Free Volume and Entropy in Condensed Systems II. Entropy of Vaporization in Liquids and the Pictorial Theory of the Liquid State

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II. Entropy of Vaporization in Liquids and the Pictorial Theory of the Liquid State

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The results of the first paper of this series, and a generalization of a method due to Eyring, are used to obtain an expression for the free volume of a liquid, $V_f = f b^3 g^3 / h^3 n^3 \times [RT/\Delta E_v]^3$, and an equation for the entropy of vaporization. $\Delta S = R[\ln V_g - \ln V_l - \ln \beta + 3 \ln (\Delta H/RT - 1)]$. Here $\beta = \gamma f b^3 g^3 / h^3 n^3$, where γ measures the interference in the liquid with the internal motions (rotations, vibrations) of the molecule, and f, b, g, h, n are quantities which depend on the geometry of the liquid and the energetic and dynamic interaction of the molecules. The rule of Barclay and Butler, that the 25°C value of ΔS for various pure liquids has a rough linear relationship to the corresponding ΔH of vaporization, is shown to imply a general tendency for a liquid to have a smaller β the larger its ΔH of vaporization. In many cases this means a smaller γ, resulting from increased interference with rotation of the molecules in the liquid. Pitzer's perfect liquid has a value $\beta = 16$, sensibly independent of ΔH. This is taken to mean that in such a liquid as benzene or carbon tetrachloride ($\beta \approx 6$) the interference with free rotation is considerable. For CS_2 there is evidence that the intermolecular force field differs from "normal," and the difference in potential function between liquid metals and normal liquids shows up strongly. Accepting the value $\beta = 16$ found for the ideal liquid as a norm, it is proposed to call $R \ln (16/\beta)$ for any liquid the hypothetical entropy defect (HED) and interpret it as the amount by which the entropy of the liquid (referred to the same substance as a perfect gas) is less than that of the ideal liquid in the "corresponding" state.

INTRODUCTION

IN the preceding paper[1] (hereinafter to be referred to as I) it was shown that, by relating it to entropy changes, the free volume of a condensed system may be determined in a usefully exact way. It was also shown that the free volume so determined bears a usefully exact relationship to a pictorial free volume based on cells or cages in which the center of gravity of a molecule is "free" to move. The latter result can be expressed in the equation

$$V_f = Nvf, \qquad (1)$$

where V_f is the molal free volume, v is the average free volume of the cell, or cage, N is Avogadro's number, and f a fluctuation factor which takes account of (a) the temperature variability of v, (b) the encroachment of the molecules on each other's free volume, and (c) whether or not a molecule is counted as being able to occupy the physical volume element assigned to another without exchanging places with it.

Using the ideas developed in I we proceed in this paper to investigate the liquid state. It is found that this makes possible the interpretation of the entropy rules of Barclay and Butler,[2] Bell,[3] and others,[4] and moreover makes it possible to use the information these rules contain to extend, and make more precise, our ideas regarding the molecular make-up of real liquids. The way in which one molecule interferes with the motions of another in a "normal" liquid is found to be related, in a rough, but more than qualitative way, to the heat of vaporization, and to the molal volume of the liquid. This gives a new criterion for "normal" behavior,[5] and paves the way for a realistic distinction between "normal" and "associated" liquids.

CALCULATION OF FREE VOLUME

For estimating the free volume of a liquid or solid an ingenious method due in essence to

[1] H. S. Frank, J. Chem. Phys. **13**, 478 (1945).

[2] I. M. Barclay and J. A. V. Butler, Trans. Faraday Soc. **34**, 1445 (1938).

[3] R. P. Bell, Trans. Faraday Soc. **33**, 496 (1937).

[4] M. G. Evans and M. Polyani, Trans. Faraday Soc. **32**, 1333 (1936).

[5] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (The Macmillan Company, New York, 1940), 800, p. 319, discuss the commonly accepted distinction between normal and associated liquids. We shall use the words to refer to the substances to which these authors apply them, but shall find it necessary to reject their hypothesis that molecular rotations are unhindered in the liquids they consider typically normal.

Eyring[6] is available. Equation (50) of I is equivalent to writing

$$S = R \ln (\gamma V_f) + B(T), \qquad (2)$$

whence

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] = R\left(\frac{\partial \ln [\gamma V_f]}{\partial V}\right)_T. \quad (3)$$

$(\partial E/\partial V)_T$ is often used for the "internal pressure" of the liquid, and is, in all ordinary cases, far greater than P, so that, to all intents and purposes

$$\left(\frac{\partial E}{\partial V}\right)_T = RT\left(\frac{\partial \ln V_f}{\partial V}\right)_T + RT\left(\frac{\partial \ln \gamma}{\partial V}\right)_T. \quad (4)$$

Now the liquid may be thought of as subdivided into cells, of average volume V_l/N, one per molecule. The diameter of such a cell will be proportional to $(V_l/N)^{\frac{1}{3}}$, the proportionality constant depending on the assumed shape.

To describe the motion of a molecule in its cell, Eyring has used a smooth potential, hard-sphere model, and Fowler and Guggenheim,[7] following Mie,[8] have discussed a harmonic oscillator model. Neither of these is very realistic, but presumably either of them could serve as a point of departure, from which successive approximations would enable one to represent the true motion with considerable accuracy. Kincaid and Eyring[9] have made one such "improvement" on the smooth-potential model. We shall follow a more general method.

In Fig. 1, the distance l between two molecules is proportional to $(V_l/N)^{\frac{1}{3}}$, say $c(V_l/N)^{\frac{1}{3}}$. Of this, a portion $l-d$, or $c(V_l/N)^{\frac{1}{3}}-d$, is equal to the free length in which the molecule can move in the dimension considered. d is the excluded length per molecule. It is a function of temperature and volume, but corresponds to the hard-sphere diameter in the cruder model. The volume of the cell in which the molecule is free to move is then $b^3[(V_l/N)^{\frac{1}{3}}-d/c]^3$ where b^3 is a proportionality constant depending on the geometry of the packing. For a simple cubic arrangement and a

cubic cell, Eyring[6] writes $b=2$, $b^3=8$. For a spherical cell, and hexagonal close packing Fowler and Guggenheim[10] write $b^3=(4/3)\pi\sqrt{2} = 5.92$. We shall leave b^3 undetermined, but expect it to have a value somewhere in this neighborhood. The constant c equals 1 for simple cubic packing, and $2^{1/6}$ for hexagonal close packing. We shall write $d/c=d'$, and note that d' is strictly proportional to d and almost equal to it.

Using (1), we may now write

$$V_f = Nfb^3[(V_l/N)^{\frac{1}{3}} - d']^3 = fb^3[V_l^{\frac{1}{3}} - N^{\frac{1}{3}}d']^3. \quad (5)$$

Here f is the fluctuation factor, containing both encroachment and temperature variability fluctuations. For a crystalline solid, we would expect it to have a value corresponding to $e^{\frac{1}{3}}\alpha$ as in I (54) and so to be equal to 6 or thereabouts. In a liquid the actual physical fluctuations are doubtless greater, but, on the other hand, the "looser" the relation between the molecules, the more we expect the effect of the fluctuations to be included in the "natural" size of the cell volumes, and the smaller the factor $T(\partial \ln v/\partial T)$ in f. Thus in the extreme case of the perfect gas, f as we are using it here equals 1. We shall therefore expect that in a liquid f will have a value between 1 and 5, say about 2 or 3. Its exact value will of course depend on the choice of b, but the product fb^3 could reasonably, for a liquid, be between 10 and 20.

To make use of (4) we differentiate (5) logarithmically obtaining

$$\left(\frac{\partial \ln V_f}{\partial V}\right)_T = \left(\frac{\partial \ln [b^3 f]}{\partial V}\right)_T + (V_l^{\frac{1}{3}} - N^{\frac{1}{3}}d')^{-1}$$

$$\times \left[V_l^{-\frac{2}{3}} - 3N^{\frac{1}{3}}\left(\frac{\partial d'}{\partial V}\right)_T\right]$$

$$= f^{\frac{1}{3}}bg V_f^{-\frac{1}{3}} V_l^{-\frac{2}{3}} + \left(\frac{\partial \ln [b^3 f]}{\partial V}\right)_T$$

$$\tag{6}$$

where

$$g = 1 - 3\left(\frac{N}{V_l}\right)^{\frac{1}{3}}\left(\frac{\partial d'}{\partial \ln V}\right)_T = 1 - \left(\frac{\partial d}{\partial l}\right)_T.$$

g measures the effect of change in volume on the exclusion diameter.

[6] H. Eyring and J. O. Hirschfelder, J. Phys. Chem. 41, 249 (1937).

[7] Fowler and Guggenheim, reference 5, 802, p. 325.

[8] G. Mie, Ann. d. Physik 11, 657 (1903).

[9] J. F. Kincaid and H. Eyring, J. Chem. Phys. 5, 587 (1937).

[10] Fowler and Guggenheim, reference 5, 806, p. 332.

With (4) this gives

$$V_f = \frac{fb^3g^3}{h^3V_l{}^2}\left[\frac{RT}{(\partial E/\partial V)_T}\right]^3, \qquad (7)$$

h being defined as

$$1 - \frac{RT(\partial \ln [b^3f\gamma]/\partial V)_T}{(\partial E/\partial V)_T}.$$

Now Hildebrand[11] has shown that for many liquids under atmospheric pressure,

$$(\partial E/\partial V)_T = \Delta E_v/V_l,$$

where ΔE_v is the energy of vaporization of the liquid. This is true when

$$E_l = E_g - \frac{a}{V}; \quad \left(\frac{\partial E}{\partial V}\right)_T = \frac{a}{V^2} = \frac{E_g - E_l}{V}. \qquad (8)$$

Even when the relation is not as simple as this, over a small volume range it must be possible to represent E_l as $E_g - a'/V^n$, which gives

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{na'}{V^{n+1}} = \frac{n(E_g - E_l)}{V} = \frac{n\Delta E_v}{V}. \qquad (9)$$

With (7), this gives

$$V_f = \frac{fb^3g^3}{h^3n^3}V_l\left[\frac{RT}{\Delta E_v}\right]^3. \qquad (10)$$

This is Eyring's[6] equation, "refined" by the introduction of the factors f, g, and h.

Equation (10) is now a perfectly general expression for V_f in any condensed phase. The appearance in it of the factors f, b, g, n, and h is repellent in so far as we desire a clear-cut relationship involving only experimentally measurable quantities. It would be idle, however, to try to treat a liquid as being simpler than it is, and each of the factors introduced has a physical meaning, as may be seen from the defining equations. Each of them is a property of the substance under discussion, with a definite value under given conditions of temperature and volume, and though we may not be able to estimate these values with great precision, we can tell enough about each of the quantities to

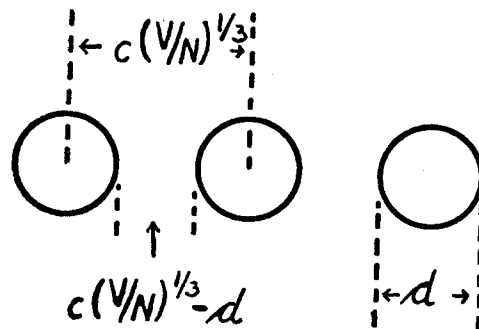[11] J. H. Hildebrand, *Solubility* (New York, 1936), second edition, p. 99.

Fig. 1.

be able to say, if a value is proposed, whether it is plausible or not. Actually, as will be seen, we shall use the quotient $\beta = \gamma fb^3g^3/n^3h^3$ as a property of the liquid (or solid) and shall find that its value can be calculated from experimental data. The values so obtained can, moreover, be correlated with other properties with interesting results.

APPLICATION TO CRYSTALS

Since (10) is a general equation, it should be applicable to the elementary crystals studied in I. Comparison of (10) with I (54) should therefore give information about the factor g, since f, b, h, and n can be evaluated for those cases. For solid argon at 77.5°K, n can be evaluated from $\Delta E(=\Delta H - RT = 1724$ cal./mole$)$, V, the molal volume of the crystal $(=22.4$ cc$)$, and $(\partial E/\partial V)_T$, obtainable from Simon and Kippert's[12] value of 38 atmos./deg. for $(\partial P/\partial T)_V$ and equal to 2945 atmos. $= 71.3$ cal./cc. This makes $n = 0.927$. h should be very close to 1, since $\gamma = 1$ and b^3f as a quasi-geometrical quantity should not be very sensitive to volume changes. The last statement agrees with the fact that for the process of fusion, with the large expansion and the shift from solid to liquid fluctuation, ΔS is only 3.5 e.u. Again, the solid model used in

[12] F. Simon and F. Kippert, Zeits. f. physik. Chemie **135**, 113 (1928). Rice (J. Am. Chem. Soc. **63**, 3 (1941)) has shown that this value is too high to be reasonably accounted for by a plausible inter-atomic potential curve for solid argon, and has (J. Chem. Phys. **12**, 289 (1944)) proposed a very different sort of curve to fit this datum. We shall not enter into a discussion of the relative plausibilities of the various assumptions which may be made to resolve the difficulty, but note that a smaller value than Simon and Kippert's for $(\partial P/\partial T)_V$ of solid argon would also fit better into the picture we are presenting here, giving a smaller value for n, and therefore a smaller one for g and a larger one for $(\partial d/\partial l)_T$.
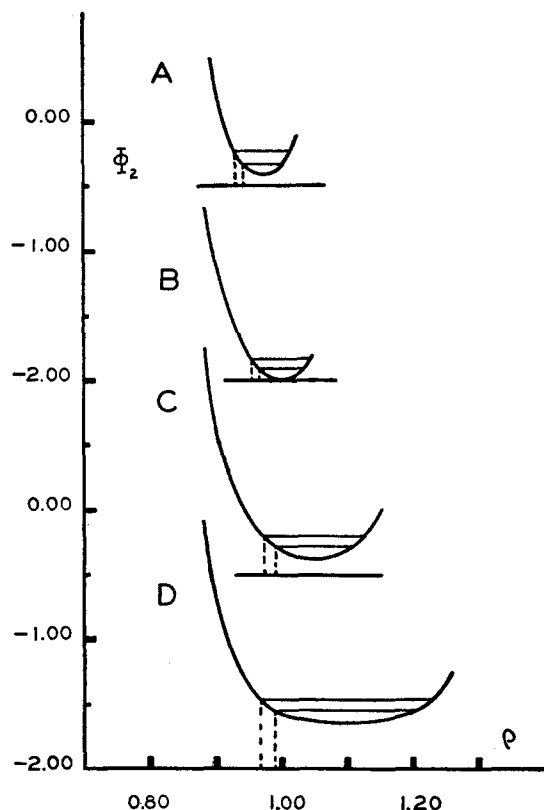
FIG. 2. $\Phi_2(=\varphi_2/D)$, the reduced potential of a molecule between two fixed neighbors, as a function of $\rho(=r/r_0)$, the reduced distance from one of them. The different curves are for different values of $\lambda(=L/r_0)$, the reduced distance apart of the "boundary" particles; for A, $\lambda=1.95$; B, $\lambda=2.00$; C, $\lambda=2.10$; D, $\lambda=2.20$. The two sets of numbers on the Φ_2 axis are for curves B and D. For A and C the ordinates $\Phi_2=-2.00$ are also shown by horizontal lines.

getting I (54) corresponds to $b=2$, $f=e^{\frac{1}{2}}\alpha=6.46$. (10) thus makes

$$\frac{V_f}{V_s}=6.46\cdot8\cdot g^3\left[\frac{1.99\times77.5}{1724\times0.927}\right]^3=4.61\times10^{-2}g^3.$$

Since the other treatment gave $V_f/V_s=5.25$ $\times10^{-3}$ we have $g^3=0.114$ or $g=0.48$. From the definition of g, this means that $(\partial d/\partial l)_T=0.52$. In words, this states that a small isothermal increment in V increases d by 52 percent of the increase in l. A corresponding calculation for cadmium at 523°K gives $g=0.27$ or

$$(\partial d/\partial l)_T=0.73.$$

RELATION TO POTENTIAL CURVE

The relation of the quantity $\partial d/\partial l$ to the kind of potential curve usually assumed to represent

the interaction of molecules in solids or liquids is shown in Figs. 2 and 3. If the intermolecular potential for two particles is assumed[13] to be $\phi_1=ar^{-12}-br^{-6}$ where r is the distance apart of their centers, this can be thrown into the form $\phi_1/D=\rho^{-12}-2\rho^{-6}$. Here D is the "dissociation energy" of the pair, the depth of the lowest point on the curve, and $\rho=r/r_0$, where r_0 is the "equilibrium separation," or distance apart corresponding to the minimum potential. If, now, one molecule is allowed to move back and forth between two fixed molecules whose centers are separated by a distance $L=\lambda r_0$, the potential ϕ_2 of the system, ignoring the interaction of the fixed molecules with each other, is given by

$$\Phi_2=\phi_2/D=\rho^{-12}+(\lambda-\rho)^{-12}-2\rho^{-6}-2(\lambda-\rho)^{-6}.$$

This function is plotted in Fig. 2 for various values of λ in the range of interest, and shows the potential energy relationship in a simplified 1-dimensional liquid or solid. Ignoring quantum effects, the actual energy of the middle molecule will be higher than the lowest point in the curve by an amount kT. Two sets of horizontal lines
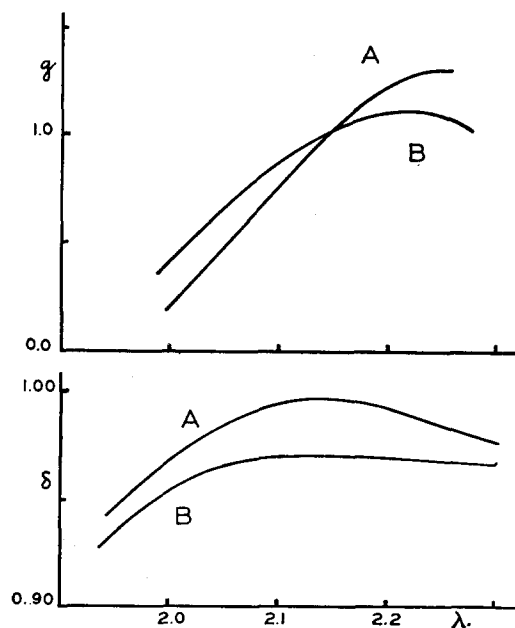

FIG. 3. $\delta(=d/r_0)$, the reduced exclusion diameter of a molecule, and $g(=1-dd/dl)$, as functions of $\lambda(=L/r_0)$ the reduced distance apart of its bounding neighbors. A, $kT/D=1/6$; B, $kT/D=1/12$.

[13] Cf., for example, J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. London **A163**, 53 (1937).

are shown in Fig. 2, representing $kT/D = \frac{1}{6}$ and $kT/D = \frac{1}{12}$, respectively. The intersections of these lines with the potential curves give the limits of the motion of the middle molecule, so that $\rho_{int} = d/r_0 = \delta$. δ has been evaluated graphically, and its approximate variation with λ is shown in Fig. 3, along with $g(= 1 - 2(\partial\delta/\partial\lambda))$. It is seen that $\partial\delta/\partial\lambda$ has rather sizable positive values when the system is highly condensed, and becomes somewhat negative when it is highly expanded. Qualitative considerations make it seem likely that this sort of trend will be found for almost any potential curve of plausible shape, and for models more realistic in detail than that considered here.

A simple generalization to three dimensions makes it possible to give a qualitative discussion of $\Delta E_v/V$, $(\partial E/\partial V)_T$ and n. We write $V = \sigma\lambda^3$ and $E = \tau D\epsilon_t$ where σ and τ are constants, and $-\epsilon_t = \phi_{2\,min}/D - 1/t$ is the distance from the zero of energy down to the line $kT/D = 1/t$ before referred to. Then

$$\frac{\Delta E_v}{V} = \frac{\tau D}{\sigma}\frac{\epsilon_t}{\lambda^3}, \quad \text{and} \quad \left(\frac{\partial E}{\partial V}\right)_T = \frac{\tau D}{\sigma}\cdot\frac{1}{3\lambda^2}\frac{\partial\epsilon_t}{\partial\lambda}.$$

$$\frac{\epsilon_t}{\lambda^3} \quad \text{and} \quad \frac{1}{3\lambda^3}\frac{\partial\epsilon_t}{\partial\lambda}$$

are shown in Fig. 4, along with their quotient, which is n in (9) and (10). It is seen that n is less than unity for highly condensed systems and rises to values somewhat above 1 as the system is expanded. Here again, it is probable that any plausible form of potential curve and of physical model will show this qualitative behavior.

Of particular interest is the ratio g/n which occurs in (10). Figure 4 shows that for $t = 6$ this ratio is near unity when n itself is near unity, and for $t = 12$ the ratio is never far from 1 except when λ is very small. How much these numbers would be influenced by changes in the model or in the form of the potential curve could be determined only by a more extended study than would be appropriate here. This is also the case with the question how far the molecules of a liquid must depart from spherical symmetry before such a discussion as this becomes inapplicable. We are going to assume that for normal liquids under ordinary laboratory conditions, the
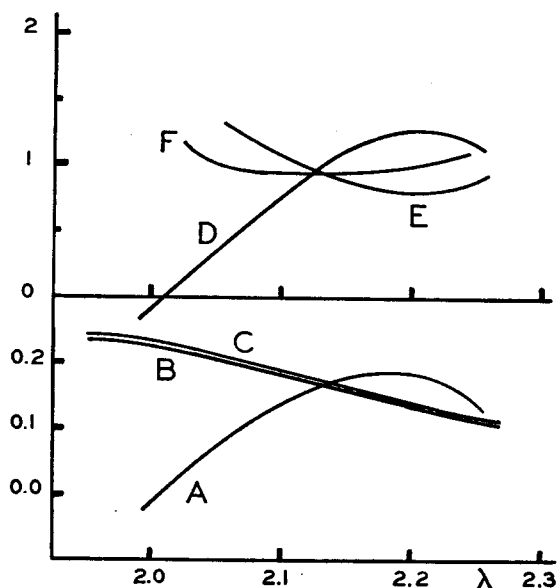

FIG. 4. Various properties of a liquid (corresponding to the simplified model described in the text) as functions of λ, which measures the degree of expansion of the liquid. Curve A represents $(1/3\lambda^2)(d\epsilon_t/d\lambda)$, which is proportional to $(\partial E/\partial V)_T$; Curves B and C represent ϵ_t/λ^3 (proportional to $\Delta E/V$), for $kT/D = 1/6$ and $1/12$, respectively. Curve D represents $n(= A/B$ or $A/C)$ practically the same for either temperature. Curves E and F represent g/n for $kT/D = 1/12$ and $1/6$, respectively (these correspond, respectively, to curves B and A of Fig. 3, divided by curve D.

ratio g/n has the qualitative physical meaning we have given to it, and a value which does not change much from liquid to liquid, and is not far from unity. This value is supported by the better-than-qualitative success of the calculation of compressibility made by Eyring and Hirschfelder,[6] and, as seen above, is not in conflict with the low values of g obtained here for solid (contracted) argon and cadmium. The values for cadmium correspond, of course, to averages, due to the anisotropy of the crystal.

APPLICATION TO LIQUIDS

Equation (10) gives an expression for V_f which may be introduced into the general Eqs. (50) and (51) of I. Taking the latter first and introducing (10) we get the general expression for the vapor pressure of a liquid

$$P_{vap} = \frac{RT}{\beta V_l}\left[\frac{\Delta E_v}{RT}\right]^3 e^{-\Delta H/RT}, \quad (11)$$
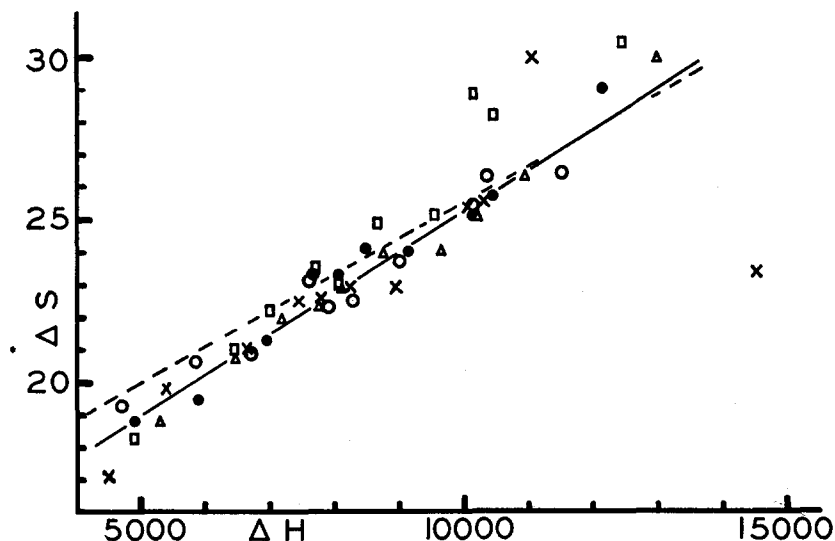
where

$$\beta = \gamma f b^3 g^3/h^3 n^3. \quad (12)$$

FIG. 5. ΔS of vaporization, in calories per degree per mole vs. ΔH of vaporization in calories per mole, at 25°C for the substances listed in Table I, which also contains the key to the symbols. The dotted line represents Eq. (16a) $\Delta S = 14.5 + 0.0011\Delta H$. The solid line represents Eq. (17) $\Delta S = 12.75 + 0.00124\Delta H$.

If b^3/n^3 is used instead of β (11) is identical with Eyring's[6] Eq. (17). We also follow Eyring in throwing (11) into the form

$$\frac{P_{vap}}{RT} = \frac{1}{V_{vap}} = \frac{1}{\beta V_l}\left[\frac{\Delta H}{RT} - 1\right]^3 e^{-\Delta H/RT}, \quad (13)$$

and pointing out that this can be made to give the Hildebrand rule[14] for entropy of vaporization, i.e., for equilibrium vaporization to the same molàl concentration of vapor all liquids should have the same molal entropy change. Eyring derives this from (13) by calling βV_l constant, remarking that most common liquids have molal volumes in the range 80–100 cc. This does not do justice to the rule, however, for it is far more accurate than such statement would imply. This may be caused in part by the fact that the function $(x-1)^3 e^{-x}$ changes so rapidly with small changes of $x(=\Delta S/R = \Delta H/RT)$ in the relevant range of ΔS values (≈ 20 e.u.), that even a considerable variation in βV_l calls for only a small change in ΔS_{vap}. We shall discuss variations in βV_l presently in another light, however, and shall find that this product may, in fact, be expected to be much the same for most liquids under the conditions envisaged in the Hildebrand rule.

[14] J. H. Hildebrand, Solubility (New York, 1936), second edition, p. 102.

ENTROPY OF VAPORIZATION OF LIQUIDS

Inserting (10) and (12) into (50) of I gives

$$\Delta S = R[\ln V_g - \ln (\beta V_l) + 3 \ln (\Delta E/RT)]$$
$$= R[\ln V_g - \ln (\beta V_l)$$
$$+ 3 \ln ((\Delta H/RT) - 1)]. \quad (14)$$

This tells how ΔS of vaporization of a liquid should vary with ΔH of vaporization, and gives a way of interpreting and of using the empirical rules of Bell,[3] and of Barclay and Butler,[2] which relate to these quantities. The empirical finding is that there are numerous groups of substances, pure liquids, or solutes in dilute solution, which, when compared at the same temperature and between the same standard states, give experimental values of ΔS and of ΔH which are more or less accurately represented by an equation of the form

$$\Delta S = A + B\Delta H. \quad (15)$$

A given A and B will describe a single group of substances (e.g., pure non-polar liquids, gases in benzene, aliphatic amines in water, etc.) more or less well. Moreover, Barclay and Butler[2] have shown that there is a value of A and one of B, which give a line ΔS vs. ΔH from which no normal substance, pure liquid nor solute, deviates very greatly. Their "normal" curve is given by

$$\Delta S = 0.0277 + 0.0011\Delta H \quad (16)$$

TABLE I.

Substance	ΔH	ΔS	Log βV_l	V_l	Log V_l	Log β	β	$\beta/16$	HED
x 2-methyl propene	4500 LR	17.1	3.11	94.9 E	1.977	1.13	13.5	0.84	0.3
c CH₃Cl	4700 B	19.3	2.70						
d 1-butene	4900 LR	18.8	2.87	95.1 E	1.978	0.89	7.8	0.49	1.4
s trans-2 butene	4900 LR	18.3	2.98	(93.5) E	1.971	1.01	10.2	0.64	0.9
t C(CH₃)₄	5300 AM	18.8	2.98	122.3 E	2.087	0.89	7.8	0.49	1.4
x cis-2 butene	5400 LR	19.8	2.79	(93.5) E	1.971	0.82	6.6	0.41	1.7
c C₂H₅Cl	5870 B	20.65	2.72	72.0 LB	1.858	0.86	7.2	0.45	1.55
d 1,4-pentadiene	5900 LR	19.5	2.99	106.5 E	2.027	0.96	9.1	0.57	1.1
s (C₂H₅)₂O	6430 B	21.0	2.79	104.6 I	2.019	0.77	5.9	0.37	2.0
t 2-methyl 2-butene	6450 LR	20.7	2.86	106.8 E	2.028	0.83	6.8	0.425	1.7
x Ge(CH₃)₄	6640 K	21.0	2.83	137.7 LB	2.136	0.69	4.9	3.1	2.3
c CS₂	6680 K	20.9	2.86	60.65 I	1.783	1.08	12.0	0.75	0.55
d Si₃H₈	6950 K	21.3	2.82	132.7 LB	2.123	0.70	5.0	0.31	2.3
s Ni(CO)₄	7000 K	22.2	2.64	131.5 I	2.119	0.52	3.3	0.21	3.1
t SiCl₄	7190 K	21.9	2.74	115.4 I	2.062	0.68	4.8	0.30	2.4
x CHCl₃	7450 I	22.3	2.68	81.10 I	1.909	0.77	5.9	0.37	2.0
c CH₃COCH₃	7600 I	23.1	2.56	74.00 I	1.869	0.69	4.9	0.31	2.3
d Br₂	7685 K	23.3	2.54	51.5 LB	1.712	0.83	6.8	0.425	1.7
s B₅H₉	7700 K	23.5	2.49	108.9 LB	2.037	0.45	2.8	0.175	3.4
t CCl₄	7760 I	22.3	2.76	97.18 I	1.988	0.77	5.9	0.37	2.0
x PCl₃	7780 K	22.5	2.71	87.65 I	1.943	0.77	5.9	0.37	2.0
c CSeS	7900 K	22.3	2.78	62.3 LB	1.794	0.99	9.8	0.61	1.0
d CH₃OH	8040 K	23.3	2.58	40.72 I	1.610	0.97	9.3	0.58	1.1
s C₆H₆	8050 B	23.0	2.67	89.50 I	1.952	0.72	5.25	0.33	2.2
t GeCl₄	8090 K	22.9	2.69	114.5 LB	2.019	0.67	4.7	0.29	2.7
x PBr₃	8230 K	22.9	2.72	95.5 LB	1.980	0.74	5.5	0.34	2.1
c 2,2,4-trimethyl pentane	8275 P	22.5	2.81	166.1 E	2.220	0.59	3.9	0.24	2.8
d Cl₂O₇	8480 K	24.1	2.49						
s CH₃COOC₂H₅	8670 B	24.9	2.34	98.50 I	1.993	0.35	2.2	0.14	3.9
t n-heptane	8740 P	23.9	2.58	147.4 E	2.168	0.41	2.6	0.16	3.6
x Zn(C₂H₅)₂	8960 K	22.9	2.83	105.3 LB	2.022	0.81	6.5	0.41	1.8
c 2,3,4-trimethyl pentane	9000 P	23.7	2.66	161.9 E	2.209	0.45	2.8	0.175	3.4
d Toluene	9115 PS	24.0	2.62	107.0 I	2.029	0.59	3.9	0.24	2.8
s SnCl₄	9550 K	25.1	2.44	117.8 I	2.071	0.37	2.3	0.14	3.8
t TiCl₄	9620 K	24.0	2.69	110.6 I	2.044	0.65	4.5	0.28	2.5
x C₂H₄Br₂	10050 RA, I	25.3	2.47	86.60 I	1.937	0.53	3.4	0.21	3.1
c C₆H₅Cl	10110 ZS, I	25.4	2.46	102.1 I	2.009	0.45	2.8	0.175	3.4
d p-xylene	10110 PS	25.1	2.52	123.9 LB	2.093	0.43	2.7	0.17	3.5
s C₂H₅OH	10120 B	28.9	1.70	58.65 I	1.768	−0.07	0.85	0.053	5.8
t m-xylene	10160 PS	25.1	2.53	123.6 LB	2.092	0.44	2.8	0.175	3.5
x S₂Cl₂	10300 K	25.7	2.41	81.10 I	1.909	0.50	3.2	0.20	3.2
c 1-C₃H₇NO₂	10380 H	26.3	2.30	89.9 LB	1.954	0.35	2.2	0.14	3.9
d o-xylene	10470 PS	25.7	2.43	123.6 LB	2.092	0.34	2.2	0.14	3.9
s H₂O	10470 I	28.22	1.88	18.07 I	1.257	0.62	4.2	0.26	2.7
t mesitylene	10930 B	26.3	2.36	140.0 LB	2.146	0.21	1.6	0.10	4.5
x n-C₃H₇OH	11050 B	29.9	1.60	75.05 I	1.875	−0.28	0.52	0.032	6.8
c GeBr₄	11510 K	26.4	2.42	126.0 LB	2.100	0.32	2.1	0.13	4.0
d H₂O₂	12130 K	29.0	1.92	23.69 I	1.374	0.55	3.55	0.22	3.0
s n-C₅H₁₁OH	12450 B	30.4	1.66	108.8 LB	2.037	−0.38	0.42	0.026	7.2
t n-C₆H₁₃OH	13050 B	29.90	1.82	128.2 LB	2.108	−0.29	0.51	0.032	6.8
x Hg	14540 K	23.30	3.40	14.84 I	1.171	2.23	170.0	10.6	−4.7
c Cs	18340 K	30.0	4.34	72.2 I	1.858	2.48	304.0	18.9	−5.85

The letters x, c, d, s, t, refer, respectively, to the symbols, cross, circle, dot (filled circle), square, and triangle, by which the substances so denoted are plotted in Figs. 5–9.

AM = J. G. Aston and G. H. Messerly, J. Am. Chem. Soc. **58**, 2354 (1936).
B = I. M. Barclay and J. A. V. Butler, Trans. Faraday Soc. **34**, 1445 (1938).
E = G. Egloff, *Physical Constants of Hydrocarbons* (Reinhold Publishing Corporation, New York, 1939).
H = E. B. Hodges, Ind. Eng. Chem. **32**, 748 (1940).
I = *International Critical Tables*.
K = K. K. Kelley, U. S. Bureau of Mines, Bull. 434 (Washington, D. C., 1941).

LB = Landolt-Börnstein, *Physikalisch-chemische Tabellen*, fifth edition and supplements.
LR = A. B. Lamb and E. E. Roper, J. Am. Chem. Soc. **62**, 806 (1940).
P = K. S. Pitzer, J. Am. Chem. Soc. **62**, 1227 (1940); **63**, 2413 (1941).
PS = K. S. Pitzer and D. W. Scott, J. Am. Chem. Soc. **65**, 803 (1943).
RA = D. Radulescu and M. Alexa, Chem. Abs. **34**, 934 (1940).
ZS = A. A. Zil'bermann-Granovskaya and E. A. Shugam, J. Phys. Chem., USSR **14**, 1004 (1940).

Note.—Where ΔH values had to be obtained by the application of the Clausius-Clapeyron equation, estimated corrections were applied to account for gas imperfection.

in their units, which are kg. cal./deg./mole for ΔS, and kg. cal./mole for ΔH. They take for the standard state of the gas a partial pressure of 1 mm of mercury at 25°C, and for the liquid, the
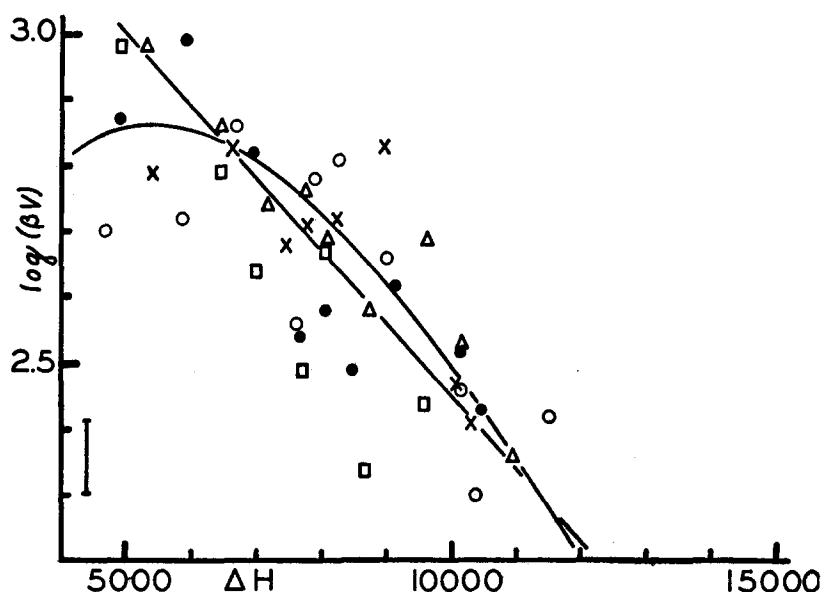
FIG. 6. Log_{10} (βV_l) vs. ΔH of vaporization in calories per mole for the liquids of Table I. The curved line represents Eq. (18) log (βV_l) = 1.600 − 0.0002712ΔH + 3 log ($\Delta H/RT$ − 1). The straight line represents Eq. (19) log (βV_l) = 3.55 − 0.00011ΔH. The vertical line has a length of 0.114 units in the logarithm, corresponding to a range of 0.5 calories per degree per mole in entropy.

pure liquid, at 25°C. We prefer to use different units, calories per degree per mole, and calories per mole, for ΔS and ΔH. We also prefer to use 1 atmosphere at 25°C as the standard state for the gas, but shall keep their standard state for liquids. In these units, and between our standard states, then, (16) becomes

$$\Delta S = 27.7 - R \ln 760 + 0.0011 \Delta H$$
$$= 27.7 - 13.2 + 0.0011 \Delta H$$
$$= 14.5 + 0.0011 \Delta H. \quad (16a)$$

An alternative line, which seem slightly better, is given by

$$\Delta S = 12.75 + 0.00124 \Delta H. \quad (17)$$

In Fig. 5 (16a) is plotted as the dotted line, and (17) as the solid one. The experimental points are for the substances presented in Table I. Some of the data are those used by Barclay and Butler, and some are from other sources, as noted.

The reality of the rule depends both on the accuracy of the data and on whether enough liquids of enough different kinds have been used to insure against a "proof by selection." As to the first point, Table I shows, in fact, that ΔH and ΔS values calculated from *International Critical*

Tables data, or from more recent sources, often disagree with those given by Barclay and Butler. The disagreements, however, are not such as to weaken the support given to the rule. As for the generality of the relationship as a rule for unassociated liquids, this is strongly supported by the points for inorganic liquids. The experimental uncertainty in the ΔS values may, in unfavorable cases, exceed 0.5 e.u., and to this order of accuracy the constants of (16a) represent the data fairly well. It seems, however, that a slightly better representation of the less polar liquids is given by (17).

There is under way in this laboratory a more extensive examination of data which have been critically chosen, and to which corrections for gas imperfection have been applied in evaluating ΔH and ΔS. The results will be communicated in a separate publication. Several points may be mentioned here, however. First, the gas imperfection corrections may be important, and if detailed theoretical questions are to be discussed, corrected values should be considered. Second, the conjecture of Barclay and Butler that different groups of substances might be representable with high precision by separate straight lines which differed somewhat from
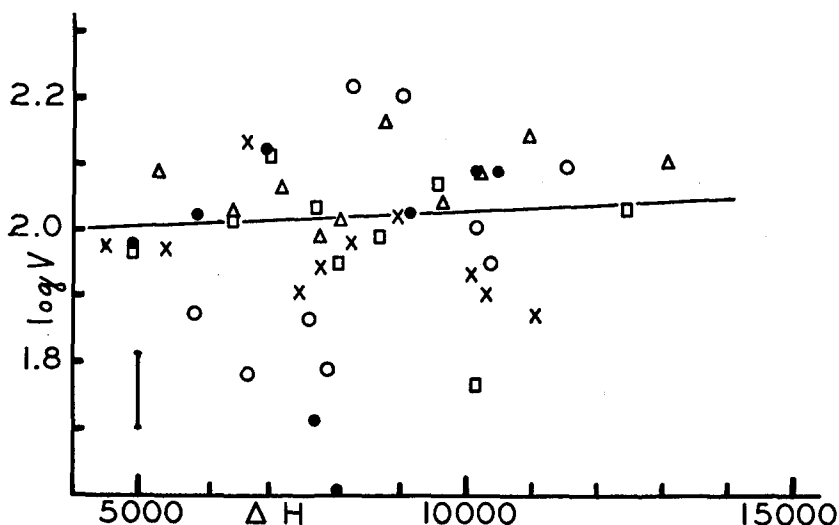
FIG. 7. $\log_{10} V$ vs. ΔH of vaporization in calories per mole, for the liquids of Table I. The line represents Eq. (20) $\log V = 1.98 + 0.000005 \Delta H$. The vertical line has a length of 0.114 units in the logarithm, corresponding to a range of 0.5 calories per degree per mole in entropy.

group to group is confirmed in several cases. Third, the differences between these group lines seem, in some cases at least, to be related to the structural features of the molecules in a way which is intelligible in terms of the discussion of the next few paragraphs.

A ROUGH NUMERICAL RULE FOR β

It is clear that (17) does represent a sort of normal behavior, and comparison with (14) shows that this is equivalent to an assertion that $\ln (\beta V_l)$ must, in a general sort of way, be a function of ΔH. Combining (14) and (17) one obtains, after a little arithmetic,

$$\log_{10} (\beta V_l) = 1.600 - 0.000271 \Delta H$$
$$+ 3 \log_{10} \left(\frac{\Delta H}{RT} - 1 \right). \quad (18)$$

(18) is plotted in Fig. 6, along with values of $\log (\beta V_l)$ for the substances of Table I, computed from (14) and the experimental ΔS and ΔH values. It is seen that in the range $\Delta H = 6,000$–12,000 cal./mole both (18) and the experimental points for normal liquids show something like a linear decrease in $\log (\beta V_l)$ as ΔH increases. One infers that there is some sort of general influence at work here, modified in each substance by more or less pronounced specific effects. The

strongly curved portion of (18) (ΔH below 6000–7000 cal./mole) falls among the liquids whose 25° vapor pressures are so high that gas imperfections become considerable. These cases present no difficulty in principle, and it may be that a future study of substances falling in this region will yield interesting results. For the present, however, we limit our discussion of pure liquids, both from the standpoint of (18) and of (17), to cases in which ΔH exceeds 5 or 6 kg cal./mole. In this range (18) can be approximated very well by the linear equation

$$\log (\beta V_l) = 3.55 - 0.00011 \Delta H. \quad (19)$$

The spread of the experimental points about the line (19) in Fig. 6 is considerably greater than the spread about (17) in Fig. 5. This is only partly due to the scale of plotting, as shown by comparison with the vertical line drawn in Fig. 6, which corresponds to an entropy discrepancy of 0.5 e.u. The reason is doubtless that there is some compensation between ΔH and ΔS, as discussed below, so that either experimental error or anomalous behavior will be accentuated in $\log (\beta V_l)$, which involves a difference between quantities which depend on ΔH and ΔS, respectively. Comparison of the discrepancies from (19) with those from (17) indicate that many of them, at least, represent real physical effects,
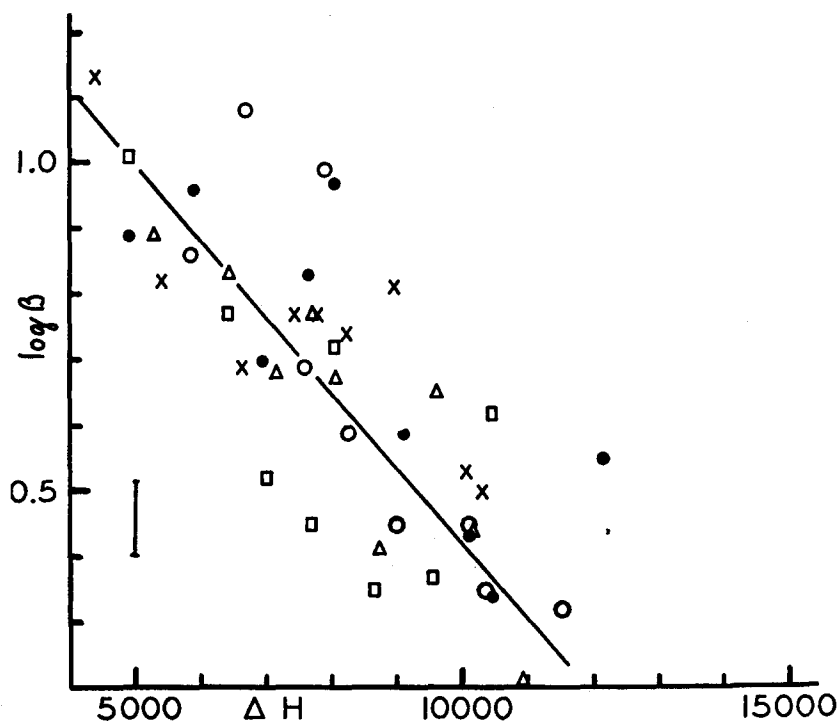
FIG. 8. $\log_{10} \beta$ vs. ΔH of vaporization in calories per mole for the liquids of Table I. The line represents Eq. (21) $\log \beta = 1.57 - 0.000115\Delta H$. The vertical line has a length of 0.114 units in the logarithm, corresponding to a range of 0.5 calorie per degree per mole in entropy.

which are therefore specific, over and above the general rules represented by (17) and (19).

Since specific effects enter as largely as they do, there would be no utility, at this stage, in a discussion of hypothetical exact functional relationships to which (17), (18), and (19) approximate. It is enough for the present to have discovered so good a linear trend in log (βV_1) with ΔH as the Barclay-Butler rule has been shown to imply, and to inquire into its qualitative physical significance.

For this purpose we must first separate out the dependence, if any, of log V upon ΔH. In Fig. 7, these quantities are plotted for the liquids of Table I, and it would be rash to claim that any marked dependence stands out. The ordinary expectation would be that log V_l should, in a general sort of way, increase with ΔH, from the Trouton rule and the idea that variations in density within a group of liquids are not extreme. It is clear, however, that for this miscellaneous series of liquids, specific, or constitutive, effects are so great as to mask any obvious emergence of such a rule.

The equation

$$\log V_l = 1.98 + 0.000005 \, \Delta H \qquad (20)$$

is derived from (21) and (19), and is plotted as the solid line in Fig. 7. While it would seem foolish to say that it describes a "normal trend" in the experimental points, closer examination suggests that it may not be devoid of significance. Substances which lie very much below, or to the right of (20) are, in striking majority, polar. That is, they have forces acting between the molecules which are absent in the non-polar liquids and which may pull the liquid together "too much," or may raise ΔH to values higher than their volumes (number of electrons which can participate in van der Waals interaction) correspond to. Substances which lie very much above, or to the left of (20) have "balled-up" molecules, or electron distributions which separate the electrons of neighboring molecules "too far," so that the van der Waals attraction is below par, ΔH is too small, and the liquid is "abnormally" expanded.

The points for H_2O and H_2O_2, and the normal

aliphatic alcohols, are in agreement with this picture. In the cases of the metals Hg and Cs, the forces holding the liquid together are different in kind (cf. discussion below).

When the individual values of $\log V_l$ are used to obtain $\log \beta$, results are obtained which are plotted against ΔH in Fig. 8. Here a rather good linear trend reappears and Eq. (21) represents the line which has been chosen to express it.

$$\log \beta = 1.57 - 0.000115 \Delta H. \qquad (21)$$

Examination of the deviations of the individual points from (21), and comparison with them of the deviations of points for $\log (\beta V_l)$ from (19), indicates a correlation which seems more than random. This lends some additional support to the idea that (20), and deviations from it, can be interpreted in a physically significant way. A closer analysis of these questions belongs to a more detailed study than is attempted here. As to order of magnitude, however, the liquids for which ΔH is greater than 6000 cal./mole, excluding the hydrogen bonded substances and the metals, show average deviations from (19), (20), and (21) of just under 0.10 in the logarithm in each case. These correspond to deviations of about 0.4 e.u., or in (19) and (21) to deviations of 800 cal./mole in ΔH. The existence of such large deviations is undoubtedly due in part to the attempt to fit so miscellaneous a group of liquids with a single representation.

PHYSICAL INTERPRETATION

To interpret (21) in terms of the physical picture, we recall that $\beta = (\gamma f b^3 g^3 / h^3 n^3)$. The product $f b^3$ may change somewhat from liquid to liquid, but we do not expect the change to be great. g/n, as we have seen, should be close to 1 for all ordinary liquids but small variations in this ratio should show up as specific effects in β. h should be close to 1 when $\gamma = 1$, and will be somewhat less than 1 otherwise, as γ should increase with V, though perhaps not greatly. The chief burden of a general variation in β with ΔH therefore falls on γ, and (21) thus shows that γ decreases with increase in ΔH. This, again, is qualitatively what is to be expected for the kinds of molecules that make up real liquids. The larger the molecules, the greater, normally, will be the van der Waals attraction between them, and the greater, therefore, the repulsive forces

between them for equilibrium. This means more intimate contact, and therefore, for polyatomic molecules, more interference with internal motions—chiefly rotation and internal rotation. It is striking that, for a series of hypothetical monatomic liquids with ΔH in the range of interest, calculations from Pitzer's[15] reduced equation of state data indicate that β would be practically independent of ΔH, and have the high value of about 16. For these liquids $\gamma = 1$ identically, and it appears that 16 is a sort of normal or "unperturbed" value for β for any non-metallic liquid. This would mean that except for peculiarities in f, b^3, or g/n the factor by which β is less than 16 measures the extent to which the internal motions are interfered with when the vapor condenses. As pointed out above, this is qualitatively reasonable as an explanation of (21), and the discussion following (5) shows that 16 is a very reasonable par value for β to have.

SOME ABNORMALITIES

The β values for several abnormal liquids stand out prominently as exceptions to what has just been said. In the case of mercury, $\beta = 170$, the explanation is undoubtedly to be found in the fact that the forces between the atoms are of a different sort from those existing in non-

[15] K. S. Pitzer, J. Chem. Phys. **7**, 583 (1939).

Pitzer tabulates $\phi_l (= V_l/V_c)$, $\log \pi (\pi = P_{vap}/P_c)$, V_g/V_l, and ΔS_{vap}, for variable values of $\vartheta (= T/T_c)$ for the ideal liquid in equilibrium with its saturated vapor. Corrections can be made for gas imperfection using the Berthelot equation. Then ΔS_{vap} yields V_g/V_l, which, with the tabulated V_g/V_l gives V_f/V_l. Since this ΔS is an equilibrium quantity $\Delta S/R = \Delta H/RT$, so that β is easily obtained. It is noteworthy that ΔH_{vap} contains T_c as a factor, and, if T is to be 25°C, T_c cannot be higher than about 533°K without making ϑ so low (<0.56) that the ideal liquid would freeze. On the other hand, this makes ΔH only some 5600 cal./mole.

The fact that $\Delta H = 5600$ is the highest value for which β can be calculated for an ideal liquid at 25°C detracts somewhat from the comparison here made. The meaning of the calculation, however, is that β is sensibly independent of temperature for these liquids, which justifies using the value 16.0 as a "norm" for any liquid at any temperature.

Incidentally, it appears that most ordinary liquids, with $\Delta H \geqslant 6000$ cal./mole, would be solids at room temperature if they behaved as ideal substances. The reason that they are liquids at room temperature, then, is that in melting they gain entropy from sources which are not available to the ideal liquid—orientations and bendings. It is very striking that hexamethyl ethane, which is so bunched up and symmetrical as to be of nearly "ideal" shape, melts at about 102°C (G. Egloff, *The Physical Constants of Hydrocarbons* (Reinhold Publishing Corporation, New York, 1939), p. 57), compared with melting points well below 0°C for all the other open chain hydrocarbons of C_8 or below. The high melting points of benzene and cyclohexane also support this point of view.

metallic liquids.[15] This results in the higher degree of condensation of the liquid (small molal volume), which is reflected in the low value of $n (=0.33^{11})$. It may also change f, b, and g/n to values different from those found in non-metallic liquids. Taking $\gamma = 1$, and putting the whole burden of the anomaly on g/n, we get $(g/n)^3 = 170/16 = 10.7$. This makes $g/n = 2.2$, approximately, a value not incompatible with the qualitative results of Fig. 4.

In the case of methyl alcohol, $\beta = 9.3$, approximately, about twice the normal value for $\Delta H = 8040$. Here, however, we know that n is again about 0.33^{11}. This might well lead to a value of $(g/n)^3$ somewhere about 10, so that if γ were equal to 1 we would expect β to be about as far from the normal curve as in the case of mercury. The conclusion is that γ is very much less than unity in this case, in excellent agreement with what we know about hydrogen bonding in the alcohols.

For ethyl alcohol $n \approx \frac{1}{2}$. This should cause a reduction in $(g/n)^3$ as compared with methyl alcohol. This should hardly cause a so pronounced decrease in β as is observed, however, the value here being about 0.85 (the increase of about 2000 calories in ΔH should normally reduce β by about 60 percent). A plausible explanation is that the longer C_2H_5OH molecules are relatively more hindered in their rotations by hydrogen bonding than are the CH_3OH molecules, so that β is smaller here.

As mentioned later, the alcohols provide cases where the free-volume concept is less clear-cut than we could wish, and it seems scarcely worth while to pursue the details of their behavior further. Empirically, it appears that the effect of the OH group becomes relatively less and less important as the hydrocarbon chain is lengthened, so that n-hexyl alcohol behaves very much like a hydrocarbon with the corresponding ΔH of vaporization.

CS_2 and $CSeS$ seem also to have β values which are higher than might be expected, particularly in view of their straight-line structure, which should cause marked interference with free rotation in the liquids. Their small molal volumes suggest that here again we have liquids which are more "condensed" than normal, and that the high β is due to large g/n. Hildebrand's figure 0.89 for n for CS_2 can be taken as being

in harmony with this conjecture. Hildebrand's value of $n = 1.21$ for $TiCl_4$ is in the opposite direction, however, in relation to the large value of β for this compound, and the tetrahalides of C, Si, Ge, Ti, and Sn will presumably require special discussion. The large β for $Zn(C_2H_5)_2$ may also reflect some difference in force field as compared with the "standard."

THE BARCLAY-BUTLER RULE

The physical meaning of the Barclay-Butler rule may now be stated in words. When a vapor condenses, a molecule, so to speak, falls into a potential well. The deeper this well, i.e., the greater the loss of energy on condensation, the narrower it is, and the smaller the free volume, therefore the greater the loss in entropy. In addition, the deeper and narrower the well the greater the interference tends to be, not only with moving back and forth, but also with squirming into different positions. This also means more loss of entropy in deeper wells. The fact that the resultant dependence of ΔS on ΔH turns out to be approximately linear, may or may not be significant—this is a point which it does not seem profitable to discuss further at this time. The fact that individual substances show specific deviations from the Barclay-Butler line is not surprising, since there are so many factors which might cause such deviation. The fact that there are so many substances of such diverse types for which the deviations are comparatively small seems to justify setting up an equation like (17) as a rough definition of normal behavior. It is to be noted that this sort of normality does not mean correspondence with such a reduced equation of state as Pitzer's[15] for an "ideal" substance, nor with the model described by Fowler and Guggenheim,[5] but rather with the normal, i.e., usual, tendency which real polyatomic substances have to depart from these.

THE HILDEBRAND RULE

Since a small value of β usually means a small γ, which means that the free rotation of a vapor molecule has been replaced by a librational motion in the liquid, small β should mean large negative ΔC_P of vaporization. This agrees with the correlation found by Pitzer[15] between ΔS and ΔC_P of vaporization for substances deviating from his figures for ideal liquids.

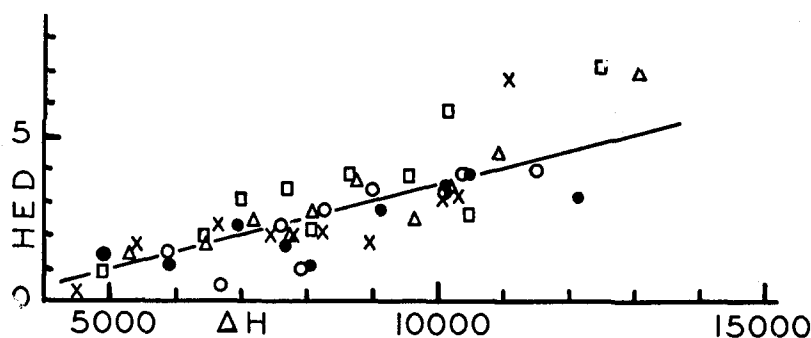This correlation also enables us to add another

FIG. 9. The hypothetical entropy defect in calories per degree per mole vs. ΔH of vaporization in calories per mole, for the liquids of Table I. The line represents Eq. (23) HED $= -1.70+0.00053\Delta H$.

point to the discussion of the Hildebrand rule. Our rule (21) for variation of β from substance to substance was derived from measurements all at one temperature, in this case 25°C. The product βV_l in Hildebrand's rule (13), however, is to be taken at a different temperature for each substance, and since it is the constancy of $\Delta H/T$ that is under discussion, it follows that the greater ΔH for a given substance, the higher the temperature at which βV_l must be taken. Since ΔC_P values more negative than -7 cal./deg./mole correspond to an increase in βV_l with temperature,[16] and since the real liquids under consideration have $-\Delta C_P$ values of about 10, we have the following kind of compensation:[17] the greater ΔH of vaporization (and ΔH is in general so great that there is no qualitative difference between the values at 25°C and at the Hildebrand temperature) the lower βV_l at 25°C, but the greater the upward correction to be made to it in going to the Hildebrand temperature. Qualitatively, therefore, it is not surprising that βV_l has similar values for all normal liquids at the Hildebrand temperatures.

THE HYPOTHETICAL ENTROPY DEFECT

The qualitative success of the Trouton rule is

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[16] Without entering here into a full discussion of the variation of β with T in real liquids, we may remark that (14) leads to the relation

$$\frac{\partial \ln \beta}{\partial \ln T}=1-\frac{\partial \ln V_l}{\partial \ln T}-3\left(1-\frac{RT}{\Delta H}\right)^{-1}$$
$$-\frac{\Delta C_P}{R}\left(1-\frac{4RT}{\Delta H}\right)\left(1-\frac{RT}{\Delta H}\right)^{-1}.$$

This shows that the more negative ΔC_P, the more strongly β increases with T in qualitative agreement with our physical picture. Numerically $\partial \ln \beta/\partial \ln T$ at 25°C is predicted to be positive for ΔC_P more negative than about -7.0 at $\Delta H=7200$, or about -6.0 at $\Delta H=10,800$.

[17] Cf. note at end of reference 2.

due to the fact that boiling liquids are, roughly, in corresponding states. Hildebrand's rule is an improvement on Trouton's because[14] it compares liquids in states which "correspond" more accurately than do the normal boiling points. According to Pitzer,[15] a further theoretical improvement could be made by comparing liquids at equal liquid to vapor volume ratios instead of at equal molal concentrations of vapor. Now the fact that β can be calculated unambiguously as a function of ϑ for an ideal liquid means that β is a *reduced quantity*. Furthermore, the empirical fact that β has a constant value, independent of ϑ, for Pitzer's ideal liquid, seems suggestive. We are going to propose, as a tentative hypothesis, that β is strictly invariant for the perfect liquid. If this is true, then comparison of β values for real liquids is logically equivalent to the comparison of ΔS under corresponding conditions, and the departure of β from the value 16.0 found for the ideal liquid is a measure of the departure of the real liquid from ideality. We therefore define

$$HED = R \ln\left(\frac{16.0}{\beta}\right) \qquad (22)$$

as the *hypothetical entropy defect* of a real liquid. By our hypothesis this is the amount by which the entropy of the real liquid is less (compared with its vapor as an ideal gas in some standard state) than that of an ideal liquid would be under corresponding conditions. HED values (for 25°C) are listed in Table I and plotted in Fig. 9. (21) requires that, as a rough empirical rule,

$$HED = -1.70+0.00053 \, \Delta H \qquad (23)$$

give a line which shall represent the 25°C values

for the normal liquids here treated with an average discrepancy of about 0.5 e.u. This is illustrated in Fig. 9 by the solid line.

What is said above shows that a good part of the HED of a normal liquid must be caused by the fact that the molecular rotation is less free in the liquid than in the gaseous state. This relates the HED to the discussion given by Hildebrand[18] of liquid structure and entropy of vaporization, with this difference, that Hildebrand, in effect, is comparing βV_l values at the Hildebrand temperature rather than β values at 25°C. The discussion by Halford[19] of the connection between ΔS and the length of free swing required for rotational motion in a liquid is also closely related to the present treatment.

As implied by the remarks made above on CS_2, CSeS, etc., however, the HED is not restricted to effects of hindered rotation, for the derivation of (14) is general enough to free (22) from the limitations of the approximate rules (17)–(21). We have seen that differences from a "normal" potential function must affect β through g and n. Differences from normal packing and dynamical behavior will be accounted for through b, f, g, h, and n. So long, therefore, as the general conditions for the physical meaningfulness of the free volume representation are fulfilled, and in so far as the concept of corresponding states is useful, the deviation of β from 16.0 should be able to express the entropy anomaly of any real liquid, arising from any cause or combination of causes. It should then be both useful and correct to use the large negative HED of mercury, for example, to express the fact that this liquid has a molal entropy considerably larger than an ideal, and very much larger than an "ordinary" liquid would have under corresponding conditions.

SIZE OF FREE VOLUME

We conclude the discussion of pure normal liquids by calculating the numerical values of V_f and V_f/V_l in sample "standard" cases. From (2)

$$\Delta S = 4.575(\log V_g - \log(\gamma V_f)),$$

or, with $V_g = 24,400$ cc,

$$\log \gamma V_f = 4.389 - \frac{\Delta S}{4.575}. \quad (24)$$

For a liquid of $\Delta H = 7000$ cal./mole, (17) gives $\Delta S = 21.4$ e.u. so that $\gamma V_f = 0.512$ cc. We can estimate γ as $\beta/16 = 0.36$ taking β from (21). This makes $V_f = 1.42$ cc. Taking V_l from (20) as 102 cc, $V_f/V_l = 0.014$ approximately. Making the same calculation for $\Delta H = 10,000$ cal./mole, $\gamma V_f = 0.078$ cc, $\gamma = 0.165$, $V_f = 0.47$ cc, $V_l = 107$ cc, so that there $V_f/F_l = 0.0044$. These values for V_f/V_l, while rather artificial, show the expected relation to the V_f/V_s values found in I for monatomic solids, which were about ½ percent. Our V_f's for liquids are by definition larger by the factor $16.0/\beta$ than the values obtained from vapor pressures by Kincaid and Eyring,[20] who also, in effect, took $\beta = 8$. This factor disturbs the otherwise almost exact agreement they found between "vapor-pressure" and "sound-velocity" values of V_f. It seems, however, that a factor of 2 is not too great a discrepancy to expect between V_f as defined here and that obtained by the sound-velocity method.

ASSOCIATED LIQUIDS

In view of the wide, and well-known, deviations of "associated" liquids from such rules as those of Trouton or Hildebrand and of Ramsay and Shields, it seems at first rather remarkable that the points for the alcohols, for the amines, and particularly for water, fall as close as they do to the Barclay-Butler line for pure liquids (cf. Fig. 5 where the "excess" ΔS for these substances is seen to be about 2 e.u. as compared with 5 or 6 e.u. discrepancies from the other rules. 2.2 e.u. is about $R \ln 3$). The explanation of course is in part that different factors tend to compensate each other, as found above with γ and $(g/n)^3$ and, to some extent, with β and V_l. Another compensation comes about in that the heats and entropies of vaporization of these liquids turn out to be about "equally abnormal." The hydrogen bond, or surface dipole, interactions between the molecules act to increase both the energy of separation and the restriction of motion beyond what is typical for liquids which are non-polar or have "buried" dipoles. It appears that the relation between the extra ΔH contribution and extra ΔS contribution due to "association" is not very different from the "normal" relation between

[18] J. H. Hildebrand, J. Chem. Phys. 7, 233 (1939).
[19] R. S. Halford, J. Chem. Phys. 8, 496 (1940).
[20] J. F. Kincaid and H. Eyring, J. Chem. Phys. 6, 620 (1938).

ΔH and ΔS, so that instead of falling far away from the Barclay-Butler line they fall somewhere near it, but in the "wrong" places—i.e., in a range of ΔH and ΔS values higher than their molecular weights and molecular volumes would normally correspond to.

Another point which needs to be mentioned here is that these substances constitute the cases in which the free volume picture is least clear-cut. The occurrence of hydrogen bonds in these liquids introduces a specific non-classical element into the motions (both translational and rotational) of the molecules in the liquid state. On the other hand, by using a sort of principle of correspondence, we can see that, however bad the focus, the free volume camera we have used

to make pictures of the simpler liquids must also give some sort of picture for these. And until some better basis is devised for comparing the associated liquids with the non-associated it seems probable that the free volume concept will continue to be useful for this purpose.

SOLUTIONS

The interpretation of liquids which has been given above receives further, and not inconsiderable, support from data on solutions. It also permits interesting conclusions to be drawn from solution data. The necessary extension of the theory, together with an analysis of experimental results, will be found in the following paper, No. III of this series.

Free Volume and Entropy in Condensed Systems

III. Entropy in Binary Liquid Mixtures; Partial Molal Entropy in Dilute Solutions; Structure and Thermodynamics in Aqueous Electrolytes

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The ideas of the first and second papers in this series, which make it possible to interpret entropy data in terms of a physical picture, are applied to binary solutions, and equations are derived relating energy and volume changes when a solution is formed to the entropy change for the process. These equations are tested against data obtained by various authors on mixtures of normal liquids, and on solutions of non-polar gases in normal solvents. Good general agreement is found, and it is concluded that in such solutions the physical picture of molecules moving in a "normal" manner in each others' force fields is adequate. As would be expected, permanent gases, when dissolved in normal liquids, loosen the forces on neighboring solvent molecules producing a solvent reaction which increases the partial molal entropy of the solute. Entropies of vaporization from aqueous solutions diverge strikingly from the normal behavior established for non-aqueous solutions. The nature of the deviations found for non-polar solutes in water, together with the large effect of temperature upon them, leads to the idea that the water forms frozen patches or microscopic icebergs around such solute molecules, the extent of the iceberg increasing with the size of the solute molecule. Such icebergs are apparently formed also about the non-polar parts of the molecules of polar substances such as alcohols and amines dissolved in water, in agreement with Butler's observation that the increasing insolubility of large non-polar molecules is an entropy effect. The entropies of hydration of ions are discussed from the same point of view, and the conclusion is reached that ions, to an extent which depends on their sizes and charges, may cause a breaking down of water structure as well as a freezing or saturation of the water nearest them. Various phenomena recorded in the literature are interpreted in these terms. The influence of temperature on certain salting-out coefficients is interpreted in terms of entropy changes. It appears that the salting-out phenomenon is at least partly a structural effect. It is suggested that structural influences modify the distribution of ions in an electrolyte solution, and reasons are given for postulating the existence of a super-lattice structure in solutions of $LaCl_3$ and of $EuCl_3$. An example is given of a possible additional influence of structural factors upon reacting tendencies in aqueous solutions.

INTRODUCTION

IN the first of two preceding papers[1] (hereinafter to be referred to as I and II) the concept of free volume was re-examined, and relations were worked out between free volume changes and changes in entropy in isothermal processes. In the second paper these free volume relation-

[1] H. S. Frank, J. Chem. Phys. **13**, 478, 493 (1945).