the negative surface tension when the density is less than  $1/v_0'$ , the bubbles probably form a continuous matrix within the drops. On the other hand, as we approach the density  $1/u_0$  from the high density side we have bubbles of density  $1/v_0'$  dispersed in a medium of considerably higher density; these bubbles, in turn, consist of material of lower density with droplets dispersed inside them. To go from the state existing at the low density side of the horizontal part of the isotherm to that existing at the high density side thus requires an exceedingly complex rearrangement of interior surfaces. The general picture which we have developed as to the nature of the phenomena which take place in the neighborhood of the critical point has some points of resemblance to, and some differences from, descriptions which have been previously

given.<sup>23</sup> As far as I am aware, the connection of these ideas with the equations of the theory of associating systems has not been brought out.

We conclude this section with a remark on the experiments of Mason, Naldrett, and Maass.<sup>2</sup> These writers state that only a very small portion of the apparently horizontal section of the coexistence curve ("coexistence" meaning that there is a stable meniscus) is absolutely flat, although a considerable section is horizontal to within about 0.001°C. This is based on the behavior of the meniscus in vigorously shaken tubes whose total molal volumes lie between  $U_0$  and  $V_0'$ . One would naturally expect that for any volume in this range the meniscus would stand near the center of the tube and simply fade out as the temperature was increased. Actually, it was found that for an appreciable range of volumes greater than  $U_0$  the meniscus appeared to disappear through the bottom of the tube, as though there were evaporation of the liquid. Of course this occurred over an extremely minute range of temperature. Also, for an appreciable range of volumes less than  $V_0'$  the meniscus seemed to disappear through the top of the tube. Maass and Naldrett interpreted this as meaning that the "critical range" of volumes, though finite, in contradiction to the van der Waals theory, was somewhat smaller than one would suppose from the appearance of the coexistence curve. However, if the isotherm of  $T_m$  is truly horizontal over a region, it is possible to have material of any density along the isotherm in equilibrium with material of any other density. This allows the possibility of an apparent shortening of the horizontal portion. For it may be that sufficient gradients of temperature or pressure are set up in the tubes in the process of shaking so that the state finally approached is one in which the densities of the two phases in equilibrium (or nearly in equilibrium) are close to the middle, rather than exactly at the ends of the horizontal part of the coexistence curve. If the coexistence curve is

really geometrically flat only over a small region near the center of the apparently horizontal portion, it presumably means that the isotherm is geometrically flat only over the same region.

## 7. PHENOMENA AT TEMPERATURES ABOVE $T_m$

At the temperature  $T_m$  the horizontal part of the isotherm corresponds to the squeezing out of the holes and the decrease in the total surface of the spongy but connected mass of liquid which is formed when  $\alpha=0$ . Above  $T_m$  the liquid has a negative surface tension, and in order to cause the spongy mass to disappear it will be necessary to increase the pressure. The isotherms, therefore, slope upward toward lower values of  $V$  just above the region where the isotherm is horizontal at  $T_m$ .

At volumes somewhat greater than this critical region the clusters will, since the surface tension is negative, have a wrinkled surface. As the volume is decreased, there will be a tendency for these to smooth out and for the bubbles inside the clusters to be squeezed out, in order to make the best use of the space. This tendency will be resisted by the negative surface tension. The net result will be that the spongy mass will form at a larger volume than is the case at  $T_m$ . This will happen when the free energy increase caused by formation of a single connected large particle is less than the increase which would be occasioned by the decrease in surface necessary in order to keep the individual large clusters separated from each other.

It would not be expected that the slope would be uniform over any great range of volumes in the region in which the spongy mass occurred. The surface would act somewhat like a spring, the force tending to uncoil it, increasing as it is squeezed up. (Since the compression of the spongy mass is only a continuation of the compression of the clusters at larger volumes, the first point at which the spongy mass occurs does not correspond to a completely uncoiled spring; if this were the case one might expect one point, a point of inflection, at which the isotherm was horizontal.) This effect of "coiling the spring" will be counteracted to some extent by the very fact that the pressure does increase as the volume is decreased, for this would tend to cause the surface tension to become less negative. Also it

<sup>23</sup> See, e.g., Wo. Ostwald, *Kolloid Zeits.* **64**, 50 (1933); J. Frenkel, *Acta Physicochimica U.R.S.S.* **8**, 261 (1938). The illustrations of Ostwald's are especially suggestive but do not reproduce the situation existing at the critical point in its full complication. Many of Ostwald's considerations have to do with phenomena which are not equilibrium phenomena.

is difficult to see to just how greatly the compressibility of the liquid itself would be involved. So it is apparent that the exact shape of the isotherm is determined by a rather complex interplay of forces as soon as the temperature  $T_m$  is passed. It is clear, however, that there will be a critical region in which we may speak in a rough way of the vapor being changed, on compression, into the liquid.

Some discussion of the way in which an isotherm approaches the critical region may be of interest. The discussion resulting in Eqs. (9) and (10) will remain largely unchanged. But, as we have noted, when the surface tension is negative we may expect the extent of the surface to be proportional to  $s$  instead of  $s^3$ . In place of the term  $\gamma s^3$  in Eq. (9) we will, therefore, write  $\gamma \nu s$ , where  $\nu$  is a further proportionality factor, related to the fraction of molecules at the surface and, therefore, dependent on the volume. (In the light of the discussion at the end of Section 4,  $\gamma$  may be expected to depend on the average curvature of the surface, but this will not affect our considerations.) Equation (10) will remain unchanged. We see now that the expression for  $c_s$  diverges when  $\alpha + \nu\gamma$ , rather than  $\alpha$  itself, becomes less than zero.  $\alpha + \nu\gamma$  will also replace  $\alpha$  in Eq. (37). We shall be interested in finding  $[\partial(\alpha + \nu\gamma)/\partial V]_T$  rather than  $(\partial\alpha/\partial V)_T$ , and comparing it with  $[\partial(\alpha + \nu\gamma)/\partial p]_T$  rather than with  $(\partial\alpha/\partial p)_T$ .  $[\partial(\alpha + \nu\gamma)/\partial p]_T$  cannot, however, be evaluated in the same way as  $(\partial\alpha/\partial p)_T$ ; in fact,  $T_m$  will be the last temperature at which an equation like Eq. (15) will hold. This may be seen in the following way. Equation (12) will hold as before, but  $\phi_\infty$  is not the actual free energy of an infinitely large cluster, since  $\phi_\infty$  does not include the surface energy. Actually we should write for the actual free energy  $\phi_\infty + \nu\gamma$ , and we can put Eq. (12) in the form

$$F = N(\phi_\infty + \nu\gamma) - N(\alpha + \nu\gamma).$$

When  $\alpha + \nu\gamma$  is zero, we have  $F = N(\phi_\infty + \nu\gamma)$ . But now this relation corresponds to one definite volume, since there is no horizontal place in the isotherm. At this pressure the large cluster fills the space, and its volume becomes equal to the total volume  $V$ . Hence when  $\alpha + \nu\gamma = 0$ , instead of Eqs. (13) and (14) we have

$$N[\partial(\phi_\infty + \nu\gamma)/\partial p]_T = V = (\partial F/\partial p)_T$$

and

$$[\partial(\alpha + \nu\gamma)/\partial p]_T = 0.$$

Thus, instead of Eq. (40) we get an indeterminate expression; if it could be evaluated this would presumably give a finite, non-zero value of  $(\partial p/\partial T)_V$ .

Equation (15) can hold only because below and at  $T_m$ , as the pressure on the vapor is increased, the density of the large clusters approaches a value different from that of the whole system as the point is approached at which a two-phase system is in equilibrium; even at  $T_m$  the system cannot be compressed until the volume is down to the value  $U_0$ . Above  $T_m$  the large clusters approach a specific volume equal to that of the whole system and on further compression no phase change occurs, but the properties of the system, including the pressure, gradually change. Obviously  $N[\partial(\phi_\infty + \nu\gamma)/\partial p]$  cannot, when  $\alpha + \nu\gamma = 0$ , be set equal to any smaller volume than the total volume of the system, since such a smaller volume corresponds to a higher pressure. On the other hand, Eq. (14) must hold at  $T_m$ , since between  $V$  and  $U$  it is impossible to produce any change in the pressure on the large clusters. Actually, however, no discontinuity is involved, as the isotherm at  $T_m$  can equally well be considered to be the limiting case for those above or those below  $T_m$ .

## 8. RELATION TO MAYER AND HARRISON'S STATISTICAL THEORY

As we noted in Section 1, Mayer and Harrison came to the conclusion that not only is there a critical region above the temperature  $T_m$ , but that there should be a series of isotherms above that temperature, which would still have a portion which was exactly horizontal. These isotherms would further have the property that there was no apparent discontinuity in slope at the ends of these flat portions of the isotherms. According to our conclusions, the last horizontal isotherm occurs at  $T_m$ . It is desirable to reconcile these apparently contradictory conclusions.<sup>24</sup>

Mayer and Harrison's theory is based upon the setting up of the partition function for the

<sup>24</sup> In the discussion which follows we shall use the notation of J. E. Mayer and M. Goeppert Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), Chapters 13 and 14.



condensing vapor in terms of certain "cluster integrals,"  $b_l$ , where  $l$  is a running subscript which takes values from 1 to  $N$ , where  $N$  is the number of molecules in the system, and it is based upon the assumption that the  $b_l$ 's are independent of the volume of the system. The cluster integrals are in turn expressed in terms of irreducible integrals,  $\beta_k$ , where  $k$  is a running subscript which goes from 1 to  $l-1$ . The  $\beta_k$  are independent of  $l$ ; that is, the same set of  $\beta_k$  serves to evaluate all the  $b_l$ . (Since the  $\beta_k$  will always be written with a subscript, they need not be confused with  $\beta$  used in the earlier sections of this paper.)

It is shown that for large  $l$  we may write  $b_l$  in the form

$$b_l = f(l, \beta) b_0^l \quad (50)$$

where

$$b_0 = \rho^{-1} \exp \sum_{k=1}^{\infty} \beta_k \rho^k \quad (51)$$

and

$$f(l, \beta) = \rho l^{-5/2} (2\pi \sum_{k=1}^{\infty} k^2 \beta_k \rho^k)^{-1/2}. \quad (52)$$

$\rho$  is the solution of the equation

$$\sum_{k=1}^{\infty} k \beta_k \rho^k = 1. \quad (53)$$

This holds as long as there is a real positive root of Eq. (53) and  $\sum k^2 \beta_k \rho^k$  converges. These conditions, however, can hold only at relatively high temperatures, where the  $\beta_k$  are not too large.

At low temperatures  $\sum_{k=1}^{\infty} k \beta_k x^k$  diverges as  $x$  increases from  $x=0$  before reaching the value 1. In this case Eq. (52) does not hold, but  $f(l, \beta)$  will still not vary faster than as a power of  $l$ . Also, we must then define  $b_0$  by

$$b_0 = \lim_{l \rightarrow \infty} \rho^{-1} \exp \sum_{k=1}^l \beta_k \rho^k \quad (54)$$

where  $\rho$  is the limit of  $\rho'$  as  $l \rightarrow \infty$ , with  $\rho'$  the root of the equation,

$$\sum_{k=1}^l k \beta_k \rho'^k = 1.$$

The limiting value,  $\rho$ , then, will obviously co-

incide with the value of  $x$  which just causes the series to diverge.

Condensation occurs when a certain parameter  $Z$ , which may be shown to be equal to  $v^{-1} \exp(-\sum_{k=1}^{\infty} \beta_k v^{-k})$  where  $v$  is the volume per molecule, becomes equal to or greater than  $b_0$ . The value of  $v$  at which this occurs is called  $v_*$ , and it is shown that  $v_* = \rho^{-1}$ . The sum  $\sum_{l=1}^{\infty} v b_l Z^l$ , which appears in the partition function, may readily be seen to diverge as soon as  $Z b_0$  becomes greater than 1.

It is proved that

$$(\partial p / \partial v)_T = -(kT/v^2) [1 - \sum_{k=1}^{\infty} k \beta_k v^{-k}] \quad (55)$$

provided  $v > v_*$ . At  $v_*$  the isotherm becomes horizontal. However, the slope of the isotherm may or may not approach zero as  $v$  decreases toward  $v_*$ . To get this information about the isotherm from Eq. (55), it is necessary to know something about the  $\beta_k$  as functions of  $T$ . Mayer and Harrison make the assumption that<sup>25</sup>

$$\beta_k = f(k, T) \beta_0^k (|\beta_0|/\beta_0)^{k+1} \quad (56)$$

where  $\beta_0$  is a function of  $T$  and  $f(k, T)$  is a positive factor and, at least, for large  $k$  a smooth function of  $k$ , such that

$$\lim_{k \rightarrow \infty} k^{-1} \ln f(k, T) = 0. \quad (57)$$

According to Eq. (57), the factor  $f(k, T)$  may not increase with  $k$  as rapidly as a constant raised to the  $k$ th power, but it may contain a factor of the form  $k^a$ , where  $a$  is a constant, and a factor of the form  $e^{-\gamma k^{1/2}}$ , where  $\gamma$  is a surface tension term.<sup>26</sup>

<sup>25</sup> Mayer and Harrison did not actually apply Eq. (56) for  $\beta_0 < 0$ , and they did not have the factor  $(|\beta_0|/\beta_0)^{k+1}$  in their equation. This factor simply has the effect of making all the terms in the series have the same sign as  $\beta_0$ . Even if Eq. (56) is not strictly applicable for values of  $\beta_0$  very close to or less than zero, I believe that it may be used in order to see how the series behaves when the  $\beta_k$ 's change sign.

<sup>26</sup> It may be questioned whether we are allowed to identify the  $\gamma$  of this section with the  $\gamma$  we have used previously. Mayer and Harrison identified their  $\gamma$  with the surface tension (within a constant factor) by an argument which essentially assumed that a mathematical cluster was the same thing as a physical cluster. Since this would be strictly true only for a dilute gas, it would appear that their  $\gamma$  is identified with the surface tension of a cluster under these conditions, rather than under conditions existing near the critical point.

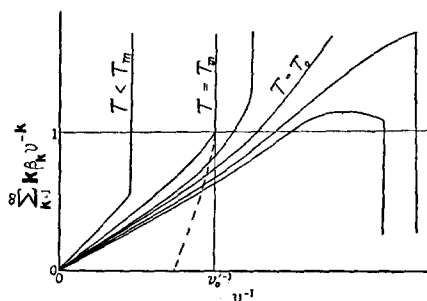


FIG. 5.

It is known that at very low temperatures all the  $\beta_k$  are positive. In general they will be expected to decrease with the temperature, and some or all will become negative. The assumption is made that  $\beta_0$  decreases with the temperature and eventually becomes negative. It is also implied that the smaller the value of  $k$  the more positive the corresponding values of  $\beta_k$ ; in other words, as the temperature increases, the  $\beta_k$  become negative in order, starting with those with large values of  $k$ .

The  $\beta_k$  are integrals whose integrands have large numbers of positive and negative parts. There is no doubt that the positive parts predominate at low temperatures. Their behavior as the temperature increases is not so clear, and it is possible that Eq. (56) may not continue to hold. The  $\beta_k$ 's, for example, could have, at least in some range of temperatures, alternating positive and negative values. Nevertheless, we shall accept the assumptions formulated in Eqs. (56) and (57) and those described in the accompanying paragraphs. I believe, however, that the validity of Mayer and Harrison's conclusions is limited, because the region in which the  $b_i$ 's are volume independent is limited in a way which will become clear as the discussion proceeds.

On the basis of Eq. (56) we may write

$$\sum_{k=1}^{\infty} k \beta_k v^{-k} = \sum_{k=1}^{\infty} k f(k, T) (\beta_0/v)^k (|\beta_0|/\beta_0)^{k+1}. \quad (58)$$

As the volume decreases the sum diverges when  $\beta_0/v > 1$ . When the temperature is low and  $\beta_0$  is strongly positive this occurs at a small value of  $v^{-1}$ , as is indicated by the first curve ( $T < T_m$ ) in Fig. 5. Because  $f(k, T)$  will be largely determined by the factor  $e^{-\gamma k^{\frac{1}{2}}}$ , and, since  $\gamma$  decreases rapidly

with  $T$ , the actual value of the sum when divergence sets in increases with  $T$ . There will be a temperature  $T_0$  at which  $\beta_0 = 0$ . In this case, the series will not diverge, but its value will continue to increase with  $v^{-1}$  because of the early terms in the series, which are positive. Above  $T_0$  the series will diverge with negative sign. The negative terms will also cause the value of the sum to increase at a less rapid rate; finally, at high  $T$ , it will decrease before the divergence occurs.

At low values of  $T$  the divergence of  $\sum_{k=1}^{\infty} k \beta_k v^{-k}$

occurs before it is equal to 1; by Eq. (55), then,  $(\partial p / \partial v)_T$  is still negative for values of  $v$  very slightly greater than  $v_s$ , which is, of course, the value of  $v$  at which the divergence occurs. This corresponds to the break in the slope of the isotherm in ordinary condensation. The temperature at which the point of divergence of the sum coincides with its reaching the value 1 is the last temperature at which the ordinary type of condensation occurs, and we identify it with our previously defined  $T_m$ . We see from Eq. (55) that above  $T = T_m$  the slope of the isotherm approaches zero as the point of condensation is approached. According to Mayer and Harrison, then, we have a smooth approach to a horizontal stretch of the isotherm.

However, as Mayer and Harrison pointed out, and as we have already noted, these calculations break down as soon as the  $b_i$ 's become volume dependent. The  $b_i$ 's become volume dependent as soon as one of the mathematical clusters which contribute appreciably to the partition function contains an appreciable fraction of all the molecules. As soon as the vapor is all condensed, and all the molecules are in one mathematical cluster, the breakdown will occur. The volume involved will be the volume of the liquid phase. But, as we have seen, at the temperature  $T_m$  the system has been coagulated into one spongy mass at the large volume end of the horizontal part of the isotherm. One cannot identify the true physical clusters with the mathematical clusters of Mayer and Harrison's theory; however, there is enough resemblance between them so that it seems reasonable to conclude that when the spongy mass is formed the cluster integrals of Mayer and Harrison's theory become volume dependent.

This happens at still larger values of  $v$  when  $T$  is greater than  $T_m$ . Thus only the portion of the curves to the left of the broken line in Fig. 5 will be susceptible of physical interpretation. This will not include the region above  $T_m$ , in which Mayer and Harrison believed the isotherms to be horizontal.

At first it might appear that a situation such as is described in the preceding paragraph is automatically excluded by the theory of Mayer and Harrison. For the sum  $\sum v b_l Z^l$  which appears in the partition function will not be expected to diverge until  $v$  has reached the value which makes  $\sum k \beta_k v^{-k} = 1$ . Therefore, we should expect that terms for which  $l \sim N$ , the total number of molecules, would not contribute appreciably to the sum, and since it is these terms which are volume dependent, it would appear that this volume dependence would not have an appreciable effect. However, actually it may become quite important. As we approach the point at which the series would normally diverge, any influence which changes the character of the higher terms can cause the series to diverge sooner because of these terms alone. A  $b_l$  for which  $l$  is large may be expected to be extremely sensitive to such influences because  $b_0$  occurs to the  $l$ th power in Eq. (50).

If, on account of the variation of  $b_l$  with the volume, the series  $\sum v b_l Z^l$  is to diverge at a larger value of  $v$  and hence a smaller value of  $Z$  than is normally to be expected, this can only result because  $b_l$  has attained a larger absolute value than its asymptotic value for large  $v$ .  $b_l$  is a complex sum and product of integrals, each of which has an integrand with many positive and negative parts. It is, therefore, difficult to decide *a priori* whether it is possible for its absolute value to increase as the system is compressed. Mayer, in a private communication, states his belief that it will not happen; however, it cannot be proved either way, and I believe that the experimental results and the considerations of this paper lend strength to the inference that  $b_l$  does actually, at least ultimately, increase as  $v$  is decreased. ( $b_l$  may decrease, passing through zero, and finally passing its asymptotic absolute value on the negative side.) If this were not true, it could be reconciled with Section 7 only by the supposition that it is possible to compress a

system with negative surface tension, when the spongy mass is formed, for at least a short range without increasing the pressure, and, therefore, without decreasing the total surface. Such a situation is geometrically possible, with condensation of some of the less dense portions into the denser portions of the material. It would, presumably, however, involve an increase in the average curvature of the surface, that is, an approach to sharper edges and corners. In the region where the surface tension is negative this process has presumably gone as far as is profitable in the normal proliferation of the surface. Therefore, further increase in curvature would be resisted, and would not be expected to occur unless forced by an increase in pressure, which is just what we wished to avoid.

As Mayer has pointed out in a private communication, wherever the sum  $\sum v b_l Z^l$  does diverge, and from whatever cause it may diverge, a phase transition of some order will occur. For the divergence of the sum at a given  $v$  means that beyond that  $v$  the partition function must be expressed by a new analytic function. This means that at least some derivation of the partition function, and hence some derivative of  $p$  with respect to  $v$ , must be discontinuous. It seems probable, however, that above  $T_m$  this is a transition of higher order and that at least  $(\partial p / \partial v)_T$  is continuous though  $(\partial^2 p / \partial v^2)_T$  may not be.

It is not, perhaps, absolutely certain that the theory of Mayer and Harrison will not break down even slightly to the left of the broken line in Fig. 5. This, however, would mean a transition of higher order at some temperatures below  $T_m$  just before the first order transition of ordinary condensation. Such an occurrence does not seem indicated by the theory of the present paper. Discounting the possibility, then, and assuming that Eq. (55) can be used up to the broken line, certain further conclusions can be drawn. Then, according to the discussion at the end of Section 5, at  $T_m$  the isotherm should diverge at a value of

$$\sum_{k=1}^{\infty} k \beta_k v^{-k} \text{ just equal to } 1, \text{ as shown in Fig. 5, since}$$

by Eq. (55) this will make  $(\partial p / \partial V)_T = 0$  at the point of divergence in agreement with Eq. (40). Furthermore, we see that  $(\partial p / \partial V)_T$  approaches

zero as  $V - V_0'$ . This will be consistent with Eq. (40) only if  $V - V_0'$  is proportional to  $(V - V_0')^{4/3}$ , which makes  $1 - dV'/dV$  proportional to  $(V - V_0')^{1/3}$ .

### 9. CONCLUSIONS

The net result of our discussion is that, apparently in agreement with experiment, the isotherm at the highest temperature  $T_m$  at which a meniscus is distinguishable has a horizontal portion. Above  $T_m$  there is a critical region, in which a transition from vapor to liquid takes place over a finite range of volumes, but where the isotherms never have zero slope. To get a final check on this, more experimental data are needed, and particular attention needs to be paid to possible effects of impurities. More surface tension measurements, correlated as well as possible with the other phenomena which occur at the critical point would also be valuable. It should be remarked that in order to compare any experimental results with the theory, it is necessary that the measurements should be made under equilibrium conditions. It seems to be true that near the critical point it is especially difficult to attain equilibrium and various kinds of hysteresis effects are common. These non-equilibrium phenomena are of considerable interest in themselves, but the theory presented here makes no attempt to explain them.

Our results appear not to be in contradiction to the more exact mathematical theory of Mayer and Harrison. Their equations are exact for the range over which they hold, whereas our discussion involves a number of assumptions and approximations. However, it seems to be reasonable to assume that the methods used in this paper can penetrate into a region where Mayer's equations break down.

It would seem best, on the basis of the results

obtained, to define the critical temperature as being identical with  $T_m$ .

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### APPENDIX

The number of molecules on the surface of a large spherical cluster can be calculated roughly if we assume the molecules are themselves spherical and in close-packed array. Neither assumption is exactly correct, but the result will suffice for our purpose.

Let  $r$  be the radius of the cluster and let  $a$  be the distance between the centers of nearest neighbors. Let  $\tau$  be the total volume of the cluster,  $\sigma$  its total surface area,  $s$  the number of molecules in it, and  $n$  the number of molecules at the surface. The volume per molecule in a close-packed array is  $2^{-1/3}a^3$ . Hence

$$\tau = 2^{-1/3}sa^3 = (4/3)\pi r^3.$$

From this we get

$$s^{1/3} = 3.28(r/a)^2.$$

Let us suppose that the sphere is sufficiently large so that its surface is practically a plane and that the molecules form a two-dimensional hexagonal close-packed array on the surface. The area per molecule on such a surface is  $(3/4)a^2$ . Hence

$$\sigma = (3/4)na^2 = 4\pi r^2.$$

So

$$n = 14.5(r/a)^2.$$

Hence

$$n = 4.4s^{1/3},$$

or

$$s^{1/3} = 0.23n.$$