

On Transitions in Condensed Systems

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Citation: [The Journal of Chemical Physics](#) **5**, 492 (1937); doi: 10.1063/1.1750061

View online: <http://dx.doi.org/10.1063/1.1750061>

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On Transitions in Condensed Systems

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(Received March 12, 1937)

In this paper there is presented a method of studying transitions in condensed phases based on the thermodynamic equation $(\partial E/\partial V)_T = T(\partial S/\partial V)_T$, which holds for low pressures. $(\partial E/\partial V)_T$ and $T(\partial S/\partial V)_T$ are plotted as functions of V , the latter for various temperatures. Intersections of these curves give the points of equilibrium and the transition points. It is shown that very general and qualitative considerations, taking into account only facts that we definitely know to be true of these curves, with one very reasonable assumption, are sufficient to indicate

that as the temperature of a system is increased from absolute zero there must be at least one change of phase, which is taken to be fusion. Changes of phase due to setting in of molecular rotation in the solid are also considered. Curves of N_2 and O_2 are constructed from available experimental data. Finally, an equation of Eyring and Hirschfelder, which would give the trend of the function $V(\partial S/\partial V)_T$ with V for liquids, is tested by a new method, and found not to accord very well with the experimental data, especially for low boiling substances.

§1. INTRODUCTION

RECENTLY a number of papers have appeared which deal with the theory of liquids and the nature of the transition between the liquid state and the solid state.¹ It is the purpose of the present communication to discuss these phenomena from a slightly different point of view, whose possibilities have not, so far as I am aware, been fully exploited. The method proposed is, we believe, of value because of the clear qualitative picture which it gives of the process of fusion and certain other types of transition. Further, it appears to be possible to predict, on extremely general premises, that on increasing the temperature from absolute zero, a condensed system must always go through at least one transition point, corresponding presumably to fusion. (At any rate, this is true if one can ignore the effect of vaporization, resulting in the possibility of sublimation, which nevertheless does not alter the fact that, as far as the *condensed* phase is concerned, at least one transition must occur.)

¹ See, for example, (a) Braunbeck, *Zeits. f. Physik* **99**, 259 (1936); (b) Kudar, *Physik. Zeits.* **35**, 560 (1934); (c) Franchetti, *Atti Accad. Lincei* **22**, 433, 585 (1935); (d) Herzfeld and Goepfert Mayer, *Phys. Rev.* **46**, 995 (1934); (e) Hill, *Physik. Zeits. Sowjetunion* **8**, 401 (1935); (f) Bijl, *Physica* **1**, 1125 (1934); (g) Frenkel, *Acta Physicochim. U. S. S. R.* **3**, 633, 913 (1935); (h) Tarschisch, *Zeits. f. Physik* **99**, 259 (1936); (i) Mayer, *J. Chem. Phys.* **5**, 67 (1937); Mayer and Ackermann, *ibid.* **5**, 74 (1937); (j) Eyring and Hirschfelder, *J. Phys. Chem.* **41**, 249 (1937); (k) Rice, *J. Chem. Phys.* **5**, 353 (1937) (cited hereafter as I). For a general discussion of much of the recent work see (l) *Trans. Faraday Soc.* **33**, 1-104 (1937).

The essence of our procedure lies in the use of the thermodynamic equation

$$P + (\partial E/\partial V)_T = T(\partial S/\partial V)_T, \quad (1)$$

where E is the molal energy, S the molal entropy, V the molal volume, and T the temperature of the system, and where P is the applied pressure.

In the case of solids and liquids at ordinary pressures P is negligible compared to $(\partial E/\partial V)_T$, so to determine the state of a solid or liquid, we may write the condition equation, which must be obeyed if $P=0$,

$$(\partial E/\partial V)_T = T(\partial S/\partial V)_T. \quad (2)$$

One of the essential differences between equilibria involving only condensed phases at ordinary pressures and equilibria in which a vapor phase is present is that in the former case Eq. (2) may be used, but in the latter case Eq. (1) is necessary.

The condition (2) is just the condition that the free energy F (which is equal to $E - TS$ when $P=0$) should be a minimum or maximum. In order for the equilibrium to be stable F must be a minimum, or

$$(\partial^2 F/\partial V^2)_T = (\partial^2 E/\partial V^2)_T - T(\partial^2 S/\partial V^2)_T > 0. \quad (3)$$

Let us now assume, what is no doubt not strictly true but can be used as an approximation (which is discussed in §3, below), that E and S can both be divided into two parts, one of which is a function of the temperature alone, and the other a function of the volume alone. This makes $(\partial E/\partial V)_T$ and $(\partial S/\partial V)_T$ functions only of V .

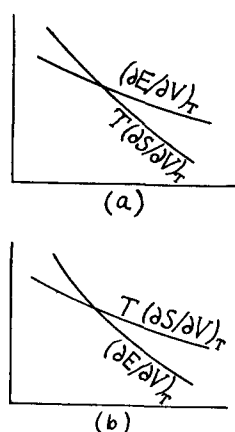


FIG. 1. Illustrating the types of intersection which can occur when $(\partial E/\partial V)_T$ and $T(\partial S/\partial V)_T$ are plotted as a function of the volume V ; (a) represents a stable intersection (b) an unstable one.

Then Eq. (2) and the inequality (3) offer a convenient means of studying the changes of equilibrium as the temperature varies, and thus changes of phase such as occur on fusion. We simply plot out $(\partial E/\partial V)_T$ as a function of V , and on the same diagram $(\partial S/\partial V)_T$ multiplied by T , and note the points where these curves intersect. As T changes the curve $T(\partial S/\partial V)_T$ simply expands proportionately, and the series of intersections gives us all necessary information regarding the various changes of phase. The intersections of these curves give the points at which Eq. (2) holds. There are two kinds of possible intersections, as shown in Fig. 1. The type in which $(\partial E/\partial V)_T$ is below $T(\partial S/\partial V)_T$ to the left of the intersection, shown in 1(a) is, of course, the type for which (3) holds and hence represents a stable equilibrium.

§2. EQUILIBRIUM IN SIMPLE LIQUIDS AND SOLIDS

We shall now consider the application of these principles to the case of solids and liquids in which the forces are of the van der Waals type. With this type of substance we can assume, at least as a first approximation, that if V is large enough $E = -a/V$, where a is a positive constant,² and thus

$$(\partial E/\partial V)_T = a/V^2. \quad (4)$$

² For very large volumes (i.e., for the gas phase) this van der Waals type correction holds for any substance, but for simple liquids it appears to hold approximately down into a part of the range of liquid volumes. See Hildebrand,

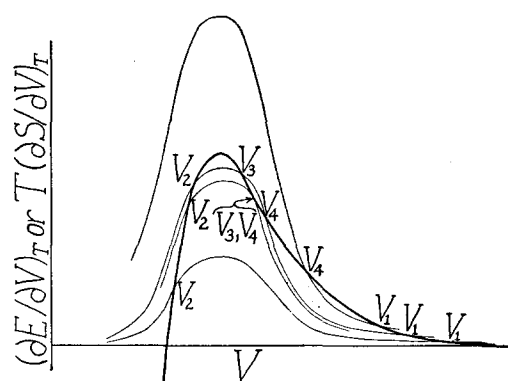


FIG. 2. Schematic curves illustrating the course of the phenomena of the condensed phase as the temperature is changed.

However, as the volume becomes smaller, and the average distance between molecules approaches the minimum of the potential curve for a pair of molecules, $(\partial E/\partial V)_T$ must reach a maximum and finally, at a volume such that most of the molecular pairs are practically at their equilibrium distance, pass through zero and become negative. The shape of the curve is illustrated in Fig. 2 (heavy curve). For S on the other hand, if V is sufficiently large, we have

$$(\partial S/\partial V)_T = R/V. \quad (5)$$

From the results ^{1(k)} of I we can make some attempt to evaluate $(\partial S/\partial V)_T$ for smaller volumes (around the boiling point of the liquid). We have defined an effective internal volume, V_e , by the equation $\Delta S = R \ln (V_v/V_e)$ where ΔS is the entropy of vaporization and V_v is the molal volume of the vapor, so that

$$(\partial S/\partial V)_T = R V_e^{-1} (\partial V_e/\partial V)_T. \quad (6)$$

Also, it has been shown that $(\partial V_e/\partial V)_T (V/V_e)$ is approximately 10 near the boiling point of the simple liquids considered. We thus see that for this range of volumes

$$(\partial S/\partial V)_T \sim 10R/V. \quad (7)$$

However, as we approach very small volumes, $(\partial S/\partial V)_T$ must eventually reach a maximum and return to zero, since the entropy must approach zero asymptotically as the volume is

Solubility, second edition (Reinhold Pub. Co., 1936) Chap. V. Setting E equal to the van der Waals correction, of course, simply amounts to taking the zero of energy at $V = \infty$.

decreased.³ Thus $(\partial S/\partial V)_T$ will have the general shape shown by the light curves, $T(\partial S/\partial V)_T$, in Fig. 2. We make the assumption that the decrease in $(\partial S/\partial V)_T$ occurs in the range of volumes indicated.

These curves also indicate the course of the phenomena of the condensed state. At sufficiently low temperatures there will be an intersection at a large volume, in the region where Eqs. (4) and (5) both hold. The volume will be given by $V=a/RT$, and is thus inversely proportional to T . This point of intersection, which we shall designate as V_1 , does not correspond to a state of stable equilibrium. There will, however, be a stable intersection very near the point at which the heavy curve crosses the axis if the temperature is very low. This occurs at a volume to be designated as V_2 , and corresponds to the solid state. As the temperature rises V_2 increases, as it should. When the temperature has risen sufficiently two more intersections appear, an unstable one at V_3 and a stable one at V_4 , corresponding to the liquid state.⁴ This happens because of the sharp rise in $(\partial S/\partial V)_T$ in going from the region where Eq. (5) holds to the region where Eq. (7) holds. The liquid, of course, does not become the most stable phase as soon as the intersection corresponding to it appears, but only when its free energy is less than that of the solid, which requires that

$$\int_{V_2}^{V_4} [(\partial E/\partial V)_T - T(\partial S/\partial V)_T] dV < 0,$$

i.e., the area enclosed between the curves between the intersections at V_2 and V_3 must become less than that included between V_3 and V_4 . Equality of these areas determines the melting point. As the temperature increases the intersections V_2 and V_3 finally coalesce and disappear as do V_4 and V_1 . Which of these disappearances takes place first is not certain, but only the latter is of importance, and it corresponds roughly to

the critical point.⁵ We have thus been able to outline the behavior of solid and liquid from absolute zero to the critical point.

It will be clear that if the curves for $(\partial E/\partial V)_T$ and $(\partial S/\partial V)_T$ are known, various thermodynamic properties of solid and liquid may be readily calculated. In particular, the coefficient of expansion may be immediately deduced, since the diagram gives directly the equilibrium volume at any temperature. And the difference between the specific heat at constant volume, C_v , and that at constant pressure, C_p , can be calculated from the relation,

$$C_p - C_v = (\partial E/\partial V)_T (\partial V/\partial T)_P, \quad (8)$$

which holds when $P=0$.

It is of interest to note that the intersection V_2 , corresponding to the solid, will, unless the $(\partial S/\partial V)_T$ curve has a very peculiar shape, always be to the left of, or very near the maximum of the $(\partial E/\partial V)_T$ curve, while V_4 is always well to the right of the maximum.⁶

It is also of interest to remark that this analysis of the phenomena of the condensed phase appears to favor Frenkel's view that the transition between liquid and solid is a perfectly continuous one in the same sense that, according to van der Waals' theory, the transition between liquid and gas is continuous. Our treatment is similar to Frenkel's in that we consider the change of certain thermodynamic quantities with the volume, though he has considered only how the pressure varies as a function of volume for equilibrium states of the system. It is possible to construct Frenkel's P - V curve by holding T constant and letting the left-hand side of Eq. (1) vary with P , watching the intersections. Of course, part of Frenkel's curve corresponds to unstable equilibrium. This does not necessarily imply, however, that there will be a critical point for fusion like the critical point for vaporization;⁷ this depends upon the respective shapes of the $P + (\partial E/\partial V)_T$ and $T(\partial S/\partial V)_T$ curves.

³ See Lewis, *Zeits. f. physik. Chemie* **130**, 532 (1927).

⁴ It is, of course, an assumption that this phase actually corresponds to the liquid state, since there is nothing in the theory to tell us about the fluidity of any phase. It remains true, however, that with this assumption the phenomena given by the theory can be brought into correspondence with those observed.

⁵ The correspondence can only be rough, because P is not negligible compared to $(\partial E/\partial V)_T$ at the critical point.

⁶ In the case of the metal mercury $(\partial E/\partial V)_T$ actually appears to be increasing with V for the liquid state. See Hildebrand, reference 2, p. 100.

⁷ This matter has recently been discussed by Simon, reference 1 (*l*), pp. 65 ff.

§3. LIMITATIONS AND SHORTCOMINGS OF THE THEORY

One objection to the theory we have just outlined consists in the fact that the assumption, that $(\partial E/\partial V)_T$ and $(\partial S/\partial V)_T$ are functions of V and independent of the temperature, is undoubtedly not strictly correct. However, this may be corrected for by allowing the shape of the curves to gradually change as the temperature is changed, and it seems unlikely that the phenomena will be altered in any of their qualitative features. It is rather important to note that the asymptotic approach of $(\partial S/\partial V)_T$ to zero at small volumes will begin at a larger value of V the lower the temperature. Thus the value of V at which $(\partial E/\partial V)_T=0$ is already in the range of volumes for which $(\partial S/\partial V)_T=0$ when the temperature is near the absolute zero. At these temperatures, then, the volume remains practically stationary for a short temperature range, giving the necessary zero values for the coefficient of expansion and C_p-C_v . As the region where $(\partial S/\partial V)_T$ approaches zero pushes over toward smaller volumes the coefficient of expansion increases. $(\partial E/\partial V)_T$ is largely determined by the forces between the molecules, and its dependence on temperature should not be as important as that of $(\partial S/\partial V)_T$.

As Professor K. F. Herzfeld has remarked to me, it is easy to derive an expression for $(\partial S/\partial V)_T$ for a simple Debye solid, in the limiting region of very low temperatures or very low volumes. For in this region, according to the Debye theory, $S=(4/5)\pi^4 R(T/\Theta)^3$, where Θ is the characteristic temperature. We have then $(\partial S/\partial V)_T = -(12/5)\pi^4 R(T/\Theta)^3 d \ln \Theta/dV$, whence it is seen that $(\partial S/\partial V)_T$ varies as T^3 . On the other hand, in the classical region of high temperatures and large volumes $(\partial S/\partial V)_T$ will be expected to be independent of T .

Another difficulty with the picture we have presented rests in the fact that in the solid state S and E probably also depend to some extent on the arrangement of the molecules, as well as the actual volume they occupy. We thus need to introduce an "arrangement parameter." Some such parameter is necessary to account for some of the transitions between allotropic solid forms, which, however, would not be important for the picture in large outline.

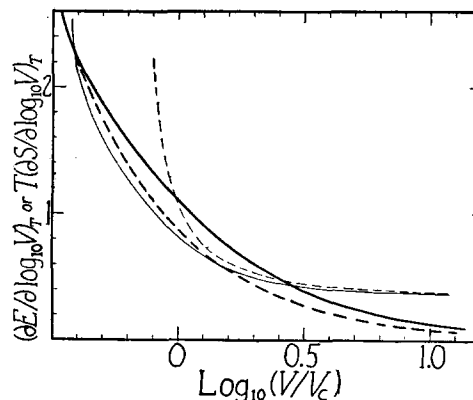


FIG. 3. Curves for N_2 , large volumes. Heavy curve, $(\partial E/\partial \log V)_T$; heavy broken curve, approximation from Eq. (4); light curve $T(\partial S/\partial \log V)_T$; light broken curve, approximation from van der Waals' equation. The temperature for the $T(\partial S/\partial \log V)_T$ curves is 77.3°K, the boiling point of N_2 . Energy units (for Figs. 3, 4, and 5) kilogram calories.

§4. ROTATION OF MOLECULES IN SOLIDS

Certain transitions occur between solid phases which, in contrast to the type just mentioned, may probably be profitably considered from the point of view developed in this paper. These are the transitions which are believed to be associated with the setting in of rotation of molecules which are not spherically symmetrical.⁸ Such molecules, if not too unsymmetrical, may often be treated as though they were symmetrical if the temperature is high enough so that rotation has become established. However, at low temperatures we must expect a restriction on the rotation of the molecules, due to the presence of the other molecules, just as the translational motion is restricted.

The earlier sections of this paper suggest that we consider the extent of freedom of the rotation in relation to the molal volume at a given temperature. When the molal volume is small, the rotation is restricted, and we will have an extra contribution to $(\partial S/\partial V)_T$, because as the volume increases the rotational, as well as the translational degrees of freedom, are loosening up. Then, as we approach the point at which the rotation becomes practically completely free, there will be a certain range of volumes over which $(\partial S/\partial V)_T$ will decrease rapidly as the volume increases, till it reaches the value char-

⁸ Pauling, Phys. Rev. **36**, 430 (1930).

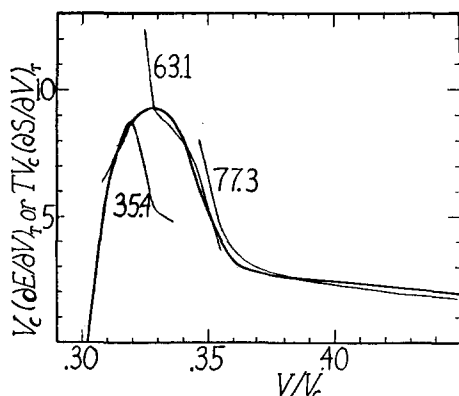


FIG. 4. Curves for N_2 , small volumes. Heavy curve, $V_c(\partial E/\partial V)_T$; light curves, $TV_c(\partial S/\partial V)_T$ at temperatures indicated.

acteristic for translational degrees of freedom only. Such behavior could easily result in a transition point at which rotation sets in, or at least becomes considerably freer, as will be seen in §5. It is true that the same influences which change the $(\partial S/\partial V)_T$ curve may also cause some corresponding changes in the $(\partial E/\partial V)_T$ curve, but this should not alter the qualitative character of the phenomena.

Fowler⁹ has recently developed a statistical theory of the rotation of molecules in which he considers the effect of an increase of temperature, any influence of the concomitant change of volume being neglected or relegated to a minor role. It is assumed that the probability of a given molecule rotating is much greater if its neighbors are already rotating, and he shows that under certain circumstances it is possible to get a sharp transition even though the volume does not change at all. However, we believe that it is probable that in the actually observed transitions the dependence of $(\partial S/\partial V)_T$ on volume plays an important part. Nevertheless, it seems altogether probable that there is a good deal of truth in Fowler's theory. Thus the greater ease of rotation for a molecule already in the neighborhood of rotating molecules would show up in a fairly great, though not completely sharp, increase of $(\partial S/\partial V)_T$ when the volume increases over a fairly narrow critical range just before the marked decrease of $(\partial S/\partial V)_T$ sets in. This would naturally affect the details of the transi-

tion. Furthermore, the exact volume at which $(\partial S/\partial V)_T$ decreases would depend upon the temperature, an effect which, in our first approximation, we neglect.

§5. APPLICATION TO SPECIFIC CASES

We shall now consider the application of the above ideas to a couple of specific cases, and attempt to construct $(\partial E/\partial V)_T$ and $(\partial S/\partial V)_T$ curves from the experimental data which are at hand. While it is not possible to get these curves exactly, a fairly good idea of their course may be obtained.

We start with N_2 . In Fig. 3, we give the results for volumes down to the boiling point. It has been found convenient to divide all volumes by the critical volume V_c and present Fig. 3 in logarithmic form. This figure was constructed with the aid of the material in I^(k), and to avoid extensive repetition we shall, in explaining it, refer directly to I, using the symbols as there defined, and referring to the equations as Eq. I(1), for example. From Eq. (6) above, and from Eq. I(11), using the corrected value of γ obtained from I(23), we can obtain $(\partial S/\partial \log V)_T$, hence $T(\partial S/\partial \log V)_T$ and $(\partial E/\partial \log V)_T$ for the boiling point. This gives us one point on each of our curves. Next we construct a tentative curve for $(\partial E/\partial \log V)_T$, using Eq. (4). This enables us to construct the true $(\partial E/\partial \log V)_T$ curve with reasonable accuracy, inasmuch as we demand that the integral of $(\partial E/\partial \log V)_T$ taken between the volumes of the liquid and the vapor in equilibrium with it, be equal to γ times the integral under the curve obtained from Eq. (4).

Now, as stated, we already have $(\partial S/\partial \log V)_T$ at the boiling point. In addition, from I(15), we can, if we assume that γ is independent of V , and using again Eq. (6), obtain $(\partial^2 S/\partial (\ln V)^2)_T$, which gives us the slope of the curve for the point where V is equal to the volume of the liquid at the boiling point. We also know $(\partial S/\partial \log V)_T$ for large volumes where the vapor is a perfect gas, and furthermore we know the change of entropy on vaporization. These pretty well fix the curve. In the figure we also give the curve for $(\partial S/\partial \log V)_T$ which would be obtained by setting $(\partial S/\partial V)_T = R/(V-b)$, where b is an excluded volume similar to that introduced in

⁹ Fowler, *Statistical Mechanics*, second edition (Macmillan, 1936) p. 810 ff.

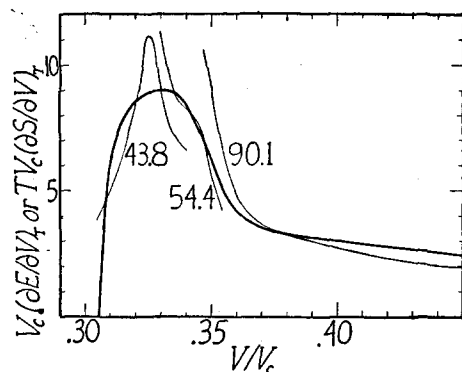


FIG. 5. Curves for O_2 , small volumes. Heavy curve, $V_c(\partial E/\partial V)_T$; light curves $TV_c(\partial S/\partial V)_T$ at temperatures indicated.

the van der Waals equation. We have set $V_c = 1.5b$. The van der Waals equation, if it held down to such low values of V , would give $V_c = 3b$, while Loeb¹⁰ suggests that the relation between V_c and the van der Waals constant is actually given approximately by $V_c = 2b$, but this seems to lead to insuperable difficulties.¹¹ For the true value of $(\partial S/\partial V)_T$ must always be less than that given by the van der Waals equation, but it is impossible to fulfill this condition and at the same time have the curve fit the other data if V_c is set equal to $2b$. On the other hand, setting $V_c = 1.5b$ gives very reasonable results, as will be seen from the figure.¹²

In Fig. 4, we give the $(\partial E/\partial V)_T$ curve for small values of V , and $T(\partial S/\partial V)_T$ for several temperatures, i.e., the boiling point, the melting point, and the transition point. These curves are very nearly fixed by the known molal volumes of liquid and solid N_2 at the melting point (31.6 and 29.6 cc, respectively),¹³ the known heats of fusion and transition (172.3 and 54.7 calories per

mole, respectively),¹⁴ and the volume at absolute zero,¹⁵ at which, at least approximately, $(\partial E/\partial V)_T = 0$, and the volume at¹⁶ 45°K. Further, the integral under the curve, taken between the respective volumes of the phases which are in equilibrium at any transition point, must equal the heat of transition. And, of course, the $T(\partial S/\partial V)_T$ curves must intersect the $(\partial E/\partial V)_T$ curve in just the right way at the transition point, as explained in §2.

In a similar manner curves for O_2 have been constructed. The figure for large volumes is very similar to Fig. 3, and is not reproduced. The result for small volumes is given in Fig. 5. In this figure the heats of fusion and transition check those of Giauque and Johnston¹⁷ (106 and 178 calories per mole, respectively), the change in volume on fusion checks that found by Lisman and Keesom¹⁸ (about 1.0 cc per mole) while the volumes below and above the transition just about coincide with the volumes derived from the densities of β and γ oxygen (1.395 and 1.30, respectively) found by Vegard.¹⁹ The measured value of the liquid density seems to be in error,²⁰ but the value used in the diagram is consistent with the data on the solid and the volume change on fusion. We have made no attempt to account for the transition at 24°K, which has a small heat of transition. Taken as a whole, the picture which we have of the transitions in O_2 seems to be quite satisfactory, in spite of the fact that we have neglected entirely the possibility of special forces, connected with the magnetic moment of O_2 , which might result in

¹⁴ Giauque and Clayton, J. Am. Chem. Soc. **55**, 4875 (1933).

¹⁵ Density of N_2 is 1.026 at liquid hydrogen temperatures, according to *International Critical Tables*.

¹⁶ Vegard, Zeits. f. Physik **79**, 471 (1932). The value of V/V_c for β N_2 at 45°K, from Vegard's x-ray determination of the density is found to be 0.317. Actually I have taken 0.3195 for V/V_c for β N_2 for the transition point at 35.4°K, but the difference is small, and on applying Eq. (8) my value gives a slightly smaller and, I believe, a somewhat more reasonable value for $C_p - C_v$. The average value of $C_p - C_v$ obtained for the β range is approximately 3 calories per degree, which would give C_v an average value of about 7 calories per degree as compared to the value of C_v of 7.8 calories per degree for liquid air found by Eucken and Hauck, Zeits. f. physik. Chemie **134**, 161 (1928).

¹⁷ Giauque and Johnston, J. Am. Chem. Soc. **51**, 2300 (1929).

¹⁸ Lisman and Keesom, Physica **2**, 905 (1935).

¹⁹ Vegard, Zeits. f. Physik **98**, 1 (1935).

²⁰ Keesom and Taconis, Physica **3**, 141 (1936).

¹⁰ Loeb, *Kinetic Theory of Gas*, second edition (McGraw-Hill Book Co., 1934) p. 194.

¹¹ These difficulties are related to those mentioned in §2 of I (just after Eq. (15)), and I believe the matter is cleared up by the assumption that $V_c = 1.5b$. It is still necessary, however, to suppose that $\phi(v)$ varies slightly from liquid to liquid.

¹² If a depends on the temperature, we have, from the thermodynamic relation $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ and van der Waals equation, $(\partial S/\partial V)_T = R/(V-b) - (da/dT)/V^2$. If V is large this becomes, approximately, $R/V + (Rb - da/dT)/V^2$. Since da/dT will be expected to be negative (as a is closely related to a sort of association constant which gives the concentration of molecular pairs due to the van der Waals forces), b will be effectively increased, as far as the effect on $(\partial S/\partial V)_T$ is concerned.

¹³ Landolt-Börnstein, *Tabellen*, 3. Ergänzungsband.

the formation of a rather specific compound,²¹ O₄.

Having constructed these curves, it is possible to apply Eq. (8), after integrating it over the range of existence of the liquid phase, and compare the experimental value of

$$\int_{T_f}^{T_b} (C_p - C_v) dT \quad \text{with} \quad \int_{V_f}^{V_b} (\partial E / \partial V)_T dV$$

taken from the curves. (In these equations the indices *b* and *f* refer to boiling and freezing points respectively.) We use the values of Giauque and his students for *C_p* and Eucken and Hauck's value for *C_v* for air. We find for

$$\int_{T_f}^{T_b} (C_p - C_v) dT$$

the values 82 and 178 calories for N₂ and O₂, respectively, while from the curves we get for

$$\int_{V_f}^{V_b} (\partial E / \partial V)_T dV$$

the values 107 and 127 calories for N₂ and O₂, respectively. The differences are probably not significant, as an error of a few percent in the densities could account for them. It is possible that the discrepancies indicate that some alteration of the curves would be desirable. However, it did not seem worthwhile to attempt to make them check in such detail, and it would probably not be possible to make the check absolute without assuming some error either in the densities at the boiling or freezing points, or in the coefficients of expansion at the boiling point.

It will be noted that the peculiar shape of the $(\partial S / \partial V)_T$ curve, which we use to account for the transition point in the solid, is just that to be expected for the setting in of molecular rotation,²² as discussed in §4. We have not attempted

²¹ See Lewis, J. Am. Chem. Soc. **46**, 2027 (1924), and Vegard, reference 19. Wahl, Proc. Roy. Soc. London **A88**, 61 (1913), reports that liquid O₂ can be supercooled down to the transition point, where the crystal modification, stable below that point, is formed almost instantaneously. This behavior is certainly not to be expected from Fig. 5, and if Fig. 5 comes anywhere near giving a correct picture of the equilibrium behavior of oxygen, it can only be explained on the assumption that internal equilibrium is not established rapidly in oxygen at low temperatures. It is to be remarked, however, that Giauque and Johnston found the melting point to be sharp, which is more nearly in accord with our expectations.

²² It should be noted that the setting in of rotation will not necessarily be accomplished by a sharp change in phase. If the $(\partial E / \partial V)_T$ curve is at all points steeper than

to take into account any dependence on temperature of the value of *V* at which the sharp decrease in $(\partial S / \partial V)_T$ occurs. Thus the actual rate of the decrease at any given temperature can at best be roughly estimated from our curves. Nor have we attempted to take account of any possible effect on $(\partial E / \partial V)_T$.

It should perhaps be remarked that the transition temperatures of both oxygen and nitrogen, and the volumes at which these transitions occur, are sufficiently small so that quantization of the molecular motion is undoubtedly important. The bending over of the $(\partial S / \partial V)_T$ curve at small volumes, which accounts for the phenomenon of fusion, is itself undoubtedly connected with the setting in of quantization. One cannot, therefore, in general, assume that the $(\partial S / \partial V)_T$ curve will remain unaltered in shape when the temperature drops below the melting point, and insofar as this assumption is made it must be considered purely provisional.

§6. SOME QUANTITATIVE CONSIDERATIONS REGARDING THE $(\partial S / \partial V)_T$ CURVE FOR LIQUIDS

As appears from I, the function $V(\partial S / \partial V)_T R^{-1} = (\partial V_e / \partial V)_T (V / V_e)$ plays a very important role in the theory of liquids. Since any information regarding the behavior of this function is of obvious interest in connection with the considerations of this paper, and since such information can be gleaned from the data already assembled in I, it seems worthwhile to close this paper with a few remarks on this subject. Eyring and Hirschfelder¹⁽ⁱ⁾ have suggested that it should be possible to set

$$(\partial V_e / \partial V)_T (V / V_e) = b (V / V_e)^{1/3}, \quad (9)$$

where *b* does not vary with *V*, but, according to these authors, may depend on temperature. However, in the note²³ to I, we have given reasons for believing that $(\partial V_e / \partial V)_T (V / V_e)$ does not depend on temperature. If we make this assumption it is possible to test the correctness of setting the exponent in Eq. (9) equal to 1/3 by a

T($\partial S / \partial V$)_T there will be no definite change of phase, but there may well occur an anomaly in the specific heat. This would be particularly likely to occur if the transition takes place at a small volume. A number of cases of gradual transitions are known. For discussion and references see Pauling, reference 8, p. 441.

²³ Just following §3 of I.

method which we shall now develop. In general, of course, we can set, at least for a small range of volumes,

$$(\partial V_e/\partial V)_T(V/V_e) = b(V/V_e)^{1/n}, \quad (10)$$

where n is a constant. We then have

$$\frac{\partial \ln [(\partial V_e/\partial V)_T(V/V_e)]}{\partial \ln V} = n^{-1} \frac{\partial (\ln V - \ln V_e)}{\partial \ln V} = n^{-1}(1 - \partial \ln V_e/\partial \ln V). \quad (11)$$

The last term in Eq. (11) can be evaluated from I(11) where, of course, the corrected value of γ should be used. We have

$$\partial \ln V_e/\partial \ln V = (\Delta S/R - 1)\gamma_{\text{corr.}}^{-1} = C'/\alpha RT, \quad (12)$$

where $C' = C_p(\text{liq.}) - C_v(\text{liq.})$. The last equation of Eq. (12) comes from I(23). On the other hand we have from Eq. I(15)

$$\frac{\partial \ln \phi}{\partial \ln V} = \frac{\partial \ln [(\partial V_e/\partial V)_T(V/V_e)]}{\partial \ln V} = -(1/\alpha T + 1/\gamma), \quad (13)$$

where now we must use the *uncorrected* value of γ , as explained in the note to I. This equation involves the assumption that γ is independent of V , but since γ never differs greatly from 1, this should be a good approximation. It also involves the assumption that $(\partial V_e/\partial V)_T(V/V_e)$ is independent of T , which has already been discussed, and which we believe to be correct. From Eqs. (11), (12) and (13), then, n can be determined, and the results for a number of the liquids considered in I are as follows: N_2 , 1.59; CO , 1.82; A , 1.42; O_2 , 1.49; HBr , 1.84; Cl_2 , 2.05; SiCl_4 , 3.10; Br_2 , 2.23; CCl_4 , 2.77. It should be noted that, though α may be in some error, the value of n is almost independent of α , since the calculation of γ also depends on α and since $C'/\alpha RT$ is considerably larger than 1. C' is obtained as explained in the note to I.

It is seen that n , for the most part, is considerably smaller than 3, and that the higher boiling substances have larger values of n . This result would appear to indicate that the assumption of Eyring and Hirschfelder can be only a rough approximation.

The New Absorption System of Cyanogen Gas in the Near Ultra-violet System I. Errata

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(J. Chem. Phys. 5, 161 (1937)).

IN the following, we wish to correct a few typographical errors which appeared in our paper with the above title. On page 163, Table II, 33722 should read 33272. On page 165, ninth line below Table IV ν_2'/ν_2' should read ν_2'/ν_1' . :N:::C:C::N: should read :N::C:C::N:

The Absorption Spectra and Dissociation Energies of Cyanic Acid and Some Isocyanates—A Correction

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On page 545, Table I, third column, 112.4 should read 114.6. On page 546, last paragraph, fifth line from bottom 52.4 should read 54.6; second line from bottom, C_2C_5 should read C_2H_5 . The conclusion reached before remains unaltered by the above corrections.