131. *Physical Properties and Chemical Constitution. Part XIV. The Parachors and the Refractivities of the Halogens.*

By Arthur I. Vogel.

Determination have been made of the refractivities for the C, D, F, and G′ lines at 20° and of the parachors of a number of miscellaneous halogen compounds, which include polymethylene chlorides, bromides, and iodides, alkyl chloro-, bromo-, and iodo-acetates, alkyl fluorides, and aromatic fluorine compounds. The new experimental data and those for the alkyl chlorides, bromides, and iodides (Part VIII, *J.*, 1943, 636) have been employed for the calculation of the parachors and refractivities of chlorine, bromine, and iodine by three independent methods, *viz.*, (1) from the alkyl halides and hydrocarbons (Part IX, *J.*, 1946, 133) or alkyl groups (Part XI, this vol., p. 610); (2) from the polymethylene dihalides $X{\cdot}[CH_2]_n{\cdot}X$ and CH_2 (Part IX, *loc. cit.*); and (3) from the alkyl monohalogenoacetates $CH_2X{\cdot}CO_2R$ and the dialkyl succinates $[CH_2]_2(CO_2R)_2$. The results by these three methods are in reasonable agreement and the mean values are :

	P.	R_{C}.	R_{D}.	R_{F}.	$R_{\mathrm{G'}}$.	$Mn_{\mathrm{D}}^{20°}$.
Cl	55·2	5·821	5·844	5·918	5·973	50·41
Br	68·8	8·681	8·741	8·892	9·011	118·07
I	90·3	13·825	13·954	14·310	14·620	196·27
F	26·1	0·81	0·81	0·79	0·78	21·84

The constants for fluorine, derived from four alkyl fluorides, must be regarded as preliminary and approximate.

THE methods of derivation and the published values of the parachors and refractivities of the halogen elements cannot be regarded as altogether trustworthy. For instance, the parachor of chlorine has been deduced (Sugden, "The Parachor and Valency", 1930, p. 37) from the parachors of CCl_4, $CHCl_3$, CH_2Cl_2, $C_2H_2Cl_4$, $CH_2Cl{\cdot}CH_2Cl$, $CH_3{\cdot}CHCl_2$, C_3H_7Cl, and $C_5H_{11}Cl$: the extreme values were 52·0 and 57·7, and the "weighted mean" 54·3. The evaluation of the chlorine contribution from such a heterogeneous collection of halogen compounds is clearly unsatisfactory; the individual variations may be due *inter alia* to real deviations attributable to the presence of more than one Cl atom on the same carbon atom. For Br and I, Sugden (*J.*, 1924, **125**, 1177) gives the values of 68·0 and 91·0, respectively, without disclosing how or from what data they are derived, whilst, for F, Allen and Sugden (*J.*, 1932, 760) deduce a value of 25·0 from measurements upon aromatic fluorine compounds. Eisenlohr (*Z. physikal. Chem.*, 1911, **75**, 585) utilises the data for 19 miscellaneous chloro-compounds for evaluating "Chlor in Chloriden", 11 heterogeneous bromo-compounds for bromine, and 5 alkyl iodides for iodine. His results were:

	R_{C}.	R_{D}.	R_{F}.	$R_{\mathrm{G'}}$.
Cl	5·933	5·967	6·043	6·101
Br	8·803	8·865	8·999	9·152
I	13·757	13·900	14·224	14·521

Apart from the obvious criticism as to the types of compound selected for Br and Cl, it must be remembered that the calculations are open to error because of the values for CH_2 employed (see Part IX, *J.*, 1946, 133).

The present author has deduced the constants for Cl by three independent methods: (1) From the experimental data for alkyl chlorides (Part VIII, *J.*, 1943, 636) and the aliphatic hydrocarbons (Parts IX and XI, *locc. cit.*). (2) From polymethylene dichlorides $Cl{\cdot}[CH_2]_n{\cdot}Cl$

TABLE I.

Parachors and refractivities for chlorine.

	P.	R_{C}.	R_{D}.	R_{F}.	$R_{\mathrm{G'}}$.	Mn_{D}^2
From alkyl chlorides and aliphatic hydrocarbons.						
$\mathrm{Pr}^n\mathrm{Cl}$	56·2	5·86	5·88	5·96	6·01	49·78
$\mathrm{Pr}^i\mathrm{Cl}$ *	58·1	5·98	6·01	6·08	6·15	49·30
$\mathrm{Bu}^n\mathrm{Cl}$	54·9	5·81	5·84	5·91	5·97	49·97
$\mathrm{Bu}^i\mathrm{Cl}$	54·4	5·73	5·76	5·83	5·89	50·19
$\mathrm{Bu}^s\mathrm{Cl}$ *	58·3	6·06	6·09	6·17	6·22	49·12
$\mathrm{Am}^n\mathrm{Cl}$	55·2	5·78	5·81	5·86	5·91	50·05
$\mathrm{Am}^i\mathrm{Cl}$	55·7	5·88	5·91	5·98	6·04	50·00
$\mathrm{CHMePr}^n\mathrm{Cl}$ *	58·7	6·07	6·11	6·19	6·25	49·25
$\mathrm{CHEt_2Cl}$ *	60·9	6·20	6·23	6·33	6·37	49·17
$\mathrm{C_6H_{13}}^n\mathrm{Cl}$	55·5	5·85	5·88	5·97	6·02	50·17
$\mathrm{C_7H_{15}}^n\mathrm{Cl}$	55·3	5·76	5·78	5·86	5·90	50·22
$\mathrm{C_8H_{17}}^n\mathrm{Cl}$	54·5	5·80	5·82	5·89	5·95	50·27
$\mathrm{C_9H_{19}}^n\mathrm{Cl}$	56·0	5·83	5·86	5·93	5·96	50·51
$\mathrm{C_{10}H_{21}}^n\mathrm{Cl}$	57·8	5·86	5·89	5·95	5·99	50·56
$\mathrm{C_{11}H_{23}}^n\mathrm{Cl}$	57·0	5·79	5·84	5·90	5·95	50·61
$\mathrm{C_{12}H_{25}}^n\mathrm{Cl}$	55·4	5·85	5·87	5·94	6·01	50·67
From polymethylene dichlorides, $Cl{\cdot}[CH_2]_n{\cdot}Cl$ and CH_2.						
$Cl{\cdot}[CH_2]_2{\cdot}Cl$	54·3	5·83	5·86	5·93	5·98	50·91
$Cl{\cdot}[CH_2]_3{\cdot}Cl$	54·7	5·76	5·78	5·85	5·90	50·97
From alkyl monochloroacetates and dialkyl succinates, $Cl{\cdot}CH_2{\cdot}CO_2R - 0{\cdot}5(CH_2{\cdot}CO_2R)_2$.						
$Cl{\cdot}CH_2{\cdot}CO_2Me$	53·7	5·82	5·84	5·92	5·96	50·60
$Cl{\cdot}CH_2{\cdot}CO_2Et$	54·3	5·88	5·91	5·98	6·03	50·56
$Cl{\cdot}CH_2{\cdot}CO_2\mathrm{Pr}^n$	54·2	5·87	5·89	5·96	5·98	50·57
$Cl{\cdot}CH_2{\cdot}CO_2\mathrm{Bu}^n$	54·2	5·82	5·85	5·91	5·96	50·68
Mean (excluding *)	55·2	5·821	5·844	5·918	5·973	50·41

and CH_2 (it is hoped to extend the series later). (3) From alkyl monochloroacetates, $Cl = Cl{\cdot}CH_2{\cdot}CO_2R - 0{\cdot}5(CH_2{\cdot}CO_2R)_2$; the experimental data for the dialkyl succinates are those given in Part XIII (preceding paper). The results are collected in Table I.

TABLE II.

Parachors and refractivities for bromine.

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
From alkyl bromides and aliphatic hydrocarbons.						
EtBr	69·5	8·67	8·73	8·89	9·01	116·55
Pr^{n}Br	68·4	8·66	8·72	8·87	8·99	117·26
Pr^{i}Br *	71·3	8·92	8·98	9·14	9·27	116·39
Bu^{n}Br	68·5	8·69	8·74	8·90	9·02	117·50
Bu^{i}Br	70·3	8·84	8·90	9·05	9·16	117·07
Bu^{s}Br *	72·3	9·09	9·15	9·31	9·45	116·65
Am^{n}Br	68·1	8·67	8·74	8·87	9·00	117·84
Am^{i}Br †	67·5	8·63	8·69	8·85	8·98	117·65
Am^{i}Br ‡	70·0	8·85	8·92	9·07	9·26	117·50
$CHMe_2Pr^nBr$ *	71·2	8·90	8·97	9·13	9·26	116·98
$CHEt_2Br$ *	73·2	9·08	9·14	9·32	9·44	117·06
$C_6H_{13}{}^nBr$	68·3	8·69	8·74	8·91	9·03	117·90
$C_7H_{15}{}^nBr$	67·8	8·65	8·71	8·86	8·98	118·05
$C_8H_{17}{}^nBr$	68·1	8·71	8·76	8·92	9·04	118·04
$C_9H_{19}{}^nBr$	69·1	8·61	8·67	8·80	8·90	118·48
$C_{10}H_{21}{}^nBr$	70·4	8·81	8·87	9·01	9·13	118·43
$C_{11}H_{23}{}^nBr$	68·8	8·58	8·65	8·80	8·91	118·63
$C_{12}H_{25}{}^nBr$	72·0	8·79	8·84	9·00	9·11	118·67
$C_{14}H_{25}{}^nBr$	69·2	8·59	8·64	8·79	8·90	118·92
$C_{16}H_{33}{}^nBr$	70·1	8·67	8·73	8·88	9·00	119·02
From polymethylene dibromides, $Br{\cdot}[CH_2]_n{\cdot}Br$ and CH_2.						
$Br{\cdot}[CH_2]_2{\cdot}Br$	67·6	8·77	8·84	9·00	9·12	123·98 *
$Br{\cdot}[CH_2]_3{\cdot}Br$	68·3	8·54	8·60	8·74	8·85	122·91 *
From alkyl monobromoacetates and dialkyl succinates, $Br{\cdot}CH_2{\cdot}CO_2R - 0{\cdot}5(CH_2{\cdot}CO_2R)_2$.						
$Br{\cdot}CH_2{\cdot}CO_2Pr^n$	67·1	8·68	8·74	8·89	8·99	118·71
$Br{\cdot}CH_2{\cdot}CO_2Bu^n$	66·1	8·52	8·58	8·72	8·84	118·87
Mean (excluding *)	68·8	8·681	8·741	8·892	9·011	118·07

† From Bisol fermentation *iso*amyl alcohol. ‡ From Sharples synthetic *iso*amyl alcohol.

TABLE III.

Parachors and refractivities for iodine.

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
From alkyl iodides and aliphatic hydrocarbons.						
MeI*	91·0	13·46	13·60	13·93	14·21	199·27
EtI	90·7	13·75	13·90	14·25	14·55	197·39
Pr^{n}I	90·7	13·83	13·97	14·32	14·62	196·67
Pr^{i}I *	92·1	14·20	14·35	14·73	15·01	195·93
Bu^{n}I	89·3	13·77	13·90	14·25	14·55	197·20
Bu^{i}I	90·9	13·80	13·94	14·28	14·58	195·75
Bu^{s}I *	95·4	14·38	14·53	14·91	15·24	195·67
Am^{n}I	90·1	13·85	13·98	14·32	14·62	197·60
Am^{i}I †	89·6	13·88	14·01	14·36	14·66	195·43
Am^{i}I ‡	91·7	13·86	14·00	14·35	14·65	195·58
$CHMePr^nI$ *	92·1	14·18	14·33	14·71	15·03	195·49
$CHEt_2I$ *	93·6	14·36	14·51	14·91	15·24	195·70
$C_6H_{13}{}^nI$	90·8	13·88	14·01	14·37	14·65	194·45
$C_7H_{15}{}^nI$	90·9	13·89	14·02	14·37	14·67	195·09
$C_8H_{15}{}^nI$	90·0	13·85	13·97	14·34	14·64	195·12
From $I{\cdot}[CH_2]_3{\cdot}I$ and CH_2.						
$I{\cdot}[CH_2]_3{\cdot}I$	88·6	13·66	13·79	14·14	—	212·05 *
From alkyl monoiodoacetates and dialkyl succinates, $I{\cdot}CH_2{\cdot}CO_2R - 0{\cdot}5(CH_2{\cdot}CO_2R)_2$.						
$I{\cdot}CH_2{\cdot}CO_2Pr^n$	91·1	13·77	13·89	14·25	14·53	197·39
$I{\cdot}CH_2{\cdot}CO_2Bu^n$	90·5	13·94	14·09	14·43	14·72	196·54
Mean (excluding *)	90·3	13·825	13·954	14·310	14·620	196·27

Refractivities refer to a temperature of 20°. In the calculation of the mean values, the figures for secondary alkyl chlorides (which give consistently high results) were omitted. The satisfactory agreement between the values deduced by the three entirely independent methods is noteworthy.

Analogous methods were employed in the calculation of the constants for Br; the experimental data for alkyl bromides (Part VIII, *loc. cit.*), to which have been added *n*-tetradecyl and *n*-hexadecyl bromides, were used. The results are summarised in Table II.

The results for I are collected in Table III: the data for alkyl iodides are those given in Part VIII (*loc. cit.*).

The results for the constants of F are not so satisfactory as those for the other halogens, chiefly because of the difficulty of preparing the pure alkyl fluorides in quantity. The figures are collected in Table IV and must be regarded as provisional. It will be noted that data for fluorobenzene, *p*-fluorotoluene, and α-fluoronaphthalene are included: the constants for Ph were deduced from PhCl, PhBr, and PhI; for *p*-$C_6H_4Me^-$ from *p*-C_6H_4MeCl — Cl; and for $C_{10}H_7{}^{\alpha}$ from $C_{10}H_7{}^{\alpha}CH_3$ — CH_3 (see following paper).

TABLE IV.

Preliminary values for the parachor and refractivities of fluorine.

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$C_5H_{11}{}^nF$	26·6	0·74	0·74	0·71	0·70	21·89
$C_6H_{13}{}^nF$	27·0	0·83	0·82	0·82	0·81	21·72
$C_7H_{15}{}^nF$	25·0	0·72	0·72	0·70	0·70	21·81
$C_8H_{17}{}^nF$	25·6	0·93	0·93	0·93	0·92	21·94
C_6H_5F *	26·0	0·75	0·73	0·69	0·65	12·37
p-$CH_3{\cdot}C_6H_4F$ *	26·5	0·61	0·61	0·55	0·50	19·63
$C_{10}H_7{}^{\alpha}F$ *	27·9	0·76	0·73	0·69	—	22·28
Mean (excluding *)	26·1	0·81	0·81	0·79	0·78	21·84

EXPERIMENTAL.

Ethylene Dichloride.—Method 1. A mixture of 62 g. of dry ethylene glycol, b. p. 196—196·5°/764 mm., and 158 g. of pure, dry pyridine was placed in a 500-ml. Claisen flask fitted with a double-surface condenser and a dropping-funnel: the side arm was closed with a cork. 480 G. of redistilled thionyl chloride were added slowly during 5 hours; a very vigorous reaction occurred and the liquid darkened considerably. The mixture was refluxed for 6 hours and then poured, with stirring, into ice-cold water. The dark heavy layer was separated, washed once with 5% sodium hydroxide solution, then twice with water and dried ($MgSO_4$). Upon distillation, pure ethylene dichloride (30 g.) passed over at 83°/756 mm.

Method 2. The pure commercial product (B.D.H.) was washed successively with saturated sodium hydrogen carbonate solution and water, dried ($MgSO_4$), and fractionated through a 3-section, Pyrex Young and Thomas column: about 95% passed over at 83°/748 mm. About 100 g. of this were distilled through a Widmer column and a middle fraction, b. p. 83°/762 mm., collected.

Propylene Dichloride.—A commercial sample was purified as for ethylene dichloride and distilled through an efficient fractionating column; b. p. 96°/770 mm.

Benzyl Chloride.—A pure commercial sample was twice redistilled from an all-glass apparatus; b. p. 177°/760 mm.

Trimethylene Dichloride.—76 G. of trimethylene glycol, b. p. 213—214°/758 mm., were placed in a 750-ml. round-bottomed Pyrex flask fitted with a dropping-funnel, a double-surface condenser, and a device for absorbing the hydrogen chloride evolved. 476 G. of redistilled thionyl chloride were added during 4 hours, and the mixture was refluxed for a further 4 hours. The reaction mixture was then distilled through an efficient column; the excess of thionyl chloride passed over at 76°, the temperature rose sharply to 116°, and the crude trimethylene dichloride (48 g.) was collected at 117—118°. This was washed and dried as above. Distillation gave pure trimethylene dichloride, b. p. 119—119·5°/756 mm.

Methyl Chloroacetate.—A mixture of 65 g. of A.R. monochloroacetic acid, 88 g. of pure absolute methyl alcohol, and 10 g. of concentrated sulphuric acid was refluxed for 7 hours, then poured into excess of water, and the lower layer separated. When purified as above, the ester (27 g.) boiled constantly at 129°/756 mm.

Ethyl Chloroacetate.—A mixture of 65 g. of A.R. monochloroacetic acid, 95 g. of absolute ethyl alcohol, and 11 g. of concentrated sulphuric acid was refluxed for 36 hours. This yielded, when worked up as above, 65 g. of pure ethyl chloroacetate, b. p. 142°/751 mm.

n-*Propyl Chloroacetate.*—A mixture of A.R. monochloroacetic acid, 115 g. of pure *n*-propyl alcohol, and 12 g. of concentrated sulphuric acid, refluxed for 30 hours, yielded by the above procedure 48 g. of *n*-propyl chloroacetate, b. p. 160—161°/764 mm.

n-*Butyl Chloroacetate.*—A mixture of 31·5 g. of A.R. monochloroacetic acid, 37 g. of pure *n*-butyl alcohol, 80 ml. of sodium-dried A.R. benzene, and 10 g. of concentrated sulphuric acid was refluxed for 30 hours, and then poured into excess of water. The benzene layer was washed with saturated sodium hydrogen carbonate solution and water, dried, and distilled. The yield of ester, b. p. 179—179·5°/766 mm., was 38 g.

Ethylene Dibromide.—To a mixture of 2500 g. of A.R. 48% hydrobromic acid and 750 g. of concentrated sulphuric acid were added 372 g. of ethylene glycol, b. p. 196—196·5°/760 mm., followed by 1200 g. of concentrated sulphuric acid slowly. The mixture was refluxed for 11 hours and then distilled until no water-insoluble liquid passed over. The resulting crude dibromide (945 g.) was washed twice with an equal volume of concentrated hydrochloric acid, then successively with water, saturated sodium hydrogen carbonate solution, and water, and dried and distilled. The dibromide passed over constantly at 130·5°/758 mm.

Propylene Dibromide.—To a mixture of 2000 g. of A.R. 48% hydrobromic acid and 600 g. of concentrated sulphuric acid were added 367 g. of propylene glycol, b. p. 186—187°/749 mm., followed by 960 g. of concentrated sulphuric acid slowly. The mixture was refluxed gently for 10 hours: there was a considerable evolution of hydrogen bromide during the first 2 hours of heating and some charring (the quantity of concentrated sulphuric acid could be reduced with advantage). The bromide (457 g.) was distilled off directly from the reaction mixture and after purification, as for ethylene dibromide, yielded upon distillation 30 g. of a liquid, b. p. *ca.* 40°, and 400 g. of pure propylene dibromide, b. p. 141—142°/770 mm.

Trimethylene Dibromide.—This was prepared in the usual manner from trimethylene glycol, b. p. 213—214°/758 mm., and purified by washing with concentrated hydrochloric acid, etc., as above. It boiled constantly at 165—165·5°/759 mm.

n-*Propyl Bromoacetate.*—A mixture of 35 g. of bromoacetic acid (m. p. 50°), 24 g. of pure *n*-propyl alcohol, 95 ml. of sodium-dried A.R. benzene, and 8 g. of concentrated sulphuric acid was refluxed for 31 hours, then poured into excess of water, the benzene layer removed, washed with saturated sodium hydrogen carbonate solution and water, and dried and distilled. The yield of *n*-propyl bromoacetate, b. p. 175—177°/762, a slightly lachrymatory liquid (compare literature), was 30 g.

n-*Butyl Bromoacetate.*—A mixture of 35 g. of bromoacetic acid, 29 g. of pure *n*-butyl alcohol, 95 ml. of dry benzene, and 8 g. of concentrated sulphuric acid was refluxed for 31 hours and yielded, as for the *n*-propyl ester, 35 g. of *n*-butyl bromoacetate, b. p. 196—197°/760 mm.

Ethyl α-*Bromopropionate.*—In a 1500-ml. three-necked flask, equipped with a dropping-funnel, a double-surface condenser and a device for absorbing the sulphur dioxide evolved, were placed 440 g. of redistilled thionyl chloride, and the whole heated to boiling. 250 G. of pure propionic acid were added at such a rate that the mixture refluxed gently (1 hour). The mixture was then refluxed for 30 minutes to expel dissolved sulphur dioxide, allowed to cool, and 1 g. of purified red phosphorus added. 620 G. of dry bromine were then introduced during 7 hours to the gently boiling propionyl chloride; the mixture was then refluxed for 7 hours, by which time the evolution of hydrogen bromide had almost ceased. The crude α-bromopropionyl chloride was then introduced during 2·5 hours into 500 ml. of absolute ethyl alcohol contained in a three-necked flask equipped with a mechanical stirrer and reflux condenser: the reaction was completed by heating on a water-bath for 4 hours, hydrogen chloride being slowly evolved. The crude ester was filtered into 1 l. of distilled water, the oil separated and washed successively with water, sodium hydrogen carbonate solution and water, and then dried. Distillation gave about 150 g. of a low-b. p. fraction (largely ethyl bromide) and 442 g. of ethyl α-bromopropionate, b. p. 69—70°/25 mm. Redistillation yielded the pure ester, b. p. 71°/26 mm., as a colourless liquid, which was kept in the dark.

n-*Tetradecyl Bromide.*—*n*-Tetradecyl alcohol, m. p. 37·5—38° (Deutsche Hydrierwerke), was converted into the bromide by the hydrogen bromide procedure (*Org. Synth.*, 1935, **15**, 25); this boiled at 181°/21 mm. and had m. p. 5°. The red phosphorus–bromine procedure (Vogel, B.P. 565,452, 1944) gave an excellent yield of a product, b. p. 180°/20 mm., m. p. 5°, $d_{4^\circ}^{20^\circ}$ 1·0169, $n_D^{20^\circ}$ 1·46045.

n-*Hexadecyl Bromide.*—60 G. of *n*-hexadecyl alcohol, m. p. 48° (Deutsche Hydrierwerke), were warmed to 100—110° and treated with hydrogen bromide for 7 hours. The crude bromide was warmed to 25° and one-third of the volume of concentrated sulphuric acid was added; the ammonia–methanol purification procedure of *Org. Synth.* (*loc. cit.*) could not be applied because of the difficulty in dealing with the emulsions formed. The bromide was accordingly extracted with ether, washed with water, and dried ($CaSO_4$). Distillation yielded 51 g. of the pure bromide, b. p. 201°/19 mm., m. p. 14°.

2-*Phenylethyl Bromide.*—This was prepared from 2-phenylethyl alcohol, b. p. 216·5—217°/755 mm., purified red phosphorus, and A.R. bromine (Vogel, *loc. cit.*) and had b. p. 98°/12 mm.

2-*Ethoxyethyl Bromide.*—The reaction between 80 g. of A.R. bromine and a mixture of 100 g. of 2-ethoxyethyl alcohol, 15·5 g. of purified red phosphorus, and 3 g. of pure pyridine (Vogel, *loc. cit.*) gave, after the product had been washed with water, dried (K_2CO_3), and carefully fractionated, 28 g. of ethyl bromide and 32 g. of 2-ethoxyethyl bromide, b. p. 128°/768 mm.

Tetrahydrofurfuryl Bromide.—60 G. of A.R. bromine were added slowly to a boiling mixture of 76·5 g. of tetrahydrofurfuryl alcohol (b. p. 175·5—176°/762 mm.) and 11·6 g. of purified red phosphorus (B.P. 565,452, 1944); 5 g. of pure pyridine and 75 ml. of water were then added, and the mixture distilled. The crude bromide was separated, washed, dried, and distilled, first at normal pressure (b. p. 170°/755 mm.) and then under reduced pressure (b. p. 52°/4·8 mm.). The yield of colourless product was 35 g.

Trimethylene Di-iodide.—25·3 G. of trimethylene glycol, b. p. 213—214°/758 mm., and 440 g. of constant-b. p. hydriodic acid were distilled slowly (7 hours) from a 500-ml. Pyrex distilling flask. The crude di-iodide (96 g.) was separated from the distillate, and the acid layer was similarly distilled with a further 25·3 g. of trimethylene glycol, affording 84 g. more of the crude di-iodide. The combined products were washed with 10% sodium hydroxide solution and water, dried ($MgSO_4$), and then shaken mechanically with a little silver powder, which removed most of the colour. Upon distillation from a little silver powder, pure colourless trimethylene di-iodide passed over at 90·5°/9 mm.

The preparation by the red phosphorus–iodine method (Vogel, *loc. cit.*) gave a product of b. p. 88—89°/6 mm., $d_{4^\circ}^{20^\circ}$ 2·5702, $n_D^{20^\circ}$ 1·6471.

2-*Phenylethyl Iodide.*—This was prepared by the red phosphorus–iodine procedure from 2-phenylethyl alcohol (b. p. 216·5—217°/755 mm.) and boiled at 114—116°/12 mm. Upon redistillation most of it passed over at 116°/12 mm. and was a perfectly colourless liquid.

n-*Propyl Iodoacetate.*—A mixture of 41·5 g. of pure monoiodoacetic acid, m. p. 82°, 24 g. of pure *n*-propyl alcohol, 95 ml. of sodium-dried A.R. benzene, and 8 g. of concentrated sulphuric acid was refluxed for 30 hours and then poured into excess of water. The lower layer was separated, washed with saturated sodium hydrogen carbonate solution and water, dried, and distilled from a little silver powder. The yield of crude ester, b. p. 197·5—198·5°/760 mm., was 39 g. This was slightly coloured and the pale red colour could be removed by shaking with a little silver powder but not by distillation from it at atmospheric pressure. Distillation under reduced pressure from silver powder gave the pure, colourless ester, b. p. 72°/7 mm.

n-*Butyl Iodoacetate*.—A mixture of 41·5 g. of pure iodoacetic acid, 29 g. of pure *n*-butyl alcohol, 95 ml. of sodium-dried A.R. benzene, and 8 g. of concentrated sulphuric acid was refluxed for 30 hours and yielded, as for the *n*-propyl ester, 44 g. of n-*butyl iodoacetate*, b. p. 214—216°/765 mm., which, however, was coloured deep red. The colour was removed by allowing it to stand over silver powder for 2 days: it was then distilled from a little silver powder and had b. p. 86°/7 mm. (Found: C, 29·7; H, 4·6; I, 52·7. $C_6H_{11}O_2I$ requires C, 29·8; H, 4·6; I, 52·4%).

Alkyl Fluorides.—The alkyl fluorides were prepared by the action of mercurous fluoride upon the corresponding alkyl bromide by a modification of the method of Swarts (*Bull. Acad. roy. Belg.*, 1921, **7**, 438); the addition of a little iodine, as suggested by Desreux (*ibid.*, 1934, **20**, 47; *Bull. Soc. chim. Belg.*, 1935, **44**, 1), was not advantageous except for *n*-amyl and *n*-hexyl fluorides. Contrary to the experience of the latter author, no secondary alkyl fluorides appeared to be formed in the reactions: the yields were uniformly poor. In all cases, the ethylenic hydrocarbon was a by-product.

Mercurous fluoride. Commercial mercurous fluoride gave a negligible yield of alkyl fluoride. Mercurous fluoride was accordingly prepared as follows. To a solution of 281 g. of A.R. mercurous nitrate in 5 l. of water and 35 ml. of concentrated hydrochloric acid was slowly added with vigorous mechanical stirring a solution of 125 g. of pure potassium hydrogen carbonate in 300 ml. of water. The resulting yellow precipitate was kept in the dark for 3 days with occasional stirring to decompose any basic nitrate. The mercurous carbonate was filtered off and washed successively with water, methyl alcohol, and ether: after drying in a vacuum desiccator over anhydrous calcium chloride the yield was 240 g. This mercurous carbonate was added in small portions to exceess of A.R. 40% hydrofluoric acid contained in a beaker coated inside with a layer of wax. The resulting yellow precipitate was washed with a *little* water by decantation, filtered off, and dried in a vacuum desiccator over anhydrous calcium chloride. The yield of mercurous fluoride was 188 g.

n-*Amyl fluoride*. An intimate mixture of 164 g. of dry mercurous fluoride, 108 g. of *n*-amyl fluoride, and 3 g. of iodine, contained in a copper flask fitted with a screw-on copper still-head to which were attached a double-surface condenser and a receiver cooled in ice, was heated in a bath at 115—118° for 9 hours: 12 g. of distillate were collected. After standing overnight, heating was continued at 135—140° for 3 hours, and a further 32 g. of liquid was collected. The combined distillates were treated with water and a little calcium chloride (to facilitate separation of the upper organic layer). Small volumes of saturated sodium hydrogen carbonate solution were added to the upper layer until reaction ceased, the silica was filtered off, and the liquid dried and fractionated: this gave fractions of b. p. 50—80° (12 g.) and 80—128° (12 g.). The latter was returned to the flask and yielded a further small quantity of crude *n*-amyl fluoride upon heating at 115—120° for 4 hours. The fraction of b. p. 50—80° (crude *n*-amyl fluoride + amylene) was cooled in ice and titrated with a solution of bromine in potassium bromide solution (90 g. Br_2; 60 g. KBr in 500 ml. of water) until a slight excess of bromine was present. The lower layer was removed, washed with potassium bromide solution until colourless, then with water, and dried ($MgSO_4$). Fractional distillation then gave 4 g. of *n*-amyl fluoride, b. p. 62—63°/767 mm.

n-*Hexyl fluoride*. An intimate mixture of 145 g. of mercurous fluoride, 101 g. of *n*-hexyl bromide, and 2·5 g. of iodine was heated, as for *n*-amyl fluoride, at 140—150° for 16 hours and at 160° for 8 hours. The distillate (49 g.) was diluted with water, treated with saturated sodium hydrogen carbonate solution then water, filtered from the silica, and the upper layer separated, dried, and fractionated: two fractions were collected of b. p. 80—140° (10 g.) and 140—155° (18 g.) respectively. The latter was mixed with 72·5 g. of mercurous fluoride, 3 g. of iodine, and 60·5 g. of *n*-hexyl bromide, and heated in a bath at 120—130° for 12 hours, 130—150° for 24 hours, and 150—155° for 12 hours. The distillate (combined with the fraction of b. p. 80—140° from the first distillation) was largely diluted with water, the upper organic layer (15 g.) removed, washed with saturated sodium hydrogen carbonate solution then water, dried, and distilled. This gave 12 g. of liquid, b. p. 80—100°, and consisted of a mixture of *n*-hexyl fluoride and hexene. The latter was removed by titration with bromine in potassium bromide solution as before and the product afforded, after two fractionations, 4 g. of *n*-hexyl fluoride, b. p. 88°/765 mm.

n-*Heptyl fluoride*. A mixture of 82·5 g. of *n*-heptyl bromide (VIII, **79**) and 110 g. of mercurous fluoride in a copper flask was heated, as for *n*-amyl fluoride, at 100° for 3 hours; the temperature was raised to 140° during 6 hours and finally to 160° during 3 hours. The upper layer (22 g.) of the distillate was removed, washed with saturated sodium hydrogen carbonate solution and water, dried, and fractionated. The liquid of b. p. 102—130° (13 g.) was freed from unsaturated hydrocarbons by means of bromine in potassium bromide solution as before, and upon distillation gave 8 g. of crude *n*-heptyl fluoride, b. p. 115—122°, the dibromoheptane remaining in the flask as a dark oil. Redistillation afforded 6 g. of the pure fluoride, b. p. 117°/779 mm.

n-*Octyl fluoride*. A mixture of 90 g. of *n*-octyl bromide (VIII, **80**) and 128 g. of mercurous fluoride was gradually heated, as before, to 150°, kept at this temperature for 2 hours and then at 150—190° for 6 hours. The distillate was poured into excess of water, the pale yellow upper layer (32 g.) removed, washed with sodium hydrogen carbonate solution and water, and the residual 26 g. of organic liquid were titrated directly without previous distillation, with bromine in potassium bromide solution, washed, dried, and distilled. 14 G. of liquid were collected at 140—145°/760 mm. (mainly at 142—143°), fuming (due to hydrogen bromide) then commenced, and a liquid passed over at 145—165° which contained little octyl fluoride. The liquid, b. p. 140—145°, after treatment with anhydrous potassium carbonate, distilled at 142—143°/760 mm.

Fluorobenzene. This was prepared from phenyldiazonium chloride (*ex* A.R. aniline) and fluoboric acid in wax-coated vessels according to *Org. Synth.*, 1933, **13**, 46 (compare Balz and Schiemann, *Ber.*, 1927, **60**, 1188), and boiled constantly at 84·5°/760 mm. Subsequently it was found that the fluoboric acid could be replaced by sodium borofluoride in this and other preparations of aromatic fluorine compounds.

p-*Fluorotoluene.* This was prepared from pure *p*-toluidine and boiled constantly at 115·5°/756 mm.

α-*Fluoronaphthalene.* 71·5 G. of pure α-naphthylamine were dissolved in 174 g. of concentrated hydrochloric acid contained in a 1-l. three-necked flask, fitted with a mechanical stirrer and dropping-funnel, and cooled in ice. A cold solution of 37·5 g. of pure sodium nitrite in 47 ml. of water was added slowly to an end-point with starch–iodide paper, the temperature being kept below 7° throughout. A solution of fluoboric acid (from 17·6 of pure boric anhydride and 101 g. of A.R. 40% hydrofluoric acid contained in a Bakelite beaker) was poured into the well-stirred diazonium salt solution at such a rate that the temperature did not rise above 10°. Stirring was continued for 60 minutes, and the precipitated borofluoride filtered off at the pump, washed with 25 ml. of ice-cold water, 25 ml. of methyl alcohol, and 25 ml. of ether, then dried between absorbent filter-paper for 12 hours and in a vacuum desiccator over anhydrous calcium chloride for several days. The resulting α-naphthyldiazonium fluoborate (82 g.) was decomposed in 20-g. lots in the usual manner and afforded, after dissolution in ether and washing with 10% sodium hydroxide solution, etc., a 90% yield of α-fluoronaphthalene, b. p. 214°/758 mm. For the physical measurements this was redistilled and a middle fraction, b. p. 98°/17 mm., taken.

p-*Chlorotoluene.* This was prepared from pure *p*-toluidine (*Org. Synth.*, 1923, **3**, 33) and boiled at 161·5°/769 mm.

m-*Dichlorobenzene.* The pure commercial product was washed successively with 10% sodium hydroxide solution and then with water until the washings were neutral, dried ($MgSO_4$), and distilled in an all-glass apparatus. It boiled constantly at 172·5°/760 mm. The compound attacks rubber corks.

Benzenesulphonyl fluoride. Benzenesulphonyl chloride, b. p. 247°/757 mm., was refluxed with aqueous potassium fluoride solution for 90 minutes (Davies, *J.*, 1931, 2104) and allowed to stand for 12 hours; 100 ml. of water were then added, and the fluoride extracted with 100 ml. of ether, the extract dried, the solvent removed, and the residue twice fractionated from an all-glass apparatus; b. p. 208—209°/753 mm.; yield 30 g.

Benzenesulphonyl chloride. A commercial product was first distilled from an all-glass apparatus, and the fraction, b. p. 247°/757 mm., collected. This was redistilled from an all-glass apparatus and had b. p. 135°/25 mm.

279. *Ethylene dichloride.* B. p. 83°/762 mm.; *M* 98·97; n_{C} 1·44252, n_{D} 1·44485, n_{F} 1·45076, $n_{\mathrm{G'}}$ 1·45506; R_{C} 20·91, R_{D} 21·00, R_{F} 21·24, $R_{\mathrm{G'}}$ 21·42; $Mn_{\mathrm{D}}^{20^\circ}$ 143·00. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·2538, $d_{4^\circ}^{41.4^\circ}$ 1·2234, $d_{4^\circ}^{60.5^\circ}$ 1·1968. 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.*
13·7°	10·74	1·2627	33·49	188·6	41·4°	9·76	1·2234	29·49	188·7
18·4	10·57	1·2561	32·79	188·5	61·5	9·03	1·1954	26·66	188·4
								Mean	188·6

Another sample, prepared by the thionyl chloride–pyridine method, had b. p. 83°/756 mm., $d_{4^\circ}^{20^\circ}$ 1·2540, n_{C} 1·44254, n_{D} 1·44495, n_{F} 1·45088, $n_{\mathrm{G'}}$ 1·45519.

280. *Propylene dichloride.* B. p. 96°/770 mm.; *M* 113·00; n_{C} 1·43693, n_{D} 1·43928, n_{F} 1·44510, $n_{\mathrm{G'}}$ 1·44931; R_{C} 25·56, R_{D} 25·69, R_{F} 26·04, $R_{\mathrm{G'}}$ 26·19; $Mn_{\mathrm{D}}^{20^\circ}$ 144·95. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·1578, $d_{4^\circ}^{42.1^\circ}$ 1·1294, $d_{4^\circ}^{61.5^\circ}$ 1·1046. Apparatus *D*.

14·9°	10·27	1·1644	29·53	226·2	41·4°	9·41	1·1303	26·27	226·4
17·1	10·22	1·1615	29·32	226·4	62·3	8·70	1·1036	23·71	226·2
24·8	9·97	1·1516	28·35	226·4				Mean	226·3

281. *Benzyl chloride.* B. p. 177°/760 mm.; *M* 126·59; n_{C} 1·53398, n_{D} 1·53887, n_{F} 1·55142, n_{G} 1·56134; R_{C} 35·76, R_{D} 36·03, R_{F} 36·72, $R_{\mathrm{G'}}$ 37·27; $Mn_{\mathrm{D}}^{20^\circ}$ 194·81. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·1004, $d_{4^\circ}^{40.7^\circ}$ 1·0806, $d_{4^\circ}^{60.5^\circ}$ 1·0621, $d_{4^\circ}^{86.8^\circ}$ 1·0372. Apparatus *A*.

20·6°	18·19	1·0998	37·46	284·8	62·2°	16·22	1·0605	32·21	284·4
26·3	17·94	1·0944	36·76	284·8	88·5	15·03	1·0356	29·15	284·0
41·2	17·16	1·0801	34·71	284·5				Mean	284·5

282. *Trimethylene dichloride.* B. p. 119·5°/756 mm.; *M* 113·00; n_{C} 1·44632, n_{D} 1·44871, n_{F} 1·45455, $n_{\mathrm{G'}}$ 1·45883; R_{C} 25·39, R_{D} 25·50, R_{F} 25·79, $R_{\mathrm{G'}}$ 26·00; $Mn_{\mathrm{D}}^{20^\circ}$ 163·70. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·1878, $d_{4^\circ}^{41.5^\circ}$ 1·1615, $d_{4^\circ}^{61.7^\circ}$ 1·1382, $d_{4^\circ}^{86.2^\circ}$ 1·1050. Apparatus *A*.

15·7°	15·42	1·1930	34·45	229·5	60·9°	13·37	1·1392	28·52	229·2
19·0	15·26	1·1890	33·97	229·5	87·4	12·21	1·1043	25·25	229·4
41·6	14·24	1·1614	30·97	229·5				Mean	229·4

283. *Methyl chloroacetate.* B. p. 129°/756 mm.; *M* 108·53; n_{C} 1·41976, n_{D} 1·42196, n_{F} 1·42716, $n_{\mathrm{G'}}$ 1·43104; R_{C} 22·24, R_{D} 22·34, R_{F} 22·59, $R_{\mathrm{G'}}$ 22·76; $Mn_{\mathrm{D}}^{20^\circ}$ 154·33. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·2343, $d_{4^\circ}^{41.1^\circ}$ 1·2072, $d_{4^\circ}^{60.8^\circ}$ 1·1809, $d_{4^\circ}^{86.8^\circ}$ 1·1463. Apparatus *A*.

12·8°	15·56	1·2437	36·24	214·1	41·2°	14·31	1·2071	32·34	214·4
18·1	15·33	1·2368	35·50	214·2	63·0	13·40	1·1780	29·56	214·9
24·9	15·17	1·2279	34·88	214·8	86·2	12·47	1·1471	26·78	215·4
								Mean	214·6

284. *Ethyl chloroacetate.* B. p. 142°/751 mm.; M 122·56; n_C 1·41933, n_D 1·42151, n_F 1·42675, $n_{G'}$ 1·43055; R_C 26·94, R_D 27·06, R_F 27·36, $R_{G'}$ 27·57; $Mn_D^{20^\circ}$ 174·22. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·1498, $d_{4^\circ}^{40\cdot7^\circ}$ 1·1248, $d_{4^\circ}^{61\cdot6^\circ}$ 1·0995, $d_{4^\circ}^{86\cdot2^\circ}$ 1·0684. Apparatus *D*.

t.	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	*P.*	*t.*	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	*P.*
21·4°	11·18	1·1481	31·70	253·3	61·9°	9·86	1·0991	26·76	253·6
25·9	11·05	1·1426	31·18	253·5	86·8	9·12	1·0677	24·05	254·2
41·5	10·54	1·1238	29·25	253·6				Mean	253·6

285. n-*Propyl chloroacetate.* B. p. 161°/764 mm.; M 136·58; n_C 1·42327, n_D 1·42546, n_F 1·43074, $n_{G'}$ 1·43432; R_C 31·58, R_D 31·72, R_F 32·06, $R_{G'}$ 32·29; $Mn_D^{20^\circ}$ 194·69. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·1020, $d_{4^\circ}^{41\cdot3^\circ}$ 1·0791, $d_{4^\circ}^{61\cdot4^\circ}$ 1·0558, $d_{4^\circ}^{85\cdot3^\circ}$ 1·0275. Apparatus *A*.

14·6°	15·12	1·1080	31·37	291·7	41·3°	14·00	1·0791	28·29	291·9
20·2	14·89	1·1018	30·72	291·8	61·4	13·23	1·0558	26·15	292·6
25·0	14·77	1·0964	30·32	292·3	86·1	12·32	1·0266	23·68	293·5
								Mean	292·3

286. n-*Butyl chloroacetate.* B. p. 179·5°/766 mm.; M 150·61; n_C 1·42746, n_D 1·42967, n_F 1·43505, $n_{G'}$ 1·43887; R_C 36·14, R_D 36·30, R_F 36·69, $R_{G'}$ 36·97; $Mn_D^{20^\circ}$ 215·33. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0713, $d_{4^\circ}^{40\cdot8^\circ}$ 1·0492, $d_{4^\circ}^{61\cdot9^\circ}$ 1·0262, $d_{4^\circ}^{86\cdot7^\circ}$ 0·9989. Apparatus *D*.

19·3°	11·49	1·0720	30·42	330·8	62·2°	10·26	1·0259	25·99	332·3
23·9	11·46	1·0670	30·20	331·7	86·7	9·58	0·9989	23·63	333·3
42·0	10·81	1·0479	27·98	331·3				Mean	331·9

287. *Ethylene dibromide.* B. p. 130·5°/758 mm.; M 187·89; n_C 1·53491, n_D 1·53891, n_F 1·54899, $n_{G'}$ 1·55690; R_C 26·79, R_D 26·96, R_F 27·38, $R_{G'}$ 27·70; $Mn_D^{20^\circ}$ 289·14. Densities determined: $d_{4^\circ}^{20^\circ}$ 2·1829, $d_{4^\circ}^{41\cdot6^\circ}$ 2·1388, $d_{4^\circ}^{64\cdot8^\circ}$ 2·0915, $d_{4^\circ}^{85\cdot8^\circ}$ 2·0469. Apparatus *A*.

13·7°	9·67	2·1959	39·76	214·9	62·0°	8·46	2·0972	33·22	215·1
24·3	9·47	2·1741	38·56	215·3	87·5	7·85	2·0432	30·03	215·4
41·4	8·99	2·1392	36·01	215·2				Mean	215·2

288. *Propylene dibromide.* B. p. 141·5°/770 mm.; M 201·92; n_C 1·51631, n_D 1·52006, n_F 1·52956, $n_{G'}$ 1·53668; R_C 31·58, R_D 31·77, R_F 32·26, $R_{G'}$ 32·62; $Mn_D^{20^\circ}$ 306·94. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·9324, $d_{4^\circ}^{41\cdot9^\circ}$ 1·8958, $d_{4^\circ}^{62\cdot1^\circ}$ 1·8602, $d_{4^\circ}^{87\cdot1^\circ}$ 1·8139. Apparatus *A*.

20·7°	9·52	1·9312	34·43	253·3	61·3°	8·52	1·8616	29·70	253·2
42·5	8·99	1·8948	31·90	253·3	88·3	7·85	1·8118	26·63	253·2
								Mean	253·3

289. *Trimethylene dibromide.* B. p. 165°/759 mm.; M 201·92; n_C 1·51973, n_D 1·52330, n_F 1·53209, $n_{G'}$ 1·53880; R_C 30·95, R_D 31·13, R_F 31·57, $R_{G'}$ 31·90; $Mn_D^{20^\circ}$ 307·59. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·9822, $d_{4^\circ}^{42\cdot3^\circ}$ 1·9444, $d_{4^\circ}^{60\cdot5^\circ}$ 1·9128, $d_{4^\circ}^{86\cdot7^\circ}$ 1·8662. Apparatus *D*.

12·3°	8·36	1·9954	41·20	256·4	62·0°	7·35	1·9102	34·67	256·5
22·1	8·17	1·9786	39·92	256·5	87·4	6·84	1·8650	31·50	256·5
42·4	7·79	1·9442	37·40	256·8				Mean	256·5

290. n-*Propyl bromoacetate.* B. p. 176°/762 mm.; M 181·04; n_C 1·44914, n_D 1·45177, n_F 1·45814, $n_{G'}$ 1·46288, $n_{G'}$ 1·46288; R_C 34·39, R_D 34·57, R_F 34·99, $R_{G'}$ 35·30; $Mn_D^{20^\circ}$ 262·83. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·4122, $d_{4^\circ}^{41\cdot6^\circ}$ 1·3849, $d_{4^\circ}^{61\cdot0^\circ}$ 1·3588, $d_{4^\circ}^{86\cdot7^\circ}$ 1·3228. Apparatus *A*.

19·2°	12·13	1·4132	32·10	304·9	61·6°	10·77	1·3580	27·39	305·0
26·4	11·91	1·4039	31·31	305·0	87·3	10·08	1·3220	24·95	306·1
41·5	11·45	1·3848	29·69	305·2				Mean	305·2

291. n-*Butyl bromoacetate.* B. p. 196°/760 mm.; M 195·07; n_C 1·45078, n_D 1·45337, n_F 1·45969, $n_{G'}$ 1·46439; R_C 38·84, R_D 39·03, R_F 39·50, $R_{G'}$ 39·85; $Mn_D^{20^\circ}$ 283·52. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·3519, $d_{4^\circ}^{41\cdot3^\circ}$ 1·3252, $d_{4^\circ}^{62\cdot4^\circ}$ 1·2992, $d_{4^\circ}^{86\cdot4^\circ}$ 1·2687. Apparatus *D*.

21·0°	9·50	1·3506	31·69	342·6	62·4°	8·64	1·2992	27·72	344·5
26·2	9·43	1·3441	31·30	343·3	87·3	8·04	1·2671	25·16	344·8
41·8	9·09	1·3246	29·74	343·9				Mean	343·8

292. *Ethyl α-bromopropionate.* B. p. 71°/26 mm.; M 181·04; n_C 1·44629, n_D 1·44896, n_F 1·45551, $n_{G'}$ 1·46029; R_C 34·17, R_D 34·35, R_F 34·78, $R_{G'}$ 35·10; $Mn_D^{20^\circ}$ 262·33. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·4135, $d_{4^\circ}^{41\cdot5^\circ}$ 1·3843, $d_{4^\circ}^{59\cdot7^\circ}$ 1·3578, $d_{4^\circ}^{87\cdot0^\circ}$ 1·3200. Apparatus *D*.

25·9°	8·56	1·4053	29·71	300·8	60·7°	7·75	1·3564	25·97	301·1
28·9	8·51	1·4011	29·45	301·0	86·6	7·14	1·3206	23·29	301·1
40·8	8·23	1·3853	28·16	301·0				Mean	301·0

293. n-*Tetradecyl bromide*. B. p. 181°/21 mm., m. p. 5°; *M* 277·29; n_{C} 1·45794, n_{D} 1·46050, n_{F} 1·46661, $n_{\mathrm{G'}}$ 1·47120; R_{C} 74·35, R_{D} 74·71, R_{F} 75·56, $R_{\mathrm{G'}}$ 76·20; $Mn_{\mathrm{D}}^{20^\circ}$ 404·98. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0175, $d_{4^\circ}^{40\cdot0^\circ}$ 1·0018, $d_{4^\circ}^{60\cdot1^\circ}$ 0·9852, $d_{4^\circ}^{86\cdot20}$ 0·9638. Apparatus *A*.

t.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
17·2°	16·50	1·0197	31·50	644·3	58·3°	15·05	0·9866	27·80	645·4
19·3	16·40	1·0181	31·26	644·0	86·3	14·08	0·9637	25·41	645·9
40·0	15·60	1·0018	29·26	643·8				Mean	644·9

294. n-*Hexadecyl bromide*. B. p. 201°/19 mm., m. p. 14°; *M* 305·34; n_{C} 1·45980, n_{D} 1·46205, n_{F} 1·46812, $n_{\mathrm{G'}}$ 1·47269; R_{C} 83·56, R_{D} 83·97, R_{F} 84·91, $R_{\mathrm{G'}}$ 85·62; $Mn_{\mathrm{D}}^{20^\circ}$ 446·44. Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9998, $d_{4^\circ}^{40\cdot2^\circ}$ 0·9841, $d_{4^\circ}^{59\cdot5^\circ}$ 0·9687, $d_{4^\circ}^{86\cdot1^\circ}$ 0·9477. Apparatus *A*.

18·3°	16·95	1·0012	31·78	724·1	61·4°	15·46	0·9671	28·00	726·2
25·3	16·76	0·9956	31·25	725·1	87·3	14·61	0·9467	25·90	727·6
41·5	16·18	0·9831	29·78	725·6				Mean	725·7

295. 2-*Phenylethyl bromide*. B. p. 98°/12 mm.; *M* 185·07; n_{C} 1·55124, n_{D} 1·55635, n_{F} 1·56894, $n_{\mathrm{G'}}$ 1·57899; R_{C} 43·47, R_{D} 43·81, R_{F} 44·62, $\mathrm{R}_{\mathrm{G'}}$ 45·27; $Mn_{\mathrm{D}}^{20\cdot}$ 288·04. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·3587, $d_{4^\circ}^{41\cdot2^\circ}$ 1·3360, $d_{4^\circ}^{61\cdot1^\circ}$ 1·3148, $d_{4^\circ}^{85\cdot7^\circ}$ 1·2881. Apparatus *A*.

16·3°	15·37	1·3627	39·23	339·9	41·1°	14·66	1·3361	36·68	340·9
20·9	15·30	1·3577	38·90	340·4	60·9	13·97	1·3150	34·40	340·8
27·2	15·07	1·3510	38·12	340·4	87·0	13·08	1·2865	31·51	340·8
								Mean	340·5

296. 2-*Ethoxyethyl bromide*. B. p. 128°/768 mm.; *M* 153·03; n_{C} 1·44590, n_{D} 1·44856, n_{F} 1·45513, $n_{\mathrm{G'}}$ 1·46007; R_{C} 29·26, R_{D} 29·41, R_{F} 29·78, $R_{\mathrm{G'}}$ 30·06; $Mn_{4^\circ}^{20^\circ}$ 221·68. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·3944, $d_{4^\circ}^{40\cdot7^\circ}$ 1·3649, $d_{4^\circ}^{61\cdot0^\circ}$ 1·3343, $d_{4^\circ}^{88\cdot6^\circ}$ 1·2943. Apparatus *D*.

15·6°	8·75	1·4010	30·27	256·2	41·0°	8·13	1·3645	27·40	256·6
21·1	8·58	1·3928	29·51	256·1	61·0	7·60	1·3343	25·04	256·6
27·1	8·47	1·3841	28·94	256·5	87·2	6·92	1·2963	22·15	256·1
								Mean	256·3

297. *Tetrahydrofurfuryl bromide*. B. p. 170°/755 mm. and 52°/4·8 mm.; *M* 165·04; n_{C} 1·48524, n_{D} 1·48811, n_{F} 1·49516, $n_{\mathrm{G'}}$ 1·50057; R_{C} 32·31, R_{D} 32·40, R_{F} 32·80, $R_{\mathrm{G'}}$ 33·10; $Mn_{\mathrm{D}}^{20^\circ}$ 245·60. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·4679, $d_{4^\circ}^{41\cdot6^\circ}$ 1·4397, $d_{4^\circ}^{60\cdot8^\circ}$ 1·4155, $d_{4^\circ}^{86\cdot9^\circ}$ 1·3823. Apparatus *A*.

17·8°	13·59	1·4708	37·43	277·5	40·2°	12·87	1·4415	34·74	278·0
19·3	13·52	1·4688	37·18	277·5	60·3	12·23	1·4162	32·43	278·1
24·1	13·36	1·4626	36·59	277·5				Mean	277·7

298. *Trimethylene di-iodide*. B. p. 90·5°/9 mm.; *M* 295·92; n_{C} 1·63579, n_{D} 1·64230, n_{F} 1·65893; R_{C} 41·18, R_{D} 41·51, $x_{\mathrm{G'}}$ R_{F} 42·36; $Mn_{\mathrm{D}}^{20^\circ}$ 485·99. Densities determined : $d_{4^\circ}^{20^\circ}$ 2·5755, $d_{4^\circ}^{41\cdot3^\circ}$ 2·5356, $d_{4^\circ}^{60\cdot6^\circ}$ 2·4986, $d_{4^\circ}^{86\cdot0^\circ}$ 2·4489. Apparatus *D*.

19·9°	6·92	2·5757	44·02	295·9	62·2°	6·44	2·4956	39·69	297·6
41·9	6·61	2·5345	41·37	296·1	87·3	6·30	2·4464	38·06	299·0
								Mean	297·2

This compound does not appear to wet glass well; the surface tension results may therefore be somewhat low.

299. 2-*Phenylethyl iodide*. B. p. 116°/12 mm.; *M* 232·07; n_{C} 1·59599, n_{D} 1·60216, n_{F} 1·61802, $n_{\mathrm{G'}}$ 1·63095; R_{C} 48·38, R_{D} 48·78, R_{F} 49·81, $R_{\mathrm{G'}}$ 50·65; $Mn_{\mathrm{D}}^{20^\circ}$ 371·82. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·6323, $d_{4^\circ}^{40\cdot2^\circ}$ 1·6087, $d_{4^\circ}^{59\cdot9^\circ}$ 1·5845, $d_{4^\circ}^{85\cdot5^\circ}$ 1·5528. Apparatus *A*.

14·4°	13·46	1·6390	41·31	359·0	61·2°	12·22	1·5829	36·22	359·7
19·0	13·28	1·6335	40·62	358·8	86·2	11·56	1·5520	33·59	360·0
42·2	12·85	1·6063	38·65	360·2				Mean	359·5

300. n-*Propyl iodoacetate*. B. p. 72°/7 mm.; *M* 228·04; n_{C} 1·49395, n_{D} 1·49762, n_{F} 1·50690, $n_{\mathrm{G'}}$ 1·51425; R_{C} 39·48, R_{D} 39·72, R_{F} 40·35, $R_{\mathrm{G'}}$ 40·84; $Mn_{\mathrm{D}}^{20^\circ}$ 341·51. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·6817, $d_{4^\circ}^{41\cdot3^\circ}$ 1·6490, $d_{4^\circ}^{61\cdot2^\circ}$ 1·6193, $d_{4^\circ}^{86\cdot0^\circ}$ 1·5816. Apparatus *D*.

17·4°	8·35	1·6857	34·76	328·5	62·1°	7·46	1·6179	29·81	329·3
24·3	8·26	1·6752	34·17	329·1	87·1	7·03	1·5799	27·43	330·3
42·1	7·82	1·6478	31·82	328·7				Mean	329·3

301. n-*Butyl iodoacetate*. B. p. 86°/7 mm.; *M* 242·07; n_{C} 1·48860, n_{D} 1·49213, n_{F} 1·50093, $n_{\mathrm{G'}}$ 1·50782; R_{C} 44·26, R_{D} 44·54, R_{F} 45·21, $R_{\mathrm{G'}}$ 45·73; $M_{\mathrm{D}}^{20^\circ}$ 361·19. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·5773, $d_{4^\circ}^{41\cdot1^\circ}$ 1·5507, $d_{4^\circ}^{61\cdot0^\circ}$ 1·5255, $d_{4^\circ}^{87\cdot0^\circ}$ 1·4958. Apparatus *D*.

21·8°	8·46	1·5750	32·91	368·1	61·4°	7·72	1·5251	29·08	368·6
28·3	8·40	1·5669	32·50	368·9	87·0	7·25	1·4958	26·78	368·2
41·5	8·05	1·5502	30·82	367·9				Mean	368·2

302. n-*Amyl fluoride*. B. p. 62—63°/767 mm.; M 90·14; n_C 1·35564, n_D 1·35725, n_F 1·36122, $n_{G'}$ 1·36392; R_C 24·88, R_D 24·99, R_F 25·23, $R_{G'}$ 25·40; $Mn_D^{20^\circ}$ 122·35. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·7909, $d_{4^\circ}^{40\cdot6^\circ}$ 0·7663. Apparatus *D*.

t.	*H*.	$d_{4^\circ}^{t^\circ}$	γ.	*P*.	*t*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
15·4°	10·50	0·7964	20·65	241·5	24·8°	10·07	0·7851	19·52	241·6
17·5	10·37	0·7939	20·33	241·3	41·3	9·27	0·7655	17·61	241·4
22·6	10·26	0·7878	19·96	242·0				Mean	241·6

303. n-*Hexyl fluoride*. B. p. 88°/765 mm.; M 104·16; n_C 1·36939, n_D 1·37118, n_F 1·37544, $n_{G'}$ 1·37835; R_C 29·56, R_D 29·68, R_F 29·98, $R_{G'}$ 30·20; $Mn_D^{20^\circ}$ 142·82. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·7960, $d_{4^\circ}^{41\cdot0^\circ}$ 0·7745, $d_{4^\circ}^{60\cdot2^\circ}$ 0·7548. Apparatus *D*.

16·9°	11·02	0·7992	21·75	281·5	61·5°	9·29	0·7535	17·29	282·5
41·5	10·04	0·7740	19·19	282·0				Mean	282·0

304. n-*Heptyl fluoride*. B. p. 117°/779 mm.; M 118·19; n_C 1·38211, n_D 1·38394, n_F 1·38822, $n_{G'}$ 1·39154; R_C 34·12, R_D 34·27, R_F 34·61, $R_{G'}$ 34·87; $Mn_D^{20^\circ}$ 163·56. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8063, $d_{4^\circ}^{42\cdot2^\circ}$ 0·7841, $d_{4^\circ}^{58\cdot5^\circ}$ 0·7678. Apparatus *D*.

16·9°	11·54	0·8094	23·07	320·1	42·2°	10·48	0·7841	20·77	321·8
23·2	11·33	0·8031	22·47	320·4	61·0	9·78	0·7652	18·48	320·3
								Mean	320·7

305. n-*Octyl fluoride*. B. p. 142·5°/760 mm.; M 132·22; n_C 1·39244, n_D 1·39345, n_F 1·39898, $n_{G'}$ 1·40220; R_C 38·89, R_D 39·07, R_F 39·47, $R_{G'}$ 39·75; $Mn_D^{20^\circ}$ 184·37. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8103, $d_{4^\circ}^{41\cdot3^\circ}$ 0·7926, $d_{4^\circ}^{61\cdot1^\circ}$ 0·7747, $d_{4^\circ}^{86\cdot9^\circ}$ 0·7518. Apparatus *A*.

17·7°	15·98	0·8123	24·31	361·4	43·0°	14·72	0·7911	21·81	361·2
20·4	15·77	0·8100	23·92	361·0	62·3	13·80	0·7737	19·99	361·4
26·9	15·61	0·8044	23·51	361·9	87·9	12·59	0·7509	17·70	361·2
								Mean	361·3

306. *Fluorobenzene*. B. p. 84·5°/760 mm.; M 96·10; n_C 1·46162, n_D 1·46573, n_F 1·47068, $n_{G'}$ 1·48445, R_C 25·78, R_D 25·98, R_F 26·48, $R_{G'}$ 26·87; $Mn_D^{20^\circ}$ 140·85. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0240, $d_{4^\circ}^{43\cdot9^\circ}$ 0·9958, $d_{4^\circ}^{61\cdot1^\circ}$ 0·9757. Apparatus *C*.

19·2°	11·24	1·0249	27·35	214·4	62·1°	9·58	0·9745	22·16	214·3
42·4	10·39	0·9976	24·61	214·7				Mean	214·4

307. p-*Fluorotoluene*. B. p. 115·5°/756 mm.; M 110·13; n_C 1·46483, n_D 1·46884, n_F 1·47897, $n_{G'}$ 1·48705; R_C 30·51, R_D 30·74, R_F 31·31, $R_{G'}$ 31·76; $Mn_D^{20^\circ}$ 161·76. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9975, $d_{4^\circ}^{40\cdot7^\circ}$ 0·9784, $d_{4^\circ}^{60\cdot8^\circ}$ 0·9575, $d_{4^\circ}^{85\cdot7^\circ}$ 0·9304. Apparatus *D*.

23·1°	11·37	0·9946	27·93	254·5	61·1°	10·00	0·9572	23·64	253·6
26·9	11·17	0·9911	27·34	254·1	86·0	9·11	0·9301	20·92	253·6
41·1	10·74	0·9780	25·95	254·1				Mean	254·0

308. α-*Fluoronaphthalene*. B. p. 214°/759 mm. and 98°/17 mm.; M 146·16; n_C 1·58604, n_D 1·59388, n_F 1·61464; R_C 43·26, R_D 43·73, R_F 44·96; $Mn_D^{20^\circ}$ 232·96. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·1340, $d_{4^\circ}^{40\cdot0^\circ}$ 1·1168, $d_{4^\circ}^{60\cdot8^\circ}$ 1·0999, $d_{4^\circ}^{86\cdot7^\circ}$ 1·0781. Apparatus *A*.

16·3°	18·35	1·1371	39·07	321·4	60·5°	16·69	1·1001	34·38	321·6
24·9	18·13	1·1299	38·35	321·2	87·4	15·63	1·0775	31·54	321·4
41·2	17·45	1·1166	36·48	321·7				Mean	321·5

309. p-*Chlorotoluene*. B. p. 161·5°/769 mm.; M 126·59; n_C 1·51629, n_D 1·52096, n_F 1·53301, $n_{G'}$ 1·54255; R_C 35·72, R_D 35·99, R_F 36·68, $R_{G'}$ 37·23; $Mn_D^{20^\circ}$ 192·54. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0710, $d_{4^\circ}^{41\cdot5^\circ}$ 1·0513, $d_{4^\circ}^{61\cdot7^\circ}$ 1·0317, $d_{4^\circ}^{86\cdot7^\circ}$ 1·0077. Apparatus *D*.

18·3°	12·42	1·0726	32·90	282·6	62·1°	11·05	1·0312	28·14	282·7
26·0	12·27	1·0653	32·28	283·2	86·3	10·30	1·0082	25·65	282·6
41·9	11·67	1·0509	30·29	282·6				Mean	282·7

310. m-*Dichlorobenzene*. B. p. 172·5°/760 mm.; M 147·01; n_C 1·54142, n_D 1·54641, n_F 1·55924, $n_{G'}$ 1·56946; R_C 35·89, R_D 36·16, R_F 36·86, $R_{G'}$ 37·42; $Mn_D^{20^\circ}$ 227·34. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·2880, $d_{4^\circ}^{41\cdot0^\circ}$ 1·2654, $d_{4^\circ}^{61\cdot5^\circ}$ 1·2430, $d_{4^\circ}^{86\cdot5^\circ}$ 1·2155. Apparatus *A*.

14·3°	15·08	1·2942	36·54	279·3	61·7°	13·37	1·2428	31·11	279·4
20·0	14·96	1·2880	36·16	279·7	86·4	12·50	1·2156	28·45	279·3
41·8	14·16	1·2645	33·53	279·8				Mean	279·5

311. *Benzenesulphonyl fluoride*. B. p. 208·5°/753 mm.; M 160·16; n_C 1·48816, n_D 1·49229, n_F 1·50285, $n_{G'}$ 1·51135; R_C 34·62, R_D 34·87, R_F 35·50, $R_{G'}$ 36·01; $Mn_D^{20^\circ}$ 239·01. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·3334, $d_{4^\circ}^{39\cdot7^\circ}$ 1·3114, $d_{4^\circ}^{61\cdot4^\circ}$ 1·2879, $d_{4^\circ}^{85\cdot6^\circ}$ 1·2608. Apparatus *A*.

15·0°	15·23	1·3389	38·18	297·4	60·4°	13·73	1·2887	33·13	298·2
17·5	15·18	1·3361	37·98	297·5	85·9	12·96	1·2605	30·59	298·8
39·4	14·47	1·3117	35·54	298·1				Mean	298·0

312. *Benzenesulphonyl chloride.* B. p. 135°/25 mm.; M 176·62; n_{C} 1·54721, n_{D} 1·55236, n_{F} 1·56553, $n_{G'}$ 1·57624; R_{C} 40·71, R_{D} 41·03, R_{F} 40·71, $R_{G'}$ 42·48; $Mn_{D}^{20^\circ}$ 274·18. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·3762, $d_{4^\circ}^{40·6^\circ}$ 1·3563, $d_{4^\circ}^{62·2^\circ}$ 1·3345, $d_{4^\circ}^{86·7^\circ}$ 1·3092. Apparatus *D*.

t.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	P.	t.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	P.
20·9°	12·72	1·3753	43·20	329·2	60·3°	11·74	1·3364	38·75	329·7
24·9	12·61	1·3713	42·70	329·3	87·4	11·06	1·3085	35·74	330·0
41·1	12·19	1·3558	40·81	329·3				Mean	329·5

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