

It has been pointed out that the solubility or melting-point method of determining latent heat of fusion of organic compounds gives very accurate results when interpreted in the light of the principles outlined above.

Some generalizations regarding the nature of the binary systems obtained with various types of mixtures have been given.

The uses of these principles in determining the choice of solvent for crystallizations and molecular-weight determinations are suggested.

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THE VAPOR PRESSURES AND HEATS OF VAPORIZATION OF NON-ASSOCIATED LIQUIDS

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In the application of physico-chemical principles to industrial and manufacturing processes, few questions are of more frequent occurrence than those dealing with distillation problems. The questions take a variety of forms but most of them may be answered when the vapor pressures of the substances involved are known. Occasionally the desired information may be found in, or calculated directly from, data given in the literature. More commonly this is not the case and it is then necessary either to make the measurements or to resort to some method of calculation of the desired values.

Many expressions have been developed for calculating vapor pressures and heats of vaporization of liquids. Probably the most useful of them is that obtained from the integration of the Clausius-Clapeyron equation. This integration, assuming that the heat of vaporization is constant, gives the well known expression,

$$\log P = -L/4.58 T + C \quad (1)$$

in which P is the vapor pressure measured at the absolute temperature T , L is the molecular latent heat of vaporization and C is a constant of integration.

Equation 1 indicates that if the common logarithm of the vapor pressure be plotted against the reciprocal of the absolute temperature a straight line should result, the slope,

$S \left(S = \frac{\Delta \log P}{\Delta (1/T)} \right)$ of which is given by the expression $-L/4.58$, or,

$$\log P = C - S/T. \quad (2)$$

Hildebrand¹ has shown that these $\log P$ vs. $1/T$ curves for normal liquids may be superimposed upon that of some closely related substance by the use of a factor which he calls a . This factor is simply the ratio of the molecular latent heats of vaporization of the substances involved, or it is the ratio of the absolute temperatures at which the vapors of the

¹ Hildebrand, *THIS JOURNAL*, **37**, 975 (1915).

two liquids will be evaporated to the same concentration of molecules.

Recently the writer undertook to determine graphically the slopes of the $\log P$ vs. $1/T$ curves for all of the normal liquids the vapor pressures of which had been measured. Although many were investigated only a few need be given here. In Table I, Col. 3, are given the slopes obtained in this manner for a representative number of liquids. As indicated by the principles outlined by Hildebrand,² there is a regular change in the slope of the $\log P$ vs. $1/T$ curves as one passes from substances having low to those having high boiling points.

When these slopes were plotted against the normal boiling points of the liquids the points were found to lie very close to a smooth curve the equation of which may be represented by

$$S = -68 + 4.877 T_b + .0005 T_b^2 \quad (3)$$

in which S is the calculated slope and T_b is the absolute boiling point of the liquid under normal pressure.

Under (4), Table I, are given the slopes of the $\log P$ vs. $1/T$ curves calculated from Equation 3, and in Col. 5 the differences between the observed and calculated slopes are recorded. It is quite evident, except at the very lowest temperatures where negative results are obtained, that this equation expresses the true slope with remarkable accuracy, the variations being both positive and negative. Indeed it may be said that at all temperatures above about 30°Å. , Equation 3 expresses the true slope with a degree of precision approaching that often found in the recorded experimental results.

When the expression for the slope, given in Equation 3, is inserted in Equation 2, and any simultaneous values of pressure and temperature (conveniently $P = 760$ and $T = T_b$) are introduced, it is then possible to evaluate the constant C . This then gives a very simple method for determining the constants in Equation 2 from the boiling point alone, a constant which is known or easily determined for many liquids.

Equation 3 also furnishes a very direct method for calculating the molecular latent heat of vaporization, since $L_v = 4.58 S$. The results obtained from such a calculation are shown in Col. 7, Table I. In Col. 6 are given the experimentally determined latent heats for comparison. Col. 8 then shows the ratio of the calculated to the observed latent heats. It will be observed that in all cases below hydrogen the calculated result is larger than the observed. This difference averages about 8%. This, then, is equivalent to changing the constant 4.58 to 4.23. Accordingly, a new empirical equation for calculating latent heats of vaporization may be developed by combining Equations 2 and 3 and using the constant 4.23 instead of 4.58, viz.,

$$L_v = 4.23 (-68 + 4.877 T_b + .0005 T_b^2) \quad (4)$$

² Hildebrand, THIS JOURNAL, 40, 45 (1918).

TABLE I

Substance	(2) T_b	(3) $S_{obs.}$	(4) $S_{calc.}$	(5) Diff.	(6) $L_{obs.}$	(7) $L_{calc.}$	(8) (7)/(6)	(9) $4.23 \times S_{calc.}$	(10) Trouton	(11) Bingham	(12) Nernst
Helium.....	4.3	5.8	-47	-52.8	...	26.5	92.5	73.5	25.8
Hydrogen.....	20.2	50	45	-5	248	228	0.92	190	435	350	250
Oxygen.....	90.1	380	380	0	1630	1740	1.068	1610	1940	1620	1630
Hydrogen chloride..	190.0	900	870	-30	3860	4110	1.065	3680	4080	3630	3850
Ether.....	308.0	1450	1480	30	6460	6630	1.025	6265	6620	6280	6600
Bromine.....	331.6	1610	1615	5	6960	7360	1.057	6840	7115	6840	7180
Benzene.....	353.3	1720	1720	0	7350	7860	1.070	7285	7590	7390	7670
Stannic chloride....	387.2	1890	1890	0	7900	8650	1.094	8000	8315	8240	8490
Chlorobenzene.....	405.0	1980	1980	0	8350	9055	1.084	8380	8700	8690	8890
Benzonitrile.....	463.6	2300	2300	0	9040	10520	1.164	9750	9960	10220	10280
Naphthalene.....	491.0	2460	2450	-10	10250	11250	1.097	10380	10580	11000	10880
Phenanthrene.....	611.0	3090	3100	10	...	14130	...	13120	13140	14500	13550
Carbazole.....	624.0	3170	3170	0	...	14500	...	13420	13410	14900	13880
Sulfur.....	720.0	3700	3700	0	...	16920	...	15670	15500	17950	15900
Cadmium.....	1057	5750	5650	-100	23480	26300	1.118	23920	22720	30200	22550
Antimony.....	1600	9000	9020	20	...	41150	...	38200	34420	55350	30800
Silver.....	2218	13150	13210	60	...	60100	...	55900	47650	91900	40600
Gold.....	2885	18600	18200	-400	...	85000	...	77000	62100	140800	36500
Platinum ^a	4270	25800	29900	4100	...	118200	...	126700	91900	273200	19500
Tungsten ^a	5280	44000	39600	-4400	...	201200	...	167800	94600	344000	-8560
Water.....	373.0	2160	1820	340	9650	9880	1.022
Ethyl alcohol.....	351.4	2170	1700	470	9500	9920	1.044
Phenol.....	454.4	2520	2240	280	10680	11510	1.078
Acetic acid.....	392.2	2200	1920	380	5650	10050	1.778
Aniline.....	456.9	2510	2250	260	10500	11470	1.091
Acetophenone.....	474.5	2550	2360	190	10700	11650	1.090

^a Calculated from the sublimation-pressure data determined by Langmuir³ using the thermodynamic relations discussed in the latter part of this paper.

³ Langmuir, *Phys. Rev.*, **3**, 340 (1913); **4**, 384 (1914).

The results obtained for such a calculation are shown in Col. 9.

In Cols. 10, 11 and 12, Table I, are given first, the latent heats of vaporization calculated from Trouton's equation

$$L_v = 21.5 T_b \quad (5)$$

second from Bingham's equation,

$$L_v = (17 + .011 T_b) T_b \quad (6)$$

and third from Nernst's equation,

$$L_v = (9.5 \log T_b - .007 T_b) T_b \quad (7)$$

Comparing the results obtained by these various equations with those obtained by direct measurement it will be observed that at the very lowest temperatures, Nernst's equation gives the best results. At all other temperatures, except for isolated cases, Equation 4 gives results as good as, if not better than, any of the others. At high temperatures it is very evident that Equation 4 gives much the best results. Nernst's equation actually goes through a maximum and finally yields negative results. The results obtained from Trouton's rule are also much too low at high temperatures, while those from Bingham's equation are much too high.

In order to show the limitations of this method of calculating vapor pressures and heats of vaporization, there are collected at the bottom of Table I the data for some typical associated liquids. In general it may be said that the simpler compounds containing hydroxyl, amino, carbonyl and carboxyl groups and most molten salts deviate more or less from the general rule for normal liquids. For these classes of liquids there will be needed at least two values of the vapor pressure, or one value of the vapor pressure and the heat of vaporization in order to write the vapor pressure equation. It should also be noted that the vapor pressures of the more strongly associated substances may not be accurately represented by the straight line equation except through relatively narrow ranges of temperature.

Having given a simple expression for the vapor pressure of liquids, the question may be asked: Can a similar expression be derived for the sublimation pressure of solids? Happily the answer is that a similar expression exists and that for many substances the constants may be empirically calculated from existing data.

It has been shown that in the expression,

$$\log P = C - S/T \quad (8)$$

the constants C and S may be calculated for normal liquids from the boiling point alone. In any case they may be calculated from two simultaneous values for $\log P$ and T . Richards⁴ has shown that there is an exactly similar expression for sublimation pressure,

$$\log P_s = C_s - S_s/T \quad (9)$$

⁴ Richards, *J. Franklin Inst.*, **187**, 581 (1919).

in which P_s is the sublimation pressure at the absolute temperature T , C_s and S_s are constants having the same significance as in Equation 8. Richards has also shown how the constants may be evaluated especially in the case of metals.

The constant S_s is related to the heat of sublimation by the expression,

$$S_s = -L_s/4.58 \quad (10)$$

Now the latent heat of sublimation is equal to the sum of the heats of fusion and of vaporization, or

$$L_s = L_f + L_v \quad (11)$$

Now, Equation 4 furnishes a method for calculating L_v for normal liquids, leaving then only the latent heat of fusion to be obtained. A careful search has revealed the fact that there are relatively very few reliable measurements of the latent heats of fusion recorded in the literature and almost no data are available for substances melting below 0° . Several empirical methods for calculating heats of fusion have been proposed. Probably the simplest and most generally useful is that proposed by Walden⁵ by which the molecular latent heat of fusion is equal to the absolute melting point times a constant.

$$L_f = T_m \cdot K \quad (12)$$

Walden⁵ has shown that the constant K has a value equal to about 13.5 for many organic compounds. This value is, however, too high for many classes of compounds. After considering all of the available data upon the latent heats of fusion we have concluded that the following tentative values for Walden's constant may be used for calculating the latent heats of fusion of these classes of substances here represented.

Substances	No. of substances investigated	Mean value of $L_f/T_m = K$	Av. deviation from mean
Metals.....	18	2.6	0.3
Aromatic hydrocarbons.....	10	12.8	0.5
Halogen compounds.....	15	13.5	0.5
Nitro compounds.....	6	13.5	0.5
Amino compounds.....	7	11.0	1.4
Aromatic hydroxy compounds.....	5	6.9	0.3
Aromatic acids, anhydrides and ketones....	7	12.1	1.0

There are insufficient data to indicate what would be the value of this constant for mixed derivatives, but in general, it may be said that the higher the molecular weight and the higher the melting point the larger will the constant tend to become in any of the series of compounds so far investigated.

It should be remembered that there is an independent method of calculating the latent heat of fusion of solids from their solubility and freezing-point curves. For this method to yield accurate results, however,

⁵ Walden, *Z. Elektrochem.*, **14**, 713 (1908).

the substance chosen as solvent must be one which will form a thermodynamically ideal mixture or, otherwise, there must be introduced a factor which will correct for the non-ideality of the given mixture. In a recent paper the writer⁶ has described a method for determining this factor, and hence for finding the heat of fusion from such data for several classes of organic compounds. It is probable that the principles there discussed would apply to other classes of substances as well, but at present there are too few data to enable one to make a comparison.

Assuming then that L_s , the latent heat of sublimation, is known or may be calculated from Equations 11 and 12, it is then possible to calculate the slope, S_s , of the $\log P_s$ vs. $1/T$ curve from Equation 10. There are insufficient data on sublimation pressures to indicate whether, in Equation 10, the latent heat of sublimation should be divided by the constant 4.58 or some other value, in order to obtain the slope. We have preferred to use the value 4.58 until this can be determined. With the constant S_s evaluated there still remains the integration constant C_s to be determined. This is readily accomplished when it is remembered that, at the melting point the vapor pressure is equal to the sublimation pressure. Hence, we may write

$$C_s - S_s/T_m = C - S/T_m \quad (13)$$

from which C_s may be determined. Thus it is evident that for solids which melt to form normal liquids, and especially if the melting point and boiling point of the substances are relatively high so that the slopes of the vapor pressure and sublimation pressure curves are not widely different, it should be possible to calculate very closely approximating equations for the vapor pressure and sublimation pressure and also the heats of vaporization, of sublimation and of fusion when only the melting and boiling points of the substance are known.

Summary

1. Empirical methods for evaluating the constants in the vapor-pressure and sublimation-pressure equations, $\log P_v = C_v - S_v/T$ and $\log P_s = C_s - S_s/T$, have been given and their significance discussed.

2. It is shown that S_v , the slope of the $\log P$ vs. $1/T$ curves is, for normal liquids given by the expression, $S_v = -68 + 4.877 T_b + 0.0005 T_b^2$.

3. It has been made evident from experimental data that the molecular heat of vaporization is equal to $4.23 \times S_v$ rather than $4.58 \times S_v$.

4. It is shown that the values of the molecular latent heat of vaporization calculated from the equation $L_v = 4.23 S_v$, are generally in better agreement with the experimental results than those calculated from the equations proposed by Trouton, by Bingham or by Nernst. The ad-

⁶ Unpublished results.

vantage is especially marked when applied to substances boiling at high temperatures.

5. The thermodynamical equations relating heats of vaporization, of sublimation and of fusion and their relation to the vapor pressure and sublimation pressure are briefly reviewed and empirical methods for calculating each from the freezing and boiling points for normal liquids are proposed.

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INVESTIGATION BY MEANS OF THE HYDROGEN ELECTRODE OF THE CHEMICAL REACTIONS INVOLVED IN WATER PURIFICATION¹

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Although titration of calcium and magnesium carbonates and precipitation of calcium carbonate, magnesium and aluminum hydroxides are common chemical reactions encountered in one way or another in a variety of instances, few definite or direct data are available concerning the course of these reactions. The titration of the alkalinity of calcium carbonate or magnesium carbonate solutions assumes that the end-points are the same as those obtained when titrating sodium carbonate solutions. Little is known concerning the velocities of the precipitation reactions and the optimum conditions for complete precipitation.

The use of the hydrogen electrode for following the courses of these reactions seemed to promise a method for obtaining more exact data both as to the end-point in alkalinity titrations and with respect to conditions for the precipitations. The reactions thus studied were: (1) the titrations of calcium carbonate and magnesium carbonate with a strong acid; (2) the precipitation of calcium carbonate (a) by the addition of hydroxide to the bicarbonate (b) by the addition of carbonate to calcium chloride; (3) the precipitation of magnesium hydroxide (a) from the carbonate (b) from the sulfate; (4) the precipitation of aluminum hydroxide.

Hildebrand² had titrated sodium carbonate with a strong acid using the hydrogen electrode but had not titrated calcium carbonate or magnesium carbonate. He also followed the precipitation of aluminum hydroxide with the same device. The apparatus used was, however, much less sensitive than that now available. The concentrations of his solutions were not given by Hildebrand but they were presumably 0.1 *N* or more concentrated. The concentrations dealt with in water analysis and purification are so very low that it seemed advisable to repeat his work using more dilute solutions and a sensitive apparatus.

¹ Abstract of thesis submitted by R. E. Greenfield in partial fulfillment of the requirements for the degree of Doctor of Philosophy, at the University of Illinois, August, 1921.

² Hildebrand, *THIS JOURNAL*, **35**, 847-71 (1913).