31. *Physical Properties and Chemical Constitution. Part V. Alkyl Ketones.*

By David M. Cowan, George H. Jeffery, and Arthur I. Vogel.

The refractive indices for the C, D, F and G′ lines at 20·0° and the surface tensions and densities over a range of temperatures have been determined for the following pure ketones: acetone, methyl ethyl, diethyl, methyl *n*-propyl, ethyl *n*-propyl, di-*n*-propyl, methyl *n*-butyl, methyl *iso*butyl, methyl *n*-amyl, methyl *n*-hexyl, and di*iso*butyl ketones. The molecular refractivities and the parachors have been evaluated.

A detailed study has been made of the preparation of diethyl, methyl *n*-propyl, ethyl *n*-propyl, and di-*n*-propyl ketones by passage of the appropriate acids over manganous oxide at 400°.

In the present investigation the refractive indices for the C, D, F, and G′ lines at 20·0°, the surface tensions and densities over a range of temperatures have been determined for the 11 ketones enumerated above, which were purified through their semicarbazones. Some of these ketones have been studied by other workers, *e.g.*, the surface tension and densities by Morgan and Owen (*J. Amer. Chem. Soc.*, 1911, **33**, 1713), by Morgan and Stone (*ibid.*, 1913, **35**, 1505), and by Morgan and Kramer (*ibid.*, p. 1834), and the refractive indices by Eisenlohr (*Z. physikal. Chem.*, 1910, **55**, 588), but the compounds used were purified by fractionation only, and their absolute purity is therefore open to question. The results of other investigators which appear to be of value are given for comparison in the experimental section.

The values for the parachor, molecular refractivity for the D line, molecular refraction coefficient $Mn_D^{20°}$, and dispersions $[R_L]_{F-C}$ and $[R_L]_{G'-C}$ for the homologous ketones are collected in Table I. The parachor for methyl *n*-hexyl ketone is not regarded as very satisfactory since the substance does not appear to wet glass completely and its contact angle is probably slightly removed from zero; the difference for this compound is therefore not included in the table. The figures for di*iso*butyl ketone are given since those for di-*n*-butyl ketone are not available. The chief feature of these results is the steady increase in the parachor difference for CH_2 in passing from acetone to methyl *n*-amyl ketone: this may be due largely to the Thorpe–Ingold valency deflexion effect. Table II contains the corresponding values for isomeric ketones.

Table I.

Ketone.	Parachor.	Diff.	$[R_L]_D$.	Diff.	$Mn_D^{20°}$.	Diff.	$[R_L]_{F-C}$.	$[R_L]_{G'-C}$.
Me,Me	161·6		16·11		79·00		0·26	0·39
		37·9		4·56		20·41		
Me,Et	199·5		20·67		99·41		0·32	0·50
		38·5		4·58		20·33		
Me,Pr^{α}	238·0		25·25		119·74		0·39	0·59
		39·5		4·79		20·55		
Me,Bu^{α}	277·5		30·04		140·29		0·48	0·72
		41·6		4·74		20·54		
Me,Am^{α}	319·1		34·78		160·83		0·55	0·84
				4·51		20·64		
Me,He^{α}	355·7		39·29		181·47		0·62	0·91
Me,Me	161·6		16·11		79·00		0·26	0·39
		2 × 37·9		2 × 4·55		2 × 20·46		
Et,Et	237·4		25·21		119·91		0·39	0·59
		2 × 38·9		2 × 4·65		2 × 20·37		
Pr^{α},Pr^{α}	315·1		34·50		160·64		0·54	0·82
		2 × 38·3		2 × 4·73		2 × 20·10		
Bu^{β},Bu^{β}	391·6		43·96		200·84		0·70	1·05

Diethyl, methyl *n*-propyl, ethyl *n*-propyl, and di-*n*-propyl ketones were prepared from the corresponding acids by passage over manganous oxide at 400°. This catalyst was first employed by Sabatier and Mailhe (*Compt. rend.*, 1914, **158**, 831) but no experimental details were given, so the reaction has been investigated in detail. The catalyst could

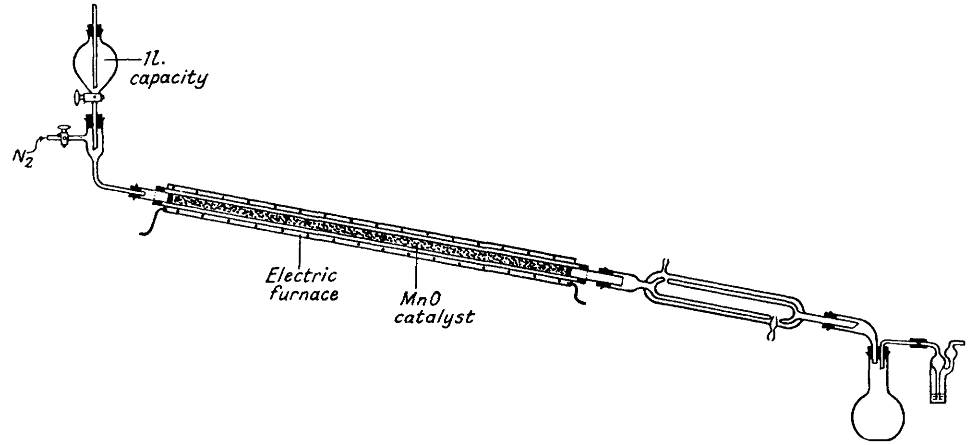
TABLE II.

Ketone.	Parachor.	$[R_L]_D$.	$Mn_D^{20°}$.	$[R_L]_{F-C}$.	$[R_L]_{G'-C}$.	Ketone.	Parachor.	$[R_L]_D$.	$Mn_D^{20°}$.	$[R_L]_{F-C}$.	$[R_L]_{G'-C}$.
Me,Pr^a	238·0	25·25	119·74	0·39	0·59	Et,Pr^a	277·3	29·96	140·30	0·47	0·80
Et′,Et	237·4	25·21	119·91	0·39	0·59	Me,Bu^a	277·5	30·04	140·29	0·48	0·72
Pr^a,Pr^a	315·1	34·50	160·64	0·54	0·82	Me,Bu$^\beta$	276·5	30·15	139·78	0·48	0·72
Me,Am^a	319·1	34·78	160·83	0·55	0·84						

not be employed for the preparation of methyl *n*-butyl and methyl *n*-amyl ketone owing to the production of resinous compounds which tended to block the tube containing the catalyst.

EXPERIMENTAL.

Preparation of Ketones from Acids with Manganous Oxide as Catalyst.—Construction of electric furnace. A thin-walled iron tube, 78 cm. long and 2·8 cm. in internal diameter, was securely wrapped with asbestos cloth (*ca.* 2 mm. thickness), and the central 70 cm. was evenly wound with about 10 m. of nichrome wire, No. 30 S.W.G., covered with two thicknesses of the asbestos cloth and held in position by copper wire ligatures; the insulation was completed by wrapping a further two thicknesses of the asbestos cloth round the tube. With a mains voltage of 220 and the introduction of a resistance in the circuit, any temperature between 130° and 450° could be readily produced; *e.g.*, with a current of 1·0 amp. the temperature is 200°, and with 1·5 amps. it is 400°. The temperature was constant to within 1° up to 28 cm. from the ends of the iron tube and to within 5° 20 cm. from the ends.



Preparation of the manganous oxide catalyst. Small pieces of pumice (3—8 mesh) sufficient to fill a length of 70 cm. in a tube of 1·5 cm. diameter were thoroughly stirred with a thick suspension of 40 g. of freshly precipitated manganous carbonate (from A.R. manganous chloride and A.R. sodium carbonate); the volume of water used should be so adjusted that most of it is absorbed by the pumice, since if much water has to be evaporated the manganous carbonate does not adhere satisfactorily. The beaker was heated on a hot plate with vigorous stirring until most of the water was expelled, then transferred to a shallow porcelain basin and the heating continued until the lumps no longer clung together: great care must be taken to avoid local over-heating.

Description of apparatus and method of use. The catalyst is packed into a hard-glass or Pyrex tube, 100 cm. long and 1·5 cm. in diameter, and held in position by means of plugs of purified glass wool. The glass tube is then inserted into the electric furnace and fixed centrally with the aid of asbestos pulp inserted in the annular space at the two ends. The whole apparatus is then fitted up as shown in the figure; attention is particularly directed to the constant-pressure device in the separating funnel, which permits of dropping the liquid in the funnel at a constant rate without the need of adjustment during the addition. The pumice is first heated in a gentle stream of nitrogen for 8 hours at 400—450° in order to convert the manganous carbonate into manganous oxide, and then allowed to cool in a stream of this gas. The acid (or mixture of acids), previously purified by careful fractionation, is then placed in the separating funnel, the tap of which is smeared with a special vacuum grease (*e.g.*, Edwards's, soft for stop-cocks), the furnace heated to 400° whilst a slow stream of nitrogen is passed through the catalyst tube, and the acid allowed to drop from the funnel at such a rate that not more than one bubble of gas per second passes through the " bubbler " at the extreme end of the apparatus; the stream of nitrogen is, of course, stopped during the addition of the acid. The apparatus requires very little attention, and 72—94 hours are usually required for circulating 1 l. of acid over the catalyst. The distillate consists of two layers; the lower, aqueous layer is separated, the ketone salted out with potassium carbonate, and added to the main ketonic layer. The combined liquids are then treated with small quantities of potassium carbonate until effervescence ceases (whereby the ketone is both freed from acid and dried), filtered, and fractionated. For the simple ketones an ordinary 4-pear column is employed; for the mixed ketones a rough separation is first effected with a 12″ glass-bead column, and the final separation by several distillations though a 5′ Dufton column provided with a spiral of nickel wire. The results of the various experiments are collected below.

Prepn.	Wt. of acids used.*	Ketone obtained.	B. p. range of ketones.	Wt. of ketone, g.	Yield, %, of ketone calc. on smaller wt. of acid.
$COEt_2$	738 g. P.A.	$COEt_2$	101—103°	252	59
$COPr^{\alpha}_2$	840 g. B.A.	$COPr^{\alpha}_2$	142—143	270	50
$COMePr^{\alpha}$	480 g. (8 mols.)	$COMe_2$	56—57	72	31
	A.A. + 352 g.	$COMePr^{\alpha}$	102—104	122	35·5
	(4 mols.) B.A.	$COPr^{\alpha}_2$	144—146	36	16
	240 g. (4 mols.)	$COMe_2$	56—57	37	32
	A.A. + 352 g.	$COMePr^{\alpha}$	102—104	116	34
	(4 mols.) B.A.	$COPr^{\alpha}_2$	144—146	43	19
	120 g. (2 mols.)	$COMe_2$	56—57	9	15·5
	A.A. + 528 g.	$COMePr^{\alpha}$	102—104	73	42
	(6 mols.) B.A.	$COPr^{\alpha}_2$	144—146	105	31
	360 g. (6 mols.)	$COMe_2$	56—57	75	43
	A.A. + 176 g.	$COMePr^{\alpha}$	102—104	75	44
	(2 mols.) B.A.	$COPr^{\alpha}_2$	144—146	nil	0
	120 g. (2 mols.)	$COMe_2$	56—57	12	21
	A.A. + 352 g.	$COMePr^{\alpha}$	102—104	75	44
	(4 mols.) B.A.	$COPr^{\alpha}_2$	144—146	62	27
$COEtPr^{\alpha}$	592 g. (8 mols.)	$COEt_2$	100—102	204	59
	P.A. + 352 g.	$COEtPr^{\alpha}$	122—124	195	49
	(4 mols.) B.A.	$COPr^{\alpha}_2$	144—146	35	15
	296 g. (4 mols.)	$COEt_2$	100—102	98	57
	P.A. + 352 g.	$COEtPr^{\alpha}$	122—124	214	54
	(4 mols.) B.A.	$COPr^{\alpha}_2$	144—146	66	29
	148 g. (2 mols.)	$COEt_2$	100—102	18	21
	P.A. + 352 g.	$COEtPr^{\alpha}$	122—124	81	41
	(4 mols.) B.A.	$COPr^{\alpha}_2$	144—146	58	25
	148 g. (2 mols.)	$COEt_2$	100—102	27	31
	P.A. + 528 g.	$COEtPr^{\alpha}$	122—124	132	66
	(6 mols.) B.A.	$COPr^{\alpha}_2$	144—146	104	30
	444 g. (6 mols.)	$COEt_2$	100—102	157	62
	P.A. + 172 g.	$COEtPr^{\alpha}$	122—124	35	18
	(2 mols.) B.A.	$COPr^{\alpha}_2$	144—146	nil	0

* A.A. = Acetic acid; P.A. = propionic acid; B.A. = butyric acid.

General Method of Purification of Ketones.—The ketones were first distilled, and a fraction boiling over 1—2° collected. This was converted into the semicarbazone, which was recrystallised to constant m. p., dried in a vacuum desiccator over calcium chloride and paraffin wax (drying at 100° often produced slight superficial discoloration), refluxed for 30 minutes with excess of a solution of " AnalaR " oxalic acid, and the ketone separated by steam distillation and salting out with " AnalaR " potassium carbonate. (No ether was employed in the extraction because of the danger of the presence of ketonic substances and the difficulty of complete separation by fractional distillation particularly for the ketones of low b. p.) The ketone was dried with anhydrous sodium sulphate, and distilled twice through an all-Pyrex glass apparatus. The thermometers were standardised against a set which had recently been calibrated at the N.P.L.

Physical Measurements.—The densities, surface tensions, and refractive indices were determined exactly as described in earlier papers of this series (compare Part III; J., 1938, 1325). Two surface-tension apparatus *A* and *B* were employed, the constants of which, when determined with pure benzene, were 1·8725 and 2·3449 respectively.

In the tabulated results, t is the temperature, h the observed difference in height (in mm.) in the two arms of the U-tube, H the corrected value, $d_{4^\circ}^{t^\circ}$ the density (calculated from the observed densities by assuming a linear variation with temperature), γ the surface tension (dynes/cm.) computed from the equation $\gamma = KHd$, P the parachor, M the molecular weight, and $Mn_{\mathrm{D}}^{20\cdot0^\circ}$ the molecular refraction coefficient. The parachor was calculated in the usual way, allowance for the density of the vapour (calculated by Sugden's method; J., 1925, **127**, 1540) being made when the temperature of measurement was within 60° of the b. p. The number in parenthesis following the value of γ_{20° is the temperature coefficient of surface tension. All the measurements of the refractive indices were carried out at 20·0° ± 0·05°. Where 20° is used, 20·0° is to be understood; n_{C}, n_{D}, n_{F}, etc., are to be taken as referring to $n_{\mathrm{C}}^{20\cdot0^\circ}$, etc.; and R_{C}, etc., to $[R_L]_{\mathrm{C}}$, etc.

Previous work. The parachor values are taken from Sidgwick, Sugden, and Adam (*Brit. Assoc. Rep.*, 1932, 265; also given by Sugden, "The Parachor and Valency," 1932). Only what appear to be the most trustworthy of the earlier values of the refractive indices are given for purposes of comparison.

Acetone. The "AnalaR" product was used; semicarbazone, m. p. 190° (*ex* ethyl alcohol). 105 G. of the semicarbazone gave 18 g. of pure acetone; b. p. 56°/762 mm.; $M = 58\cdot08$; n_{C} 1·35827; n_{D} 1·36023, n_{F} 1·36490, $n_{\mathrm{G'}}$, 1·36818; R_{C} 16·04, R_{D} 16·11, R_{F} 16·30, $R_{\mathrm{G'}}$16·43; $R_{\mathrm{G'-C}}$ 0·39, $R_{\mathrm{F-C}}$ 0·26; $Mn_{\mathrm{D}}^{20^\circ}$ 79·00.

Densities determined : $d_{4^\circ}^{20^\circ}$ 0·7960, $d_{4^\circ}^{42\cdot0^\circ}$ 0·7711.

$\gamma_{20^\circ} = 23\cdot90$ (0·10). (* = Apparatus *A*. ** = Apparatus *B*.)

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
26·3°	12·74 **	12·50	0·7906	23·17	161·4
26·0	16·04 *	15·80	0·7908	23·40	161·7
42·0	15·19 *	14·95	0·7711	21·75	161·7
				Mean	161·6

[*P* 160·9—162·0; Eisenlohr (*Z. physikal. Chem.*, 1910, **75**, 585) gives $d_{4^\circ}^{19\cdot4^\circ}$ 0·79115, $n_{\alpha}^{19\cdot4^\circ}$ 1·35672, $n_{\mathrm{D}}^{19\cdot4^\circ}$ 1·35886, $n_{\beta}^{19\cdot4^\circ}$ 1·36366, $n_{\gamma}^{19\cdot4^\circ}$ 1·36750.]

Methyl ethyl ketone. Hopkin and Williams's pure liquid was distilled and a fraction, b. p. 80—81°, collected; semicarbazone, m. p. 145° (*ex* ethyl alcohol); 82 g. yielded 24 g. of the pure ketone; b. p. 81°/762·5 mm.; $M = 72\cdot10$; n_{C} 1·37683, n_{D} 1·37881, n_{F} 1·38333; $n_{\mathrm{G'}}$ 1·38712; R_{C} 20·57, R_{D} 20·67, R_{F} 20·89, $R_{\mathrm{G'}}$ 21·07; $R_{\mathrm{G'-C}}$ 0·50, $R_{\mathrm{F-C}}$ 0·32; $Mn_{\mathrm{D}}^{20^\circ}$ 99·41.

Densities determined : $d_{4^\circ}^{20^\circ}$ 0·8058, $d_{4^\circ}^{42\cdot3^\circ}$ 0·7838.

$\gamma_{20^\circ} = 24\cdot50$ (0·10). (* = Apparatus *A*. ** = Apparatus *B*.)

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
26·5°	16·09 *	15·85	0·7993	23·72	199·3
42·1	15·23 *	14·99	0·7840	22·01	199·3
22·5	13·15 **	12·91	0·8023	24·29	199·6
41·9	12·31 **	12·07	0·7842	22·19	199·7
				Mean	199·5

[*P* 198·2—198·8; Einsenlohr (*loc. cit.*) gives $d_{4^\circ}^{15\cdot9^\circ}$ 0·80870; $n_{\alpha}^{15\cdot9^\circ}$ 1·37844, $n_{\mathrm{D}}^{15\cdot9^\circ}$ 1·38071, $n_{\beta}^{15\cdot9^\circ}$ 1·38554, $n_{\gamma}^{15\cdot9^\circ}$ 1·38938.]

Diethyl ketone. Diethyl ketone, b. p. 102°, prepared from propionic acid, was employed; semicarbazone, m. p. 139° (*ex* ethyl alcohol). 78 G. of the pure semicarbazone yielded 24 g. of the pure ketone; b. p. 102°/751 mm.; $M = 86\cdot13$; n_{C} 1·39012; n_{D} 1·39220, n_{F} 1·39702, $n_{\mathrm{G'}}$ 1·40064; R_{C} 25·10, R_{D} 25·21, R_{F} 25·49, $R_{\mathrm{G'}}$ 25·69; $R_{\mathrm{G'-C}}$ 0·59, $R_{\mathrm{F-C}}$ 0·39; $Mn_{\mathrm{D}}^{20^\circ}$ 119·91.

Densities determined : $d_{4^\circ}^{20^\circ}$ 0·8138, $d_{4^\circ}^{40\cdot9^\circ}$ 0·7944, $d_{4^\circ}^{61\cdot3^\circ}$ 0·7745.

$\gamma_{20^\circ} = 25\cdot29$ (0·11). Apparatus *A*.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
21·0°	16·78	16·54	0·8129	25·18	237·3
40·9	15·70	15·46	0·7944	23·00	237·5
61·7	14·53	14·29	0·7741	20·71	237·5
				Mean	237·4

[$P = 236\cdot2$; Eisenlohr (*loc. cit.*) gives $d_{4^\circ}^{16\cdot6^\circ}$ 0·81750, $n_{\alpha}^{16\cdot6^\circ}$ 1·39168, $n_{\mathrm{D}}^{16\cdot6^\circ}$ 1·39385, $n_{\beta}^{16\cdot6^\circ}$ 1·39877, $n_{\gamma}^{16\cdot6^\circ}$ 1·40298.]

Methyl n-*propyl ketone.* Methyl *n*-propyl ketone, b. p. 102°, prepared from propionic and acetic acids, was used; semicarbazone, m. p. 110° (*ex* "AnalaR" benzene); b. p. 102°/756 mm.;

$M = 86{\cdot}13$; n_C 1·38815, n_D 1·39018, n_F 1·39511, $n_{G'}$ 1·39846; R_C 25·14, R_D 25·25, R_F 25·53, $R_{G'}$ 25·73; $R_{G'-C}$ 0·59, R_{F-C} 0·39; Mn_D^{20} 119·74.

Densities determined : $d_{4°}^{20°}$ 0·8089, $d_{4°}^{40·5°}$ 0·7870, $d_{4°}^{60·8°}$ 0·7673.

$\gamma_{20°} = 24{\cdot}82$ (0·11). Apparatus *A*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
15·6°	16·85	16·61	0·8135	25·30	237·5
41·3	15·44	15·20	0·7868	22·39	238·3
62·2	14·23	13·99	0·7659	20·06	238·3
				Mean	238·0

[*P* = 233·0 (?), 238·0; Eisenlohr (*loc. cit.*) gives $d_{4°}^{20·2°}$ 0·8089, $n_{\alpha}^{20·2°}$ 1·38754, $n_{D}^{20·2°}$ 1·38946, $n_{\beta}^{20·2°}$ 1·39461, $n_{\gamma}^{20·2°}$ 1·39881.]

Ethyl n-*propyl ketone.* Ethyl *n*-propyl ketone, b. p. 125°, prepared from propionic and butyric acids, was employed; semicarbazone, m. p. 113° (*ex* ethyl alcohol); the ketone had b. p. 125°/760 mm.; $M = 100{\cdot}16$; n_C 1·39844, n_D 1·40072, n_F 1·40563, $n_{G'}$ 1·41064; R_C 29·81, R_D 29·96, R_F 30·28, $R_{G'}$ 30·61; $R_{G'-C}$ 0·80; R_{F-C} 0·47; $Mn_D^{20°}$ 140·30.

Densities determined : $d_{4°}^{20°}$ 0·8118, $d_{4°}^{41·5°}$ 0·7945, $d_{4°}^{62·1°}$ 0·7761, $d_{4°}^{86·3°}$ 0·7536.

$\gamma_{20°} = 25{\cdot}54$ (0·11). Apparatus *A*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
25·0°	16·80	16·56	0·8076	25·04	277·4
42·1	15·90	15·66	0·7940	23·28	277·1
62·9	14·86	14·62	0·7754	21·23	277·4
86·9	13·57	13·33	0·7531	18·80	277·3
				Mean	277·3

[Eisenlohr (*loc. cit.*) gives $d_{4°}^{22·0°}$ 0·81491, $n_{\alpha}^{22·0°}$ 1·39683, $n_{D}^{22·0°}$ 1·39889, $n_{\beta}^{22·0°}$ 1·40402, $n_{\gamma}^{22·0°}$ 1·40813.]

Di-n-*propyl ketone.* Di-*n*-propyl ketone, b. p. 144—146°, prepared from butyric acid, was used; semicarbazone, m. p. 134° (*ex* ethyl alcohol). The ketone had b. p. 145°/767 mm.; $M = 114{\cdot}18$; n_C 1·40465, n_D 1·40692, n_F 1·41185, $n_{G'}$ 1·41568; R_C 34·34, R_D 34·50, R_F 34·88, $R_{G'}$ 35·16; $R_{G'-C}$ 0·82, R_{F-C} 0·54; $Mn_D^{20°}$ 160·64.

Densities determined : $d_{4°}^{20°}$ 0·8145, $d_{4°}^{41·5°}$ 0·7964, $d_{4°}^{62·5°}$ 0·7783, $d_{4°}^{87·5°}$ 0·7559.

$\gamma_{20°} = 25{\cdot}38$ (0·10). Apparatus *A*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
16·2°	17·06	16·82	0·8179	25·76	314·5
42·1	15·93	15·69	0·7958	23·38	315·4
62·5	14·86	14·62	0·7783	21·31	315·2
87·5	13·66	13·42	0·7559	18·99	315·4
				Mean	315·1

[*P* = 314·1; Bruhl (*J. pr. Chem.*, 1894, **50**, 141) gives $d_{4°}^{21·7°}$ 0·8160, $n_{\alpha}^{21·7°}$ 1·40521, $n_{D}^{21·7°}$ 1·40732, $n_{\gamma}^{21·7°}$ 1·41650.]

Methyl n-*butyl ketone.* This was prepared from ethyl *n*-propylacetoacetate, the experimental details for methyl *n*-amyl ketone ("Organic Syntheses," 1927, **7**, 61) being suitably modified. The fraction, b. p. 127—128°, was used; semicarbazone, m. p. 126° (*ex* " AnalaR " benzene). The ketone had b. p. 127·5°/757 mm.; $M = 100{\cdot}16$; n_C 1·39861, n_D 1·40072, n_F 1·40585, $n_{G'}$ 1·40943; R_C 29·90, R_D 30·04, R_F 30·38, $R_{G'}$ 30·62; $R_{G'-C}$ 0·72, R_{F-C} 0·48, $Mn_D^{20°}$ 140·29.

Densities determined : $d_{4°}^{20°}$ 0·8095, $d_{4°}^{60·5°}$ 0·7750, $d_{4°}^{85·6°}$ 0·7523.

$\gamma_{20°} = 25{\cdot}43$ (0·10). Apparatus *A*.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
21·1°	16·96	16·72	0·8086	25·32	277·8
61·3	14·91	14·67	0·7744	21·27	276·9
85·4	13·69	13·45	0·7525	18·95	277·9
				Mean	277·5

Methyl iso*butyl ketone.* The fraction, b. p. 118°/763 mm., from an Eastman Kodak product was employed; semicarbazone, m. p. 137° (*ex* " AnalaR " benzene). Ketone : b. p. 118·5°/766 mm.; $M = 100{\cdot}16$; n_C 1·39352, n_D 1·39562, n_F 1·40064, $n_{G'}$ 1·40420; R_C 30·01, R_D 30·15, R_F 30·49, $R_{G'}$ 30·73; $R_{G'-C}$ 0·72, R_{F-C} 0·48; $Mn_D^{20°}$ 139·78.

Densities determined : $d_{4^\circ}^{20^\circ}$ 0·7978, $d_{4^\circ}^{61\cdot5^\circ}$ 0·7631, $d_{4^\circ}^{86\cdot6^\circ}$ 0·7402.

$\gamma_{20^\circ} = 23{\cdot}64\ (0{\cdot}09_5)$. Apparatus *A*.

t.	*h.*	*H.*	$d_{4^\circ}^{t^\circ}$.	*γ.*	*P.*
23·7°	15·89	15·65	0·7947	23·29	277·0
62·1	13·98	13·74	0·7626	19·62	276·5
87·0	12·69	12·45	0·7398	17·25	276·0
				Mean	276·5

[Eisenlohr (*loc. cit.*) gives $d_{4^\circ}^{17\cdot4^\circ}$ 0·80316, $n_{\alpha}^{17\cdot4^\circ}$ 1·39500, $n_{\mathrm{D}}^{17\cdot4^\circ}$ 1·39694, $n_{\beta}^{17\cdot4^\circ}$ 1·40235, $n_{\gamma}^{17\cdot4^\circ}$ 1·40638.]

Methyl n-*amyl ketone*. This was prepared from ethyl *n*-butylacetoacetate (" Organic Syntheses," 1927, **7**, 61), and the fraction, b. p. 150—151°, collected. This was purified through the semicarbazone, m. p. 125° (*ex* " AnalaR " benzene). Identical results were obtained with commercially pure methyl *n*-amyl ketone (General Metallurgical and Chemical Ltd.; Carbide and Carbon Chemicals Corporation). B. p. 151°/766 mm.; $M = 114{\cdot}18$; n_{C} 1·40640, n_{D} 1·40860, n_{F} 1·41380, $n_{\mathrm{G'}}$ 1·41755; R_{C} 34·61, R_{D} 34·78, R_{F} 35·16, $R_{\mathrm{G'}}$ 35·45; $R_{\mathrm{G'-C}}$ 0·84, $R_{\mathrm{F-C}}$ 0·55; $Mn_{\mathrm{D}}^{20^\circ}$ 160·83.

Densities determined : $d_{4^\circ}^{20^\circ}$ 0·8111, $d_{4^\circ}^{61\cdot7^\circ}$ 0·7799; $d_{4^\circ}^{84\cdot9^\circ}$ 0·7597.

$\gamma_{20^\circ} = 26{\cdot}60\ (0{\cdot}10)$. Apparatus *A*.

t.	*h.*	*H.*	$d_{4^\circ}^{t^\circ}$.	*γ.*	*P.*
24·0°	17·56	17·32	0·7979	26·20	319·8
61·9	15·60	15·36	0·7797	22·43	318·7
87·2	14·38	14·14	0·7579	20·07	318·9
				Mean	319·1

Methyl n-*hexyl ketone*. A fraction, b. p. 172—173·5°, from an Eastman Kodak product was used; semicarbazone, m. p. 124° (*ex* " AnalaR " benzene). Ketone : b. p. 175°/758 mm.; $M = 128{\cdot}21$; n_{C} 1·41309, n_{D} 1·41536, n_{F} 1·42058, $n_{\mathrm{G'}}$ 1·42409; R_{C} 39·10, R_{D} 39·29, R_{F} 39·72, $R_{\mathrm{G'}}$ 40·01; $R_{\mathrm{G'-C}}$ 0·91, $R_{\mathrm{F-C}}$ 0·62; $Mn_{\mathrm{D}}^{20^\circ}$ 181·47.

Densities determined : $d_{4^\circ}^{20^\circ}$ 0·8179, $d_{4^\circ}^{61\cdot5^\circ}$ 0·7848, $d_{4^\circ}^{87\cdot9^\circ}$ 0·7630.

$\gamma_{20^\circ} = 25{\cdot}73\ (0{\cdot}07_5)$. Apparatus *A*.

t.	*h.*	*H.*	$d_{4^\circ}^{t^\circ}$.	*γ.*	*P.*
22·1°	16·97	16·73	0·8163	25·57	353·2
62·0	15·64	15·40	0·7844	22·62	356·5
87·5	14·57	14·33	0·7634	20·48	357·3
				Mean	355·7

[$P = 355{\cdot}7$, 356·8; Eisenlohr (*loc. cit.*) gives $d_{\alpha^\circ}^{20^\circ}$ 0·8185, $n_{\alpha}^{20^\circ}$ 1·41390, $n_{\mathrm{D}}^{20^\circ}$ 1·41613, $n_{\beta}^{20^\circ}$ 1·42133, $n_{\gamma}^{20^\circ}$ 1·42569.]

*Dï*iso*butyl ketone*. A fraction, b. p. 166—168°, of a commercial product (General Metallurgical and Chemical Ltd.; Carbide and Carbon Chemicals Corporation) was employed; semicarbazone, m. p. 123° (*ex* " AnalaR " benzene). Ketone : b. p. 168°/760·5 mm.; $M = 142{\cdot}23$; n_{C} 1·40990; n_{D} 1·41206, n_{F} 1·41727, $n_{\mathrm{G'}}$ 1·42109; R_{C} 43·75, R_{D} 43·96, R_{F} 44·45, $R_{\mathrm{G'}}$ 44·80; $R_{\mathrm{G'-C}}$ 1·05, $R_{\mathrm{F-C}}$ 0·70; $Mn_{\mathrm{D}}^{20^\circ}$ 200·84.

Densities determined : $d_{4^\circ}^{20^\circ}$ 0·8053, $d_{4^\circ}^{61\cdot3^\circ}$ 0·7726, $d_{4^\circ}^{85\cdot4^\circ}$ 0·7533.

$\gamma_{20^\circ} = 24{\cdot}09\ (0{\cdot}08_5)$. Apparatus *B*.

t.	*h.*	*H.*	$d_{4^\circ}^{t^\circ}$.	*γ.*	*P.*
22·0°	12·93	12·69	0·8037	23·92	391·4
61·9	11·56	11·32	0·7731	20·52	391·6
86·5	10·70	10·46	0·7524	18·45	391·8
				Mean	391·6

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WOOLWICH POLYTECHNIC, LONDON, S.E. 18.

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