

$$\frac{\Delta n_A}{\Delta t} = k_2 \bar{V} \bar{c}_B^2$$

where  $\bar{V}$  and  $\bar{c}_B$  are the average volume and the average concentration of  $B$ , based on the entering and exit gases.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

## ELECTRIC MOMENT AND MOLECULAR STRUCTURE. V. THE POLYMETHYLENE BROMIDES

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RECEIVED JUNE 10, 1931

PUBLISHED AUGUST 5, 1931

These measurements upon compounds containing two dipoles separated by a carbon chain of varying length were undertaken with the object of studying the effect of the carbon chain upon the positions of the dipoles relative to one another and thus of extending our knowledge of the shape and behavior of the chain. The bromide doublets were used as being simple dipoles obtainable in compounds with chains of different length. Subsequent measurements have been made upon the diethyl esters of dicarboxylic acids<sup>1</sup> and upon the glycols,<sup>2</sup> in both of which classes of compounds the dipoles are more complex.

### Apparatus

The dielectric constants of the solutions of the substances under investigation have been measured with a capacity bridge, part of which was presented by the Bell Telephone Laboratories. This part consisted of two fixed resistance arms with small adjustable resistances and capacities for balancing small inequalities and shielded in-put and out-put transformers, the whole mounted in a case with the parts carefully shielded. The other two arms of the bridge consisted of two condensers with series resistances as used previously in this Laboratory.<sup>3</sup> The source of current was a Western Electric Company variable oscillator, which was operated at a frequency of 50,000 cycles in these measurements. The balance of the bridge was obtained by passing the current through a six-tube amplifier with a detector and a multimeter, adjustable to read microamperes, as null instrument. The condenser in which the liquid was measured consisted of concentric gold-plated cylinders fitting closely into a small glass vessel similar to that used in earlier measurements.<sup>4</sup> The densities of the liquids were determined with a pycnometer of the type previously employed<sup>5</sup> and

<sup>1</sup> Smyth and Walls, *THIS JOURNAL*, **53**, 527 (1931).

<sup>2</sup> Smyth and Walls, *ibid.*, **53**, 2115 (1931).

<sup>3</sup> Smyth, Morgan and Boyce, *ibid.*, **50**, 1536 (1928).

<sup>4</sup> Smyth and Stoops, *ibid.*, **51**, 3312 (1929).

<sup>5</sup> Smyth and Morgan, *ibid.*, **50**, 1547 (1928).

the temperatures were controlled with a special form of thermostat also used before.<sup>5</sup> The solutions of ethylene bromide were measured at a wave length of 600 meters with a slightly more accurate bridge, which has been previously described,<sup>6</sup> and the measurements on decamethylene bromide were checked at 1000 meters on a heterodyne beat apparatus also previously described.<sup>1,2</sup>

### Preparation of Materials

**Heptane and benzene** were purified as in earlier work.<sup>7</sup>

**Ethylene Bromide.**—Ethylene bromide from the Eastman Kodak Company was washed with cold concentrated sulfuric acid, sodium carbonate solution and water, and, after drying with calcium chloride, was fractionally distilled. The middle fraction, boiling at 131.0° (756 mm.), was used;  $n_D^{20}$  1.53801;  $d_4^{20}$  2.1760.

**Trimethylene Bromide.**—Trimethylene bromide from the Eastman Kodak Company was washed with sodium carbonate solution and water and, after drying with calcium chloride, was fractionally distilled under reduced pressure. The middle fraction, boiling constantly at 80.5° (50 mm.), was used;  $n_D^{20}$  1.52319;  $d_4^{20}$  1.9790.

**Pentamethylene Bromide.**—Pentamethylene bromide was loaned by Dr. Wallace H. Carothers of E. I. du Pont de Nemours and Company; b. p. 122–125° (36 mm.);  $n_D^{20}$  1.5126.

**Decamethylene Bromide.**—Decamethylene bromide, loaned by Dr. Carothers, was distilled under reduced pressure (b. p. 172–174° (12 mm.)) and recrystallized.

### Experimental Results

The dielectric constants,  $\epsilon$ , and the densities,  $d$ , are given in Table I together with the polarizations,  $P_2$ , of the bromides calculated by means of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{c_1 M_1 + c_2 M_2}{d} \quad \text{and} \quad P_2 = \frac{P_{12} - P_1}{c_1} + P_1$$

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 dielectric constants were actually measured at intervals of about 10° and the densities at intervals of about 20°, with the exception of the measurements upon the benzene solutions of ethylene bromide which were made at the stated temperatures. Although the data were graphically interpolated to obtain values at definite 10° intervals, the results are shown, for the most part, at 20° intervals only, in order to save space. The values for the pure solvents, which have been repeatedly determined, are omitted also for the same reason.

The values of  $P_2$  have been plotted against those of  $c_2$  and extrapolated to  $c_2 = 0$  to obtain the values of  $P$  given in Table II as  $P_\infty$ . The values of  $P_\infty$  when plotted against  $1/T$  should give a straight line, 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  $b = 4\pi N\mu^2/9k$ ,  $N$

<sup>6</sup> Smyth and Dornte, *THIS JOURNAL*, **52**, 3546 (1930).

<sup>7</sup> Smyth and Rogers, *ibid.*, **52**, 2227 (1930).

being the Avogadro constant,  $6.061 \times 10^{23}$ ,  $\mu$ , the electric moment, and  $k$ , the molecular gas constant,  $1.372 \times 10^{-16}$ . As the temperature range possible in these measurements is not as wide as might be wished for the accurate establishment of the  $P_\infty - 1/T$  curves and as  $b$  is not constant for some of these substances,  $P_A$  is neglected and  $a$  set equal to  $MR_D$ .  $b$  is then obtained approximately as  $(P_\infty - MR_D)T$  and the moment is calculated from the relation  $\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - MR_D)T}$ . At the bottom of the set of data for each substance in Table II, the very approximate values of  $P_A$  and of the moments obtained from the  $P_\infty - 1/T$  curves are given in parentheses. The measurements of the decamethylene bromide solutions made with a heterodyne beat apparatus at 1000 meters wave length as a check gave values of the moment of  $2.73 \times 10^{-18}$  at  $25^\circ$  and  $2.72 \times 10^{-18}$  at  $50^\circ$  in excellent agreement with those in Table II.

TABLE I

INTERPOLATED VALUES OF DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS AND POLARIZATION OF POLAR COMPONENTS

Heptane-Ethylene Bromide				Benzene-Ethylene Bromide		
Mole fr. of $C_2H_4Br_2 =$	0.0303	0.0650	0.0913	0.0258	0.0487	0.0490
$t, ^\circ C.$						
-40	2.030	2.053				
-30	2.018	2.044	2.066			
-10	1.996	2.023	2.047			
10	1.969	1.996	2.024	2.378	2.428	2.428
30	1.940	1.967	1.997	2.337	2.387	2.393
50	1.906	1.935	1.965	2.290	2.336	2.333
70	1.870	1.901	1.930	2.243	2.286	2.285
90	1.832	1.866	1.892			
$d$						
-40	0.7628	0.7962				
-30	.7545	.7874	0.8122			
-10	.7370	.7697	.7944			
10	.7197	.7515	.7761	0.9212	0.9496	0.9503
30	.7019	.7330	.7570	.8991	.9270	.9278
50	.6839	.7145	.7380	.8761	.9044	.9052
70	.6648	.6954	.7073	.8545	.8815	.8822
90	.6445	.6749				
$P_2$						
-40	40.5	36.1				
-30	42.3	40.8				
-10	47.2	43.4	43.6			
10	47.8	44.3	45.4	67.7	62.5	62.2
30	50.1	45.7	47.3	68.9	64.1	67.3
50	47.4	45.6	47.5	66.6	62.4	61.3
70	43.3	44.6	47.2	65.8	60.9	60.2
90	37.2	43.1	46.5			

TABLE I (Continued)  
 Heptane-Trimethylene Bromide

Mole fr. of $C_3H_5Br_2 =$ $t, ^\circ C.$	0.0340	0.0353	0.0383	0.0413	0.0507	0.1471
-30	2.146	2.148	2.156	2.159	2.180	2.694
-10	2.109	2.112	2.120	2.122	2.141	2.603
10	2.071	2.075	2.081	2.084	2.102	2.518
30	2.033	2.035	2.041	2.045	2.062	2.437
50	1.994	1.997	1.999	2.006	2.020	2.360
70	1.955	1.957	1.957	1.965	1.979	2.285
<i>d</i>						
-30	0.7561	0.7575	0.7580	0.7604	0.7646	0.8806
-10	.7391	.7403	.7410	.7428	.7474	.8514
10	.7216	.7231	.7241	.7252	.7300	.8320
30	.7040	.7056	.7067	.7074	.7122	.8129
50	.6863	.6875	.6887	.6896	.6943	.7927
70	.6678	.6692	.6692	.6719	.6756	.7726
<i>P<sub>2</sub></i>						
-30	133.9	131.6	134.1	131.0	130.5	120.4
-10	130.4	129.3	131.8	128.9	127.5	119.3
10	126.8	126.2	127.2	126.1	124.6	114.9
30	123.8	120.7	122.7	123.2	121.8	110.5
50	117.9	117.0	115.6	118.4	116.0	106.4
70	111.9	109.0	109.0	110.6	110.8	101.6

Heptane-Pentamethylene Bromide

Mole fr. of $C_3H_{10}Br_2 =$ $t, ^\circ C.$	0.0311	0.0361	0.0492	0.0665
-40	2.193	2.222	2.294	2.392
-30	2.173	2.203	2.271	2.366
-10	2.135	2.164	2.225	2.314
10	2.097	2.124	2.179	2.261
30	2.058	2.081	2.132	2.208
50	2.018	2.038	2.085	2.154
70	1.974	1.995	2.036	2.097
<i>d</i>				
-40	0.7642	0.7694	0.7826	0.7996
-30	.7557	.7610	.7741	.7910
-10	.7386	.7436	.7565	.7738
10	.7214	.7264	.7391	.7556
30	.7042	.7091	.7216	.7376
50	.6864	.6912	.7041	.7194
70	.6680	.6730	.6864	.7007
<i>P<sub>2</sub></i>				
-40	171.5	170.4	166.3	164.2
-30	169.3	169.5	164.5	162.6
-10	166.0	166.9	160.5	158.3
10	161.9	163.4	156.1	154.2
30	158.6	158.0	151.2	150.0
50	152.1	151.9	144.7	144.0
70	144.6	144.2	135.9	136.2

TABLE I (Concluded)  
 Heptane-Decamethylene Bromide

Mole fr. of $C_{10}H_{20}Br_2 =$ $t_i, ^\circ C.$	0.0329	0.0355	0.0435	0.0475	0.0574	0.0675
0	2.164	2.182	2.227	2.251	2.315	2.370
20	2.126	2.139	2.180	2.207	2.264	2.315
40	2.083	2.095	2.134	2.160	2.213	2.258
60	2.039	2.050	2.087	2.113	2.161	2.201
80	1.994	2.003	2.041	2.063	2.106	2.143
<i>d</i>						
0	0.7342	0.7380	0.7449	0.7488	0.7597	0.7690
20	.7171	.7200	.7279	.7317	.7424	.7515
40	.6996	.7021	.7103	.7141	.7245	.7335
60	.6820	.6843	.6924	.6961	.7065	.7155
80	.6637	.6665	.6744	.6781	.6884	.6977
<i>P<sub>2</sub></i>						
0	216.9	215.3	212.9	211.8	211.8	207.3
20	213.8	212.1	207.5	209.1	207.4	203.4
40	208.3	206.4	202.1	204.2	202.1	198.0
60	199.3	197.3	194.9	198.4	195.8	191.0
80	192.2	189.2	189.2	191.3	189.0	184.1

TABLE II

VALUES OF  $P_\infty$  ( $P_\infty - MR_D$ ) $T$ , AND THE MOMENT

$T, ^\circ A.$	$P_\infty$	$C_2H_4Br_2(MR_D = 27.0)$ (in $C_7H_{16}$ )			$C_3H_6Br_2(MR_D = 31.0)$ (in $C_6H_6$ )				
		$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	$P_\infty$	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	$P_\infty$	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$
243	43	3890	0.79			140.2	26540	2.07	
263	48	5520	0.94			136.2	27670	2.11	
283	48	5940	0.98	74.0	13300	1.46	132.0	28580	2.15
303	49	6660	1.04	74.3	14330	1.52	128.7	29600	2.18
323	48	6780	1.05	72.0	14550	1.52	122.8	29650	2.19
343	47	6860	1.05	70.7	14990	1.55	(115.8)	(29090)	(2.17)

 $(P_A = 17.5; \mu = 1.12 \times 10^{-18})$   $(P_A = 45; \mu = 1.56 \times 10^{-18})$ 

$T, ^\circ A.$	$C_8H_{10}Br_2(MR_D = 40.6)$			$C_{10}H_{20}Br_2(MR_D = 64.6)$		
	$P_\infty$	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	$P_\infty$	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$
233	178.8	32200	2.28			
253	174.4	33850	2.34			
273	169.8	35270	2.39	229	44880	2.69
293	156.6	36620	2.43	221	45830	2.73
313	161.6	37870	2.47	214.5	46920	2.75
333	155.0	38100	2.48	206.0	47090	2.76
353				197.0	46740	2.75

 $(P_A = 60; \mu = 1.60 \times 10^{-18})$ 
 $(P_A = 37; \mu = 2.40 \times 10^{-18})$ 

### Discussion of Results

The values of  $P_2$  for ethylene bromide in dilute solution in heptane increase with rising temperature, pass through a maximum at about  $30^\circ$ , and

then decrease, although, according to the Debye equation,  $P_2$  should be a linear function of  $1/T$ . Obviously, it is useless to attempt to determine  $b$  as the slope of the  $P_\infty - 1/T$  curve since  $b$  is not a constant. When the moment is calculated as  $\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - MR_D)T}$ , it is found to increase with rise of temperature. The measurements of ethylene bromide in benzene solution give much higher values of the polarization, a difference analogous to that found by Meyer in the case of ethylene chloride.<sup>8</sup> The polarizations in benzene solution also show a maximum at 30°, but, as the only values below this temperature were determined not far above the freezing point, where the tendency toward association is greater, great significance cannot be attached to this. The temperature range is here too short for an accurate determination of the moment from temperature variation, but the 30, 50 and 70° values lie on an approximately straight line, which gives  $\mu = 1.12 \times 10^{-18}$  and  $P_A = 17.5$ . It is more satisfactory to use the refraction to obtain the values of the moment given in Table II, where the temperature variation of  $\mu$  from 30 to 70° is negligible.

The polarizations of the higher bromides in dilute solution do not increase with rising temperature even at the lowest temperatures investigated, but the values of  $b$  obtained on the slope of the  $P_\infty - 1/T$  lines give surprisingly large values of  $P_A$  and, consequently, low values of the moment. When the molar refraction is used in the calculation of the moment, the values obtained for trimethylene bromide show a small increase with rising temperature at the low temperatures. Pentamethylene bromide shows a more appreciable increase with temperature and decamethylene bromide a negligible increase. An increase in the moment with rising temperature, while tending to cause a departure from linearity in the  $P_\infty - 1/T$  curve, would at the same time reduce the slope of the curve and hence reduce the value of  $b$  and increase  $P_A$ , which, as it is obtained by a long extrapolation, is very dependent upon the slope of the curve. The value of  $P_A$  for pentamethylene bromide which shows the most marked temperature variation of the moment, is the highest of the three, while that for decamethylene bromide, which shows negligible temperature variation of the moment, is much the lowest. Actually, one would expect the large molecule of decamethylene bromide to have the largest value of  $P_A$ . It appears probable,<sup>9</sup> therefore, that these apparent values of  $P_A$  are much too high, although the value for decamethylene bromide is less than double those found for some of the alkyl halides.<sup>10</sup> Considerable doubt must, however, exist as to whether these latter values are not too high.<sup>9</sup> Morgan and Lowry<sup>11</sup> obtained a value of 21.4 for the  $P_A$  of methyl bromide from the

<sup>8</sup> Meyer, *Z. physik. Chem.*, [B] **8**, 27 (1930).

<sup>9</sup> Cf. Smyth, *THIS JOURNAL*, **51**, 2051 (1929).

<sup>10</sup> Smyth and Rogers, *ibid.*, **52**, 2227 (1930).

<sup>11</sup> Morgan and Lowry, *J. Phys. Chem.*, **34**, 2385 (1930).

temperature variation in solution and a value of 2.8 from the polarization of solid methyl bromide. The reason for this discrepancy is not apparent. In view, however, of the uncertainty which exists in regard to the  $P_A$  values for these bromides, it seems best to use the values of the moments calculated from  $(P_\infty - MR_D)$ . They are presumably a little high because of the neglect of  $P_A$ , but, for the most part, this cannot materially alter the conclusions to be drawn from them.

In order to interpret the results, it is necessary to know the moment of the dipole at each end of the carbon chain. The moment of methyl bromide reported by Morgan and Lowry<sup>11</sup> is  $1.45 \times 10^{-18}$ , but, in obtaining this value, they used the curve which gave the high value, 21.4, for  $P_A$ . As  $P_A$  has been neglected in the values of the moments which we are to interpret, it is best to use for our purposes the value of the moment obtained from a calculation in which the almost negligible value of  $P_A$ , 2.8, found from the solid, is used. The result of this calculation is  $1.7 \times 10^{-18}$ . Eucken and Meyer<sup>12</sup> have used a value of  $1.5 \times 10^{-18}$  for the moment of the C-Br bond obtained as the moment of bromobenzene and a value of  $0.4 \times 10^{-18}$  for that of the C-H bond calculated from that of toluene. The assumptions underlying the assignment of the values to these bonds are exceedingly doubtful in character, although the empirical method used by Eucken and Meyer is often effective in calculating moments. As the use of these bond moments gives the decidedly high value  $1.9 \times 10^{-18}$  for methyl bromide, it is best to adopt tentatively the value  $1.7 \times 10^{-18}$  as the moment of the dipole at each end of the carbon chain.

Williams<sup>13</sup> has treated the molecule  $XCH_2CH_2X$  as containing two dipoles, each of moment  $m$ , with their axes in the lines joining the carbon nuclei to the X groups, these lines making an angle with the extension of the line joining the carbon nuclei. The mean effective moment of the molecule is then calculated as  $\mu = 1.41 m \sin \theta$ . The values which Williams observed for molecules of this type were all much lower than the calculated, a fact which he attributed to repulsion between the X groups and consequent decrease in  $\theta$ . Meyer<sup>8</sup> has considered the mutual potential energies of the doublets and obtained a much more complicated expression, which, when the mutual potential energies are small in comparison with the energy of rotation of the dipoles around the C-C line, may be simplified to the equation given by Williams. When the distance between the doublets is small, the mutual potential energy is large, and it is only at very high temperatures, not practically obtainable, that the energy of rotation around the C-C line is sufficient to make the doublets independent of one another. As the mutual potential energy is a minimum when the doublets oppose one another, it is evident that the moment of the

<sup>12</sup> Eucken and Meyer, *Physik. Z.*, **30**, 397 (1929).

<sup>13</sup> Williams, *Z. physik. Chem.*, [A] **138**, 75 (1928).

molecule as a whole will increase as rising temperature gives a rotational energy which tends to overcome this effect of the mutual potential energy.

Meyer has found that the polarization of ethylene chloride in solution in hexane shows a variation with temperature in conformity with the requirements of his equation, deviating from the linearity required by the simple Debye equation. So many approximations and assumptions are necessary in a treatment of this sort that even an exact quantitative agreement between a single set of observed and calculated values is not necessarily convincing, but Meyer has experimentally demonstrated the success of his equation in predicting an increase in the moment of ethylene chloride with rising temperature. The results of the present work show a similar increase in the moment of ethylene bromide with rising temperature.


It is interesting to calculate the moment for the limiting case in which the rotational energy is large in comparison to the mutual potential energy of the doublets, or, expressed in another way, in which all positions in the rotation about the C-C bond are equally probable. Assuming the usual tetrahedral carbon valence angles and taking the moment of each dipole as  $m = 1.7 \times 10^{-18}$ , we may apply the simple equation of Williams to this limiting case:  $\mu = 1.41 \times 1.7 \times 10^{-18} \sin 70^\circ = 2.25 \times 10^{-18}$ . The large difference between this value and those observed for ethylene bromide shows how far the actual conditions are from those assumed in the derivation of the equation. The reduction of the moment of each dipole by the inductive effect of the other has been neglected in this calculation. The moment of ethyl bromide has been found to be  $1.86 \times 10^{-18}$ .<sup>5</sup> The rounding off of this figure to  $1.9 \times 10^{-18}$  makes it comparable with the values of the moments in the calculation of which  $P_A$  has been neglected. The difference of  $0.2 \times 10^{-18}$  between this value and the moment of methyl bromide may be attributed mainly to the moment induced in the second carbon in the former.<sup>10</sup> This suggests that in ethylene bromide each dipole tends to induce a moment in the second carbon from it opposite to that induced by the other dipole. It would seem reasonable, therefore, to subtract a moment of at least  $0.2 \times 10^{-18}$  from the value  $1.7 \times 10^{-18}$  used for  $m$  in the calculation. If  $m$  is taken as  $1.5 \times 10^{-18}$ , the result obtained for  $\mu$  is  $2.0 \times 10^{-18}$ , still much higher than the observed values, which should approach this value with rising temperature.

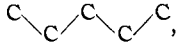
The temperature variation of the moment of ethylene bromide in benzene solution is small and uncertain and the moment is higher than that found in heptane solution. Meyer observed a similar difference in the case of ethylene chloride, finding a larger moment without temperature variation in the benzene solutions. The reason for this discrepancy probably lies in the effect of the benzene upon the forces between the dipoles in the molecule for results, as yet not published in detail,<sup>14</sup> confirm the tem-

<sup>14</sup> Smyth and Dornte, THIS JOURNAL, 53, 2005 (1931).



perature variation of the moment in the cases of ethylene chloride and ethylene chlorobromide, in at least qualitative conformity with the prediction of Meyer's equation.

In trimethylene bromide, the  $110^\circ$  valence angle of the central carbon should bend the chain thus, . This should tend to reduce the opposition between the dipoles at the ends of the chain and so increase the resultant moment. If we take 1.52 Å. as the internuclear separation of the carbons and 1.85 Å. as the separation of the carbon and the bromine nuclei,<sup>15</sup> we may calculate the distance which would separate the two bromine nuclei if they were able to lie on the inside of the angle of the carbon chain in the plane of the three carbon atoms, the  $110^\circ$  valence angles being maintained throughout. The result of this calculation, 1.53 Å., is considerably smaller than the atomic diameter of bromine, 2.18 Å., calculated from x-ray data,<sup>16</sup> which shows that this particular arrangement of the atoms in the molecule is impossible without great distortion of the valence angles. A similar calculation for ethylene bromide gives 2.79 Å. for the separation of the bromine nuclei when they lie on the same side of the molecule in the plane of the carbon atoms. Evidently there is reason to expect a moment for trimethylene bromide larger than that of ethylene bromide and showing some increase as the increasing energy of rotation about the C-C bonds accompanying rising temperature tends to overcome the effects of the mutual potential energy of the dipoles and the repulsion between the bromine atoms.

If the carbon chain in pentamethylene bromide were the zigzag structure, , with the carbons all in the same plane, its moment should differ from that of trimethylene bromide only as the result of an increase of 2.5 Å. in the separation of the two dipoles. This obviously should increase the moment and decrease its variation with temperature. Actually, there is no reason why there should not be turning about the other C-C bonds and it is easy to picture this turning as sometimes giving rise to a ring structure in which the dipoles overlap and oppose one another. This is somewhat analogous to the ring structure suggested to account for the lowering of the moment and its increase with rising temperature in the case of diethyl succinate.<sup>1</sup> The existence of a portion of the molecules in this ring structure, which would diminish with rising temperature, would account for the fact that the increase of moment on going from trimethylene to pentamethylene bromide is not greater and that the increase of moment with rising temperature is not inconsiderable. However, this must be regarded as a very tentative and speculative explanation rather than as definite evidence of ring formation. There is uncertainty in the experi-

<sup>15</sup> Pauling, *Z. Krist.*, **67**, 377 (1928).

<sup>16</sup> Huggins, *Phys. Rev.*, **28**, 1086 (1926).

mental accuracy of the temperature variation of the moments of trimethylene and pentamethylene bromide. In the latter it may be merely that the mutual potential energy of the dipoles renders less probable those positions in which the chains are bent by turning around the C-C bonds so as to bring the two dipoles near together on the same side of the molecule and give increased moment. Increasing rotational energy with rising temperature would then overcome the effect of the mutual potential energy of the dipoles and increase the moment.

Probably in pentamethylene bromide and, certainly, in decamethylene bromide, it is justifiable to assign to the dipole at each end of the chain the moment of ethyl bromide,  $1.9 \times 10^{-18}$ , which has been found indistinguishable from that of heptyl bromide in value. If the carbon chain is rod-like with the  $110^\circ$  valence angles maintained, we can apply the simple equation used to calculate the limiting value of the moment of ethyl bromide, that is,  $\mu = 1.41 \times 1.9 \times 10^{-18} \sin 70^\circ = 2.5 \times 10^{-18}$ . In decamethylene bromide, the dipoles are so far apart that we should expect no lowering of the resultant moment because of their mutual potential energy and, therefore, no temperature variation of the moment because of this effect. The difference between the observed and the calculated values of the moments is no greater than the possible absolute error in the observed value and the absence of appreciable variation of the values with temperature accords with the theoretical prediction. As any considerable permanent bending of the chain would cause a moment larger than that calculated and, probably, varying with temperature, which should affect the bending, it may be concluded that the long carbon chain in the liquid does not differ much from the rod-like shape commonly assigned to it. Another conclusion to be drawn is that the chain does not bend appreciably in the electric field used in measuring the dielectric constant, for such bending would increase the effect of the dipoles and give an apparent increase in the value of the electric moment observed.

In conclusion the writers wish to express their gratitude to the Bell Telephone Laboratories for a portion of the apparatus used in these measurements and to Dr. Wallace H. Carothers of E. I. du Pont de Nemours and Company for the loan of the pentamethylene and decamethylene bromide.

### Summary

The dielectric constants and densities of heptane solutions of dibromides with two, three, five and ten carbon atoms between the bromines have been measured over a range of temperature and the results have been used to calculate the electric moments of the molecules.

The moment of ethylene bromide is found to increase with rising temperature in accordance with theoretical predictions. The moments of methyl

and ethyl bromide are used to calculate the moments which might be expected in the molecules. The observed values are lowered by proximity of the two bromide dipoles, which also gives rise to the temperature variation of the moment. In decamethylene bromide the two dipoles are so far apart that the observed and calculated moments agree satisfactorily and the moment shows no variation with temperature.

Rotation around the C-C bonds probably causes some bending of the carbon chain, but there is no evidence of pronounced bending of the supposedly rod-like structures of the long chains, even in the external electric fields used in the measurement of the dielectric constants.

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[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH]

## THE GLASS ELECTRODE. THE STUDY OF VARIOUS CHARACTERISTICS

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RECEIVED JUNE 15, 1931

PUBLISHED AUGUST 5, 1931

### Introduction

The theory of the glass cell which so far is the most widely accepted is that of Haber.<sup>1</sup> He derived several expressions for the potential difference across a glass membrane when the two surfaces are in contact with solutions whose hydrogen-ion concentrations (activities) are  $1a$  and  $1b$ . All of these expressions may be summarized into the equation  $E = RT \log (1a/1b) - F(G)$ , where by  $F(G)$  is meant a function of the glass, when immersed in different solutions.

The difference between the equations of Haber as well as between different hypotheses which have since been stated, arises from differences assumed for  $F(G)$ . When  $F(G)$  is a small constant the glass is said to be "good," since it then has the theoretical slope for the calibration curve and also a small zero correction. Haber made the hypothesis that the glass is hydrated at its surfaces, this hydrated layer having the product  $[H^+][OH^-]$  constant. In his paper, under certain conditions,  $F(G) = RT \log (IIa/IIb)$ , where  $IIa$  and  $IIb$  are the hydrogen-ion concentrations (activities) in the two hydrated layers.  $F(G)$  then is small only when  $IIa$  is nearly equal to  $IIb$ , which occurs when the hydrated layer is uninfluenced by the successive solutions coming in contact with the glass, or  $[H^+]$  and  $[OH^-]$  are constant. Hughes<sup>2</sup> pointed out that this constancy could be attributed to the sodium silicate buffer system in the hydrated layer at the phase boundary. It is also evident that any increase in the buffer capacity of the hydrated layer improves the electrode performance.

<sup>1</sup> Haber and Klemensiewicz, *Z. physik. Chem.*, **67**, 385 (1909).

<sup>2</sup> Hughes, *J. Chem. Soc.*, 491 (1928).