THE VAPOR PRESSURE AND HEAT 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 directly or to resort to some method of calculation of the required data.

Many expressions have been developed for calculating vapor pressures and heats of vaporization, probably the most useful of which is that obtained from the integration of the Clausius-Clapeyron equation. Assuming the gas laws to apply and also assuming that the heat of vaporization is a constant throughout the desired range, and introducing common logarithms, there is obtained the expression:

$$\text{Log } P = \frac{-L}{4.58\ T} + C, \qquad (1)$$

in which P is the vapor pressure and T is the absolute temperature at which P is measured. C is an integration constant, the value of which depends upon the units used.

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. In view of the rather bold assumptions concerning the applicability of the gas laws and the constancy of the latent heat of vaporization, it is quite remarkable how closely experimental data may be represented by this linear equation throughout relatively wide ranges of temperature.

In equation (1) the term L/4.58 represents the slope of the log P vs 1/T vapor pressure curve. The integration constant, C, is the value which log P would have when the temperature is some hypothetical maximum. Numerically, the value of C, assuming the pressure to be measured in mm. of mercury, varies from about 4.2 for helium to about 11.2 for tungsten. The exact value for any substance may be calculated when the latent heat and the boiling point at some particular pressure are known. The integration constant may be eliminated if the vapor pressures at two different temperatures are known. Equation (1) may then be transformed into:

$$\frac{\log P_2 - \log P_1}{1/T_2 - 1/T_1} = \frac{\triangle \log P}{\triangle (1/T)} = \frac{-L}{4.58} = \text{Slope} = S \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Thus it is evident that if the slope of the logarithmic vapor pressure curve be determined, the molecular latent heat of vaporization may be calculated, or vice versa.

Having shown that there is a simple expression for vapor pressures involving only two constants, the question naturally arises, Can these constants be evaluated from existing data? Since the slope of the straight line vapor pressure equation is directly related to the latent heat of vaporization (equation 2), and since the heat of vaporization is closely related to the normal boiling point as shown by the well known rules of Trouton[3], Nernst[5] and Bingham[4], it is probable that the slope, S, is a function of the normal boiling point, a constant which is known for many liquids.

In order to show the nature of this function we shall make use of the data collected in Table I. The data from which this table was constructed have been taken mainly from the Landolt und Boernstein, "Physickalisch Chemisch Tabellen" and the French Tables. For the vapor pressures of the metals, the most recent determinations of Ruff and Bergdahl[1] and of Langmuir[2] have been consulted as well. The vapor pressures of tungsten and platinum have not been directly determined above the melting point. Langmuir has determined the sublimation pressures, however, throughout wide ranges of temperatures. The values here given for the vapor pressures of these two metals have been calculated from the thermodynamic relations existing between the vapor pressure and the heats of vaporization, of sublimation and of fusion, in accordance with the principles discussed in a later section of this paper. The latent heat of fusion of tungsten is not known, but it may be shown that for most metals the molecular latent heat of fusion, expressed in small calories, is about 2.6 times the absolute melting temperature. The values used for making the calculations for these two substances are,

	M. Pt. (Abs.)	Ht. of sublimation	Ht. of fusion	Ht. of vaporization
Tungsten	3540	210,400	9200	201,200
Platinum	2028	123,500	5300	118,200

Under column 3, Table I, are recorded the slopes of the log P vs 1/T curves which have been determined from the experimental curves plotted on large scale coordinate paper. Now it is very evident that there is a gradual change in the slopes of the log P vs. 1/T curves as one passes from the substances having low normal boiling points to those having higher boiling points. This change is observed readily when the experimental slopes are plotted against the normal boiling points for these substances. The points on this plot lie very close to a line which may be represented by the equation:

$$S = -68 + 4.877 T_b + 0005 T \frac{2}{b} \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

In this equation S is the calculated slope and T_b the absolute boiling point of the substance under normal pressure.

Under (4), Table 1, are given the slopes of the log P vs. 1/T curves calculated from equation (3), and in column 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 slope with a high degree of precision. Applied to the high boiling metals, the 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 20° Abs., equation (3) expresses the true slope of

TABLE I.

TAB

(1)	(2)	(3)	(4)	(5)	(6)
Substance	Tb	Sobs.	Scalc	Dif.	Lobs
Helium...................	4.3	5.8	–47	–52.8	.....
Hydrogen	20.2	50	45	–5	248
Nitrogen	77.3	314	315	1	1362
Oxygen	90.1	380	380	0	1630
Methane	108.8	440	463	23	.....
Phosphine	187.5	800	864	64	.....
Hydrogen chloride	190.0	900	870	–30	3860
Hydrogen bromide	205.0	920	950	30	3940
Hydrogen sulphide	211.5	1000	980	–20	4500
Hydrogen iodide	234.0	1150	1100	–50	4332
Chlorine	240.0	1080	1130	50	4650
Ethyl chloride..........	285.6	1310	1365	55	5760
Boron trichloride	291.2	1320	1400	80	5700
Isopentane	301.0	1400	1450	50	5870
Ether	308.0	1450	1480	30	6460
N–pentane	308.8	1470	1490	20	6180
Carbon disulphide........	319.0	1450	1540	90	6380
Silicon tetrachlor.........	329.8	1580	1590	10	6350
Diisopropyl	330.5	1580	1600	20	.....
Bromine	331.6	1610	1615	5	6960
Chloroform	333.2	1620	1620	0	.....
N–hexane	341.6	1660	1660	0	6840
Phosphorous Trichlor....	346.2	1690	1685	–5	7070
Carbon tetrachlor	350.7	1660	1710	50	7130
Benzole	353.3	1720	1720	0	7350
Hexamethylene	353.5	1720	1720	0	.....
Flourbenzole	358.0	1750	1750	0	7600
N–heptane	371.0	1800	1815	15	7590
Diisobutyl	382.2	1890	1870	–20	7990
Toluole	383.4	1880	1875	–5	7940
Stannic chloride	387.2	1890	1890	0	7900
N–octane	398.5	1970	1955	–15	8100
Chlorbenzole	405.0	1980	1980	0	8350
Propylene bromide	414.0	2050	2040	–10	.....
Brombenzole	428.5	2120	2120	0	8800
Trimethylene brom.......	437.4	2190	2160	–30	.....
Benzoic aldehyde	451.3	2320	2235	–85	.....
Iodobenzole	461.0	2250	2280	30	9430
Benzonitrile	463.6	2300	2300	0	9040
Benzoyl chloride.........	470.1	2380	2335	–45	.....
Nitrobenzole	485.0	2440	2420	–20	10050
Naphthalene	491.0	2460	2450	–10	10250
Chlornaphthalene	532.3	2675	2675	0	12100
Acenaphthene	550.5	2780	2770	–10	.....
Bromnaphthalene	554.0	2800	2795	–5	.....
Phthalic anhydride.......	556.5	2825	2800	–25	.....
Fluorene	570.5	2930	2880	–50	.....
Phenanthrene	611.0	3090	3100	10	.....
Anthracene	615.0	3120	3125	5	.....
Carbazol	624.0	3170	4170	0	.....
Mercury	630.0	3070	3200	130	13630
Sulphur	720.0	3700	3700	0	.....
Cadmium	1057	5750	5650	–100	23480
Zinc	1198	6880	6500	–380	25500
Antimony	1600	9000	9020	20	.....
Bismuth	1780	10100	10200	100	.....
Lead	1830	10200	10560	360	.....
Silver	2218	13150	13210	60	.....
Tin	2545	16600	15600	–1000	.....
Copper	2600	17000	16000	–1000	.....
Gold	2885	18600	18200	–400	.....
Platinum	4270	25800	29900	4100	.....
Tungsten	5280	44000	39600	–4400	.....
Water	373.0	2160	1820	340	9650
Ethyl alcohol	351.4	2170	1600	570	9500
Phenol	454.4	2520	2240	280	10680
Acetic acid	392.2	2200	1920	380	5650
Aniline	456.9	2510	2250	260	10500
Acetophenone	474.5	2550	2360	190	10700

LE I.

(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
	Lcalc / Lobs.					Sobs / Tb	
Lcalc		4.23 x Scale	Trouton	Binghan	Nernst		(13) + 2.881
26.5	.....	......	92.5	73.3	25.8	1.350	4.231
228	0.92	190	435	350	250	2.475	5.356
1435	1.062	1333	1660	1380	1345	4.060	6.941
1740	1.068	1610	1940	1620	1630	4.214	7.095
2010	.....	1960	2340	2150	2020	4.046	6.927
3660	.....	3675	4025	3575	3810	4.260	7.141
4110	1.065	3680	4080	3630	3850	4.732	7.613
4200	1.065	4020	4400	3950	4210	4.487	7.368
4570	1.015	4145	4540	4090	4370	4.720	7.601
5260	1.213	4660	5030	4580	4885	4.915	7.796
4940	1.062	4785	5150	4720	5020	4.500	7.381
5990	1.040	5780	6140	5750	6090	4.590	7.471
6035	1.040	5925	6250	5870	6240	4.530	7.411
6400	1.090	6140	6460	6120	6450	4.650	7.531
6630	1.025	6265	6620	6280	6600	4.702	7.583
6720	1.087	6310	6630	6300	6650	4.755	7.636
6630	1.050	6520	6850	6550	6880	4.545	7.426
7225	1.138	6735	7080	6810	7130	4.792	7.673
7225	.....	6775	7100	6820	7145	4.780	7.661
7360	1.057	6840	7115	6840	7180	4.857	7.738
7410	.....	6860	7155	6890	7230	4.860	7.741
7600	1.111	7030	7340	7090	7410	4.860	7.741
7730	1.092	7140	7445	7210	7520	4.877	7.758
7600	1.067	7240	7540	7320	7640	4.727	7.608
7860	1.070	7285	7590	7390	7670	4.865	7.746
7860	.....	7285	7600	7395	7680	4.860	7.741
8000	1.052	7410	7690	7500	7800	4.888	7.769
8230	1.085	7685	7970	7830	8090	4.850	7.731
8650	1.082	7915	8200	8150	8380	4.944	7.825
8600	1.082	7940	8230	8170	8400	4.900	7.781
8650	1.094	8000	8315	8240	8490	4.880	7.761
9010	1.111	8280	8560	8510	8740	4.940	7.821
9055	1.084	8380	8700	8690	8890	4.890	7.771
9380	.....	8640	8895	8920	9090	4.954	7.835
9700	1.102	8980	9205	9310	9450	4.950	7.831
10020	.....	9150	9400	9550	9650	5.004	7.885
10610	.....	9470	9700	9910	9960	5.140	8.021
10300	1.092	9655	9910	10200	10190	4.874	7.755
10520	1.164	9750	9960	10220	10280	4.910	7.791
10890	.....	9895	10110	10420	10600	5.059	7.940
11160	1.111	10240	10440	10820	10740	5.027	7.908
11250	1.097	10380	10580	11000	10880	5.000	7.881
12220	1.011	11320	11450	12190	11870	5.020	7.901
12710	.....	11720	11850	12700	12200	5.045	7.926
12810	.....	11820	11900	12800	12300	5.059	7.940
12920	.....	11860	11980	12880	12380	5.074	7.955
13400	.....	12200	12290	13300	12630	5.130	8.011
14130	.....	13120	13140	14500	13550	5.055	7.936
14280	.....	13240	13220	14600	13650	5.070	7.951
14500	.....	13420	13410	14900	13880	5.080	7.961
14050	1.030	13550	13550	15100	14000	4.874	7.755
16920	.....	15670	15500	17950	15900	5.140	8.021
26300	1.118	23920	22720	30200	22550	5.435	8.316
31500	1.235	27500	25780	36200	24900	5.746	8.627
41150	.....	38200	34420	55350	30800	5.622	8.503
46170	.....	43150	38300	65100	32750	5.674	8.555
48300	.....	44650	39400	67950	33300	5.573	8.454
60100	.....	55900	47650	91900	40600	5.930	8.811
75950	.....	66000	54800	114600	36600	6.518	9.399
77700	.....	67700	56000	118800	36900	6.540	9.421
85000	.....	77000	62100	140800	36500	6.448	9.329
118200	.....	126700	91900	273200	19500	6.050	8.931
201200	.....	167800	94600	344000	−8560	8.320	11.201
9880	1.022	......	.....	......	.....	.....	......
9920	1.044	......	.....	......	.....	.....	......
11510	1.078	......	.....	......	.....	.....	......
10050	1.778	......	.....	......	.....	.....	......
11470	1.091	......	.....	......	.....	.....	......
11650	1.090	......	.....	......	.....	.....	......

the log P vs 1/T curves for normal liquids with a degree of precision approaching that often found in the recorded experimental results.

In column 6, Table 1, are given the molecular latent heats of vaporization of some of these liquids. These results have been calorimetrically determined. Column 7 shows the values of the latent heats calculated as shown in equation (2). These values have been obtained by multiplying the observed slope (column 3) by 4.58. Column 8 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.,

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

In columns 9, 10, 11 and 12, Table I, are given, first, the latent heats of vaporization calculated from equation (4), second, from Trouton's[3] equation, $L_v = 21.5 \,.\, T_b$:— ......(5) third, from Bingham's[4] equation, $L_v = (17 + .011\, T_b)\, T_b$, ...(6) and fourth, from Nernst's[5] equation, $L_v = (9.5 \,.\, \log T_b - .007\, T_b)\, T_b$..........(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 as good, if not better, results 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 to negative results. The results obtained by Trouton's rule are also much too low at high temperatures, while those from Bingham's equation are much too high.

Finally, Table I contains the values for the constant, C, in equation (1). In column 13 are given the values of the constant which should be used when the pressure is to be calculated in atmospheres. This constant is found by dividing the observed slope of the log P vs 1/T curves by the absolute boiling point. By adding the value of the logarithm of 760, which is practically 2,881, to the numbers given in column 13 there is obtained the value of the constant to be used in order to represent the vapor pressure in mm. of mercury. These values are given in column 14. This constant increases as the boiling point of the substance in question increases.

In order to show the limitations of this method of calculating vapor pressures and heats of evaporation, 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 will 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 latent heat of evaporation in order to write the vapor pressure equation. It should be noted also 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,

$$\text{Log } P = C - S/T \qquad \text{(8)}$$

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. Now it may be shown that there is an exactly similar expression for sublimation pressure, viz.,

$$\text{Log } P_S = C_S - S_S/T \qquad \text{(9)}$$

in which P_s is the sublimation pressure at the temperature T, and C_s and S_s are constants having the same significance as in equation (8).

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

$$S_s = L_s / 4.58 \quad \text{(10)}$$

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

$$L_s = L_f + L_v \quad \text{(11)}$$

Equation (4) furnishes a method for calculating L_v, 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 heat of fusion recorded in the literature, and almost no data are available for substances melting below 0°. Several empirical rules for calculating the latent heat of fusion have been proposed. Probably the simplest and most generally useful is that proposed by Walden[6], by which the molecular latent heat of fusion is equal to the absolute melting point times a constant, or,

$$L_f = T_m K \quad \text{(12)}$$

Walden 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 substances 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.

Substance.	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	0.1
Nitro Halides	6	13.5	0.5
Amino Compounds	7	11.0	1.4
Aromatic Hydroxy Substances	5	6.9	0.3
Aromatic Acids, Anhydrides and Ketones	7	12.1	1.0

There is insufficient data to indicate what would be the value of this constant for mixed derivitives, 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 investigated.

Assuming, then, that L_s, the latent heat of sublimation, is known or may be calculated from equations (11) and (12) there still remains the constant C_s to be determined. This is accomplished readily when it is remembered that, at the melting point, the vapor pressure is equal to the sublimation pressure. Hence,

$$C_S - S_S/T_m = C - S/T_m \qquad \text{(13)}$$

from which C_s may be calculated.

It should be remembered that there is an independent method of calculating the latent heat of fusion of solids from their solubilities and freezing point lowering. In order for this method to yield accurate results, however, 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 Author[7] has described a method for determining this factor, and hence for finding the latent heat of fusion, for several classes of organic substances. It is probable that the principles there discussed would apply to other classes of compounds as well, but at present there is too little data to enable one to make a comparison.

In conclusion, it may be said that, from the principles outlined above, it should be possible to determine the vapor pressures, the sublimation pressures and the heats of vaporization, of sublimation and of fusion for normal substances when only the freezing point and normal boiling points are known.

SUMMARY

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

An empirical method for calculating the latent heat of vaporization of normal liquids has been given which gives very good results for liquids boiling from about 20° Abs. up to those boiling at the highest temperature so far investigated.

BIBLIOGRAPHY.

(1) Ruff and Bergdahl, Z. anorg. u. Allg. Chem. 106, 89 (1919).
(2) Langmuir, Phys. Rev., 340, (1913) and 384, (1914).
(3) Trouton, See Nernst's Theoretical Chemistry.
(4) Bingham, See Nernst's Theoretical Chemistry.
(5) Nernst, See Nernst's Theoretical Chemistry.
(6) Walden, Zeit. fur Electrochemie, 14, 713, (1908).
(7) Author. This issue.

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