247. *Correlation of Vapour Pressure, Temperature, and Molar Entropy of Vaporisation.*

By Leo H. Thomas.

It is shown that the ratio of the values of the differential $\boldsymbol{R}T\ \mathrm{d}\log_e p/\mathrm{d}T$ (where T is the absolute temperature) for any two non-associated liquids at the same vapour pressure p is a constant, and a generalised vapour pressure–temperature relation is presented. A reliable and accurate method is then given for comparison of vapour pressures, and procedures are developed for interpolation and extrapolation of vapour-pressure data.

In continuation of work on comparison of latent heats of vaporisation at corresponding states (Thomas, *J.*, 1949, 3415), it has been found that the ratio of the values of the function $E/T = \boldsymbol{R}T\ \mathrm{d}\log_e p/\mathrm{d}T$ for any two non-associated liquids at temperatures corresponding to the same saturated vapour pressure p is a constant. At temperatures somewhat below the normal b. p., when the vapour behaves approximately as a perfect gas, E/T becomes, of course, L/T, the molar entropy of vaporisation.

Values of E/T have been calculated by numerical differentiation of recorded vapour-pressure data over as wide a range as possible, and then plotted as log E/T against log p. A series of sixteen selected vapour pressures log p_1, log p_2, . . . log p_n then being taken, the corresponding values of $\log(E/T)_1$, etc., were read off for a number of substances. Ideally, then, $\log(E/T)_n - \log(E/T)_{n-1}$ should be constant. These increments were averaged over the whole of the range to represent the behaviour of an ideal reference substance, and the latter assigned a convenient value E/T at 0·1 atm. of 100 cal. per mole per degree, *i.e.*, a Trouton constant of 100 at this pressure. Values of E/T at other vapour pressures then read as in Table 1.

Table 1.

V. p., atm.	E/T	V. p., atm.	E/T	V. p., atm.	E/T	V. p., atm.	E/T
0·001	141·1	0·020	115·4	1	77·8	20	52·6
0·002	135·7	0·050	106·8	2	71·3	30	50·0
0·005	127·9	0·25	91·3	5	62·6	40	48·1
0·010	121·8	0·50	84·6	10	57·1	50	47·2

The behaviour of a number of substances is compared with that of the ideal reference substance in Table 2. The figures represent $(E/T)_{\text{ideal}}$ divided by the corresponding values for the substances tabulated, and are constant within the limits of accuracy obtainable by the method.

The above definition of E leads to the expression $(T/E)\,\mathrm{d}\log_{10}p = \mathrm{d}T/2{\cdot}303\boldsymbol{R}T$, and integration gives

$$\log_{10} T_2/T_1 = \boldsymbol{R}\int_{\log_{10}p_1}^{\log_{10}p_2} (T/E)\,\mathrm{d}\log_{10}p$$

or, in terms of our ideal reference substance (suffix s) :

$$\log_{10} T_2/T_1 = \boldsymbol{R}K\int_{\log_{10}p_1}^{\log_{10}p_2} (T/E)_s\,\mathrm{d}\log_{10}p \qquad . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\log_{10} T = \log_{10}\theta + \boldsymbol{R}K\int_{0}^{\log_{10}p} (T/E)_s\,\mathrm{d}\log_{10}p \qquad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where θ is the absolute temperature corresponding to a vapour pressure of unity (1 mm. Hg), and K is a constant for a given substance as recorded in Table 2.

$(T/E)_s$ cannot apparently be expressed by a simple mathematical expression (compare Thodos, *Ind. Eng. Chem.*, 1950, **42**, 1514); instead, values of the standard integral have been evaluated graphically.

TABLE 2.

	Substance	Refs.*	p_c	Vapour pressure, in atmospheres							
				0·001	0·002	0·005	0·010	0·020	0·050	0·10	0·25
(I)	Et_2O	1, 2, 3	36	3·56	3·57	3·57	3·57	3·57	3·58	3·57	3·57
(II)	CCl_4	1	45	—	—	—	—	3·67	3·67	3·66	3·67
(III)	$CH_3{\cdot}CO_2Et$	1	38	—	—	—	—	—	3·44	3·41	3·41
(IV)	C_6H_5Cl	1, 2	45	3·61	3·60	3·59	3·59	3·57	3·57	3·57	3·57
(V)	C_2H_6	4	49	—	—	—	—	—	3·91	3·96	3·95
(VI)	HCl	4	82	—	—	—	—	—	—	—	—
(VII)	n-C_5H_{12}	1	33	—	—	—	—	3·71	3·70	3·71	3·73
(VIII)	CO	5	35	—	—	—	—	—	—	—	4·22
(IX)	n-C_6H_{14}	1, 2, 6	30	3·57	3·59	3·59	3·59	3·59	3·62	3·63	3·66
(X)	C_6H_6	1	48	—	—	—	—	—	—	3·61	3·59
(XI)	CCl_2F_2	7	40	—	—	—	—	—	—	—	3·81
(XII)	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Me$	1	34	—	—	—	—	—	3·41	3·39	3·39

	Substance	Vapour pressure, in atmospheres								Mean deviation, %
		0·50	1	2	5	10	20	30	40	
(I)	Et_2O	3·59	3·59	3·61	3·59	3·59	3·58	3·57	—	0·3
(II)	CCl_4	3·66	3·67	3·69	3·71	3·71	3·69	3·67	3·64	0·5
(III)	$CH_3{\cdot}CO_2Et$	3·41	3·39	3·39	3·38	3·37	3·35	3·35	—	0·6
(IV)	C_6H_5Cl	3·57	3·58	3·59	3·57	3·51	—	—	—	0·4
(V)	C_2H_6	3·93	3·92	3·91	3·91	3·89	3·90	3·91	—	0·4
(VI)	HCl	—	3·65	3·63	3·59	3·59	3·59	3·63	—	0·6
(VII)	n-C_5H_{12}	3·73	3·72	3·73	3·70	3·69	3·67	3·67	—	0·5
(VIII)	CO	4·21	4·18	4·19	4·20	4·22	4·23	4·22	—	0·3
(IX)	n-C_6H_{14}	3·67	3·65	3·66	3·62	3·63	3·59	—	—	0·7
(X)	C_6H_6	3·57	3·58	3·59	3·61	3·61	3·61	3·59	3·58	0·3
(XI)	CCl_2F_2	3·79	3·79	3·79	3·77	3·77	3·80	3·82	—	0·3
(XII)	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Me$	3·39	3·41	3·41	3·43	3·42	—	—	—	0·3

* (1) Young, *Sci. Proc. Roy. Soc. Dublin*, 1909–10, **12**, 374. (2) Mündel, *Z. phys. Chem.*, 1913, **85**, 435. (3) Taylor and Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 2450. (4) International Critical Tables. (5) Crommelin, Byleveld, and Brown, *Proc. K. Akad. Wetensch.*, 1931, **34**, 1314. (6) Drücker, Jimeno, and Kangro, *Z. phys. Chem.*, 1915, **90**, 513. (7) Gilkey, Gerard, and Bixler, *Ind. Eng. Chem.*, 1931, **23**, 364.

TABLE 3. *Evaluation of the standard integral.*

$\log_{10} p_{(\mathrm{mm.})}$; range, 0 to	−0·4	−0·2	+0·2	+0·4	+0·6	+0·8	1·0
Corr. value for integral from zero	0·002804	0·001420	0·001458	0·002956	0·004500	0·006092	0·007738
$\log_{10} p_{(\mathrm{mm.})}$; range, 0 to	1·2	1·4	1·6	1·8	2·0	2·2	2·4
Corr. value for integral from zero	0·009442	0·011216	0·013062	0·014986	0·016992	0·019088	0·021288
$\log_{10} p_{(\mathrm{mm.})}$; range, 0 to	2·6	2·8	3·0	3·2	3·4	3·6	3·8
Corr. value for integral from zero	0·023608	0·26058	0·028650	0·031394	0·034306	0·037402	0·040712
$\log_{10} p_{(\mathrm{mm.})}$; range, 0 to	4·0	4·2	4·4	4·6			
Corr. value for integral from zero	0·044228	0·047954	0·051896	0·056060			

Solution of (2) by application of Campbell's "zero-sum" method (*Phil. Mag.*, 1920, **39**, 177; 1924, **47**, 816) then gave for ether

$$\log_{10}(T/100) = 0{\cdot}29506 + 7{\cdot}1280\int_{0}^{\log_{10}p}(T/E)_{,}\, \mathrm{d}\log_{10}p$$

(0° K = −273·15° C). The measure of agreement between T at the published vapour pressures and those calculated from the equation is shown in Table 4 (t = °C). In view of the fact that the measurements over the three ranges 0·444—0·949, 3·95—437·7 mm., and 921 mm. to the critical point are those of three independent experimenters (see refs. in Table 2), the agreement is remarkable, and must surely be within the limits of absolute experimental accuracy. An examination of the mean % deviations printed in Table 2 suggests that a comparable degree of accuracy is to be generally expected from critical conditions to at least as low a vapour pressure as, say, 0·5 mm. of mercury.

TABLE 4.

V. p., mm.	*t*, calc.	*t*, exptl.	Error	V. p., mm.	*t*, calc.	*t*, exptl.	Error
0·443	−83·8°	−83·5°	−0·3°	921	40·11°	40·00°	+0·11°
0·949	−76·4	−76·2	−0·2	1,734	60·12	60·00	+0·12
3·95	−60·85	−60·80	−0·05	4,855	99·80	100·00	−0·20
12·62	−46·01	−46·00	−0·01	7,513	120·03	120·00	+0·03
34·03	−31·25	−31·33	+0·08	15,778	139·98	160·00	−0·02
104·8	−11·52	−11·64	+0·12	21,775	179·85	180·00	−0·15
437·7	19·84	19·87	−0·03	27,060 *	194·2	193·8 *	+0·4

* Critical values.

From (2) we get for two substances at the same vapour pressure :

$$\log_{10} T_1/\theta_1 = (K_1/K_2)\log_{10} T_2/\theta_2$$

or,

$$\log_{10} T = I + (K_1/K_2)\log_{10} T_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where I is a constant—a modification of the well-known Ramsay–Young relationship.

Equation (3) is far easier to use than that previously proposed by the author (*loc. cit.*), and it does not suffer from the limitation that it can be used only in regions where the ideal-gas laws can be considered as valid. A knowledge or reliable estimation of critical data is also not now required. The previously proposed equation is still, however, useful as a method of extrapolating to low vapour pressures (*loc. cit.*, p. 3419).

Table 5 records the behaviour of a number of substances compared with that of benzene. Most probable vapour-pressure values for the latter have been determined graphically (direct p–T plot) from Timmermans's data ("Physico-chemical Constants of Pure Organic Compounds," Elsevier Pub. Co. Ltd., 1950, 142), supplemented above 100° by those of von Huhn (*Forsch. Gebiete Ingenieurw.*, 1931, *A*, 2, 109), Gornowski, Amick, and Hixson (*Ind. Eng. Chem.*, 1947, **39**, 1348), and Bender, Furukawa, and Hyndman (*ibid.*, 1952, **44**, 387).

The most recent and probably the most accurate measurements are those of Forziati, Norris, and Rossini (*J. Res. Nat. Bur. Stand.*, 1949, **43**, 555) in the range 48—780 mm. They differ from the author's most probable values by $\not>$0·2° at any of the twenty literature values (mean difference = 0·1°) and are related to the latter by the equation

$$\log_{10}(T/100) = 1{\cdot}0030 \log_{10}(T/100)_{\text{selected}} - 0{\cdot}0015 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The constants of Table 5, evaluated in the manner already described, were calculated by expressing each temperature to the nearest 0·1°—a procedure which, apart from experimental error, would result in a mean difference between actual and calculated temperatures of 0·01—0·05% depending on the b. p. of the substance. The vapour pressures used in this table ranged in general from about 36 mm. (v. p. of benzene at its f. p.) to ~760 mm. Four-figure logarithms were used in the calculations so the average agreement between actual and calculated temperatures cannot, except by chance, be better than corresponds to an error of 0·02—0·03%.

The average error in using measurements carried out by the National Bureau of

Standards and by similar methods (refs. 5—9) is 0·02%. The errors for other measurements, however, average 0·04%, corresponding to an error of ~0·1° for a substance of b. p. −100° and to 0·2° for one of b. p. 300°. In no case have the errors in the individual determinations been such as to imply departure from linearity in the log T–log T_{benzene} plot.

A more stringent test is possible for measurements by the National Bureau of Standards since b. p.s are taken at a series of set and almost constant pressures. It is then possible to apply (3) without involving interpolation uncertainties. Thus to the nearest 0·01°, the behaviour of nonane may be expressed in terms of that of benzene (both sets of vapour pressure being due to Willingham *et al.*, *loc. cit.*) by the equation

TABLE 5.

$\log_{10}(T/100) = A + B \log_{10}(T/100)_{\text{benzene}}$

Substance	B	A	Mean error, %	B. p., ° K	Ref.*
H_2	1·800	−1·6761	0·03°	20	1
O_2	1·159	−0·6804	0·03	90	2
CH_4	1·182	−0·6005	0·05	111	3
C_2H_6	1·097	−0·3355	0·01	184	3
C_3H_8	1·065	−0·2199	0·04	231	3
Cl_2	1·030	−0·1873	0·03	238	4
C_4H_{10}	1·052	0·1410	0·01	273	3
cis-CHMe:CHMe	1·032	0·1235	0·01	277	5
C_5H_{12}	1·029	0·0741	0·05	309	3
CS_2	1·054	0·0739	0·03	319	4
$COMe_2$	0·9761	0·0173	0·03	329	4
$CHCl_3$	0·9954	0·0221	0·04	334	4
C_6H_{14}	1·015	0·0222	0·03	342	3
C_7H_{16}	0·9943	0·0251	0·04	353	3
$CH_2Pr^nPr^i$	1·008	0·0075	0·03	363	6
$[CH_2]_4{>}CHEt$	1·015	0·0193	0·02	376	6
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}NO_2$	0·9703	0·0753	0·03	404	7
Bu^nCN	0·9754	0·0827	0·02	414	8
n-$(C_5H_{11})_2O$	0·9404	0·1472	0·03	460	8
$C_{20}H_{42}$	0·9322	0·1788	0·02	489	9
$COPh_2$	0·9154	0·2610	0·02	579	8
SnI_4	1·032	0·2284	0·06	621	10
Hg	1·006	0·2489	0·02	630	11
Zn	0·9548	0·5537	0·02	1180	12
KOH	1·092	0·6060	0·08	1600	12
Bi	0·5690	0·9177	0·09	1693	12

* (1) Henning, *Z. Physik*, 1926, **40**, 775. (2) Jaquerod, Travers, and Senter, *Proc. Roy. Soc.*, 1902, **70**, 484. (3) From Thodos's compilation, *loc. cit.* (4) International Critical Tables. (5) Scott, Ferguson, and Brickwedde, *J. Res. Nat. Bur. Stand.*, 1944, **33**, 1. (6) Forziati, Norris, and Rossini, *loc. cit.* (7) Holcomb and Dorsey, *Ind. Eng. Chem.*, 1949, **41**, 2788. (8) Dreisbach and Shrader, *ibid.*, p. 2879. (9) Willingham, Taylor, Pignocco, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **35**, 219. (10) Kabesh and Nyholm, *J.*, 1951, 3245. (11) Ramsay and Young, *J.*, 1886, **49**, 37. (12) From " Chemical Engineers' Handbook " (Perry, 2nd edn., McGraw-Hill Co., 1941).

TABLE 6.

T_{nonane}, exptl. (to nearest 0·01°)	T_{benzene}, exptl.	Error	Δ $\log_{10} T$, benzene	Δ $\log_{10} T$, nonane	B
424·84°	354·02°	±0·00°	0·00854	0·00827	0·969
416·83	347·13	±0·00	0·01690	0·01635	0·968
401·43	333·88	±0·00	0·01551	0·01505	0·970
387·78	322·17	−0·01	0·01368	0·01320	0·965
376·15	312·18	±0·00	0·01138	0·01101	0·967
366·73	304·10	+0·01	0·01119	0·01082	0·967
357·71	296·37	+0·01	0·01297	0·01258	0·970
347·50	287·65	−0·01			

$$\log_{10}(T/100)_{\text{nonane}} = 0{\cdot}09687 + 0{\cdot}96781 \log_{10}(T/100)_{\text{benzene}}$$

The error in no single temperature exceeds 0·01°, so the actual mean error is less than this—in fact, the authors claim a reproducibility at a given vapour pressure of ±0·002°. It should also be observed that the value of the constant $B = K_1/K_2$ can be accurately ascertained by the slope between any two successive temperatures differing by not more than a few degrees (Table 6).

Remaining critical data are those tabulated by Timmermans (*op. cit.*).

Interpolation of Vapour Pressures.—It is obvious from the constancy of B in Table 6 that interpolation errors in the case of nonane, and indeed for substances in general, will be no greater than the experimental error.

Extrapolation of Vapour Pressures.—Method 1. Use of the constants of Table 5 and the critical temperatures recorded in the literature leads to calculated critical pressures for some paraffins as shown in Col. 4 of Table 7. They are seen to be too low by a mean of 2·2%. Modified values calculated by use of equation (4) and the accurate measurements of the National Bureau of Standards lie nearer to the experimental. A further slight adjustment of the vapour pressure of benzene, either below the b. p. or in the region above, say, 25 atm., could completely account for the discrepancy.

TABLE 7.

Substance	T_c, °K	Corr. temp., benzene	p_c, calc., atm.	Lit. values	Error, % (method 1)	Error, % (modified)	Error, % (method 2)	V. p. used *
Ethane ...	305·3	286·2°	46·7	48·6, 48·8, 48·2	−3·7	−2·3	−3·0	1138·0 57·68
Propane ...	369·9	276·5	41·6	42·0	−1·0	±0·0	−1·7	760·0 37·39
Butane ...	426·3	266·9	36·8	35·7	−0·3	+1·1	+1·4	760·0 36·26
,, ...	425·2 †	265·6	36·2	37·5 †				
Pentane ...	470·3	257·9	32·7	33·1	−1·2	±0·0	+0·6	760·0 44·64
Hexane ...	507·9	248·6	28·8	29·9, 29·6, 30·1	−3·3	−2·3	−1·6	760·0 41·35
Heptane ...	540·0	241·4	26·1	27·0, 26·9	−3·0	−2·2	−0·6	760·0 36·15

* Refs. as in Table 5.

† Beattie, Simard, and Su, *J. Amer. Chem. Soc.*, 1939, **61**, 924.

Method 2. Col. 8 shows values calculated from equation (2) by using only two vapour pressures, ~760 and ~40 mm. The average error is now 1·6% but the distribution is more normal.

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