the viscous concentrated solutions, or it may be due to the fact that the density of the solutions was neglected in calculating the values of the concentrations. The equilibrium must involve not less than two compounds, one of which has a ratio of antimony to sodium greater than two, and one less than two. In dilute solution the compound of low antimony content is present in relatively larger quantities. While the electrolyses have not yielded any conclusive quantitative results, they do show that antimony is present in solution as anion and that more than one atom of antimony is associated with each negative charge. The only compounds previously investigated which bear any resemblance to those just described, aside from the corresponding lead compounds, are the polyiodides.

In conclusion, I wish to express my appreciation of interest and assistance of Professor Charles A. Kraus, under whose direction this work was carried out.

WORCESTER, MASS.

THE ELECTRICAL CONDUCTANCE OF SOLUTIONS IN BROMINE.

BY EDWARD H. DARBY.

Introduction.—The dielectric constant of a solvent is largely determinative of its power to ionize substances dissolved in it, the ionizing power increasing with the dielectric constant according to the Thomsen-Nernst hypothesis. This influence is very marked at low concentrations, but at higher concentrations solvents of low dielectric constant appear to possess an ionizing power comparable with that of solvents of high dielectric constant.

Solutions of strong electrolytes do not obey the mass-action law at higher concentrations and consequently a direct comparison between ionizing power and dielectric constant for different solvents is impossible. According to Kraus and Bray,[1] however, the ionization of a binary electrolyte in any solvent may be expressed as a function of its concentration by the equation

$$\frac{(c\gamma)^2}{c(1-\gamma)} = D(c\gamma)^m + K.$$

Where D, m and K are constants, γ is the degree of ionization and c the concentration. It is thus possible to relate the effect of the dielectric constant on the ionization of a given electrolyte in different solvents by means of the values of the constants D, m and K. Since the relation between ionization and dielectric constant is a very involved one, it is obvious

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[1] Kraus and Bray, THIS JOURNAL, **35**, 1315 (1913).

that the ratio of the ionization values for a given salt in two different solvents will depend on the concentration.

Kraus and Bray have shown that the value of K becomes very small for solvents of low dielectric constant. For a dielectric constant below ten, the mass-action constant is too small to admit of ready experimental determination. The value of m increases with increasing dielectric constant, reaching a value a little less than two in the case of solvents of very low dielectric constant. The value of D, however, is practically independent of the value of the dielectric constant of the solvent and lies in the neighborhood of 0.35.[1] It follows then, that a concentration of about $4 N$ solutions of strong electrolytes in different solvents are ionized to the same extent. At higher concentrations, solutions in solvents of lower dielectric constant should possess the higher ionization.[2]

If a concentrated solution of a strong electrolyte can be obtained in any solvent, it will be highly ionized, irrespective of the value of the dielectric constant of the solvent. Conductance values obtained for solutions in such solvents as amylamine, hydrobromic acid, liquid iodine, etc., beart his out. The strongly electronegative character of liquid iodine makes this solvent a particularly interesting one with which to work, but its dielectric constant has not been measured and a comparison with other solvents is impossible.

The dielectric constant of bromine, however, is 3.18 at 20° and it seemed that, in view of the solvent and ionizing powers of iodine, bromine might exhibit similar properties. Plotnikow and Rokotjan[3] have shown that a number of substances such as IBr, and PBr_5, yield conducting solutions in bromine, although the conductance of such solutions is very low. Judging by the results obtained with other solvents, strong solutions of typical electrolytes in bromine should be very much better conductors than the solutions investigated by Plotnikow.

At the suggestion of Dr. Kraus, an investigation of bromine solutions was, therefore, undertaken. Potassium bromide did not appear to be appreciably soluble in bromine. It was to be expected, however, that salts of the organic nitrogen bases would prove to be soluble and such was found to be the case. Tetramethylammonium bromide was found to be soluble to the extent of about 0.10 N, but this concentration was not sufficiently high for the purpose of this investigation. Trimethylammonium chloride was then tried and found to be extremely soluble. Other salts of organic bases are doubtless soluble in bromine but the investigation has not been extended any further in this direction.

[1] The only marked exception is water, in which case D has the value approximately 2.5.

[2] This result can not well be verified owing to other factors which enter at high concentration, such as viscosity for example.

[3] Plotnikow and Rokotjan, *Ztschr. f. phys. Chem.*, **84**, 365 (1913).

Trimethylammonium chloride is very readily soluble in bromine, in fact, the salt absorbs bromine vapor so rapidly that it was found necessary to make the salt up into pellets in order to introduce it into the cell. The vapor pressure of the bromine is greatly lowered by the addition of the salt, as is evident from the decrease in color intensity of the bromine vapor over the solution. The color of the liquid also becomes less intense. At high concentrations the solution is transparent with a yellowish color. The viscosity of these solutions increases enormously with concentration. It is evident from these facts that the addition of an electrolyte to bromine has an enormous effect on the condition of the solvent. Wherein this consists, cannot be determined without further investigation.

Apparatus.—The Kohlrausch method was used in determining the conductance of the solutions. A drum-wound bridge of three meters' length was employed, using a telephone and induction coil. Two resistance boxes were employed, one of 111,000 ohms' capacity with Curtis wound coils for higher resistances and an ordinary box for the lower resistances. A variable air condenser was placed in the circuit for the purpose of compensating the effects of capacity and induction.

The temperature was maintained at $18° \pm 0.01°$, the thermostat being adjusted by means of a thermometer, divided in tenth degrees, and calibrated by the Reichsanstalt.

The cell employed consisted of a glass cylinder about 35 cm. long and 3 cm. in diameter. At the top it was provided with a neck bent at an angle of 90° to the axis of the cylinder to allow of tipping the cell and mixing the solution without danger of loss around the ground-glass stopper. Platinum electrodes, of one cm. square, were sealed into the bottom of the cell by stiff platinum wires to which tubular extensions were sealed extending outside the cell and bent upwards. These tubes were filled with mercury and provided contact with the bridge wires.

The platinum electrodes were not coated with platinum black since polarization effects in bromine are negligible. This necessitated a modification in the method of calibration as usually followed. The constant of a second cell platinized in the usual manner was determined with a potassium chloride solution using salt that had been subjected to repeated recrystallization from conductivity water. A solution of potassium iodide was then made up of arbitrary concentration and saturated with iodine. Using this solution, the resistance of the reference cell and that of the cell used in the experiments were measured. After correcting for the resistance of the leads, the cell constant of the latter cell is obtained at once.

In Table I are given the results obtained in the standardization of the reference cell. The concentration of the solution is given in the first column, the resistance of the solution after correction R is given in the

second column, the specific conductance L as determined by Kohlrausch is given in the third, and the cell constant $K = LR$ is given in the last column.

TABLE I.

Conc.	R.	L (Kohlrausch).	K.
0.01 N	2800.2	0.001225	3.43029
0.02 N	1429.9	0.002397	3.42749

The resistance of the reference cell with the potassium iodide solution was 2986 ohms, while that for the other was 161.07 ohms. This gives 0.1850 for the constant of the cell employed in this investigation.

Materials.—The bromine used was purified by distillation. The conductance of bromine was so small that it could not be determined with the apparatus available. It was certainly so low as to be entirely negligible.

The trimethylammonium chloride was Kahlbaum's product. Since it has a strong tendency to take up water, it was dried in a vacuum over phosphorus pentoxide and was then used without further purification. For convenience in handling, it was made up into pellets, which were again dried over phosphorus pentoxide in vacuum before introducing into the cell. These pellets weighed from 0.1 to 0.50 g.

The density of the bromine solution of trimethylammonium chloride decreases with increasing concentration. It was, therefore, necessary to determine this change in density. A Westphal balance was employed using a heavier bob than the one furnished, since the former would not sink in the bromine. This made a calibration necessary which was obtained by making another determination of the density of pure bromine, using a pycnometer consisting of a glass bulb of 21 cc. capacity and having a stem of 1 mm. diameter. The instrument was calibrated with water in the usual way, and the ratio of the two values found for the density of bromine was taken as the calibration correction of the balance. At 18° the weight of water was found to be 21.3953 g., the weight of bromine 67.0458 g. In making the density determinations with the balance it was found necessary to suspend the bob by a platinum wire about one meter in length in order that the balance might not be attacked by the bromine vapors. The densities are given below. Concentrations, expressed in mols of salt per liter of solution, are given in the first column, the densities in the second, and the concentration expressed in mols of bromine per mol of salt in the third. Within the limits of error the density is a linear function of the fractional concentration.

TABLE II.

Concentration.	Density.	Mols of bromine per mol of salt.
0.00 (pure bromine)	3.134	..
0.5923	3.073	141.3
0.9237	3.06	90.78
1.917	2.956	44.12

Procedure.—The method followed in making up the solutions was to weigh the amount of bromine introduced into the cell and then to add the weighed pellets of salt. In this way the concentration was gradually increased from the most dilute to the most concentrated solution.

The salt went into solution very readily, most of it dissolving in the course of a half hour. A slight shaking, which the bent neck of the cell made very simple, served to get the remainder of the salt into solution.

Experimental Results.—In Table III are given the results of three independent series of measurements. All measurements were made at 18.00°. No correction was made for the conductance of the solvent.

TABLE III.

No.	Weight, salt. g.	Conc.	Resistance.	$L \times 10^5$.	Λ.	Log V.	Log (cΛ).	Log (cΛ²).
Temperature 18° ± 0.01°.						Cell constant 0.1950.		
			Run No. 1, 73.07 g. of Bromine.					
1....	0.2027	0.09076	6,399.0	0.3893	0.3186	1.042	2.4611	3.9644
2....	0.4115	0.1843	618.2	3.992	1.624	0.736	1.4702	1.6886
3....	0.6160	0.2750	215.5	8.580	3.121	0.5608	1.9334	0.4227
4....	0.8156	0.3800	114.5	16.14	4.346	0.4304	0.2077	0.8457
5....	1.2447	0.5520	49.44	37.32	6.761	0.2581	0.5719	1.4020
6....	1.6560	0.7320	29.65	62.09	8.484	0.1355	0.7930	1.7213
7....	2.0401	0.8910	21.24	86.52	9.699	0.0460	0.9371	1.9238
8....	2.4427	1.0665	16.12	113.8	10.43	1.9720	1.0561	2.0843
9....	2.8401	1.2356	13.04	141.9	11.49	1.9073	1.1520	2.2122
			Run No. 2, 116.05 g. of Bromine.					
1....	0.1029	0.029	252,300.0	0.007334	0.02529	1.5376	4.8653	5.2682
2....	0.2104	0.0595	30,061.0	0.06115	0.1038	1.2269	3.7892	4.8054
3....	0.3404	0.0954	4,971.0	0.3722	0.3880	1.0421	2.5708	2.15962
4....	0.4539	0.1285	1,809.0	1.023	0.7945	0.8900	1.0098	2.90992
5....	0.5646	0.1592	922.1	2.006	1.261	0.7892	1.3024	1.4031
6....	0.7423	0.2093	428.6	4.316	2.063	0.6794	1.6351	1.9496
7....	0.9320	0.2618	241.1	7.669	2.929	0.4817	1.8847	0.3515
8....	1.1106	0.3110	161.5	11.44	3.683	0.5072	0.0587	0.6247
9....	6.469	0.3427	82.25	22.45	5.259	0.3688	0.3513	1.0713
10....	6.469	0.5334	53.59	34.50	6.469	0.2730	0.5378	1.3438
11....	8.008	0.6887	33.46	55.07	8.008	0.1630	0.7409	1.6444
12....	9.865	0.9323	19.99	98.65	9.865	0.0302	0.9636	1.9577
			Run No. 3, 54.72 g. of Bromine.					
1....	0.9937	0.4944	43.77	42.18	8.531	0.2059	0.6250	1.5561
2....	1.1297	0.5599	29.86	51.3	9.163	0.1519	0.7101	1.6717
3....	1.7316	0.8546	15.90	115.4	10.73	1.9968	1.0623	2.1929
4....	2.2742	1.314	10.94	157.0	11.00	1.9814	1.2227	2.3258

At the head of the table is given the weight of bromine in the cell. In the first column is given the number of the observation, in the second the weight of the salt, in the third the concentration is given in gram equivalents per liter, in the fourth the resistance of the solution, corrected for the resistance of the leads, 0.14 ohm; in the fifth column is given the
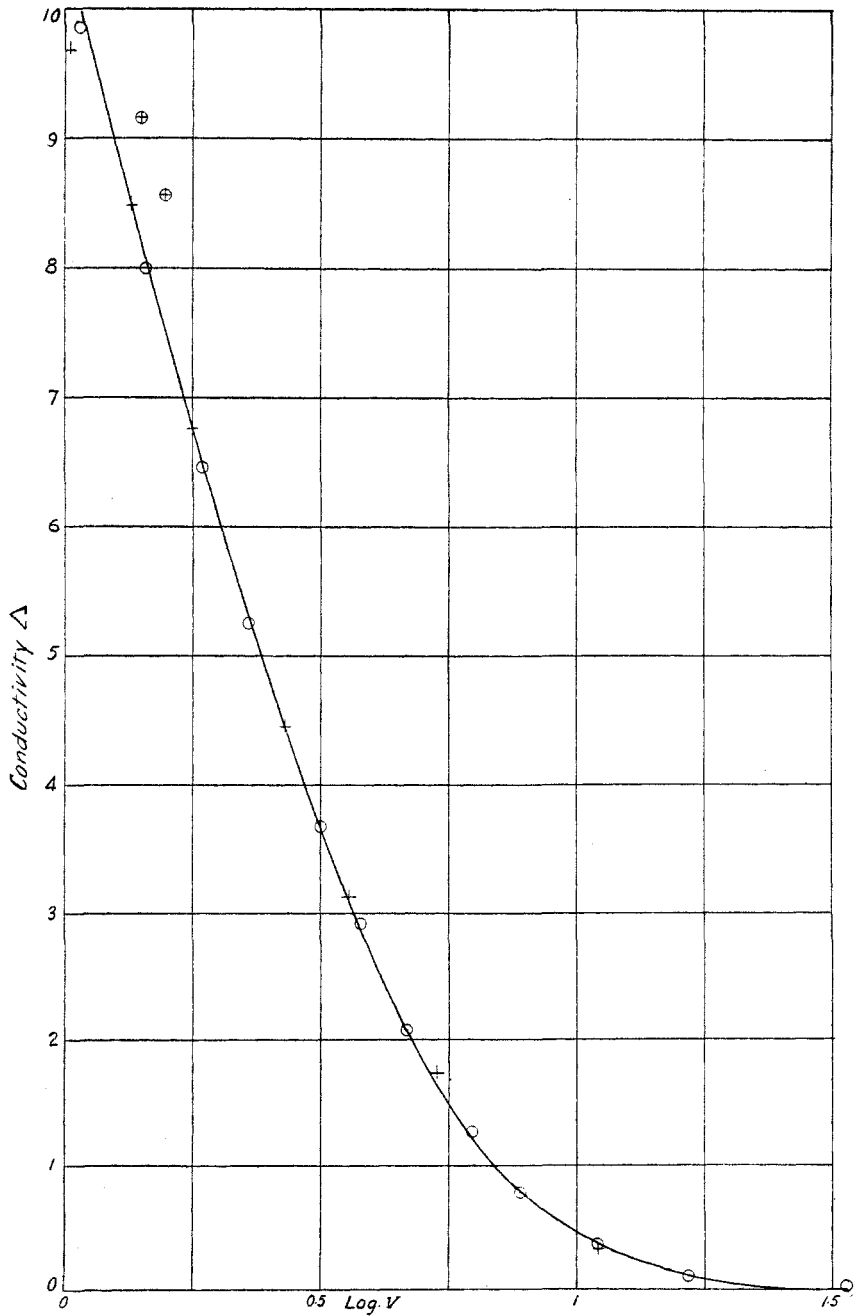
Fig. 1.—Conductance-concentration curves. Trimethylammonium chloride in bromine.

specific conductance L of the solution multipled by ten, the equivalent conductance Λ is given in the sixth, the logarithm of the dilution V in liters per equivalent is given in the seventh column, and in the eighth and ninth columns are given log $(c\Lambda)$ and log $(c\Lambda^2)$, respectively.
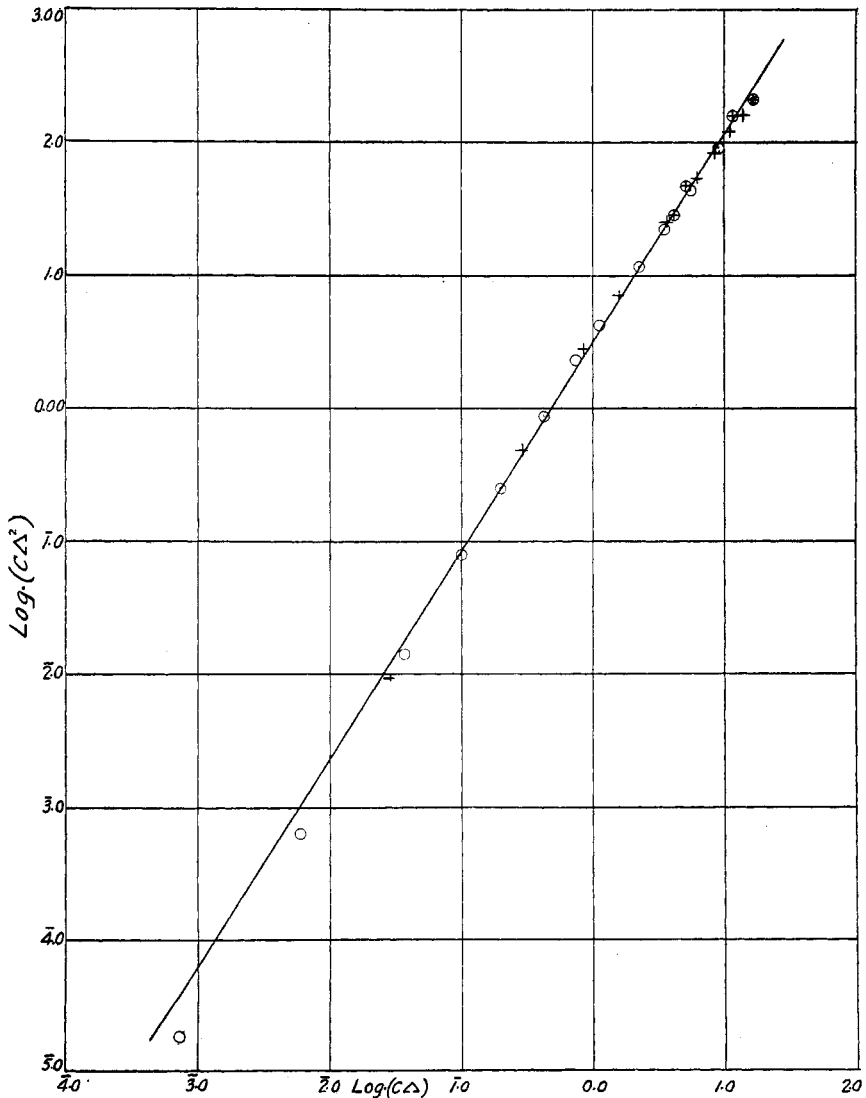

Fig. 2.—m-P plot for solutions of trimethylammonium chloride in bromine.

Discussion.—The results are shown graphically in Figs. 1, 2 and 3. In Fig. 1, values of Λ are plotted against log V, Fig. 2 is an M-P plot,[1] values

[1] Kraus and Bray, THIS JOURNAL, **35**, 1324 (1913).

of log $(c\Lambda)$ being plotted against those of log $(c\Lambda^2)$. As is generally the case with solutions in solvents of low dielectric constant, there is no tendency for the conductance to rise with increasing values of V. That is, the conductance curve continues to drop as the dilution increases. This
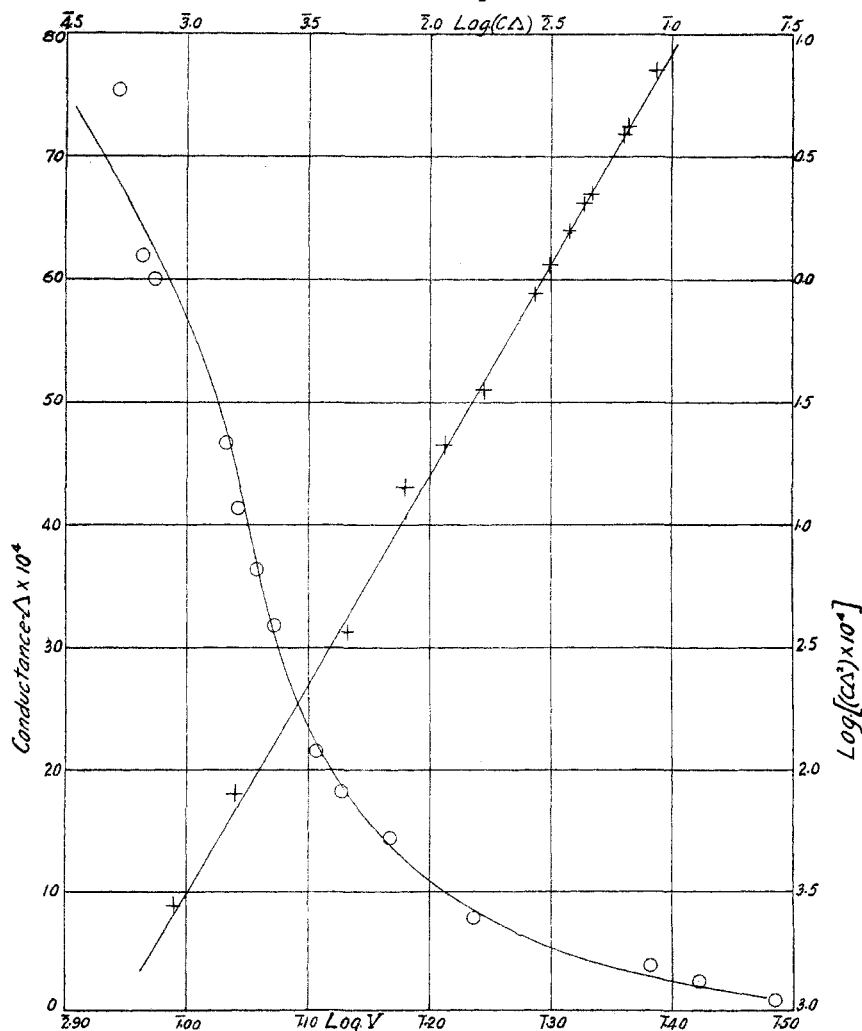

Fig. 3.—m-P and conductance-concentration plot.   Iodine and bromine.

is in contrast to the behavior of the ordinary solutions in solvents of moderately high dielectric constant in which there is a minimum in the conductance curve with a marked rise at higher dilution.

The values of Λ increase less rapidly at higher ion concentrations. This is a characteristic phenomenon of conducting solutions in general and is doubtless due to the rapid increase in the viscosity of the solution.

The m-P plot (Fig. 2) shows that the solution conforms to the equation of Kraus and Bray. Even in the most dilute solutions, whose resistance was about 250,000 ohms, the points conform reasonably well to a straight line.

From the plot, the values of the constants m and P may be determined giving

$$\log (c\Lambda^2) = 1.62 \log (c\Lambda) + \log 0.55.$$

If Λ_0 is known, the value of D in the general equation may be determined from the equation

$$D = P/\Lambda_0^{2-m}$$

Λ_0 cannot be directly determined, but Λ_0 is approximately a linear function of the fluidity of the solvent. We may then determine Λ_0 from the equation

$$\Lambda_0 = Kf,$$

where f is the fluidity and $K = 0.517$ (approximately). The viscosity of bromine at the temperature used is 0.010. This gives $\Lambda_0 = 51.7$. With this value of Λ_0 we obtain $D = 0.849$. This value of D is higher than that of most solvents. It may be that for solvents of very low dielectric constant the value of D rises. On the other hand, it may be that the mobility of the ions is not correctly given by the equation assumed above.

In order to have a basis of comparison, Plotnikow's results in the case of solutions of iodine in bromine were also examined. The method of procedure was similar to that used above.

These values are plotted in Fig. 3. The values of m, P and D are obtained in the same way as for trimethylammonium chloride and are as follows: $m = 1.7354$; $P = 0.048$; $D = 0.1691$.

In Fig. 3 are also plotted values of $\log V$ against Λ. The rise in conductance with increasing concentration is very much smaller than it is in the case of trimethylammonium chloride. It should be noted than the concentrations in the case of solutions of iodine in bromine are much larger than those of trimethylammonium chloride. It would seem to show that, when viscosity effects are not too great, the equation applies to very high concentrations.

The other substances with which Plotnikow worked hardly afford a basis of comparison. He found that, while a few metallic bromides are soluble in bromide, for example, aluminium bromide, they do not give conducting solutions. Antimony bromide gave a solution of very slight conducting power. Only phosphorus pentabromide gave a solution having an appreciable conductance and then only in very concentrated solutions.

Summary.—The conductance of a typical electrolyte in bromine has been measured.

The conductance values were found to be greater than those of any of the compounds studied by Plotnikow, none of which are typical electrolytes.

The values of m and D for trimethylammonium chloride are in fair agreement with those usually found for solutions in different solvents.

The conductance follows the dilution equation of Kraus and Bray.

WORCESTER, MASS.

A PRELIMINARY STUDY OF REVERSIBLE REACTIONS OF SULFUR COMPOUNDS.

BY GILBERT N. LEWIS, MERLE RANDALL AND F. RUSSELL V. BICHOWSKY.

Before publishing the details of a number of investigations which have extended over a period of eight years and which have finally permitted the calculation of the free energy of important sulfur compounds, we shall discuss briefly the nature and difficulties of the problem, and shall describe a large number of preliminary experiments. Designed as a means of orientation, these experiments were for the most part rough and qualitative. Some were selected for extensive quantitative investigation, and of these a few led to the successful results to be described later. They all help to throw light upon the extremely complicated behavior of sulfur compounds.

Sulfur is an element which appears in so many various types of compounds, in which it displays different valences, that the difficulty in obtaining data suitable for free energy calculations is due not to the paucity but to the wealth of reversible reactions. Indeed here, as with the nitrogen compounds, it is hard to find a reversible reaction which is not attended by numerous side reactions.

In studying the oxygen compounds of sulfur, the first important substance to consider is sulfur dioxide. Its free energy could be determined most directly from measurements of its thermal dissociation. Deville[1] passed sulfur dioxide through a "hot-cold" tube, and found evidence of a slight dissociation at 1200° C. We have, however, repeated these experiments between 1000 and 1500° and found, even at the highest temperatures, that the dissociation is too small to furnish a reliable method for obtaining the free energy of formation.

Turning, therefore, to a more complicated system, we have studied equilibria is *systems* containing sulfur, oxygen and hydrogen. *This system*, under varying conditions, yields, besides hydrogen and oxygen, gaseous S_8, S_6, S_2, S, the numerous solid and liquid forms of sulfur, steam,

[1] Deville, *Ann. chim.*, **145**, 94 (1865).