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Citation: [The Journal of Chemical Physics](#) **5**, 353 (1937); doi: 10.1063/1.1750035

View online: <http://dx.doi.org/10.1063/1.1750035>

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Internal Volume and the Entropy of Vaporization of Liquids

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(Received December 29, 1937)

An effective internal volume, V_e , of a liquid is defined by the equation $\Delta S = R \ln V_e/V_v$, where ΔS = entropy of vaporization, and V_v = molal volume of the vapor in equilibrium. A condition for equilibrium is found which gives ΔS in terms of V_e/V and dV_e/dV , where V is the actual molal volume of the liquid. The experimental data are considered in the light of this relationship, and the reason for the approximate validity of Trouton's or Hildebrand's rule is discussed. The nature of the relation between the internal and actual volume and its connection with the specific heat of the liquid is considered. Finally suggestions are made in way of explanation of the fact that entropies of vaporization of associated liquids are practically invariably high.

§1. INTRODUCTION

THE idea of the covolume of a liquid, that is, the portion of the volume in which the molecules are free to move, is one which was brought forward early in the development of the theory of liquids. It appears in, perhaps, its simplest form in van der Waals' equation, in which the molal volume, V , is corrected by subtraction of the "excluded volume," b . That this covolume, $V - b$, is closely related to the heat of vaporization has also long been realized. Thus it is shown in Nernst's *Theoretische Chemie* that, if one assumes van der Waals' equation to be correct, the heat of vaporization at equilibrium is given by the equation¹

$$\Delta H = RT \ln [(V_v - b)/(V - b)], \quad (1)$$

in which V_v is the molal volume of the vapor in equilibrium with the liquid, whose molal volume is V . The entropy of vaporization is accordingly

$$\Delta S = R \ln [(V_v - b)/(V - b)]. \quad (2)$$

In view of the way the entropy of a gas depends upon its volume, it will be seen that the validity of Eq. (2) does not depend upon whether the vapor is in equilibrium with the liquid or not. The statement holds for all entropy equations of this general type, such as Eq. (3) below. However, unless otherwise specified, we shall write ΔS for the equilibrium entropy of vaporization.

¹ English translation (Macmillan, 1923), p. 251. For more recent applications see Evans and Polanyi, *Trans. Faraday Soc.* **31**, 891 (1935); Horiuti, *Zeits. f. Elektrochem.* **39**, 22 (1933); Svenson, *Ann. d. Physik*, **87**, 424 (1928); also reference 3.

The deduction of these equations in the form given depends upon the assumption that b is actually constant. Now b , the effective excluded volume, is equal to 4 times the volume of (one mole of) the gas molecules, and since the volume of a liquid can actually become less than this, b cannot be a true constant. Deviations begin to occur when V is around² $3b$, and they must be such that b appears to decrease.

Thus Eqs. (1) and (2) cannot be universally valid, but they suggest the definition of an effective volume, V_e , of the liquid by means of the equation³

$$\Delta S = R \ln (V_v/V_e). \quad (3)$$

This quantity V_e will not be equal to $V - b$, even though b be considered to be a function of V , but in the region in which $[\partial(V - b)/\partial V]_T < 1$ it will also be true that

$$(\partial V_e/\partial V)_T < 1. \quad (4)$$

It is interesting to note that, if we do assume that $(\partial V_e/\partial V)_T = 1$, the volume V_e and what Hildebrand calls the thermal pressure, P_t ($= P + (\partial E/\partial V)_T$, where P is applied pressure and E the energy of the system) have the same relation as the volume and pressure of a perfect gas. For we have the thermodynamic relationships

² Compare Loeb, *Kinetic Theory of Gases*, second edition (McGraw-Hill Book Co. 1934), p. 175.

³ See Rice, *J. Chem. Phys.* **4**, 369-370 (1936). This equation assumes that V_v is large enough so that the vapor may be considered to be a perfect gas. The equation is essentially equivalent to Eq. (296) of Herzfeld, *Kinetische Theorie der Wärme* (Vieweg u. Sohn, Braunschweig, 1925).

$$P_t = P + (\partial E / \partial V)_T = T(\partial P / \partial T)_V = T(\partial S / \partial V)_T \\ = T(\partial S / \partial V_e)_T (\partial V_e / \partial V)_T \\ = (RT / V_e) (\partial V_e / \partial V)_T, \quad (5)$$

the last expression following from Eq. (3). Now if $(\partial V_e / \partial V)_T = 1$ it is seen that the required relationship holds. However, such a hypothetical "perfect" liquid does not exist.

§2. THE ENTROPY OF VAPORIZATION OF NORMAL LIQUIDS

We shall now consider the factors which determine the entropy of vaporization of liquids in which the forces are of the van der Waals type, and in which the molecules are sufficiently symmetrical so that we are probably justified in supposing that they rotate freely in the liquid phase. If the external pressure, P , is of the order of a few atmospheres it is negligible, and we may write, from Eq. (5),

$$(\partial E / \partial V)_T = (RT / V_e) (\partial V_e / \partial V)_T, \quad (6)$$

and, in general, treat the liquid under its own vapor pressure as though it were at zero pressure.

On évaporation at equilibrium the change of entropy is related to the heat, ΔH , and the energy, ΔE , of vaporization by the equations

$$\Delta S = \Delta H / T = \Delta E / T + R. \quad (7)$$

If now we select the zero-point of energy so that the vapor has zero energy, we may set $\Delta E = -E$, and then eliminating T between (6) and (7) we obtain

$$\Delta S = - (ER / V_e) (\partial E / \partial V)_T^{-1} (\partial V_e / \partial V)_T + R. \quad (8)$$

In order to use this equation it is necessary to evaluate E as a function of V . Fortunately it seems to be possible to do this with some degree of approximation, for we may undoubtedly consider that the vaporization causes a change only in the *potential* energy of the system, and there are good experimental and theoretical reasons for believing that the change of E with V does not depend on whether the temperature changes or not, and is given over a certain range of values of V by an expression of the form⁴

$$dE / dV = a / V^2. \quad (9)$$

As (9) does not hold over the whole range of

⁴ Hildebrand, *Solubility* (Reinhold Publishing Co. 1936), p. 98.

values of V from liquid to vapor, we cannot write $E = -a/V$, but instead set

$$E = -\gamma a / V, \quad (10)$$

where γ is a function of V , but never very different from 1. Eqs. (8), (9) and (10) give⁵

$$\Delta S = R \ln (V_e / V_e) \\ = R [\gamma (V / V_e) (\partial V_e / \partial V)_T + 1]. \quad (11)$$

By a few simple considerations we can see something about the form the function $\gamma(V/V_e) \times (\partial V_e / \partial V)_T$ must have in the case of molecules which are sufficiently near to being spherically symmetrical. It is reasonable to suppose that if the volume of the liquid is expressed in terms of the actual volume occupied by the molecules (measured by van der Waals' b) and V_e is expressed in the same terms, then all cases being reduced to geometrical similarity the effective volume should be the same function of the total volume for all cases. In other words

$$V_e / b = f(V / b) = f(v) \quad (12)$$

where $v = V/b$ and $f(v)$ is a universal function, from which it is clear that $(V/V_e)(\partial V_e / \partial V)_T$ should also be a universal function of v . Likewise γ should be such a function, so that we may write from (11)

$$\Delta S / R - 1 = \phi(v), \quad (13)$$

where ϕ is a universal function.

TABLE I.

Subs.	b.p. (°K)	V (cc) (at b.p.)	$\frac{\Delta S}{R} - 1$	V_e (cc)	V/V_e	V/V_e	V_e/V $\times 10^{-2}$
Ne	27.2	16.7	7.2	0.64	26	0.401	1.33
N ₂	77.4	34.7	7.69	1.08	32	.385	1.83
CO	81.5	35.3	7.94	.90	39	.392	1.89
A	87.3	28.4	7.7	1.25	23	.379	2.52
O ₂	90.1	28.1	8.10	.83	34	.377	2.63
CH ₄	111.7	38.6	8.85	.49	79	.390	2.37
Kr	120.2	32	8.68	.63	51		3.1
Xe	166.0	42.5	8.92	.68	62	.378	3.21
HCl	188.1	30.5	9.32	.51	60	.35	5.05
HBr	206.1	37.4	9.28	.59	64		4.52
Rn	208	50	9.4	.52	98		3.4
HI	237.7	44.8	9.01	.87	51		4.34
Cl ₂	238.5	45.5	8.3	1.86	24	.368	4.30
SiCl ₄	330.9	121.3	9.95	.48	251		2.24
Br ₂	331.9	53.5	10.02	.44	122	.394	5.08
CCl ₄	349.9	104	9.48	.81	128	.377	2.76
GeCl ₄	356.2	123	12.0	.066	1860		2.4
SnCl ₄	387.2	132.9	9.4	.98	135		2.40

ΔS is calculated from ΔH values given in Bichowsky and Rossini's *Thermochemistry of Chemical Substances* (Reinhold Publishing Co. 1936). Other data from Landolt Börnstein, *Tabellen*, and *International Critical Tables*. All data are taken at, or corrected to, the boiling point.

⁵ It should be emphasized that Eq. (11) is a condition equation; namely, it is the condition that the external pressure be negligible.

It is generally assumed that the critical volume, V_c , is a measure of b . van der Waals' equation gives $V_c = 3b$, but it is probably more nearly correct to set⁶ $V_c = 2b$. With the aid of this relation, Eq. (13) can be tested. Of course Eq. (13) can only be approximately correct, and that it is not exactly correct is readily seen from Table I, in which the various relevant quantities are given for a number of liquids at their boiling points, inasmuch as V/V_c appears to be approximately constant while $\Delta S/R - 1$ is not. $\phi(v)$ may, however, be sensitive to small changes in v . This we can investigate by considering the temperature coefficient, provided we assume that the function ϕ is independent of temperature and that dV_c/dV does not depend upon whether there is a change in temperature or not.

We first note that

$$d\Delta S/dT = R[d \ln V_v/dT - d \ln V_c/dT]. \quad (14)$$

Now since we assume that the vapor is a perfect gas we have $d \ln V_v/dT = d \ln T/dT - d \ln P/dT$, where P is the vapor pressure. The last term can be evaluated sufficiently accurately by the Clapeyron equation, and we have $d \ln P/dT = \Delta S/RT$. And it is easy to see, from our assumption that dV_c/dV does not depend on whether T changes, and from Eq. (11), that $d \ln V_c/dT = (v/v_c)(dV_c/dV)\alpha = (\Delta S/R - 1)\alpha/\gamma$, where $\alpha = V^{-1}dV/dT$ is the coefficient of expansion. Since, from the same assumption, $d/d \ln v = d/d \ln V = \alpha^{-1}d/dT$, we see, using these expressions and Eq. (13), and assuming γ is constant, that

$$d \ln \phi(v)/d \ln v = \alpha^{-1}d \ln (\Delta S - R)/dT = -(1/\alpha T + 1/\gamma). \quad (15)$$

The right-hand side of (15) turns out to be around 3 for practically all substances. A range of v of about 10 percent would then account for the range of values of $\Delta S/R - 1 = \phi(v)$ observed in the liquids in Table I. In view of the difficulty in measuring the critical density there might be this much error in the observed values of v at the boiling point. However, if we make this assumption we run into a rather puzzling difficulty. It is seen that for the liquids listed V/V_c has approximately a tenfold range (if we neglect GeCl_4 , which is probably in error). Now since $\gamma^{-1}\phi(v)$

$= d \ln v_c/d \ln v$ (where $v_c = V_c/b$) we can calculate the range of v_c and hence the range of $v/v_c = V/V_c$ for a given range of v , and if v changes by 10 percent it is readily seen that with $\phi(v)$ in the neighborhood of 10 and γ always about 1, the ratio v/v_c should not vary more than two or threefold. This difficulty suggests that $\phi(v)$ differs slightly for various liquids. This, indeed, is also suggested by other facts, as we shall see immediately, but I have been unable to find any hypothesis regarding this variation of $\phi(v)$ which seems at all reasonable and at the same time is adequate to remove the difficulty just discussed.⁷ If we ignore this difficulty, however, we are now in a position to consider the significance of such approximate empirical generalizations as Trouton's rule and its more accurate modification, Hildebrand's rule. Some such rule should follow from Eq. (11), which we now rewrite in the more convenient form

$$R \ln v_v/v_c = R[\phi(v) + 1]. \quad (16)$$

Since v_c is a function of v this equation may be regarded as a condition equation on v , hence on v_c and V_c ; thus the value of ΔS for any value of v_c or V_c is fixed by Eq. (16). If v_c (and hence $\phi(v)$) were the same function of v for all substances, then we should expect that all liquids would have the same value of the entropy of vaporization if it were measured at such a temperature that v_c were the same for all liquids. And we must remember that, at this temperature v and $v_v/v = V_v/V$, as well as ΔS would be fixed by Eq. (16) and have the same value for all liquids. Thus Trouton's rule would be expected to be obeyed if V_v/V were the same for all liquids at the boiling point, and Hildebrand's rule (which says that ΔS is the same for all liquids at such a temperature that the liquid is in equilibrium with vapor at some fixed value of V_v) is seen to require that V should be the same for all liquids at the Hildebrand temperature. Neglecting the small change in V on going from the Hildebrand temperature to the boiling point (or assuming, if V_c as chosen is far from the volume at the boiling point, that the change is about the same for all liquids) we see that

⁷ It is perhaps significant that the tetrahalides, which may not rotate freely in the liquid phase, are the liquids which are most out of line.

⁶ Reference 2, p. 194.

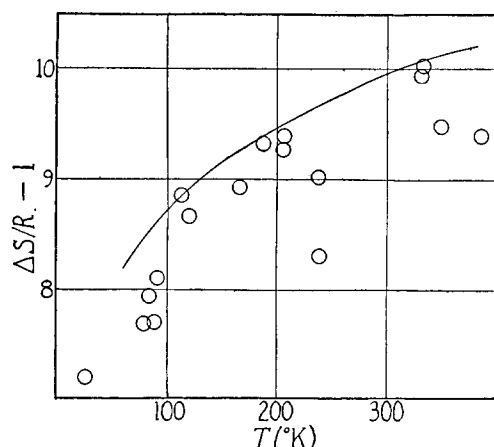


FIG. 1. $\Delta S/R-1$ as a function of T for the liquids of Table I, except GeCl_4 . The curve is calculated from Table III, p. 103 of Hildebrand's *Solubility*, second edition, and gives the result to be expected from Hildebrand's rule, with benzene as the reference liquid. The use of benzene displaces the curve upward, but the shape should be approximately the same.

Hildebrand's rule demands that V should be practically the same for all liquids at the boiling point. Now, as may be seen from Table I, neither V_v/V nor V are the same for all liquids, so neither Trouton's rule nor Hildebrand's rule would hold if v_e were truly an absolutely definite universal function of v , but rather something in between. It is true that Hildebrand's rule is obeyed better than Trouton's rule, as will be clear from Fig. 1, but they do not after all differ very greatly from each other, and the approximate theoretical result may be considered to be in reasonably good agreement with the experimental facts.⁸

⁸ Just as the present paper was being finished, I saw the preprint of the paper to be given at the Princeton symposium by Eyring and Hirschfelder, which parallels the development of §2 and §3 of this paper. However, the present paper takes up the questions involved from a

§3. THE QUANTITY γ AND THE HEAT CAPACITY

We can get at the evaluation of γ in another way, if we assume, as we have throughout, that the functional relationship between V_e and V is independent of the temperature,⁹ and that the change of V_e with temperature is conditioned solely by the change of V . Suppose, now, we hold V_e constant and allow T to change. We may consider the change of entropy under these conditions in which equilibrium is not maintained, and write

$$(\partial \Delta S / \partial T)_{V_e} = -C/T \quad (17)$$

where C is equal to the specific heat per mole of the liquid at constant pressure minus the specific heat per mole of the vapor at constant volume. From (3), then (see statement directly following Eq. (2)), we see that

$$dR \ln V_e/dT = C/T. \quad (18)$$

Noting now that

$$d \ln V_e/dT = V_e^{-1} dV_e/dT = (V/V_e)(dV_e/dV)\alpha$$

we get from Eqs. (11) and (18)

$$C/\alpha RT = \gamma^{-1}(\Delta S/R-1), \quad (19)$$

where, in this equation, ΔS once more refers to somewhat different point of view, and discusses a different series of liquids, so it seems worthwhile to publish it in its entirety. If b of Eyring and Hirschfelder is considered to be the same for all liquids, then they may be said to have used a special form of $\phi(v)$, which has the advantage of giving approximately the correct magnitude for $\Delta S/R-1$, though all the difficulties as regards trends from liquid to liquid remain the same.

⁹ In a paper which I saw in process of publication, Stearn and Eyring, *J. Chem. Phys.* 5, 113 (1937), have treated the change of effective volume with temperature in a different way.

TABLE II.

Subs.	$T(^{\circ}\text{K})$ (b.p.)	$\alpha \times 10^3$	C_p (liq.) (calories per deg.)	C_v (gas)	C	$C/\alpha RT$	γ	$\gamma_{\text{corr.}}$	γ_H
N_2	77.4	5.88	13.64	4.97	8.67	9.6	0.80	1.19	
CO	81.5	5.2	14.43	4.97	9.46	11.2	0.71	1.01	
A	87.3	4.54	10.51	2.98	7.53	9.6	0.80	1.21	
O_2	90.1	4.14	12.99	4.98	8.01	10.8	0.75	1.16	
HBr	206.1	2.12	14.31	4.96	9.35	10.8	0.86	1.26	
Cl_2	238.5	1.61	16.25	5.82	10.43	13.7	0.60	0.85	
SiCl_4	330.7	1.83	35.2	20.25	15.0	12.5	0.80	1.00	0.98
Br_2	331.9	1.22	17.12	6.56	10.56	13.1	0.76	1.06	
CCl_4	349.9	1.36	32.43	19.11	13.32	14.1	0.67	0.87	0.93

Data from Landolt Börnstein, *Tabellen* and *International Critical Tables* (for α see especially density formulas in I.C.T.). On account of considerable discrepancies in the various values given, we note particularly that Pearson and Robinson's value of α was used for HBr and Latimer's value of C_p for SiCl_4 .

the entropy of vaporization at equilibrium. Thus if γ is less than 1 we see that $C/\alpha RT$ should be greater than $\Delta S/R - 1$, and a comparison of these quantities should enable us to evaluate γ . We have made this comparison in Table II for those substances in Table I for which data that seem reasonably reliable are at hand. It is seen that $C/\alpha RT$ is in general larger than $\Delta S/R - 1$, but the relation between them is rather irregular, and if $(dV_e/dV)(V_e/V)^{-1}$ were calculated from $\Delta S/R - 1$ by use of the values of γ obtained from Table II, the regularity in Fig. 1 would be lost. It seems likely that the irregularity is due to a large extent to experimental error in the determination of α .

We have the opportunity of comparing γ at the boiling point as obtained in the above manner with γ at 25°C (tabulated as γ_H) obtained by direct comparison of $(\partial E/\partial V)_T$ (as obtained by Hildebrand and his co-workers) with $\Delta E/V$ in the case of SiCl_4 and CCl_4 . We have done this (reducing ΔH , from the tabulation of Bichowsky and Rossini, to 25°C and calculating ΔE) for these liquids and exhibited the results in Table II. It is seen that the agreement is only fair.

Note added, March, 1937: Doctors Eyring and Hirschfelder have called my attention to experimental data of Eucken and Hauck* which, as they remarked, shows that the assumption made at the beginning of §3 and the resulting equation

$$d \ln V_e/dT = (V/V_e)(dV_e/dV)\alpha \quad (20)$$

cannot be exactly true. Eucken and Hauck have found that C_v for the liquid is greater than one would expect for the gas by about the amount that the specific heat of a three-dimensional oscillator differs from that of a monoatomic gas. In other words, the liquid is more like a solid with respect to the translational motion of its molecules than it is like a gas. Now, we see from Eq. (3), holding V_e and V constant that

$$R(\partial \ln V_e/\partial T)_V = [C_v(\text{liq.}) - C_v(\text{gas.})]/T. \quad (21)$$

Hence

$$d \ln V_e/dT = (\partial \ln V_e/\partial T)_V + (\partial \ln V_e/\partial V)_T(dV/dT) \\ = C_v(\text{liq.})/RT - C_v(\text{gas.})/RT + (V/V_e)(\partial V_e/\partial V)_T \alpha, \quad (22)$$

it being understood that $V^{-1}(dV/dT) = \alpha$ refers to the expansion of the liquid at zero pressure, or, what amounts to the same thing, under its vapor pressure. Combining (22) with (18) and (11) we get in place of (19)

$$C'/\alpha RT = \gamma_{\text{corr.}}^{-1}(\Delta S/R - 1), \quad (23)$$

where $C' = C_p(\text{liq.}) - C_v(\text{liq.})$ and $\gamma_{\text{corr.}}$ is the true value of γ , as contrasted to the value γ tabulated in Table II.

* Zeits. f. physik. Chemie **134**, 161 (1928).

We have added a column of $\gamma_{\text{corr.}}$ obtained (except in the case of argon, where $C_v(\text{liq.})$ was taken directly from Eucken and Hauck's data, and the cases of O_2 , N_2 and CO , where Eucken and Hauck's value for air was used) by assuming that $C_v(\text{liq.}) - C_v(\text{gas.}) = 3R/2 = 2.98$ calories per mole. It is to be noted that there is now reasonably good agreement between $\gamma_{\text{corr.}}$ and γ_H for SiCl_4 and CCl_4 .

Since the assumption of Eq. (20) was used in Eq. (15), we must, in order to be consistent, use the uncorrected value of γ when applying Eq. (15). If this is done the assumption embodied in Eq. (20) cancels out. The assumption remains that $d\phi(v)/dv$ is independent of temperature changes. If we can assume that γ is approximately independent of temperature (and since it does not vary greatly at all, this seems reasonable) this will be true if $d \ln v_e/d \ln v = V(\partial S/\partial V)_T R^{-1}$ is independent of temperature. Now $(\partial S/\partial V)_T$ is independent of temperature if $C_v(\text{liq.}) - C_v(\text{gas.})$ is independent of volume. The measurements of Eucken and Hauck, while not extensive enough to prove this definitely, indicate that probably $C_v(\text{liq.}) - C_v(\text{gas.})$ is constant for simple liquids at the volumes which prevail at and below the boiling point. Therefore, we believe that we can conclude that Eq. (15) is valid if the uncorrected value of γ is used.

§4. ASSOCIATED LIQUIDS

There are a number of substances which have abnormally high entropies of vaporization, and it has long been customary to assume that that is due to molecular association. A similar effect might be expected if the molecules were prevented from rotating by mere mechanical interference. Such phenomena undoubtedly result in a decrease of the entropy of a liquid, and it is assumed that the substance must acquire the extra entropy in evaporating. This would be undoubtedly true if the substance boiled at the same temperature as if it were not associated or its rotation unimpeded, but as a matter of fact the boiling point is higher, being determined ultimately by Eq. (8), and there is no reason why the entropy of association might not be balanced or overcome by changes in other types of entropy at the point of equilibrium.

In the case of an associated liquid the situation is complicated by the fact that we cannot use Eq. (11) for Eq. (9) will not be followed when the energy of association is included, and γ is thus unknown. However, we can gain some understanding of the fact that the ΔS of vaporization is higher than normal at the boiling point, or at least see the conditions which must hold for this to be true. Let us suppose that we

wish to know the entropy of vaporization at a temperature, T , such that the liquid is in equilibrium with vapor at a definite pressure, say, 1 atmosphere. If the liquid were *not* associated, this equilibrium would take place at a temperature T_0 and the effective volume of the liquid would be V_e' . The entropy of vaporization would be, say, $\Delta S' = \Delta E'/T_0 + R$; in the actual liquid, however, there is an extra entropy of vaporization due to the necessity of first dissociating the molecules. Call it $\Delta S''$ and the corresponding extra energy of vaporization $\Delta E''$. The total entropies and energies of vaporization are thus given by $\Delta S = \Delta S' + \Delta S''$ and $\Delta E = \Delta E' + \Delta E''$. We must, at any temperature, have $\Delta E''/T > \Delta S''$, else the liquid would not be associated. Hence, we see that, at T_0 we have for the free energy of vaporization at atmosphere (what is, in itself, obvious)

$$\Delta F = \Delta E + RT - T\Delta S > 0. \quad (24)$$

As the liquid warms up the free energy decreases. We have the general thermodynamic equation

$$d\Delta F/dT = -\Delta S. \quad (25)$$

So equilibrium will occur at a higher temperature. At the same time ΔS will change. We have

$$d\Delta S/dT = \Delta C_p/T. \quad (26)$$

Since C_p for the vapor is less than that for the liquid, ΔS also decreases with the temperature. The question we now have to answer is: Will ΔF reach zero before ΔS reaches the value which $\Delta S'$ had at T_0 (which is, of course, the normal entropy of vaporization of an unassociated liquid)? This will generally be the case if, at $T = T_0$,

$$\frac{-d\Delta F/dT}{\Delta F} > \frac{-d\Delta S/dT}{\Delta S - \Delta S'}, \quad (27)$$

$$\text{or} \quad \frac{\Delta S}{\Delta F} > \frac{-\Delta C_p}{T(\Delta S - \Delta S')}. \quad (28)$$

Putting in the values of these quantities at $T = T_0$, we can write, specifically,

$$\frac{\Delta S}{\Delta E'' - T_0\Delta S''} > \frac{-\Delta C_p}{T_0\Delta S''} \quad (29)$$

$$\text{or we must have} \quad -\frac{\Delta S}{\Delta C_p} > \frac{\Delta E'' - T_0\Delta S''}{T_0\Delta S''}. \quad (30)$$

Now ΔS will always be considerably greater than $-\Delta C_p$, for in case of any appreciable tendency toward association ΔS will be considerably greater than 20, while, with water, methyl and ethyl alcohols, typical associated liquids, $-\Delta C_p$ is not over 10 or 11 calories per degree per mole.¹⁰ The observed energy of vaporization at the boiling point will, therefore, be greater than normal unless $\Delta E''$ is three or four times as great as $T_0\Delta S''$. If this were the case, and $\Delta S''$ were at all large, we should expect appreciable association in the gas phase. For example, if $\Delta S'' = 10$ and $T_0 = 300$ and $\Delta E'' = 3T_0\Delta S''$, we have $\Delta E'' = 9000$, which would correspond to an energy of dissociation of the double molecules of about 18,000. This is greater than the energy of dissociation of N_2O_4 .

I wish to thank Professor J. H. Hildebrand for helpful discussions during the early stages of the preparation of this paper.

¹⁰ Landolt-Börnstein, *Tabellen*. The specific heat values for the vapors of methyl and ethyl alcohols obtained from the data of Fiock, Ginnings, and Holton, Nat. Bur. Stand. J. Research 6, 886 (1931) are very low. This is probably because they measured the heat content of the saturated vapor, and the number of associated molecules, while small, is not entirely negligible and increases as the temperature and pressure go up. In our argument we neglect the presence of associated molecules in the vapor, which in these liquids is the correct procedure for our purposes.