677. *Thermodynamic Properties of Organic Oxygen Compounds. Part XV.*[1] *Purification and Vapour Pressures of Some Ketones and Ethers*

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Samples of four ketones (methyl ethyl, diethyl, methyl propyl, and ethyl propyl) and three ethers (methyl phenyl, ethyl phenyl, and diphenyl) of purity greater than 99·9 moles %, as established by cryoscopy, have been prepared. Their freezing points and the vapour pressures in the range 150—1000 mm. have been measured. Antoine and Kirchhoff equations have been fitted to the experimental vapour pressures. Normal boiling points and heats of vaporisation have been calculated.

The vapour pressures of the four ketones and three ethers with which this Paper is concerned have been measured previously (methyl ethyl ketone,[2-7] diethyl ketone,[4-6,8] methyl

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propyl ketone,[3,4,6,7] ethyl propyl ketone,[9] methyl phenyl ether,[4,5,10] ethyl phenyl ether,[4,5] and diphenyl ether [4,5,11]). Of the observations published, some cover only a limited temperature range and most appear to be of a lower precision than those obtained by comparative ebulliometry on samples of known high purity. The freezing points of the ketones have also been measured, and the results differ by 0·4—0·8° from previously published values.[4,12,13]

Antoine equations, $\log_{10} P$ (mm.) $= A - B/(C + t)$, and Kirchhoff equations, $\log_{10} P$ (mm.) $= a - b/T - c \log T$, have been fitted to the experimental vapour pressures (t is the temperature in °c, $T = t + 273{\cdot}15°$, and A, B, C, a, b, and c are constants). The Antoine equation usually gives a close fit for accurate experimental data, and permits easy calculation of the temperature corresponding to any particular value of pressure. The Kirchhoff equation for vapour pressure has a sounder theoretical basis but possesses the disadvantage that temperatures cannot readily be calculated from pressures. The results of the measurements tabulated in this Paper have a standard deviation ($P_{obs.} - P_{calc.}$) of $\pm 0{\cdot}02$ mm. for the Antoine equations and $\pm 0{\cdot}1$ mm. for the Kirchhoff equations.

Experimental

Purification.—Commercial samples of the four ketones were distilled under reduced pressure (700 mm.) through columns of 100 theoretical plates with a reflux ratio of 100 : 1. A series of fractions was collected, and those of highest purity (gas chromatography) were combined. The boiling range and gas chromatograms of methyl ethyl ketone and ethyl propyl ketone indicated the absence of impurities. Further purification of diethyl ketone and methyl propyl ketone was necessary; fractional freezing was effective for the former but not for the latter, which was purified by azeotropic distillation at 700 mm. with water. The ketones were dried over calcium sulphate (methyl ethyl and methyl propyl) or calcium hydride (diethyl and ethyl propyl), and redistilled.

Pure samples of methyl phenyl ether and ethyl phenyl ether were prepared from commercial products by fractional distillation at 650 mm. through 100-plate columns. Fractions of constant boiling point which showed no impurities (gas chromatography) were combined, dried over calcium hydride, and redistilled under reduced pressure. Commercial diphenyl ether was distilled at atmospheric pressure from flask to receiver without the use of a column, and was further purified by fractional freezing. In the later stages of purification, all the compounds were kept under dry nitrogen.

Freezing Points, and the Quantitative Determination of Purity.—The purities of six of the compounds were determined by melting- or freezing-point procedures.[14,15] Initial freezing points and the freezing-point depressions produced by addition of measured amounts of 2,3,3-trimethylpentane were found by means of a U-tube apparatus.[14] These methods could not be used for methyl propyl ketone because of its erratic freezing behaviour; its purity was assessed by low-temperature calorimetry.[16] The results of the measurements are given in Table 1.

Vapour Pressure–Temperature Relationships, Normal Boiling Points, Values of (dP/dt) *at* 760 *mm., and Latent Heats of Vaporisation.*—Vapour pressures from near 150 or 200 mm. to near 1000 mm. were measured in an ebulliometric apparatus.[17] The apparatus and procedure were as described previously except that calculations were carried out on a digital computer, which calculated temperatures and corresponding vapour pressures from bridge readings of the platinum resistance thermometers, and also the following. Antoine equations and Kirchoff equations were fitted by the method of least squares to the observed values of t and P for each compound, and the values of pressure at the experimental temperatures were calculated from both equations for each compound. The experimental vapour pressures are given in Table 2, and

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TABLE 1

Purities and freezing points

Compound	Purity (moles %) and method of assessment	F. p. of sample	F. p. for 100% purity
Methyl ethyl ketone	99·95 ± 0·01 (f. p.)	−86·73° ± 0·01°	−86·69° ± 0·01°
Diethyl ketone	99·95 ± 0·01 (f. p.)	−39·00 ± 0·01	−38·97 ± 0·01
Methyl propyl ketone	99·93 ± 0·01 (calorimetric)	−76·88 ± 0·01	−76·86 ± 0·01
Ethyl propyl ketone	99·96 ± 0·01 (m. p.)	−55·67 ± 0·01	−55·65 ± 0·01
Methyl phenyl ether	99·993 ± 0·002 (m. p.)	—	—
Ethyl phenyl ether	99·96 ± 0·01 (m. p.)	—	—
Diphenyl ether	99·997 ± 0·001 (m. p.)	—	—

TABLE 2

Vapour pressures (t in °C; P in mm. Hg at 0° and standard gravity)

t	P	t	P	t	P	t	P
			Methyl ethyl ketone				
42·788	199·28	64·005	449·69	74·839	651·42	83·161	850·78
48·148	247·70	67·009	499·73	76·950	698·03	85·013	901·02
53·026	299·75	69·734	548·93	79·221	751·08	86·715	949·18
57·080	349·46	72·343	599·55	81·268	801·72	88·444	1000·23
60·821	401·05						
			Diethyl ketone				
56·544	153·32	82·114	401·08	96·897	650·69	105·737	850·67
63·032	198·99	85·494	449·88	99·177	698·25	107·682	900·53
68·735	247·83	88·612	499·03	101·566	751·03	109·486	948·79
73·908	300·09	91·605	550·15	103·724	801·33	111·303	999·49
78·158	349·45	94·314	599·94				
			Methyl propyl ketone				
56·649	153·31	82·326	401·03	97·179	650·75	106·114	852·16
63·184	199·11	85·708	449·64	99·470	698·36	108·023	900·92
68·897	247·82	88·893	499·63	101·845	750·53	109·830	949·09
74·077	299·96	91·834	549·67	104·031	801·30	111·655	999·78
78·340	349·29	94·549	599·34				
			Ethyl propyl ketone				
75·613	153·19	102·558	400·90	118·125	650·07	127·509	851·28
82·486	199·14	106·128	449·80	120·532	697·61	129·522	900·24
88·481	247·87	109·419	498·99	123·080	750·99	131·435	948·81
93·872	299·58	112·558	549·82	125·345	801·07	133·365	999·80
98·385	349·27	115·416	599·62				
			Methyl phenyl ether				
109·876	199·12	135·078	449·66	147·890	650·54	157·810	850·44
116·255	247·70	138·640	499·65	150·429	697·72	160·009	900·72
122·045	299·77	141·919	549·54	153·143	751·08	162·087	950·32
126·854	349·43	145·003	599·99	155·554	801·21	164·114	1000·80
131·266	400·72						
			Ethyl phenyl ether				
117·431	153·32	146·908	400·94	163·972	650·77	174·190	851·22
124·908	198·96	150·795	449·59	166·622	698·70	176·407	900·51
131·478	247·70	154·432	499·32	169·315	750·31	178·511	949·37
137·430	299·86	157·829	549·63	171·821	800·98	180·608	1000·09
142·338	349·27	160·982	599·84				
			Diphenyl ether				
204·213	199·18	235·186	449·40	250·991	650·61	263·290	851·84
212·102	248·07	239·618	499·95	254·089	697·34	265·939	901·01
219·226	300·19	243·667	550·00	257·458	751·14	268·416	949·02
225·105	349·61	247·413	599·79	260·469	801·86	270·949	1000·08
230·561	401.15						

the constants of the vapour-pressure equations in Table 3. The values of the normal boiling points, (dP/dt) at 760 mm., and latent heats of vaporisation calculated from the Antoine equations are given in Table 4. Latent heats of vaporisation, ΔH_v, at the normal boiling point were calculated from 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 molar volume of the liquid. Values of B were calculated from measured [18] or estimated (T_c and P_c for ethyl phenyl

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TABLE 3

Constants of vapour-pressure equations

	Antoine equation $\log P = A - B/(C + t)$			Kirchhoff equation $\log P = a - b/T - c \log T$		
Compound	A	B	C	a	b	c
Methyl ethyl ketone	7·06376	1261·455	221·982	19·48332	2328·00	3·92657
Diethyl ketone	7·02427	1309·653	214·118	22·02258	2614·85	4·72805
Methyl propyl ketone ...	7·01753	1311·145	214·693	21·71880	2594·12	4·63307
Ethyl propyl ketone	7·00083	1365·798	208·007	22·90884	2812·27	4·97916
Methyl phenyl ether	7·05236	1489·756	203·543	22·84299	3033·20	4·88720
Ethy phenyl ether	7·01980	1507·267	194·357	24·97404	3295·20	5·53743
Diphenyl ether	7·01188	1800·415	177·826	24·66548	3897·50	5·30117

TABLE 4

Normal boiling points, dP/dt at 760 mm., second virial coefficients, molar volumes of liquids, and molar heats of vaporisation

Compound	B. p. at 760 mm.	(dP/dt) at 760 mm. (mm. Hg/°c)	B (ml.)	V_L (ml.)	ΔH_v at 760 mm. (cal./mole)
Methyl ethyl ketone ...	79·589°	24·27	−1085	100	7570
Diethyl ketone	101·959	22·94	−1250	122	8060
Methyl propyl ketone ...	102·260	22·84	−1260	122	8040
Ethyl propyl ketone ...	123·496	21·75	−1430	144	8520
Methyl phenyl ether ...	153·580	20·44	−1300	129	9330
Ethyl phenyl ether	169·806	19·89	−1530	151	9730
Diphenyl ether............	257·997	16·59	−1995	195	11,620

ether and P_c for diphenyl ether) [19] values of the critical temperatures and critical pressures by the use of Pitzer and Curl's equation.[20] The molar volumes, V_L, at the boiling points were obtained from volume equivalents of the elements.[21]

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