366. *Physical Properties and Chemical Constitution. Part XX. Aliphatic Alcohols and Acids.*

By Arthur I. Vogel.

The refractivities at 20° and the parachors of a number of alcohols and aliphatic acids have been determined. Subtraction of the constants for alkyl groups (Part XI, this vol., p. 610) lead to the following mean values for the contributions of the OH and the CO_2H group:

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
OH	30·2	2·536	2·546	2·570	2·588	23·94
CO_2H	73·7	7·191	7·226	7·308	7·368	63·98

Summation of the constants for CO (Part XI, *loc. cit.*) and OH gives values approximately equal to those determined directly for CO_2H; this is in contrast to COO (esters), the constants of which are very different from those deduced from CO (ketones) + O (ethers) (Part XII, this vol., p. 624).

Contrary to Sugden's views ("The Parachor and Valency", 1930, p. 167) no "negative anomaly" of the parachor nor its steady decrease with temperature over the normal temperature range studied could be detected; it is improbable, therefore, that the parachor can be employed to detect association in aliphatic alcohols and acids.

The objects of the present investigation were: (*a*) The direct determination of the contributions of the OH and the CO_2H group to the parachor and refractivities. (*b*) A comparison of the constants calculated from {CO (Part XI, *loc. cit.*) + OH} with those determined directly for CO_2H. Eisenlohr (*Z. physikal. Chem.*, 1911, **75**, 585; "Spektrochemie organischer Verbindungen: Molekularrefraktion und -dispersion", Ferdinand Enke, 1912, p. 48) computed the refractivity constants for "carbonyl oxygen" O″ from aldehydes and ketones, $C_nH_{2n}O'' - [CH_2]_n$, and for "hydroxyl oxygen" O′ from acids, $C_nH_{2n}O''O' - [CH_2]_n$. It seems surprising, that although the refractivities for some 10 aliphatic alcohols $C_nH_{2n+2}O'$ are collected (*loc. cit.*, p. 590), yet these figures are not employed for the calculation of the constants for "hydroxyl oxygen" but merely for the evaluation of the CH_2 constants and for H (from $C_nH_{2n+2}O' - [CH_2]_n - O'$). Eisenlohr's figures for CH_2 differ considerably from the author's (compare Part IX, *J.*, 1946, 133), and in consequence all the derived constants are subject to appreciable error.

Sugden (*op. cit.*, p. 167; *J.*, 1924, **125**, 38, 1185) utilises the so-called "negative anomaly" between the observed and the predicted value of the parachor and its steady decrease with rise of temperature as evidence for the association of the lower aliphatic alcohols and acids. The results for methyl alcohol, ethyl alcohol, and acetic acid quoted by Sugden in support of this view cover a range of temperatures approaching that of the critical temperature; furthermore, Sugden (*op. cit.*, p. 36) agrees that at high temperatures both the surface tensions and the densities are difficult to measure with accuracy. The author's own parachor determinations of the lower aliphatic alcohols and acids extending to temperatures within 20—25° of the boiling point do not reveal any such "negative anomaly": the use of the parachor in the detection of association must therefore be accepted with considerable reserve.

The constants for OH have been deduced from the author's own measurements upon aliphatic alcohols by subtracting the values for the alkyl groups (Part XI, *loc. cit.*). The constants for the *n*-nonyl, *n*-decyl, and *n*-undecyl groups have been evaluated from the corresponding hydrocarbons (Part IX, *loc. cit.*), *e.g.*, $n\text{-}C_9H_{20} - H$; $R_{G'}$ for *n*-nonane appears to be slightly in error and the value has been deduced from $C_8H_{17}{}^a + CH_2$. The parachor values are not given for those compounds which give erratic surface tensions by the method of capillary rise.

It will be observed that, unlike most other homologous series, the first member of the series and the secondary alcohol (*iso*propyl alcohol) do not give abnormally high values; they have accordingly been included in the calculation of the mean values. The results for methyl cellosolve, cellosolve, and butyl cellosolve, computed from the relationship

$$OH = Alkyl{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OH - \{Alkyl + 2CH_2 + O \text{ (in ethers)}\}$$

fall into line. For purposes of comparison the figures deduced for benzyl alcohol and 2-phenylethyl alcohol are included in Table I: the constants for $C_6H_5{\cdot}CH_2$ were calculated from $C_6H_5{\cdot}CH_2Cl$ (XIV, **261**) − Cl, and $C_6H_5{\cdot}CH_2{\cdot}CH_2$ was assumed to be $C_6H_5{\cdot}CH_2 + CH_2$.

The refractivities at 20° and, wherever possible, the parachors of a number of aliphatic carboxylic acids have been determined, and the contributions of the CO_2H group calculated by subtracting the constants for the alkyl groups. The results are summarised in Table II: the

TABLE I.

Values for the OH *group in alcohols.*

Alcohol.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$
MeOH	32·8	2·54	2·57	2·58	2·61	24·44
EtOH	31·4	2·58	2·60	2·63	2·65	24·00
Pr^nOH	29·7	2·56	2·57	2·60	2·62	24·07
Pr^iOH	30·6	2·59	2·60	2·62	2·64	23·80
Bu^nOH	30·0	2·54	2·55	2·57	2·58	23·91
Bu^iOH	28·8	2·54	2·55	2·57	2·58	23·89
Am^nOH	29·2	2·58	2·59	2·61	2·63	23·83
Am^iOH (synthetic)	—	2·54	2·56	2·58	2·59	23·88
$C_6H_{13}{}^nOH$	—	2·52	2·53	2·57	2·57	23·80
$C_7H_{15}{}^nOH$	—	2·48	2·49	2·51	2·53	23·66
$C_8H_{17}{}^nOH$	—	2·52	2·53	2·57	2·60	23·79
$C_9H_{19}{}^nOH$	—	2·56	2·55	2·59	2·60	23·73
$C_{10}H_{21}{}^nOH$	—	2·53	2·53	2·54	2·56	23·89
$C_{11}H_{23}{}^nOH$	—	2·51	2·52	2·54	2·56	23·90
C_3H_5·OH	29·4	2·45	2·46	2·47	2·49	24·45
Mean OH	30·2	2·536	2·546	2·570	2·588	23·94
MeO·CH_2·CH_2·OH	31·8	2·45	2·45	2·47	2·48	24·69
EtO·CH_2·CH_2·OH	30·2	2·53	2·54	2·54	2·56	24·29
Bu^nO·CH_2·CH_2·OH	—	2·51	2·50	2·53	2·54	23·91
Ph·CH_2·OH	—	2·28	2·28	2·28	2·26	21·65
Ph·CH_2·CH_2·OH	34·0	2·30	2·28	2·29	2·27	22·16

constants for acetic acid have been omitted in the calculation of the mean values. The parachor results are in good agreement with those of Hunter and Maass (*J. Amer. Chem. Soc.*, 1929, **51**, **153**); their "experimental values of the parachors were the average obtained over 80° temperature range" over which the variation was less than 1%.

TABLE II.

Values for the CO_2H *group in aliphatic carboxylic acids.*

Acid.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
Me·CO_2H *	76·0	7·29	7·34	7·42	7·49	64·23
Et·CO_2H	74·1	7·17	7·21	7·29	7·36	63·97
Pr^n·CO_2H	73·8	7·21	7·25	7·33	7·39	63·89
Pr^i·CO_2H	74·0	7·16	7·19	7·26	7·33	63·74
Bu^n·CO_2H	73·2	7·21	7·24	7·33	7·38	63·99
Bu^i·CO_2H	73·5	7·19	7·23	7·31	7·37	63·78
Am^n·CO_2H	—	7·20	7·23	7·30	7·37	64·06
$C_6H_{13}{}^n$·CO_2H	—	7·19	7·22	7·32	7·37	64·22
$C_7H_{15}{}^n$·CO_2H	—	7·20	7·24	7·32	7·37	64·15
Mean CO_2H (excluding *)	73·7	7·191	7·226	7·308	7·368	63·98

It is of interest to compare the above mean values for CO_2H with those obtained by the summation of CO (Part XI, *loc. cit.*; the mean values of CO deduced from all the ketones were used) and OH. The results are:

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
CO + OH	75·3	7·180	7·214	7·293	7·360	66·33

The difference in the parachor is 1·6 units; the agreement between the refractivities must be regarded as fairly satisfactory in view of the slight variation of the individual CO constants (compare Part XI, *loc. cit.*). These results should be compared with those for COO in esters, the values for which differ considerably from those computed from CO (ketones) + O (ethers) (Part XIII, *loc. cit.*).

If the values for H deduced from CH_2 in aliphatic hydrocarbons (Part IX, *loc. cit.*) are subtracted from those found for OH, the following constants for O (hydroxyl) are obtained:

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
O (in OH; Vogel)	14·7	1·510	1·518	1·527	1·548	26·50
O (in OH; Eisenlohr)	—	1·522	1·525	1·531	1·541	—

The agreement of the refractivities with Eisenlohr's figures would seem to be fortuitous owing to his use of what must now be regarded as approximate values for CH_2. These values differ from the constants for O (ethers) and O (acetals) (Part XII, this vol., p. 616).

Added October 14th, 1948.—The author is now of the opinion that two series of values for the constants of CO in ketones are required. The following mean values have been deduced from the date given in Part XI (this vol., p. 611; Table II).

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
CO (in ketones).....................	44·4	4·579	4·601	4·654	4·702	42·41
CO (in methyl ketones)	46·7	4·730	4·758	4·814	4·874	42·42

If the former constants are employed, the results for CO + OH are:

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
CO + OH	74·6	7·115	7·147	7·224	7·290	66·35

Experimental.

Methyl alcohol. One litre of Burrough's synthetic absolute methyl alcohol was dried by Lund and Bjerrum's method (*Ber.*, 1931, **64**, 210) and carefully fractionated through a three-section Pyrex Young and Thomas column, a middle fraction being collected; b. p. 64·5/766 mm. (In the purification of this and the other alcohols precautions were taken to prevent the entrance of moisture; similar precautions were taken during the actual physical measurements.)

Ethyl alcohol. One litre of Burrough's absolute ethyl alcohol was similarly purified; b. p. 78°/760 mm.

The following nine alcohols were dried (A.R. K_2CO_3) and fractionated.

n-*Propyl alcohol.* Redistilled Bisol *n*-propyl alcohol, b. p. 96·5—97°/760 mm., gave b. p. 96·5°/764 mm.

iso*Propyl alcohol.* Redistilled Bisol *iso*propyl alcohol, b. p. 82·1—82·4°/760 mm., gave b. p. 82·3°/760 mm.

n-*Butyl alcohol.* Redistilled Bisol *n*-butyl alcohol, b. p. 117·0—117·2°/750 mm., gave b. p.117°/754 mm.

iso*Butyl alcohol.* Redistilled Bisol product, b. p. 106—108°/752 mm., gave b. p. 107·5°/752 mm.

n-*Amyl alcohol.* Boots synthetic *n*-amyl alcohol gave alcohol of b. p. 136°/746 mm.

iso*Amyl alcohol.* Sharples synthetic *iso*butylcarbinol afforded alcohol of b. p. 130°/746 mm.

iso*Amyl alcohol.* Bisol fermentation *iso*amyl alcohol finally had b. p. 130·5°/764 mm. The physical properties varied slightly from sample to sample, and hence were not employed in the calculation of the OH constants.

n-*Hexyl alcohol.* The redistilled Carbon and Carbide Corporation product, b. p. 156—157°/752 mm., was purified to b. p. 155·5°/736 mm.

n-*Heptyl alcohol.* A large sample, b. p. 175—177°/771 mm., prepared by reduction of redistilled *n*-heptaldehyde with iron and acetic acid (*Org. Synth.*, 1926, **6**, 52), ultimately had b. p. 175°/764 mm.

The starting material for the next four alcohols was the Deutsche Hydrierwerke product.

n-*Octyl alcohol.* About 250 g. were carefully fractionated, and a middle fraction collected; b. p. 193·5°/764 mm.

n-*Nonyl alcohol.* The alcohol was dried, twice distilled, and a middle fraction collected; b. p. 212°/765 mm.

n-*Decyl and* n-*undecyl alcohol.* The dried product was twice distilled, and a middle sample taken; b. p. 229°/760 mm. and 243·5°/769 mm., respectively.

Allyl alcohol. The B.D.H. pure product was dried (A.R. K_2CO_3) and fractionated through a three-section Pyrex Young and Thomas column; b. p. 97°/760 mm.

The initial alcohol in the following three cases was a Carbon and Carbide Corporation product.

"*Methyl cellosolve*" (*2-methoxyethyl alcohol*). The alcohol was dried (A.R. K_2CO_3) and distilled in an all-glass apparatus through a lagged Widmer column; b. p. 124°/757 mm.

"*Cellosolve*" (*2-ethoxyethyl alcohol*). This was similarly purified; b. p. 135°/761 mm.

"*Butyl cellosolve*" (*2-butoxyethyl alcohol*). This was dried (A.R. K_2CO_3,) fractionated through a well-lagged all-glass Dufton column, and then distilled in an all-glass apparatus; b. p. 168°/754 mm.

Benzyl alcohol. The B.D.H. pure product was dried (K_2CO_3) and fractionated; b. p. 203°/754 mm.

2-Phenylethyl alcohol. A pure commercial product was dried and fractionally distilled; b. p. 216·5°/755 mm.

Tetrahydrofurfuryl alcohol. The B.D.H. product was dried ($CaSO_4$) and carefully fractionated; b. p. 176°/762 mm.

Acetic acid. The procedure employed is based upon that described by Bousfield and Lowry (*J.*, 1911, **99**, 1432). 200 G. of B.D.H. A.R. glacial acetic acid were mixed with 4 g. of A.R. potassium permanganate and distilled from a 250-ml. round-bottomed flask through a three-section Pyrex Young and Thomas column, precautions being taken to prevent ingress of moisture: more than one-third distilled below 116·5°, the remainder at 117·0°, thus proving that purification by direct distillation with potassium permanganate is unsatisfactory. About 600 g. of A.R. glacial acetic acid were partly frozen, and *ca.* 300 g. of liquid poured off. The residual 300 g. was melted, mixed with 6 g. of A.R. potassium permanganate and fractionally distilled as before. The fraction, b. p. 116·5—117·5°/765 mm. (*ca.* 225 g.), was collected, partly frozen and about half of the fluid portion rejected. Repetition of the distillation afforded pure acetic acid of b. p. 118·0°/765 mm.

Propionic acid. About 1 l. of Boake Roberts commercial acid were dried (Na_2SO_4) and fractionated through a three-section Pyrex Young and Thomas column, that boiling at 139—141°/760 mm. (mainly 140·8—141·0°) being collected separately. 300 G. of this redistilled acid were mixed with 6 g. of A.R. potassium permanganate and fractionated as before; the first half was rejected, and the remainder distilled constantly at 140·7°/760 mm., from which a middle fraction was separated for the physical measurements.

n-*Butyric acid.* 250 G. of the redistilled commercial product, b. p. 161·5—163°/756 mm., were mixed with 5 g. of A.R. potassium permanganate and fractionated as before. The first third was discarded, and the remainder distilled constantly at 162·5°/767 mm.

iso*Butyric acid.* About 500 g. of Hopkin and Williams pure acid were dried (Na_2SO_4) and fractionally distilled through a two-section Pyrex Young and Thomas column. After a small fraction of low b. p. had passed over, the acid boiled constantly at 154·5°/775 mm., from which a middle fraction was set aside for the physical measurements.

n-*Valeric acid.* This acid was synthesised in quantity according to the scheme : *n*-Butyl bromide ⟶ *n*-butyl cyanide ⟶ *n*-valeric acid. A large sample was distilled, and a middle fraction, b. p. 184°/768 mm., was collected.

iso*Valeric acid.* About 500 g. of Kahlbaum's pure acid was dried (Na_2SO_4) and fractionally distilled as before; b. p. 176·5°/762 mm.

n-*Hexoic acid.* Boots pure acid was dried and redistilled; b. p. 203°/756 mm.

n-*Heptoic acid.* A large commercial sample was dried and twice fractionated; b. p. 222°/764 mm.

n-*Octoic acid.* The redistilled Deutsche Hydrierwerke product, b. p. 235·5—238°/762 mm., was carefully fractionated; b. p. 236°/769 mm.

453. *Methyl alcohol.* B. p. 64·5°/766 mm.; *M* 32·04; n_C 1·32694, n_D 1·32855, n_F 1·33225, $n_{G'}$ 1·33477; R_C 8·18, R_D 8·22, R_F 8·30, $R_{G'}$ 8·36; $Mn_D^{20°}$ 42·57. Densities determined : $d_{4°}^{20°}$ 0·7924, $d_{4°}^{40·9°}$ 0·7727. Apparatus *A*.

(These headings apply to all subsequent tables in this paper.)

t.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
15·2°	15·33	0·7969	22·88	87·9	28·2°	14·86	0·7847	21·83	88·3
19·0	15·21	0·7934	22·60	88·0	40·2	14·38	0·7733	20·96	88·7
								Mean	88·2

454. *Ethyl alcohol.* B. p. 78°/760 mm.; *M* 46·07; n_C 1·35959, n_D 1·36139, n_F 1·36565, $n_{G'}$ 1·36855; R_C 12·84, R_D 12·90, R_F 13·04, $R_{G'}$ 13·13; $Mn_D^{20°}$ 62·72. Densities determined : $d_{4°}^{20°}$ 0·7910, $d_{4°}^{41·3°}$ 0·7735, $d_{4°}^{57·2°}$ 0·7597. Apparatus *A*.

16·8°	15·18	0·7937	22·56	126·5	40·3°	14·32	0·7743	20·76	127·0
22·3	15·02	0·7891	22·19	126·7	59·3	13·43	0·7580	19·06	127·1
25·8	14·93	0·7862	21·98	126·9				Mean	126·8

455. n-*Propyl alcohol.* B. p. 96·5°/764 mm.; *M* 60·13; n_C 1·38364, n_D 1·38556, n_F 1·39015, $n_{G'}$ 1·39341; R_C 17·46, R_D 17·54, R_F 17·73, $R_{G'}$ 17·86; $Mn_D^{20°}$ 83·32. Densities determined : $d_{4°}^{20°}$ 0·8043, $d_{4°}^{41·6}$ 0·7880, $d_{4°}^{59·4°}$ 0·7745. Apparatus *A*.

17·8°	15·84	0·8060	23·91	165·0	41·6°	14·90	0·7880	21·99	165·3
21·0	15·73	0·8035	23·61	165·0	59·9	14·23	0·7741	20·63	165·7
								Mean	165·2

456. iso*Propyl alcohol.* B. p. 82·3°/760 mm.; *M* 60·09; n_C 1·37523, n_D 1·37711, n_F 1·38168, $n_{G'}$ 1·38484; R_C 17·50, R_D 17·58, R_F 17·77, $R_{G'}$ 17·90; $Mn_D^{20°}$ 82·75. Densities determined : $d_{4°}^{20°}$ 0·7864, $d_{4°}^{41·2°}$ 0·7697, $d_{4°}^{59·2°}$ 0·7532. Apparatus *A*.

17·1°	14·68	0·7888	21·68	164·4	41·9°	13·60	0·7691	19·59	164·4
21·0	14·50	0·7858	21·34	164·3	59·5	12·75	0·7530	17·98	164·5
								Mean	164·4

457. n-*Butyl alcohol.* B. p. 117°/754 mm.; *M* 74·12; n_C 1·39732, n_D 1·39929, n_F 1·40407, $n_{G'}$ 1·40744; R_C 22·04, R_D 22·14. R_F 22·37, $R_{G'}$ 22·53; $Mn_D^{20°}$ 103·72. Densities determined : $d_{4°}^{20°}$ 0·8104, $d_{4°}^{40·4°}$ 0·7956, $d_{4°}^{61·0°}$ 0·7793, $d_{4°}^{85·0°}$ 0·7594. Apparatus *A*.

16·0°	16·91	0·8134	25·76	205·3	61·8°	14·85	0·7787	21·65	205·3
24·0	16·53	0·8074	24·99	205·3	86·5	13·70	0·7582	19·45	205·3
41·9	15·80	0·7945	23·51	205·4				Mean	205·3

458. iso*Butyl alcohol.* B. p. 107·5°/752 mm.; *M* 74·12; n_C 1·39343, n_D 1·39549, n_F 1·40016, $n_{G'}$ 1·40361; R_C 22·07, R_D 22·17, R_F 22·41, $R_{G'}$ 22·57; $Mn_D^{20°}$ 103·43. Densities determined : $d_{4°}^{20°}$ 0·8021, $d_{4°}^{42·7°}$ 0·7852, $d_{4°}^{61·5°}$ 0·7699, $d_{4°}^{85·0°}$ 0·7501. Apparatus *D*.

15·9°	11·69	0·8053	23·25	202·1	61·9°	10·34	0·7696	19·65	202·8
23·2	11·46	0·7996	22·63	202·2	86·5	9·52	0·7489	17·61	202·7
41·3	10·98	0·7863	21·32	202·6				Mean	202·6

459. n-*Amyl alcohol.* B. p. 136°/746 mm.; *M* 88·15; n_C 1·40793, n_D 1·40999, n_F 1·41498, n_G 1·41854; R_C 26·72, R_D 26·84, R_F 27·13, $R_{G'}$ 27·33; $Mn_D^{20°}$ 124·29. Densities determined : $d_{4°}^{20°}$ 0·8136, $d_{4°}^{41·4°}$ 0·7981, $d_{4°}^{60·6°}$ 0·7835, $d_{4°}^{85·0°}$ 0·7640. Apparatus *D*.

14·3°	13·04	0·8178	26·31	244·2	62·2°	11·46	0·7823	22·14	244·4
17·2	12·92	0·8157	26·03	244·1	87·0	10·56	0·7625	19·93	244·1
40·9	12·14	0·7958	23·94	244·2				Mean	244·2

460A. iso*Amyl alcohol* (fermentation; Bisol). B. p. 130·5°/764 mm.; *M* 88·15; n_C 1·40527, n_D 1·40731, n_F 1·41227, $n_{G'}$ 1·41582; R_C 26·64, R_D 26·75, R_F 27·03, $R_{G'}$ 27·24; $Mn_D^{20^\circ}$ 124·05. Densities determined: $d_{4^\circ}^{2\cdot0}$ 0·8118, $d_{4^\circ}^{42\cdot3^\circ}$ 0·7952, $d_{4^\circ}^{61\cdot4^\circ}$ 0·7813, $d_{4^\circ}^{87\cdot0^\circ}$ 0·7598. Apparatus *D*.

t.	*H.*	d_{4°.	γ.	*P.*	*t.*	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	*P.*
19·3°	12·07	0·8123	24·21	240·8	60·9°	10·78	0·7817	20·81	240·9
24·3	11·87	0·8085	23·70	240·6	86·5	9·93	0·7602	18·64	240·9
42·3	11·36	0·7952	22·31	240·9					Mean 240·8

460B. iso*Amyl alcohol* (synthetic; Sharples). B. p. 130°/746 mm.; n_C 1·40657, n_D 1·40865, n_F 1·41361, $n_{G'}$ 1·41708; R_C 26·64, R_D 26·76, R_F 27·04, $R_{G'}$ 27·24; $Mn_D^{20^\circ}$ 124·18. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8139, $d_{4^\circ}^{40\cdot0^\circ}$ 0·7994, $d_{4^\circ}^{60\cdot2^\circ}$ 0·7844, $d_{4^\circ}^{86\cdot0^\circ}$ 0·7639.

461. n-*Hexyl alcohol.* B. p. 155·5°/736 mm.; *M* 102·17; n_C 1·41606, n_D 1·41816, n_F 1·42325, $n_{G'}$ 1·42694; R_C 31·25, R_D 31·39, R_F 31·73, $R_{G'}$ 31·96; $Mn_D^{20^\circ}$ 144·90. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8205, $d_{4^\circ}^{41\cdot0^\circ}$ 0·8058, $d_{4^\circ}^{61\cdot8^\circ}$ 0·7909, $d_{4^\circ}^{86\cdot4^\circ}$ 0·7713. The surface-tension results by the method of capillary rise were erratic.

462. n-*Heptyl alcohol.* B. p. 175°/764 mm.; *M* 116·20; n_C 1·42137, n_D 1·42351, n_F 1·42870, $n_{G'}$ 1·43243; R_C 35·88, R_D 36·04, R_F 36·42, $R_{G'}$ 36·70; $Mn_D^{20^\circ}$ 165·41; $d_{4^\circ}^{20^\circ}$ 0·8219.

463. n-*Octyl alcohol.* B. p. 212°/765 mm.; *M* 144·25; n_C 1·43105, n_D 1·43325, n_F 1·43856, $n_{G'}$ 1·44241; R_C 45·14, R_D 45·34, R_F 45·83, $R_{G'}$ 46·17; $Mn_D^{20^\circ}$ 206·75; $d_{4^\circ}^{20^\circ}$ 0·8273.

464. n-*Nonyl alcohol.* B. p. 212°/765 mm.; *M* 144·25; n_C 1·43105, n_D 1·43325, n_F 1·43856, $n_{G'}$ 1·44241; R_C 45·14, R_D 45·34, R_F 45·83, $R_{G'}$ 46·17; $Mn_D^{20^\circ}$ 206·75; $d_{4^\circ}^{20^\circ}$ 0·8273.

465. n-*Decyl alcohol.* B. p. 229°/760 mm.; *M* 158·26; n_C 1·43440, n_D 1·43660, n_F 1·44197, $n_{G'}$ 1·44591; R_C 49·78, R_D 50·00, R_F 50·53, $R_{G'}$ 50·92; $Mn_D^{20^\circ}$ 227·36; $d_{4^\circ}^{20^\circ}$ 0·8287.

466. n-*Undecyl alcohol.* B. p. 243·5°/769 mm.; *M* 172·30; n_C 1·43697, n_D 1·43918, n_F 1·44460, $n_{G'}$ 1·44859; R_C 54·40, R_D 54·64, R_F 55·22, $R_{G'}$ 55·65; $Mn_D^{20^\circ}$ 247·97; $d_{4^\circ}^{20^\circ}$ 0·8298.

467. *Allyl alcohol.* B. p. 97°/760 mm.; *M* 58·08; n_C 1·40994, n_D 1·41266, n_F 1·41941, $n_{G'}$ 1·42456; R_C 16·88, R_D 16·98, R_F 17·22, $R_{G'}$ 17·41; $Mn_D^{20^\circ}$ 82·05. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8524, $d_{4^\circ}^{41\cdot5^\circ}$ 0·8345, $d_{4^\circ}^{61\cdot0^\circ}$ 0·8176. Apparatus *A*.

17·1°	16·25	0·8549	26·01	153·4	41·2°	15·23	0·8348	23·81	153·7
28·5	15·75	0·8452	24·93	153·5	60·2	14·43	0·8183	22·11	154·4
									Mean 153·7

468. 2-*Methoxyethyl alcohol* ("*methyl cellosolve*"). B. p. 124°/757 mm.; *M* 76·07; n_C 1·40039, n_D 1·40238, n_F 1·40713, $n_{G'}$ 1·41049; R_C 19·10, R_D 19·18, R_F 19·38, $R_{G'}$ 19·52; $Mn_D^{20^\circ}$ 106·68. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9663, $d_{4^\circ}^{40\cdot9^\circ}$ 0·9465, $d_{4^\circ}^{61\cdot9^\circ}$ 0·9277, $d_{4^\circ}^{86\cdot1^\circ}$ 0·9043. Apparatus *A*.

14·9°	17·50	0·9710	31·82	186·1	61·5°	15·68	0·9281	27·25	187·3
41·0	16·52	0·9464	29·28	187·0	85·6	14·68	0·9048	24·87	187·8
									Mean 187·1

469. 2-*Ethoxyethyl alcohol* ("*cellosolve*"). B. p. 135°/761 mm.; *M* 90·12; n_C 1·40547, n_D 1·40751, n_F 1·41224, $n_{G'}$ 1·41591; R_C 23·78, R_D 23·89, R_F 24·13, $R_{G'}$ 24·32; $Mn_D^{20^\circ}$ 126·84. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9297, $d_{4^\circ}^{41\cdot0^\circ}$ 0·9114, $d_{4^\circ}^{60\cdot9^\circ}$ 0·8941, $d_{4^\circ}^{86\cdot4^\circ}$ 0·8713. Apparatus *D*.

24·7°	12·45	0·9255	28·46	224·9	60·3°	11·33	0·8946	25·03	225·3
29·1	12·33	0·9218	28·07	225·0	87·2	10·64	0·8706	22·88	226·4
40·3	11·92	0·9120	26·85	224·9					Mean 225·3

470. n-*Butoxyethyl alcohol* ("*butyl cellosolve*"). B. p. 168°/754 mm.; *M* 118·17; n_C 1·41745, n_D 1·41956, n_F 1·42458, $n_{G'}$ 1·42833; R_C 32·99, R_D 33·13, R_F 33·48, $R_{G'}$ 33·73; $Mn_D^{20^\circ}$ 167·75. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9018, $d_{4^\circ}^{40\cdot0^\circ}$ 0·8850, $d_{4^\circ}^{60\cdot5^\circ}$ 0·8681, $d_{4^\circ}^{86\cdot4^\circ}$ 0·8457. Apparatus *A*.

17·9°	15·73	0·9036	26·62	297·0	60·1°	14·25	0·8684	23·17	297·9
40·9	15·13	0·8843	25·05	299·0	86·5	13·34	0·8456	21·12	299·4
									Mean 298·3

The surface-tension measurements were not altogether satisfactory and require confirmation by the method of maximum bubble pressure

471. *Benzyl alcohol.* B. p. 203°/754 mm.; *M* 108·13; n_C 1·53552, n_D 1·54033, n_F 1·55259, $n_{G'}$ 1·56227; R_C 32·22, R_D 32·47, R_F 33·08, $R_{G'}$ 33·56; $Mn_D^{20^\circ}$ 166·55. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0454, $d_{4^\circ}^{41\cdot1^\circ}$ 1·0301, $d_{4^\circ}^{61\cdot0^\circ}$ 1·0152, $d_{4^\circ}^{86\cdot6^\circ}$ 0·9952. The surface tension results were unsatisfactory.

472. 2-*Phenylethyl alcohol.* B. p. 216·5°/755 mm.; *M* 122·16; n_C 1·52760, n_D 1·53210, n_F 1·54363, $n_{G'}$ 1·55259; R_C 36·86, R_D 37·12, R_F 37·79, $R_{G'}$ 38·31; $Mn_D^{20^\circ}$ 187·15. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0198, $d_{4^\circ}^{40\cdot0^\circ}$ 1·0053, $d_{4^\circ}^{60\cdot5^\circ}$ 0·9904, $d_{4^\circ}^{86\cdot4^\circ}$ 0·9701. Apparatus *D*.

24·5°	16·09	1·0165	40·39	303·0	59·5°	14·98	0·9911	36·67	303·3
40·9	15·55	1·0047	38·58	303·0	86·7	14·16	0·9699	33·92	303·9
									Mean 303·3

473. *Tetrahydrofurfuryl alcohol.* B. p. 176°/762 mm.; M 102·13, n_C 1·44987, n_D 1·45197, n_F 1·45731, $n_{G'}$ 1·46173; R_C 26·05, R_D 26·15, R_F 26·42, $R_{G'}$ 26·64; $Mn_D^{20°}$ 148·29. Densities determined: $d_{4°}^{20°}$ 1·0535, $d_{4°}^{41·3°}$ 1·0365, $d_{4°}^{61·5°}$ 1·0194, $d_{4°}^{86·5°}$ 0·9984. Apparatus *A*.

t.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
21·6°	14·55	1·0522	37·81	240·7	60·5°	13·43	1·0202	33·84	241·4
22·8	14·50	1·0512	37·64	240·7	87·0	12·67	0·9971	31·20	242·1
40·7	14·00	1·0370	35·85	241·0					Mean 241·5

474. *Acetic acid.* B. p. 118·0°/765 mm.; M 60·05; n_C 1·36952, n_D 1·37151, n_F 1·37615, $n_{G'}$ 1·37941; R_C 12·93, R_D 12·99, R_F 13·14, $R_{G'}$ 13·24; $Mn_D^{20°}$ 82·36. Densities determined: $d_{4°}^{20°}$ 1·0492, $d_{4°}^{41·4°}$ 1·0267, $d_{4°}^{61·4}$ 1·0044, $d_{4°}^{87·1°}$ 0·9769. Apparatus *D*.

20·1°	10·64	1·0491	27·57	131·2	42·3°	10·01	1·0257	25·36	131·4
23·1	10·55	1·0459	27·25	131·2	61·8	9·46	1·0040	23·46	131·9
26·9	10·48	1·0418	26·96	131·3	87·5	8·65	0·9765	20·86	131·4
									Mean 131·4

475. *Propionic acid.* B. p. 140·7°/760 mm.; M 74·08; n_C 1·38425, n_D 1·38623, n_F 1·39098, $n_{G'}$ 1·39430; R_C 17·43, R_D 17·51, R_F 17·70, $R_{G'}$ 17·84; $Mn_D^{20°}$ 102·69. Densities determined: $d_{4°}^{20°}$ 0·9942, $d_{4°}^{42·3°}$ 0·9715, $d_{4°}^{62·1°}$ 0·9510, $d_{4°}^{86·5°}$ 0·9263. Apparatus *A*.

14·6°	14·52	0·9997	27·24	169·2	61·5°	12·65	0·9516	22·54	169·6
26·1	14·13	0·9880	26·14	169·5	86·3	11·62	0·9265	20·16	169·4
42·1	13·42	0·9717	24·42	169·5					Mean 169·4

476. n-*Butyric acid.* B. p. 162·5°/767 mm.; M 88·10; n_C 1·39552, n_D 1·39768, n_F 1·40256, $n_{G'}$ 1·40612; R_C 22·11, R_D 22·22, R_F 22·46, $R_{G'}$ 22·63; $Mn_D^{20°}$ 123·14. Densities determined: $d_{4°}^{20°}$ 0·9563, $d_{4°}^{41·2°}$ 0·9373, $d_{4°}^{61·0°}$ 0·9187, $d_{4°}^{86·8°}$ 0·8938. Apparatus *A*.

22·5°	14·70	0·9540	26·26	209·0	42·0	13·96	0·9366	24·48	209·2
24·4	14·64	0·9522	26·10	209·1	61·4	13·20	0·9183	22·70	209·4
29·8	14·46	0·9473	25·65	209·3	87·3	12·15	0·8933	20·32	209·4
									Mean 209·3

477. iso*Butyric acid.* B. p. 154·5°/775 mm.; M 88·10; n_C 1·39096, n_D 1·39300, n_F 1·39782, $n_{G'}$ 1·40129; R_C 22·07, R_D 22·17, R_F 22·41, $R_{G'}$ 22·59; $Mn_D^{20°}$ 122·69. Densities determined: $d_{4°}^{20°}$ 0·9483, $d_{4°}^{41·3°}$ 0·9276, $d_{4°}^{60·8°}$ 0·9090, $d_{4°}^{85·2°}$ 0·8843. Apparatus *D*.

15·1°	10·88	0·9531	25·61	207·9	41·8°	10·02	0·9271	22·96	207·8
20·1	10·71	0·9482	25·08	207·9	59·5	9·46	0·9103	21·27	207·9
23·5	10·63	0·9459	24·83	207·8	87·5	8·61	0·8821	18·76	207·6
									Mean 207·8

478. n-*Valeric acid.* B. p. 184°/768 mm.; M 102·13; n_C 1·40589, n_D 1·40800, n_F 1·41305, $n_{G'}$ 1·41672; R_C 26·71, R_D 26·83, R_F 27·13, $R_{G'}$ 27·33; $Mn_D^{20°}$ 143·80. Densities determined: $d_{4°}^{20°}$ 0·9390, $d_{4°}^{41·0°}$ 0·9211, $d_{4°}^{60·8°}$ 0·9039, $d_{4°}^{85·5°}$ 0·8819. Apparatus *A*.

19·2°	15·51	0·9397	27·29	248·4	60·4°	13·92	0·9042	23·57	248·7
27·2	15·16	0·9328	26·48	248·4	86·1	12·90	0·8815	21·29	248·9
41·7	14·54	0·9205	25·06	248·2					Mean 248·5

479. iso*Valeric acid.* B. p. 176·5°/762 mm.; M 102·13; n_C 1·40123, n_D 1·40331, n_F 1·40832, $n_{G'}$ 1·41188; R_C 26·72, R_D 26·85, R_F 27·15, $R_{G'}$ 27·36; $Mn_D^{20°}$ 143·32. Densities determined: $d_{4°}^{20°}$ 0·9286, $d_{4°}^{40·8°}$ 0·9102, $d_{4°}^{60·8°}$ 0·8926, $d_{4°}^{86·9°}$ 0·8687. Apparatus *D*.

19·9°	11·14	0·9289	25·55	247·2	63·1°	9·87	0·8920	21·74	247·2
26·4	10·96	0·9229	24·98	247·4	85·7	9·17	0·8698	19·70	247·4
43·4	10·39	0·9079	23·30	247·1					Mean 247·3

480. n-*Hexoic acid.* B. p. 203°/756 mm.; M 116·16; n_C 1·41412, n_D 1·41626, n_F 1·42143, $n_{G'}$ 1·42516; R_C 31·34, R_D 31·48, R_F 31·82, $R_{G'}$ 32·07; $Mn_D^{20°}$ 164·52; $d_{4°}^{20°}$ 0·9265.

481. n-*Heptoic acid.* B. p. 222°/764 mm.; M 130·18; n_C 1·42138, n_D 1·42361, n_F 1·42896, n_G 1·43281; R_C 35·92, R_D 36·08, R_F 36·48, $R_{G'}$ 36·76; $Mn_D^{20°}$ 185·32; $d_{4°}^{20°}$ 0·9200.

482. n-*Octoic acid.* B. p. 236°/769 mm.; M 144·21; n_C 1·42557, n_D 1·42777, n_F 1·43311, $n_{G'}$ 1·43693; R_C 40·60, R_D 40·79, R_F 41·23, $R_{G'}$ 41·54; $Mn_D^{20°}$ 205·90; $d_{4°}^{20°}$ 0·9093.

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