161. A Relationship Between Viscosity, Density, and Vapour Pressure of Liquids.

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An equation is proposed connecting the fluidity (ϕ) and the density (d) of a liquid with vapour pressure, and a comparison made of $\phi\sqrt{d}$ at corresponding pressures. The value of $\phi\sqrt{d}$ at the same reduced pressure is approximately a constant for all non-associated non-symmetrical substances. The significance of this constant is discussed.

It was pointed out by Porter (*Phil. Mag.*, 1912, **23**, 458) that, for mercury and water, the logarithm of the viscosity (η) or fluidity is a linear function of the logarithm of the vapour pressure (p); *i.e.*, $\log_{10}\phi = b' + a'\log_{10} p$. Assuming the equation to hold up to the critical point, we may write

$$\log \phi/\phi_c = a'\log p/p_c \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ϕ_c and p_c are the critical fluidity and pressure respectively.

Graphically determined values of a' and b' are printed in Table I. It can be seen that for non-associated liquids, $a' \approx 0{\cdot}238$. Hence, in general, non-associated liquids in equilibrium with their vapours at the same reduced pressure have approximately the same reduced fluidity.

For highly symmetrical molecules, a' is found to be appreciably greater than 0·238, indicating that even at corresponding pressures, such substances are considerably more viscous than those possessing non-symmetrical molecules.

In a previous publication (*J.*, 1946, 573) the author discussed the relationship between viscosity and reduced temperature T_c and put forward the equation

$$\log\left[\frac{\eta\sqrt{v}}{\eta_c\sqrt{v_c}}\right] = k\left[\frac{T_c}{T} - 1\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where v is the specific volume at absolute temperature T, or,

$$\log_{10} \eta\sqrt{v} = \alpha + \beta/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It was also shown that $\eta_c\sqrt{v_c} \approx 1{\cdot}167$ (η in 10^3 poise); but log p is a linear function of $1/T$ (below) and therefore

$$\log_{10} \phi\sqrt{d} = b + a \log_{10} p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or, introducing the critical pressure,

$$\log \phi\sqrt{d}/\phi_c\sqrt{d_c} = a \log p/p_c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which is a modification of (1).

Values of a, b, and log $\phi_c\sqrt{d_c}$ are also given in Table I. The introduction of $\sqrt{d}$ into the variable ϕ somewhat alters the slope so that $a \approx 0{\cdot}220$. The average deviation of a' from the mean 0·238 is 3·8% as compared with 4·2% deviation of a from the mean 0·220 for the same 46 liquids. However, unlike ϕ_c which is approximately constant only for one particular homologous series, $\phi_c\sqrt{d_c}$ is tolerably constant for all the non-associated liquids examined irrespective of type.

The fair constancy of a implies, of course, that at corresponding pressures, all the liquids—with the exception of those possessing highly symmetrical molecules—have approximately the same reduced value of $\phi\sqrt{d}$. Further, since $\log_{10} \phi_c\sqrt{d_c} \approx 2{\cdot}901$, the value of $\phi\sqrt{d}$ for a particular substance depends primarily on its " distance " from the critical state.

It should be pointed out that (5) leads to a value of 1·256 (η in 10 poise) for $\eta\sqrt{v}$ whereas (2) gives 1·167—a difference of 8%. Measurements in the region of the normal b. p. to the critical point, which at present are lacking, might therefore decide between (2) and (5) if indeed either equation represents the true viscosity behaviour in this region.

The nature of the experimental data is such as to necessitate calculation of a and b by the following methods :

(A) Actual vapour pressures at 10° intervals have been taken from the literature, and corresponding viscosities from Thorpe and Rodger (*Phil. Trans.*, 1894, **185**, 397; 1897, **189**, 71).

(B) When vapour pressures havé been recorded only in the form of the equafion log $p = A - B/T$, a and b have been calculated from the values of α and β (Thomas, *loc. cit.*) and A and B. The percentage agreements between the calculated and the experimental values of $\eta\sqrt{v}$ are then necessarily the same as those involved in (3) which, with the corresponding temperature ranges, have previously been given (*ibid.*).

(C) For other liquids, vapour pressures have been recorded in the form of other p–T equations such as that of Dupré and Kirchoff, *viz.*: $\log p = C - D/T - F \log T$. Vapour pressures corresponding to the experimental viscosities have then been calculated from these equations.

(D) In a few cases, vapour pressures have been mathematically interpolated from p–T tables for temperatures corresponding to the viscosity data.

The procedure adopted for a particular substance is indicated in the table by use of the above letters. Values of a and b recorded under (A), (C), and (D) have been evaluated by application of Campbell's " zero sum " method (*Phil. Mag.*, 1920, **39**, 177; 1924, **47**, 816). The measure of agreement between the experimental values of $\eta\sqrt{v}$ and those calculated from (4) is shown in col. 10. Corresponding deviations from (3) over the same temperature ranges are tabulated in the preceding column. Vapour pressure references are given as footnotes to the table; viscosity references have previously been given (*loc. cit.*).

Discussion of Results.—It is well known that often great discrepancies exist between vapour pressure measurements of different observers, especially the lower values, such differences arising partly from the use of insufficiently purified materials (Ramsay and Young, *J.*, 1885, 44). Large errors may also arise in the " static " method due to insufficient preliminary degassing of the material. Perhaps extreme cases are those of *o*- and *p*-xylenes. The values from 80° to 130° of Woringer (International Critical Tables) do not even approximately fall on the same p–T curve as that constructed from the data of Kassel (*loc. cit.*). Accordingly two values of a and b are recorded for *o*- and *p*-xylenes; they are seen to differ very widely indeed.

TABLE I.

	b'.	a'.	$\log_{10} \phi_c$.	b.	a.	Deviation, %, in a.	a, calc., from b. p.	Deviation, %, in a (from b. p.).	Mean % error, eqn. (4).	Mean % error, eqn. (3).	$\log_{10} \phi_c\sqrt{d_c}$.	Deviation, %, in $\phi_c\sqrt{d_c}$.	Approx. temp. range.		Ref.
Propane	—	—	—	1·900	0·229	4·1	0·208	5·5	—	—	2·932	7·4	—	B	1
Butane	—	—	—	1·952	0·213	3·2	0·197	10·4	—	—	2·897	0·9	—	B	1
*iso*Butane	—	—	—	1·717	0·262	19·1	0·224	1·8	—	—	2·884	4·0	—	B	1
Pentane	2·002	0·241	3·062	1·953	0·221	0·4	0·210	4·5	—	—	2·925	5·7	—	B	1
*iso*Pentane	2·017	0·230	3·028	1·8994	0·2332	6·0	0·215	2·3	0·1	0·1	2·924	5·4	0—30°	A	1
Hexane	2·015	0·231	3·020	1·960	0·215	2·3	0·210	4·5	—	—	2·896	1·2	—	B	1
Heptane	2·031	0·230	3·022	1·9650	0·2169	1·4	0·215	2·3	0·7	0·4	2·900	0·2	0—90	A	1
Octane	2·027	0·230	3·010	1·9592	0·2183	0·8	0·221	0·4	0·7	0·3	2·891	2·3	20—120	A	1
Methyl formate	1·821	0·237	2·924	1·8687	0·2182	0·8	0·223	1·4	0·1	0·1	2·883	4·2	0—30	A	1
Methyl acetate..............	1·898	0·232	2·952	1·9235	0·2155	2·4	0·232	5·5	0·2	0·2	2·903	0·5	0—50	A	1
Ethyl acetate	1·906	0·236	2·958	1·9135	0·2213	0·6	2·238	8·2	0·3	0·1	2·899	0·5	0—70	A	1
Propyl formate	1·841	0·244	2·935	1·8520	0·2296	4·4	0·243	10·4	0·1	0·1	2·880	5·0	0—70	A	1
Methyl propionate	1·922	0·230	2·951	1·9345	0·2129	3·2	0·229	4·1	0·2	0·1	2·887	3·3	0—70	A	1
Ethyl propionate...........	1·940	0·232	2·961	1·9421	0·2136	2·9	0·235	6·8	0·3	0·1	2·882	4·5	0—80	A	1
Propyl acetate	1·887	0·247	2·973	1·8803	0·2328	5·8	0·245	11·3	0·8	0·1	2·904	0·7	20—100	A	1
Methyl butyrate	1·901	0·241	2·965	1·8887	0·2327	5·8	0·244	10·9	0·6	0·2	2·916	3·5	0—100	A	1
Methyl *iso*butyrate	1·893	0·244	2·969	1·8960	0·2268	3·1	0·236	7·3	0·6	0·1	2·896	1·2	0—90	A	1
Ethyl ether	2·000	0·237	3·046	1·9839	0·2169	1·4	0·208	5·5	0·3	0·1	2·899	0·5	0—30	A	1
Methyl propyl ether	1·996	0·235	—	2·010	0·215	2·3	0·213	3·2	—	—	—	—	—	B	1
Ethyl propyl ether	1·993	0·234	3·019	1·9558	0·2214	0·6	0·222	0·9	0·4	0·1	2·925	5·7	0—60	A	1
Propyl ether.................	1·955	0·246	—	1·919	0·231	5·0	0·229	4·1	—	—	—	—	—	B	1
Butyl ether	—	—	—	1·914	0·231	5·0	0·233	5·9	—	—	—	—	—	B	2
Methyl cyanide	—	—	—	1·9773	0·2100	4·5	0·207	5·9	0·1	0·2	2·934	7·9	16—77	C	3
Ethyl cyanide	—	—	—	1·9881	0·2071	5·9	0·206	6·4	0·0	0·1	2·920	4·5	20—93	C	3
Propyl cyanide	—	—	—	1·9053	0·2242	1·9	0·224	1·8	0·3	0·2	2·903	0·5	18—113	C	3
Butyl cyanide	—	—	—	1·9000	0·2225	1·1	0·225	2·3	0·2	0·2	—	—	19—134	C	3
Ethyl bromide	1·803	0·233	—	1·9167	0·2194	0·3	0·208	5·5	0·1	0·1	—	—	0—30	A	1
Propyl bromide	1·825	0·228	—	1·910	0·217	1·4	0·216	1·8	—	—	—	—	—	B	1
*iso*Propyl bromide	1·758	0·250	—	1·850	0·234	6·4	0·228	3·6	—	—	—	—	—	B	1
Nitromethane	1·820	0·243	—	1·894	0·217	1·4	0·224	1·8	—	—	—	—	—	B	1
Nitroethane..................	—	—	—	1·855	0·226	2·7	0·231	5·0	—	—	—	—	—	B	4
Nitropropane	—	—	—	1·8632	0·2249	2·2	0·236	7·3	0·5	0·2	—	—	15—122	C	5
Nitrobutane	—	—	—	1·9110	0·2134	3·0	0·233	5·9	0·8	0·4	—	—	15—143	C	5
Propyl chloride	1·844	0·249	—	1·875	0·227	3·2	0·218	0·9	—	—	2·905	0·9	—	B	1
*iso*Propyl chloride	1·771	0·273	—	1·799	0·251	14·1	0·237	7·2	—	—	—	—	—	B	1
Benzene *	1·616	0·301	2·988	1·6049	0·2925	—	0·291	—	0·3	0·4	2·937	8·9	0—80	A	6
Toluene	1·900	0·244	2·998	1·8928	0·2265	3·0	0·227	3·2	0·3	0·2	2·911	2·3	30—100	A	1
Ethylbenzene	1·858	0·264	—	1·8604	0·2436	10·7	0·214	2·7	0·3	0·2	—	—	0—130	A	1
o-Xylene	1·845	0·264	—	1·8931	0·2258	2·6	0·228	3·6	0·2	0·3	—	—	0—80	A	7
o-Xylene	,,	,,	—	1·8512	0·2419	—	,,	,,	0·1	0·1	—	—	90—140	A	1

p-Xylene	1·890	0·267		2·0061	0·1986	9·7	0·214	2·7	0·2	0·1	—	—	10—80	A	7
p-Xylene	,,	,,	—	1·8806	0·2479	—	,,	,,	0·1	0·1	—	—	90—130	A	1
m-Xylene	2·018	0·219	—	2·0213	0·1968	10·5	0·205	6·8	0·4	0·2	—	—	0—130	A	1
Methyl iodide	1·726	0·230	—	1·9373	0·2194	0·2	0·209	5·0	0·0	0·0	—	—	0—30	A	1
Ethyl iodide	1·775	0·225	—	0·9500	0·2099	4·6	0·205	6·8	0·2	0·2	—	—	0—60	A	1
Propyl iodide	1·789	0·225	—	1·926	0·215	2·3	0·212	3·6	—	—	—	—	—	B	1
*iso*Propyl iodide	1·739	0·241	—	1·873	0·232	5·5	0·222	0·9	—	—	—	—	—	B	1
Acetone	1·985	0·224	3·005	1·9763	0·2052	6·7	0·210	4·5	0·0	0·1	2·909	1·9	10—50	A	1
Methyl ethyl ketone	1·935	0·232	—	1·9241	0·2144	2·5	0·226	2·7	0·4	0·1	—	—	10—50	A	8
Methyl propyl ketone	—	—	—	1·931	0·218	0·9	0·218	0·9	—	—	—	—	—	B	8
Acetaldehyde	2·011	0·223	—	2·019	0·201	8·6	0·204	7·3	—	—	—	—	—	B	1
Butaldehyde	—	—	—	1·869	0·225	2·3	0·231	5·0	—	—	—	—	—	B	2
Methyl sulphide	1·957	0·220	2·973	1·9675	0·2024	8·0	0·200	9·1	0·2	0·1	2·903	0·5	0—30	A	1
Ethyl sulphide	1·906	0·246	2·906	1·8913	0·2354	7·0	0·211	4·1	0·2	0·1	2·944	10·4	10—80	A	1
Methylene chloride	1·754	0·239	2·857	1·8597	0·2224	1·1	0·216	1·8	0·1	0·1	2·884	4·0	0—30	A	1
Chloroform	1·734	0·234	2·815	1·8590	0·2162	1·7	0·216	1·8	0·3	0·1	2·858	10·4	0—60	A	1
Carbon tetrachloride *	1·383	0·318	2·825	1·5232	0·3018	—	0·293	—	0·1	0·3	2·890	2·6	20—70	A	1
Ethylene chloride *	1·581	0·279	2·866	1·677	0·258	—	0·270	—	—	—	2·864	8·9	—	B	1
Ethylene chloride	,,	,,	,,	1·625	0·278	—	,,	—	—	—	2·905	0·9	—	B	1
Ethylidene chloride	1·743	0·251	2·897	1·817	0·233	5·9	0·237	7·7	—	—	2·889	2·8	—	B	1
Ethylidene chloride	,,	,,	,,	1·803	0·241	9·5	,,	,,	—	—	2·911	2·3	—	B	1
s-Tetrachlorethane *	1·519	0·302	—	1·612	0·300	—	0·300	—	—	—	—	—	—	B	1
Styrene	—	—	—	1·9452	0·2258	2·6	0·223	1·4	1·0	1·7	—	—	0—140	C	9
β-*iso*Amylene	—	—	—	2·058	0·202	8·2	0·192	12·7	—	—	2·948	11·4	—	B	2
Isoprene	—	—	—	2·035	0·206	6·4	0·195	11·3	—	—	—	—	—	B	2
Fluorobenzene	1·782	0·258	2·951	1·8026	0·2475	12·5	0·246	11·8	0·5	0·6	2·925	5·7	0—81	D	6
Chlorobenzene	1·852	0·241	2·943	1·9142	0·2155	2·4	0·223	1·4	0·5	0·5	2·891	2·3	0—120	D	6
Bromobenzene	1·795	0·241	2·886	1·9250	0·2135	2·9	0·223	1·4	0·9	0·6	2·892	2·1	28—142	D	6
Iodobenzene	1·790	0·229	2·804	1·9351	0·2122	3·5	0·227	3·2	0·3	0·5	2·896	1·2	28—149	D	6
Nitrobenzene	—	—	—	1·894	0·209	5·0	0·216	1·8	—	—	—	—	—	B	1
Acetic anhydride	—	—	—	1·944	0·206	6·4	0·236	7·3	—	—	—	—	—	B	1
Propane-1-thiol	—	—	—	1·901	0·218	0·9	0·213	3·2	—	—	—	—	—	B	10
*cyclo*Hexene *	—	—	—	1·497	0·317	—	0·271	—	—	—	—	—	—	B	11
Ethylene bromide *	1·497	0·275	—	1·670	0·268	—	0·261	—	—	—	—	—	—	B	1
Dioxan *	—	—	—	1·4374	0·3126	—	0·324	—	0·3	0·5	—	—	0—80	A	12
Diphenyl	—	—	—	1·8567	0·2413	9·7	0·251	14·1	0·1	0·1	—	—	139—210	C	13
*cyclo*Hexane *	—	—	—	1·2495	0·3677	—	0·354	—	0·9	0·6	2·899	0·5	11—76	C	14
Ethylene oxide	1·891	0·227	—	1·9134	0·2082	5·4	0·211	4·1	0·4	0·5	—	—	−50—+9	D	1
Average values	—	0·238	—	—	0·220	4·2	—	5·2	0·33	0·25	2·901	3·5	—	—	—

* These symmetrical substances were excluded when calculating the mean values of *a* and *a′* and the deviations from them.

(1) *I.C.T.*
(2) Kuchinskaya, *Khim. Referat. Zhur.*, 1939, **2**, No. 4, 23.
(3) Heim, *Bull. Soc. chim. Belg.*, 1933, **42**, 467.
(4) Goodeve, *Trans. Faraday Soc.*, 1934, **30**, 501.
(5) Hodge, *Ind. Eng. Chem.*, 1940, **32**, 748.
(6) Young, *Sci. Proc. Roy. Dublin Soc.*, 1910, **12**, 374.
(7) Kassel, *J. Chem. Physics*, 1936, **4**, 276.
(8) Mayberry and Aston, *J. Amer. Chem. Soc.*, 1934, **56**, 2682.
(9) Patnode and Scheiber, *ibid.*, 1939, **61**, 3449.
(10) Taylor and Layng, *J. Chem. Physics*, 1933, **1**, 798.
(11) Harrison and Berg, *Ind. Eng. Chem.*, 1946, **38**, 117.
(12) Crenshaw, Cope, Finkelstein, and Rogan, *J. Amer. Chem. Soc.*, 1938, **60**, 2308.
(13) Chipman and Peltier, *Ind. Eng. Chem.*, 1929, **21**, 1106.
(14) Nagornov, *Chem. Zentr.*, 1927, ii, 2668.

Fairly large errors in a might also be expected to arise from the viscosity measurements. It is instructive to compare the data of Thorpe and Rodger (*locc. cit.*) for benzene with those of Bingham and Harrison (*Z. physikal. Chem.*, 1909, **66**, 1). Taking the same vapour pressure over the range 0—70°, the a value of the latter is 2% higher than that calculated from the viscosities of the former.

It seems probable then that errors in a of from 2 to 6% may reasonably be expected.

Of the 74 liquids examined, 66 show a mean error in a of 4·2%, of which 61 show errors of $< 7\%$. The remaining 8 liquids—unsubstituted ring compounds and certain of the polyhalides—are quite exceptional, this being due apparently to the fact that they all possess highly symmetrical molecules. The introduction of even one substituent group into the ring effectively destroys the symmetry and normal values of a are then exhibited.

Over a relatively small temperature range, it can hardly be expected that (4) would reproduce the experimental data as accurately as (3), for experimental errors in the determination of vapour pressure are superimposed on those incurred in the viscosity measurements. In fact, the average deviations are 0·33% and 0·25% respectively for the same 47 liquids.

Now

$$\frac{\mathrm{d}\log_e \phi\sqrt{d}}{\mathrm{d}\log_e p} = \frac{\mathrm{d}\log_e \phi\sqrt{d}}{\mathrm{d}(1/T)} \times \frac{\mathrm{d}(1/T)}{\mathrm{d}\log_e p} = a$$

and it has been shown (Thomas, *loc. cit.*) that $\mathrm{d}\log \phi\sqrt{d}/\mathrm{d}(1/T)$ (β) is sensibly constant only at temperatures near the b. p., but increases at lower temperatures. However, it is well known that $\mathrm{d}(1/T)/\mathrm{d}\log p$ *decreases* at lower temperatures (below). The effects are therefore compensatory; possibly, then, over more extended ranges, (4) may be more accurate than (3). Unfortunately, the necessarily low vapour pressures of those substances showing a noticeable increase in β at the lower temperatures, are not available. It is hoped to make this the subject of immediate experimental study.

From the Clapeyron equation we get

$$\mathrm{d}\log_e p/\mathrm{d}(1/T) = -LT/p(V_v - V_l)$$

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

At temperatures up to the b. p., $V_v \gg V_l$. Assuming the perfect gas laws to hold for the saturated vapour, we may therefore write $\mathrm{d}\log_e p/\mathrm{d}(1/T) = -L/\boldsymbol{R}$.

The gas laws do not in fact apply to saturated vapours except at temperatures well below the b. p. as is shown by the observation of Young and Thomas (*J.*, 1893, **63**, 1191) that at a reduced pressure of 0·04423 the ratio of the actual vapour densities to the theoretical values for ten lower esters is $\sim 1{\cdot}06$. It is suggested that the equation

$$\mathrm{d}\log_e p/\mathrm{d}(1/T) = -E/\boldsymbol{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

or

$$\log_e p = A - E/\boldsymbol{R}T$$

represents liquid–vapour equilibrium, where E is a quantity greater than L at the b. p. or somewhat below the b. p. and becoming equal to L only at still lower temperatures.

Between the b. p. and the critical point, (6) is found to hold with fair accuracy even though L rapidly decreases with rising temperature to zero *at* the critical point. The table below, compiled from the data in the I.C.T., shows the average percentage deviations between observed pressures and those calculated from (6) for twelve substances at 10° intervals between their b. p.s and critical points.

Carbon tetrachloride	0·7	Octane	0·5	Hexane	0·5
Pentane	0·2	Xenon	0·4	Ethyl propionate	0·8
Methyl butyrate	0·8	Benzene	0·7	*cyclo*Hexane	0·5
Chlorobenzene	0·3	Ethyl acetate	0·8	Heptane	0·6

(Mean deviation = 0·6%.)

A recent publication by Gouq-jen Su (*Ind. Eng. Chem.*, 1946, **38**, 923) shows a graph of $\log p/p_c$ against T_c/T for a number of substances for P/p_c values of 0·001 to unity. The plots show no noticeable curvature.

From the above relationships, $E = L\boldsymbol{R}T/p(V_v - V_l)$. Values of this function are printed below. Vapour pressures and molar volumes were taken from I.C.T. The latent heats used are those based on direct calorimetric data.

t.	$E/10$, cals. per mole.	Devn., %, from mean.	*t.*	$E/10$, cals. per mole.	Devn., %, from mean.	*t.*	$E/10$, cals. per mole.	Devn., %, from mean.	*t.*	$E/10$, cals. per ole.	Devn., %, from mean.
Benzene (t_c = 288°).			*Benzene* (t_c = 288°).			*Carbon dioxide* (t_c = 31°).			*Carbon dioxide* (t_c = 31°).		
100°	727	+1·2	200°	707	−1·5	−30°	384	−0·8	0°	390	+0·8
120	728	+1·2	220	715	−0·4	−25	386	−0·3	5	385	−0·5
140	722	+0·6	240	727	+1·2	−20	391	+1·0	10	380	−1·8
160	711	−1·0	260	742	+3·3	−15	395	+2·0	15	383	−1·0
180	711	−1·0	280	757	+5·5	−10	395	+2·0	20	377	−3·0
						− 5	393	+1·5	25	350(?)	

The average deviations from the mean values are 1·3% for benzene (100—260°) and 1·3% for carbon dioxide (− 30° to + 20°). The large *positive* deviation for benzene and the large *negative* deviation for carbon dioxide at the two top temperatures might well be due to experimental errors in the difficult determinations of latent heats, vapour pressures, and specific volumes. For temperatures between the b. p. and the critical point the error involved in (6) does not then *demonstrably* exceed the probable experimental error.

At temperatures somewhat below the b. p., $-\mathrm{d}\log_e p/\mathrm{d}(1/T)$ becomes $\approx L/\boldsymbol{R}$, and therefore E slowly increases with fall in temperature.

The fair constancy of E would seem to imply that it represents some fundamental characteristic of liquid–vapour equilibria. In general, it cannot be equated to L except presumably at temperatures sufficiently below the b. p.

Since the constants in Table I were evaluated by means of logarithms to the base 10, (6) becomes :

$$\log_{10} p = A/2{\cdot}303 - E/2{\cdot}303\,\boldsymbol{R}T$$

but

$$\log_{10} \eta\sqrt{v} = -b - a\log_{10} p$$

therefore

$$\log_{10} \eta\sqrt{v} = -b - aA/2{\cdot}303 + aE/2{\cdot}303\,\boldsymbol{R}T = \alpha + \beta/T$$

therefore $a = 2{\cdot}303\,\boldsymbol{R}\beta/E = 4{\cdot}571\,\beta/E$. But $\beta = E_{\mathrm{visc.}}/2{\cdot}303\boldsymbol{R}$, where $E_{\mathrm{visc.}}$ is the activation energy of viscous flow defined by the equation

$$\eta\sqrt{v} = \text{constant} \times e^{E_{\mathrm{visc.}}/\boldsymbol{R}}$$

Therefore $a = E_{\mathrm{visc.}}/E$, or, at temperatures somewhat lower than the b. p., $a = E_{\mathrm{visc.}}/L$.

It has been shown by Kistiakowsky (*Z. physikal. Chem.*, 1923, **107**, 65) that the value of L in calories at the b. p., T_B, is given by

$$L = 2303\,\boldsymbol{R}T_B \log_{10} 82{\cdot}07\,T_B$$

The relationship holds with a satisfactory degree of accuracy (the average percentage error between $L_{\mathrm{calc.}}$ and $L_{\mathrm{obs.}}$ is 3%) over a b. p. range of − 196° for nitrogen to 1554° for silver chloride which includes fused metals and salts. It is not obeyed for associated liquids such as alcohols. Therefore $a \approx \beta/T_B \log_{10} 82{\cdot}07\,T_B$.

The mean value of a so determined is 0·245, being higher than the previous value 0·220 owing to the fact that $L < E$. For purposes of comparison the values of a in col. 8 have been obtained by multiplying the values calculated as above by the factor 0·220/0·245 = 0·8975, so that

$$a \approx 0{\cdot}8975\,\beta/T_B \log_{10} 82{\cdot}07\,T_B \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

or

$$E = 5{\cdot}093\,T_B \log_{10} 82{\cdot}07\,T_B$$

In addition to the above tabulated values, Table II has been compiled from (7) for a number of substances whose vapour pressures have not been determined.

As mentioned above, (3) is accurate only at temperatures approaching the b. p., and at lower temperatures the plots of $\log \eta\sqrt{v}$–$1/T$ are decidedly convex to the $1/T$ axis (see graph, Thomas, *loc. cit.*). Within the approximate temperature range 0—100° therefore the β values of

TABLE II.

Substance.	*a*.	Substance.	*a*.
*iso*Pentane	0·215	Amyl cyanide	0·225
*iso*Hexane	0·214	Phenyl cyanide	0·213
*iso*Heptane	0·214	Benzyl cyanide	0·220
Nonane	0·230	Ethyl ketone	0·213
Ethyl valerate	0·238	Propionic anhydride	0·239
Butyl propionate	0·239	Allyl chloride	0·218
Butyl bromide	0·212	Allyl bromide	0·214
*iso*Butyl bromide	0·233	Allyl iodide	0·212
Amyl bromide	0·215	Diallyl	0·213
Hexyl bromide	0·223	Nitropentane	0·236
Heptyl bromide	0·231	Nitro*iso*pentane	0·256
Butane-1-thiol	0·216	Propyl nitrite	0·216
Pentane-1-thiol	0·217	Butyl nitrite	0·222
Pentane-2-thiol	0·223	Amyl nitrite	0·220
Hexane-2-thiol	0·220	*iso*Amyl nitrite	0·210
Hexane-1-thiol	0·223	Anisole	0·257
Heptane-1-thiol	0·231	Phenetole	0·246
Heptane-2-thiol	0·231	*o*-Chlorotoluene	0·223
*iso*Butyl iodide	0·224	*m*-Chlorotoluene	0·211
*iso*Butyl chloride	0·241	*m*-Bromotoluene	0·215
Propaldehyde	0·249	*p*-Bromotoluene	0·209
*iso*Valeraldehyde	0·247	Acetophenone	0·223
Methylene bromide	0·207	Methyl*cyclo*hexane	0·251

(Mean % deviation from $a = 0{\cdot}220$ is 4·9.)

liquids of sufficiently high b. p. will be too great to correspond with the values of E calculated from (7). High values of a are then to be expected :

Decane	0·239	Octyl bromide	0·241
Undecane	0·244	Octane-1-thiol	0·240
Dodecane	0·254	Propylene bromide	0·253
Butyl valerate	0·247	*iso*Butylene bromide	0·286
Ethyl heptoate	0·249	*p*-Methyl*cyclo*hexanone	0·263
Heptyl acetate	0·264		

These are precisely those higher-boiling liquids which show large (1—2%) errors in equation (3).

The data for symmetrical substances in Table I are scanty. They may be supplemented to a certain extent by the following values calculated from (7) :

Thiophen	0·253	*cyclo*Hexanone	0·311
*cyclo*Hexene	0·271	*cyclo*Hexyl chloride	0·281
Chloral	0·283	*cyclo*Hexyl bromide	0·269

The high values exhibited by *cyclo*hexanone and by the *cyclo*hexyl halides are surprising in view of the fact that the benzenoid analogues of the latter are normal. The case of chloral seems anomalous. Clearly, further experimental study is necessary before the effect of molecular symmetry can be confidently assessed.

Assuming $a = 0{\cdot}220$, (7) enables one to calculate β for a given compound from its b. p. at atmospheric pressure with an average error of $\sim$ 5%. By using this value ($\beta_{\text{calc.}}$), $\eta\sqrt{v}$ at any temperature T_2 may be calculated from one measured value at another temperature T_1 by the use of (3).

It may easily be shown that the error in $\log(\eta\sqrt{v})_{T_2}$ is given by

$$\Delta \log \eta\sqrt{v} = \Delta\beta\,[1/T_2 - 1/T_1]$$

where $\Delta\beta$ is the difference between $\beta_{\text{calc.}}$ and the actual value.

Between 0° and 100° the above becomes $\Delta \log \eta\sqrt{v} = 0{\cdot}000982\,\Delta\beta$. Putting $\beta = 400$ (*e.g.*, from butane to nonane, β increases from 261 to 492), we have

$$\Delta \log \eta\sqrt{v} = 20 \times 0{\cdot}000982 = 0{\cdot}01964 \text{ or } \Delta\ \eta\sqrt{v} = 4{\cdot}6\%$$

The error involved in this procedure will naturally be $>$ or $<$ 4·6% according as $\beta >$ or < 400.

A treatment similar to that above, but involving the internal latent heat L_i, has been given by Eyring *et al.* (an excellent review of which is given by Kincaid, Eyring, and Stearn, *Chem. Rev.*, 1941, **28**, 301), who have developed a general theory of the liquid state.

The activation energy of viscous flow $E_{\text{visc.}}$ [which equals $\boldsymbol{R}$ d $\log_e\eta/\text{d}(1/T)$] is regarded as that required for the formation of a " hole " into which the unit of flow can be transferred by rotation. The theorem is derived that " the energy necessary to make a hole in the liquid the size of a molecule equals the energy of vaporisation (the internal latent heat of vaporisation) ". The hole necessary for viscous flow will in general be a fraction of the full size of the molecule, the fraction depending on the shape of the flowing unit; $E_{\text{visc.}}$ will then be some fraction of L_i such that $L_i/E'_{\text{visc.}} = n$. For normal molecules, $n \approx 4$, but for symmetrical molecules, $n \approx 3$.

The values of L_i used were those at the b. p. Now, L_i increases quite rapidly as the temperature drops from the b. p.; for instance, for benzene, from 80° to 0° there is an increase in L_i of 17%. Presumably, if viscosity measurements were conducted over a given temperature range, then the mean value of L_i over that range should have been used.

Between the b. p. and the critical point, L_i of course decreases to zero at the latter temperature. If n is taken to be constant, then $E_{\text{visc.}}$, and hence the slope of the log η–$1/T$ curve, should likewise decrease to zero. The only substance on which viscosity measurements have been carried out in this range is carbon dioxide. Solution of (3) gives $\alpha = -0{\cdot}8519$ and $\beta = 513{\cdot}7$, between 5° and 29°. The average agreement between viscosity calculated from these constants and the experimental values is 1·0%, showing that a sensibly linear relationship holds.

The treatment given in this paper is free from such objections since $\boldsymbol{R}\text{d} \log_e p/\text{d}(1/T) = E$ is constant, at least above the b. p. The physical significance to be attributed to E, beyond the fact that it can be equated to L at temperatures well below the b. p., is, however, not clear.

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