

character of the carbon-bromine bond in cyanogen bromide was found to be 33%.

The contribution of structure II to the actual structure is 24% for cyanogen chloride and 33% for cyanogen bromide. That structure II should contribute more in the case of the bromide than in the case of the chloride is to be expected from the electronegativities. Chlorine is more electronegative than bromine. Therefore structure II, which imposes a positive formal charge on the halogen, would be less favorable for the chloride than for the bromide.

The relation found between bond distances and vibration frequencies<sup>21</sup> suggests that the stretching force constants for the carbon-chlorine bond in cyanogen chloride would be greater than that for a normal single carbon-chlorine bond. This is found to be the case. The force constant for the carbon-chlorine bond in carbon tetrachloride<sup>22</sup> is 0.4 megadyne/cm., while in cyanogen chloride it is 0.5 megadyne/cm.<sup>23</sup>

Dipole moment measurements of the cyanogen halides have not been made yet. If no resonance occurred, the moments would be expected to be

(21) Badger, *J. Chem. Phys.*, **2**, 128 (1934).

(22) Voge and Rosenthal, *ibid.*, **4**, 137 (1936).

(23) Linnet and Thompson, *Nature*, **139**, 509 (1937).

the difference between the C≡N and the C—Cl bond moments. The C≡N moment is greater than the C—Cl moment and so the resultant would be toward the N. Structure II has a large moment toward the N due to the separation of a charge. Because of the resonance, therefore, the moments of the molecules should be greater than the difference between the C≡N and the C—X bond moments. This effect of resonance on the dipole moment has already been noticed in the case of molecules similar to the cyanogen halides, namely, in the chloro and cyano derivatives of acetylene.<sup>24</sup>

### Summary

The molecular structures of cyanogen chloride and cyanogen bromide have been investigated by electron diffraction. The molecules were assumed to be linear nitriles. The results for the chloride are: carbon-chlorine  $1.67 \pm 0.02$  Å.; carbon-nitrogen  $1.13 \pm 0.03$  Å. The results for the bromide are: carbon-bromine  $1.79 \pm 0.02$  Å.; carbon-nitrogen  $1.13 \pm 0.04$  Å. The double bond character of the carbon-halogen bond is 24% in the chloride and 33% in the bromide.

(24) Curran and Wenzke, *THIS JOURNAL*, **59**, 943 (1937).

PRINCETON, N. J.

RECEIVED OCTOBER 29, 1938

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## Internal Rotation in Ethylene Chlorobromide and Ethylene Bromide

BY J. Y. BEACH<sup>1</sup> AND ANTHONY TURKEVICH

### Introduction

In a recent<sup>2</sup> paper the molecular structure of ethylene chloride was investigated by the electron diffraction method in order to determine the extent of internal rotation about the carbon-carbon bond. It was shown that there is a high potential barrier to such internal rotation. The configuration with the lowest internal potential energy is the *trans* configuration and the height of the barrier is between 5 kcal./mole and infinity. An attempt to duplicate this potential curve was then made by calculating the exchange repulsions and electrostatic interactions of the six atoms at the ends of the molecule. The potential curve obtained by adding these terms together was used to calculate a theoretical intensity of scattering

curve, assuming a Boltzmann distribution of molecules among all possible configurations. This curve did not agree with the electron diffraction photographs of ethylene chloride. In order to obtain a potential function compatible with the electron diffraction data it was necessary to re-evaluate the chlorine-chlorine exchange repulsions. The Morse curve for use in calculating the chlorine-chlorine repulsions was obtained<sup>2</sup> from the observed Morse curve by multiplying by 14/8. The chlorine-chlorine repulsions obtained using this Morse curve lead to a corrected potential barrier. The theoretical intensity curve for this corrected potential function was in agreement with the electron diffraction photographs.

In the present investigation we have undertaken to determine the potential barrier to internal rotation in ethylene chlorobromide and ethyl-

(1) National Research Fellow in Chemistry.

(2) Beach and Palmer, *J. Chem. Phys.*, **6**, 639 (1938).

ene bromide by electron diffraction and to find out if it is necessary to calculate steric repulsions by the same method that was required in the case of ethylene chloride.

The electron diffraction apparatus was the same as used previously.<sup>3</sup> The wave length of the electrons was 0.0590 Å., and the distance from the nozzle to the photographic films was 12.19 cm. The photographs were treated by the radial distribution method<sup>4</sup> and by the visual method.<sup>5</sup>

**Ethylene Chlorobromide.**—Eastman ethylene chlorobromide was carefully fractionated in a thirty-inch (76-cm.) column in which the reflux ratio could be controlled. The photographs, taken with the sample reservoir at 60° showed eleven rings. No measurements were made on the first as it was too close to the central image. The measured values of  $s (= 4\pi \sin \theta/2/\lambda)$  for the maxima and minima and the estimated intensities of the maxima are given in Table I.

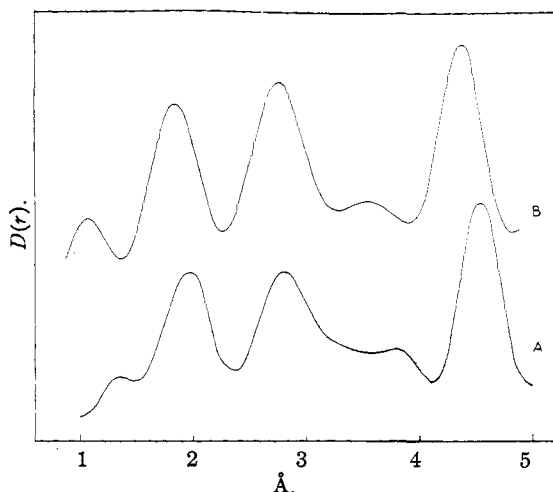


Fig. 1.—Modified radial distribution curves for A, ethylene bromide, and B, ethylene chlorobromide.

The radial distribution function,<sup>4</sup> calculated directly from the values of  $s_{\text{obsd.}}$  and  $I$ , is shown in Fig. 1, curve B. The peaks are at 1.08, 1.85, 2.75, and 4.37 Å. The small maximum at 3.55 Å. is without significance and will be discussed later. The first peak (at 1.08 Å.) gives the carbon-hydrogen distance, but because the hy-

(3) Beach and Stevenson, *J. Chem. Phys.*, **6**, 75 (1938); Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(4) The radial distribution method was developed by Pauling and Brockway, *THIS JOURNAL*, **57**, 2684 (1935), and applied by them to a large number of molecules. Recently this method has been modified by Degard, *Bull. Soc. Sci. Liège*, **1**, 36 (1938), and Schomaker (to be published) to give slightly more reliable results. In this paper we shall use only the modified radial distribution method.

(5) Pauling and Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

TABLE I

ETHYLENE CHLOROBROMIDE

Values in parentheses are not included in the average

Max.	Min.	$I$	$s_{\text{obsd.}}$	$s^a$	$s^a/s_{\text{obsd.}}$	$s^b$	$s^b/s_{\text{obsd.}}$
2	20		2.492	2.35	(0.943)	2.31	(0.927)
2	20		3.212	3.22	1.002	3.15	.981
3			4.037	3.98	0.986	3.86	.956
3	20		4.779	4.72	.988	4.68	.979
4			5.555	5.64	1.015	5.55	.999
4	6		6.070	6.12	1.008	6.01	.990
5			6.786	6.55	0.965	6.52	.961
5	16		7.489	7.52	1.004	7.43	.992
6			8.348	8.43	1.010	8.28	.992
6	4		9.007	9.07	1.007	8.91	.989
7			9.771	9.63	0.986	9.61	.984
7	4		10.38	10.40	1.002	10.36	.998
8			11.18	11.04	0.987	10.95	.979
8	3		11.85	11.80	.996	11.65	.983
9			12.67	12.62	.996	12.48	.985
9	2		13.28	13.52	1.018	13.30	1.002
10			13.92	13.92	0.996	13.83	0.989
10	1		14.68	14.47	.986	14.47	.986
11	1		16.16	16.21	1.003	16.08	.995
			Av.	0.998		Av.	0.986

C-Cl = 1.76 Å. C-Cl = 1.74 Å.  
C-Br = 1.91 Å. C-Br = 1.88 Å.

<sup>a</sup> Calculated for a model having a cosine potential barrier of 5 kcal./mole. <sup>b</sup> Calculated for the *trans* model.

drogen scattering is such a small fraction of the total, it is surprising that its position is so near the actual carbon-hydrogen distance, 1.09 Å. The second peak, at 1.85 Å., is a weighted average of the carbon-chlorine and the carbon-bromine distances. The carbon-chlorine and carbon-bromine single bond distances given in the table of covalent radii<sup>6</sup> are 1.76 and 1.91 Å., respectively. The weighted average of these distances, using their atomic numbers as weighting factors, is 1.86 Å. The peak at 2.75 Å. is an average of the long carbon-chlorine and the long carbon-bromine distances. If the carbon-carbon distance is taken to be 1.54 Å.<sup>6</sup> and the bond angles are assumed to be tetrahedral, the long carbon-chlorine and the long carbon-bromine distances are 2.69 and 2.82 Å., respectively. The weighted average of these is 2.78 Å. The most probable chlorine-bromine distance is represented by the peak at 4.37 Å. The chlorine-bromine distance for a *trans* molecule having tetrahedral angles and the above carbon-halogen distances is 4.43 Å. This peak shows that the molecule is roughly *trans*, there being slight deviations from this configuration. The extent to which these occur is estimated more reliably from the visual method.

(6) Pauling and M. L. Huggins, *Z. Krist.*, **87A**, 205 (1934); Pauling and L. O. Brockway, *THIS JOURNAL*, **59**, 1223 (1937).

In applying the visual method, theoretical intensity curves were calculated only for models in which the bond distances were normal single covalent bond distances<sup>6</sup> and bond angles were all tetrahedral. The carbon-carbon distance, 1.54 Å., is observed by electron diffraction in numerous hydrocarbons and by X-rays in diamond. The carbon-chlorine distance, 1.76 Å., has been observed in the chlorinated methanes.<sup>7</sup> The carbon-bromine distance, 1.91 Å., is that found in the brominated methanes.<sup>8</sup> The bond angles are probably not distorted appreciably from the tetrahedral values because even in methylene chloride, where the chlorine atoms are much closer together, the distortion is not over 5°. In Fig. 2, curve A is calculated for a *cis* model, curve B is calculated for a freely rotating model, and curve E is based on a *trans* model for the molecule. Curves C and D are calculated for a model having a potential barrier of the type  $V(\phi) = V_0/2(\cos \phi + 1)$ .  $V_0$  is the height of the potential barrier, and  $\phi$  is the angle between the two C-C-X planes.  $V_0 = 2$  kcal./mole for curve C, and 5 kcal./mole for curve D. On curve A the fourth maximum is too high, rendering the *cis* model unsatisfactory. The fourth and sixth maxima, observed on the photographs, do not occur on curve B, ruling out the freely rotating model. Curve C is unsatisfactory because it does not possess the observed fourth maximum and because the ninth and tenth maxima are not resolved. Curves D and E are both similar in appearance to the photographs. We can say, therefore, that  $5 \text{ kcal./mole} \leq V_0 \leq \infty$ . Quantitative comparisons of the photographs with curves D and E are given in Table I. The final results for ethylene chlorobromide are: if  $V(\phi) = V_0/2(\cos \phi + 1)$ , then  $5 \text{ kcal./mole} \leq V_0 \leq \infty$ . C-Cl =  $1.75 \pm 0.02$  Å., and C-Br =  $1.90 \pm 0.02$  Å.

**Ethylene Bromide.**—Eastman ethylene bromide was purified by the same method used for the ethylene chlorobromide. The photographs were taken with the sample at 70° and showed ten maxima. The first was too close to the central image to be measured. The measured values of  $s$  ( $= (4\pi \sin \theta/2)/\lambda$ ) for the maxima and minima, as well as the visually estimated intensities of the maxima, are tabulated in Table II.

The radial distribution function is shown in

(7) L. E. Sutton and L. O. Brockway, *THIS JOURNAL*, **57**, 473 (1935).

(8) Lévy and L. O. Brockway, *ibid.*, **59**, 1662 (1937); Finbach and Hassel, *Z. physik. Chem.*, **86**, 301 (1937).

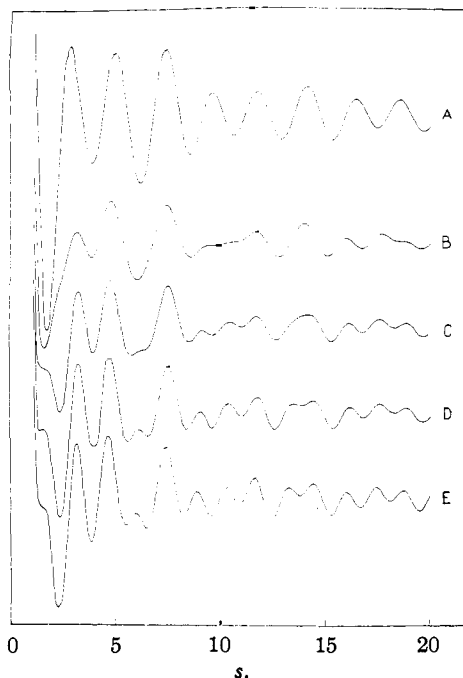


Fig. 2.—Theoretical intensity curves for ethylene chlorobromide: A, *cis*; B, free rotation; C, cosine barrier of 2 kcal./mole; D, cosine barrier of 5 kcal./mole; E, *trans* model.

Fig. 1, curve A. The peaks at 1.97, 2.81, and 4.54 Å. represent, respectively, the carbon-bromine, the long carbon-bromine, and the bromine-bromine distances. The values expected

TABLE II

ETHYLENE BROMIDE

Values in parentheses are not included in the average

Max.	Min.	$I$	$s_{\text{obsd.}}$	$s^a$	$s^a/s_{\text{obsd.}}$	$s^b$	$s^b/s_{\text{obsd.}}$
	2		2.426	2.33	(0.960)	2.27	(0.936)
2	20		3.142	3.13	(.996)	3.06	(.974)
	3		3.867	3.83	.990	3.79	.980
3	18		4.543	4.57	1.006	4.51	.993
	4		5.289	5.40	1.021	5.28	.998
4	8		5.813	5.88	1.012	5.80	.998
	5		6.555	6.45	0.984	6.40	.976
5	14		7.227	7.33	1.014	7.25	1.003
	6		8.043	8.20	1.020	8.03	0.998
6	5		8.663	8.71	1.005	8.61	.994
	7		9.452	9.31	0.985	9.25	.979
7	8		9.980	10.09	1.011	10.00	1.002
	8		10.81	10.74	0.994	10.65	0.985
8	4		11.42	11.41	.999	11.29	.989
	9		12.81	13.05	1.019	12.88	1.007
10	1		14.13	14.07	0.996	14.05	0.994
11	1		15.56	15.75	1.012	15.55	.999
			Av.		1.004	Av. 0.993	

C-Br = 1.92 Å. C-Br = 1.90 Å.

<sup>a</sup> Calculated for a model having a cosine potential barrier of 5 kcal./mole. <sup>b</sup> Calculated for the *trans* model.

for these distances from a *trans* tetrahedral molecule having a carbon-bromine distance of 1.91 Å.

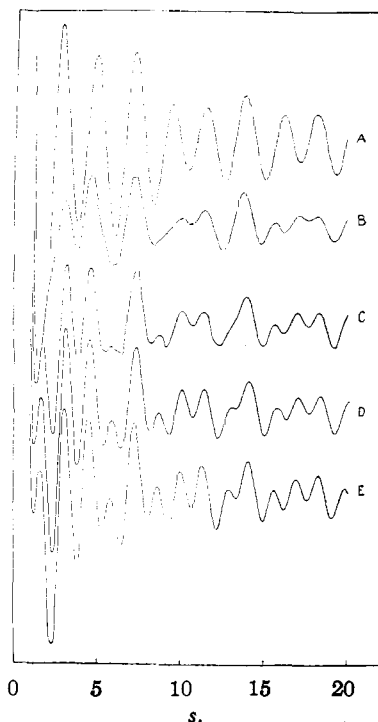


Fig. 3.—Theoretical intensity curves for ethylene bromide. A, *cis*; B, free rotation; C, cosine barrier of 2 kcal./mole; D, cosine barrier of 5 kcal./mole; E, *trans* model.

are: 1.91, 2.82, and 4.56 Å. There is excellent agreement on all but the first peak.

Again the visual method is resorted to in order to determine the extent of the oscillation about the *trans* position. All models for which theoretical intensity curves were calculated have tetrahedral angles, a carbon-carbon distance of 1.54 Å., and a carbon-bromine distance of 1.91 Å. The curves are shown in Fig. 3. Curve A is for a *cis* model, curve B for a freely rotating model, and curve E is for a *trans* model. Curves C and D are for models having a cosine potential barrier of 2 kcal./mole and 5 kcal./mole, respectively. Curve A is unsatisfactory because the fourth maximum is too high. Curve B is unsatisfactory because the sixth maximum is too high. On curve C, the fourth maximum is too low and the ninth and tenth maxima are not resolved as they are on the photographs. The *cis* model, the freely rotating model, and the model with a 2 kcal./mole barrier are therefore ruled out. Curves D and E are qualitatively satisfactory and are compared quantitatively with the photographs in Table II. The final results are: if  $V(\phi) = V_0/2(\cos \phi + 1)$ , then  $5 \text{ kcal./mole} \leq V_0 \leq \infty$ ; C-Br =  $1.92 \pm 0.02 \text{ Å}$ .

**Discussion.**—We now attempt, on theoretical grounds, to duplicate the potential barrier to internal rotation that we have observed experimentally for ethylene chlorobromide and ethylene

TABLE III

INTERACTIONS IN ETHYLENE CHLORIDE, ETHYLENE CHLOROBROMIDE AND ETHYLENE BROMIDE IN KCAL./MOLE							
$\phi$	0°	30°	60°	90°	120°	150°	180°
Electrostatic Interactions							
Ethylene chloride	1.80	1.46	0.85	0.18	-0.29	-0.59	-0.65
Ethylene chlorobromide	1.52	1.24	.65	.07	-.35	-.61	-.69
Ethylene bromide	1.37	1.12	.56	.04	-.34	-.57	-.67
Exchange Repulsions							
Ethylene chloride	14.03	13.30	12.83	13.83	14.58	14.38	13.75
Ethylene chlorobromide	14.36	13.66	12.71	13.47	14.00	13.76	13.09
Ethylene bromide	14.10	13.28	12.10	12.75	13.22	13.00	12.29
Corrected Exchange Repulsions							
Ethylene chloride	17.37	15.82	14.22	14.45	14.87	14.56	13.89
Ethylene chlorobromide	18.26	16.78	14.39	14.26	14.37	13.99	13.29
Ethylene bromide	18.13	16.43	13.71	13.63	13.53	13.18	12.45
Exchange Interactions Plus Electrostatic Interactions, $E(\phi) - E(\pi)$							
Ethylene chloride	2.73	1.66	0.58	0.91	1.19	0.67	0.0
Ethylene chlorobromide	3.48	2.50	0.96	1.14	1.25	.75	.0
Ethylene bromide	3.85	2.78	1.04	1.17	1.26	.81	.0
Corrected Exchange Interactions Plus Electrostatic Interactions, $E(\phi) - E(\pi)$							
Ethylene chloride	5.93	4.04	1.83	1.39	1.34	0.73	0.0
Ethylene chlorobromide	7.18	5.42	2.44	1.73	1.42	.78	.0
Ethylene bromide	7.72	5.77	2.59	1.89	1.41	.83	.0

bromide. The electrostatic interactions, consisting of nine terms, were calculated from the dipole moments of the bonds as given by Smyth.<sup>9</sup> The results for ethylene chloride, ethylene chlorobromide, and ethylene bromide are tabulated as a function of  $\phi$  in Table III.

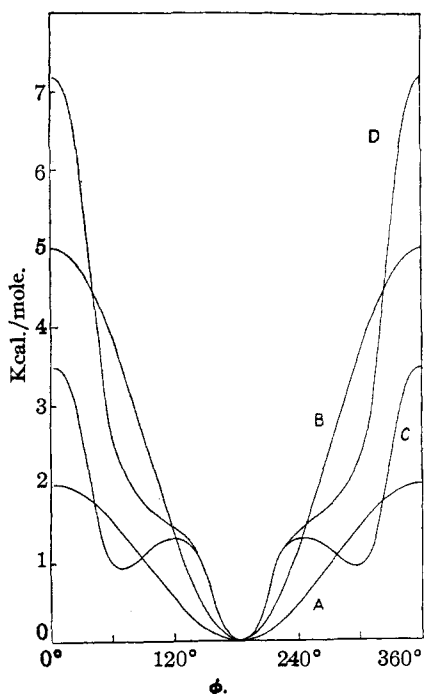


Fig. 4.—Potential barriers for ethylene chlorobromide: Curve A, 2 kcal./mole cosine curve; Curve B, 5 kcal./mole cosine curve; Curve C, exchange interactions plus electrostatic interactions; Curve D, corrected exchange interactions plus electrostatic interactions.

The values for ethylene chloride are taken from a previous paper.<sup>2</sup> Normal single covalent bond distances<sup>6</sup> and tetrahedral angles were assumed in making these calculations. The barrier due to this type of interaction is seen to vary from about 2.5 kcal./mole in the chloride to about 2.0 kcal./mole in the bromide.

The steric repulsions were calculated by the method of Eyring.<sup>10</sup> The Morse curves were assumed to be 20% coulombic. The sums of the nine steric repulsions calculated in this way for ethylene chloride, ethylene chlorobromide, and ethylene bromide are tabulated in Table III. The sums of the exchange and electrostatic interactions are also given in Table III. The ethyl-

ene chloride barrier is shown in reference 2, Fig. 4, curve A. The barrier for ethylene chlorobromide is shown in this paper in Fig. 4, curve C; the ethylene bromide barrier is shown in Fig. 5, curve C. As in the case of ethylene chloride,<sup>2</sup> it was

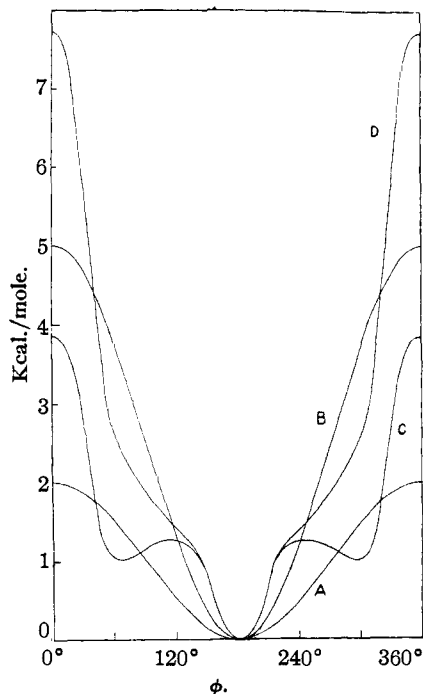


Fig. 5.—Potential barriers for ethylene bromide: Curve A, 2 kcal./mole cosine curve; Curve B, 5 kcal./mole cosine curve; Curve C, exchange interactions plus electrostatic interactions; Curve D, corrected exchange interactions plus electrostatic interactions.

found that the theoretical intensity curves calculated from the potential barrier determined in this way were in disagreement with the photographs. For both compounds the theoretical intensity curves calculated from these potential barriers are indistinguishable from the theoretical curves calculated from the 2 kcal./mole potential curve. This might have been suspected in advance because, as seen in Fig. 4 and Fig. 5, the theoretical potential barriers follow, in a general way, the 2 kcal./mole curve.

To achieve an agreement between the calculated and the observed potential barriers, resort is made to the same procedure that was used for ethylene chloride<sup>2</sup> (p. 643). The corrected steric repulsions are given in Table III. The sums of these interactions and the electrostatic interactions are also given in Table III. This poten-

(9) Smyth, *J. Phys. Chem.*, **41**, 209 (1937).

(10) Eyring, *THIS JOURNAL*, **54**, 3191 (1932).

TABLE IV  
APPROXIMATE FRACTION OF MOLECULES HAVING VARIOUS INTERNAL CONFIGURATIONS AT 300°K.

$\phi$	Fraction at an angle $\phi$ (including those at $-\phi$ )						
	0°	30°	60°	90°	120°	150°	180°
Ethylene chloride	0.0	0.001	0.044	0.093	0.101	0.282	0.478
Ethylene chlorobromide	.0	.0	.018	.059	.099	.289	.535
Ethylene bromide	.0	.0	.015	.047	.105	.277	.556

tial function for ethylene chloride is shown in reference 2, Fig. 4, curve B. For the chlorobromide and the bromide these potential functions appear in Fig. 4, curve D, and Fig. 5, curve D, respectively. They follow the 5 kcal./mole curves quite closely and the electron scattering functions obtained from them are identical with those calculated assuming a potential barrier of 5 kcal./mole. We have therefore obtained potential functions that are compatible with the electron diffraction photographs of these substances.

In Fig. 1 both curves show a small maximum at positions corresponding to halogen-halogen separations due to a value of  $\phi$  of about 80°. The shortcomings of the radial distribution method as applied at present prohibit the placing of any definite significance to these small peaks. In both radial distribution curves the distance between the large peaks is so great that it is not surprising that the curve is not flat throughout the whole region between them.

Ethylene chlorobromide has not been investigated previously by electron diffraction. Wierl,<sup>11</sup> from electron diffraction photographs showing only four maxima, concluded that ethylene bromide was a *trans* molecule rather than a *cis* or a

(11) Wierl, *Ann. Physik*, **13**, 453 (1932).

freely rotating molecule. He reported a bromine-bromine distance of  $4.75 \pm 0.15 \text{ \AA}$ .

From the final potential curves for the three molecules we have calculated the fractions of the molecules that possess any given configuration. These fractions are given in Table IV.

### Summary

The electron diffraction investigation of the molecular structures of ethylene chlorobromide and ethylene bromide leads to the following results. For both molecules, if  $V(\phi) = V_0/2 (\cos \phi + 1)$ , then  $5 \text{ kcal./mole} \leq V_0 \leq \infty$ . In ethylene bromide the carbon-bromine distance is  $1.91 \pm 0.02 \text{ \AA}$ . In ethylene chlorobromide the carbon-chlorine distance is  $1.75 \pm 0.02 \text{ \AA}$  and the carbon-bromine distance is  $1.90 \pm 0.02 \text{ \AA}$ . The carbon-carbon distance was assumed to be  $1.54 \text{ \AA}$  and the carbon-hydrogen distance was assumed to be  $1.09 \text{ \AA}$  in both cases.

The observed potential barriers can be calculated by taking into account the electrostatic interactions and the exchange repulsions of the two ends of the molecules. The exchange repulsions, however, must be calculated by the method required for ethylene chloride in reference 2.

PRINCETON, N. J.

RECEIVED NOVEMBER 10, 1938

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

## The Thermodynamics of Bi-univalent Electrolytes. IV. Cadmium Bromide in Aqueous Solution

BY ROGER G. BATES<sup>1</sup>

Cadmium bromide, in common with the other cadmium halides, has been shown to display extreme deviations from normal behavior in aqueous solution as indicated by its low activity coefficient<sup>2</sup> and the formation of rather stable ion aggregates with alkali bromides.<sup>3</sup>

(1) Sterling Fellow.

(2) (a) Getman, *J. Phys. Chem.*, **32**, 91 (1928); (b) Lucasse, *This Journal*, **51**, 2597 (1929).

(3) The stability of cadmium bromide complex ions has been determined by (a) cryoscopy, Cornec and Urbain, *Bull. soc. chim.*, **25**, 215, 218 (1919); (b) ebullioscopy, Rouyer, *Ann. chim.*, [10] **13**, 423 (1930), and Hun, *Compt. rend.*, **193** 355 (1931); (c) ultraviolet

This investigation was undertaken with the two-fold purpose of obtaining accurate measurements of the thermodynamic behavior of this abnormal salt in solution over a wide range of concentration and of ascertaining, from studies of very dilute solutions, the extent to which the Debye-Hückel theory is applicable to an intermediate electrolyte of this type.

absorption spectra, Job, *Ann. chim.*, **9**, 113 (1928); and (d) potentiometric studies of mixtures of cadmium salt and alkali bromide, Knobloch, *Zotos*, **78**, 110 (1930), and Riley and Gallafent, *J. Chem. Soc.*, 514 (1932).