713. *Correlation of Critical Temperature, Vapour Pressure, and Latent Heat of Vaporisation.*

By Leo H. Thomas.

It is shown that the ratio of the latent heats of vaporisation of any two liquids at the same reduced temperature is a constant, and an empirical equation is presented for latent heat as a function of temperature.

This leads to an accurate vapour pressure–temperature equation and to a method of plotting vapour pressures.

Methods are also given whereby the latent heat of a given substance at any temperature up to the critical may be reliably estimated from vapour-pressure data extending only to the boiling point.

A comparison of reduced latent heats of vaporisation at corresponding temperatures cannot, of course, be made owing to the fact that the value of the latent heat approaches zero with increasing proximity to the critical state. However, it has been found that, in general, the ratio of the latent heats for any two substances is sensibly constant at the same reduced temperature.

In compiling Table I, latent heats have been evaluated by graphical interpolation for a variety of substances at various reduced temperatures, and the results tabulated as the ratio of the g.-molar latent heat of these substances divided by the corresponding values for benzene.

All critical temperatures and latent-heat data have been taken from the International Critical Tables, the data for benzene being selected for comparison purposes as being probably the most reliable. The data of those substances marked * are those based on direct calorimetric determinations, whereas all other latent-heat values are those compiled by Young (*Proc. Roy. Dublin Soc.*, 1910, **12**, 374) by application of the Clapeyron equation to his measurements of vapour pressure and specific volumes of liquid and saturated vapour.

It can at once be seen that the ratios of the latent heats are constant over wide temperature ranges. In general, the ratios are printed to two or three significant figures only so that the constancy is apparent within the limits of experimental accuracy.

Table I.

Ratios of g.-molar latent heat to that of benzene at corresponding reduced temperatures.

	Reduced temperatures.										Estimated accuracy of data, % (I.C.T.).
Compound.	0·50.	0·55.	0·60.	0·65.	0·70.	0·75.	0·80.	0·85.	0·90.	0·95.	
CCl_4	0·965	0·965	0·973	0·973	0·967	0·963	0·965	0·970	0·978	0·982	±0·3
*Et_2O	—	—	0·88	0·88	0·89	0·86	0·85	0·85	0·83	0·80	±2·0
Et_2O	—	—	0·88	0·88	0·89	0·86	0·86	0·87	0·86	0·85	—
*CO_2 (1)	—	—	—	—	0·56	0·57	0·56	0·56	0·55	—	±2·0
*CO_2 (2)	—	—	—	—	0·52	0·53	0·53	0·54	0·53	0·52	—
*CS_2	0·822	0·823	0·833	0·833	0·824	0·817	—	—	—	—	±0·3
C_5H_{12}	—	—	—	0·86	0·85	0·85	0·85	0·86	0·85	0·82	—
*NH_3	—	0·72	0·73	0·73	0·73	0·73	0·73	—	—	—	±2·0
$SnCl_4$	—	—	1·12	1·12	1·10	1·11	1·09	1·10	1·08	—	—
$CH_3{\cdot}CO_2Me$	—	—	—	1·02	1·01	1·00	0·99	1·00	0·98	0·95	—
$CH_3{\cdot}CO_2Et$	—	—	—	—	1·08	1·07	1·06	1·06	1·05	1·03	—
*N_2O	—	—	—	—	—	—	0·51	0·53	0·55	0·50	—
*$CHCl_3$	0·94	0·94	0·95	0·96	0·97	—	—	—	—	—	±1·0
*MeOH	—	1·13	1·06	1·07	1·08	1·07	1·06	1·07	1·07	1·12	±2·0
*EtOH	—	1·26	1·31	1·34	1·36	1·35	1·34	1·32	1·29	1·22	±4·0
*H_2O	1·24	1·24	1·26	1·26	1·27	—	—	—	—	—	—

Variation of Latent Heat with Temperature.—It follows from the above observation that a very simple relation should exist between latent heat and reduced temperature, and the form of the equation must be such that the latent heat vanishes at the critical temperature (T_c). Such an equation is

$$L = a(T_c - T)^b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a is a constant for a particular substance and b a constant which should have approximately the same numerical value for all non-associated substances.

The equation has been solved for all the substances tabulated above by application of Campbell's "zero-sum" method (*Phil. Mag.*, 1920, **39**, 177; 1924, **47**, 816) to its linear logarithmic form

$$\log L = \log a + b \log (T_c - T)$$

Table II shows the values of a and b so obtained. The maximum positive and negative %-deviations between the experimental values of latent heat and those calculated from (1) are tabulated, as well as the average deviations (%) over the whole temperature range for each substance. For all the substances, the errors are obviously within the limits of experimental accuracy.

It is seen that the values of b are approximately constant for all the substances except water, and the mean value is 0·400. Equation (1) therefore becomes

$$L = a'(T_c - T)^{0 \cdot 4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Table II also shows the average deviations % between observed values of latent heat and those calculated from (2). Here again, although agreement is naturally not so satisfactory as when using the two-constant equation, the errors are still, probably, within the limits of experimental accuracy with the possible exception of benzene and carbon tetrachloride. It is instructive in this connection to compare the different values of b (0·401 and 0·425) obtained for carbon dioxide when using two independent sets of experimental data. Comparison should also be made between the value 0·413 based on direct calorimetric data for ether, and the value 0·394 derived from Young's calculated values (*loc. cit.*).

TABLE II.

Compound.	b.	a, cals. per g.-mol.	Maximum error, %,		Mean error, %, in (1).	Mean error, %, in (2).	Temp. range.
			+.	−.			
*Carbon tetrachloride	0·378	9,480	0·7	0·5	0·2	1·3	0— 260°
*Ethyl ether	0·413	7,730	1·4	1·4	0·7	0·8	0— 160
Ethyl ether	0·394	8,490	1·9	1·6	0·8	0·8	0— 180
*Carbon dioxide (1)	0·401	6,050	2·1	1·4	0·9	0·9	− 50—− 20
*Carbon dioxide (2)	0·425	5,690	0·9	0·7	0·5	0·6	− 60— 0
*Carbon disulphide	0·395	7,480	0·9	0·7	0·5	0·5	0— 140
Pentane	0·395	8,260	1·4	0·2	0·3	0·3	40— 180
*Ammonia	0·377	8,130	0·2	0·2	0·1	0·4	− 20—− 50
Tin tetrachloride	0·412	8,970	0·5	0·5	0·2	0·6	100— 280
Methyl acetate	0·410	8,790	0·5	0·7	0·3	0·8	60— 220
Ethyl acetate	0·408	9,310	0·9	0·7	0·5	0·6	80— 220
*Benzene	0·377	9,840	1·2	0·5	0·2	1·4	0— 260
*Methyl alcohol	0·391	11,170	2·3	1·2	0·9	1·0	20— 220
*Ethyl alcohol	0·418	11,120	3·0	1·9	1·3	1·4	40— 200
*Water	0·329	15,280	0·5	0·5	0·0	1·3	0— 180
Means (excluding water)	0·400	—	1·3	0·9	0·5	0·8	—

It might be thought surprising that (2) applies equally well to methyl and to ethyl alcohol and to ammonia as to the "non-associated" substances. However, the author has previously (*J.*, 1948, 1345) supplied viscometric evidence to show that these two alcohols and also amines show degrees of association which probably do not change from room temperature to the critical.

Variation of Vapour Pressure with Temperature.—From the Clapeyron equation we get

$$\frac{1}{p} \cdot \frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{pT(V_v - V_l)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where L is the g.-molar latent heat of vaporisation, and V_l and V_v the g.-molar volumes of liquid and saturated vapour, respectively.

Assuming the perfect-gas laws to hold for the saturated vapour, and neglecting V_l, which is negligible for temperatures up to the b. p., in comparison with V_v, we get the well-known relationship $L = \boldsymbol{R}\, T^2 \mathrm{d} \log_e p/\mathrm{d}T$. Further assumptions that L remains constant over a given temperature range, or is a linear function of temperature, lead to well-known vapour-pressure equations.

The gas laws do not, however, apply to saturated vapours except at temperatures well below the b. p. In fact such vapours at temperatures near the b. p. are more compressible by 4—6% than a perfect gas (*e.g.*, Young and Thomas *J.*, 1893, **63**, 1191).

According to Nernst (" Theoretical Chemistry," Macmillan and Co. Ltd., 1923, p. 317) the following expression holds for fluorobenzene for pressures up to ~15 atm., *viz.*, $p(V_v - V_l) = \mathbf{R}T(1 - p/p_c)$, where p_c is the critical pressure. From the theorem of corresponding states, he assumed the expression to be generally applicable. Further examination has shown, however, that the most *generally* applicable expression, which may be employed for temperatures up to but not much above the b. p., is

$$p(V_v - V_l) = \mathbf{R}T(1 - \alpha p/p_c) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where α is a constant $\neq$ unity. Combining (3) and (4) we get

$$\mathbf{R}\,\mathrm{d}\log_e p/\mathrm{d}(1/T) = -L/(1 - \alpha p/p_c) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The most serviceable value of α has been obtained by the following methods : (*a*) numerical differentation of vapour-pressure data given at fixed temperature intervals led to a value of d $\log_e p/\mathrm{d}T$ and hence to a value at the b. p. of the differential expression in (5) ; α was then calculated by using published values of L_B, the value of the latent heat at the b. p., (*b*) by direct evaluation from (4) using data for V_v and V_l.

Selection of the more reliable data for latent heats, vapour pressures, and molar volumes has been made from the International Critical Tables, and the most probable value of α (1·8) arrived at after examination of ten substances by method (*a*) and ten by method (*b*). Within the limits of accuracy of the method, α does not seem to be dependent on the chemical nature of the substances or on the b. p.

A general serviceable vapour-pressure equation can now be obtained by combining equations (2), (3), and (4), *viz.*

$$(1/p)\ \mathrm{d}p/\mathrm{d}T = a(T_c - T)^{0{\cdot}4}/\mathbf{R}T^2(1 - 1{\cdot}8p/p_c)$$

or

$$(1/p - 1{\cdot}8/p_c)\mathrm{d}p = a(T_c - T)^{0{\cdot}4}\mathrm{d}T/\mathbf{R}T^2$$

Therefore

$$\log_e p - 1{\cdot}8\ p/p_c = I' + \frac{a}{\mathbf{R}T_c^{\,0{\cdot}6}}\int \frac{T_c(1 - T/T_c)^{0{\cdot}4}}{T^2}\,.\,\mathrm{d}T$$

where I' is the constant of integration.

By expansion and integration of this equation we get

$$\log_{10}p - 0{\cdot}782p/p_c = I - aE/4{\cdot}571T_c^{\,0{\cdot}6} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where

$$E = 0{\cdot}921\log_{10}T + \left(\frac{T_c}{T}\right) + 0{\cdot}120\left(\frac{T}{T_c}\right) + 0{\cdot}0320\left(\frac{T}{T_c}\right)^2 + 0{\cdot}0139\left(\frac{T}{T_c}\right)^3 + 0{\cdot}00750\left(\frac{T}{T_c}\right)^4 + 0{\cdot}00460\left(\frac{T}{T_c}\right)^5$$

This equation, although somewhat unwieldy, should be generally applicable to temperatures up to or a little above the b. p. It is sufficient for this purpose to take only the first 4 or 5 terms of the expansion series into account. Inasmuch as the numerical values of the coefficients are known, the equation contains only two characteristic constants. The critical temperature of a given substance may be reliably estimated by the method given in the previous paper. Its critical pressure, a method of estimation for which is also given in this paper, need not be known with any accuracy, for p_c occurs only in the small correction term.

The arithmetical labour involved in the use of the equation may be greatly lessened by evaluating the series sum at selected reduced temperatures and reading off the values for a particular reduced temperature from a large-scale graph.

Table III shows the measure of agreement between Willingham, Taylor, Pignocco, and Rossini's accurately measured vapour pressures (*J. Res. Nat. Bur. Stand.*, 1945, **35**, 219) for benzene, and those calculated from (6). Taking $I = 20{\cdot}0804$ and $a = 4{\cdot}2725$, the average error is less than 0·1%.

TABLE III.

t	80·92°	74·03°	60·78°	49·07°	39·08°	31·00°	23·27°	17·72°
p (mm.), calc.	780·3	628·2	402·4	261·3	175·9	124·5	87·80	67·23
p (mm.), exptl.	779·3	627·9	402·4	261·7	175·9	124·7	87·75	67·22
Error, %	−0·1	−0·0	±0·0	+0·2	±0·0	+0·2	−0·1	−0·0

By changing the variable in (5) from T to T/T_c we get

$$(1/p)\mathrm{d}p/\mathrm{d}(T/T_c) = L/RT_c(T/T_c)^2(1 - 1{\cdot}8p/p_c)$$

Therefore for two liquids at the same reduced temperature, we can write

$$\frac{(1/p_1)\mathrm{d}p_1}{(1/p_2)\mathrm{d}p_2} = \frac{L_1T_{c_2}}{L_2T_{c_1}} \cdot \frac{1 - 1{\cdot}8p_2/p_{c_2}}{1 - 1{\cdot}8p_1/p_{c_1}}$$

and since L_1/L_2 is constant,

$$\int\left(\frac{1}{p_1} - \frac{1{\cdot}8}{p_{c_1}}\right)\mathrm{d}p_1 = \frac{L_1T_{c_2}}{L_2T_{c_1}}\int\left(\frac{1}{p_2} - \frac{1{\cdot}8}{p_{c_2}}\right)\mathrm{d}p_2$$

whence

$$\log_e p_1 - \frac{1{\cdot}8p_1}{p_{c_1}} = K' + \frac{L_1T_{c_2}}{L_2T_{c_1}}\left(\log_e p_2 - \frac{1{\cdot}8p_2}{p_{c_2}}\right)$$

where K' is the constant of integration.

Converting this to common logarithms we have

$$\log_{10}p_1 - \frac{0{\cdot}782p_1}{p_{c_1}} = K + \frac{L_1T_{c_2}}{L_2T_{c_1}}\left(\log_{10}p_2 - \frac{0{\cdot}782p_2}{p_{c_2}}\right) \quad . \quad . \quad . \quad . \quad (7)$$

In (7) it is to be understood that p_1 and p_2 are vapour pressures at corresponding temperatures.

Equation (7) provides an alternative and simpler method of representing vapour pressures; the vapour pressure of the substance under consideration (after application of the small correction for non-perfect vapour behaviour) may be plotted against the vapour pressure of a standard liquid (suitably " corrected ") at the same reduced temperature. The standard liquid selected by the author was chlorobenzene—chosen in view of the fact that its vapour pressure has been reliably measured (Young, *loc. cit*) right down to ~2 mm. of mercury.

Table IV shows values of the constant K and the slope $L_1T_{c_2}/L_2T_{c_1}$ for 15 liquids determined in the same manner as above. Their vapour pressures have been taken at the temperatures tabulated in the International Critical Tables, with the exception of benzene for which Young's values (*loc. cit.*) have been used, the corresponding temperatures for chlorobenzene were calculated, and the vapour pressures of the latter interpolated from a large-scale graph. In no case were the deviations in the individual vapour-pressure values such as to indicate any departure from linearity, and the mean of the average deviations is seen to be 0·6%, which is certainly within the limits of reliability of most of the vapour-pressure determinations.

TABLE IV.

Compound.	K.	$\frac{L_1T_{c_2}}{L_2T_{c_1}}$.	Error, %, in (7).	Temp. range.	$L/10$ (calc.), joules/g.-mol.	Temp.	$L/10$, exptl. values.	Error, %.	$L/10$ (calc.), method (C).	Error %.
C_6H_6	0·169	0·968	0·7	−10—80°	—	—	—	—	—	—
C_6H_5Cl	0·000	1·000	—	—	355	130·6°	365, 348	+0·4	353	+1·0
$H{\cdot}CO_2Me$	0·077	1·014	0·5	0—40	276	31·3	282	+2·1	283	−0·4
$CH_3{\cdot}CO_2Me$	−0·336	1·093	0·8	0—50	305	60	305	±0·0	303	+0·7
$CH_3{\cdot}CO_2Et$	−0·608	1·133	0·9	0—70	321	80	316	−1·6	315	+0·3
$CH_3{\cdot}CO_2Pr$	−0·814	1·172	0·7	20—100	346	100	343, 340	−1·3	338	+1·0
C_7H_{16}	−0·656	1·105	0·5	0—90	319	97·5	319	±0·0	314	+1·6
C_6H_5Me	−0·034	0·997	0·7	30—100	331	109·6	333	+0·6	—	—
CCl_4	0·235	0·948	0·7	20—70	296	80	296, 298	−0·3	295	−0·7
$CHCl_3$	0·247	0·958	0·2	0—60	292	61·5	295	+1·0	298	−1·0
NH_3	0·453	0·978	0·6	−77— −35	225	−20	226	+0·4	228	−0·9
SO_2	0·219	1·004	0·7	−60— −10	249	−10	246	−1·2	250	−1·6
CH_3Cl	0·660	0·867	0·2	−50— −10	210	−23·8	216	+2·8	211	+2·3
PrOH	−0·228	1·055	0·4	10—90	427	97	413, 416	−3·2	419	−1·1
Pr^{i}OH	−0·382	1·074	0·8	20—80	407	82	406, 399, 400	−1·2	402	±0·0
Bu^{i}OH	−0·423	1·066	0·7	60—100	422	108	427, 428	+1·3	431	−0·8
Averages	—	—	0·6	—	—	—	—	1·1	—	1·0

For application of this method to alcohols, ethyl alcohol has been used as standard in place of chlorobenzene. The selected vapour pressure of this alcohol, up to 70°, is that of the International Critical Tables, and above 70° that of Ramsey and Young (*Phil. Trans.*, 1887, **177**, 123). The method would be expected to be accurate for lower alcohols and higher straight-chain homologues in view of the fact that, as for unassociated liquids, the ratio of their latent heats at the same reduced temperature is constant (see Table I). However, with higher branched-chain alcohols it may be expected that, owing to changes in the degrees of association with changing temperature (Thomas, *J.*, 1948, 1349), this ratio will no longer be accurately constant. Nevertheless, this ratio is not likely to change greatly over small temperature ranges so that, as a method of plotting vapour pressures, the above is still of use even for such cases.

The accurate measurement of vapour pressures of the order of 0·1—5 mm. of mercury is difficult, and few, if any, such values are to be found in the literature apart from recent measurements on commercial plasticizers and low-vapour-pressure vacuum oils, etc., and also for water and liquid metals. Such values, however, may be reliably estimated for a given liquid by plotting vapour pressures from ~10 mm. to the b. p. against a *suitably selected* standard, and then extrapolating to the lower vapour pressures required. For example, for propyl acetate with chlorobenzene as standard, we have at low vapour pressures

$$\log_{10} p = 1{\cdot}172 \log_{10} p_{\text{standard}} - 0{\cdot}814$$

At 20°, the vapour pressure of chlorobenzene is 8·83 mm., so that at the same reduced temperature (— 18°) the vapour pressure of the ester would be 0·170 mm. Similarly, the vapour pressure of propyl acetate at —36° would be 0·073 mm. to correspond with a vapour pressure of 2·56 mm. for the standard at 0°.

Estimation of Latent Heat.—The following methods can be adopted :

(*A*) By application of (6) to the published vapour-pressure values. From the value of a so obtained, the magnitude of L may then be calculated from (2). Table V shows the measure of agreement between L so calculated and the experimental values for benzene, the mean error being only 1·2% over the range 0—260°. The agreement for other liquids might well be even better, for, as we have previously seen, benzene is somewhat exceptional in giving a value of b rather different from the mean value 0·400. Thus, in general, the latent heat of a given substance may be reliably estimated at temperatures approaching the critical even though the vapour-pressure data may not extend above the b. p.

TABLE V.

Temp.	0°	40°	80°	120°	160°	200°	240°
$L/10$, cals. per g.-mol.	836	786	735	677	613	534	422
$L/10$, calc.	841	792	738	678	608	523	411
Error, %	−0·6	−0·8	−0·4	−0·1	+0·8	+2·1	+2·6

(*B*) An easier method is to plot the vapour pressure of the given substance against that of a standard in the manner already explained. The slope of the plot then provides a measure of the constant ratio of the latent heat of that substance to that of the standard at the same reduced temperature, from which the ratio of the latent heat of the substance to that of *benzene* at the same reduced temperature may be calculated.

Columns 6—9 of Table IV show the experimental value(s) of the latent heat either at the b. p.s or at temperatures near to the b. p.s, the values calculated by method (*B*), and the deviations (%) between the experimental and calculated values. All latent-heat data are those of the International Critical Tables and/or of Young (*loc. cit.*), with the exception of *iso*propyl and *iso*butyl alcohols, additional more recent values for which are due to Matthews (*J. Amer. Chem. Soc.*, 1926, **48**, 562) and Parks and Nelson (*J. Physical Chem.*, 1928, **32**, 61).

(*C*) The easiest method of calculating the latent heat at a given temperature is by calculating $d \log_e p/d(1/T)$ by numerical differentiation of the $\log_e p/T$ values in the neighbourhood of that temperature; *e.g.*, from the I.C.T. vapour-pressure values of carbon tetrachloride, we get $d \log_e p/dT$ at 80° = 0·299. Hence $d \log_e p/d(1/T) = -3720$, and from (5) $L = 7070$ cals., which compares favourably with the experimentally derived values 7075 and 7130 cals.

The latent heat at any other temperature may now be calculated from (2). Thus for carbon tetrachloride, $a' = 7070/(556 - 353)^{0{\cdot}4}$ cals., so the latent heat at, say, 200° is 4940 cals. The mean experimental value at this temperature is 5030 cals.

Of the above three methods, the last is to be preferred for alcohols, for it is free from the objection that (5) cannot in general hold with sufficient accuracy for associated substances except over small temperature ranges.

GLAMORGAN TECHNICAL COLLEGE, TREFOREST.

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