[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. IX. THE ELECTRIC MOMENTS OF THE ALKYL HALIDES AND HALOGENATED METHANES

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The electric moments of butyl chloride, bromide and iodide and heptyl bromide have been determined with a view to ascertaining the effect of the length of the hydrocarbon chain upon the moment of the molecule and to observing whether the variation from chloride to bromide to iodide is the same in large molecules as in small. At the same time it is possible to study the dependence of the mutual orienting effects of the molecules upon molecular size. The previously unmeasured bromine and iodine substituted methanes have been investigated in order to throw further light upon the mutual repulsion of atoms or groups in the same molecule.

Method of Measurement

The methods of measurement and calculation used in the present work have been described in the first two papers of the series[1] on dielectric polarization, and a subsequently developed cell with four different fixed capacities, which was used in some of the measurements, has been described in a later paper. The dielectric constants[2] were measured with the capacity bridge originally used, a frequency of 5×10^5 cycles, corresponding to a wave length of 600 meters, being employed as before. The errors were similar to those described in the last mentioned paper, dielectric constant values below 5 having a probable error of 0.2% and those above 5 having a probable error of 0.5%. The relative error within a given series of measurements was much smaller in both cases. Since the same type of pycnometer was used as in the earlier work, the probable error in the densities was the same, being about 0.07% in the low temperature determinations and not more than 0.03% in the measurements above 0°.

Preparation of Materials

Heptane.—Pure normal heptane was obtained from the Ethyl Gasoline Corporation. As the boiling point, refractive index, and dielectric constant of a sample were not appreciably different after washing with sulfuric acid, followed by sodium carbonate solution and water, drying over calcium chloride and finally distilling over sodium, the heptane was used without purification.

Benzene.—Merck's C. P. benzene was washed three times with concentrated sulfuric acid, followed by dilute sodium hydroxide solution and water, dried over calcium chloride and crystallized twice; m. p. 5.47°. It was then allowed to stand over sodium and distilled from it; b. p. 80.1°; n^{20}_{D} 1.50135.

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[1] Smyth, Morgan and Boyce, THIS JOURNAL, **50**, 1536 (1928); Smyth and Morgan, *ibid.*, **50**, 1547 (1928).

[2] Smyth and Stoops, *ibid.*, **51**, 3312 (1929).

Butyl Chloride.—*n*-Butyl chloride obtained from the Eastman Kodak Company was refluxed gently with concentrated sulfuric acid, distilled, washed with water, dried over calcium chloride and distilled; b. p. 77.5°; n_D^{20} 1.40148.

Butyl Bromide.—*n*-Butyl bromide obtained from the Eastman Kodak Company was washed with cold concentrated sulfuric acid, then with sodium carbonate solution. dried over calcium chloride and distilled; b. p. 101.0°; n_D^{20} 1.43985.

Butyl Iodide.—*n*-Butyl iodide obtained from the Eastman Kodak Company was shaken once with ice-cold concentrated sulfuric acid and eight times with dilute sodium hydroxide, washed with water, dried over calcium chloride and distilled at reduced pressure; d_4^{20} 1.616.

Heptyl Bromide.—*n*-Heptyl bromide obtained from the Eastman Kodak Company was washed with cold concentrated sulfuric acid, sodium carbonate solution, and water, dried over calcium chloride and distilled at reduced pressure. A fraction boiling within a 0.2° interval was taken; d_4^{16} 1.144; n_D^{20} 1.44972. "International Critical Tables" give d_4^{16} 1.133, in good agreement with the value d_4^{16} 1.134 obtained for the unpurified material. The purified material was treated again in the same way and the product obtained had the same density as before, d_4^{16} 1.144. This was, therefore, concluded to be the correct value for the pure material.

Methylene Bromide.—Material obtained from the Eastman Kodak Company was washed with dilute sodium carbonate solution and water, dried over calcium chloride and distilled at reduced pressure; d_4^{20} 2.4921; n_D^{20} 1.53559.

Methylene Iodide.—Kahlbaum's methylene iodide was washed with dilute sodium hydroxide solution and water, dried over calcium chloride and distilled at reduced pressure; d_4^{25} 3.3104.

Bromoform.—Material obtained from the Eastman Kodak Company was washed with concentrated sulfuric acid, followed by dilute sodium hydroxide solution and water, dried over anhydrous potassium carbonate and distilled at reduced pressure; d_4^{20} 2.889.

Iodoform.—Kahlbaum's iodoform, which melted at 119.0°, was used without purification.

Experimental Results

The densities, which showed but slight departure from a linear dependence upon temperature, were determined at approximately 25° intervals and the dielectric constants at 15° intervals. The majority of the densities, d, and dielectric constants, ϵ, in Table I were obtained at 10° intervals by graphical interpolation, and the polarizations, P_2, of the polar components were calculated from them by means of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{c_1M_1 + c_2M_2}{d} \text{ and } P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2, M_1 and M_2, and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the individual components. The solutions of methylene bromide, methylene iodide and bromoform were measured at the same two or three fixed temperatures and, therefore, require no interpolation to make them comparable.

Discussion of Results

When the P_2–c_2 curves are extrapolated to $c_2 = 0$, the values of P obtained, designated as P_∞, give a straight line when multiplied by T and

Table I

Dielectric Constants and Densities of Solutions and Polarizations of Polar Components

Heptane–Butyl Chloride

Mole fr. of C_4H_9Cl = t, °C.	0	0.0242	0.0653	0.0889	0.1562	0.2191	0.2617	0.5619	0.8623	1.000
					ϵ					
−90	2.083	2.219	2.440	2.567	2.954	3.359	3.659	6.302	10.16	12.24
−70	2.055	2.175	2.376	2.485	2.837	3.184	3.453	5.792	9.228	10.98
−50	2.027	2.135	2.315	2.413	2.732	3.038	3.266	5.322	8.465	9.940
−30	1.999	2.096	2.259	2.347	2.635	2.904	3.122	4.924	7.743	9.073
−10	1.972	2.058	2.206	2.285	2.547	2.792	2.986	4.586	7.077	8.320
10	1.944	2.022	2.157	2.227	2.466	2.688	2.861	4.285	6.518	7.663
30	1.916	1.985	2.108	2.174	2.393	2.591	2.745	4.025	6.062	7.090
50	1.888	1.950	2.059	2.122	2.319	2.494	2.642	3.792	5.676	6.558
70	1.858	1.913	2.007	2.070	2.248	2.410	2.543	3.570	5.250	6.045
					d					
−90	0.7752	0.7778	0.7836	0.7864	0.7993	0.8025	0.8205	0.8820	0.9618	1.0050
−70	.7587	.7613	.7678	.7700	.7826	.7872	.8029	.8630	.9400	.9794
−50	.7420	.7448	.7513	.7539	.7659	.7718	.7853	.8438	.9191	.9580
−30	.7252	.7280	.7347	.7375	.7488	.7561	.7673	.8247	.8980	.9375
−10	.7088	.7114	.7181	.7209	.7317	.7402	.7490	.8057	.8769	.9157
10	.6921	.6947	.7011	.7043	.7148	.7243	.7313	.7867	.8559	.8950
30	.6755	.6775	.6843	.6878	.6975	.7070	.7130	.7675	.8355	.8736
50	.6576	.6606	.6668	.6708	.6790	.6889	.6949	.7475	.8148	.8513
70	.6392	.6428	.6486	.6528	.6603	.6708	.6759	.7271	.7925	.8275
					$P_2(C_4H_9Cl)$					
−90	157.7	153.2	141.2	137.1	127.5	124.5	118.1	96.76	79.52	72.68
−70	146.5	143.6	133.7	129.4	122.0	118.1	113.3	94.82	79.12	70.98
−50	136.5	134.6	126.3	122.5	116.8	112.7	108.4	92.50	78.72	72.32
−30	128.5	126.5	120.2	116.7	112.1	107.9	105.2	90.34	78.12	71.96
−10	121.7	120.7	114.6	111.3	107.9	103.9	102.0	88.30	77.33	71.67
10	116.1	115.0	110.1	106.3	103.8	101.1	98.62	86.32	76.60	71.29
30	111.3	109.6	105.4	102.4	100.8	97.73	95.64	84.57	76.02	70.96
50	106.6	101.5	99.10	97.44	97.01	94.35	92.75	82.88	75.58	70.59
70	102.4	94.48	92.42	93.45	93.61	90.02	90.13	81.04	74.70	70.12

Heptane–Butyl Bromide

Mole fr. of C_4H_9Br = t, °C.	0.0456	0.0930	0.1409	0.2579	0.4154	0.5959	0.8413	1.000
					ϵ			
−90	2.349	2.588	2.854	3.548	4.687	6.280	8.970	11.08
−70	2.289	2.513	2.751	3.379	4.389	5.810	8.220	10.14
−50	2.239	2.441	2.653	3.226	4.119	5.405	7.565	9.258
−30	2.193	2.373	2.568	3.086	3.886	5.044	6.984	8.520
−10	2.149	2.310	2.491	2.957	3.679	4.732	6.474	7.880
10	2.107	2.251	2.417	2.843	3.499	4.454	6.039	7.315
30	2.064	2.197	2.346	2.737	3.336	4.203	5.640	6.799
50	2.022	2.146	2.279	2.640	3.187	3.966	5.290	6.345
70	1.979	2.097	2.217	2.547	3.050	3.761	4.969	5.930
90	1.938	2.049	2.158	2.455	2.914	3.577	4.662	5.535

TABLE I (*Continued*)

Mole fr. of C_4H_9Br =	0.0456	0.0930	0.1409	0.2579	0.4154	0.5959	0.8413	1.000
t, °C.	d							
−90	0.7960	0.8195	0.8432	0.9072	0.9986	1.1152	1.2967	1.4310
−70	.7783	.8022	.8260	.8884	.9781	1.0927	1.2708	1.4040
−50	.7616	.7849	.8087	.8694	.9575	1.0698	1.2449	1.3735
−30	.7456	.7679	.7913	.8505	.9372	1.0472	1.2188	1.3450
−10	.7295	.7510	.7740	.8318	.9170	1.0245	1.1926	1.3170
10	.7125	.7337	.7560	.8127	.8964	1.0017	1.1663	1.2880
30	.6949	.7159	.7375	.7931	.8750	.9780	1.1397	1.2592
50	.6775	.6977	.7183	.7723	.8528	.9542	1.1129	1.2300
70	.6589	.6786	.6993	.7514	.8307	.9298	1.0853	1.2005
90	.6397	.6590	.6803	.7306	.8073	.9043	1.0562	1.1695

	P_∞	$P_2(C_4H_9Br)$							
−90	157.8	153.2	136.3	129.7	118.6	105.2	94.2	80.9	73.8
−70	146.5	144.4	130.9	124.2	114.7	102.4	92.2	80.2	73.5
−50	138.6	136.2	124.7	118.5	111.0	99.53	90.6	79.4	73.2
−30	131.7	129.7	118.9	113.9	107.5	96.88	88.9	78.7	72.8
−10	124.2	124.1	113.4	110.6	104.0	94.35	87.0	77.9	72.4
10	118.6	119.3	109.2	106.1	100.9	92.18	86.0	77.2	72.1
30	113.4	115.1	105.7	102.1	98.02	90.28	84.7	76.5	71.7
50	109.2	109.3	101.9	98.94	95.85	88.46	83.2	75.9	71.3
70	106.2	104.5	99.57	95.81	93.56	86.77	82.0	75.2	70.9
90	103.0	102.9	98.34	93.84	91.21	85.13	81.1	74.6	70.5

Heptane–Butyl Iodide

Mole fr. of C_4H_9I =	0.0386	0.0831	0.1698	0.2943	0.5462	0.8090	1.000
t, °C.	ε						
−80	2.247	2.450	2.862	3.529	5.044	7.085	8.890
−60	2.201	2.386	2.760	3.351	4.729	6.543	8.180
−40	2.157	2.325	2.668	3.195	4.445	6.082	7.534
−20	2.115	2.271	2.585	3.063	4.188	5.673	7.002
0	2.076	2.219	2.506	2.939	3.971	5.304	6.542
20	2.038	2.169	2.432	2.820	3.783	5.005	6.117
40	2.001	2.119	2.360	2.718	3.614	4.755	5.737
60	1.964	2.073	2.295	2.630	3.465	4.507	5.421
80	1.925	2.027	2.229	2.556	3.318	4.254	5.108

	d						
−80	0.7993	0.8352	0.9082	1.0221	1.2619	1.5497	1.7842
−60	.7818	.8172	.8892	.9993	1.2361	1.5187	1.7505
−40	.7644	.7992	.8702	.9771	1.2109	1.4883	1.7168
−20	.7470	.7810	.8509	.9549	1.1854	1.4582	1.6832
0	.7296	.7628	.8314	.9329	1.1596	1.4278	1.6495
20	.7118	.7446	.8112	.9111	1.1339	1.3976	1.6158
40	.6940	.7263	.7912	.8900	1.1079	1.3674	1.5824
60	.6757	.7075	.7711	.8675	1.0816	1.3369	1.5485
80	.6571	.6885	.7505	.8449	1.0551	1.3063	1.5144

Table I (*Continued*)

t, °C.	Mole fr. of C_4H_9I = P_∞	0.0386	0.0831	0.1698	0.2943	0.5462	0.8090	1.000
		$P_2(C_4H_9I)$						
−80	136.6	137.6	124.6	116.4	107.6	93.1	81.7	74.6
−60	127.1	123.0	119.0	111.9	104.0	91.2	80.6	74.1
−40	120.9	116.3	114.0	108.2	100.8	89.1	79.6	73.5
−20	115.4	111.2	110.1	104.8	98.2	87.4	78.6	72.9
0	111.1	107.1	106.3	101.6	95.5	85.9	77.5	72.4
20	107.6	104.4	103.1	98.9	92.7	84.6	76.8	71.8
40	103.0	100.3	99.0	95.8	90.2	83.4	76.2	71.1
60	98.4	96.7	95.9	93.2	88.7	82.5	75.5	70.8
80	95.6	92.9	93.1	90.5	87.9	81.4	74.5	70.2

Heptane–Heptyl Bromide

t, °C.	Mole fr. of $C_7H_{15}Br$ =	0.0488	0.0889	0.1626	0.3330	0.5327	1.000
		ϵ					
−70		2.297	2.491	2.862	3.704	4.809	7.385
−50		2.247	2.422	2.755	3.515	4.498	6.875
−30		2.198	2.356	2.656	3.348	4.214	6.392
−10		2.152	2.294	2.567	3.200	3.969	5.957
10		2.109	2.237	2.489	3.067	3.767	5.582
30		2.067	2.184	2.417	2.950	3.595	5.255
50		2.024	2.133	2.349	2.840	3.437	4.970
70		1.980	2.083	2.278	2.734	3.284	4.711
90		1.936	2.033	2.210	2.632	3.134	4.476
		d					
−70		0.7831	0.8039	0.8428	0.9348	1.0243	1.2370
−50		.7667	.7871	.8249	.9166	1.0044	1.2160
−30		.7502	.7702	.8075	.8981	.9849	1.1944
−10		.7333	.7533	.7895	.8793	.9657	1.1725
10		.7165	.7359	.7712	.8606	.9456	1.1507
30		.6988	.7184	.7534	.8420	.9255	1.1285
50		.6810	.7004	.7354	.8227	.9056	1.1065
70		.6632	.6821	.7171	.8032	.8858	1.0847
90		.6442	.6633	.6978	.7836	.8648	1.0622
	P_∞	$P_2(C_7H_{15}Br)$					
−70	...	152.3	146.1	139.0	123.8	115.7	98.5
−50	149.6	145.3	139.7	133.6	119.9	112.8	97.5
−30	141.6	138.4	133.7	128.4	116.5	109.9	96.3
−10	134.6	132.7	128.0	124.0	113.4	107.1	95.1
10	128.3	127.7	123.3	120.5	110.6	105.0	94.0
30	125.5	124.4	119.6	117.3	108.2	103.4	93.0
50	...	118.2	115.2	113.9	105.7	101.6	92.1
70	...	112.1	111.6	109.9	103.3	99.7	91.3
90	...	108.4	108.8	106.9	101.0	97.0	90.5

Benzene–Methylene Bromide

t, °C.	Mole fr. of CH_2Br_2 =	0.0496	0.0947	0.2038	0.5618	0.8114	1.000
		ϵ					
10		2.460	2.596	2.957	4.420	5.884	7.772
40		2.383	2.502	2.815	4.088	5.335	6.678
70		2.293	2.401	2.676	3.841	4.848	

TABLE I (*Continued*)

t, °C.	Mole fr. of CH_2Br_2 =	0.0496	0.0947	0.2038	0.5618	0.8114	1.000
		d					
10		0.9530	1.0117	1.1607	1.7015	2.1418	2.5438
40		.9192	.9759	1.1202	1.6463	2.0734	2.4442
70		.8844	.9395	1.0795	1.5984	2.0042	
	P_∞	$P_2(CH_2Br_2)$					
10	64.4	62.4	60.8	58.6	52.7	49.3	47.1
40	62.1	60.1	58.5	56.5	51.4	48.5	46.5
70	59.0	56.9	56.5	54.7	50.6	47.6	

Benzene–Methylene Iodide

t, °C.	Mole fr. of CH_2I_2 =	0.0268	0.0449	0.0636	0.1337	0.1943	1.000
		ϵ					
25		2.341	2.384	2.425	2.592	2.734	5.316
50		2.282	2.322	2.359	2.524	2.646	
		d					
25		0.9330	0.9721	1.0137	1.1728	1.3065	3.3105
50		.9045	.9432	0.9832	1.1351	1.2706	
	P_∞	$P_2(CH_2I_2)$					
25	56.3	54.4	56.2	55.7	55.1	56.1	47.74
50	54.6	52.2	54.2	54.2	55.6	53.0	

Benzene–Bromoform

t, °C.	Mole fr. of $CHBr_3$ =	0.0409	0.0573	0.0718	0.0929	0.2340	0.5047	0.7358	1.000
		ϵ							
10		2.308	2.411	2.438	2.477	2.726	3.232	3.726	4.404
40		2.315	2.340	2.365	2.399	2.623	3.075	3.506	4.084
70		2.234	2.258	2.284	2.313	2.522	2.924	3.315	3.816
		d							
10		0.9711	1.0045	1.0330	1.0751	1.3591	1.9068	2.3818	2.9189
40		.9366	.9689	.9969	1.0380	1.3144	1.8487	2.3134	2.8383
70		.8997	.9333	.9603	1.0004	1.2692	1.7898	2.2446	2.7597
	P_∞	$P_2(CHBr_3)$							
10	51.0	48.5	50.8	50.1	50.4	49.1	47.5	46.6	46.05
40	49.9	48.6	49.1	49.2	49.1	48.0	46.6	45.6	45.17
70	48.5	45.0	47.3	46.8	46.8	46.9	45.6	44.9	44.37

Benzene–Iodoform

Mole fr. of CHI_3 =	ϵ							
t, °C.	0	0.0063	0.0222	0.0352	0	0.0063	0.0222	0.0352
10	2.315	2.323	2.361	2.387	0.8896	0.9096	0.9663	1.0100
20	2.295	2.307	2.341	2.366	.8786	.8991	.9550	.9989
30	2.274	2.291	2.321	2.345	.8682	.8880	.9436	.9869
40	2.253	2.272	2.298	2.322	.8574	.8768	.9322	.9750
50	2.232	2.252	2.275	2.299	.8466	.8657	.9210	.9631
60	2.210	2.230	2.250	2.274	.8357	.8546	.9096	.9512
70	2.188	2.206	2.226	2.248	.8246	.8434	.8979	.9392

TABLE I (*Concluded*)

	Mole fr. of CHI_3 =	0.0063	0.0222	0.0352
t, °C.	P_∞	$P_2(CHI_3)$		
10	...	56.5	59.6	53.5
20	61.5	63.6	60.1	59.5
30	...	66.8	61.0	60.1
40	...	73.2	60.1	59.5
50	59.6	87.6	58.8	59.0
60	...	87.6	57.0	58.1
70	...	84.4	55.7	56.4

plotted against T (Fig. 1), as required by the Debye equation: $P = a + b/T$, in which $a = P_E + P_A$, the sum of the electronic polarization, P_E, and the atomic, P_A, and $b = 4\pi N\mu^2/9k$, N being the Avogadro number, 6.061×10^{23}, μ, the electric moment, and k, the molecular gas constant, 1.372×10^{-16}. When the equation is written in the form $(P_\infty - a)\ T = b$, it is evident that it can be tested by the constancy of $(P_\infty - a)T$, the values of which are given in Table II.

TABLE II

VALUES OF $(P_\infty - a)T$

T, °A.	$(P_\infty - a)T$			
	C_4H_9Cl	C_4H_9Br	C_4H_9I	$C_7H_{15}Br$
183	21810	20290	...	...
193	21920	20270	15900	...
203	21920	20220	16180	...
213	21940	20380	15530	20510
223	21850	20450	15500	20590
233	21800	20130	15540	20780
243	21870	20610	15650	20630
253	21960	20420	15480	20440
263	21880	20330	15520	20490
273	22170	20280	15530	20310
283	21960	20280	15730	20260
293	21920	20330	15650	20690
303	22060	20150	15630	20850
313	21910	20410	15270	20630
323	22000	20120	14660	...
333	21910	20280	15060	...
343	21920	20340	14750	...
353	...	20400	14620	...

In the case of butyl iodide, a small decrease in the values of $(P_\infty - a)T$ accompanies rising temperature at the higher temperatures, probably because of slight decomposition of the substance. Below 30° for the butyl iodide and over the entire temperature range within which the other substances are liquid, the values of $(P_\infty - a)T$ are constant, giving further proof, if further proof is needed, of the applicability of the Debye equation to polar liquids highly diluted by non-polar.

The best values of a and b were obtained from the curves in Fig. 1 and the electric moments were then calculated from b. The values of P_E at infinite wave length were calculated from the molar refractions given in Landolt–Börnstein (5th ed.) by means of the equation, $P_E = [1 - \lambda_0^2/\lambda^2][(n^2 - 1)M/(n^2 + 2)d]$, in which n is the refractive index for light of wave length λ, λ_0 is the wave length corresponding to a characteristic vibration frequency in the ultraviolet region, and d is the density. As dispersion data were not available for heptyl bromide, the value of P_E at infinite wave length was estimated by subtracting 1.0, a difference analogous to those found for the other halides, from 42.20, the molar refraction for the sodium D-line. The result, 41.2, should be within 0.3 of the correct value. The atomic polarization, P_A, has been obtained by subtracting P_E from a. The results are shown in Table III.

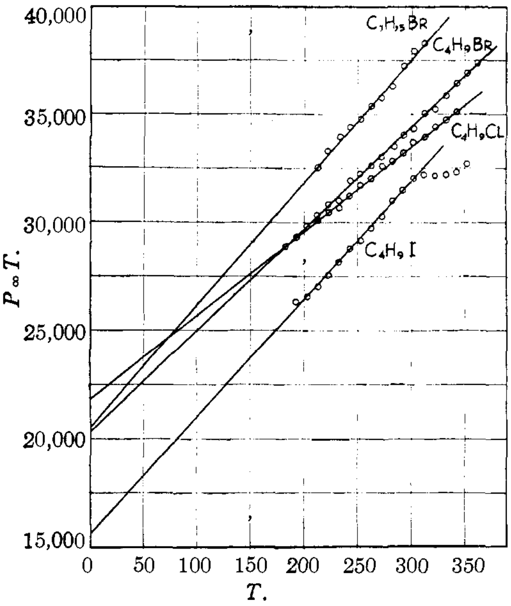

Fig. 1.—Variation of $P_\infty T$ with T.

TABLE III

VALUES OF FUNDAMENTAL CONSTANTS

	a	P_E	P_A	b	$\mu \times 10^{18}$
C_4H_9Cl	38.5	24.9	13.6	21920	1.88
C_4H_9Br	46.9	27.6	19.3	20300	1.81
C_4H_9I	54.2	32.3	21.9	15530	1.59
$C_7H_{15}Br$	56.7	41.2	15.5	20610	1.83

The values of P_A are surprisingly high and may be considerably in error, as a small change in the curve has a large effect upon a and, consequently, an even greater effect upon the difference, $a - P_E$, but the accuracy of the curves is such as to render a small P_A for these substances highly improbable. Moreover, a value of 12.3 has been determined with some accuracy for ethyl iodide[2] and a rough value of 11 has been found for ethyl bromide.[1] Preliminary measurements carried out in this Laboratory upon heptyl bromide in the solid state indicate a value for P_A of the same order of magnitude as that here found. In the butyl halides, the values increase from chloride to bromide to iodide, but, in view of the uncertainty of the values, great significance cannot be attached to this.

The substituted methanes were measured over too limited a range of temperature to permit of an accurate determination of a and b by plotting P_∞ against $1/T$. As is very commonly done, a was assumed equal to MR_D, the molar refraction for the D-sodium line, and the electric moment was calculated from $P_\infty - MR_D$. The values of MR_D for methylene bromide and bromoform were taken directly from Landolt–Börnstein (5th ed.), while those for methylene iodide and iodoform were calculated as the sum of the atomic refractions, the accuracy of the values thus obtained being quite sufficient for the purpose. Values of the electric moments calculated at different temperatures showed very close agreement except in the case of iodoform, the results for which are less accurate than the others because of its low solubility and decomposition in solution. The small values of the difference $P_\infty - MR_D$ for this substance increase the relative error of the moment. At 20° the value obtained was 0.84×10^{-18}, and at 70°, 0.77×10^{-18}. The necessary neglect of P_A in calculating this moment causes the mean value 0.8×10^{-18} given in Table IV to be too high. Indeed, if iodoform had a value of P_A comparable to those given in Table III, its moment would be zero. It seems probable that the true value of the moment of iodoform is little more than half the value given in Table IV, while the values for methylene bromide and iodide and bromoform are also a little high because of neglect of P_A, which, however, affects these moments less than that of iodoform because of their higher values. As most investigators have neglected P_A[3] in calculating the moment, it seems best, for the sake of comparison, to use these values, bearing in mind the fact that they are a little high, rather than to subtract fictitious values of P_A of reasonable size, which might be expected to give more nearly correct values for the moments. The good agreement of the values at different temperatures, except in the case of iodoform, indicates that they are not far from the true values. The significance of the results shown in Table IV, together with the moments of other similar molecules, will be discussed presently.

Earlier papers have discussed the variation of the polarization with concentration as evidence of the mutual effects of the polar molecules in producing orientation or association.[4] It has been shown that the orienting effect of the molecules of a liquid upon one another depends not only on the size of their electric doublets, but also upon the location of the doublet or doublets in the molecule and upon the geometrical shape of the molecule. It is interesting to compare these effects in the closely related molecules investigated in the present work.

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[3] See Smyth, THIS JOURNAL, 51, 2051 (1929).

[4] See particularly Smyth and Stoops, *ibid.*, 51, 3330 (1929); also Smyth, *Chem. Reviews*, **6**, 549 (1929).

The molecule of an alkyl halide may be regarded as containing a single electric doublet located in the neighborhood of the bond between the halogen and the carbon chain. The effect of this doublet upon neighboring molecules depends upon its moment and upon the sizes of the halogen and the hydrocarbon chain which screen its force field. The deviation of the P_{12}–c_2 curves from linearity has been used as a qualitative indication of association or orientation. The effect is so great in hexane–ethyl bromide mixtures[1] that the curve actually passes through a maximum, which flattens out with rising temperature as increased thermal agitation reduces the molecular orientation. The moment of the ethyl iodide molecule is slightly smaller than that of the bromide and the screening effect[2] of the iodine is somewhat larger than that of the bromine. Consequently, the mutual effect of the molecules is not sufficient to cause a maximum in the P_{12}–c_2 curves as in the case of ethyl bromide. When butyl chloride, bromide and iodide are compared with one another, the differences are not pronounced as the screening effect of the large butyl groups so reduces the intermolecular action that the differences between the effects of the halogens are small.

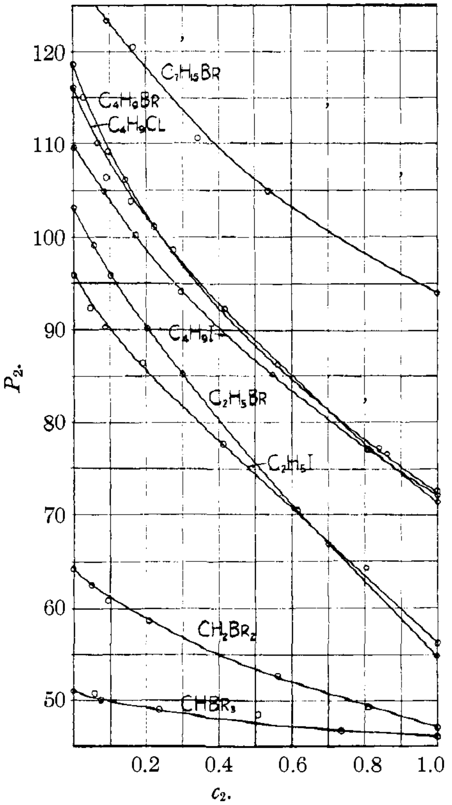

Fig. 2.—Variation of P_2 with concentration at 10°.

In comparing the P_{12}–c_2 curves for different substances, it must be borne in mind that differences in P_E affect the relative rate of change of P_2 with c_2 and hence the shape of the P_{12}–c_2 curves. Indeed, this seems to be the principal cause of the differences in these curves, for the P_2–c_2 curves in Fig. 2 show only small differences in curvature. The heptyl bromide curve has the smallest slope. The butyl halide curves have a slightly greater slope and lie close together. The ethyl bromide and ethyl iodide curves are very similar, the slope of the latter being slightly less. Differences in P_E and P_A for the different substances are responsible for the spacing of the curves.

At the bottom of the diagram lie the curves for methylene bromide and bromoform, which, because of the small size of their moments and the screening of the doublets by the bromines, show little intermolecular action. The corresponding iodine compounds are not shown, as some of their P_2 values are in error because of decomposition.

The temperature variation of P_2 for the pure substance gives further evidence of the intermolecular action. The values of P_2 for pure ethyl bromide increase slightly with rising temperature until the boiling point is approached, instead of decreasing according to the requirements of the Debye equation, because increasing thermal agitation decreases the intermolecular action which reduces the polarization. In ethyl iodide the intermolecular action is enough smaller to permit decrease of polarization with rising temperature even at the lower temperatures where its effect is greater. In the butyl halides the decrease of P_2 with rising temperature is greater and, in heptyl bromide, still greater.

The moments calculated from the values of P_∞ are given in Table IV together with a number of values previously determined, the latter being followed by their literature references.

TABLE IV

ELECTRIC MOMENTS OF HALOGEN COMPOUNDS × 10^{18}

X =	Cl	Br	I
CH_3X	1.7[a]	..	1.31[b]
C_2H_5X	2.0[a]	1.86[c]	1.66[d]
C_4H_9X	1.88	1.81	1.59
$C_7H_{15}X$	..	1.83	..
CH_2X_2	1.6[e]	1.39	1.08
CHX_3	1.05[c]	0.99	0.8
CX_4	0[e]	..	..
CH_3CHX_2	2.05[f]	..	..

[a] Sircar, *Indian J. Phys.*, **12**, 197 (1928); [b] Mahanti and Sen Gupta, *ibid.*, **12**, 181 (1928); [c] Smyth and Morgan, Ref. 1; [d] Smyth and Stoops, Ref. 2; [e] Sänger, *Physik. Z.*, **27**, 556 (1926); [f] Ghosh, Mahanti and Sen Gupta, *Z. Physik*, **54**, 711 (1929).

The influence of the length of the carbon chain upon the moment of the molecule has been discussed previously, but a quantitative treatment of the theory has been attempted in the present investigation.[5] As the result of the treatment is not conclusive, the details are not given. The moments induced throughout the molecule by the principal doublet at the end of the chain and the moments induced in turn by these induced moments are calculated from the polarizabilities of the different parts of the molecule, which are obtained from the refractions associated with the bonds.[6] The calculated increase in moment due to the direct effect of the principal doublet is very small in the third carbon of the chain and negligible thereafter, which is in agreement with the absence of any increase in the observed

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[5] Smyth, THIS JOURNAL, **51**, 2380 (1929).

[6] *Cf.* Smyth, *Phil. Mag.*, **50**, 361 (1925).

moments with increase in the size of the alkyl group beyond ethyl. However, the secondary moments induced by those already induced by the principal doublet are calculated as continuing with decreasing size through a chain much longer than two carbons. This would cause an increase in moment with increase in the size of the alkyl group far beyond ethyl, which the agreement of the values for the ethyl and the butyl halides and, in the case of the bromides, the heptyl as well, shows to be non-existent. The rough approximations necessary in these calculations are much more apt to cause serious error in the case of the secondary moments. Indeed, they are quite sufficient to cause the not inconsiderable values calculated for these secondary moments, which the experimental results show to be negligible in the longer molecules. In view of this, it may be concluded that the results of theory and experiment are not irreconcilable, but the failure to obtain positive agreement is unsatisfactory.

The moments of the chlorinated methanes were considered at a time when very inadequate values were available.[7] It was shown that, if the tetrahedral structure of the molecule remained undistorted, the moment of methylene chloride should be 1.15 times that of methyl chloride, which should be identical with that of chloroform, while that of the symmetrical carbon tetrachloride molecule should be zero. The same relations should, of course, hold among the bromine and iodine compounds. Sänger obtained a higher value for methyl chloride than that given in Table IV, but, as Sircar's value 1.69×10^{-18} agrees well with an unpublished result obtained by Dr. S. O. Morgan, the value 1.7×10^{-18} has been adopted as correct.

The deviations of the observed values from those calculated on the basis of an undistorted tetrahedral structure may be conveniently explained by resolving the system of charges making up the methylene halide molecule into two doublets with their axes in the two imaginary lines joining the halogen nuclei to the carbon nucleus. The moment of the molecule, as a whole, is the resultant of the moments of these two doublets and is, of course, smaller the larger the angle between the axes of the doublets. The distance between a carbon nucleus and the nucleus of an attached chlorine atom is calculated to be 1.70 Å.[8] If there were no distortion of the tetrahedral structure of methylene chloride, the angle between the axes of the two doublets would be 110° and the distance between the two chlorine nuclei would, therefore, be 2.78 Å. The radius of the chlorine atom calculated by Huggins[9] from x-ray data is 0.97 Å., from which the distance between the outermost electrons in the two chlorines, a very vague quantity, would be calculated as 0.84 Å. A quantity more significant for these considerations is the atomic diameter obtained from the kinetic theory of gases, which

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[7] Smyth, *Phil. Mag.*, **47**, 530 (1924).

[8] Pauling, *Z. Krist.*, **67**, 377 (1928).

[9] Huggins, *Phys. Rev.*, **28**, 1086 (1926).

might be expected to set a limit to the distance of nearest approach of the chlorine nuclei in the absence of strong forces of compression. Approximate values for this diameter may be calculated by an indirect method. The radius of the collision sphere of the argon atom determined by Rankine and Smith[10] from viscosity measurements is 1.44 Å. as compared with an atomic radius 0.93 Å. calculated by Huggins. If a proportionate difference exists for the chlorine atom, the latter has a collision sphere of radius 1.50 Å., which necessitates a distance of 3.0 Å. between the chlorine nuclei in methylene chloride if the spheres are in actual contact and uncompressed, instead of the 2.78 Å. calculated for the undistorted tetrahedral structure. A widening of the angle between the doublet axes from 110 to 124° is, therefore, required and, as a result, the moment of the molecule, as a whole, is reduced from the value calculated for the undistorted molecule, $1.15 \times 1.7 \times 10^{-18}$, to $0.94 \times 1.7 \times 10^{-18} = 1.6 \times 10^{-18}$, in agreement with the observed value. Similarly, in methylene bromide, the distance between the nuclei of the bromines and that of the carbon is given as 1.85 Å., from which the separation of the bromine nuclei may be calculated as 3.02 Å. in the absence of distortion of the tetrahedral structure. The bromine radius given by Huggins is 1.09 Å. and that of krypton is 1.06 Å., while the radius of the collision sphere of krypton found by Rankine and Smith is 1.55 Å., which figures give a radius for the sphere of repulsion of the bromine atom of 1.60 Å. The nuclear separation of the bromines in methylene bromide should, therefore, be 3.20 Å. instead of 3.02 Å., the angle between the doublets would be widened to 120°, and the resultant moment would be identical with that of methyl bromide. No accurate value for the latter is available in the literature, but an unpublished value determined by Dr. S. O. Morgan agrees within the limit of the experimental error with the moment of methylene bromide in Table IV. For methylene iodide, the distance between the carbon and iodine nuclei is taken as the sum of the atomic radii, 1.96 Å., and the calculation carried out as before. The angle between the doublet axes is found to be 135° and the resultant moment, therefore, 0.78 times that of methyl iodide, or $0.78 \times 1.31 \times 10^{-18} = 1.02 \times 10^{-18}$, in excellent agreement with the value in Table IV.

In similar fashion the chloroform molecule may be resolved into three doublets with their axes in the imaginary lines joining the carbon nucleus to the three chlorine nuclei which lie at the apices of an equilateral triangle. If there were no compression of the spheres of repulsion used in the calculation for methylene chloride, the carbon–chlorine bonds would be stretched even if the tetrahedral structure were so distorted that the carbon and the three chlorine nuclei were in the same plane. It appears reasonable to suppose that the hypothetical atomic spheres are somewhat compressed, but it is evident that the distortion of the tetrahedral structure of the mole-

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[10] Rankine and Smith, *Phil. Mag.*, **42**, 601 (1921).

cule is greater than in the case of the methylene compound, which should cause the decrease in moment below that calculated for the undistorted tetrahedral structure to be greater. The separation of the chlorine nuclei is still considerably greater than the atomic diameter estimated from x-ray data, so that there is no need to suppose that the electron shells are appreciably deformed. This is in harmony with the fact that the atomic refraction of chlorine shows no significant variation between molecules containing one, two, three and four chlorines attached to the same carbon,[11] which would certainly not be the case if the electron shells of the halogens suffered increasing deformation as the number of halogens attached to one carbon increased.

Calculation leads to similar conclusions for bromoform and iodoform, although the distortion of the tetrahedral structure in the bromoform molecule should be less than in the molecules of the other two substances. Table IV shows the much lower values for the trihalogenated molecules. The moment of bromoform differs from Morgan's unpublished value for methyl bromide, to which it should be equal if the tetrahedral structure were undistorted, by an amount smaller than the differences observed for the chlorine and iodine compounds, thereby conforming with the result of the calculation. As the inductive effect of a doublet in one part of the molecule upon the rest of the molecule has been disregarded in these calculations and in view of the speculative nature of the argument concerning the atomic dimensions and the possible errors in some of the experimental values of moments quoted, the excellence of the agreement between the observed and the calculated moments of the methylene compounds must be somewhat fortuitous. It is evident, however, that the theory of the distortion of the molecule by repulsion explains satisfactorily the moments of the halogenated methanes.

Summary

The dielectric constants and densities of several alkyl halides and halogenated methanes in heptane or benzene have been determined over a wide range of temperature, and the data have been used to calculate the polarizations of the substances and the electric moments of their molecules.

The polarizations show that the orientation or association of the polar molecules depends upon the size of the electric moments of the molecules and the screening of their doublets by the molecular structure.

In the alkyl halides no measurable increase of electric moment accompanies increase of the number of carbon atoms beyond two.

In the di- and tri-halogenated methanes, repulsive forces between the halogens distort the structures and reduce the moments of the molecules.

PRINCETON, NEW JERSEY

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[11] *Cf.* Smyth, *Phil. Mag.*, 50, 361 (1925).