128. *Physical Properties and Chemical Constitution. Part XI. Ketones.*

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New experimental data for the parachors and refractivities of higher alkyl ketones and aryl alkyl ketones are presented. The CO contributions of aliphatic ketones have been calculated with the aid of the experimental data for aliphatic hydrocarbons (Part IX, *J.*, 1946, 133), and the following are regarded as the most probable values :

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
CO	45·9	4·684	4·713	4·768	4·830	42·38

These differ appreciably from the values previously accepted. The CO contributions for the aryl alkyl ketones have been computed by direct comparison with the experimental figures for *n*-alkylbenzenes (preceding paper).

Eisenlohr (*Z. physikal. Chem.*, 1910, **55**, 600) has computed the contribution of the carbonyl oxygen, O¨, to the molecular refractivity by subtracting nCH$_2$ from the molecular refractivities of 12 aldehydes and ketones $[CH_2]_nO^{\cdot\cdot}$ and gives the following mean values [the figures for the CO contribution (= C + O¨) are also included for comparison with the author's results] :

	R_C.	R_D.	R_F.	$R_{G'}$.
O¨	2·189	2·211	2·247	2·267
CO	4·602	2·629	4·685	4·733

Sugden, Reed, and Wilkins (*J.*, 1925, **127**, 1525; see also " The Parachor and Valency ", 1930, **38**) state that a double bond gives an increment in parachor of about **23·2** in compounds containing the links C=C, C=O, C=S, C=N, and N=O; the value for the parachor contribution of the carbonyl group is therefore C + O + ⊨ or 4·8 + 20·0 + 23·2 = 48·0. In Part V (*J.*, **1940**, 171) experimental data were presented for the physical properties of a number of alkyl ketones which had been purified through the semicarbazones. The results of measurements upon further alkyl ketones and a number of aryl alkyl ketones are now given. To calculate the CO contribution, the author has subtracted the experimental figures for the corresponding hydrocarbon (Part IX, *J.*, 1946, 133) wherever this was possible [*e.g.*, $Bu^n_2CO - 2Bu^n$ ($\equiv n\text{-}C_8H_{18}$) = CO] or the calculated values for the alkyl groups. The figures for the alkyl groups employed in these calculations and also in succeeding papers of this series are collected in Table I; the values for higher alkyl groups (*n*-nonyl *et seq.*) may be obtained by subtracting H from the *n*-alkyl hydrocarbons (Part IX, *loc. cit.*). The values for CH_3 were the mean figures deduced by subtracting $(n - 2)CH_2$ from the normal hydrocarbons C_nH_{2n+2}; C_2H_5 from $CH_3 + CH_2$; $C_3H_7{}^{\beta}$ from 0·5 (di*iso*butyl − $2CH_2$); and C_3H_5 from diallyl.

TABLE I.

Constants for alkyl groups.

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
CH_3	55·4	5·636	5·653	5·719	5·746	18·13
C_2H_5	95·4	10·260	10·300	10·414	10·481	38·72
$C_3H_7{}^n$	135·5	14·895	14·965	15·125	15·235	59·25
$C_3H_7{}^i$	133·8	14·905	14·975	15·145	15·255	58·95
$C_4H_9{}^n$	175·3	19·500	19·585	19·800	19·950	79·81
$C_4H_9{}^i$	173·8	19·530	19·620	19·840	19·990	79·54
$C_4H_9{}^s$	171·2	19·330	19·420	19·625	19·775	80·21
$C_5H_{11}{}^n$	215·0	24·140	24·250	24·515	24·700	100·46
$C_5H_{11}{}^i$ *	212·6	24·095	24·195	24·460	24·650	100·30
$C_5H_{11}{}^i$ †	213·1	24·170	24·280	24·540	24·720	100·21
CHMePr^n (2-pentyl)	209·7	23·895	24·000	24·255	24·440	100·83
$CHEt_2$ (3-pentyl)	208·5	23·815	23·925	24·170	24·355	100·95
$C_6H_{13}{}^n$	255·0	28·725	28·855	29·160	29·385	121·10
$C_7H_{15}{}^n$	295·7	33·395	33·550	33·905	34·170	141·75
$C_8H_{17}{}^n$	335·7	37·960	38·135	38·535	38·830	162·43
C_3H_5 (allyl)	124·3	14·425	14·520	14·745	14·920	57·60

* From di*iso*amyl prepared from *iso*amyl bromide (*ex* Sharples synthetic *iso*amyl alcohol) and sodium.
† From di*iso*amyl prepared from *iso*amyl bromide (*ex* Bisol fermentation *iso*amyl alcohol) and sodium.

The contributions of the CO group for the various alkyl ketones are collected in Table II. The lines marked with an asterisk are those for ketones which were regenerated from the semicarbazones (Part V, *J.*, **1940**, 171); the other ketones were purified by fractionation only, and the data are therefore not quite so trustworthy. Two series of mean values are given:

TABLE II.

CO *Values for aliphatic ketones.*

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
Me_2CO *	50·9	4·77	4·80	4·86	4·94	42·74
MeEtCO *	47·7	4·68	4·72	4·76	4·84	42·56
Et_2CO *	46·7	4·58	4·61	4·66	4·73	42·47
MePr^{n}CO *	46·6	4·61	4·63	4·69	4·75	42·36
EtPr^{n}CO *	45·5	4·65	4·68	4·73	4·78	42·32
MeBu^{n}CO *	45·7	4·74	4·76	4·83	4·89	42·31
MeBu^{i}CO *	46·8	4·84	4·88	4·93	4·99	42·11
Pr^n_2CO *	44·2	4·55	4·57	4·63	4·69	42·15
EtBu^{n}CO	44·9	4·55	4·56	4·62	4·67	42·37
MeAm^{n}CO *	48·2	4·82	4·85	4·91	4·98	42·34
EtAm^{n}CO	42·7	4·48	4·49	4·55	4·58	42·43
$C_6H_{13}{}^n$MeCO *	43·7	4·66	4·69	4·75	4·77	42·43
$C_6H_{13}{}^n$EtCO	44·8	4·55	4·57	4·63	4·67	42·61
Bu^n_2CO	43·5	4·56	4·59	4·64	4·68	42·29
Bu^i_2CO *	44·1	4·69	4·72	4·77	4·82	42·77
Me$C_7H_{15}{}^n$CO	43·9	4·74	4·77	4·82	4·88	42·50
Et$C_7H_{15}{}^n$CO	45·1	4·57	4·60	4·64	4·68	42·46
Am^n_2CO	42·5	4·61	4·62	4·67	4·72	42·23
Me$C_9H_{19}{}^n$CO	—	4·71	4·72	4·78	4·83	42·45
Mean (excluding Me_2CO)	45·1	4·644	4·668	4·723	4·772	42·39
Mean * (excluding Me_2CO)	45·9	4·684	4·713	4·768	4·830	42·38

the first (excluding acetone) includes all the ketones, and the second (which one would expect to be the more trustworthy) is deduced from the ketones *ex* semicarbazones. These results differ appreciably from those of Sugden (parachor) and Eisenlohr (refractivities). In view of the somewhat large individual variations from the mean, it is proposed to reinvestigate the whole subject later.

The results for a number of aryl alkyl ketones, which were purified by fractionation only, are collected in Table III; the values were obtained by subtraction of the experimental figures of the appropriate alkylbenzenes (preceding paper). It will be observed that the parachor contributions, except for the methyl ketones, approximate to those for the alkyl ketones, whilst the refractivities for those compounds in which the keto-group is directly attached to the aromatic ring appear to be uniformly high.

TABLE III.

CO *Values for aryl alkyl ketones.*

Ketone.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
Ph·COMe	47·9	5·12	5·17	5·40	5·58	46·34
Ph·COEt	44·4	5·01	5·08	5·27	5·35	46·04
Ph·COPr^n	43·4	5·08	5·15	5·33	5·50	45·96
Ph·CH$_2$·COMe	48·6	4·70	4·73	4·80	[4·80]	44·64
Ph·CH$_2$·COEt	46·2	4·53	4·56	4·61	4·66	44·71
Ph·CH$_2$·COPr^n	44·3	4·50	4·54	4·61	4·66	44·42
Ph·CH$_2$·CH$_2$·COMe	49·8	4·60	4·64	4·68	4·73	44·85
Ph·CH$_2$·CH$_2$·COEt	47·4	4·47	4·50	4·56	4·59	44·77
Ph·CH$_2$·CH$_2$·COPr^n	44·5	4·45	4·47	4·52	4·58	44·14

EXPERIMENTAL.

Preparation of Ketones.—All the ketones, except those in which the CO group is directly attached to the benzene ring, were prepared by passing the appropriate acid or mixture of acids over thoria at 430—450°.

Preparation of thoria catalyst. 276 G. of commercially pure, finely-powdered thorium nitrate were dissolved in the minimum volume of water (*ca.* 450 ml.) and a solution of 106 g. of A.R. anhydrous sodium carbonate in 400 ml. of water was added slowly and with mechanical stirring. The heavy white precipitate was allowed to settle, as much as possible of the mother-liquor was decanted, and the precipitate washed once by decantation with 500 ml. of water. The resulting moist precipitate was made into a thick paste with distilled water, and pumice (4—8 mesh) was stirred in until most of the suspension appeared to be absorbed and the pumice was completely covered. The impregnated pumice was dried in *ca.* 200-g. lots by heating in a large evaporating dish upon an electric hot plate with constant stirring until the lumps no longer clung together. The cold product was sieved: about 250 g. of a white powder (largely thorium carbonate but containing some oxide) are recovered and can be used for impregnating more pumice. The total weight of impregnated pumice is about 1400 g.; the exact weight will, of course, depend upon the grade of the pumice.

The catalyst was packed into a hard-glass or Pyrex tube, 100 cm. long and 1·5 cm. in diameter. Small plugs of purified glass wool were inserted after each 15-cm. column of the catalyst; this device reduced the danger of carbonisation blocking the tube. The apparatus was set up as detailed in Part V (*J.*, 1940, 172) and the tube was heated to 430—450° in a slow stream of nitrogen; carbon dioxide (and generally oxides of nitrogen) were evolved. The decomposition of the thorium salt deposited upon the pumice was complete in 6—12 hours.

A temperature of 430—450° was employed in all the preparations.

*Di-*n*-butyl ketone.* 200 G. of *n*-valeric acid, b. p. 182·5—185·5°/750 mm. (Eastman Kodak), were circulated over the catalyst during 18 hours. The product was worked up as detailed in Part V (*loc. cit.*) and yielded, upon fractionation through a Pyrex Young and Thomas column, 50 g. of the crude ketone, b. p. 181—185°/756 mm. Upon refractionation, most boiled at 184°/750 mm., and a middle fraction was collected for the physical measurements. The poor yield of the ketone is probably due to the unsatisfactory character of the sample of the commercial acid used.

*Di-*n*-amyl ketone.* 200 G. of *n*-hexoic acid, b. p. 203—206° (Deutsche Hydrierwerke), were circulated over the catalyst during 22 hours; the distillate weighed 159 g., of which 15 g. constituted the aqueous layer. After removal of excess of acid and drying, distillation gave the following fractions: (1) 200—221°, 10 g.; (2) 221—225°, 100 g.; (3) 225—227°, 12 g.; and (4) 227—235°, 12 g. Upon redistillation of fraction (2), it boiled largely at 223°/760 mm. and a middle portion was taken for the physical measurements.

Ethyl n*-butyl ketone.* A mixture of 51 g. of *n*-valeric acid, b. p. 184—184·5°/768 mm. (*ex* *n*-butyl cyanide), and 111 g. of propionic acid, b. p. 139—141°/760 mm., was passed over the catalyst during 9 hours. The aqueous layer in the distillate was separated, and the organic layer washed successively with 10% sodium hydroxide solution and water and dried ($CaSO_4$). The mixture of ketones (74 g.) was distilled through a Widmer column and afforded 38 g. of diethyl ketone, b. p. 101—105°, 26 g. of ethyl *n*-butyl ketone, b. p. 145—146°/767 mm., and 8 g. of a high-b. p. residue composed largely of di-*n*-butyl ketone. Redistillation from a Claisen flask with fractionating side arm yielded the pure ethyl *n*-butyl ketone, b. p. 146·5°/765 mm.

Ethyl n*-amyl ketone.* A mixture of 77 g. of pure *n*-hexoic and 99 g. of pure propionic acid when circulated over thoria during 6 hours afforded 93 g. of the crude mixture of ketones. This was separated by distillation into 32 g. of diethyl ketone, b. p. 101—104°, 40 g. of crude ethyl *n*-amyl ketone, b. p. 165—185°, and 14 g. of a high-b. p. residue (largely di-*n*-amyl ketone). The fraction, b. p. 165—185°, when distilled through a well-lagged, all-glass Dufton column, boiled largely at 166—168°, and a middle fraction, b. p. 167°/749 mm., was employed for the physical measurements.

Ethyl n-*hexyl ketone.* A mixture of 130 g. of *n*-heptoic acid, b. p. 216—218°/744 mm., and 148 g. of pure propionic acid was circulated over a thoria catalyst during 15 hours. The crude mixture of ketones (128 g.), isolated as detailed under ethyl *n*-butyl ketone, was distilled through a well-lagged, all-glass Dufton column and thus separated into 40 g. of diethyl ketone, b. p. 100—105°, 58 g. of ethyl *n*-hexyl ketone, b. p. 184—190° (largely 185—186°), and 27 g. of a dark residue composed largely of di-*n*-hexyl ketone. Upon redistillation of the ethyl *n*-hexyl ketone, it boiled largely at 187°/751 mm. and a middle fraction was used in the physical measurements.

Ethyl n-*heptyl ketone.* A mixture of 72 g. of *n*-octoic acid, b. p. 235—239°/762 mm. (Deutsche Hydrierwerke), and 111 g. of pure propionic acid was passed over the catalyst during 10 hours and afforded 98 g. of the crude mixture of ketones. A preliminary distillation gave 30 g. of diethyl ketone, b. p. 100—105°, 45 g. of crude ethyl *n*-heptyl ketone, b. p. 200—210°, and 6 g. of crude di-*n*-heptyl ketone. Redistillation of the main fraction through a well-lagged, all-glass Dufton column afforded pure ethyl *n*-heptyl ketone, b. p. 203°/754 mm.

Methyl n-*heptyl ketone.* A mixture of 96 g. of *n*-octoic acid (as above) and 320 g. of A.R. glacial acetic acid upon circulation over a thoria catalyst during 36 hours yielded, after thorough washing to remove acetone, 125 g. of the mixed ketones. The following fractions were collected upon distillation : (1) 180—190°, 7 g.; (2) 190—194°, 90 g.; (3) 194—206°, 15 g.; and (4) a high-b. p. residue (8 g.) which solidified on cooling. Fraction (4), after two crystallisations from dilute alcohol, gave 6 g. of pure di-*n*-heptyl ketone, m. p. 41°. Redistillation of fraction (2) yielded pure methyl *n*-heptyl ketone, b. p. 193°/749 mm.

Methyl n-*nonyl ketone.* A solution of 86 g. of decoic acid, m. p. 31—32° (Deutsche Hydrierwerke), in 120 g. of A.R. glacial acetic acid was circulated over the thoria catalyst during 16 hours. A small hot plate was placed immediately below the adaptor through which the mixture entered the catalyst tube in order to prevent solidification. It was necessary to warm the reaction product in order to keep it fluid while being worked up in the usual manner. Distillation of the resulting mixture of ketones (57 g.) through a well-lagged, all-glass Dufton column gave 7 g. of acetone, b. p. 56°, 40 g. of crude methyl *n*-nonyl ketone, b. p. 224—226°, and 6 g. of a high b. p. residue (largely di-*n*-nonyl ketone). Pure methyl *n*-nonyl ketone, b. p. 228·5°/748 mm., was obtained upon redistillation of the main fraction.

Benzyl methyl ketone. A solution of 170 g. of pure phenylacetic acid in 225 g. of A.R. glacial acetic acid was circulated over the catalyst during 18 hours : a slow stream of carbon dioxide was passed through the catalyst tube to keep the gases in motion. The distillate was worked up as detailed under ethyl *n*-butyl ketone except that the aqueous layer was extracted with two 50-ml. portions of benzene. After the removal of the solvent at atmospheric pressure, the mixture was distilled under reduced pressure and yielded 88 g. of benzyl methyl ketone, b. p. 100—102·5°/20 mm. (mainly 102—102·5°/20 mm.) (compare *Org. Synth.*, 1936, **16**, 47, in which different proportions of the acids are employed and the b. p. of the crude ketone is given as 110—120°/21—22 mm.), and a residue (16 g.) of crude dibenzyl ketone. Redistillation gave the pure benzyl methyl ketone, b. p. 102·5°/19 mm.

Benzyl ethyl ketone. A mixture of 204 g. of pure phenylacetic acid and 333 g. of pure propionic acid was circulated over the catalyst during 16 hours. The distillate was worked up as for benzyl methyl ketone except that the extraction with benzene was omitted. The dry, crude mixture of ketones (320 g.) was distilled through a three-section Pyrex Young and Thomas column to separate the diethyl ketone, b. p. 99—103° (165 g.). The residue was distilled under reduced pressure and gave 110 g. of crude benzyl ethyl ketone, b. p. 118—123°/22 mm., and a residue (34 g.) of impure dibenzyl ketone. Upon redistillation the main fraction boiled at 113—115°/17 mm., from which a middle fraction, b. p. 113·5°/17 mm., was removed for the physical measurements.

Benzyl n-*propyl ketone.* A solution of 204 g. of pure phenylacetic acid in 396 g. of *n*-butyric acid, b. p. 162—163°/765 mm., was circulated over a thoria catalyst during 20 hours. The distillate yielded 368 g. of the dry, crude mixture of ketones, which was separated, as for ethyl benzyl ketone, into 185 g. of di-*n*-propyl ketone, b. p. 140—145°, 108 g. of crude benzyl *n*-propyl ketone, b. p. 240—260°, and 49 g. of impure dibenzyl ketone. Redistillation of the main fraction yielded the pure ketone, b. p. 243—247°/757 mm., from which a middle fraction, b. p. 244°/757 mm., was employed in the physical measurements.

Methyl 2-phenylethyl ketone. A solution of 100 g. of β-phenylpropionic acid, m. p. 48°, in 160 g. of A.R. glacial acetic acid was slowly circulated over a thoria catalyst. The dry, crude mixture of ketones (88 g.) upon distillation yielded 70 g. of crude methyl 2-phenylethyl ketone, b. p. 230—235°. The pure ketone, b. p. 234·5°/770 mm., was obtained upon redistillation.

Ethyl 2-phenylethyl ketone. A solution of 100 g. of pure β-phenylpropionic acid in 200 g. of pure propionic acid was circulated over a thoria catalyst during 11 hours. The distillate yielded 171 g. of the crude, dry mixed ketones. This was worked up as for benzyl ethyl ketone and afforded 75 g. of diethyl ketone, b. p. 100—103°, 72 g. of crude ethyl 2-phenylethyl ketone, b. p. 245—249°, and 15 g. of impure di-2-phenylethyl ketone. The main fraction gave the pure ketone, b. p. 248°/763 mm., upon redistillation.

2-Phenylethyl n-*propyl ketone.* A solution of 200 g. of pure β-phenylpropionic acid in 469 g. of pure *n*-butyric acid was circulated over a thoria catalyst during 15 hours. The distillate yielded 338 g. of crude, dry mixed ketones. This was worked up as for benzyl ethyl ketone and gave 194 g. of di-*n*-propyl ketone, b. p. 140—144°, 130 g. of 2-phenylethyl *n*-propyl ketone, b. p. 139—143°/17 mm., and 44 g. of impure di-2-phenylethyl ketone. Redistillation yielded the pure ketone, b. p. 138·5°/16 mm.

Acetophenone. A pure commercial sample was distilled and a middle fraction, b. p. 200°/759 mm., collected.

Propiophenone. 238 G. of redistilled thionyl chloride were placed in a 500-ml. Claisen flask with fractionating side arm; this was fitted with a dropping-funnel in the long neck, a reflux condenser (attached to a gas absorption device) in the short neck, and a small cork in the side arm. The flask was heated on a water-bath, 148 g. of pure propionic acid were added during 2 hours, and the mixture was then refluxed for 30 minutes, and fractionally distilled. The yield of propionyl chloride, b. p. 78—81°/777 mm., was 100 g.

A mixture of 234 g. of sodium-dried A. R. benzene and 135·5 g. of anhydrous aluminium chloride was placed in a 1·5-l. three-necked flask provided with a dropping-funnel, a mercury-sealed mechanical stirrer, and an efficient reflux condenser. The dropping-funnel was charged with 90 g. of propionyl chloride and about 2—3 ml. were added to the stirred mixture. Evolution of hydrogen chloride commenced after 1—2 minutes' warming, the flame was removed, and the chloride added dropwise during 2—3 hours, after which the reaction mixture was refluxed for 0·5 hour, allowed to cool, and added to 1 l. of water, which was vigorously stirred in a 3 l. beaker; the temperature was kept below 10° by addition of ice. The benzene layer was separated, washed twice with 10% sodium hydroxide solution, then with water and dried ($MgSO_4$). The benzene was removed and the residue distilled; 78 g. of propiophenone, b. p. 214·5—216·5°/763 mm., were obtained. Redistillation gave pure propiophenone, b. p. 215°/763 mm.

Butyrophenone. The reaction between 134 g. of anhydrous aluminium chloride, 234 g. of sodium-dried A.R. benzene, and 105 g. of *n*-butyryl chloride, b. p. 100·5—102·5°/777 mm., as detailed under propiophenone, yielded 90 g. of butyrophenone, b. p. 227—229°/777 m. Redistillation gave the pure compound, b. p. 228°/777 mm.

124. *Di-*n*-butyl ketone.* B. p. 184°/750 mm.; *M* 142·23; n_C 1·41730, n_D 1·41946, n_F 1·42467, $n_{G'}$ 1·42852; R_C 43·56, R_D 43·76, R_F 44·22, $R_{G'}$ 44·58; $Mn_D^{20^\circ}$ 201·90. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8217, $d_{4^\circ}^{40\cdot7^\circ}$ 0·8056, $d_{4^\circ}^{60\cdot6^\circ}$ 0·7895, $d_{4^\circ}^{86\cdot6^\circ}$ 0·7700. Apparatus *D*.

(These headings apply to corresponding columns in all the following tables.)

t.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
21·1°	13·12	0·8208	26·60	393·5	62·6°	11·73	0·7879	22·82	394·5
26·9	12·95	0·8163	26·11	393·8	87·4	10·91	0·7694	20·73	394·4
41·1	12·41	0·8053	24·68	393·7				Mean	394·0

125. *Di-*n*-amyl ketone.* B. p. 223°/760·5 mm.; *M* 170·19; n_C 1·42571, n_D 1·42782, n_F 1·43321, $n_{G'}$ 1·43711; R_C 52·89, R_D 53·12, R_F 53·70, $R_{G'}$ 54·12; $Mn_D^{20^\circ}$ 243·14. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8245, $d_{4^\circ}^{41\cdot5^\circ}$ 0·8097, $d_{4^\circ}^{60\cdot5^\circ}$ 0·7956, $d_{4^\circ}^{86\cdot0^\circ}$ 0·7762. Apparatus *A*.

19·4°	17·74	0·8249	27·40	472·3	62·4°	15·81	0·7943	23·51	472·1
41·8	16·76	0·8095	25·40	472·3	87·7	14·77	0·7750	21·43	472·8
								Mean	472·4

126. *Ethyl* n*-butyl ketone.* B. p. 146·5—147°/765 mm.; *M* 114·18; n_C 1·40671, n_D 1·40880, n_F 1·41390, $n_{G'}$ 1·41759; R_C 34·34, R_D 34·49, R_F 34·87, $R_{G'}$ 35·14; $Mn_D^{20^\circ}$ 160·86. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8181, $d_{4^\circ}^{40\cdot5^\circ}$ 0·8008, $d_{4^\circ}^{61\cdot9^\circ}$ 0·7829, $d_{4^\circ}^{86\cdot5^\circ}$ 0·7611. Apparatus *A*.

16·1°	17·26	0·8214	26·55	315·5	61·6°	15·09	0·7832	22·13	316·2
20·0	17·17	0·8181	26·30	316·1	87·2	13·73	0·7605	19·55	315·7
40·9	16·00	0·8005	23·98	315·4				Mean	315·8

127. *Ethyl* n*-amyl ketone.* B. p. 167°/749 mm.; *M* 128·21; n_C 1·41328, n_D 1·41541, n_F 1·42060, $n_{G'}$ 1·42431; R_C 38·92, R_D 39·09, R_F 39·52, $R_{G'}$ 39·82; $Mn_D^{20^\circ}$ 181·47. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8220, $d_{4^\circ}^{41\cdot2^\circ}$ 0·8054, $d_{4^\circ}^{61\cdot0^\circ}$ 0·7903, $d_{4^\circ}^{86\cdot1^\circ}$ 0·7693. Apparatus *A*.

14·5°	17·58	0·8263	27·20	354·3	40·9°	16·36	0·8056	24·68	354·7
19·7	17·42	0·8223	26·82	354·8	61·0	15·47	0·7903	22·89	354·9
22·9	17·21	0·8197	26·42	354·6	87·1	14·21	0·7685	20·45	354·8
								Mean	354·7

128. *Ethyl* n*-hexyl ketone.* B. p. 187°/751 mm.; *M* 142·23; n_C 1·41861, n_D 1·42081, n_F 1·42608, $n_{G'}$ 1·42990; R_C 43·55; R_D 43·74, R_F 44·23, $R_{G'}$ 44·57; $Mn_D^{20^\circ}$ 202·22. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8241, $d_{4^\circ}^{40\cdot7^\circ}$ 0·8014, $d_{4^\circ}^{60\cdot1^\circ}$ 0·7921, $d_{4^\circ}^{84\cdot9^\circ}$ 0·7725. Apparatus *A*.

17·3°	17·92	0·8263	27·73	395·0	60·7°	15·82	0·7916	23·45	395·4
20·4	17·76	0·8238	27·40	395·0	87·2	14·65	0·7707	21·14	395·7
40·0	16·86	0·8080	25·50	395·6				Mean	395·3

129. *Ethyl* n*-heptyl ketone.* B. p. 203°/754 mm.; *M* 156·26; n_C 1·42302, n_D 1·42521, n_F 1·43052, $n_{G'}$ 1·43447; R_C 48·23, R_D 48·45, R_F 48·97, $R_{G'}$ 49·37; $Mn_D^{20^\circ}$ 222·70. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8251, $d_{4^\circ}^{39\cdot6^\circ}$ 0·8109, $d_{4^\circ}^{60\cdot6^\circ}$ 0·7951, $d_{4^\circ}^{85\cdot7^\circ}$ 0·7761. Apparatus *A*.

21·2°	18·02	0·8242	27·68	435·4	61·3°	16·24	0·7946	24·16	436·0
40·9	17·15	0·8099	26·01	435·7	86·1	15·11	0·7758	21·95	436·0
								Mean	435·8

130. *Methyl* n*-heptyl ketone.* B. p. 193°/749 mm.; *M* 142·23; n_C 1·41878, n_D 1·42096, n_F 1·42625, $n_{G'}$ 1·43021; R_C 43·74, R_D 43·94, R_F 44·42, $R_{G'}$ 44·78; $Mn_D^{20^\circ}$ 202·11. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8208, $d_{4^\circ}^{40\cdot5^\circ}$ 0·8059, $d_{4^\circ}^{60\cdot7^\circ}$ 0·7901, $d_{4^\circ}^{85\cdot5^\circ}$ 0·7705. Apparatus *A*.

20·3°	17·14	0·8206	26·34	392·7	61·5°	15·49	0·7985	22·90	394·1
41·0	16·50	0·8055	24·89	394·4	88·2	14·62	0·7685	21·04	396·4
								Mean	394·4

131. *Methyl* n-*nonyl ketone.* B. p. 228·5°/748 mm.; *M* 170·29; n_{C} 1·42686, n_{D} 1·42907, n_{F} 1·43448, $n_{\mathrm{G'}}$ 1·43843; R_{C} 52·99, R_{D} 53·22, R_{F} 53·81, $R_{\mathrm{G'}}$ 54·23; $Mn_{\mathrm{D}}^{20^\circ}$ 243·36. Densities determined : $d_{4^\circ}^{20^\circ}$ 0·8250, $d_{4^\circ}^{41\cdot5}$ 0·8098, $d_{4^\circ}^{60\cdot6^\circ}$ 0·7955, $d_{4^\circ}^{85\cdot8^\circ}$ 0·7770. The results of the surface tension measurements were unsatisfactory (P = 470—480) and the meniscus was not always clear; presumably the contact angle is not zero and determinations should be made by the maximum bubble-pressure method.

132. *Benzyl methyl ketone.* B. p. 102·5°/19 mm.; *M* 134·17; n_{C} 1·51195, n_{D} 1·51635, n_{F} 1·52756, $n_{\mathrm{G'}}$ 1·5370 (approximate; line difficult to see); R_{C} 40·19, R_{D} 40·48, R_{F} 41·21, $R_{\mathrm{G'}}$ 41·83; $Mn_{\mathrm{D}}^{20^\circ}$ 203·46. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0018, $d_{4^\circ}^{40\cdot3^\circ}$ 0·9850, $d_{4^\circ}^{59\cdot9^\circ}$ 0·9690, $d_{4^\circ}^{85\cdot3^\circ}$ 0·9470. Apparatus *A*.

t.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
19·2°	20·28	1·0025	38·07	332·4	60·7°	18·40	0·9683	33·36	333·0
23·1	20·15	0·9992	37·70	332·7	86·0	17·26	0·9464	30·59	333·4
40·2	19·37	0·9851	35·73	333·0				Mean	332·9

133. *Benzyl ethyl ketone.* B. p. 113·5°/17 mm.; *M* 148·20; n_{C} 1·50728, n_{D} 1·51146, n_{F} 1·52205, $n_{\mathrm{G'}}$ 1·53061; R_{C} 44·68, R_{D} 44·99, R_{F} 45·77, $R_{\mathrm{G'}}$ 46·39; $Mn_{\mathrm{D}}^{20^\circ}$ 224·00. Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9877, $d_{4^\circ}^{40\cdot4^\circ}$ 0·9717, $d_{4^\circ}^{60\cdot8^\circ}$ 0·9556, $d_{4^\circ}^{85\cdot9^\circ}$ 0·9344. Apparatus *A*.

19·7°	19·82	0·9879	36·66	369·1	61·2°	18·03	0·9553	32·25	369·7
20·3	19·74	0·9875	36·50	368·9	87·3	16·87	0·9333	29·48	370·0
41·2	18·87	0·9711	34·31	369·4				Mean	369·4

134. *Benzyl* n-*propyl ketone.* B. p. 243·5—244°/757 mm.; *M* 162·21; n_{C} 1·50227, n_{D} 1·50627, n_{F} 1·51649, $n_{\mathrm{G'}}$ 1·52465; R_{C} 49·28, R_{D} 49·62, R_{F} 50·46, $R_{\mathrm{G'}}$ 51·13; $Mn_{\mathrm{D}}^{20^\circ}$ 244·34. Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9718, $d_{4^\circ}^{40\cdot2^\circ}$ 0·9550, $d_{4^\circ}^{61\cdot4^\circ}$ 0·9386, $d_{4^\circ}^{85\cdot9^\circ}$ 0·9188. Apparatus *A*.

20·0°	19·21	0·9718	34·96	405·6	60·9°	17·45	0·9390	30·68	406·6
21·3	19·14	0·9708	34·79	405·8	86·9	16·43	0·9180	28·24	407·3
40·5	18·36	0·9548	32·83	406·6				Mean	406·3

135. *Methyl 2-phenylethyl ketone (benzylacetone).* B. p. 234·5°/770 mm.; *M* 148·20; n_{C} 1·50824, n_{D} 1·51237, n_{F} 1·52285, $n_{\mathrm{G'}}$ 1·53130; R_{C} 44·75, R_{D} 45·07, R_{F} 45·84, $R_{\mathrm{G'}}$ 46·46; $Mn_{\mathrm{D}}^{20^\circ}$ 224·14. Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9875, $d_{4^\circ}^{41\cdot1^\circ}$ 0·9711, $d_{4^\circ}^{60\cdot8^\circ}$ 0·9562, $d_{4^\circ}^{86\cdot9^\circ}$ 0·9348. Apparatus *D*.

19·0°	15·60	0·9867	38·01	372·9	62·0°	14·17	0·9533	33·43	373·0
26·8	15·37	0·9822	37·28	372·8	86·7	13·36	0·9350	30·85	373·5
41·3	14·85	0·9709	35·61	372·9				Mean	373·0

136. *Ethyl 2-phenylethyl ketone.* B. p. 247·5—248·5°/763 mm.; *M* 162·22; n_{C} 1·50451, n_{D} 1·50851, n_{F} 1·51864, $n_{\mathrm{G'}}$ 1·52664; R_{C} 49·25, R_{D} 49·58; R_{F} 50·41, $R_{\mathrm{G'}}$ 51·06; $Mn_{\mathrm{D}}^{20^\circ}$ 244·69. Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9760, $d_{4^\circ}^{41\cdot0^\circ}$ 0·9597, $d_{4^\circ}^{60\cdot8^\circ}$ 0·9439, $d_{4^\circ}^{86\cdot7^\circ}$ 0·9240. Apparatus *A*.

18·7°	20·00	0·9770	36·59	408·4	61·2°	18·30	0·9436	32·33	410·0
28·5	19·74	0·9694	35·83	409·4	85·8	17·25	0·9247	29·87	410·1
40·7	19·11	0·9599	34·35	409·1				Mean	409·4

137. *2-Phenylethyl* n-*propyl ketone.* B. p. 138·5°/16 mm.; *M* 176·25; n_{C} 1·49852, n_{D} 1·50232, n_{F} 1·51196, $n_{\mathrm{G'}}$ 1·51976; R_{C} 53·85, R_{D} 54·20, R_{F} 55·08, $R_{\mathrm{G'}}$ 55·79; $Mn_{\mathrm{D}}^{20^\circ}$ 264·78. Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9602, $d_{4^\circ}^{40\cdot9^\circ}$ 0·9445, $d_{4^\circ}^{59\cdot0^\circ}$ 0·9310, $d_{4^\circ}^{85\cdot9^\circ}$ 0·9100. Apparatus *A*.

19·7°	19·43	0·9604	34·94	446·2	59·9°	17·75	0·9303	30·92	446·8
23·2	19·28	0·9577	34·57	446·3	85·0	16·75	0·9107	28·56	447·3
40·5	18·46	0·9448	32·66	446·0				Mean	446·5

138. *Acetophenone.* B. p. 200°/759 mm.; *M* 120·14; n_{C} 1·52803, n_{D} 1·53349, n_{F} 1·54782, $n_{\mathrm{G'}}$ 1·55982; R_{C} 35·98, R_{D} 36·27, R_{F} 37·10, $R_{\mathrm{G'}}$ 37·77; $Mn_{\mathrm{D}}^{20^\circ}$ 184·23. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0282, $d_{4^\circ}^{41\cdot2^\circ}$ 1·0113, $d_{4^\circ}^{60\cdot8^\circ}$ 0·9949, $d_{4^\circ}^{85\cdot7^\circ}$ 0·9739. Apparatus *A*.

17·8°	20·69	1·0300	39·90	293·2	61·0°	18·67	0·9947	34·77	293·3
25·1	20·35	1·0240	39·02	293·2	86·2	17·58	0·9734	32·04	293·6
40·0	19·69	1·0119	37·31	293·4				Mean	293·3

139. *Propiophenone.* B. p. 215°/763 mm.; *M* 134·17; n_{C} 1·52181, n_{D} 1·52688, n_{F} 1·54008, $n_{\mathrm{G'}}$ 1·55106; R_{C} 40·50, R_{D} 40·83, R_{F} 41·68, $R_{\mathrm{G'}}$ 42·38; $Mn_{\mathrm{D}}^{20^\circ}$ 204·86. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0101, $d_{4^\circ}^{41\cdot8^\circ}$ 0·9934, $d_{4^\circ}^{61\cdot2^\circ}$ 0·9776, $d_{4^\circ}^{85\cdot5^\circ}$ 0·9572. Apparatus *D*.

22·3°	14·95	1·0082	37·22	328·7	60·1°	13·69	0·9785	33·08	328·8
24·5	14·80	1·0065	36·79	328·3	86·7	12·80	0·9562	30·23	329·0
41·4	14·29	0·9937	35·07	328·7				Mean	328·7

140. *Butyrophenone.* B. p. 228°/777 mm.; *M* 148·20; n_{C} 1·51511, n_{D} 1·51988, n_{F} 1·53234, n_{G} 1·54248; R_{C} 45·23, R_{D} 45·58, R_{F} 46·49, $R_{\mathrm{G'}}$ 47·23; $Mn_{\mathrm{D}}^{20^\circ}$ 225·25. Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9885, $d_{4^\circ}^{41\cdot5^\circ}$ 0·9727, $d_{4^\circ}^{61\cdot0^\circ}$ 0·9575, $d_{4^\circ}^{86\cdot0^\circ}$ 0·9370. Apparatus *D*.

24·5°	14·41	0·9851	35·06	366·1	61·4°	13·30	0·9572	31·44	366·6
29·3	14·34	0·9814	34·76	366·7	86·9	12·61	0·9363	29·16	367·8
41·0	13·87	0·9731	33·33	365·9				Mean	366·6

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