364. *Thermodynamic Properties of Organic Oxygen Compounds. Part VIII.* Purification and Vapour Pressures of the Propyl and Butyl Alcohols.*

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The purification of n- and iso-propyl and n-, iso-, s-, and t-butyl alcohol is described. The purities of the compounds have been established by cryoscopic methods or by gas chromatography. The freezing point of t-butyl alcohol and the vapour pressures of all the alcohols have been measured and the latent heats of vaporization have been calculated.

ACCURATE measurements of the physicochemical properties of industrially important, organic, oxygen compounds are being made in this Laboratory with samples of high purity. Previous publications on alcohols from this Laboratory have given results of measurements of second virial coefficients of the propyl and the butyl alcohols [1] and the heat of combustion of butan-1-ol.[2] The methods used to purify the alcohols and the results of vapour-pressure measurements on the pure compounds in the pressure range 250—1000 mm. Hg are given below.

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* Part VII, Andon, Counsell, Herington, and Martin, *Trans. Faraday Soc.*, in the press.

[1] Cox, *Trans. Faraday Soc.*, 1961, **57**, 1674.

[2] Gundry, Head, and Lewis, *Trans. Faraday Soc.*, 1962, **58**, 1309.

Previous measurements[3-7] of the vapour pressures of these alcohols were often of lower precision than is attainable by modern techniques or were made on materials of undefined purity. The compounds used in the present work were dried by treatment with calcium hydride and were >99·9% pure. The precision of the vapour-pressure results was better than ±0·1 mm. Hg. The new values for the vapour pressure of n-propyl and n-butyl alcohol are appreciably lower than the recent results of Brown and Smith[6] and those for n-butyl alcohol are lower than, but in better agreement with, the values of Butler *et al.*[4] The pressures reported by Butler *et al.*[4] for iso- and t-butyl alcohol are considerably lower but for s-butyl alcohol they are higher than the values now reported. Parks and Barton's values[3] for isopropyl and t-butyl alcohol differ by several mm. from the new measurements. The values of the boiling points at 760 mm. given below agree to better than 0·1° with recently published[8] selected values for all these compounds except t-butyl alcohol.

An accurate freezing point was measured for t-butyl alcohol and the value obtained was identical with that of Simonsen and Washburn.[9] Values for the freezing points of the other alcohols are not reported because they either undercooled considerably before crystallizing or formed glasses.

EXPERIMENTAL

Purification.—All the specimens were purified by distillation and t-butyl alcohol was further fractionally frozen. Commercially available materials were twice fractionally distilled in columns of 50—75 theoretical plates and the best fractions were selected by examination of gas–liquid chromatograms (column packing: 10% of tetrakis-*N*-2-hydroxyethylethylenediamine on Celite; 75°; detection by argon ionisation). Purity was assessed by comparison with samples containing known amounts of added impurities. Usually the impurities were selected from the adjacent homologues of the main component. Further purification by fractional freezing was possible only with t-butyl alcohol since, of the other alcohols, isopropyl and n-butyl crystallized only after prolonged undercooling, and n-propyl and iso- and s-butyl alcohol solidified as glasses. For this reason, it was not possible to establish the concentration of impurity in the last three compounds by cryoscopy.

The methods used for the quantitative determination of purity by melting-point procedure and for the measurement of the freezing point and cryoscopic constant have been described.[10,11] In all purity determinations by cryoscopy, 2,2,4-trimethylpentane was used to produce additional depression of the freezing point. Before determination of purity, the samples were dried over calcium hydride and the pure compounds were stored in sealed containers

TABLE 1.

Purification and purity of alcohols.

Alcohol	Quality of starting material	No. of theor. plates used in each distn.	No. of distns.	Purity by gas chromatography (moles %)	Purity by cryoscopy method	moles %
n-Propyl ...	Tech.	50	2	99·94		
Isopropyl...	" AnalaR "	75	2	99·96	M. p.	99·96
n-Butyl ...	Tech.	50	2	99·94	,,	99·92
Isobutyl ...	" AnalaR "	50	2	99·93		
s-Butyl ...	,,	50	3	99·95		
t-Butyl ...	,,	50	2 *	—	F. p.	99·96

* The sample was also fractionally frozen twelve times.

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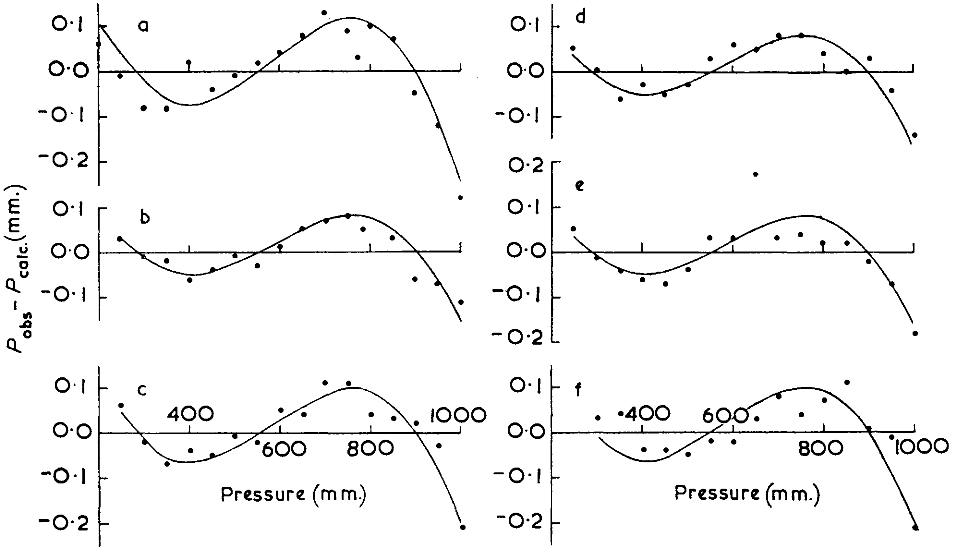
[3] Parks and Barton, *J. Amer. Chem. Soc.*, 1928, **50**, 24.
[4] Butler, Ramchamdemi, and Thomson, *J.*, 1935, 280.
[5] Williamson and Harrison, *J. Chem. Phys.*, 1957, **26**, 1409.
[6] Brown and Smith, *Austral. J. Chem.*, 1959, **12**, 407.
[7] Mathews and McKetta, *J. Phys. Chem.*, 1961, **65**, 758.
[8] " Selected Values of Properties of Chemical Compounds," Manufacturing Chemists Association Research Project, Pittsburgh, 1960.
[9] Simonsen and Washburn, *J. Amer. Chem. Soc.*, 1946, **68**, 235.
[10] Herington, *Analyt. Chim. Acta*, 1957, **17**, 15.
[11] Handley, *Analyt. Chim. Acta*, 1957, **17**, 115.

under dry nitrogen. The purification procedures and the results of purity measurements are summarized in Table 1.

The following properties of t-butyl alcohol were also measured: f. p. 25·61°; depression produced by one mole % of impurity: 1·056°; calc. f. p. for 100% purity: 25·70°.

Vapour Pressure–Temperature Relations, Normal Boiling Points, Values of $(dP/dt)_{760\,\text{mm.}}$*, and Latent Heats of Vaporization.*—The vapour pressures were measured by the ebulliometric method previously described.[12,13] Results are given in Table 2. They were fitted to the Antoine equation, $\log_{10} P = A - B/(t + C)$, which generally gives a satisfactory fit for accurate vapour-pressure data and has the advantage over other vapour-pressure equations in ease of calculation of the b. p. at any pressure within the range of measurements. The differences, shown in the Figure, between observed vapour pressures and those calculated from the equations were generally less than 0·1 mm. Hg. However, the Figure shows that the deviations from the Antoine equations were not randomly distributed and followed the same trend for all six alcohols. The Antoine equations give the vapour pressure of these alcohols to 0·1 mm. Hg, but, to utilise the full accuracy of the data, it is necessary to add to the values calculated by the equations small corrections which can be read off from the Figure. Similarly, the values of dP/dt calculated from the Antoine equations require small corrections which can be derived from the Figure. These corrections are negligible at 760 mm. and, at other pressures, very small, *e.g.*, for isobutyl alcohol, $(dP/dt)_{1000\,\text{mm. Hg}}$ was decreased from 36·04 to 35·93 mm. Hg/°c.



Differences between observed and calculated vapour pressures for (a) n-propyl, (b) isopropyl, (c) n-butyl, (d) isobutyl, (e) s-butyl, and (f) t-butyl alcohol.

The Antoine equations and the Figure were used to calculate the boiling points at 760 mm. and values of $(dP/dt)_{760\,\text{mm.}}$. The latent heats of vaporization were calculated by using the equation $\Delta H_v = T[(\boldsymbol{R}T/P) + B - V_L]dP/dt$, where B is the second virial coefficient in the equation of state, $PV = \boldsymbol{R}T + BP$, and V_L is the molal volume of the liquid. The following values were used in the calculations: 0°c = 273·15°K; $\boldsymbol{R}$ = 1·98725 cal. deg.$^{-1}$ mole^{-1} = 0·082057 l. atm. deg.$^{-1}$ mole^{-1}. The molecular weights were calculated from the 1961 Table of International Atomic Weights,[14] based on ^{12}C = 12. Using these values instead of atomic weights based on the previous chemical scale affected the physical properties now reported by amounts less than the experimental errors. Second virial coefficients of the alcohols have been published [1] and the molal volumes were calculated from published densities.[8] It is

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[12] Herington and Martin, *Trans. Faraday Soc.*, 1953, **49**, 154.
[13] Biddiscombe and Martin, *Trans. Faraday Soc.*, 1958, **54**, 1316.
[14] *Pure Appl. Chem.*, 1962, **5**, 258.

TABLE 2.

Vapour pressures of the alcohols.

t in °c; P in mm. Hg at 0°c and standard gravity.

	P		P	t	P	t	P		P
				n-Propyl					
65·599	199·37	81·174	400·79	91·026	599·68	97·594	772·81	103·166	949·94
70·256	247·70	83·931	449·84	93·143	651·62	98·512	800·06	104·576	999·54
74·507	300·03	86·490	499·83	94·955	698·99	100·155	850·62		
78·023	350·10	88·856	550·04	96·837	751·04	101·667	899·35		
				Isopropyl					
56·779	247·85	69·704	449·52	76·455	600·02	81·931	750·65	86·550	900·43
60·798	300·14	72·131	499·54	78·431	651·21	82·958	782·04	87·922	949·38
64·091	349·61	74·372	549·69	80·160	698·88	85·090	850·70	89·261	999·22
67·088	400·33								
				n-Butyl					
89·212	247·86	103·636	449·53	111·161	598·97	117·393	751·13	122·564	899·66
93·662	299·83	106·367	499·78	113·429	651·11	119·193	800·35	124·155	949·79
97·357	349·54	108·885	550·03	115·324	697·52	120·940	850·66	125·686	1000·00
100·742	400·91								
				Isobutyl					
80·207	247·96	94·205	449·73	101·546	599·92	107·568	751·21	112·624	900·61
84·524	299·99	96·815	499·15	103·696	650·79	109·326	800·68	114·101	948·40
88·063	349·02	99·289	549·99	105·589	698·46	111·017	850·70	115·623	999·73
91·381	400·86								
				s-Butyl					
72·392	247·75	86·112	449·91	93·303	600·13	99·201	751·23	104·186	901·34
76·600	299·59	88·693	499·85	95·394	650·76	100·931	800·87	105·647	949·55
80·131	349·65	91·068	549·69	97·252	698·26	102·611	851·57	107·146	1001·12
83·340	400·89								
				t-Butyl					
60·781	300·46	69·707	450·08	76·439	598·90	81·996	749·56	86·730	900·41
64·054	349·69	72·138	499·89	78·509	651·90	83·625	799·03	88·127	949·27
67·076	400·77	74·338	548·75	80·198	697·88	85·272	851·67	89·560	1001·39

TABLE 3.

Constants of Antoine equation, $\log_{10} P = A - B/(t + C)$; normal boiling points; $(\mathrm{d}P/\mathrm{d}t)_{760\ \mathrm{mm.}}$; and molar latent heats of vaporization.

Alcohol	Temp. range	A	B	C	B. p./760 mm.	$(\mathrm{d}P/\mathrm{d}t)_{760\ \mathrm{mm.}}$ (mm. Hg/°c)	Heat of vaporization at 760 mm. (cal./mole)
n-Propyl ...	65—105°	7·72911	1428·977	197·585	97·151°	28·79	9950
Isopropyl ...	56—90	7·72589	1351·627	196·726	82·241	30·39	9650
n-Butyl	89—126	7·36762	1307·445	173·670	117·726	26·95	10,350
Isobutyl ...	80—116	7·29914	1233·095	171·197	107·888	27·70	10,050
s-Butyl	72—108	7·20428	1158·543	168·452	99·513	28·23	9800
t-Butyl	60—90	7·20616	1094·341	170·658	82·347	29·92	9400

known that virial coefficients higher than the second are required to correct for non-ideal behaviour of some alcohol vapours and consequently, as the values of the heat of vaporization obtained by using the above equation may be in error by about 1%, the calculated values were rounded to the nearest 50 cal./mole. The constants of the Antoine equations and the values of the properties calculated are given in Table 3.

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