

**183.** *Studies in Dielectric Polarisation. Part XXII. The Series Effect on the Dipole Moments of Some Alkyl Halides in Solution.*

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The effects of induction in the polar molecule and in the solvent by the principal dipole of various alkyl halides have been examined and a comparison has been made between the theoretical predictions and the experimental moments, measured in benzene at 20°. It has been found that the moments of the compounds increase as the series of *n*-alkyl iodides and bromides are ascended, and that the effect is greater in the former series. This is probably due to differences in properties between the polar groups.

THE present paper gives an account of some measurements of the dipole moments of two series of *n*-alkyl halides. The results are of interest as they give information concerning the influence of the series effect on solution results and, since the moments of these compounds in the vapour state are available, a comparison can be made of this effect upon the moments as measured in the vapour state and in solution. It formerly appeared that the moments of the vapours of these compounds attained a constant value in the second member of the series (see, *e.g.*, Smyth and McAlpine, *J. Chem. Physics*, 1934, **2**, 499) and a similar result was established for other series from solution measurements, *e.g.*, *n*-alkyl nitriles in benzene (Part XIII, Cowley and Partington, *J.*, 1935, 604) and the chlorides of *n*-fatty acids in benzene (Part XVI, Martin and Partington, *J.*, 1936, 158). More recent work, however, has shown that in the vapour state several series, notably the alkyl halides, exhibit small increases in moment extending over more than four carbon atoms in the case of the iodides, when a uniform method of correction for atomic polarisation is adopted (Groves and Sugden, *J.*, 1937, 158). From the earlier solution data it is impossible to reach any definite conclusion on the variation of the moment in the *n*-alkyl halide series, as no measurements for the whole series made under uniform conditions are available. The moments reported in this paper refer to alkyl bromides and iodides. The corresponding chlorides were not used, because the volatility of the lower members of this series, upon

which interest would be mainly centred, would make it difficult to work with them in solutions. Since small changes in moment were found between successive earlier members of these series, the *n*-compounds as far as the amyl member were investigated, the moment then being found to have reached a constant value.

A comparison of the earlier results with those of this research is given in the table. The solvent and temperature are stated after each figure obtained from solution measurements, and the vapour results are the means of several determinations. The values found from solutions by the temperature method are in all probability too small, as the values of the atomic polarisation of alkyl halides found by this method are anomalously large (cf. Cowley and Partington, J., 1937, 132; Table II). The moments are expressed throughout the paper in Debye units.

Compound.	Solution results.*		Present results <sup>11</sup> (B., 20°).	Vapour result.
C <sub>2</sub> H <sub>5</sub> I .....	1.35 (H., temp.†) <sup>1</sup>	1.6 (B., 25°) <sup>2</sup>	1.41	1.64 <sup>3</sup>
C <sub>3</sub> H <sub>7</sub> I .....	1.66 (Hp., temp.) <sup>4</sup>	1.7 (B., 25°) <sup>2</sup>	1.78	1.87 <sup>3</sup>
<i>n</i> -C <sub>3</sub> H <sub>7</sub> I .....	—	1.85 (B., 20°) <sup>5</sup>	1.84	2.01 <sup>3</sup>
<i>iso</i> -C <sub>3</sub> H <sub>7</sub> I .....	—	1.99 (B., 20°) <sup>5</sup>	1.95	—
<i>n</i> -C <sub>4</sub> H <sub>9</sub> I .....	1.59 (Hp., temp.) <sup>6</sup>	1.88 (B., 10°) <sup>7</sup>	1.88	2.08 <sup>3</sup>
<i>n</i> -C <sub>5</sub> H <sub>11</sub> I .....	—	—	1.88	—
<i>iso</i> -C <sub>5</sub> H <sub>11</sub> I .....	—	1.93 (B., 20°) <sup>5</sup>	—	—
C <sub>2</sub> H <sub>5</sub> Br .....	1.86 (H., temp.) <sup>8</sup>	1.91 (H., 20°) <sup>10</sup>	1.89	2.01 <sup>3</sup>
—	1.71 (C., 20°) <sup>10</sup>	2.12 (B., —) <sup>9</sup>	—	—
<i>n</i> -C <sub>3</sub> H <sub>7</sub> Br .....	2.00 (B., —) <sup>9</sup>	1.94 (B., 20°) <sup>5</sup>	1.93	2.13 <sup>3</sup>
<i>iso</i> -C <sub>3</sub> H <sub>7</sub> Br .....	2.20 (B., —) <sup>9</sup>	2.09 (B., 20°) <sup>5</sup>	2.04	2.19 <sup>3</sup>
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br .....	1.81 (Hp., temp.) <sup>6</sup>	1.97 (B., 10°) <sup>7</sup>	1.93	2.15 <sup>3</sup>
<i>n</i> -C <sub>5</sub> H <sub>11</sub> Br .....	—	—	1.95	—
<i>iso</i> -C <sub>5</sub> H <sub>11</sub> Br .....	—	1.93 (B., 20°) <sup>5</sup>	—	—

\* Solvents: B. benzene; C. carbon disulphide; H. hexane; Hp. heptane.

† Moment determined by the temperature method.

<sup>1</sup> Morgan and Lowry, *J. Physical Chem.*, 1930, **34**, 2385. <sup>2</sup> Williams, *Z. physikal. Chem.*, 1928, **A**, **138**, 75. <sup>3</sup> Groves and Sugden, *J.*, 1937, 158. <sup>4</sup> Smyth and Stoops, *J. Amer. Chem. Soc.*, 1929, **51**, 3312. <sup>5</sup> Parts, *Z. physikal. Chem.*, 1931, **B**, **12**, 312. <sup>6</sup> Smyth and Rogers, *J. Amer. Chem. Soc.*, 1930, **52**, 2227. <sup>7</sup> Parts, *Z. physikal. Chem.*, 1930, **B**, **7**, 327. <sup>8</sup> Smyth and Morgan, *J. Amer. Chem. Soc.*, 1928, **50**, 1547. <sup>9</sup> Daily, *Physical Rev.*, 1929, **30**, 548. <sup>10</sup> Cowley and Partington, *J.*, 1937, 130. <sup>11</sup> See also preliminary note, Cowley and Partington, *Nature*, 1937, **140**, 1100.

Parts's values (*loc. cit.*) are in fairly good agreement with some of the present results, examination of which shows that there is a gradual increase in moment in the *n*-iodide series as far as the butyl compound, the moment of which is identical with that of *n*-amyl iodide. *iso*Propyl iodide possesses a moment greater than that of its *n*-isomer and also of the higher *n*-compounds. An analogous result is found for the bromide series, but in this case the moment reaches its limiting value in the *n*-series at the third member, the moment of *n*-propyl bromide being practically equal to those of *n*-butyl and *n*-amyl bromides. Of the two propyl bromides, the *iso*-compound has the greater moment.

The increases in moment with extension of the hydrocarbon chain shown by the vapours are on the whole larger and continue to higher members of the series than those in solution. Both solution and vapour results indicate that the change in the iodide series is greater than in the bromide series and that this increase continues further along the chain, in spite of the fact that the moments of the iodides are somewhat smaller than those of the corresponding bromides. It follows that the variation of moment does not depend directly upon the magnitude of the principal dipole, as simple induction in the hydrocarbon chain would cause the increase in moment of the series to be proportional to this magnitude (cf. Smyth, "Dielectric Constant and Molecular Structure," 1931, p. 74).

The total moment of a simple molecule with one polar group, dissolved in a non-polar solvent, can be regarded as compounded vectorially from three moments: (1) the primary moment of the polar bond, (2) the resultant moment produced by its effect on other parts of the polar molecule (radical effect), and (3) the resultant moment of the induction by the principal dipole in the solvent molecules (solvent effect). There would be, in addition, the further interaction of these moments, so the separation of these

effects is somewhat arbitrary, but these three factors are the major components. Since in the vapour state only the first two effects contribute to the resultant moment of the molecule, the study of the induction effect produced in an homologous series will evidently be simpler in that case than in solution. The solvent effect will depend upon the characteristics of the solvent as well as upon those of the polar molecule, particularly upon its shape. Methods for computing these moments have been given by Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171) and by Higasi (*Sci. Papers Inst. Phys. Chem. Res., Japan*, 1936, **28**, 284). It has been shown that if the shape of the polar molecule and the location and magnitude of its dipole are known, together with the polarisability of the solvent, then an estimate of the moment due to the solvent effect can be made, and in certain cases of simple molecules these estimates are in fairly good agreement with experimental figures (cf. Cowley and Partington, Part XX, *J.*, 1936, 1184; Part XXI, *J.*, 1937, 130). The radical effect will depend upon the location of the principal dipole and upon the hydrocarbon chain to which it is attached, and the importance of this effect is largely governed by spatial considerations.

If the molecule can be treated approximately as a body of revolution, then the sign of the moment induced in various parts of the polar molecule depends upon the position of the hydrocarbon chain relative to the dipole. In those parts of the polar molecule falling within two cones of semi-angle  $55^\circ$  about the dipole axis, the induced moment will be in the sense of the primary moment, whereas the moment induced in the parts outside this space opposes it (Frank, *loc. cit.*). The magnitude of the moments induced in a solvent molecule, or hydrocarbon radical, by the principal dipole of the polar molecule will depend largely upon the position of the molecule, or radical, relative to the primary dipole. The facts that the radical is fixed and is nearer the polar group and that the bond moments may be modified by introduction of the hydrocarbon group in the polar molecule, cause a difference between the moments induced in a hydrocarbon radical and in a solvent molecule situated in similar positions. The moment induced in the radical, according to Frank's theory, will be somewhat greater than, and have the opposite sign to, that induced in the solvent molecule. In the higher members of these alkyl series, as each additional  $\text{CH}_2$  group introduces a further inflexion in the molecule (due to the carbon valency angle), the end of the chain is relatively free to rotate, and although this possibly causes parts of the molecule to occupy positions outside the cones, the bulk of the polarisable matter is added in positions such that its induced moment augments the primary moment. The theory shows that for molecules of the alkyl halide type the solvent effect is negative and so the radical effect should be positive, as is found by experiment. On this basis, however, the increase of moment in such homologous series should be proportional to the magnitude of the principal dipole and the percentage increase should be uniform. This conclusion is not supported either by the results for vapours or by those for solutions (see preceding table). The necessary approximations assumed in the development of the theory have been clearly stated by Frank (*loc. cit.*, p. 180), and to them the discrepancy between the theoretical and experimental results may well be due.

The examination of the magnitudes of the moments induced in various parts of the molecule, as discussed above, requires a knowledge of the location and magnitude of the primary dipole, the radii and polarisabilities of the atoms, and the distances between them. It has been suggested that the principal dipole of an alkyl halide molecule is situated between the carbon and the halogen nucleus at seven-eighths of the distance from the former (cf. Meyer, *Z. physikal. Chem.*, 1930, *B*, **8**, 27; Smyth and McAlpine, *J. Chem. Physics*, 1933, **1**, 190), although in reality the dipole possibly has a finite length. The atomic radii of hydrogen, carbon, bromine, and iodine may be taken as 0.29, 0.77, 1.14 and 1.33 Å. (Pauling, *Proc. Nat. Acad. Sci.*, 1932, **18**, 293; Pauling and Higgins, *Z. Krist.*, 1934, **87**, 205), and their polarisabilities are 0.654, 0.984, 3.63, and  $5.46 \times 10^{-24}$  c.c. respectively (Smallwood and Herzfeld, *J. Amer. Chem. Soc.*, 1930, **52**, 1919). If it is assumed that the primary dipole is localised in the position given above and that the distances between the centres of the nuclei are equal to the sum of the respective atomic radii (cf. Brockway and Jenkins, *ibid.*, 1936, **58**, 2036), diagrams of the alkyl bromide and iodide molecules can be

drawn to scale using these atomic dimensions. An *isopropyl iodide* molecule is represented in Fig. 1, in which the point *M* indicates the position of the primary dipole and the dotted lines represent the surfaces of the cones. [The hydrogen atoms are not shown in the diagram.] It can readily be seen that the size of the halogen atom largely determines the extent to which parts of the molecule lie within or without the cones of semi-angle  $55^\circ$ . Also the magnitudes of the moments induced in these parts, which either enhance or oppose the primary moment, will be largely dependent on the polarisability of the halogen atom, and in the lower members of the series the opposing moments will be induced solely in parts of the halogen atom (see Fig. 1, where the atoms  $C_1$  and  $C_2$  are in the cone of semi-angle  $55^\circ$ ). In the *n*-compounds higher than the ethyl member of the series, there is a possibility

FIG. 1.

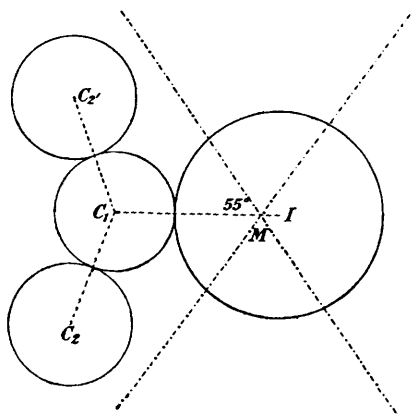
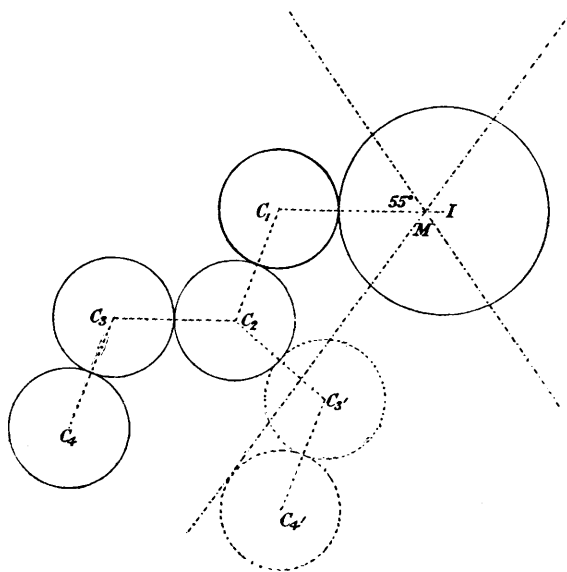


FIG. 2.



that part of the chain will not lie within the cones. An *n*-butyl iodide molecule is shown in Fig. 2, an alternative position of the chain being indicated by the broken-line circles. Since, however, the distances to the remoter carbon atoms (*e.g.*,  $C_3$  and  $C_4$ ) in this case are greater, the effect in these atoms will be smaller and will not necessarily be produced directly by the main dipole, but again in these higher molecules the main opposing moment will be located on the halogen atom.

The difference in polarisability and size of the halogen atoms would cause the induced moments in the two series to differ, and reference to the figures shows that the extent to which the halogen atom lies outside the surfaces of the cones, in which the induced moments are positive, will vary with any possible alteration in the position of the primary dipoles. The effects produced by lengthening the chain would probably differ in the two series, for the reflex polarisation induced in part of the halogen atom would be very sensitive to the factors mentioned above, since this part of the molecule is in the region where the field is strongest.

The greater increase in moment of the iodides over that of the bromides has been ascribed to a redistribution of the charges (Smyth and McAlpine, *J. Chem. Physics*, 1934, 2, 499) or to a modification of the lines of force on the parts of the halogen atom subtending an angle greater than  $55^\circ$  with the dipole (Groves and Sugden, *loc. cit.*). On this basis the difference of the radical effect shown in the series of alkyl halides can be explained, and probably accounts for the fact that the experimental figures for the vapours of the ethyl and propyl compounds exceed those calculated from the moment of the methyl compound by Groves and Sugden (J., 1937, 1992) by means of an extension of Frank's theory (*loc. cit.*). Allowance for the radical and the solvent effect and for the interactions between these

induced moments cannot be adequately made, and any quantitative calculations from solution results are necessarily somewhat uncertain.

It is of interest to examine the differences in moment between successive members of the iodide, bromide, and cyanide series as found from measurements on the vapours and solutions. They are given below.

Difference in $\mu$ of compounds.	Iodide.		Bromide.		Cyanide.	
	Vapour.	Soln.	Vapour.	Soln.	Vapour.	Soln.
$C_2H_5 - CH_3$ .....	0.23 <sup>3</sup>	0.37 <sup>11, 10</sup>	0.21 <sup>3</sup>	—	0.10 <sup>3</sup>	0.13 <sup>12</sup>
$n-C_3H_7 - C_2H_5$ .....	0.14 <sup>3</sup>	0.06 <sup>11, 10</sup>	0.12 <sup>3</sup>	0.04 <sup>11</sup>	0.01 <sup>3</sup>	0.00 <sup>12</sup>
$n-C_4H_9 - n-C_3H_7$ .....	0.07 <sup>3</sup>	0.04 <sup>11</sup>	0.02 <sup>2</sup>	0.00 <sup>11</sup>	0.04 <sup>3</sup>	0.00 <sup>12</sup>
$n-C_5H_{11} - n-C_4H_9$ .....	—	0.00 <sup>11</sup>	—	0.02 <sup>11</sup>	—	—

For references see preceding table; all values of  $\mu$  from solutions relate to solutions in benzene at 20°.

<sup>12</sup> Cowley and Partington, J., 1935, 604.

(In the results obtained from solutions no correction for atomic polarisation has been made: this will have a negligible effect on the differences given above.)

These figures show that the respective maximum moments in these  $n$ -series are attained more quickly in the values determined in solution than in those found for the vapours, and that on the whole the variations between the moments of successive members of a series are smaller in the former measurements. The modification produced by the surrounding solvent molecules in this case apparently causes the difference. The change in molecular arrangement between a polar molecule dissolved in a non-polar solvent and another higher molecule of the same series in the same solvent would arise from the displacement of some solvent molecules by the hydrocarbon chain, and the variation of moment observed in the series would be dependent on the differences between the displaced molecules of solvent and the radical. Lengthening of the chain makes the shape of the molecule more elongated, and the solvent effect would increase somewhat as the series is ascended (cf. Higasi, *loc. cit.*). Since in these halides the radical and the solvent effect are acting in opposition, the increase in the latter in passing from the lower to the higher members of the series would reduced the change of moment due to the radical effect alone. The variation in moment in the vapours is due to the radical effect only, and hence the changes in moment between successive members of these series should be smaller in solution than in the vapour state, a result confirmed by experiment.

The moments measured in solution clearly show the difference between the radical and the solvent effect. The second influence is considerably greater in the  $n$ -alkyl cyanides than in the iodides and bromides, the reduction in the last two series being approximately the same, since the solvent effect is largely dependent on the orientation polarisation. The actual variation between the methyl and the  $n$ -butyl member of the iodide series exceeds that between the corresponding cyanides, and the percentage increase is greater in the former. In this connexion it must be remembered that the principal dipole in the cyanides is situated at approximately 0.6 A. further from the growing hydrocarbon chain (Part XIII, *loc. cit.*, p. 609), but the difference in inducing dipole in the two series more than outweighs this greater distance. The differences between the moments found for acetonitrile and methyl iodide in the vapour state and in benzene solution are 0.5 and 0.2, whereas the excesses of the limiting values of the  $n$ -series over those of the methyl compounds in solution are 0.1 and 0.5 respectively. These facts can be most easily explained by the greater polarisability of the iodine atom than that of the cyano-group.

It seems that the chief factors governing the inductive effect in the polar molecules of these series are the characteristics of the polar group. The polarisability and the size of the group are important properties and, in the compounds examined, the larger polarisability and the greater size of the group both tend to increase the moment of the molecule as the series is ascended.

#### EXPERIMENTAL.

*Measurement of Dielectric Constants and Densities.*—The solutions of the substances were prepared in the glass vessels, and the dielectric constants and densities were measured in the glass dielectric cell containing platinum plates and the pyknometers, described in Part XX (J., 1936, 1184). The electrical circuit was that of Parts XII and XIII (J., 1935, 602).

*Preparation of Materials.*—Benzene, used as solvent, was Kahlbaum's "thiophen-free" material dried over sodium and fractionated.

*Iodides.* Methyl, ethyl, isopropyl and *n*-butyl iodides were from Kahlbaum, and *n*-propyl and *n*-amyl iodides were from B.D.H. and Fraenkel and Landau, respectively. The purest grades in each case were used and were carefully purified. In the case of the lower members of the series, the specimen was shaken with dilute sodium carbonate solution, washed repeatedly with water, and dried over anhydrous calcium chloride. It was left over phosphoric oxide for a day and then fractionated twice through a long column. The treatment of the higher members of the series, which were originally slightly coloured, was similar except that the compound was shaken with mercury and fractionated under reduced pressure (cf. Brown and Acree, *J. Amer. Chem. Soc.*, 1916, **38**, 2149; Smyth and McAlpine, *J. Chem. Physics*, 1934, **2**, 499). The physical constants of the materials used are given below.

Iodide.	B. p.	$D_4^{20}$ .	$n_D^{20}$ .	$[R_L]_D^{20}$ .
Methyl .....	42.1°/746 mm.	2.2781	1.5316	19.29
Ethyl .....	71.6/744	1.9358	1.5136	24.24
<i>n</i> -Propyl .....	102.3/763	1.7390	1.5041	28.95
<i>iso</i> Propyl .....	89.3/757	1.7037	1.4988	29.31
<i>n</i> -Butyl .....	129.2/749	1.6156	1.4998	33.49
<i>n</i> -Amyl .....	153.5—154.0/747	1.5176	1.4966	38.18

*Bromides.* The sources of the materials were: *n*-propyl and *n*-butyl from Kahlbaum, isopropyl from Fraenkel and Landau, and *n*-amyl bromide from B.D.H. The method of purification of these compounds was that used for the iodides, and their physical constants are given below.

Bromide.	B. p.	$D_4^{20}$ .	$n_D^{20}$ .	$[R_L]_D^{20}$ .
<i>n</i> -Propyl .....	71.0°/769 mm.	1.3536	1.4339	23.65
<i>iso</i> Propyl .....	59.1/762	1.3193	1.4255	23.86
<i>n</i> -Butyl .....	101.2/754	1.2758	1.4400	28.30
<i>n</i> -Amyl .....	126.5—127.0/759	1.2177	1.4448	33.00

*Results.*—The symbols have their usual significance and the values of the moments are calculated from the differences ( $P_{2\infty} - P_E$ ). All the following results relate to solutions of the various halides in benzene at 20°.

Compound.	$P_{2\infty}$ , c.c.	$P_E$ , c.c.	$\mu$ .	Compound.	$P_{2\infty}$ , c.c.	$P_E$ , c.c.	$\mu$ .
CH <sub>3</sub> I .....	61.5	19.3	1.41	<i>n</i> -C <sub>3</sub> H <sub>7</sub> I .....	109.7	38.2	1.88
C <sub>2</sub> H <sub>5</sub> I .....	90.8	24.2	1.78	<i>n</i> -C <sub>3</sub> H <sub>7</sub> Br .....	102.8	23.6	1.93
<i>n</i> -C <sub>3</sub> H <sub>7</sub> I .....	101.0	28.9	1.84	<i>iso</i> -C <sub>3</sub> H <sub>7</sub> Br .....	112.2	23.9	2.04
<i>iso</i> -C <sub>3</sub> H <sub>7</sub> I .....	109.5	29.3	1.95	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br .....	107.4	28.3	1.93
<i>n</i> -C <sub>4</sub> H <sub>9</sub> I .....	105.0	33.5	1.88	<i>n</i> -C <sub>5</sub> H <sub>11</sub> Br .....	113.7	33.0	1.95

$f_2$ .	$\epsilon$ .	$D_4^{20}$ .	$P_{12}$ , c.c.	$P_2$ , c.c.	$f_2$ .	$\epsilon$ .	$D_4^{20}$ .	$P_{12}$ , c.c.	$P_2$ , c.c.
Methyl iodide.					Ethyl iodide.				
0.000000	2.281	0.8790	26.58	—	0.000000	2.280	0.8789	26.57	—
0.010582	2.313	0.8895	26.95	61.9	0.010774	2.329	0.8892	27.25	89.6
0.022089	2.347	0.9007	27.35	61.3	0.020973	2.375	0.8990	27.87	88.5
0.032222	2.378	0.9106	27.70	61.3	0.031101	2.420	0.9087	28.46	87.4
0.041910	2.407	0.9201	28.02	61.1	0.040975	2.464	0.9180	29.04	86.8
$P_{2\infty} = 61.5$ c.c.; $P_E = 19.3$ c.c.; $P_{2\infty} - P_E = 42.2$ c.c.; $\mu = 1.41$ .					$P_{2\infty} = 90.8$ c.c.; $P_E = 24.2$ c.c.; $P_{2\infty} - P_E = 66.6$ c.c.; $\mu = 1.78$ .				
<i>n</i> -Propyl iodide.					<i>iso</i> Propyl iodide.				
0.000000	2.279	0.8788	26.56	—	0.000000	2.279	0.8788	26.56	—
0.010836	2.332	0.8889	27.35	99.8	0.010971	2.339	0.8888	27.46	108.5
0.021717	2.384	0.8990	28.12	98.5	0.020938	2.395	0.8979	28.28	109.0
0.031634	2.431	0.9082	28.80	97.4	0.031272	2.453	0.9073	29.11	108.3
0.042074	2.481	0.9178	29.51	96.6	0.041500	2.510	0.9166	29.91	107.4
$P_{2\infty} = 101.0$ c.c.; $P_E = 28.9$ c.c.; $P_{2\infty} - P_E = 72.1$ c.c.; $\mu = 1.84$ .					$P_{2\infty} = 109.5$ c.c.; $P_E = 29.3$ c.c.; $P_{2\infty} - P_E = 80.2$ c.c.; $\mu = 1.95$ .				
<i>n</i> -Butyl iodide.					<i>n</i> -Amyl iodide.				
0.000000	2.280	0.8789	26.57	—	0.000000	2.281	0.8792	26.57	—
0.011254	2.335	0.8895	27.44	104.2	0.011501	2.337	0.8897	27.53	109.7
0.022352	2.389	0.8997	28.30	104.1	0.023018	2.393	0.9000	28.48	109.6
0.032599	2.439	0.9092	29.07	103.2	0.044813	2.503	0.9194	30.29	109.6
0.044458	2.497	0.9198	29.96	102.8					
$P_{2\infty} = 105.0$ c.c.; $P_E = 33.5$ c.c.; $P_{2\infty} - P_E = 71.5$ c.c.; $\mu = 1.88$ .					$P_{2\infty} = 109.7$ c.c.; $P_E = 38.2$ c.c.; $P_{2\infty} - P_E = 71.5$ c.c.; $\mu = 1.88$ .				

$f_2$	$\epsilon$	$D_4^{20}$	$P_{12}$ , c.c.	$P_2$ , c.c.	$f_2$	$\epsilon$	$D_4^{20}$	$P_{12}$ , c.c.	$P_2$ , c.c.
<i>n</i> -Propyl bromide.					<i>iso</i> Propyl bromide.				
0-000000	2.277	0.8792	26.52	—	0-000000	2.279	0.8788	26.56	—
0-010335	2.331	0.8842	27.30	102.2	0-010693	2.343	0.8836	27.49	111.9
0-020348	2.383	0.8890	28.04	101.3	0-021383	2.407	0.8886	28.39	112.4
0-030390	2.436	0.8937	28.78	100.8	0-031177	2.468	0.8932	29.23	112.4
0-040377	2.487	0.8984	29.47	99.7	0-041754	2.531	0.8981	30.08	110.9
$P_{2\infty} = 102.8$ c.c.; $P_E = 23.6$ c.c.; $P_{2\infty} - P_E = 79.2$ c.c.; $\mu = 1.93$ .					$P_{2\infty} = 112.2$ c.c.; $P_E = 23.9$ c.c.; $P_{2\infty} - P_E = 88.3$ c.c.; $\mu = 2.04$ .				
<i>n</i> -Butyl bromide.					<i>n</i> -Amyl bromide.				
0-000000	2.280	0.8789	26.57	—	0-000000	2.281	0.8790	26.58	—
0-011203	2.338	0.8843	27.47	106.8	0-012131	2.346	0.8845	27.66	113.6
0-021696	2.392	0.8892	28.29	105.8	0-024399	2.411	0.8898	28.71	114.1
0-032839	2.451	0.8944	29.16	105.6	0-035077	2.468	0.8945	29.62	113.3
0-043382	2.504	0.8992	29.94	105.6					
$P_{2\infty} = 107.4$ c.c.; $P_E = 28.3$ c.c.; $P_{2\infty} - P_E = 79.1$ c.c.; $\mu = 1.93$ .					$P_{2\infty} = 113.7$ c.c.; $P_E = 33.0$ c.c.; $P_{2\infty} - P_E = 80.7$ c.c.; $\mu = 1.95$ .				

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