65. *Considerations of a Vapour Pressure–Temperature Equation, and their Relation to Burnop's Boiling-point Function.*

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The constants A and B in the vapour-pressure equation $\log p = A - B/T$ have been examined. The approximate constancy of A is discussed. Heats of vaporisation calculated from B are shown to be related to the formula weight M by the approximate empirical equation $\log \Delta H_0 = 4{\cdot}93 - 4/M^{\frac{1}{2}}$. Burnop's empirical function $8M^{\frac{1}{2}} + M \log T_B$ is derived, and shown to be proportional to the formula weight, from which follows its additive nature. By the use of 4, as demanded by theory, rather than 8 as the coefficient of $M^{\frac{1}{2}}$, the apparent constitutive nature disappears.

It is well known that the vapour pressures of most liquids can be represented with considerable accuracy over fairly wide ranges of temperature by Young's empirical equation $\log p = A - B/T$, where A and B are constants for a particular compound. Indeed, much of the vapour-pressure data given in the International Critical Tables is represented in this form. Examination of these data brings out two facts : (1) that A is of the same order of magnitude for most compounds, variations being about 10%, and (2) that B shows a marked and regular trend with formula weight. It is the object of this paper to examine these facts and to show what bearing some of the considerations have on a certain empirical relation involving boiling point.

The thermodynamic basis of Young's relation may be considered as follows. For a substance whose vapour is assumed to behave as a perfect gas and whose molar volume in the liquid state is negligible in comparison with the volume in the gas state, we may write

$$\delta \log_e p = (\Delta H/\boldsymbol{R}T^2)\, \delta T \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

Here $\boldsymbol{R}$ is the gas constant, p the vapour pressure at absolute temperature T, and ΔH the heat of vaporisation. The last is itself a function of temperature and can be expressed in terms of empirical constants a, b, etc., and the difference in heat capacity between the liquid and the vapour, $\Delta_0 C_p$ (the value at $T = 0°$K. calculated empirically) :

$$\Delta H = \Delta H_0 + \Delta_0 C_p T + \tfrac{1}{2}aT^2 + \tfrac{1}{3}bT^3 + \; . \; . \; .$$

Here ΔH_0 is the heat of vaporisation at the absolute zero, although a value so calculated from such an empirical relation obtained at much higher temperatures may not necessarily be identical with the true value, the error being dependent on the range of temperature over which the empirical relation is valid. Equation (1) is now integrated between the limits of p at T and 1 atmosphere (760 mm.) at the boiling point T_B, the necessity of considering a chemical constant being thus eliminated. We obtain

$$\log p = \log 760 + \Delta H_0/2{\cdot}303\boldsymbol{R}T_B - \Delta H_0/2{\cdot}303\boldsymbol{R}T + (\Delta_0 C_p/\boldsymbol{R}) \log T/T_B + \; . \quad (2)$$

The fourth and succeeding terms, which include temperature coefficients of $\Delta_0 C_p$ and powers of $(T - T_B)$, may be shown to affect (2) by not more than 10% for not too great a temperature range. A survey of the literature indicates that for normal liquids $\Delta_0 C_p/\boldsymbol{R}$ lies well within the limits of 1—10 units. However, even if a value of 10 is assumed, for a liquid boiling at 50° a range of 50° below this would give the fourth term as 0·7 unit, and for one boiling at 200° the same range below would give the value of 0·4. The succeeding terms are considerably less.

For this reason it is possible to identify A in the Young equation with log 760 + $\Delta H_0/2{\cdot}303\boldsymbol{R}T_{\mathrm{B}}$ with an accuracy of about 10% for not too large a temperature range. On the assumption that $\Delta H_0/T_{\mathrm{B}}$ is given by 87·8 (the value of Trouton's constant in Joules/degree), its value is 7·46, a value very close to the individual values of A for many substances.

Comparing B with $\Delta H_0/2{\cdot}303\boldsymbol{R}$, values of ΔH_0 (in Joules per mol.) have been calculated from the values of B given in the International Critical Tables (Vol. III), and in one or two cases from vapour-pressure–temperature data. The data are given in Table I, in which is indicated the range of temperature over which Young's simple two-term equation is valid. For compounds which exhibit normal behaviour, as distinct from those represented by alcohols and acids, it has been found that a simple relation exists between the formula weight and the heat of vaporisation.

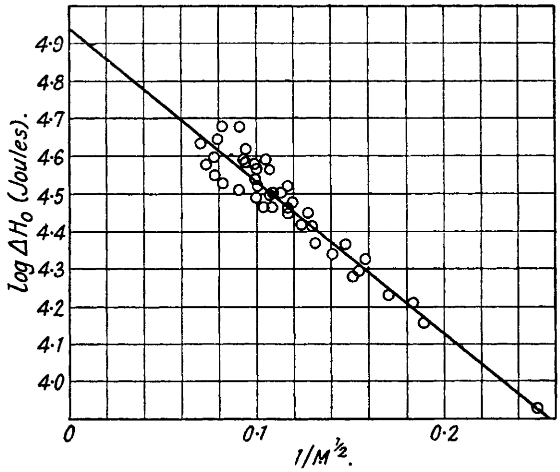

TABLE I.

Substance.	$1/M^{\frac{1}{2}}$.	Temp. range.	ΔH_0.	Substance.	$1/M^{\frac{1}{2}}$.	Temp. range.	ΔH_0.
CH_4............	0·250	−174° to −163°	8517	C_6H_5Me	0·104	− 92° to + 15°	39198
C_2H_4	0·189	−160 „ −104	14396	CH_3Br †	0·103	− 70 „ + 5	28994
C_2H_6 *	0·183	−140 „ − 90	16207	$C_2H_4Cl_2$(*cis*-)	0·102	+ 23 „ + 49	29216
CH_3F	0·170	−102 „ − 76	17053	$C_2H_4Cl_2$(*trans*-) ...	0·102	+ 27 „ + 59	31006
C_3H_4	0·158	− 73 „ − 13	21372	*n*-C_7H_{16}	0·100	− 63 „ − 40	37358
C_3H_6	0·154	− 95 „ − 48	19693	OPr_2	0·099	+ 8 „ + 90	34295
C_3H_8	0·151	−136 „ − 40	19037	$CH_3{\cdot}CO_2Pr$ *	0·099	+ 40 „ + 80	38133
OMe_2	0·147	− 70 „ − 20	23025	C_6H_5Cl	0·094	− 35 „ − 15	42250
CH_3Cl	0·140	− 19 „ + 20	21988	$C_3H_7{\cdot}CO_2Et$	0·093	+ 45 „ +121	39318
C_4H_{10}	0·131	−100 „ + 12	23450	$C_2H_5{\cdot}CO_2Pr$	0·093	+ 45 „ +125	39221
OMeEt	0·129	0 „ + 25	26262	C_3H_7Br	0·090	0 „ + 30	32430
SHEt	0·127	+ 8 „ + 45	28210	$C_6H_5{\cdot}NO_2$	0·090	+112 „ +209	48955
C_2H_5Cl	0·124	− 30 „ + 30	26319	*o*-$C_6H_4(OH)CO_2Me$	0·0811	+175 „ +215	48670
n-C_5H_{12}	0·118	− 20 „ + 50	27691	CCl_4	0·081	− 19 „ + 20	33914
OMePr	0·116	− 0·5 „ + 40	28952	$C_4H_9{\cdot}CO_2C_4H_9$(*iso*)	0·0795	+ 90 „ +170	44482
OEt_2 *	0·116	0 „ + 35	28550	$C_2H_2Cl_4$..............	0·077	+ 26 „ +145	39729
$CH_3{\cdot}CO_2Me$ *	0·116	− 10 „ + 40	33351	C_3H_7I	0·0767	0 „ + 30	35334
C_6H_6	0·113	+ 42 „ +100	32295	$C_2H_4Br_2$	0·0729	+ 10 „ +150	38082
n-C_6H_{14}	0·108	− 10 „ + 90	31679	C_6H_5I	0·070	− 30 „ + 18	43000
OEtPr	0·107	+ 20 „ + 60	31160	CH_2Cl_2	0·108	− 87 „ + 38	29357
$CH_3{\cdot}CO_2Et$ *	0·107	+ 30 „ + 70	37077				

* Calculated from vapour-pressure–temperature data (International Critical Tables, Vol. III).
† Egan and Kemp, *J. Amer. Chem. Soc.*, 1938, **60**, 2097.
Other data from values of A and B (International Critical Tables, Vol. III).

The data are plotted in the figure, from which it is apparent that there is very approximately a linear relation between log ΔH_0 and the reciprocal of the root of the formula weight. A considerable scatter is observed for substances of greater weight, but the agreement is remarkably good for those of lower weight, and is striking in view of the temperature range. The line drawn in the figure is given by

$$\log \Delta H_0 = 4{\cdot}93 - 4/M^{\frac{1}{2}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

and values of log ΔH_0 calculated from this equation rarely deviate by more than 10% from (and are usually less than 5% from) the observed value. It is doubtful whether any theoretical significance can be attached to this relation, since the heat of vaporisation would not be expected to be simply a function of mass. Furthermore, such a relation implies that isomeric substances have identical heats of vaporisation, which is of course not the case. On these considerations alone, the suggested relation is not claimed as other than an approximate rule. It can, however, be shown to lead to a number of generalisations which have been suggested.

Recently, Burnop (J., 1938, 826) has shown that the empirical relation

$$b = 8M^{\frac{1}{2}} + M \log T_{\mathrm{B}}$$

is an additive function where M and T_{B} are the formula weight and the boiling point respectively. By examining a large number of compounds of different classes, he obtained values of b from which he derived atomic and structural values. This relation can be shown to follow from the empirical rule proposed above for the heats of vaporisation, and it appears that Burnop's use of the boiling point is significant only in that it affords a comparison of this function at temperatures corresponding to equal vapour pressures. The relation is perfectly general and holds for all temperatures so long as they correspond to a given vapour pressure. Such a conclusion is probably true for most empirical relations involving boiling point. It has been shown that the vapour-pressure–temperature relation can be expressed quite accurately over a restricted temperature range by

$$\log p = \log 760 + \Delta H_0/2{\cdot}303\boldsymbol{R}T_{\mathrm{B}} - \Delta H_0/2{\cdot}303\boldsymbol{R}T$$

Transposing, and taking logarithms, we have

$$\log (\log 760 + \Delta H_0/2{\cdot}303\boldsymbol{R}T_{\mathrm{B}} - \log p) = \log \Delta H_0 - \log 2{\cdot}303\boldsymbol{R} - \log T$$

and substituting relation (3) for log ΔH_0, we have

$$\log (\log 760 + \Delta H_0/2{\cdot}303\boldsymbol{R}T_{\mathrm{B}} - \log p) = 4{\cdot}93 - 4/M^{\frac{1}{2}} - \log 2{\cdot}303\boldsymbol{R} - \log T$$

Again, transposing and multiplying throughout by M, we have

$$M\{4{\cdot}93 - \log 2{\cdot}303\boldsymbol{R} - \log (\log 760/p + \Delta H_0/2{\cdot}303\boldsymbol{R}T_{\mathrm{B}})\} = 4M^{\frac{1}{2}} + M \log T \quad . \quad (4)$$

It has been pointed out above that $\log 760 + \Delta H_0/2{\cdot}303\boldsymbol{R}T_{\mathrm{B}}$ shows only a small variation from substance to substance. Since, however, the left-hand side of (4) involves the logarithm of $\log 760 + \Delta H_0/2{\cdot}303\boldsymbol{R}T_{\mathrm{B}}$, it follows that for an arbitrarily chosen value of p the coefficient of M will remain sensibly constant for all normal substances. Relation (4) may then be written as $\alpha M = 4M^{\frac{1}{2}} + M \log T$, *i.e.*, the right-hand side is a function which is proportional to the formula weight, the proportionality constant α being a function only of the arbitrarily chosen value of p, the vapour pressure corresponding to T. It thus follows that such a function must be additive. Burnop's relation, which is of the same form, is the special case where $p = 1$ atm.

It will be noticed that the derived relation differs from Burnop's in that the coefficient of $M^{\frac{1}{2}}$ is 4 instead of 8. It will be shown later by a few examples that the value 4 does give an additivity of the same order of accuracy.

Table II shows the results of a test of this additivity at temperatures other than the boiling point. Data for two ethers, three esters, and two hydrocarbons have been interpolated from vapour-pressure–temperature data given in the International Critical Tables. Values of $4M^{\frac{1}{2}} + M \log T$ are given under the heading of the compound and have been calculated from temperatures corresponding to vapour pressures given in col. 1.

That the values are additive is shown by the increment for a CH_2 group given under

ΔCH_2. These values are, at a given pressure, in good agreement for the three classes of compound. Furthermore, the relation certainly holds over the wide pressure range 760—100 mm. These facts are considered sufficient indication of the essential correctness of the theory.

Now Burnop has shown that his function is constitutive and, in addition to atomic values, has calculated values for various constitutional features. For example, he finds it necessary to assign a value of 16·1 to a double bond, and 17·6 to a six-membered ring. Clearly, the theory worked out above cannot account for constitutive influences. A recalculation of his data, however, clears up this difficulty and further establishes the theoretical relation.

TABLE II.

p, mm.	Et_2O.	ΔCH_2.	EtPrO.	$CH_3{\cdot}CO_2Me$.	ΔCH_2.	$CH_3{\cdot}CO_2Et$.	ΔCH_2.	$CH_3{\cdot}CO_2Pr$.	CH_4.	ΔCH_2.	C_2H_6.
760	218·5	41·4	259·9	221·1	40·6	261·7	41·4	303·1	48·8	41·3	90·1
316·2	216·0	41·0	257·0	218·4	41·3	259·7	39·9	299·6	48·1	40·7	88·8
199·5	214·9	40·7	255·6	217·3	40·2	257·5	40·6	298·1	47·8	40·5	88·3
100	213·1	40·5	253·6	215·7	39·7	255·4	40·6	296·0	47·5	40·3	87·8

It has been shown that the function is proportional to the formula weight. The results of a recalculation of some of the data, using the theoretical function $4M^{\frac{1}{2}} + M \log T_{\mathrm{B}}$, are given under $b'_{\mathrm{obs.}}$ in Table III. The ratio $b'_{\mathrm{obs.}}/M = \alpha$ is given in the last column, and it will be seen that this is remarkably constant, having a mean value of 2·99. The theoretical value can be calculated from (4), according to which

$$\alpha = 4{\cdot}93 - \log 2{\cdot}303\boldsymbol{R} - \log (\log 760/p + \Delta H_0/2{\cdot}303\boldsymbol{R}T_{\mathrm{B}})$$

TABLE III.

Substance.	$b'_{\mathrm{obs.}}$.	$b'_{\mathrm{calc.}}$.	$b'_{\mathrm{obs.}}/M$.
Paraffins :			
CH_4	48·8	47·9	3·04
C_2H_6	90·1	89·7	3·00
C_3H_8	130·4	131·6	2·96
C_4H_{10}	171·8	173·5	2·96
C_5H_{12}	213·3	215·4	2·96
C_6H_{14}	255·0	257·3	2·96
*cyclo*Paraffins :			
$[CH_2]_3$	125·1	125·6	2·98
$[CH_2]_4$	167·8	167·5	3·00
$[CH_2]_5$	209·3	209·4	2·99
$[CH_2]_6$	250·9	251·3	2·99
Olefins :			
$CH_2{:}CH_2$	83·4	83·8	2·98
$CH_2{:}CH{\cdot}CH_3$	124·9	125·7	2·97
$CH_2{:}CH{\cdot}CH_2{\cdot}CH_3$	166·2	167·6	2·97
$CH_2{:}CH{\cdot}[CH_2]_2{\cdot}CH_3$	208·4	209·4	2·98
$CH_2{:}CH{\cdot}[CH_2]_3{\cdot}CH_3$	249·1	251·3	2·97
Acetylenes :			
$CH{\vdots}CH$	79·3	77·8	3·05
$CH{\vdots}C{\cdot}CH_3$	121·3	119·7	3·03
$CH{\vdots}C{\cdot}CH_2{\cdot}CH_3$	162·5	161·6	3·01
$CH{\vdots}C{\cdot}[CH_2]_2{\cdot}CH_3$	202·8	203·5	2·99
Diolefins :			
$CH_2{:}C{:}CH_2$	120·8	119·7	3·02
$CH_2{:}CH{\cdot}CH{:}CH_2$	162·6	161·6	3·01
$CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH_3$	203·0	203·5	2·99
Alkyl chlorides :			
CH_3Cl	149·6	151·1	2·96
C_2H_5Cl	190·6	193·3	2·95
C_3H_7Cl	232·3	234·8	2·96
Aromatic hydrocarbons :			
C_6H_6	234·3	233·3	3·00
$C_6H_5{\cdot}CH_3$	275·9	275·2	3·00
$C_6H_5{\cdot}C_2H_5$	318·1	317·1	3·00
$C_6H_5{\cdot}C_3H_7$	360·2	359·0	3·00
$C_6H_5{\cdot}C_4H_9$	402·6	400·9	3·00
Naphthalene	390·0	382·9	3·07
Decahydronaphthalene	404·9	402·8	2·93

and with the previously calculated value of $\log 760 + \Delta H_0/2{\cdot}303\boldsymbol{R}T_{\mathrm{B}} = 7{\cdot}46$ and $p =$ 760 mm., α can be shown to be 2·98, which agrees well with the mean value obtained above.

From the mean value, a few individual atomic values have been calculated, *viz.*, H = 2·99, C = 35·90, O = 47·84, Cl = 106·1, and by using these values, b' has been calculated by an additive process, the results obtained being given in Table III under $b'_{\mathrm{calc.}}$. It is seen that they agree well with the observed values. Such agreement is important, especially so for those compounds which contain rings and double bonds, because it is here that constitutive influences, if present, should cause disagreement with theory. It thus appears that Burnop's constitutive constants were a necessary outcome of his use of 8 as a coefficient of $M^{\frac{1}{2}}$.

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