

169. Physical Properties and Chemical Constitution. Part VIII. Alkyl Chlorides, Bromides, and Iodides.

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Determinations have been made of the refractive indices for the C, D, F, and G' lines at 20·0°, and of the surface tensions and densities over a range of temperatures, of a wide series of alkyl chlorides, bromides, and iodides. The molecular refractivities and parachors have been evaluated, and the results for the *n*-halides used for the calculation of the CH₂ differences. These differ appreciably from the values hitherto accepted.

In spite of its importance for the calculation of physical constants, no systematic investigation of the physical properties of alkyl chlorides, bromides, and iodides is on record. The data used by Eisenlohr (*Z. physikal. Chem.*, 1911, **75**, 605) for evaluation of the refractivities are limited and not always satisfactory. With regard to the parachors, Sugden ("The Parachor and Valency," 1930, p. 37) gives a table incorporating the data from which the constant for chlorine has been computed; the eight values range from 52·0 to 57·7, and the compounds include chloroform and carbon tetrachloride, which, in the author's opinion, should not be used in the initial deduction of the constant. (This subject will be discussed in a later paper.) Furthermore, for bromine and iodine, no experimental figures are disclosed and publication is confined to the statement (*op. cit.*, p. 189) "From organic compounds F = 25·7, Cl = 54·3, Br = 68·0, I = 91·0" (compare Sugden, *J.*, 1924, **125**, 1180): these are based on a CH₂ value of 39·0.

The author has determined the refractivities and parachors of a large number of alkyl halides. The chlorides were prepared by means of both zinc chloride-hydrochloric acid (cf. Norris and Taylor, *J. Amer. Chem. Soc.*, 1924, **46**, 753) and thionyl chloride (cf. Clark and Streight, *Trans. Roy. Soc. Canada*, 1929, **23**, 77). The results for chlorides are in Table I, the straight-chain and branched-chain members being separated.

The purest samples of ethyl, propyl, and butyl bromides were obtained by use of concentrated hydrobromic acid (Norris, *J. Amer. Chem. Soc.*, 1916, **38**, 1075; *Amer. Chem. J.*, 1907, **38**, 639). Bromides from *n*-amyl to *n*-nonyl were prepared by means of hydrobromic acid-sulphuric acid (cf. Kamm and Marvel, *J. Amer. Chem. Soc.*, 1920, **42**, 299; "Organic Syntheses," 1921, **1**, 5), but purification was best effected up to *n*-octyl bromide

TABLE I.

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G.</i>	<i>Mn_D^{20°}</i>
*Pr ^α Cl	191.7	20.76	20.85	21.09	21.25	109.03
*Bu ^α Cl	230.3	25.30	25.42	25.70	25.92	129.75
*Am ^α Cl	270.2	29.92	30.06	30.38	30.61	150.51
†C ₆ H ₁₃ ^α Cl	310.5	34.58	34.74	35.13	35.41	171.27
†C ₇ H ₁₅ ^α Cl	350.7	39.16	39.33	39.77	40.07	191.97
†C ₈ H ₁₇ ^α Cl	390.2	43.76	43.96	44.44	44.78	212.70
†C ₉ H ₁₉ ^α Cl	431.0	48.46	48.68	49.22	49.61	233.31
†C ₁₀ H ₂₁ ^α Cl	472.0	53.11	53.36	53.94	54.25	254.03
†C ₁₁ H ₂₃ Cl	511.9	57.68	57.96	58.58	59.04	274.68
†C ₁₂ H ₂₅ Cl	549.7	62.27	62.55	63.22	63.74	295.42
*Pr ^β Cl	191.9	20.89	20.99	21.23	21.41	108.25
†Bu ^β Cl	228.2	25.26	25.38	25.67	25.88	129.73
† <i>sec.</i> -BuCl	229.5	25.39	25.51	25.80	26.00	129.33
<i>tert.</i> -BuCl	229.4	25.57	25.69	25.99	26.20	128.37
*†Am ^β Cl	268.8	30.05	30.19	30.52	30.76	150.21
§Am ^β Cl	269.2	30.10	30.24	30.58	30.82	150.14
*CHMePr ^α Cl	268.4	29.97	30.11	30.45	30.69	150.08
*CHEt ₂ Cl	269.4	30.02	30.16	30.50	30.73	150.12
*CMe ₂ EtCl	268.2	30.07	30.22	30.55	30.80	149.79

* ZnCl₂-HCl method.† SOCl₂ method.‡ From fermentation *iso*amyl alcohol (Bisol).§ From synthetic *iso*amyl alcohol (Sharples).

by washing with concentrated hydrochloric acid (McCullough and Cortese, *J. Amer. Chem. Soc.*, 1929, 51, 225) instead of concentrated sulphuric acid. The hydrochloric acid purification is not satisfactory for *n*-nonyl and higher bromides, which are best treated by methyl alcohol-sulphuric acid (Ruhoff, Burnett, and Reid, *ibid.*, 1934, 56, 2784; "Organic Syntheses," 1935, 15, 24). Bromides from *n*-octyl to *n*-dodecyl are best prepared with gaseous hydrogen bromide at 100–120° (cf. Ruzicka, Stoll, and Schinz, *Helv. Chim. Acta*, 1928, 11, 685; Ruhoff, Burnett, and Reid, *loc. cit.*); Kamm and Marvel's method leads to carbonisation and gives lower yields (cf. "Organic Syntheses," 1921, 1, 7). The most trustworthy results for bromides are in Table II, arranged as in Table I.

TABLE II.

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G.</i>	<i>Mn_D^{20°}</i>
*EtBr	165.4	18.93	19.03	19.30	19.49	155.27
*Pr ^α Br	203.9	23.56	23.69	24.00	24.23	176.51
*Bu ^α Br	243.8	28.19	28.33	28.70	28.97	197.31
†Am ^α Br	283.1	32.81	32.99	33.39	33.70	218.30
†C ₆ H ₁₃ ^α Br	323.3	37.42	37.60	38.07	38.42	239.00
†C ₇ H ₁₅ ^α Br	363.5	42.05	42.26	42.77	43.15	259.80
†C ₈ H ₁₇ ^α Br	403.8	46.67	46.90	47.46	47.87	280.57
†C ₉ H ₁₉ ^α Br	444.1	51.24	51.49	52.09	52.55	301.28
§C ₁₀ H ₂₁ ^α Br	484.6	56.06	56.34	57.00	57.50	321.90
§C ₁₁ H ₂₃ ^α Br	523.7	60.47	60.77	61.48	62.01	342.70
§C ₁₂ H ₂₅ ^α Br	566.3	65.21	65.52	66.28	66.84	363.42
*Pr ^β Br	205.1	23.83	23.96	24.29	24.53	175.34
*Bu ^β Br	244.1	28.37	28.52	28.89	29.15	196.61
* <i>sec.</i> -BuBr	243.5	28.42	28.57	28.94	29.23	196.86
* Am ^β Br	280.6	32.80	32.97	33.39	33.70	217.86
*¶Am ^β Br	282.6	32.95	33.12	33.53	33.91	217.83
*CHMePr ^α Br	280.9	32.80	32.97	33.39	33.70	217.81
*CHEt ₂ Br	281.7	32.90	33.07	33.49	33.80	218.01

* HBr method and HCl purification.

† HBr-H₂SO₄ method and HCl purification.‡ HBr-H₂SO₄ method and MeOH-H₂SO₄ purification.§ HBr gas method and MeOH-H₂SO₄ purification.|| From fermentation *iso*amyl alcohol (Bisol).¶ From synthetic *iso*amyl alcohol (Sharples).

TABLE III

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G.</i>	<i>Mn_D^{20°}</i>
MeI	146.9	19.10	19.25	19.65	19.96	217.40
EtI	186.6	24.07	24.20	24.66	25.03	236.11
Pr ^α I	226.2	28.73	28.94	29.45	29.86	255.92
Bu ^α I	264.6	33.27	33.49	34.05	34.50	276.01
Am ^α I	305.1	37.99	38.23	38.84	39.32	296.18
C ₆ H ₁₃ ^α I	345.8	42.61	42.87	43.53	44.04	316.55
C ₇ H ₁₅ ^α I	386.6	47.29	47.57	48.28	48.84	336.84
C ₈ H ₁₇ ^α I	425.7	51.81	52.11	52.88	53.47	357.55
Pr ^β I	225.9	29.11	29.33	29.88	30.27	254.88
Bu ^β I	264.7	33.33	33.66	34.12	34.57	275.29
<i>sec.</i> -BuI	266.6	33.71	33.95	34.54	35.02	275.88
*Am ^β I	302.7	38.05	38.29	38.90	39.38	295.64
†Am ^β I	304.3	37.96	38.20	38.81	39.30	295.88
CHMePr ^α I	301.8	38.08	38.33	38.97	39.47	296.32
CHEt ₂ I	302.1	38.18	38.44	39.08	39.60	296.65

* From fermentation *iso*amyl alcohol (Bisol).† From synthetic *iso*amyl alcohol (Sharples).

The purest iodides (methyl to *n*-octyl) were prepared by distillation of the purified alcohols with constant-b. p. hydriodic acid (Norris, *loc. cit.*, 1907), followed by washing with concentrated hydrochloric acid: traces of iodine were removed by distillation from pure silver powder. If a *large* excess of yellow phosphorus is used in the ordinary phosphorus-iodine method (cf. Walker, J., 1892, 61, 717; Adams and Voorhees, *J. Amer. Chem. Soc.*, 1919, 41, 789; "Organic Syntheses," 1933, 13, 60), small quantities of phosphorus compounds may be formed, which cannot be removed by simple distillation. The results for iodides, arranged as in Table I, are in Table III.

The new data for *n*-alkyl halides have been used for the evaluation of the CH₂ differences by the method of least squares: in the iodide series, methyl iodide has been omitted from the calculation, as it appears anomalous. The results are below. These values differ appreciably from the hitherto accepted figures (*P*

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G.</i>	<i>Mn_P^{20°}</i>
Chlorides	40.10	4.621	4.641	4.691	4.734	20.71
Bromides	40.02	4.625	4.646	4.696	4.733	20.79
Iodides	39.98	4.631	4.656	4.707	4.743	20.24

39.0, Sugden, J., 1924, 125, 1180; *R_C* 4.598, *R_D* 4.618, *R_F* 4.668, *R_G* 4.710, Eisenlohr, *Z. physikal. Chem.*, 1911, 75, 605) which form the basis of the calculation of atomic and structural constants for the parachor and refractivities. The subject will be discussed further in a subsequent communication.

EXPERIMENTAL.

Physical Measurements.—Full details are given in Part VII (this vol., p. 18). Unless otherwise stated, all b. p.'s are corrected.

Previous Work.—Parachor values, the source of which is not indicated, are taken from Sidgwick, Sugden, and Adam (*Brit. Assoc. Rep.*, 1932, 265). Reference is also made to what appear to be the most trustworthy recorded values of the refractive indices for comparison; the measurements of Timmermans and his co-workers and of Deffet have been reduced to 20° with the aid of their temperature coefficients.

Alcohols.—All the liquid alcohols, except methyl and ethyl, were dried with A.R. potassium carbonate and fractionated through a special Pyrex Young fractionating column with bark corks. Burrough's alcohols: A.R. absolute methyl and ethyl alcohols. British Industrial Solvents ("Bisol") alcohols: *n*-propyl, b. p. 96—97°/760 mm.; *isopropyl*, b. p. 82—82.5°/760 mm.; *n*-butyl, b. p. 116—117°/750 mm.; *isobutyl*, b. p. 106.5—107.5°/766 mm.; *isoamyl*, b. p. 131°/763 mm. (fermentation). Boake Roberts's alcohols: *sec*.-butyl, b. p. 100—100.5°/770 mm.; *tert*.-butyl, b. p. 81.5—82.5°/761 mm., m. p. 25.5°. Sharples's alcohols: *n*-amyl, b. p. 136.5—137.5°/766, mainly 137°/766 mm.; *isoamyl*, b. p. 130—130.5°/762 mm. (synthetic); methyl-*n*-propylcarbinol, b. p. 118.5°/764 mm.; diethylcarbinol, b. p. 115.5—116°/760 mm.; *tert*.-amyl (dimethylethylcarbinol), b. p. 101—101.5°/760 mm. Carbide and Carbon Chemicals (General and Metallurgical): *n*-hexyl alcohol, b. p. 156—157°/752 mm. *n*-Heptyl alcohol, b. p. 175.5—176.5°/774 mm., was prepared by reduction of redistilled *n*-heptaldehyde with iron and acetic acid ("Organic Syntheses," 1926, 6, 52). Deutsche Hydrierwerke alcohols: *n*-octyl, b. p. 193—194°/763.5 mm.; *n*-nonyl, b. p. 211.5—212°/765 mm.; *n*-decyl, b. p. 228—229°/760 mm.; *n*-undecyl, b. p. 241—245°/769 mm.; *n*-dodecyl, m. p. 24°.

Preparation of Alkyl Chlorides.—(1) Norris and Taylor's method (*loc. cit.*) was modified as follows. The mixture of alcohol (1 g.-mol.), zinc chloride sticks (2 g.-mols.), and concentrated hydrochloric acid (2 g.-mols.) was heated for 4 hours over a free flame in a flask fitted with a long double-surface reflux condenser; the mixture was allowed to cool, and a double-surface condenser was attached to the top of the reflux condenser by a glass tube bent twice at right angles and arranged vertically so that the lower end was inside a flask cooled externally by ice. The alkyl chloride was then directly distilled from the reaction mixture: for *n*- and *iso*-propyl chlorides the water in the reflux condenser was maintained at 50—60°, but for the higher chlorides the water was removed. For purification, washing with concentrated hydrochloric acid in the cold is satisfactory for *n*-propyl and all *sec*.-alkyl chlorides, but refluxing and distillation with an equal volume of concentrated sulphuric acid was used for *n*-butyl and *n*-amyl chlorides. All the crude chlorides were washed with water, dilute sodium hydroxide or sodium carbonate solution, water, then dried with anhydrous sodium sulphate or calcium chloride (shaking) and fractionated, a middle fraction being collected. The yields of crude chlorides were: Pr^aCl 92; Pr^bCl 72; Bu^aCl 65 (by modification of method of "Organic Syntheses," 1925, 5, 27); Bu^bCl 5*; *sec*.-BuCl 78; Am^aCl 67; Am^bCl 52; CHMePr^aCl 49; CHEt₂Cl 55%.

(2) (a) To a mixture of the alcohol (0.5 g.-mol.) and pure pyridine (0.5 g.-mol.) in a 500-c.c. round-bottomed flask carrying a dropping funnel and double-surface reflux condenser, was added redistilled thionyl chloride (1 g.-mol.) during 3—4 hours (occasional shaking). The mixture was refluxed for ¾ hr. and allowed to cool, and the upper layer separated,† treated with water, 5% sodium hydroxide solution, water, dried with anhydrous sodium sulphate, and fractionated. The yields of chlorides were: Bu^aCl 33 g.; Bu^bCl 31 g.; *sec*.-BuCl 22 g.

(2) (b) When pyridine was omitted, the apparatus consisted of a 250-c.c. Pyrex Claisen flask carrying a dropping funnel and double-surface condenser (calcium chloride guard tubes); the side arm was plugged with a small cork, and the whole apparatus inclined so that the side tube was at an angle of 120°. For *n*-hexyl chloride, the redistilled thionyl chloride (1.5 g.-mols.) was placed in the flask, and the alcohol (0.5 g.-mol.) added with frequent shaking during 2—3 hours. In all other cases the alcohol (0.33 or 0.5 g.-mol.) was in the flask and the thionyl chloride (1 or 1.5 g.-mols.) was added dropwise. For *n*-undecyl and *n*-dodecyl chlorides, 4 g.-mols. of thionyl chloride were used to 1 g.-mol. of alcohol. The mixture was refluxed for 4—8 hours, the condenser, dropping funnel, and plug in the side-arm were then removed, and the mixture distilled. The crude chloride was washed with water, 10% sodium carbonate solution, water (twice), dried with anhydrous sodium sulphate, and fractionated. The yields of crude chlorides were: C₆H₁₃^aCl 63; C₇H₁₅^aCl 80; C₈H₁₇^aCl 80; C₉H₁₉^aCl 76; C₁₀H₂₁^aCl 91; C₁₁H₂₃^aCl 89; C₁₂H₂₅^aCl 84%.

The tertiary chlorides were prepared from *tert*.-butyl and *tert*.-amyl alcohol by treatment with concentrated hydrochloric acid (see "Organic Syntheses," 1928, 8, 50), dried by prolonged mechanical shaking with anhydrous sodium sulphate, and fractionated. The yield of chloride was approximately equal to that of the alcohol employed.

Clark and Streight, *loc. cit.*, claim a 15% yield of pure chloride. Although a poor yield of a fraction with approximately the correct b. p. could be isolated, the main product was a high-boiling liquid.

† With *sec*.-butyl chloride, the liquid was so dark that the line of demarcation could not be seen. Accordingly, a volume (83 c.c.) equal to that for *n*-butyl chloride was run off, and the residual liquid treated as above.

50.* *n*-Propyl chloride (Method 1). B. p. 46—46.5°/764 mm.; M 78.55; n_D † 1.38610, n_D 1.38800, n_F 1.39300, n_G 1.39636. Densities determined: $d_4^{20^\circ}$ 0.8890, $d_4^{40.7^\circ}$ 0.8609. Apparatus *D*.

<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ	<i>P.</i>
12.4°	10.51	10.27	0.8982	22.78	191.3	41.6°	9.29	9.05	0.8597	19.21	192.0
20.0	10.27	10.03	0.8890	22.02	191.7						Mean 191.7

(*P* 190.2, 187.0; Karvonen, *Ann. Acad. Sci. Fennicae*, 1912, [A], **3**, 1; 1914, [A], **5**, 128; *Chem. Zentr.*, 1912, II, 1271; 1919, III, 57, 807, gives b. p. 46.6°/770.5 mm., $d_4^{20^\circ}$ 0.8910, n_C 1.38637, n_D 1.38838, n_F 1.39321, n_G 1.39723; Timmermans and Hennaut-Roland, *J. Chim. physique*, 1930, **27**, 401, give b. p. 46.6°/760 mm., $d_4^{20^\circ}$ 0.89231, n_C 1.38664, n_F 1.39365, n_G 1.39769.)

51. isoPropyl chloride (Method 1). B. p. 34.5°/740 mm.; M 78.55; n_C 1.37612, n_D 1.37810, n_F 1.38298, n_G 1.38651. Densities determined: $d_4^{20^\circ}$ 0.8629, $d_4^{48.6^\circ}$ 0.8657.

<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ	<i>P.</i>	App.	<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ	<i>P.</i>	App.
19.6°	12.42	12.18	0.8633	19.69	192.1	<i>A</i>	24.4°	9.69	9.45	0.8590	19.27	192.0	<i>C</i>
22.9	12.26	12.02	0.8603	19.36	191.9	<i>A</i>	25.6	9.59	9.35	0.8580	19.04	191.7	<i>C</i>
16.1	9.92	9.68	0.8663	19.91	191.9	<i>C</i>						Mean 191.9	

(Timmermans and Martin, *ibid.*, 1928, **25**, 413, give b. p. 34.8°/760 mm., $d_4^{20^\circ}$ 0.86167, n_C 1.37625, n_D 1.37835, n_F 1.38340.)

52. *n*-Butyl chloride (Method 1). B. p. 77°/769 mm.; M 92.57; n_C 1.39941, n_D 1.40159, n_F 1.40656, n_G 1.41021. Densities determined: $d_4^{20^\circ}$ 0.8859, $d_4^{41.7^\circ}$ 0.8608, $d_4^{60.5^\circ}$ 0.8392. Apparatus *A*.

<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ	<i>P.</i>
23.3°	14.34	14.10	0.8821	23.29	230.5	61.0°	12.18	11.94	0.8386	18.75	230.2
42.0	13.20	12.96	0.8605	20.88	230.2						Mean 230.3

(*P* 230.5; Karvonen, *loc. cit.*, gives b. p. 77.7—77.9°/763 mm., $d_4^{20^\circ}$ 0.88387, n_C 1.39940, n_D 1.40147, n_F 1.40652, n_G 1.41063; Timmermans and Hennaut-Roland, *loc. cit.*, give b. p. 78.50°/760 mm., $d_4^{20^\circ}$ 0.88647, n_C 1.40026, n_F 1.40713, n_G 1.41161.)

52A. *n*-Butyl chloride (Method 2a). B. p. 78.0°/762 mm.; n_C 1.40014, n_D 1.40223, n_F 1.40730, n_G 1.41099; R_D 25.32, R_D 25.43, R_F 25.72, R_G 25.87; $Mn_D^{20^\circ}$ 129.80. Densities determined: $d_4^{20^\circ}$ 0.8866, $d_4^{40.9^\circ}$ 0.8650, $d_4^{60.6^\circ}$ 0.8427. Apparatus *D*.

19.0	11.02	10.88	0.8877	23.85	229.9	41.0	10.19	9.95	0.8649	21.25	230.1
26.3	10.87	10.63	0.8799	23.10	230.1	61.6	9.45	9.21	0.8416	19.14	230.3
											Mean 230.1

53. isoButyl chloride (Method 2a). B. p. 68.5°/756 mm.; M 92.57; n_C 1.39634, n_D 1.39841, n_F 1.40348, n_G 1.40729. Densities determined: $d_4^{20^\circ}$ 0.8810, $d_4^{40.5^\circ}$ 0.8587, $d_4^{58.4^\circ}$ 0.8379. Apparatus *D*.

25.5	10.27	10.23	0.8750	21.66	228.3	56.5	9.03	8.79	0.8400	18.23	228.4
41.1	9.58	9.34	0.8580	19.79	227.9						Mean 228.2

(Timmermans and Martin, *J. Chim. physique*, 1926, **23**, 746, give b. p. 68.85°/760 mm., $d_4^{20^\circ}$ 0.87735, n_C 1.39624, n_D 1.39836, n_F 1.40349, n_G 1.40779.)

54. sec-Butyl chloride (Method 2a). B. p. 68°/761 mm.; M 92.57; n_C 1.39503, n_D 1.39709, n_F 1.40215, n_G 1.40582. Densities determined: $d_4^{20^\circ}$ 0.8740, $d_4^{48.7^\circ}$ 0.8512. Apparatus *A*.

19.7	13.58	13.34	0.8743	21.84	228.9	40.5	12.61	12.37	0.8514	19.72	229.8
26.0	13.36	13.12	0.8676	21.32	229.7						Mean 229.5

(Timmermans and Martin, *loc. cit.*, 1928, give b. p. 68.25°/760 mm., $d_4^{20^\circ}$ 0.87320, n_C 1.3949, n_D 1.3970, n_F 1.4020, n_G 1.4064.)

54A. sec-Butyl chloride (Method 1). B. p. 68°/769 mm.; n_C 1.39486, n_D 1.39694, n_F 1.40197, n_G 1.40558; R_D 25.40, R_D 25.54, R_F 25.83, R_G 26.04; $Mn_D^{20^\circ}$ 129.31. Densities determined: $d_4^{20^\circ}$ 0.8726, $d_4^{41.7^\circ}$ 0.8478, $d_4^{60.8^\circ}$ 0.8250. Apparatus *A*.

12.4	14.20	13.96	0.8813	23.04	230.1	41.4	12.74	12.50	0.8481	19.85	230.8
20.7	13.72	13.48	0.8718	22.01	230.1	60.5	11.63	11.39	0.8253	17.60	230.5
											Mean 230.4

55. tert-Butyl chloride (HCl method). B. p. 49.5°/738 mm.; M 92.57; n_C 1.38362, n_D 1.38564, n_F 1.39071, n_G 1.39427. Densities determined: $d_4^{20^\circ}$ 0.8457, $d_4^{43.0^\circ}$ 0.8164. Apparatus *B*.

9.1	10.40	10.16	0.8596	20.48	229.3	40.6	8.94	8.70	0.8195	16.72	229.1
17.1	10.10	9.86	0.8493	19.64	229.7						Mean 229.4

(Timmermans and Martin, *J. Chim. physique*, 1934, **31**, 85, give b. p. 50.7°/760 mm., $d_4^{20^\circ}$ 0.84139, n_C 1.38297, n_F 1.39024; *P* 231.2.)

* The numbering of compounds in Clarendon type follows on from Part VII (this vol., p. 18).

† All the measurements of the refractive indices were carried out at 20° ± 0.02°. Where 20° is used, 20.0° is to be understood; n_C , n_D , n_F , n_G are to be taken as referring to $n_c^{20.0^\circ}$, etc.; R_D , etc., to $[R_L]_c$, etc. These abbreviations also apply to the data from the literature.

56. *n*-Amyl chloride (Method 1). B. p. 105°/764 mm.; *M* 106.60; n_D 1.40961, n_D 1.41177, n_F 1.41691, n_G 1.42053. Densities determined: $d_4^{20^\circ}$ 0.8821, $d_4^{40^\circ}$ 0.8600, $d_4^{60^\circ}$ 0.8374, $d_4^{86.5^\circ}$ 0.8125. Apparatus D.

<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>
12.9	11.95	11.75	0.8895	25.81	270.1	62.7	10.09	9.85	0.8376	20.38	270.4
23.0	11.56	11.32	0.8789	24.57	270.0	87.1	9.09	8.85	0.8119	17.75	270.1
41.9	10.82	10.58	0.8588	22.44	270.1						Mean 270.2

(*P* 270.4; Karvonen, *loc. cit.*, gives b. p. 105.7—105.8°/759 mm., $d_4^{20^\circ}$ 0.87815, n_D 1.40978, n_D 1.41192, n_F 1.41704, n_G 1.42133; Lek, Thesis, Brussels, 1930, gives $d_4^{20^\circ}$ 0.88159.)

57. isoAmyl chloride (Method 1, from Bisol fermentation isoamyl alcohol). B. p. 99°/777 mm.; *M* 106.60; n_D 1.40696, n_D 1.40909, n_F 1.41425, n_G 1.41799. Densities determined: $d_4^{20^\circ}$ 0.8732, $d_4^{41.6^\circ}$ 0.8521, $d_4^{61.4^\circ}$ 0.8315, $d_4^{86.8^\circ}$ 0.8050. Apparatus A.

<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>
14.6	14.96	14.72	0.8786	24.22	269.2	62.6	12.58	12.34	0.8308	19.18	268.9
18.3	14.63	14.39	0.8749	23.57	268.5	87.3	11.33	11.09	0.8043	16.70	268.0
41.6	13.67	13.43	0.8521	21.43	269.2						Mean 268.8

(*P* 269.8.)

57A. isoAmyl chloride (Method 1, from Sharples's synthetic isoamyl alcohol). B. p. 98.5°/765 mm.; n_D 1.40627, n_D 1.40840, n_F 1.41361, n_G 1.41738; R_D 30.10, R_D 30.24, R_F 30.58, R_G 30.82; $Mn_D^{20^\circ}$ 150.14. Densities determined: $d_4^{20^\circ}$ 0.8704, $d_4^{40.2^\circ}$ 0.8492, $d_4^{69.6^\circ}$ 0.8292. Apparatus A.

<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>
18.4	14.64	14.40	0.8721	23.52	269.2	40.3	13.54	13.30	0.8491	21.15	269.2
22.9	14.45	14.21	0.8674	23.08	269.4	60.9	12.48	12.24	0.8278	18.97	269.0
											Mean 269.2

58. β -Chloropentane (Method 1). B. p. 97°/770 mm.; *M* 106.60; n_D 1.40579, n_D 1.40791, n_F 1.41308, n_G 1.41678. Densities determined: $d_4^{20^\circ}$ 0.8732, $d_4^{40.8^\circ}$ 0.8514, $d_4^{61.8^\circ}$ 0.8308. Apparatus A.

<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>
17.8	14.62	14.38	0.8755	23.57	268.3	42.0	13.41	13.17	0.8502	20.97	268.5
19.5	14.53	14.29	0.8737	23.38	268.3	61.7	12.45	12.21	0.8309	19.00	268.2
24.8	14.36	14.12	0.8683	22.96	268.7						Mean 268.4

59. γ -Chloropentane (Method 1). B. p. 96°/753 mm.; *M* 106.60; n_D 1.40609, n_D 1.40820, n_F 1.41336, n_G 1.41709. Densities determined: $d_4^{20^\circ}$ 0.8723, $d_4^{42.4^\circ}$ 0.8509, $d_4^{69.6^\circ}$ 0.8327. Apparatus A.

<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>
19.8	14.80	14.56	0.8725	23.79	269.8	41.5	13.64	13.40	0.8518	21.37	269.3
22.1	14.67	14.43	0.8712	23.54	269.5	63.0	12.51	12.27	0.8293	19.05	269.0
27.0	14.48	14.24	0.8673	23.13	269.5						Mean 269.4

60. tert.-Amyl chloride (HCl method). B. p. 84.5°/759 mm.; *M* 106.60; n_D 1.40304, n_D 1.40520, n_F 1.41032, n_G 1.41403. Densities determined: $d_4^{20^\circ}$ 0.8650, $d_4^{40.5^\circ}$ 0.8444, $d_4^{61.6^\circ}$ 0.8215. Apparatus D.

<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>
17.8	10.86	10.62	0.8673	22.75	268.4	41.1	9.99	8.75	0.8438	20.32	268.5
23.3	10.62	10.38	0.8616	22.09	268.2	61.2	9.11	8.87	0.8219	18.00	267.7
											Mean 268.2

61. *n*-Hexyl chloride (Method 2b). B. p. 134°/759 mm.; *M* 120.62; n_D 1.41774, n_D 1.41991, n_F 1.42525, n_G 1.42907. Densities determined: $d_4^{20^\circ}$ 0.8784, $d_4^{40.6^\circ}$ 0.8600, $d_4^{61.3^\circ}$ 0.8407, $d_4^{86.7^\circ}$ 0.8163. Apparatus A.

<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>
20.3	16.18	15.94	0.8781	26.21	310.8	62.7	14.09	13.85	0.8394	21.77	310.4
20.4	16.14	15.90	0.8780	26.14	310.6	87.3	12.84	12.60	0.8157	19.25	309.7
42.6	15.19	14.95	0.8582	24.02	311.2						Mean 310.5

(Karvonen, *loc. cit.*, gives $d_4^{20^\circ}$ 0.8755, n_D 1.41731, n_D 1.41944, n_F 1.42464, n_G 1.42893; Clark and Streight, *loc. cit.*, give b. p. 135—136°, $d_4^{20^\circ}$ 0.8759, n_D 1.42364; Lek, *loc. cit.*, gives b. p. 135.10°/760 mm., $d_4^{20^\circ}$ 0.86595, n_D 1.41648, n_F 1.42408.)

62. *n*-Heptyl chloride (Method 2b). B. p. 159.5°/769 mm.; *M* 134.65; n_D 1.42354, n_D 1.42571, n_F 1.43107, n_G 1.43490. Densities determined: $d_4^{20^\circ}$ 0.8766, $d_4^{41.3^\circ}$ 0.8573, $d_4^{61.5^\circ}$ 0.8398, $d_4^{87.0^\circ}$ 0.8165. Apparatus D.

<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>
12.3	12.95	12.71	0.8835	27.73	349.7	62.3	11.30	11.06	0.8391	22.92	351.2
21.5	12.71	12.47	0.8752	26.95	350.5	87.2	10.46	10.22	0.8163	20.60	351.4
41.6	12.00	11.76	0.8570	24.89	350.9						Mean 350.7

(Clark and Streight, *loc. cit.*, give b. p. 158.5—159.5°, $d_4^{20^\circ}$ 0.8741, n_D 1.42844.)

63. *n*-Octyl chloride (Method 2b). B. p. 181.5°/765 mm.; *M* 148.68; n_D 1.42836, n_D 1.43058, n_F 1.43596, n_G 1.43990. Densities determined: $d_4^{20^\circ}$ 0.8748, $d_4^{41.2^\circ}$ 0.8565, $d_4^{61.2^\circ}$ 0.8406, $d_4^{86.6^\circ}$ 0.8192. Apparatus D.

<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>
17.9	13.17	12.93	0.8766	27.99	390.1	61.4	11.62	11.38	0.8406	23.62	390.0
22.5	13.02	12.78	0.8727	27.54	390.2	87.1	10.82	10.58	0.8188	21.39	390.5
41.3	12.32	12.08	0.8564	25.55	390.3						Mean 390.2

(Clark and Streight, *loc. cit.*, give b. p. 179—180°, $d_4^{20^\circ}$ 0.8745, n_D 1.43424.)

64. *n*-Nonyl chloride (Method 2b). B. p. 202°/760 mm.; *M* 162.70; n_D 1.43175, n_D 1.43400, n_F 1.43946, n_G 1.44348. Densities determined: $d_4^{20^\circ}$ 0.8704, $d_4^{40.60^\circ}$ 0.8551, $d_4^{61.1^\circ}$ 0.8388, $d_4^{86.8^\circ}$ 0.8204. Apparatus D.

<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	$d_4^{20^\circ}$	γ	<i>P.</i>
17.3	13.52	13.28	0.8725	28.62	431.3	61.3	12.00	11.76	0.8386	24.36	431.0
20.4	13.35	13.11	0.8701	28.17	430.8	86.6	11.10	10.86	0.8190	21.97	430.1
41.4	12.78	12.54	0.8545	26.46	431.9						Mean 431.0

(Clark and Streight, *loc. cit.*, give b. p. 98—100°/23 mm., $d_4^{20^\circ}$ 0.8679, n_D 1.43692.)

65. n-Decyl chloride (Method 2b). B. p. 222—223°/760 mm.; M 176.73; n_D 1.43502, n_D 1.43731, n_F 1.44281, n_G 1.44682. Densities determined: d_4^{20} 0.8683, d_4^{15} 0.8524, d_4^{10} 0.8372, d_4^{5} 0.8180. Apparatus D .

t .	h .	H .	d_4^t .	γ .	P .	t .	h .	H .	d_4^t .	γ .	P .
21.8	13.64	13.40	0.8679	28.72	471.4	63.0	12.27	12.03	0.8360	24.84	472.0
42.1	12.99	12.75	0.8516	26.81	472.3	86.3	11.49	11.25	0.8172	22.70	472.1
Mean 472.0											

66. n-Undecyl chloride (Method 2b). B. p. 240—241°/772 mm.; M 190.75; n_D 1.43778, n_D 1.44003, n_F 1.44559, n_G 1.44966. Densities determined: d_4^{20} 0.8677, d_4^{15} 0.8526, d_4^{10} 0.8378, d_4^{5} 0.8197. Apparatus D .

t .	h .	H .	d_4^t .	γ .	P .	t .	h .	H .	d_4^t .	γ .	P .
21.3	13.85	13.61	0.8677	29.13	511.3	61.5	12.60	12.36	0.8370	25.55	512.4
25.7	13.76	13.52	0.8635	28.83	511.9	87.3	11.76	11.52	0.8181	23.27	512.1
42.3	13.23	12.99	0.8517	27.32	512.0						Mean 511.9

67. n-Dodecyl chloride (Method 2b). B. p. 116.5°/5.0 mm.; M 204.78; n_D 1.44028, n_D 1.44255, n_F 1.44814, n_G 1.45226. Densities determined: d_4^{20} 0.8673, d_4^{15} 0.8516, d_4^{10} 0.8377, d_4^{5} 0.8181. Apparatus A .

t .	h .	H .	d_4^t .	γ .	P .	t .	h .	H .	d_4^t .	γ .	P .
24.3	18.06	17.82	0.8641	28.83	549.2	61.9	16.45	16.21	0.8367	25.40	549.4
41.5	17.30	17.04	0.8514	27.17	549.1	86.9	15.53	15.29	0.8177	23.41	550.9
Mean 549.7											

Preparation of Alkyl Bromides.—The methods used were: (1) The hydrogen bromide-sulphuric acid method (Kamm and Marvel, *loc. cit.*), A.R. hydrobromic acid (47.5%) being used with all the n -alcohols up to n -decyl and with isopropyl, *sec*-butyl, and isoamyl alcohols, and methyl- n -propyl- and diethyl-carbinols. (2) Use of 47.5% A.R. hydrobromic acid (Norris, *loc. cit.*) with ethyl, n -propyl, isopropyl, isobutyl, n -butyl, *sec*-butyl, and isoamyl alcohols: the method gave poor yields from n -amyl and higher n -alcohols. (3) The phosphorus tribromide method (Adams and Noller, *J. Amer. Chem. Soc.*, 1926, **48**, 1080; Reynolds and Adkins, *ibid.*, 1929, **51**, 280; "Organic Syntheses," 1933, **13**, 20) with isopropyl, isobutyl, n -amyl, and n -hexyl alcohols. (4) Ruhoff, Burnett, and Reid's gaseous hydrogen bromide method (*loc. cit.*) with n -octyl, n -decyl, n -undecyl, and n -dodecyl alcohols.

Preparations by method (1) were made on a large scale (to give 750—1000 g. of bromide). The refluxing period was 6—12 hours. For all bromides up to and including n -hexyl, the crude bromide could be distilled directly from the reaction mixture; for the higher bromides, where appreciable charring took place, the reaction product was filtered through glass-wool and diluted with water, and the crude bromide separated, best by ether extraction. All the bromides to n -octyl were purified by washing twice with an equal volume of concentrated hydrochloric acid (McCullough and Cortese, *loc. cit.*), then with water, 10% sodium carbonate solution, water (twice); they were then dried with calcium chloride and fractionated, a middle fraction being collected. For bromides beyond n -octyl, however, Ruhoff, Burnett, and Reid's method of purification (*loc. cit.*) must be used, as shown by the following observations for carefully fractionated samples:

$C_8H_{17}Br$ (Method 1), HCl purified: d_4^{20} 1.1124, n_D^{20} 1.4527.
$C_8H_{17}Br$ (Method 4), MeOH-H ₂ SO ₄ purified: d_4^{20} 1.1104, n_D^{20} 1.4524.
$C_9H_{19}Br$ (Method 1), HCl purified: d_4^{20} 1.0823, n_D^{20} 1.4534.
$C_9H_{19}Br$ (Method 1), MeOH-H ₂ SO ₄ purified: d_4^{20} 1.0901, n_D^{20} 1.4542.

In the preparation of n -propyl and isopropyl bromides by this method, the best yields are obtained by using the proportions described for n -butyl bromide but the slow-distillation technique given for ethyl bromide ("Organic Syntheses," 1921, **1**, 6); e.g., distillation of 360 g. of n -propyl alcohol occupied 6 hours and the yield of bromide was 655 g., but if the mixture was refluxed first and then distilled, the yield was much lower.

Details of method (2) are illustrated by the preparation of ethyl bromide. A mixture of 31 g. of absolute alcohol and 460 g. of A.R. constant-b. p. hydrobromic acid in a 500-c.c. Pyrex distilling flask was slowly distilled (6 hrs.) from an air-bath, the distillate being collected in a receiver cooled in ice. The bromide layer (64 g.) was separated, the acid layer mixed with a further 31 g. of absolute alcohol, and again distilled (5 hrs.). The resultant bromide layer was separated, combined with that from the first distillation, and washed and dried as in method (1), a middle fraction being collected on distillation. The yields of crude products for the other bromides were: n -propyl 65; isopropyl 75, n -butyl 72, isobutyl 54, *sec*-butyl 75; isoamyl (fermentation) 37%.

Isopropyl and isobutyl bromides were prepared in excellent yield at -10° to 0° by method (3), the crude product being purified by washing with concentrated hydrochloric or hydrobromic acid (instead of concentrated sulphuric acid), followed by water, 10% sodium carbonate solution, and water, and dried with anhydrous sodium sulphate. Contrary to Mann and Purdie (J., 1935, **1549**), the product obtained from higher alcohols (n -amyl to n -octyl) at 0° was far from pure; it was necessary to complete the reaction (3 mols. of alcohol and 1.3 mols. of phosphorus tribromide) by refluxing for 2—3 hours: the cold product was poured into water, neutralised with 10% sodium hydroxide solution, and steam-distilled. The crude bromide was purified as described above. For higher n -alcohols this method is not as satisfactory as method (1) or (4).

Bromides of n -alcohols above heptyl were best prepared by method (4) at 100—120° (cf. "Organic Syntheses," 1935, **15**, 35), the crude bromide being purified by Ruhoff, Burnett, and Reid's method (*loc. cit.*): the formation of emulsions sometimes encountered in the subsequent treatment with 50% methyl alcohol was considerably reduced by addition of a few grams of anhydrous calcium chloride. The yields were excellent throughout.

68. Ethyl bromide (Method 2). B. p. 38.5°/765 mm.; M 108.98; n_D 1.42212, n_D 1.42481, n_F 1.43146, n_G 1.43651. Density determined: d_4^{20} 1.4633. * = Apparatus C. † = Apparatus D.

t .	h .	H .	d_4^t .	γ .	P .	t .	h .	H .	d_4^t .	γ .	P .
18.8°	6.96	6.72	1.4653	24.32	165.4 †	18.2	7.26	7.02	1.4664	24.44	165.4 *
25.2	6.81	6.57	1.4545	23.60	165.4 †						Mean 165.4

[P 167.6 (e), 165.7; Timmermans and Martin, *J. Chim. physique*, 1926, **23**, 746, give b. p. 38.40°/760 mm., d_4^{20} 1.46063, n_D 1.42195, n_D 1.42476, n_F 1.43135, n_G 1.43686.]

68A. Ethyl bromide (Method 1). B. p. 38°/756 mm.; n_D 1.42197, n_D 1.42466, n_F 1.43135, n_G 1.43643; R_D 19.07, R_F 19.33, R_G 19.54; Mn_D^{20} 155.26. Densities determined: d_4^{20} 1.4604, $d_4^{15.7}$ 1.4676. * = Apparatus C. † = Apparatus D.

t .	h .	H .	d_4^t .	γ .	P .	t .	h .	H .	d_4^t .	γ .	P .
19.9	7.07	6.83	1.4606	23.68	164.8 *	16.9	6.96	6.72	1.4656	24.32	165.3 †
25.2	7.00	6.76	1.4517	23.30	165.2 *	21.1	6.86	6.59	1.4586	23.74	165.1
Mean 165.1											

69. *n*-Propyl bromide (Method 2). B. p. 72°/780 mm.; M 123.01; n_D 1.43218, n_D 1.43485, n_F 1.44143, n_G 1.44640. Densities determined: $d_4^{20^\circ}$ 1.3548, $d_4^{41.6^\circ}$ 1.3185, $d_4^{61.6^\circ}$ 1.3847. Apparatus *A*.

<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4°	γ	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4°	γ	<i>P.</i>
19.4	10.27	10.03	1.3558	25.46	203.8	25.3	10.11	9.87	1.3458	24.87	204.1
20.2	10.22	9.98	1.3545	25.31	203.7	42.5	9.42	9.18	1.3170	22.64	203.9
Mean 203.9											

(*P* 205.3; Karvonen, *loc. cit.*, gives b. p. 70.8°/769.2 mm.; $d_4^{20^\circ}$ 1.3539, n_C 1.43142, n_D 1.43411, n_F 1.44055, n_G 1.44591; Timmermans and Martin, *loc. cit.*, give b. p. 71.00°/760 mm., $d_4^{20^\circ}$ 1.35135, n_C 1.43180, n_D 1.43435, n_F 1.44119, n_G 1.44684.)

69A. *n*-Propyl bromide (Method 1). B. p. 70.5°/752 mm.; n_C 1.43208, n_D 1.34255, n_F 1.44136, n_G 1.44637; R_C 23.54, R_D 23.72, R_F 23.98, R_G 24.21; $Mn_D^{20^\circ}$ 176.43. Densities determined: $d_4^{20^\circ}$ 1.3556, $d_4^{42.5^\circ}$ 1.3153, $d_4^{61.9^\circ}$ 1.2799. Apparatus *B*.

9.2	8.46	8.22	1.3750	26.50	203.0	41.2	7.52	7.28	1.3176	22.49	203.3
19.3	8.13	7.89	1.3569	25.05	203.3	61.5	7.00	6.76	1.2807	20.30	204.4
Mean 203.6											

70. isoPropyl bromide (Method 2). B. p. 59°/758 mm.; M 123.01; n_C 1.42271, n_D 1.42541, n_F 1.43205, n_G 1.43711. Densities determined: $d_4^{20^\circ}$ 1.3138, $d_4^{40.6^\circ}$ 1.2777. Apparatus *A*.

15.0	9.74	9.50	1.3246	23.56	204.8	41.4	8.82	8.58	1.2763	20.51	205.5
21.8	9.47	9.23	1.3106	22.60	205.0						Mean 205.1

(*P* 205.1; Timmermans and Martin, *loc. cit.*, 1928, give b. p. 59.35°/760 mm., $d_4^{20^\circ}$ 1.31388, n_C 1.42286, n_D 1.42562, n_F 1.43235, n_G 1.43755.)

70A. isoPropyl bromide (Method 1). B. p. 58.9°/748 mm.; n_C 1.42147, n_D 1.42416, n_F 1.43073, n_G 1.43569; R_C 23.97, R_D 24.15, R_F 24.42, R_G 24.67; $Mn_D^{20^\circ}$ 175.19. Densities determined: $d_4^{20^\circ}$ 1.3030, $d_4^{40.7^\circ}$ 1.2629. Apparatus *A*.

9.8	10.05	9.81	1.3227	24.30	206.5	40.7	8.82	8.58	1.2629	20.29	207.0
19.5	9.61	9.37	1.3040	22.88	206.5						Mean 206.7

70B. isoPropyl bromide (Method 3). B. p. 59.3°/756 mm.; n_C 1.42321, n_D 1.42591, n_F 1.43238, n_G 1.43730; R_C 23.74, R_D 23.87, R_F 24.19, R_G 24.42; $Mn_D^{20^\circ}$ 175.40. Densities determined: $d_4^{20^\circ}$ 1.3202, $d_4^{40.5^\circ}$ 1.3325, $d_4^{42.1^\circ}$ 1.2783. Apparatus *A*.

14.1	9.65	9.41	1.3314	23.46	203.4	41.2	8.71	8.47	1.2800	20.30	204.3
23.3	9.37	9.13	1.3140	22.46	204.8						Mean 203.9

71. *n*-Butyl bromide (Method 2). B. p. 101°/768 mm.; M 137.03; n_C 1.43732, n_D 1.43993, n_F 1.44637, n_G 1.45125. Densities determined: $d_4^{20^\circ}$ 1.2744, $d_4^{41.0^\circ}$ 1.2474, $d_4^{60.6^\circ}$ 1.2190. Apparatus *D*.

21.3	8.60	8.36	1.2738	26.28	243.7	41.1	8.08	7.84	1.2473	24.15	243.8
24.9	8.51	8.27	1.2685	25.91	243.7	60.6	7.53	7.29	1.2190	21.95	244.0
Mean 243.8											

(*P* 243.5; Karvonen, *loc. cit.*, gives b. p. 100.2°/745.6 mm.; $d_4^{20^\circ}$ 1.2746, n_C 1.43719, n_D 1.43983, n_F 1.44613, n_G 1.45150; Timmermans and Martin, *loc. cit.*, 1926, give b. p. 101.60°/760 mm., $d_4^{20^\circ}$ 1.27567, n_C 1.43690, n_D 1.43975, n_F 1.44615, n_G 1.45145.)

71A. *n*-Butyl bromide (Method 1). B. p. 101°/758 mm.; n_C 1.43733, n_D 1.43993, n_F 1.44637, n_G 1.45125; R_C 28.11, R_D 28.26, R_F 28.62, R_G 28.89; $Mn_D^{20^\circ}$ 197.31. Densities determined: $d_4^{20^\circ}$ 1.2778, $d_4^{41.2^\circ}$ 1.2476, $d_4^{60.5^\circ}$ 1.2184, $d_4^{86.0^\circ}$ 1.1804. Apparatus *A*.

26.1	11.07	10.83	1.2689	25.73	243.2	59.9	9.76	9.52	1.2193	21.74	243.0
40.3	10.49	10.25	1.2489	23.97	242.8	86.1	8.82	8.58	1.1803	18.96	243.0
Mean 243.0											

72. isoButyl bromide (Method 2). B. p. 91—91.5°/765 mm.; M 137.03; n_C 1.43214, n_D 1.43475, n_F 1.44115, n_G 1.44594. Densities determined: $d_4^{20^\circ}$ 1.2532, $d_4^{42.6^\circ}$ 1.2205, $d_4^{63.0^\circ}$ 1.1913, $d_4^{86.8^\circ}$ 1.1548. Apparatus *D*.

12.5	8.48	8.24	1.2640	25.66	244.1	61.9	7.17	6.93	1.1929	20.42	244.6
41.5	7.64	7.40	1.2221	22.53	243.7						Mean 244.1

(*P* 243.8; Timmermans and Martin, *loc. cit.*, 1928, give b. p. 91.40°/760 mm., $d_4^{20^\circ}$ 1.26462, n_C 1.43394, n_D 1.43664, n_F 1.44317, n_G 1.44871.)

72A. isoButyl bromide (Method 3). B. p. 91—91.5°/745 mm.; n_C 1.43228, n_D 1.43490, n_F 1.44129, n_G 1.44612; R_C 28.73, R_D 28.88, R_F 29.24, R_G 29.52; $Mn_D^{20^\circ}$ 196.62. Densities determined: $d_4^{20^\circ}$ 1.2380, $d_4^{40.2^\circ}$ 1.2077, $d_4^{60.4^\circ}$ 1.1749. Apparatus *A*.

14.2	11.10	10.86	1.2469	25.36	246.6	40.5	10.20	9.96	1.2072	22.51	247.2
24.1	10.75	10.51	1.2317	24.24	246.9	60.4	9.35	9.11	1.1749	20.04	247.1
Mean 246.8											

73. sec.-Butyl bromide (Method 2). B. p. 91°/764 mm.; M 137.03; n_C 1.43397, n_D 1.43660, n_F 1.44317, n_G 1.44816. Densities determined: $d_4^{20^\circ}$ 1.2556, $d_4^{41.8^\circ}$ 1.2257, $d_4^{61.0^\circ}$ 1.1977. Apparatus *A*.

19.3	10.82	10.58	1.2556	24.89	243.6	41.7	10.01	9.77	1.2258	22.43	243.3
37.3	10.21	9.97	1.2320	23.00	243.6	60.8	9.35	9.11	1.1980	20.44	243.6
Mean 243.5											

(Timmermans and Delcourt, *loc. cit.*, give b. p. 91.2°/760 mm., $d_4^{20^\circ}$ 1.26088, n_C 1.43434, n_F 1.44369, n_G 1.44944; *P* 243.4.)

73A. *sec.-Butyl bromide* (Method 1). B. p. 91.5°/756 mm.; n_D 1.43421, n_D 1.43685, n_F 1.44340, n_G 1.44835; R_G 28.34, R_D 28.56, R_F 28.86, R_G 29.14; Mn_D^{20} 196.90. Densities determined: d_4^{20} 1.2597, d_4^{15} 1.2264, d_4^{25} 1.1935. Apparatus B.

<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4°	γ .	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4°	γ .	<i>P.</i>
10.9	9.02	8.78	1.2739	26.23	243.4	41.4	8.20	7.96	1.2266	22.89	244.4
22.2	8.75	8.51	1.2562	25.07	244.1	63.2	7.56	7.32	1.1925	20.47	244.8
Mean 244.2											

74. *n-Amyl bromide* (Method 1). B. p. 128.5°/764 mm.; M 151.06; n_D 1.44243, n_D 1.44505, n_F 1.45144, n_G 1.45619. Densities determined: d_4^{20} 1.2190, d_4^{15} 1.1936, $d_4^{17.7}$ 1.1673, $d_4^{86.5}$ 1.1352. Apparatus D.

19.4	9.31	9.07	1.2197	27.32	283.2	60.8	8.23	7.99	1.1684	23.05	283.3
22.9	9.22	8.98	1.2154	26.95	283.2	87.5	7.48	7.24	1.1340	20.28	283.0
42.4	8.65	8.41	1.1920	24.76	282.7	Mean 283.1					

(P 283.6; Karvonen, *loc. cit.*, gives b. p. 127.8—128.0°/762 mm., d_4^{20} 1.2175, n_D 1.44175, n_D 1.44435, n_F 1.45067, n_G 1.45592; Lek, *loc. cit.*, gives d_4^{20} 1.21730.)

74A. *n-Amyl bromide* (Method 3). B. p. 128.5°/762 mm.; n_D 1.44200, n_D 1.44460, n_F 1.45103, n_G 1.45579; R_G 32.72, R_D 32.89, R_F 33.30, R_G 33.60; Mn_D^{20} 218.22. Densities determined: d_4^{20} 1.2215, d_4^{15} 1.1954, $d_4^{86.4}$ 1.1714, $d_4^{86.6}$ 1.1368. Apparatus D.

20.2	9.33	9.09	1.2212	27.41	283.0	62.1	8.20	7.96	1.1693	22.99	282.9
42.0	8.74	8.50	1.1944	25.07	283.0	87.1	7.51	7.27	1.1362	20.40	282.7
Mean 282.9											

75. *isoAmyl bromide* (Method 1, from Bisol alcohol). B. p. 119.5°/760 mm.; M 151.06; n_D 1.43964, n_D 1.44225, n_F 1.44861, n_G 1.45341. Densities determined: d_4^{20} 1.2127, $d_4^{40.9}$ 1.1850, $d_4^{80.8}$ 1.1594, $d_4^{87.3}$ 1.1239. Apparatus A.

17.1	11.75	11.51	1.2165	26.22	281.0	63.2	10.08	9.84	1.1562	21.30	280.7
41.4	10.80	10.56	1.1843	23.42	280.6	87.6	9.15	8.91	1.1235	18.74	280.2
Mean 280.6											

(P 282.9; Lek, *loc. cit.*, gives d_4^{20} 1.20300.)

75A. *isoAmyl bromide* (Method 1, from Sharples's synthetic alcohol). B. p. 119.5°/755 mm.; n_D 1.43941, n_D 1.44199, n_F 1.44839, n_G 1.45416; R_G 32.95, R_D 33.12, R_F 33.53, R_G 33.91; Mn_D^{20} 217.83. Densities determined: d_4^{20} 1.2069, d_4^{15} 1.1791, $d_4^{22.6}$ 1.1529, $d_4^{87.4}$ 1.1200. Apparatus D.

15.4	9.11	8.87	1.2128	26.57	282.8	60.5	7.90	7.66	1.1556	21.86	282.6
41.9	8.36	8.12	1.1790	23.64	282.5	86.4	7.20	6.96	1.1213	19.27	282.6
Mean 282.6											

76. *β -Bromopentane* (Method 1). B. p. 117°/759 mm.; M 151.06; n_D 1.43929, n_D 1.44194, n_F 1.44840, n_G 1.45315. Densities determined: d_4^{20} 1.2122, d_4^{15} 1.1828, d_4^{11} 1.1577, $d_4^{84.8}$ 1.1263. Apparatus A.

14.3	11.80	11.56	1.2198	26.40	280.7	62.1	10.11	9.87	1.1564	21.37	280.9
18.9	11.66	11.42	1.2137	25.92	280.8	86.5	9.26	9.02	1.1240	18.99	280.9
41.6	10.85	10.61	1.1827	23.50	281.2	Mean 280.9					

77. *γ -Bromopentane* (Method 1). B. p. 118°/769 mm.; M 151.06; n_D 1.44054, n_D 1.44320, n_F 1.44967, n_G 1.45449. Densities determined: d_4^{20} 1.2051, whence d_4^{20} 1.2113 (extrap.), d_4^{13} 1.1831, $d_4^{34.0}$ 1.1566, $d_4^{84.5}$ 1.1293. Apparatus D.

23.3	8.83	8.59	1.2072	25.48	281.5	61.5	7.84	7.60	1.1597	21.94	281.9
27.3	8.73	8.49	1.2022	25.21	281.6	87.2	7.17	6.93	1.1257	19.27	281.4
41.0	8.43	8.19	1.1856	23.98	281.9	Mean 281.7					

78. *n-Hexyl bromide* (Method 1). B. p. 153.5°/746 mm.; M 165.08; n_D 1.44532, n_D 1.44781, n_F 1.45424, n_G 1.45907. Densities determined: d_4^{20} 1.1748, $d_4^{60.6}$ 1.1525, $d_4^{82.8}$ 1.1269, $d_4^{86.3}$ 1.0987. Apparatus D.

18.3	9.91	9.67	1.1767	28.10	323.0	61.1	8.82	8.58	1.1288	23.92	323.4
26.2	9.75	9.51	1.1677	27.42	323.5	85.9	8.11	7.87	1.0922	21.36	322.9
42.1	9.27	9.03	1.1508	25.66	323.6	Mean 323.3					

(P 322.8; Karvonen, *loc. cit.*, gives d_4^{20} 1.1763, n_D 1.44520, n_D 1.44778, n_F 1.45402, n_G 1.45924; Lek, *loc. cit.*, gives b. p. 156.3°/760 mm., d_4^{20} 1.17988, n_D 1.44478, n_F 1.45380.)

78A. *n-Hexyl bromide* (Method 3). B. p. 153°/751 mm.; n_D 1.44501, n_D 1.44761, n_F 1.45388, n_G 1.45856; R_G 37.49, R_D 37.68, R_F 38.14, R_G 38.48; Mn_D^{20} 238.97. Densities determined: d_4^{20} 1.1718, d_4^{15} 1.1484, $d_4^{15.8}$ 1.1250, $d_4^{84.1}$ 1.0964. Apparatus A.

28.7	12.40	12.16	1.1621	26.46	322.2	61.2	11.46	11.22	1.1257	23.65	323.4
42.2	11.98	11.74	1.1476	25.23	322.4	86.5	10.55	10.31	1.0960	21.16	323.0
Mean 322.8											

79. *n-Heptyl bromide* (Method 1). B. p. 177.5°/758 mm.; M 179.11; n_D 1.44794, n_D 1.45052, n_F 1.45681, n_G 1.46150. Densities determined: d_4^{20} 1.1401, d_4^{15} 1.1182, $d_4^{15.9}$ 1.1046, $d_4^{86.7}$ 1.0695. Apparatus A.

17.6	13.78	13.54	1.1426	28.97	363.7	61.8	12.42	12.18	1.1064	25.23	362.8
26.5	13.52	13.28	1.1333	28.25	364.1	85.7	11.39	11.15	1.0705	22.35	363.8
41.3	12.93	12.69	1.1188	26.58	363.5	Mean 363.5					

(P 363.0; Defiet, *Bull. Soc. chim. Belg.*, 1931, **40**, 385, gives b. p. 180.0°/760 mm., d_4^{20} 1.13991, n_D 1.44772, n_F 1.45678, n_G 1.46177.)

80. n-Octyl bromide (Method 1). B. p. 200°/768 mm.; M 193.14; n_D 1.45010, n_D 1.45267, n_F 1.45893, n_G 1.46356. Densities determined: $d_4^{20^\circ}$ 1.1124, $d_4^{41.8^\circ}$ 1.0918, $d_4^{61.1^\circ}$ 1.0722, $d_4^{86.2^\circ}$ 1.0454 Apparatus *D*.

<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ .	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ .	<i>P.</i>
19.2	10.88	10.64	1.1132	29.25	403.5	60.7	9.81	9.57	1.0726	25.35	404.0
22.3	10.79	10.55	1.1101	28.92	403.5	86.7	9.14	8.90	1.0449	22.97	404.6
42.0	10.29	10.05	1.0916	27.09	403.7						Mean 403.8

(*P* 402.4; Deffet, *loc. cit.*, gives b. p. 201.5°/760 mm., $d_4^{20^\circ}$ 1.11290, n_D 1.45011, n_F 1.45921, n_G 1.46435; Lek, *loc. cit.*, gives $d_4^{20^\circ}$ 1.11293.)

81. n-Nonyl bromide (Method 1). B. p. 219.5°/745 mm.; M 207.18; n_D 1.45165, n_D 1.45417, n_F 1.46044, n_G 1.46513. Densities determined: $d_4^{20^\circ}$ 1.0901, $d_4^{41.3^\circ}$ 1.0699, $d_4^{61.5^\circ}$ 1.0509, $d_4^{86.2^\circ}$ 1.0270. Apparatus *A*.

<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ .	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ .	<i>P.</i>
17.7	14.82	14.58	1.0923	29.82	443.2	63.2	13.28	13.04	1.0493	25.62	444.2
41.8	14.00	13.76	1.0704	27.58	443.6	86.9	12.56	12.32	1.0263	23.68	445.3
											Mean 444.1

(Tomecko and Adams, *J. Amer. Chem. Soc.*, 1927, **49**, 529, give b. p. 88°/4 mm., $d_4^{20^\circ}$ 1.0183, n_D 1.4533.)

82. n-Decyl bromide (Method 4). B. p. 102.5°/5.9 mm.; M 221.19; n_D 1.45274, n_D 1.45527, n_F 1.46149, n_G 1.46617. Densities determined: $d_4^{20^\circ}$ 1.0658, $d_4^{41.6^\circ}$ 1.0475, $d_4^{61.5^\circ}$ 1.0286, $d_4^{87.0^\circ}$ 1.0055. Apparatus *A*.

<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ .	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ .	<i>P.</i>
18.9	15.04	14.80	1.0668	29.56	483.5	40.9	14.38	14.14	1.0472	27.73	484.6
26.5	14.90	14.66	1.0600	29.09	484.6	61.8	13.73	13.49	1.0283	25.97	485.6
											Mean 484.6

83. n-Undecyl bromide (Method 4). B. p. 114°/5.0 mm.; M 235.21; n_D 1.45444, n_D 1.45697, n_F 1.46319, n_G 1.46788. Densities determined: $d_4^{20^\circ}$ 1.0541, $d_4^{41.0^\circ}$ 1.0367, $d_4^{61.8^\circ}$ 1.0196, $d_4^{86.7^\circ}$ 0.9976. Apparatus *A*.

<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ .	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ .	<i>P.</i>
19.9	15.55	15.31	1.0542	30.22	523.1	41.0	14.83	14.59	1.0367	28.32	523.4
21.8	15.49	15.25	1.0526	30.06	523.3	62.5	14.19	13.95	1.0190	26.62	524.3
28.2	15.32	15.08	1.0472	29.57	523.8	85.7	13.36	13.12	0.9984	24.53	524.3
											Mean 523.7

84. n-Dodecyl bromide (Method 4). B. p. 130.0°/5.7 mm.; M 249.24; n_D 1.45556, n_D 1.45807, n_F 1.46426, n_G 1.46878. Densities determined: $d_4^{20^\circ}$ 1.0382, $d_4^{41.0^\circ}$ 1.0208, $d_4^{61.7^\circ}$ 1.0055, $d_4^{84.9^\circ}$ 0.9839. Apparatus *D*.

<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ .	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ .	<i>P.</i>
19.3	12.31	12.07	1.0388	30.96	566.0	61.2	11.21	10.97	1.0043	27.21	566.8
24.9	12.11	11.87	1.0341	30.31	565.5	85.9	10.54	10.30	0.9831	25.01	566.9
40.6	11.74	11.50	1.0211	29.00	566.4						Mean 566.3

Preparation of Alkyl Iodides.—(1) This method consisted in slow distillation of the alcohol with 3–4 g.-mols. of constant-b. p. hydriodic acid ("Inorganic Syntheses," 1939, **1**, 157), the experimental details being similar to those already described for the bromides (see Norris, *loc. cit.*, 1907). For quantities of the order of 0.5 g.-mol. of alcohol the time required was 4–6 hours for C_1 – C_4 iodides and 7–9 hours for C_5 – C_8 iodides. The iodide was purified by washing with an equal volume of concentrated hydrochloric acid, then with water, 5% sodium carbonate or hydroxide solution until colourless, water (twice), and dried with anhydrous sodium sulphate or calcium chloride. For iodides up to C_4 , the fractionated sample was usually shaken with pure silver powder, filtered, and redistilled immediately before use. Higher iodides were first distilled under normal pressure in dim light, the correct b. p. fraction removed (this was generally slightly coloured), shaken mechanically with silver powder, filtered, and distilled under diminished pressure. All the samples used were colourless and were kept in the dark until required. The results of the preparations are summarised below.

Iodide, RI.	Wt. of ROH (g.).	Wt. of 57% HI (g.).	Yield of crude RI (g.).	Iodide, RI.	Wt. of ROH (g.).	Wt. of 57% HI (g.).	Yield of crude RI (g.).
MeI	16	302	61	*Am β I	44	337	90
EtI	44	302	80	†Am β I	40	297	95
Pr a I	30	302	84	CHMePr a I	44	337	90
Pr β I	30	302	85	CHEt $_2$ I	40	297	81
Bu a I	40	485	93	C $_6$ H $_{13}$ a I	51	446	111
Bu β I	30	273	65	C $_7$ H $_{15}$ a I	58	446	110
sec.-BuI	30	273	73	C $_8$ H $_{17}$ a I	65	446	120
Am a I	44	337	99				

* From Sharples's synthetic alcohol.

† From Bisol fermentation alcohol.

(2) The iodides (to C_5) were generally also prepared by the red phosphorus-iodide method or by the large-scale method of Adams and Voorhees (*loc. cit.*; cf. Adams, Kamim, and Marvel, "Organic Chemical Reagents," Univ. of Illinois Bulletin, 1919, **1**, 27; "Organic Syntheses," 1933, **13**, 60) in which equal quantities of red and yellow phosphorus are used. A relative deficiency of iodine led to an impure product. In order to obtain the purest iodides by this method, only a slight excess of phosphorus should be used, and for iodides other than methyl and ethyl the best results are obtained with the proportions 3 g.-atoms of iodine, 1.22 g.-atoms of a mixture of red and yellow phosphorus (6 : 5), and 3.05 g.-mols. of alcohol.

85. Methyl iodide (Method 1). B. p. 42.3°/761 mm.; M 141.95; n_D 1.52635, n_D 1.53152, n_F 1.54468, n_G 1.55498. Densities determined: $d_4^{20^\circ}$ 2.2829, $d_4^{41.6^\circ}$ 2.2895. Apparatus *D*.

<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ .	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4^*	γ .	<i>P.</i>
16.5	5.79	5.55	2.2895	31.38	146.8	22.9	5.68	5.44	2.2711	30.59	146.6
											Mean 146.7

(*P* 146.2; Karvonen, *loc. cit.*, gives b. p. 42.2°/753 mm., $d_4^{17^\circ}$ 2.2863, $n_D^{17^\circ}$ 1.52787, $n_D^{17^\circ}$ 1.53306, $n_F^{17^\circ}$ 1.54607, $n_G^{17^\circ}$ 1.55740; Timmermans and Delcourt, *loc. cit.*, 1934, give b. p. 42.5°/760 mm., $d_4^{20^\circ}$ 2.27900, n_D 1.52575, n_F 1.54535.)

85A. Methyl iodide (Method 2). B. p. 42°/751 mm.; n_D 1.52660, n_D 1.53173, n_F 1.54489, n_G 1.55528; R_D 19.12, R_D 19.28, R_F 19.67, R_G 19.98; Mn_D^{20} 217.42. Densities determined: d_4^{20} 2.2819, $d_4^{14.1}$ 2.2922. Apparatus $A = *$. Apparatus $C = \dagger$.

t .	h .	H .	d_4^* .	γ .	P .	t .	h .	H .	d_4^* .	γ .	P .
14.1	7.44	7.20	2.2922	30.90	146.1 *	16.0	5.94	5.70	2.2889	30.97	146.4 †
21.4	7.21	6.97	2.2795	29.75	145.6 *	22.2	5.73	5.49	2.2781	29.76	145.8 †
Mean 146.0											

86. Ethyl iodide (Method 1). B. p. 73°/765 mm.; M 155.98; n_D 1.50897, n_D 1.51369, n_F 1.52532, n_G 1.53483. Densities determined: $d_4^{15.5}$ 1.9395, $d_4^{11.5}$ 1.8881, $d_4^{9.1-8}$ 1.8419. Apparatus A .

13.3	8.33	8.09	1.9556	29.62	186.1	60.9	7.05	6.81	1.8441	23.52	186.7
41.1	7.65	7.41	1.8891	26.21	187.0	Mean 186.6					

(P 187.0; Karvonen, *loc. cit.*, gives $d_4^{16.5}$ 1.9427, $n_D^{16.5}$ 1.51077, $n_D^{15.5}$ 1.51542, $n_F^{16.5}$ 1.52715, $n_G^{16.5}$ 1.53726; Timmermans and Martin, *loc. cit.*, 1928, give b. p. 72.30°/760 mm., d_4^{20} 1.93582, n_D 1.50899, n_D 1.51367, n_F 1.52541.)

86A. Ethyl iodide (Method 2). B. p. 71.5°/745 mm.; n_D 1.50873, n_D 1.51337, n_F 1.52509, n_G 1.53428; R_D 24.04, R_D 24.23, R_F 24.69, R_G 25.05; Mn_D^{20} 236.06. Densities determined: d_4^{20} 1.9361, $d_4^{10.9}$ 1.8883, $d_4^{11.5}$ 1.8394. Apparatus D .

14.4	6.43	6.19	1.9490	29.79	187.0	40.9	5.86	5.62	1.8883	26.21	187.1
22.8	6.30	6.06	1.9297	28.88	187.4	61.5	5.49	5.25	1.8394	23.85	187.8
Mean 187.3											

87. n-Propyl iodide (Method 1). B. p. 102°/768 mm.; M 170.01; n_D 1.50103, n_D 1.50524, n_F 1.51589, n_G 1.52442. Densities determined: d_4^{20} 1.7434, $d_4^{10.1}$ 1.7036, $d_4^{9.0}$ 1.6693, $d_4^{5.4}$ 1.6198. Apparatus A .

14.5	9.14	8.90	1.7536	29.22	225.4	61.4	8.02	7.78	1.6677	24.30	226.5
25.2	8.98	8.74	1.7338	28.37	226.3	85.2	7.36	7.12	1.6202	21.60	226.7
41.5	8.51	8.27	1.7047	26.40	226.1	Mean 226.2					

(P 226.0; Karvonen, *loc. cit.*, gives b. p. 101.9°/765.5 mm., d_4^{20} 1.7471, n_D 1.50123, n_D 1.50546, n_F 1.51611, n_G 1.52513; Lek, *loc. cit.*, gives d_4^{20} 1.74892; Timmermans and Delcourt, *loc. cit.*, give b. p. 102.5°/760 mm., d_4^{20} 1.74890, n_D 1.50148, n_F 1.51600; Audsley and Goss, *J.*, 1942, 358, give d_4^{20} 1.7458, n_D^{20} 1.5050.)

87A. n-Propyl iodide (Method 2). B. p. 101°/749 mm.; n_D 1.50175, n_D 1.50599, n_F 1.51665, n_G 1.52496; R_D 28.63, R_D 28.83, R_F 29.35, R_G 29.74; Mn_D^{20} 256.03. Densities determined: d_4^{20} 1.7518, $d_4^{12.2}$ 1.7087, $d_4^{9.7}$ 1.6758, $d_4^{8.0}$ 1.6245. Apparatus A .

14.5	9.26	9.02	1.7624	29.77	225.3	60.6	7.97	7.73	1.6737	24.23	226.1
24.4	9.02	8.78	1.7433	28.66	225.6	87.5	7.27	7.03	1.6216	21.35	225.9
41.1	8.50	8.26	1.7108	26.46	225.4	Mean 225.8					

88. iso-Propyl iodide (Method 1). B. p. 89°/762 mm.; M 170.01; n_D 1.49477, n_D 1.49918, n_F 1.51021, n_G 1.51829. Densities determined: d_4^{20} 1.7025, $d_4^{11.0}$ 1.6647, $d_4^{10.0}$ 1.6228. Apparatus A .

16.4	8.65	8.41	1.7092	26.92	226.6	40.9	7.96	7.72	1.6648	24.07	226.3
25.0	8.32	8.08	1.6932	25.62	225.9	61.6	7.31	7.07	1.6235	21.49	225.8
Mean 225.9											

(Timmermans and Delcourt, *loc. cit.*, give b. p. 89.5°/760 mm., d_4^{20} 1.70416, n_D 1.49473, n_F 1.51026; Audsley and Goss, *loc. cit.*, give d_4^{20} 1.7043, n_D 1.4991.)

88A. iso-Propyl iodide (Method 2). B. p. 88°/749 mm.; n_D 1.49408, n_D 1.49840, n_F 1.50949, n_G 1.51813; R_D 29.16, R_D 29.38, R_F 29.93, R_G 30.35; Mn_D^{20} 254.74. Densities determined: d_4^{20} 1.6795, $d_4^{12.9}$ 1.6507, $d_4^{10.7}$ 1.6131. Apparatus A .

24.5	8.50	8.26	1.6882	26.11	227.6	61.2	7.57	7.33	1.6121	22.13	229.1
41.6	8.05	7.81	1.6534	24.18	228.2	Mean 228.3					

89. n-Butyl iodide (Method 1). B. p. 129°/756 mm.; M 184.03; n_D 1.49589, n_D 1.49984, n_F 1.50978, n_G 1.51769. Densities determined: d_4^{20} 1.6157, $d_4^{11.7}$ 1.5815, $d_4^{11.5}$ 1.5492, $d_4^{8.8}$ 1.5090. Apparatus A .

16.9	9.92	9.68	1.6207	29.38	264.4	60.1	8.79	8.55	1.5514	24.84	264.8
26.4	9.71	9.47	1.6055	28.47	264.8	86.0	8.07	7.83	1.5088	22.12	264.6
41.3	9.26	9.02	1.5821	26.72	264.5	Mean 264.6					

(P 264.7; Karvonen, *loc. cit.*, gives b. p. 129.3—129.5°/746.5 mm., d_4^{20} 1.6123, n_D 1.49577, n_D 1.49975, n_F 1.50962, n_G 1.51803; Lek, *loc. cit.*, gives d_4^{20} 1.61541; Timmermans and Delcourt, *loc. cit.*, give b. p. 130.4°/760 mm., d_4^{20} 1.61541, n_D 1.49635, n_D 1.50038, n_F 1.51041; Audsley and Goss, *loc. cit.*, give d_4^{20} 1.6187, n_D^{20} 1.5000.)

89A. n-Butyl iodide (Method 2). B. p. 129°/756 mm., n_D 1.49367, n_D 1.49758, n_F 1.50738, n_G 1.51520; R_D 33.48, R_D 33.70, R_F 34.26, R_G 34.79; Mn_D^{20} 275.60. Densities determined: d_4^{20} 1.5995, $d_4^{11.5}$ 1.5619, $d_4^{10.8}$ 1.5317, $d_4^{9.5}$ 1.4875. Apparatus A .

12.8	10.04	9.80	1.6117	29.58	266.3	60.6	8.83	8.59	1.5320	24.64	267.6
22.9	9.74	9.50	1.5944	28.36	266.4	87.8	8.06	7.82	1.4853	21.75	267.6
41.0	9.32	9.08	1.5628	26.57	267.4	Mean 267.2					

90. sec-Butyl iodide (Method 1). B. p. 117.5—118°/750 mm.; M 184.03; n_D 1.49497, n_D 1.49909, n_F 1.50946, n_G 1.51779. Densities determined: d_4^{20} 1.5920, $d_4^{10.1}$ 1.5595, $d_4^{10.1}$ 1.5266, $d_4^{5.5}$ 1.4838. Apparatus A .

17.3	7.49	7.25	1.5964	28.58	266.5	61.3	6.59	6.35	1.5246	23.91	267.0
25.9	7.26	7.02	1.5824	27.43	266.2	87.5	6.00	5.76	1.4806	21.06	266.7
41.9	6.98	6.74	1.5566	25.91	266.7	Mean 266.6					

(Lek, *loc. cit.*, gives d_4^{20} 1.59806; Timmermans and Delcourt, *loc. cit.*, give b. p. 120.0°/760 mm., d_4^{20} 1.59754, n_D 1.49596, n_D 1.50010, n_F 1.51054, n_G 1.51940, P 266.1; Audsley and Goss, *loc. cit.*, give d_4^{20} 1.5984, n_D^{20} 1.5000.)

91. isoButyl iodide (Method 1). B. p. 119.5°/771 mm.; M 184.03; n_D 1.49195, n_D 1.49588, n_F 1.50571, n_G 1.51357. Densities determined: d_4^{20} 1.6017, $d_4^{42.5}$ 1.5641, $d_4^{62.5}$ 1.5305, $d_4^{86.5}$ 1.4898. Apparatus *D*.

<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>	<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>
17.5	7.44	7.20	1.6059	28.55	264.9	60.3	6.52	6.28	1.5342	23.79	264.9
25.4	7.21	6.97	1.5928	27.42	264.4	85.3	5.98	5.74	1.4918	21.15	264.9
41.3	6.90	6.66	1.5663	25.76	264.7						Mean 264.7

(Timmermans and Delcourt, *loc. cit.*, give b. p. 120°/760 mm., d_4^{20} 1.60346, n_D 1.49238, n_F 1.50630, *P* 264.0; Audsley and Goss, *loc. cit.*, give d_4^{20} 1.6038, n_D^{20} 1.4961.)

92. n-Amyl iodide (Method 1). B. p. 154.5°/761 mm. (very slight decomp.), followed by 52°/20 mm.; M 198.06; n_D 1.49171, n_D 1.49540, n_F 1.50474, n_G 1.51222. Densities determined: d_4^{20} 1.5118, $d_4^{41.1}$ 1.4827, $d_4^{61.4}$ 1.4541, $d_4^{86.9}$ 1.4163. Apparatus *A*.

<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>	<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>
20.5	10.62	10.38	1.5111	29.37	305.1	61.3	9.49	9.25	1.4542	25.19	305.1
21.0	10.57	10.33	1.5104	29.22	304.9	87.2	8.75	8.51	1.4159	22.56	304.9
42.0	10.04	9.80	1.4815	27.19	305.3						Mean 305.1

(Karvonen, *loc. cit.*, gives b. p. 153.2—153.5°/743 mm., d_4^{20} 1.5095, n_D 1.49174, n_D 1.49548, n_F 1.50485, n_G 1.51277; Audsley and Goss, *loc. cit.*, give d_4^{20} 1.5108, n_D^{20} 1.4965.)

92A. n-Amyl iodide (Method 2). B. p. 155°/766 mm., followed by 42°/10 mm.; n_D 1.49229, n_D 1.49607, n_F 1.50548, n_G 1.51286; R_D 38.11, R_D 38.27, R_F 38.88, R_G 39.36; Mn_D^{20} 296.32. Densities determined: d_4^{20} 1.5122, $d_4^{41.5}$ 1.4807, $d_4^{63.2}$ 1.4503, $d_4^{86.9}$ 1.4146. Apparatus *A*.

<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>	<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>
25.5	10.42	10.18	1.5041	28.67	304.7	62.2	9.34	9.10	1.4503	24.72	304.5
41.9	9.94	9.70	1.4801	26.88	304.7	86.7	8.70	8.46	1.4149	22.41	304.6
											Mean 304.6

93. isoAmyl iodide (Method 1, from fermentation alcohol). B. p. 147.5°/768 mm.; M 198.06; n_D 1.48896, n_D 1.49269, n_F 1.50201, n_G 1.50934. Densities determined: d_4^{20} 1.5025, $d_4^{43.0}$ 1.4709, $d_4^{61.5}$ 1.4443, $d_4^{86.3}$ 1.4071. Apparatus *A*.

<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>	<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>
25.0	9.98	9.74	1.4955	27.28	302.7	61.3	9.02	8.78	1.4446	23.75	302.7
42.1	9.56	9.32	1.4722	25.69	302.9	87.0	8.32	8.08	1.4061	21.27	302.5
											Mean 302.7

93A. isoAmyl iodide (Method 1, from synthetic alcohol). B. p. 147.5°/763 mm.; n_D 1.49024, n_D 1.49394, n_F 1.50331, n_G 1.51079; R_D 37.96, R_D 38.20, R_F 38.81, R_G 39.30; Mn_D^{20} 295.88. Densities determined: d_4^{20} 1.5092, $d_4^{40.4}$ 1.4807, $d_4^{61.4}$ 1.4504, $d_4^{86.5}$ 1.4129. Apparatus *D*.

<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>	<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>
21.4	7.88	7.64	1.5072	28.40	303.5	61.1	7.15	6.91	1.4501	24.74	304.6
40.6	7.54	7.30	1.4805	26.69	304.1	86.5	6.68	6.44	1.4129	22.47	305.2
											Mean 304.3

94. γ -Iodopentane (Method 1). B. p. 141.5—142.5°/773 mm. (very slight decomp.), followed by 41.5°/17 mm.; M 198.06; n_D 1.49394, n_D 1.49781, n_F 1.50763, n_G 1.51573. Densities determined: d_4^{20} 1.5106, $d_4^{41.5}$ 1.4809, $d_4^{61.5}$ 1.4504, $d_4^{86.5}$ 1.4148. Apparatus *A*.

<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>	<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>
16.9	10.41	10.17	1.5150	28.85	303.0	61.9	9.00	8.76	1.4511	23.80	301.5
25.1	10.18	9.94	1.5034	27.98	302.4	97.3	8.38	8.14	1.4137	21.55	301.9
41.5	9.57	9.33	1.4809	25.87	301.6						Mean 302.9

(Audsley and Goss, *loc. cit.*, give d_4^{20} 1.5128, n_D^{20} 1.4979.)

95. β -Iodopentane (Method 1). B. p. 141—142°/762 mm. (very slight decomp.), followed by 44.5°/20 mm.; M 198.06; n_D 1.49222, n_D 1.49611, n_F 1.50590, n_G 1.51359. Densities determined: d_4^{20} 1.5096, $d_4^{41.5}$ 1.4785, $d_4^{60.5}$ 1.4503, $d_4^{86.5}$ 1.4114. Apparatus *A*.

<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>	<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>
17.5	10.30	10.06	1.5133	28.51	302.4	60.2	9.00	8.76	1.4507	23.80	301.5
41.2	9.48	9.24	1.4789	25.59	301.2	85.3	8.42	8.18	1.4133	21.65	302.3
											Mean 301.8

(Audsley and Goss, *loc. cit.*, give d_4^{20} 1.5020, n_D^{20} 1.4960.)

96. n-Hexyl iodide (Method 1). B. p. 180°/774 mm. (very slight decomp.), followed by 45.5°/4 mm.; M 212.08; n_D 1.48905, n_D 1.49264, n_F 1.50160, n_G 1.50862. Densities determined: d_4^{20} 1.4367, $d_4^{41.4}$ 1.4091, $d_4^{61.6}$ 1.3826, $d_4^{86.1}$ 1.3504. Apparatus *D*.

<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>	<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>
18.3	8.70	8.46	1.4389	30.06	345.1	62.1	7.79	7.55	1.3820	25.77	345.8
24.1	8.62	8.38	1.4314	29.62	345.7	85.6	7.31	7.07	1.3511	23.59	345.9
41.7	8.30	8.06	1.4087	28.04	346.4						Mean 345.8

(*P* 344.1; Karvonen, *loc. cit.*, gives b. p. 177°/743.7 mm., d_4^{20} 1.4387, n_D 1.48929, n_D 1.49290, n_F 1.50183, n_G 1.50941; Lek, *loc. cit.*, gives b. p. 180.20°/760 mm., d_4^{20} 1.43919, n_D 1.48924, n_F 1.50185; Audsley and Goss, *loc. cit.*, give d_4^{20} 1.4329, n_D^{20} 1.4930.)

97. n-Heptyl iodide (Method 1). B. p. 202°/774 mm. (very slight decomp.), followed by 62.5°/3.5 mm.; M 226.11; n_D 1.48628, n_D 1.48974, n_F 1.49832, n_G 1.50509. Densities determined: d_4^{20} 1.3734, $d_4^{41.0}$ 1.3487, $d_4^{61.1}$ 1.3248, $d_4^{85.7}$ 1.2943. Apparatus *D*.

<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>	<i>t</i>	<i>h</i>	<i>H</i>	d_4^t	γ	<i>P</i>
18.6	9.24	9.00	1.3751	30.56	386.6	61.6	8.29	8.05	1.3242	26.33	386.8
20.2	9.15	8.91	1.3732	30.22	386.1	88.3	7.75	7.51	1.2913	23.95	387.4
41.0	8.68	8.44	1.3487	28.11	386.0						Mean 386.6

(*P* 384.5; Deffet, *loc. cit.*, gives b. p. 204°/760 mm., d_4^{20} 1.37949, n_D 1.48699, n_F 1.49916, n_G 1.50567; Lek, *loc. cit.*, gives d_4^{20} 1.37961; Audsley and Goss, *loc. cit.*, give d_4^{20} 1.3792, n_D^{20} 1.4909.)

98. n-Octyl iodide (Method 1). B. p. 221—221.5°/752 mm. (very slight decomp.), followed by 86.5°/5 mm.; M 240.14; n_D 1.48554, n_D 1.48892, n_F 1.49731, n_G 1.50385. Densities determined: d_4^{20} 1.3297, d_4^{15} 1.3061, $d_4^{61.6}$ 1.2833, $d_4^{86.5}$ 1.2549. Apparatus D.

<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4°	γ .	<i>P.</i>	<i>t.</i>	<i>h.</i>	<i>H.</i>	d_4°	γ .	<i>P.</i>
21.0	9.58	9.34	1.3286	30.65	425.3	61.0	8.70	8.46	1.2840	26.83	425.6
42.4	9.11	8.87	1.3051	28.59	425.5	86.9	8.19	7.95	1.2545	24.63	426.4
											Mean 425.7

(Deffet, *loc. cit.*, gives b. p. 225.5°/760 mm., d_4^{20} 1.33008, n_D^{20} 1.48514, n_F 1.49688, n_G 1.50363; Audsley and Goss, *loc. cit.*, give d_4^{20} 1.3295, n_D^{20} 1.4890.)

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