681. *Thermodynamic Properties of Organic Oxygen Compounds. Part IX.*[1] *The Critical Properties and Vapour Pressures, above Five Atmospheres, of Six Aliphatic Alcohols.*

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The critical temperatures, pressures, and densities of the two propyl and four butyl alcohols have been determined, together with their vapour pressures in the range from 5 atm. up to the critical point. Critical temperatures were determined by the visual sealed-tube method; pressures, including critical pressures, were determined in a glass apparatus based on the original design of Andrews; and orthobaric densities in the range 20—120° below the critical (from which the critical densities were found) were determined from volumetric measurements made on sealed tubes. Equations are presented for the variation with temperature of the vapour pressures and the orthobaric densities.

IN continuation of previous work on critical properties,[2] a study has been made of the two propyl and four butyl alcohols (including measurements of critical pressures and densities in addition to the temperatures which alone were measured in the earlier work). Critical temperatures were determined by the visual method already described.[2] Critical pressures were determined in an apparatus similar to that originally used by Andrews[3] and subsequently developed by Young[4] and by Kay,[5] but only the upper part of the experimental tube was maintained at an elevated temperature, the lower part remaining at lower temperatures. The experiment was arranged so that the pressure was measured while the disappearance and the reappearance of the meniscus were observed visually, and the method was essentially a refinement of that used by Altschul.[6] Both critical temperatures

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[1] Part VIII, Biddiscombe, Collerson, Handley, Herington, Martin, and Sprake, *J.*, 1963, 1954.

[2] Ambrose and Grant, *Trans. Faraday Soc.*, 1957, **53**, 771; Ambrose, Cox, and Townsend, *ibid.*, 1960, **56**, 1452.

[3] Andrews, *Phil. Trans.*, 1869, **159**, 575.

[4] Young, *Sci. Proc. Royal Dublin Soc.*, 1910, **12**, 374.

[5] Kay, *J. Amer. Chem. Soc.*, 1947, **69**, 1273.

[6] Altschul, *Z. phys. Chem.*, 1893, **11**, 577.

and critical pressures could have been obtained simultaneously in this way, but we preferred to retain our original method for critical temperatures because its accuracy had already been well demonstrated, and our method of temperature measurement (by means of a Leeds and Northrup platinum resistance thermometer) was more accurate than that available for use in the pressure experiment. At lower temperatures the apparatus was used for the determination of vapour pressures, and equations for the vapour-pressure curves have been calculated. Critical densities were obtained by application of the law of rectilinear diameters to the orthobaric densities measured over a range of temperature by the method of Hebert, McDuffy, and Secoy.[7] The approximately linear relation [8] between ($\rho_L - \rho_V$) and the cube root of ($t_c - t$) was demonstrated (where ρ_L, ρ_V are the liquid and vapour densities and t_c, t are the critical temperature and the temperature of observation, respectively).

EXPERIMENTAL

Materials.—The alcohols had been prepared in this laboratory, by purification of commercially available samples, for use in the current programme for determining their thermodynamic properties.[1] Their purities, determined by means of gas–liquid chromatography and melting- or freezing-point measurements, are listed in Table 1. However, because alcohols in contact with air pick up water so easily, they were dried by storing them over calcium hydride for several days before transference under a vacuum into the experimental tubes. There was visible reaction with the calcium hydride, and experience showed that the treatment was necessary if consistent vapour- and critical-pressure results were to be obtained.

TABLE 1.

Critical properties.

	Critical temperatures (°c)			Critical pressures (atm.)		
Alcohol	obs.	lit.	calc.*	obs.	lit.	calc.*
Propyl	263·56°	263·7° [4]	264·5°	51·02	50·16 [4]	51·4
Isopropyl	235·25 ¶	235·6 †	247·3	47·02		53·1
Butyl	289·83	286·95 ‡ 288·0 † 289·74 §	283·1	43·55	43·58 § 48·60 ‡	43·3
Isobutyl	276·70 ¶	274·59 §	273·1	42·39	42·38 §	44·5
s-Butyl	262·80		261·3	41·39		44·5
t-Butyl	233·0		236·9	39·20		44·5

	Purities	Critical densities (g./ml.)			
	(moles %)	obs.	lit.	calc.*	ρL at 20°
Propyl	99·94	0·2754	0·273 [4]	0·269	0·8035
Isopropyl	99·96	0·2727		0·274	0·7854
Butyl	99·94	0·2699	0·267 § 0·270 ‡	0·266	0·8096
Isobutyl	99·93	0·2722	0·269 §	0·270	0·8020
s-Butyl	99·95	0·2755		0·270	0·8129
t-Butyl	99·96	0·2700		0·280	0·7792 (27°)

* Calc. by Lydersen's method (see ref. 25). † Fischer and Reichel, *Mikrochem.*, 1943, **31**, 102. ‡ Mann and Shemilt, *J. Chem. Phys.*, 1955, **23**, 1370. § Kay and Donham, *Chem. Eng. Sci.*, 1955, **1**, 1. ¶ Kreglewski, *Bull Acad. polon. Sci., Cl. III*, 1954, **2**, 191.

Critical Temperatures.—The oven, temperature measurement, filling of tubes, and method of observation have been described.[2]

Vapour Pressures and Critical Pressures.—The apparatus (Fig. 1), an adaptation of that used by Kay,[5] consisted of a vertical glass tube A (3 mm. internal diameter, sealed at its upper end) which was held in a metal fitting B and communicated *via* a mercury-filled U and another glass tube C (in which the oil–mercury interface was located) with an oil-operated, dead-weight piston-gauge (Budenberg). The tube A was heated in the electric oven originally designed for the critical-temperature measurements. The sample was confined over mercury, and the

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[7] Hebert, McDuffy, and Secoy, *J. Phys. Chem.*, 1958, **62**, 431.

[8] Jüptner, *Z. phys. Chem.*, 1913, **85**, 1.

position of the sample–mercury interface could be adjusted by means of the screw press D. This interface (the position of which could be determined accurately by means of a cathetometer) was in the part of tube A which extended below the oven, so that no mercury was raised above room temperature and there was therefore no need to correct at higher temperatures for the mercury-vapour pressure. The pressure exerted by the vapour was the sum of the barometric pressure, that determined from the gauge, and the hydrostatic heads of oil, mercury, and alcohol. (The experimental tube was of uniform bore and the hydrostatic head of the alcohol was therefore independent of the temperature; it was equivalent to the length of the column of liquid at room temperature.) The oven was suspended so that it could be raised clear of tube A.

The experimental tube was filled with an appropriate amount of the substance under study, by vacuum-manipulation in the apparatus shown in Fig. 2. The tube A was held in a larger tube designed so that the assembly could be inverted by rotation about a conical joint E when filling was complete, and air could be admitted to the system so that the remainder of the tube was filled with mercury. When filled, tube A was removed from the filling apparatus and

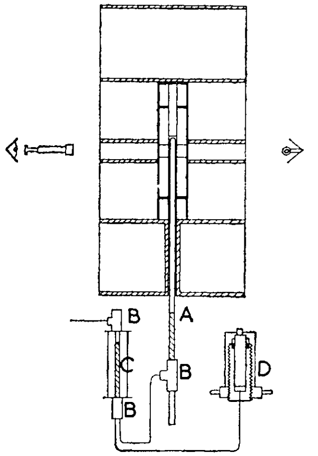

FIG. 1. Vapour pressure and critical pressure apparatus.

A, experimental tube; B, glass-to-metal couplings; C, sight glass for mercury–oil interface; D, screw press for adjustment of mercury level.

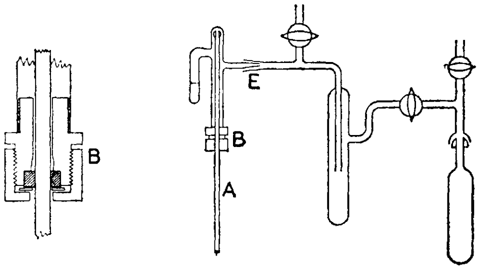

FIG. 2. Filling apparatus for vapour pressure tubes.

A, experimental tube; B, glass-to-metal coupling; E, conical joint to allow rotation of experimental tube.

inserted in the metal adapter B (Fig. 1) after the washer and elastomer sealing-ring had been moved to the end of the tube. The swelling at the end of A prevented it from being ejected under pressure from B. During the transfer from one apparatus to the other, care was taken that no bubble of air was trapped, the nut was then screwed down and the system was compressed to between 50 and 60 atm. so that a check could be made for the absence of leaks. The temperature of the oven was adjusted so that it was just below the critical, and the oven was lowered over the tube. As the tube became warm the screws on the mercury and oil presses were adjusted to allow for thermal expansion of the experimental liquid and to adjust the position of the two mercury menisci conveniently for observation. The pressure was reduced so that a vapour–liquid meniscus, visible through the window in the oven, was formed in the tube. The piston-gauge was balanced and was maintained in balance by addition of weights as the temperature was raised through the critical temperature, at which the meniscus disappeared with the same characteristic phenomena as are observed in sealed tubes. The temperature was then lowered, an observation was made as the meniscus reappeared, and the process was repeated several times. The difference in pressures at disappearance and reappearance was about 0·01 atmosphere.

After the critical pressure had been determined, similar experiments were carried out at fixed lower temperatures to determine the corresponding vapour pressures, the meniscus being adjusted on each occasion, as before, so that it was visible in the window of the oven. If the weights on the piston-gauge did not balance the pressure exactly, an indication of this lack of balance was given by the movement of the meniscus up or down.

With the butyl alcohols, decomposition at temperatures in the higher range was apparent from a gradual rise in pressure. To minimise errors due to this, results for all compounds were obtained on more than one filling of the sample tube, and after the critical pressure determinations, results were obtained in the lower range of temperatures before the higher. The design of apparatus was suitable for work on slightly unstable compounds since the oven could be raised at all times except when an experiment was actually in progress, and there was no unnecessary heating of the sample.

At temperatures for which the vapour pressure is no more than 10 atm. prolonged superheating is liable to occur, and the vapour bubble may not be formed at the top of the tube even when the balancing pressure is reduced to atmospheric or less. (Occurrence of this superheating is a good indication that the sample has been thoroughly freed from air.) The unpredictable conclusion of this condition occurs with explosive suddenness which may ruin the experiment. The difficulty was dealt with by flaming the top of the tube until vapour was formed against a pressure of a few atmospheres, and then lowering the oven immediately before the tube had cooled. Care had to be taken that faulty manipulation during the experiment did not at any time cause complete collapse of the vapour bubble since the superheating would inhibit its formation.

The standard instrument for the temperature measurements was a platinum resistance thermometer used with a Mueller bridge (Leeds and Northrup). This thermometer, however, could not be accommodated in the apparatus in addition to the vapour-pressure tube, and temperatures were measured with a small thermometer, designed to fit in the space available and made in the laboratory. Since the performance of this thermometer proved disappointing, it was frequently calibrated *in situ* against the Leeds and Northrup thermometer which was inserted in the oven in place of the experimental tube so that the resistance element occupied the position of interest, *i.e.*, was in the window. The piston and cylinder assemblies for the pressure measurement had been calibrated in the National Physical Laboratory (N.P.L.), and were subsequently used for the determination of the vapour pressure of carbon dioxide at 0·010° (*i.e.*, the vapour pressure when the bulb was inserted in a water triple-point cell[9]). The mean value obtained, 34·403 atm. (standard deviation of seven determinations ±0·004 atm.) is in good agreement with a provisional standard value, 34·400 atm., recently obtained in the N.P.L.

Orthobaric Densities.—In the method adopted for the determination of orthobaric densities (an adaptation of the classical one for making this measurement by observations on sealed tubes) observations are made on a series of tubes, instead of on two only, and the results are averaged overall.

Consider the effect of temperature upon the proportion occupied by liquid of a sealed tube containing the substance under study. If F is the fraction occupied by liquid, V is the internal volume of the tube, m is the mass of substance present, ρ_V, ρ_L are the densities of vapour and liquid, α is the cubical coefficient of expansion of glass, and the subscripts o and t refer to room temperature and t°, respectively, then

The volume of liquid $= VF_o,\ VF_t[1 + \alpha t]$ at the corresponding temperatures,

and

$$m = V[F_o\rho_{Lo} + (1 - F_o)\rho_{Vo}]$$
$$= V[1 + \alpha t][F_t\rho_{Lt} + (1 - F_t)\rho_{Vt}]. \qquad (1)$$

Whence

$$F_o(\rho_{Lo} - \rho_{Vo}) + \rho_{Vo} = (1 + \alpha t)[F_t(\rho_{Lt} - \rho_{Vt}) + \rho_{Vt}]. \qquad (2)$$

For the materials here examined $\rho_{Vo} \ngtr 0{\cdot}0001$ and may be ignored.

Therefore

$$F_o = [1 + \alpha t]\left[F_t\left(\frac{\rho_{Lt} - \rho_{Vt}}{\rho_{Lo}}\right) + \left(\frac{\rho_{Vt}}{\rho_{Lo}}\right)\right]. \qquad (3)$$

[The volume correction for thermal expansion at 300° is about $3 \times 10^{-3}V$; that due to an internal pressure of 50 atm. is about $2{\cdot}5 \times 10^{-4}V$ and may be ignored.] If a series of tubes is taken and

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[9] Barber, Handley, and Herington, *Brit. J. Appl. Phys.*, 1954, **5**, 41.

the movements of the menisci are measured as the temperature is raised, so that F_t can be plotted against F_o, then ρ_{Vt} and ρ_{Lt} can be found from the values of F_o at $F_t = 0, 1$ if ρ_{Lo} is known.

The tubes used were about 15 cm. long, and were made from glass tubing of 3 mm. precision bore. Up to ten were filled with each substance by normal vacuum-manipulation, F_o being varied between 0·15 and 0·65, as far as possible in approximately equal steps. The tubes were carefully prepared so that their lower ends were approximately hemispherical and distortion of the cylindrical wall was kept to a minimum. To determine F_o, the array of tubes was set up vertically with the hemispherical end downwards in a beaker of water (the temperature of which was measured), and measurements on each tube in turn were made with a cathetometer of the height of the liquid column h (measured from the lower end of the internal cavity to the bottom of the meniscus) and of the meniscus h'. Then the volume of liquid V_L is given by

$$V_L = \pi h'(h'^2 + 3r^2)/6 + \pi r^2(r - h) + 2\pi r^3/3, \tag{4}$$

where r is the radius of the tube. The tubes were inverted, and the volume of vapour V_V in each was determined in a similar way.

Then $$V = V_L + V_V, \text{ and } F_o = V_L/(V_L + V_V). \tag{5}$$

Since the value of F_o is used in the calculation for every experiment, two or three determinations of it were made (by more than one observer) and the mean was taken. The standard deviation from the means of 56 determinations (24 tubes) amounted to 0·0005.

In the calculation of V and F the nominal value of the radius of the tubing was used, and no check was made of its accuracy; as long as the tube is of uniform bore the exact value of the radius is not important except in the evaluation of the meniscus and end corrections which are themselves small. If reproducible results were to be obtained in the determination of V it was important that no liquid should be trapped at the upper ends of the tubes. Each tube was, therefore, heated slightly at the upper end before it was put in the water-bath, and no undue delay was allowed before observations were made. At higher temperatures liquid did not persist at the tops of the tubes, except in one set which was made from tubing of 2 mm. bore. With these tubes there was a clearly defined temperature below which surface tension was sufficient to hold a column of liquid at the top; measurements were unsatisfactory and a further set of tubes of 3 mm. bore was used.

With the internal volume known, F_t at any higher temperature can be found by measuring the liquid or vapour volume only. The tubes, placed 6 at a time in a holder which could be rotated, were heated in a vapour jacket (containing decalin, Dowtherm, or ethyl phthalate, according to the temperature range required). The jacket had been lagged, and windows cut in the lagging for observation and illumination so that each tube in turn could be examined. Readings were taken at temperatures ranging from about 120° to between 10° and 20° below the critical temperature. The temperature was adjusted by varying the pressure in the vapour jacket (which was attached to a manostat), and did not vary during an experiment by more than 0·1°. Temperatures were measured by means of a laboratory-made platinum resistance thermometer which was checked against the Leeds and Northrup instrument.

The tubes were immersed directly in the vapour and were therefore examined through only one thickness of glass so that no unnecessary distortion was introduced. The method, however, subjected the tubes to a thermal shock at the beginning of each experiment as the level of the condensing vapour rose up the jacket, and at first many exploded. The failures occurred at the points of sealing-off of the tube, and most breakages were prevented when the tubes were put in the vapour with the final seals downwards. In this way they did not have to withstand the thermal shock and high pressure at the same time. The tubes of t-butyl alcohol, however, nearly all burst eventually, no doubt because of thermal decomposition which caused excessive pressure; no effect on the density values obviously attributable to decomposition was observed.

The behaviour of individual tubes as the temperature is raised may be seen from Fig. 3. In those which contain more than the critical filling the liquid expands at an increasing rate as the temperature is increased until a point is reached at which liquid completely fills the tube. The overall effect is the same in reverse with the tubes which are underfilled, but two competing effects are apparent at first: the expansion of the liquid and its evaporation as the vapour pressure rises. At some values of F_0 the amount of liquid first increases because of the former before it decreases as a result of the latter.

When F_0 was plotted against F_t, excellent straight lines were obtained (normally with four or five points on each) and the pattern over a range of temperatures is shown in Fig. 4. After a preliminary examination, as a result of which some tubes were rejected because the residuals of the points obtained from them were consistently high (suggesting that they were distorted and that the assumption of uniform bore was incorrect), the best line was found by a least-squares treatment. In few instances were the final residuals greater than 0·0010. From the intercepts the values of ρ_L and ρ_V were calculated from the known densities at room temperature.

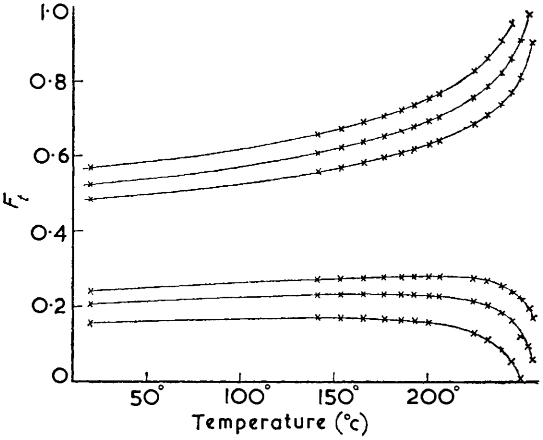

FIG. 3. Effect of temperature on sealed tubes filled to varying degrees. Plot of F_t against temperature for various tubes filled with propyl alcohol.

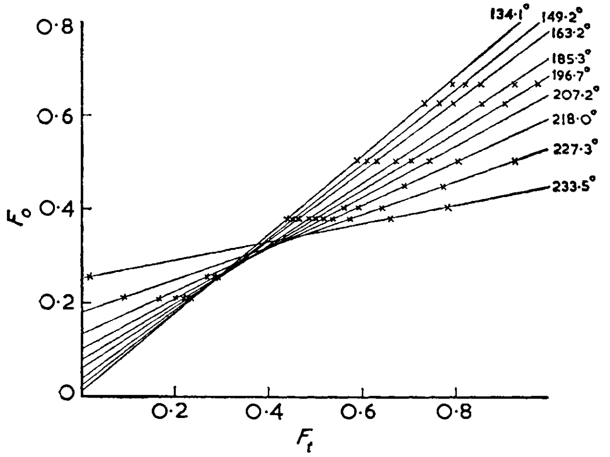

FIG. 4. Plot of F against F_0 for isopropyl alcohol.

RESULTS

Critical Properties.—The values obtained for the critical properties are given in Table 1. As in our earlier work, the critical temperatures are mean values of a series of observations on the disappearance and reappearance of the meniscus as the temperature of each tube was raised and then lowered. In most instances the range of temperature over which the phenomena occurred did not exceed a few hundredths of a degree but, taking all factors into account, we would place an uncertainty of $\pm 0{\cdot}1°$ on the final figures. That for t-butyl alcohol must be excepted since there was lack of agreement in the results obtained from different tubes; and the uncertainty in this instance must be put at $\pm 0{\cdot}2°$.

The critical pressure of each of the compounds was determined several times and, for most of them, with more than one filling of the experimental tube. The range of results was about 0·1% of the pressure, and we consider that the mean value given is within ±0·1% of the true value. Wherever possible, values of the critical properties taken from the literature have been quoted for comparison; the good agreement between our results and those of Kay (which has been reported earlier [2] for the critical temperatures of other compounds) now extends to the critical pressure measurements on n-butyl and isobutyl alcohol.[10] In addition, there is good agreement between our value and Young's value for the critical temperature of propyl alcohol,[4] but we consider his pressure value too low (that Young's values for vapour pressure tend to be low has been confirmed by other workers [11,12]). This work was started with measurements of the critical pressure of benzene; the value obtained, 48·36 atm., may be compared with the literature values, 47·9,[4] 48·34,[12] 48·7,[13] and 48·28.[14] It was finished with measurements of the critical pressure of fluorobenzene; the value obtained, 44·95 atm., may be compared with that reported from the U.S. Bureau of Mines,[15] 44·910 atm., for measurements on another sample of the same batch of fluorobenzene.

It is somewhat difficult to suggest a precision for the values of the critical densities; for propyl, butyl, and isobutyl alcohol they are some 1% higher than the results of Young [4] and of Kay and Donham.[10] The critical density is obtained by extrapolation of the rectilinear diameter to the critical temperature, and it has been pointed out by Benson and Copeland [16] that there is no valid reason why the extrapolation should be based on orthobaric densities (as is customary and has been done in this work) in preference to volumes. Exact measurements reveal, too, that the rectilinear diameter is in fact curved, and the extrapolation may be subject to considerable personal variation. It seems, therefore, that values purporting to be of high accuracy are not meaningful, but the four figures have been retained for substitution in the equations given in Table 3 for the orthobaric densities.

Vapour Pressures.—The experimental results are given in Table 2, together with their residuals from the calculated values, expressed as $\Delta\log p$, and the constants of the equations used for the calculation ($\Delta\log p = 0{\cdot}0004$ corresponds to a difference in pressure of 0·1%). A few measurements were made at pressures below 5 atm. but the apparatus was not reliable in this region.

If experimental results are to be fitted by an equation right up to the critical point, the equation must be capable of reproducing the reversal of curvature which is revealed at a reduced temperature of about 0·8 when $\log p$ is plotted against $1/T$ on a large scale. The equation of Frost and Kalkwarf [17] fulfills this requirement but, since it is not explicit in either p or T, it is inconvenient to use. In addition, the equation did not fit the results for propyl or isopropyl alcohol over the whole range without systematic deviations and we therefore adopted the following empirical equation, which fitted the results and from which the pressure p may be calculated, without difficulty, by simple substitution for the temperature, t:

$$\log p = A' - B/(C + t) - Dt + E(t - F)^3. \qquad (6)$$

A', B, C, D, E, and F are constants of which B and C are those found for the Antoine equations to fit the vapour-pressure results at lower temperatures.[1] The remaining constants were found by first plotting the results in the form of the residual of $\log p$ from the value calculated for the experimental temperature by means of the low-pressure Antoine equation. The curve of the residual was cubic in form and was solved graphically, the constants being adjusted so that the correcting terms became zero at the temperature G (20—30° above the b. p.) at which the residual was zero. Below $G°$ the normal Antoine equation is to be applied.

At the beginning of the work we made measurements on benzene and (in a silica tube) on water, and at its conclusion on water and fluorobenzene. The internal consistency of the results for benzene was at least as good as that found for the alcohols, but benzene in fact was

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[10] Kay and Donham, *Chem. Eng. Sci.*, 1955, **1**, 1.

[11] Silberberg, McKetta, and Kobe, *J. Chem. Eng. Data*, 1959, **4**, 323.

[12] Bender, Furukawa, and Hyndman, *Ind. Eng. Chem.*, 1952, **44**, 387.

[13] Gornowski, Amick, and Hixson, *Ind. Eng. Chem.*, 1947, **39**, 1348.

[14] Connolly and Kandalic, *J. Chem. Eng. Data*, 1962, **7**, 137.

[15] Douslin, Moore, Dawson, and Waddington, *J. Amer. Chem. Soc.*, 1958, **80**, 2031.

[16] Benson and Copeland, *J. Chem. Phys.*, 1955, **23**, 1180.

[17] Frost and Kalkwarf, *J. Chem. Phys.*, 1953, **21**, 264.

TABLE 2.

Vapour pressures (atm.) of alcohols. (Temp. in °c; $\Delta\log p = \log p_{\text{obs.}} - \log p_{\text{calc.}}$)

Temp.	p	$\Delta\log p$	Temp.	p	$\Delta\log p$	Temp.	p	$\Delta\log p$	Temp.	p	$\Delta\log p$
	Propyl			Isopropyl			Butyl			Isobutyl	
132·31°	3·286	0·0009	121·90°	3·983	−0·0006	146·19°	2·514	0·0013	149·49°	3·753	0·0020
138·62	3·952	0·0008	122·08	3·997	−0·0030	155·96	3·313	0·0010	159·92	4·921	0·0001
138·97	3·968	−0·0018	122·25	4·044	0·0014	160·62	3·770	0·0024	170·29	6·353	0·0001
147·52	5·062	0·0006	131·94	5·326	−0·0010	166·09	4·333	0·0008	173·25	6·804	−0·0004
148·17	5·123	−0·0018	132·08	5·349	−0·0008	166·13	4·337	0·0008	179·75	7·896	−0·0005
157·87	6·605	−0·0014	140·09	6·633	−0·0023	170·82	4·865	−0·0008	185·79	9·019	−0·0006
158·35	6·689	−0·0012	142·42	7·096	0·0004	175·48	5·477	0·0009	191·02	10·095	0
164·41	7·764	−0·0016	142·49	7·094	−0·0005	186·60	7·099	0·0006	195·16	10·982	−0·0007
167·86	8·446	−0·0011	153·14	9·282	−0·0003	189·49	7·545	−0·0010	200·42	12·236	0·0001
168·76	8·648	−0·0001	153·17	9·294	−0·0006	197·16	8·939	0·0002	202·74	12·786	0·0041
178·51	10·802	−0·0009	158·34	10·557	0·0012	199·40	9·354	−0·0006	205·86	13·598	−0·0003
178·56	10·811	−0·0010	158·37	10·510	−0·0011	207·81	11·138	0·0003	212·38	15·406	0·0002
179·18	10·974	−0·0005	165·10	12·302	−0·0004	209·17	11·436	−0·0001	223·16	18·696	−0·0008
188·38	13·398	−0·0005	165·21	12·337	−0·0002	217·72	13·293	0·0002	223·17	18·758	0·0006
189·16	13·619	−0·0005	168·57	13·328	0·0006	219·15	13·861	−0·0005	226·43	19·825	−0·0002
198·87	16·616	−0·0006	168·75	13·426	0·0020	228·91	16·612	0·0001	232·00	21·807	−0·0004
199·67	16·872	−0·0009	180·03	17·024	−0·0003	229·32	16·706	−0·0006	239·77	24·845	0
209·48	20·438	−0·0002	180·11	17·113	0·0021	239·67	19·969	−0·0018	242·32	25·871	−0·0004
210·45	20·805	−0·0003	190·06	20·941	0·0011	239·91	20·177	0·0010	250·12	29·347	0·0002
221·39	25·445	−0·0002	190·08	20·904	0·0002	249·77	23·733	0	252·45	30·392	−0·0003
221·60	25·585	0·0005	205·16	27·919	0·0006	250·05	23·810	−0·0006	252·45	30·413	−0·0001
239·95	34·991	−0·0005	216·42	34·143	0	259·70	27·816	−0·0001	263·11	35·783	−0·0003
251·93	42·478	−0·0006	220·15	36·435	−0·0001	260·08	27·909	−0·0013	266·20	37·504	0·0001
263·56	51·023	0·0003	227·04	40·978	−0·0004	269·62	32·410	−0·0001	269·92	39·676	0·0007
			235·09	47·019	0·0009	277·49	36·464	0·0002	274·56	42·386	0
						283·74	40·006	0·0009			
						289·83	43·554	0			
	s-Butyl			s-Butyl			t-Butyl			t-Butyl	
148·96	4·681	−0·0011	201·10	14·844	0·0003	103·27	2·131	−0·0017	153·68	8·729	0
150·44	4·845	−0·0028	211·01	17·772	−0·0006	115·41	3·150	0·0001	159·67	10·033	0·0004
159·68	6·146	0·0004	211·30	18·115	0·0054	125·40	4·217	−0·0004	170·70	12·733	0·0001
160·05	6·161	−0·0014	211·89	18·530	0·0106	135·63	5·559	−0·0016	172·78	13·330	0·0011
170·06	7·838	0·0007	221·44	21·408	0·0008	146·22	7·306	0·0002	233·00	39·200	0
170·37	7·840	−0·0022	221·81	22·466	0·0115						
179·94	9·800	0·0037	232·39	25·762	0·0014						
180·53	9·812	−0·0011	242·19	30·199	0·0016						
190·11	12·005	0·0009	252·76	35·557	0·0006						
190·79	12·155	0·0004	262·80	41·392	0						
200·79	14·768	0·0007									

Constants of vapour pressure equations.

$$\log_{10} p \text{ (atm.)} = A' - \frac{B}{C+t} - Dt + E(t-F)^3,\ t > G$$
$$= A - \frac{B}{C+t},\ t < G.$$

Alcohol	A	A'	B	C	10^4D	10^8E	F	G
Methyl *	5·50947	5·54194	1761·635	255·24	3·80	1·535	145°	64·5°
Ethyl *	4·33256	5·37917	1652·05	231·48	4·29	1·195	167	102
Propyl	4·84830	4·90882	1428·977	197·585	4·19	2·43	195	120
Isopropyl	4·84508	4·90388	1351·627	196·726	4·72	3·095	170	112
Butyl	4·48681	4·53285	1307·445	173·670	2·84	1·83	210	140
Isobutyl	4·41833	4·46403	1233·095	171·197	2·91	2·27	200	138
s-Butyl	4·32347	4·37118	1158·543	168·452	3·24	3·55	184	130
t-Butyl	4·32535	4·35499	1094·341	170·658	2·60	2·095	155	102

* The figures for the vapour pressures of methanol and ethanol, which can be fitted by the same type of curve, are included for comparison. The methanol curve is based on the results of Dever, Finch, and Grunwald (*J. Phys. Chem.*, 1955, **59**, 668) at low pressures, of Wojciechowski (*J. Res. Nat. Bur. Stand.*, 1936, **17**, 721) for the boiling point, and of Kay and Donham[10] for higher pressures. The ethanol curve is based on the A.P.I. Antoine equation and Young's results[4] at higher pressures.

not a good standard for use in checking the apparatus because of discrepancies between published results (~1% of the pressure); the present results were slightly higher than those of the most recent investigators[13] (maximum deviation, 0·3% of the pressure). The only substance which can be taken as a standard with confidence is water; measurements over the range 150—270° (5—55 atm.) agreed, within 0·1% of the pressure, with the values taken from the table published by Osborne and Meyers.[18] Two vapour-pressure measurements on fluorobenzene at 200·23° and 251·46° (13·23, 28·33 atm.) were about 0·5% higher than the published values.[15]

Of the alcohols themselves, there are results for three which may be compared with this work. Those of Young for propyl alcohol[4] are lower by about 1% of the pressure throughout the range from 120° to the critical; those of Kay and Donham[10] for butyl alcohol are lower by about 0·2% between 190° and 260°, and for isobutyl alcohol by about 0·5% between 220° and 260° (in both instances, as remarked above, agreement was closer for the critical pressure itself.) Vapour pressures of butyl alcohol have also been measured by Shemilt, Esplen, and Mann;[19] up to 270° these results are about 2% greater than those of the present work and between 270° and the critical the difference increases to 10%. The shape of the vapour-pressure curve in the critical region given by the results of Shemilt *et al.* is not confirmed by any other results we have examined and we believe they are in error. The fact that Young's values for vapour pressures tend to be low, the fair agreement existing between the present results and those of Kay and Donham for isobutyl alcohol, and the good agreement for butyl alcohol, all provide good support for the accuracy of our methods.

Decomposition of the butyl alcohols did not bar consistent results provided the procedure outlined in the Experimental section was followed, except that t-butyl alcohol became too unstable above 235°, and there are no experimental values between that temperature and the critical. Surprisingly, a reasonable value for the critical pressure was obtained (*i.e.*, it remained constant for an hour or more); presumably this was because two opposing tendencies, the rise in pressure due to decomposition and the fall in critical temperature with consequent fall in pressure, almost exactly counter-balanced each other. A satisfactory interpolation, based on the form of equation used for the other alcohols, was therefore possible. The results for s-butyl alcohol are also less reliable than for the remaining alcohols because of decomposition, although with this substance experimental measurements were made right up to the critical temperature.

Orthobaric Densities.—If ρ_L,ρ_V are the orthobaric densities of liquid and vapour, and t,t_c are respectively the temperature of the observation and the critical temperature, it is found that $(\rho_L - \rho_V)$ is approximately proportional to the cube root of $(t_c - t)$. This relation provides a check on the consistency of results since a smooth, and nearly linear, curve is obtained if $(\rho_L - \rho_V)$ is plotted against $(t_c - t)^{\frac{1}{3}}$. The line passes through the origin if the value of t_c used is correct. For exact representation of results the following equations were used:

$$\rho_L + \rho_V = 2\rho_c + a(t_c - t) - b(t_c - t)^2; \qquad (7)$$

$$\rho_L - \rho_V = c(t_c - t)^{\frac{1}{3}} - d(t_c - t)^2; \qquad (8)$$

ρ_c is the critical density and a, b, c, and d are constants for each substance. In Table 3 are listed the constants of these equations together with the experimental values on which they are based and the residuals of $(\rho_L - \rho_V)$ and $(\rho_L + \rho_V)$ from the calculated values. Jones and Bowden[20] have recommended the use of a fractional exponent other than one-third for expressing the temperature dependence of $(\rho_L - \rho_V)$; this form of equation does not seem to offer any advantage over that adopted here, which itself has the advantage that cube roots are easily available.

Equation (8) cannot be extrapolated beyond the range of the experimental results if the object is to obtain ρ_V since very large errors (and sometimes negative values) arise. Young[4] included a cubic term in his equation for the dependence of $(\rho_V + \rho_L)$ on temperature for alcohols, this has not been done here because the present results are not sufficiently precise to justify the introduction of another term.

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[18] Osborne and Meyers, *J. Res. Nat. Bur. Stand.*, 1934, **13**, 1.

[19] Shemilt, Esplen, and Mann, *Canad. J. Chem. Eng.*, 1959 (8), 142.

[20] Jones and Bowden, *Phil. Mag.*, 1946, **37**, 480.

TABLE 3.

Orthobaric densities of alcohols.

Temp. (c)	ρ_L obs.	ρ_V obs.	$\rho_L - \rho_V$ obs. − calc.	$\rho_L + \rho_V$ obs. − calc.	Temp. (c)	ρ_L obs.	ρ_V obs.	$\rho_L - \rho_V$ obs. − calc.	$\rho_L + \rho_V$ obs. − calc.
		Propyl					Isopropyl		
141·65°	0·6875	0·0091	−0·0015	0·0008	134·12°	0·6605	0·0146	0	0·0019
154·18	0·6700	0·0135	−0·0025	0·0009	149·18	0·6353	0·0193	0·0007	−0·0004
165·85	0·6533	0·0173	−0·0011	0·0006	163·23	0·6104	0·0278	0·0001	0·0004
176·93	0·6350	0·0220	−0·0013	−0·0008	170·57	0·5957	0·0332	−0·0007	0·0003
186·29	0·6204	0·0270	0·0006	0·0004	177·55	0·5815	0·0389	−0·0005	0·0006
192·77	0·6077	0·0314	−0·0005	−0·0003	185·30	0·5640	0·0456	−0·0002	−0·0004
201·01	0·5923	0·0384	−0·0009	0·0009	191·98	0·5480	0·0535	−0·0006	0·0001
206·40	0·5816	0·0413	0·0014	−0·0005	196·69	0·5357	0·0597	−0·0008	0
225·12	0·5376	0·0618	0·0018	−0·0009	201·74	0·5222	0·0669	−0·0001	−0·0001
232·54	0·5166	0·0742	0·0006	−0·0004	207·25	0·5055	0·0762	0·0001	−0·0003
240·11	0·4992	0·0885	0·0079	0·0061	213·19	0·4852	0·0888	−0·0002	−0·0002
245·33	0·4724	0·1034	−0·0017	0·0010	218·05	0·4658	0·1029	−0·0022	0·0009
250·22	0·4499	0·1187	−0·0030	0·0002	222·64	0·4418	0·1196	−0·0068	−0·0006
254·61	0·4267	0·1357	−0·0016	−0·0004	227·28	0·4165	0·1389	−0·0041	−0·0004
256·69	0·4127	0·1474	−0·0026	0·0001	231·07	0·3849	0·1660	−0·0061	0·0001
					233·53	0·3493	0·1975	−0·0132	−0·0006
		Butyl					Isobutyl		
166·93	0·6694	0·0142	−0·0002	0·0003	148·01	0·6775	0·0098	−0·0030	0·0027
173·57	0·6538	0·0176	0·0006	0·0002	161·25	0·6594	0·0140	−0·0038	0·0024
188·90	0·6401	0·0203	0·0010	0·0002	181·16	0·6297	0·0211	−0·0034	0·0008
196·32	0·6279	0·0238	−0·0006	−0·0005	186·40	0·6211	0·0238	−0·0038	0·0003
202·62	0·6182	0·0266	−0·0004	−0·0004	193·89	0·6111	0·0254	0·0011	0·0001
208·75	0·6087	0·0283	0·0015	−0·0014	203·73	0·5943	0·0317	0·0015	0·0002
216·63	0·5950	0·0341	0·0001	−0·0004	213·94	0·5746	0·0397	0·0012	−0·0003
226·57	0·5764	0·0409	0	−0·0008	223·89	0·5539	0·0490	0·0013	−0·0005
235·08	0·5592	0·0482	−0·0004	−0·0006	229·31	0·5416	0·0553	0·0007	−0·0003
242·44	0·5437	0·0563	0·0008	0·0007	236·17	0·5239	0·0657	−0·0017	0·0002
248·05	0·5314	0·0623	0·0004	0·0012	242·15	0·5088	0·0732	0·0005	−0·0004
256·95	0·5080	0·0740	0·0006	0·0003	248·70	0·4888	0·0852	−0·0002	−0·0010
260·90	0·4896	0·0880	−0·0140	0·0008	252·91	0·4743	0·0965	−0·0030	0·0008
275·70	0·4365	0·1224	−0·0138	0·0008	262·29	0·4313	0·1275	−0·0115	−0·0004
		s-Butyl					t-Butyl		
134·08	0·6944	0·0110	0	0·0016	146·67	0·6281	0·0217	0·0001	0·0012
150·87	0·6701	0·0156	−0·0002	0·0003	160·46	0·6035	0·0289	0·0008	0·0004
171·62	0·6377	0·0239	−0·0003	−0·0004	174·08	0·5754	0·0395	−0·0009	−0·0005
180·40	0·6233	0·0278	0·0008	−0·0008	183·05	0·5561	0·0474	−0·0001	−0·0008
188·20	0·6092	0·0330	0·0002	−0·0006	192·66	0·5330	0·0597	−0·0011	0·0004
200·10	0·5871	0·0418	0·0007	0·0001	200·37	0·5128	0·0701	0·0002	0·0005
205·41	0·5758	0·0462	−0·0002	−0·0012	207·41	0·4905	0·0835	−0·0014	0·0005
221·55	0·5390	0·0638	0·0003	0					
231·24	0·5132	0·0777	0·0008	0					

Constants in the equations.

$$\rho_L + \rho_V = 2\rho_c + a(t_c - t) - b(t_c - t)^2$$

$$\rho_L - \rho_V = c(t_c - t)^{\frac{1}{3}} - d(t_c - t)^2$$

Alcohol	10^3a	10^6b	c	10^6d	Alcohol	10^3a	10^6b	c	10^6d
Propyl	1·34	1·23	0·1410	1·29	Isobutyl	1·20	0·73	0·1368	1·00
Isopropyl ...	1·33	0·72	0·1420	1·53	s-Butyl	1·29	0·80	0·1378	0·74
Butyl	1·31	1·16	0·1357	1·28	t-Butyl	1·32	0·80	0·1308	0·96

DISCUSSION

Application of the Principle of Corresponding States.—Equations (7) and (8) for the orthobaric densities may be put in the reduced forms:

$$(\rho_L + \rho_V)/\rho_c = 2 + a'(1 - T_r) - b'(1 - T_r)^2, \qquad (9)$$

and

$$(\rho_L - \rho_V)/\rho_c = c'(1 - T_r)^{\frac{1}{3}} - d'(1 - T_r)^2, \qquad (10)$$

where T_r is the reduced temperature and a', b', c', and d' are constants simply related to those given earlier. Equations with $a' = 2{\cdot}54$, $b' = 1{\cdot}0$, $c' = 4{\cdot}123$, and $d' = 1{\cdot}1$ fit all the experimental results with nearly as good accuracy as do the individually calculated equations and deviations of $(\rho_L + \rho_V)/\rho_c$ and $(\rho_L - \rho_V)/\rho_c$ are no greater than $\pm 0{\cdot}003$. Young's values for ethanol are also fitted but those for $(\rho_L - \rho_V)$ of methanol show a systematic deviation. It seems that orthobaric densities in general behave closely according to the corresponding-states principle but, for example, for hydrocarbons the coefficients of $(1 - T_r)^2$ are smaller than for alcohols.

It is well known [21] that vapour pressures do not follow the simple law of corresponding states. Refinements of the law have been suggested by Riedel,[22] Rowlinson,[23] and Pitzer,[24] in which a parameter additional to the critical properties is introduced. The acentric factor, ω, of Pitzer, which is a measure of the departure of the vapour pressure of a substance from the behaviour of simple spherical molecules, ranges from 0·564 for methanol to 0·666 for isopropyl alcohol (*i.e.*, in the region of the normal boiling point the vapour pressures are only about one-quarter of what would be expected according to the simple corresponding-states principle). Application of Pitzer's correlation reproduces the experimental vapour pressures between $T_r = 0{\cdot}66$ and $T_r = 1$ with a maximum deviation of 8%.

Prediction of Critical Properties.—Application of these modified corresponding-states correlations to a substance requires a knowledge of its critical properties. These are frequently unknown, and much time has been devoted to the search for methods for their calculation; no method has more than a limited success because there is no direct relation between such macroscopic properties and molecular structure, but the study has a practical value provided its limitations are recognised.

The ratio of the absolute boiling point to the absolute critical temperature, T_b/T_c, is of value in predicting critical temperatures. For any series of compounds there is generally a rise in the ratio as the boiling point increases, and it was found earlier [2] that the ratio for hydrocarbons could be accurately expressed by $T_b/T_c = x + yT_b$, where x and y are constants. The values for these alcohols do not follow such an exact relation but it appears probable that the values for straight- and slightly branched-chain primary and secondary alcohols above C_4 may fall near the paraffin line [given by $T_b/T_c = 0{\cdot}51453 + (4{\cdot}6842 \times 10^{-4})T_b$]. Of the eight alcohols (including methanol and ethanol) for which data are available, this equation gives the critical temperatures of five within ±3°, the exceptions being methyl, isopropyl, and t-butyl alcohol.

Another way in which this ratio may be used is in a group-contribution method, such as has been worked out by Lydersen,[25] according to which

$$T_b/T_c = 0{\cdot}567 + \sum\Delta_T - (\sum\Delta_T)^2,$$

where $\sum\Delta_T$ is the summation of the contributions from all the groups present in the molecule. This treatment gives results which are in fair agreement (±5°) with the experimental values, except that the predicted value for n-butyl alcohol is 6·7° low and that for isopropyl alcohol is 12·2° high. A similar procedure gives fair agreement with the experimental values for the critical pressures and critical volumes (Table 1).

It is of interest that the critical pressures of most materials are higher than those found by extrapolation of the appropriate low-pressure Antoine equation. The reverse is true for the alcohols: the critical pressures of methanol, ethanol, and the six alcohols

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[21] Cope, Lewis, and Weber, *Ind. Eng. Chem.*, 1931, **23**, 887.

[22] Riedel, *Chem.-Ing.-Tech.*, 1954, **26**, 83.

[23] Rowlinson, *Trans. Faraday Soc.*, 1954, **50**, 647.

[24] Pitzer, *J. Amer. Chem. Soc.*, 1955, **77**, 3433.

[25] Lydersen, " Estimation of Critical Properties of Organic Compounds by the Method of Group Contributions," University of Wisconsin, Engineering Experiment Station, Report no. 3, 1955; quoted *in extenso* by Reid and Sherwood, " The Properties of Gases and Liquids, Their Estimation and Correlation," McGraw Hill Book Company Inc., New York, 1958.

studied in this work fall into two groups; those in the first (methanol, ethanol, and the propanols) are 11—13% below the extrapolated values, and those in the second (butyl alcohols) are 5—6% below the extrapolated values. The different behaviour of the butyl alcohols suggests that in the alcohol series, members above C_4 will show a progressive diminution of the effect of the hydroxyl group on physical properties, and that higher alcohols will behave more like non-hydroxylic materials in this respect.

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