952. Viscosity and Molecular Association. Part III.* Association of Phenols and Amides.

By Leo H. Thomas.

Following previous papers in the series, the author has calculated the degrees of association of a number of phenols and amides. The vapour pressures of a number of such compounds have also been determined.

Using the same nomenclature as in earlier papers, we define three functions, E, a, and β as

$$E = -\boldsymbol{R}\,\mathrm{d}\log_e p/\mathrm{d}(1/T),\quad a = -\mathrm{d}\log \eta\sqrt{v}/\mathrm{d}\log p,\quad \text{and}\quad \beta = \mathrm{d}\log_{10}\eta\sqrt{v}/\mathrm{d}(1/T)$$

where η is the viscosity of a liquid, p its vapour pressure, v its specific volume, and T the absolute temperature. At temperatures somewhat below the normal b. p., E becomes the g.-molar latent heat of vaporisation.

The three functions are obviously inter-related through the expression

$$a = 2{\cdot}303\boldsymbol{R}\beta/E \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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* Part II, *J.*, **1948**, 1349.

For an unassociated substance,[1] and also for certain associated liquids,[2] the plot of log $\eta\sqrt{v}$ against log p is linear, and we can write

$$\log_{10} \eta/v = b - \boldsymbol{a} \log_{10} p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where b and also $\boldsymbol{a}$ are constants. Furthermore, it was shown that $\boldsymbol{a}$ has approximately the same value (0·220) for all non-associated substances with the exception of a very few having highly symmetrical molecules. Associated liquids, however, give a (or $\boldsymbol{a}$) values mostly considerably larger than 0·220, and the plot may no longer be linear. The η–p relationship now agrees with the equation

$$\eta\sqrt{v} = A/p^{0\cdot 220} + D/p^{d} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where A, D, and $d(>0\cdot220)$ are constants. [At sufficiently high temperatures, the second term may become negligible in comparison with the first so that the behaviour would then similate that of an unassociated substance. At sufficiently low vapour pressure, on the other hand, the second term becomes the more important, and $-\mathrm{d}\log \eta\sqrt{v}/\mathrm{d}\log p$ becomes equal to d, a conclusion implying that degrees of association (γ) become constant at lowest temperatures. The author [3] has previously shown that the lower branched-chain alcohols have already attained these " ultimate " degrees of association at temperatures no lower than their b. p.s, but that dissociation of the polymers probably occurs at higher temperatures. The straight-chain alcohols, however, appear to form association complexes stable at temperatures approaching even their critical points.]

By using the methods of evaluation previously outlined (η in poises × 10^3, and p in mm. of mercury), the values of the various constants for a number of phenols and amides are as given in Table 1. All viscosity and density data are due to Friend,[4] and values of p corresponding to the measured viscosities have been graphically interpolated from vapour-pressure data (references to which are given in the Table). Col. 5 shows the average % deviation between the observed values of $\eta\sqrt{v}$ and those calculated from equations (2) or (3). In no case is there any indication of systematic departure from these equations.

The molecular weight in the liquid state of an associated substance may be larger than that in the vapour state, and E now includes an extra quantity of heat consumed in the breaking up of the polymers. Making allowance for the latter fact, and assuming that the $\eta\sqrt{v}$–p relation is otherwise normal, we can clearly write $2\cdot303\boldsymbol{R}\beta/\gamma E^1 = 0\cdot220$, E^1 being the value of the differential for the polymer as such *per formula weight.* But $2\cdot303\boldsymbol{R}\beta/E = a$, E being the experimental value, again per formula weight. (The molecular weight in the vapour is assumed to be that of the monomer.) Hence eliminating β, we have

$$\gamma = aE/0\cdot220E^1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now E^1 (in cal.) will be less than E by an amount, x cal., absorbed in the rupture of " hydrogen bonds." Writing h for the heat consumed in the breaking of N such bonds, we have

$$E - E' = x = (\gamma - 1)h/\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It was previously assumed that the value of E^1 at the normal b. p. was given by a modified Trouton relationship, the value so obtained being of course less than the experimental value by x cal. Consequently, knowing x, and evaluating a (or $\boldsymbol{a}$) by differentiation of eqn. (3), or from eqn. (2) in the event of the plot of log η/v against log p being linear, γ and h values were calculated for a number of alcohols. The numerical values of h were sensibly in agreement with estimates made by other methods.

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[1] Thomas, *J.*, 1947, 822.
[2] Part I, *J.*, 1948, 1345.
[3] Part II, *J.*, 1948, 1349.
[4] Friend, *Phil. Mag.*, 1945, **36**, 73; 1946, **37**, 120, 201.

A number of refinements are now, however, introduced arising from recent related work by the author, *viz.*:

TABLE 1.

Substance	*A*	*D* (or 10^b)	*d* or ***a***	% deviation eqn. 3 (or 2)	Approx. temp. range (° c)	*a*	***B***	Mean deviation (° c) equation (13)
Phenol	12·00	32·0	0·460	0·9	60—175	—	0·867	—
o-Cresol	12·00	27·4	0·530	0·9	72—185	—	0·885	—
m-Cresol	10·00	28·5	0·470	0·8	62—192	—	0·870	—
p-Cresol	12·00	30·0	0·510	0·8	60—190	—	0·858	—
o-Chlorophenol	10·00	16·7	0·380	0·3	41—163	0·2403	0·9464	0·3
o-Methoxyphenol	10·00	11·36	0·367	0·3	93—191	0·3694	0·9069	0·4
m- ,,	8·00	19·8	0·360	0·2	120—230	0·5726	0·8405	0·2
p- ,,	8·00	20·9	0·360	0·7	131—234	0·6067	0·8269	0·3
Methyl *p*-hydroxybenzoate	6·00	29·1	0·335	0·2	160—241	0·7641	0·7823	0·4
Acetamide	14·00	21·4	0·460	0·4	112—210	0·6479	0·8023	0·3
Propionamide	10·00	24·5	0·400	0·4	92—209	0·6262	0·8112	0·2
n-Butyramide	—	38·19	0·349	0·5	121—205	0·6297	0·8134	0·1
o-Nitrophenol	—	18·15	0·246	0·2	109—200	0·3568	0·9156	0·2
o-Hydroxyacetophenone		15·07	0·235	0·7	110—197	0·3712	0·9103	0·3
Salicylaldehyde	—	17·89	0·246	0·1	96—191	0·2391	0·9550	0·3
p-Chlorophenol	—	25·89	0·2934	0·2	99—210	0·4564	0·8776	0·4
Methyl salicylate	—	14·01	0·2304	0·5	80—215	0·2407	0·9366	0·4

References to vapour pressures: First four and last compound, Stull, *Ind. Eng. Chem.*, 1947, **39**, 517; for all others, present work.

(A) The Trouton " constant " has been shown to depend in general on structure type,[5] and in particular on the chain length of the molecule. Assumption of a constant value for the Trouton ratio would therefore bias the derived values of γ and particularly of h. Instead, values of E^1 (in cal.) at temperatures corresponding to a vapour pressure of 100 mm. (T_{100}) have been calculated from the relation

$$E^1 = 100ZT_{100}/(F - \Delta F) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where Z is the " molecular number " per formula weight, F is an additive entropy of vaporisation function evaluated by summation of the appropriate atomic and structural increments, and ΔF is dependent on the possibility of rotational isomerism in the molecule, and increases with the number of bonds (n) about which there is restricted rotation (ref. 5, equation 6; k_1 being taken as 0·0480, and k_2 as 0·000622).

[F and Z should here refer strictly to the polymer per formula weight, and E^1 should be equated to $\{100\gamma T_{100}Z_{\text{monomer}}\}/\{F_{\text{polymer}} - (\Delta F)_{\text{polymer}}\}$. However, it is assumed, at least provisionally, that the F increment in respect of a hydrogen bond surviving vaporisation is zero, so that $F_{\text{polymer}} = \gamma F_{\text{monomer}}$. It is debatable whether $(\Delta F)_{\text{polymer}}$ would be equal to $\gamma(\Delta F)_{\text{monomer}}$, but any inequality would in any case be small and practically without effect. The remarks below on the choice of n values are significant in this connection.]

(B) From the above definition of E we may write for an associated liquid

$$\mathrm{d}\log_{10}T/\mathrm{d}\log_{10}p = \boldsymbol{R}(T/E) = \boldsymbol{R}T/(E^1 + x) = \boldsymbol{R}T/E^1(1 + x/E^1)$$

and for benzene (as " comparison substance,"[6] x now being zero)

$$\mathrm{d}\log_{10}T_{\text{benzene}}/\mathrm{d}\log_{10}p = \boldsymbol{R}(T/E)_{\text{benzene}}$$

so that

$$\frac{\mathrm{d}\log_{10}T}{\mathrm{d}\log_{10}T_{\text{benzene}}} = \left(\frac{T}{E^1}\right)\left(\frac{1}{1 + x/E^1}\right)\left(\frac{E}{T}\right)_{\text{benzene}}$$

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[5] Thomas, *J.*, 1953, 2132.

[6] Thomas, *J.*, 1953, 1233.

But it has been shown [6] that the ratio of the values of E/T for any two unassociated substances at temperatures corresponding to the same vapour pressure is constant independently of the value of the vapour pressure chosen. Therefore

$$d \log_{10} T/d \log_{10} T_{\text{benzene}} = B^1/(1 + x/E^1) = B \text{ (say)} \quad . \quad . \quad . \quad . \quad (7)$$

where B^1 is a constant provided the comparison substance remains unchanged, and equals the slope of the plot of log T against log T_{benzene} in the hypothetical event of the polymers' surviving vaporisation.

In other words,

$$E = E^1B^1/B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and, since $(E/T)_{\text{benzene}}$ at a vapour pressure of 100 mm. is [5] 27·2 cal. mole^{-1} deg.$^{-1}$, equation (6) becomes

$$B^1 = 0{\cdot}272(F - \Delta F)/Z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

(C) Combining equations (4) and (8), we have

$$\gamma = aB^1/0{\cdot}220B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and, from equations (5) and (8),

$$h = \left(\frac{\gamma}{\gamma - 1}\right) E^1 \left(\frac{B^1}{B} - 1\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Thus γ and h at a vapour pressure of 100 mm. can be determined from the a value obtained by differentiation of equation (3), the B^1 value derived from equation (9), and the value of B derived from vapour-pressure data. Similar calculations can in principle be conducted at other temperatures over the entire experimental range, but, in practice, accurate and unbiased evaluation of B (or E) at each temperature by numerical differentiation is impossible unless the measurements are extensive and of great accuracy. An alternative method, presented below, has the merit of self-consistency, and should lead to more reliable evaluation over the whole range of measurements.

Eliminating E from equations (4) and (5) we get

$$\gamma^2 - \frac{a\gamma}{0{\cdot}220}\left(1 + \frac{h}{E'}\right) + \frac{ah}{0{\cdot}220E^1} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

But for a substance of constant a value, it is found that the plot of log T against log T_{benzene} at the same vapour pressure is, as for an unassociated liquid, linear within the limits of experimental error: *i.e.*, B becomes constant ($=\boldsymbol{B}$) and equation (7) simplifies to

$$\log T = \alpha + \boldsymbol{B} \log T_{\text{benzene}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Therefore, from equation (10), such substances have constant degrees of association, a fact requiring that, not only E/E^1, but [from equation (12)] also h/E^1, and hence x/E^1 be constant.

For a substance whose a value and hence γ value is not constant but decreases with rise in temperature, it is reasonable to suppose that the value of h is independent of γ as such but depends only on temperature (decreasing with rise in temperature) and on the nature of the (monomer) molecule, *i.e.*, it can be supposed that *in general* h/E^1 is constant for a particular substance. Therefore x/E^1 [$=h(\gamma - 1)/\gamma E^1$] now decreases with rising temperature, so that from equation (7), B, whilst $<B^1$, will approach the latter in numerical value at higher temperatures.

Although strictly, then, the plot of log T against log T_{benzene} is expected to be linear only for substances of constant degree of association, the % variation in the values of B

over the experimental range is such in fact that equation (13) reproduces the vapour-pressure behaviour very well even for those compounds not showing constant degrees of association. Table 1 accordingly shows the mean deviation between the experimental temperatures and those calculated from equation (13) for all the substances studied, whether γ is constant or not. It appears likely that the deviations lie within the limits of experimental error in all cases.

TABLE 2.

						Values of γ at vapour pressures:						
Substance	n	F	B'	B_{100}	a_{100}	760	250	100	40	10	3	$h/100$ (cal.)
Phenol	1	182·0	0·978	0·867	0·333	1·52	1·62	1·71	1·78	1·89	1·99	32
o-Cresol	2	212·0	0·969	0·885	0·331	1·42	1·53	1·65	1·76	1·95	—	27
m-Cresol	,,	,,	,,	0·870	0·339	1·53	1·63	1·72	1·80	1·92	2·03	32
p-Cresol	,,	,,	,,	0·858	0·335	1·48	1·61	1·72	1·83	2·01	2·15	36
p-Chlorophenol	1	238·5	0·970	0·878	0·293	1·47	constant					39
o-Chlorophenol	$\frac{1}{2}$	,,	0·977	0·943	0·291	1·31	1·34	1·37	1·40	1·44	1·48	14
o-Methoxyphenol	$1\frac{1}{4}$	239·0	0·969	0·910	0·274	1·27	1·30	1·33	1·36	1·39	—	31
m- ,, ...	$2\frac{1}{2}$	,,	0·953	0·840	0·299	1·48	1·51	1·54	1·57	1·61	—	49
p- ,, ...	,,	,,	,,	0·821	0·301	1·52	1·56	1·59	1·62	1·66	—	56
Methyl *p*-hydroxybenzoate	3	283·0	0·927	0·795	0·305	—	1·60	1·61	1·63	1·66	1·69	62
Methyl salicylate	1	283·7	0·952	0·956	0·230	1·04	constant					—
o-Nitrophenol	0	254·2	0·960	0·916	0·246	1·17	constant					39
o-Hydroxyacetophenone ...	1	257·2	0·959	0·910	0·235	1·13	constant					57
Salicylaldehyde	0	227·2	0·965	0·955	0·246	1·13	constant					10
Acetamide	2	114·0	0·944	0·810	0·301	1·42	1·51	1·60	1·68	1·80	—	55
Propionamide..................	$2\frac{1}{2}$	144·0	0·948	0·815	0·313	1·55	1·61	1·66	1·70	1·77	1·84	51
n-Butyramide	3	174·0	0·949	0·813	0·349	1·85	constant					46

The necessary steps in the calculation of the values of γ and h in Table 2 are then as follows:

(a) Calculation of $d \log T/d \log T_{\text{benzene}}$ $(=B)$ by numerical differentiation, at some point to the middle of the experimental vapour-pressure data—conveniently at 100 mm. [In the case of phenol and the cresols, the experimental data are not sufficiently accurate to allow of this, and the values of $\boldsymbol{B}$ obtained from equation (13) were assumed to be equal to the true values at the mid-points.]

(b) Evaluation of B^1 with the help of equation (9).

(c) Calculation of γ_{100} from equation (10), using values of a derived from equation (3), or $\boldsymbol{a}$ from equation (2).

(d) Calculation of the value (assumed constant) of h/E^1 from equation (11) and of h_{100} from this latter ratio and the value of E_{100} derived from equation (6).

(e) Evaluation of γ over the entire range of the experimental data by solution of the quadratic equation (12).

This treatment leads to a knowledge of h at a vapour pressure of 100 mm. only. Its value at any other vapour pressure can be obtained from the circumstance that h/E^1 is assumed constant, and that the ratio of E/T at this chosen vapour pressure to its value at 100 mm. is a constant for all substances (ref. 6, Table 1). The increase in h from the normal b. p. to a vapour pressure of, say, 10 mm. is in fact ~10%.

The " ultimate " degrees of association follow simply by putting $a = d$ in equation (12) [or in equation (10) if B is constant]—a procedure both simpler than, and preferable in principle to, that previously adopted. However, it is clear from the nature of equation (3) that any such values will be very inaccurate unless the experimental data happen to fall in the region where rapid variation in a occurs (see ref. 3, Figs. 1 and 2)—which they do not usually (as distinct from the behaviour of alcohols over the same range) for the compounds studied in this paper. In fact it is only for phenol (2·5), *o*-cresol (2·8), *m*-cresol (2·5), and *p*-cresol (2·8) that such values are at all reliable.

o-Nitrophenol, salicylaldehyde, and *o*-hydroxyacetophenone are seen from the Table to be associated to the extent of ~10% only, this being due, of course, to suppression of intermolecular association by intramolecular engagement of the hydrogen atoms concerned—a conclusion supported by a variety of evidence,[7] and in particular by the absence in the infrared spectra of strong absorption in the 7000 cm.$^{-1}$ region. Like the lower branched-chain and all n-alcohols previously referred to, the degree of association does not depend on temperature to any detectable extent. The values given for the hydrogen-bond energies for such compounds are necessarily uncertain owing to the smallness of $(B^1 - \boldsymbol{B})$.

Methyl salicylate within the limits of the method appears to be completely non-associated. Phenol and the three cresols, on the other hand, are strongly associated and approximately to the same extent, and the derived h values are sensibly constant. In common with all the remaining phenolic substances considered, they show strong absorption in the 7000 cm.$^{-1}$ region, a fact currently accepted as indicative of strong intermolecular association.

Substitution in phenol other than by the methyl group would appear to decrease somewhat the extent of association irrespective of the electronic nature of the group (*p*-chlorophenol, *m*- and *p*-methoxyphenols, and methyl *p*-hydroxybenzoate)—a fact which may be connected with interference in the flat-on-flat packing normally adopted by the benzene ring [5] in the liquid state, or simply with the increase in molecular size. The evidence is insufficient to justify further speculation.

The steric factors for the formation of a strong intermolecular bond in *o*-chloro- and *o*-methoxy-phenols are unfavourable. Nevertheless, the electrostatic attraction of the hydroxyl hydrogen atom for the adjacent chlorine or oxygen atom will stabilise the monomer (as *cis*-conformation) to a certain extent, and result in the formation of a " weak " hydrogen bond.[8] The extent of association is therefore likely to decrease somewhat, but not to the same degree as in such strongly chelated structures as those mentioned above. That these expectations are fulfilled is apparent from the γ values found for *o*-chloro- and *o*-methoxy-phenols which are significantly lower than the figures for the isomeric compounds. The energy of the intermolecular hydrogen bond for *o*-chlorophenol (1·4 kcal.) appears to be lower than could be caused by uncertainties in the method, but no explanation is possible at present.

The three amides studied are strongly associated, the energies of the N–H • • • O bonds being at least as large as, if not larger than, those for the O–H • • • O bonds in the phenols. This is in contrast with the relatively weak association in amines,[2] and is due presumably to resonance with the structure (*A*) which gives a positive charge to the nitrogen atom which donates the proton involved in hydrogen bonding, and simultaneously a negative charge to the oxygen which accepts that proton. The position is therefore analogous to the strengthening of the unsymmetrical O–H • • • O bond in fatty acids.[8]

$$\mathrm{O{\cdot}CR{:}NH_2^{+}} \quad (A)$$

The n values assigned to the non-chelate compounds are in agreement with the principles previously outlined,[5] rotation of the OH or NH_2 bonds as such being assumed (as for methyl and ethyl groups) to be restricted in the liquid state if attached either to a benzene ring or to an atom carrying a double bond.

The n values assigned to the four strongly chelate phenols are likewise unambiguous, and for these compounds the increment in the F function in respect of the chelate ring is put as 0·7—the usual value for a six-membered ring. The increment in respect of the formation of a hydrogen bond as such is assumed to be zero, this being justified at the moment solely from the observation that the experimental value of F (based on the measurements of Ramsay and Young [9]) for the completely non-associated methyl salicylate (281·2) agrees well with the value (279·9) calculated on this basis.

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[7] Klyne, " Progress in Stereochemistry," Butterworths Scientific Publications, 1954, Vol. I, 223.

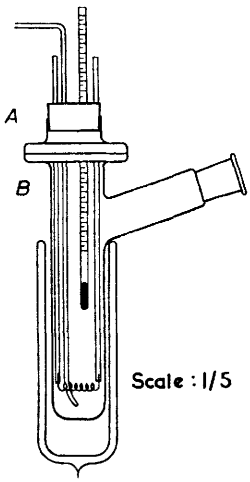
[8] Pauling, " The Nature of the Chemical Bond," Oxford Univ. Press, London, 2nd edn., 1940, Chap. 9.

[9] Ramsay and Young, *Z. physik. Chem.*, 1887, **1**, 237.

The only uncertainty in assignment of n values is for *o*-chloro- and *o*-methoxy-phenols, both compounds containing intermediate concentrations of (weakly) chelate molecules. The values actually chosen are the arithmetic means of the two extreme values, *e.g.*, $1\frac{1}{4}$ for *o*-methoxyphenol being the mean of zero (100% chelate structure) and $2\frac{1}{2}$ (no chelation). In any event, the values of γ are little affected by changing n by one or two units. The small F increment for ring formation was not applied for these two compounds.

EXPERIMENTAL

Vapour pressures were measured by the " dynamical " method, using the apparatus shown in the diagram, the upper part (A) of the boiling-tube being connected to the lower part (B) by means of a flanged ground-glass joint. The liquid was heated internally by means of a coil of platinum wire connected to a 6 v source and consuming ~60 w; and to minimise heat losses, the lower part of the boiling-tube was fitted into a Dewar flask, and the upper part lagged. In order to eliminate " bumping " at the lower pressures it was necessary to use a fine air-leak drawn from 0·5 mm. internal-diameter capillary tube.



Temperature was measured by insertion of a series of short-stem N.P.L calibrated thermometers through the rubber bung in A, and extending to ~1" above the surface of the liquid. The thermometers were periodically recalibrated in position in the apparatus and under atmospheric pressure against the b. p.s[10] of water and carefully purified samples, mostly of " AnalaR " quality, of ether, acetone, benzene, toluene, chlorobenzene, bromobenzene, aniline, nitrobenzene, and synthetic quinoline.

The side arm of B was connected *via* a ground-glass joint to a reflux condenser in turn connected in the usual way to a U tube open mercury manometer and hence to a vacuum pump. Variation and control of the pressure were accomplished by means of an Edwards and Co. Ltd. monostatic valve (Model VPC1) fitted into the vacuum line between the manometer and pump. Connection of the manometer to the vacuum line was made by a flush $\frac{1}{2}$" internal diameter T piece constructed such that the tube to the manometer did not protrude internally into the straight vacuum tube. All the usual manometer and barometer corrections were applied and the estimated uncertainty in pressure readings as such was ~±0·3 mm.

Although these are admittedly of no great absolute accuracy, the author's aim has been to produce reliable measurements free as far as possible from systematic error, and to this end, the following sources of error were taken into consideration: (*a*) All thermometer readings were taken with a rising meniscus; the " emergent column " correction never amounted to >0·1°, and the " external pressure " correction, which was measured experimentally, amounted to 0·2° at the lowest pressure. (*b*) The usual precautions against leakage of air into the apparatus other than through leak and valve, and " fouling " of the oil in the pump, were also observed. (*c*) Correction due to the head of vapour above the liquid is of increasing significance as the vapour pressure decreases, but is negligible at vapour pressures above, say, 10 mm. (*d*) It is also possible that the measured pressure is greater than the true vapour pressure of the liquid by an amount equal to the partial pressure of the admitted air, but the experimentally determined rate of leakage in of air was ~0·003 g. per min. compared with the rate of formation of vapour from the boiling liquid of at least 3 g. per min. The g.-molar fraction of air in the vapour space is therefore very small, and its pressure may be neglected. (*e*) A possible error on the premise that air is continuously flowing through the apparatus from the valve to the pump (the flow past the manometer connection is however very small, and arises only from the leak) was experimentally shown to be absent by immediate redetermination of the vapuro pressure of a given substance as outlined, but with the one difference that the pump and valve connections were closed before each measurement. Within the limits of accuracy specified above, however, no difference could be detected.

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[10] Timmermans, " Physico-chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

The method was checked by measurement of the vapour pressure of water (25—100°), chlorobenzene (40—132°), and bromobenzene (120—156°), and comparison between the temperatures (smoothed as below) at a series of set vapour pressures (at $\log_{10} p = 0{\cdot}1$ intervals) and the literature values.[11] The average difference for water and bromobenzene was 0·1°, with maximum deviation of 0·2° and 0·1° respectively. The author's values for chlorobenzene from 40° to the b. p. are consistently lower by ~0·3° than those of Young, but consistently *higher* from 60° to the b. p. by ~0·2° than the measurements of Dreisbach and Shrader (the latter being in perfect agreement with Zmaczynski's measurements carried out only >100°). Between 60° and the b. p. therefore the author's results are virtually identical with the mean literature values. The uncertainty in temperature measurement is therefore considered to be ~0·2°.

Readings at ~3° intervals were taken for all substances, covering a vapour-pressure range of ~5—760 mm., and smoothed figures read off from a large-scale plot of $\log p$ vs. $t°$. The latter are recorded in Table 3.

TABLE 3.

			Temperature (°c)			
$\log_{10} p$ (mm.)	I	II	III	IV	V	VI
1·0	76·4	60·3	100·8	93·6	88·4	126·4
1·2	85·0	68·5	109·4	102·4	96·4	134·6
1·4	94·2	77·5	118·8	112·3	105·3	143·9
1·6	104·3	87·4	129·0	123·1	115·2	154·2
1·8	115·6	98·2	140·0	134·8	126·5	165·4
2·0	128·3	109·9	152·1	147·2	138·7	177·4
2·2	142·1	122·7	165·4	160·6	152·0	190·5
2·4	156·7	136·6	179·9	175·4	166·4	204·8
2·6	172·4	151·7	195·6	191·7	181·7	220·4
2·8	189·4	168·3	212·3	209·1	198·3	237·4
2·8808	196·7	175·4	219·4	216·5	205·6	244·7
,, (lit. values)	196·5 [1]	174·5 [2]	220·0 [1]	217·2 [2]	205·0 [1]	244·3 [3]

			Temperature (°c)			
$\log_{10} p$ (mm.)	VII	VIII	IX	X	XI	XII
1·0	124·2	108·1	173·7	108·6	96·1	
1·2	133·3	116·8	182·9	116·8	104·9	124·9
1·4	143·1	126·1	192·9	125·8	114·5	134·3
1·6	153·5	136·1	203·8	135·7	124·9	144·5
1·8	164·8	146·7	215·8	146·5	136·1	155·4
2·0	177·1	158·1	228·9	158·0	148·4	167·1
2·2	190·6	170·6	243·2	170·4	161·7	179·7
2·4	205·1	184·0	—	183·5	176·3	193·2
2·6	220·7	198·2	—	197·3	192·5	207·9
2·8	237·4	212·3	—	212·1	209·9	223·8
2·8808	244·5	219·8	—	218·4	217·3	230·6
,,	245·6 [3]	222·2 [2]	—	221·1 [2]	213·4 [3]	216·0 [3]
(lit. values)		213·1 [3]			215 [4]	

References to b. p.: [1] Stull, *loc. cit.*; [2] Timmermans, ref. 10; [3] Friend, ref. 4; [4] Vogel, ref. 13.

Materials.—Salicylaldehyde (I), *o*- (II) and *p*- (III) chlorophenol, *o*-nitrophenol (IV), and *o*-methoxyphenol (V) (~250 g.; B.D.H.) were purified by repeated fractionation at atmospheric pressure (the first in an atmosphere of carbon dioxide) through a heated 12″ Dufton column into samples boiling over a range of <0·1°. *m*- and *p*-Methoxyphenol (VI), and propionamide (VIII) (~50 g.; B.D.H.) were distilled in the small-scale fractionation apparatus described by the author [12] to give reasonably sharp fractions boiling over ⯒1/3°, and comprising generally the middle third of the distillates.

Methyl p-*hydroxybenzoate* (IX). A sample (B.D.H) was recrystallised first from "AnalaR" benzene and then from benzene–methyl alcohol, and dried in a desiccator over calcium chloride. It melted sharply at 127·5° (corr.) (lit.,[4] 131°).

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[11] Water: Partington, "An Advanced Treatise on Physical Chemistry," Longmans, Green and Co., 1950, 248. Bromobenzene: ref. 9, Chlorobenzene: Young, *Sci. Proc. Royal Dublin Soc.*, 1910, **12**, 374; Zmaczynski, *J. Chim. phys.*, 1930, **27**, 503; Dreisbach and Schrader, *Ind. Eng. Chem.*, 1949, **41**, 2879.

[12] Thomas, *J.*, 1946, 820.

[13] Vogel, "Practical Organic Chemistry," Longmans, Green and Co., 1956, 676.

Acetamide (X). A sample of b. p. 217—218° (uncorr.) was obtained by fractionation and used without further purification. It was probably somewhat impure.

o-*Hydroxyacetophenone*. This was prepared by the Fries reaction as described by Vogel,[13] and finally purified by fractionation at atmospheric pressure, a middle constant-boiling fraction being collected.

n-Butyramide (XII). Fractionation of 50 g. of material (B.D.H) failed to give a sharp fraction, the greater portion distilling between 214° and 220°. It was therefore recrystallised from ~400 c.c. of " AnalaR " benzene, and dried in a vacuum desiccator over calcium chloride to give a material of sharp m. p. On subsequent fractionation, virtually the whole of the recrystallised sample distilled constantly at 230° (corr.). (Literature values are *ca.* 216°.) Its m. p., however, *viz.*, 115·8° (corr.), agreed well with the value 116·0° given by Timmermans.[10]

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