are plotted, in order that the results may be shown. A bath of ether and carbon dioxide was used, and with an automatic device it was possible to maintain the temperature within 0.3° of any temperature desired. These frozen solutions are poor conductors of heat, and the temperature must be held constant for at least thirty minutes before measurements can safely be made.

From the actual figures, the conduction is seen to increase most rapidly at about —21°, and as this is the cryohydric temperature for a solution of potassium iodide in water, it seems that even with rapid cooling a certain amount of segregation takes place.

In Fig. 2 the relative conductivities of N, 0.5 N and 0.25 N hydrochloric acid solutions are shown. These values are plotted directly, the last values being multiplied by 10. The conducting power increases fairly regularly with the temperature, so that there is no evidence of segregation. This is to be anticipated, since the cryohydric temperature for hydrochloric acid and water is far below the temperatures employed. The conductivities of the acid solutions are much greater than those of salt solutions of the same strength.

Until the experiments described here were undertaken, we were unaware that these solutions had been studied. Professor W. D. Bancroft has kindly given us a number of references to articles by Weimarn. We have been unable to consult the originals but the abstracts in the *Centralblatt* do not seem to bear directly on our work.

McGILL UNIVERSITY.

CRYOSCOPIC MEASUREMENTS AT LOW TEMPERATURES.

By H. S. REID AND D. McINTOSH.

It has been shown that organic substances containing oxygen, when dissolved in liquefied hydrobromic acid, unite with the solvent forming definite salts melting far above the melting point of either constituent.[1] Ether, for example, gives the compound $C_4H_{10}O.HBr$ melting at —46°, while ether and hydrobromic acid melt at —120° and —86°, respectively. To explain the formation of these salts it has been assumed that the oxygen at the low temperature acts as a tetravalent element, yielding with hydrobromic acid such compounds as $C_4H_{10}O\begin{smallmatrix}H\\Br\end{smallmatrix}$ or $C_4H_{10}O = BrH$.

The first of these formulae seems the more probable; for, in a study of the transport numbers,[2] it was found that the ether, or other organic body,

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[1] Archibald and McIntosh, *J. Chem. Soc.*, **85**, 919 (1904); McIntosh, THIS JOURNAL, **33**, 71 (1911); Maass and McIntosh, *Ibid.*, **34**, 1273 (1912).

[2] Steele, McIntosh and Archibald, *Phil. Trans.*, (A) **205**, 99 (1905).

under an electric stress moves towards the cathode, $i. e.$, the ether formed part of the positively charged ion.

The measurement of the conductivities of these solutions[1] showed certain anomalies as compared with water solutions, for the molecular conductivities increased with concentration. To account for this, a theory of complexes in solution of the type $(C_4H_{10}O)_x$ $(HBr)_y$ was advanced, so that in these solutions we may have very complex ions. It was proved that this theory of complexes might account for the increase in molecular conductivity with concentration, if it were assumed that two or more molecules of the solute united with the solvent to form a compound which undergoes ionic dissociation.

A careful study of the freezing-point curves from 100% hydrobromic acid to 100% substance containing oxygen, showed that the compounds in solution were largely dissociated into their constituents. In order to explain, if possible, these anomalies, and to throw light on the compounds in solution, we have made a number of determinations of the molecular weights of several oxygen compounds by the freezing-point method, and have worked to somewhat greater concentrations than are usual in these measurements.

Previous molecular-weight determinations were made by Steele, McIntosh and Archibald[2] by the boiling-point method, but their apparatus was probably defective. The most recent work has been done by Beckmann and Waentig,[3] but not much could be learned of the molecular structure of the compounds formed, on account of irregular results and also because they worked only at low concentrations.

Preparation and Purification of Reagents.

The reagents used as solutes were toluene, chloroform and carbon tetrachloride, which behave, as we shall show, normally in liquid hydrobromic acid, and methyl alcohol, ethyl alcohol, ether, acetone, ethyl acetate, acetic acid, paraldehyde and acetaldehyde, which form compounds with liquid hydrogen bromide. Bromine was also used as a solute in order to ascertain its solubility in the solvent, since on this point there is conflicting evidence.

The hydrogen bromide was made by dropping bromine into red phosphorus and water, passing the gas through water containing red phosphorus, then through phosphorus pentoxide and condensing it by solid carbon dioxide and ether.

The methyl and ethyl alcohol were purified by distillation, drying over calcium oxide and redistilling, drying over anhydrous copper sulfate and again distilling.

[1] Archibald, THIS JOURNAL, **29**, 665, 1415 (1907).

[2] *Loc. cit.*

[3] *Z. anorg. Chem.*, **67**, 17 (1910).

The ether was distilled, allowed to stand over sodium and redistilled.

The acetone was crystallized from sodium bisulfate solution; a solution of sodium carbonate was added, the acetone distilled off, dried over calcium chloride and redistilled.

The ethyl acetate was washed with a solution of sodium chloride and sodium carbonate, separated, distilled, dried over calcium chloride and redistilled.

The acetic acid was obtained by repeated freezing of glacial acetic in the ordinary way.

The pure paraldehyde was distilled and converted into the acetaldehyde by adding a drop of concentrated sulfuric acid and distilling.

The toluene had been previously purified and had stood over sodium for several years.

The chloroform was distilled, washed with water and dried over concentrated sulfuric acid.

The carbon tetrachloride was washed with a caustic soda solution, distilled, dried over calcium chloride and redistilled.

The bromine was dried by distilling from barium oxide in a glass apparatus.

Apparatus.

The apparatus used was much the same as that employed by Beckmann and Waentig. The thermometer was a platinum resistance one made by Heraeus in which the platinum was embedded in the quartz, thus enabling the thermometer to take up the temperature of the solution very quickly. The main difference between our apparatus and that used by Beckmann and Waentig was in the position of the electromagnet. They attached their magnet directly to the inner glass tube, but we placed ours above the tube, so that the thermometer wires were not cut by the magnetic lines, and thus disturbances in the galvanometer were avoided.
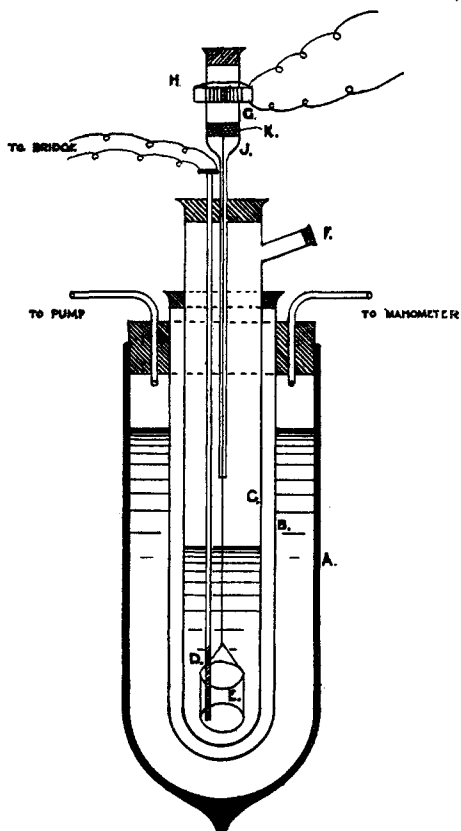
Fig. 1 shows a cross section of

Fig 1.

the large Dewar flask A used.   B is a glass tube immersed in the carbon dioxide and ether.   C is the freezing-point tube containing the platinum resistance thermometer D, and platinum stirrer E.   F is the side tube through which the solute was introduced.   G is a glass tube reaching into A, carrying the stirrer and electromagnet H.   J is the iron ring which is attracted by the magnet and so lifts and lowers the stirrer.   The pressure used corresponded to a temperature of from $-90°$ to $-92°$.

The electrical measuring apparatus was of the Carey-Foster type and consisted of two 3000 ohm resistances connected in series with a bridge wire, and two balancing resistances boxes.   A Broka galvanometer was used, and at the freezing point of hydrobromic acid one mm. on the bridge wire corresponded to $0.00158°$.   All the resistances were calibrated before and after the experiments.

<div align="center">Procedure.</div>

In order to find the value of K, the constant for hydrogen bromide, we used as solutes toluene, chloroform and carbon tetrachloride, which showed no evidence of forming compounds.   They behaved normally when dissolved, showing no apparent tendency to association or dissociation.   The second series for toluene and chloroform was made after all the experiments had been completed, in order to make sure that none of the resistances had altered in any way.   The results obtained are shown in Tables I and II.

TABLE I.—TOLUENE. M. W. $= 92.8$.

G $= 96.6$ grams.

g.	Δ.	K.	K'.
0.218	0.248	101.0	101.0
0.385	0.441	101.8	102.8
0.594	0.687	102.9	104.9
0.752	0.878	103.9	107.4
0.930	1.077	103.0	97.0

G $= 77.4$ grams.

0.292	0.424	103.5	103.5
0.526	0.745	100.8	97.6
0.675	0.964	101.7	104.5
0.779	1.114	101.9	104.6
0.866	1.244	102.3	106.3

Mean K $= 102.3$.

G = weight in grams of the solvent.
g = total weight in grams of the solute.
Δ = total lowering in degrees produced by grams of the solute.
K = the constant $\times 10^{-2}$ found from lowering of Δ degrees by g grams of the solute.
K' = constant the $\times 10^{-2}$ found from the individual measurements.

TABLE II.—CHLOROFORM. M. W. $= 119.5$.

G $= 67.9$ grams.

g.	Δ.	K.	K'.
0.218	0.284	105.8	105.8
0.421	0.541	104.2	102.5
0.565	0.723	103.8	102.6
0.755	0.975	104.8	107.6
0.955	1.239	105.2	107.2

G $= 80.7$ grams.

0.200	0.219	105.5	105.5
0.412	0.433	101.3	97.6
0.622	0.669	103.8	108.6
0.797	0.860	104.1	105.2
0.891	0.967	104.7	109.3

Carbon Tetrachloride, M. W. 154.0.

G $= 59.5$ grams.

0.358	0.389	101.7	101.7
0.577	0.633	101.9	102.1
0.770	0.847	101.9	101.7
0.940	1.039	102.1	103.5
1.109	1.234	102.8	105.9

Mean K $= 103.9$.

From these results the mean value of K is seen to be 103.1. This value was used throughout the remainder of the work to calculate the molecular weights of the solutes employed.

The latent heat of fusion, W, of hydrogen bromide can be calculated, knowing K, from the formula

$$K = 0.02T^2/W \text{ and is equal to 6.79 cal. per g.}$$

Table III shows the results obtained using ethyl alcohol as the solute. Care had to be exercised in introducing the alcohol because of the large heat of combination, which caused the alcohol to be sprayed on the walls of the tube unless added very slowly. The alcohols appeared to be most reactive, but the other solutes forming compounds with the solvent also had to be added slowly.

TABLE III.—ETHYL ALCOHOL. K = 103.1.
M. W. = 46.
G = 71.0 grams.

g.	Δ.	M.	M′.
0.107	0.140	111.0	111.0
0.238	0.287	117.7	129.9
0.589	0.723	118.2	116.8
0.964	1.265	110.6	100.6
1.164	1.546	109.3	103.5
1.436	1.929	108.0	103.2
1.674	2.334	104.3	84.5
1.816	2.592	102.0	80.0

G = 86.6 grams.

g.	Δ.	M.	M′.
0.167	0.196	101.3	101.3
0.346	0.384	107.0	113.7
0.540	0.588	109.3	113.1
0.837	0.918	108.0	107.0
1.029	1.100	111.2	125.7
1.243	1.302	113.7	126.1
1.585	1.678	112.5	108.2
1.914	2.148	106.0	83.5
2.097	2.341	106.5	112.9
2.401	2.794	102.3	79.9
2.658	3.144	100.4	87.6
2.975	3.597	98.5	83.3

TABLE IV.—METHYL ALCOHOL. K = 103.1. M. W. = 32.
G = 60.4 grams.

g.	Δ.	M.	M′.
0.200	0.309	110.5	110.5
0.406	0.601	115.2	118.4
0.642	0.978	112.2	107.0
0.812	1.313	105.4	86.7
1.054	1.664	108.1	118.0
1.305	1.988	112.2	132.1
1.565	2.335	114.3	127.5
1.764	2.486	121.3	225.1
2.023	2.651	130.4	265.4
2.486	3.515	120.3	90.6

G = 68.0 grams.

g.	Δ.	M.	M′.
0.197	0.278	107.7	107.7
0.335	0.471	108.1	108.5
0.464	0.651	108.1	108.8
0.670	0.936	108.5	109.7
0.828	1.121	112.2	129.2
1.045	1.435	110.5	104.7
1.251	1.719	110.5	110.1
1.437	1.929	113.0	134.5
1.661	2.223	113.5	115.2
1.816	2.407	114.3	127.5
2.025	2.618	117.0	148.6
2.199	2.873	115.7	102.7
2.452	3.320	111.8	85.2
2.597	3.525	111.4	106.5

In dilute solutions the alcohol is polymerized 2.3 to 2.4 times. The amount of association increases very slightly until a concentration of 1.4 to 1.8 per cent. is reached where the amount of the association is 2.5. At further concentration the molecular weight decreases quite rapidly. This seems to show that at this concentration the amount of dissociation

becomes very much greater and doubtless continues to increase, because the association would increase with greater concentration, and the amount of dissociation must be greater than the association in order to give a lower molecular weight. This view is also supported by the fact that the molecular conductivity of alcohol in hydrogen bromide increases with concentration. Table XI shows the variation in the molecular weight and molecular conduction[1] with concentration. It will be seen that the concentration where the molecular weight begins to decrease, corresponds fairly well with the concentration where the first marked bend occurs in the conductivity curve, i. e., where the dissociation first becomes marked.

Table IV shows the results obtained with methyl alcohol. The association is here seen to be greater than in the case of ethyl alcohol. Taking the results in the second part of the table, it is seen that in dilute solutions the amount of association is 3.4. The increased association is very small indeed, but it seems to reach a maximum at a concentration of 3.0%, where the amount of association is 3.6. With increased concentration the association seems to decrease a little.

As in the case of ethyl alcohol, the amount of dissociation must be quite marked after a concentration of 1.0% has been reached, as is shown by the conductivity curve. Therefore the association must be much more marked than in the case of the ethyl alcohol. The compounds formed with alcohol were found by Maass and McIntosh[2] to be $CH_3HO.HBr$ and $C_2H_5O.HBr$.

The results obtained with ethyl acetate are shown in Table V.

In very dilute solutions there appears to be a certain amount of dissociation, but very little. With increasing concentration the association steadily increases until the percentage of the acetate is about 3.0 when the amount of association is 1.6. On addition of more of the solute the value of the molecular weight decreases, showing that the amount of dissociation has increased.

No measurements of molecular conductivity are available, but it is more than probable that the same explanation would apply here as in the case of the alcohols. The compounds formed were found to be $CH_3COOC_2H_5HBr$, $(CH_3COOC_2H_5)_2(HBr)_5$ and $CH_3COOC_2H_5(HBr)_4$.[2]

Table VI shows the values obtained for the molecular weight of ether.

In dilute solutions the ether seems to be associated 1.2 times. The molecular weight is constant until a concentration of 1.5% has been reached where the amount of association increases slightly, and then gradually decreases with increasing concentration indicating increased dissociation.

[1] Archibald. *Loc. cit.*

[2] *Loc. cit.*

TABLE V.—ETHYL ACETATE. $K = 103.1$.
M. W. = 88.
G = 78.4 grams.

g.	Δ.	M.	M'.
0.102	0.167	80.6	80.6
0.321	0.483	87.4	91.0
0.483	0.683	93.0	106.6
0.661	0.842	113.3	147.6
1.035	1.105	123.3	187.1
1.353	1.305	136.5	209.1
1.683	1.494	148.3	230.3
2.051	1.855	145.5	134.3
2.401	2.202	143.3	132.5
2.605	2.457	139.5	107.5

G = 68.2 grams.

g.	Δ.	M.	M'.
0.176	0.317	83.9	83.9
0.334	0.520	97.0	117.6
0.569	0.804	106.8	125.0
0.845	1.131	112.8	127.5
1.013	1.302	117.4	148.6
1.217	1.400	131.2	312.0
1.475	1.629	136.7	170.7
1.845	2.023	137.8	142.0
2.192	2.389	138.5	143.2
2.619	2.939	134.2	115.8
2.930	3.451	128.0	91.1
3.030	3.656	122.0	73.2

TABLE VI.—ETHYL ETHER. $K = 103.1$.
M. W. = 74.
G = 75.4 grams.

g.	Δ.	M.	M'.
0.177	0.278	87.2	87.2
0.340	0.522	89.1	91.2
0.501	0.785	87.3	83.7
0.712	1.123	86.5	84.6
0.832	1.301	87.3	92.4
1.157	1.712	92.3	117.6
1.361	1.872	99.4	189.5
1.624	2.303	96.4	90.7
1.797	2.546	96.5	105.8
2.136	3.092	94.3	91.5
2.376	3.556	91.1	76.3
2.481	3.891	89.3	65.7

G = 59.5 grams.

g.	Δ.	M.	M'.
0.304	0.612	86.1	86.1
0.480	0.962	86.6	.87.2
0.609	1.203	87.8	92.8
0.755	1.372	85.5	150.0
0.936	1.611	100.8	131.4
1.125	2.009	97.1	82.2
1.226	2.223	95.6	81.0
1.542	2.789	95.6	95.7
1.759	3.203	94.9	90.1
1.909	3.525	93.5	79.9
2.286	4.241	93.0	90.4

No conductivity measurements are available here. Ether forms the compounds $(C_2H_5)_2O.HBr$ and $(C_2H_5)_2O.(HBr)_2$.

Acetone in solution gives the values for the molecular weight shown in Table VII.

The association in dilute solutions is quite marked, and is equal to 1.5, increasing quite rapidly until a concentration of 2.2% has been reached, where the amount of association is 3. With increasing concentration the molecular weight gets steadily less, showing that the dissociation is greatly increased. The only compound formed was found to be $C_3H_6O.HBr$.

Table VIII gives the results obtained with acetic acid.

In this case it was difficult to obtain concordant results on account of the high freezing point of the acid, which caused the drop coming in contact with the thermometer or stirrer to solidify immediately. The hydrogen bromide was rotated as far as possible up the sides of the tube to dissolve any adhering particles.

The association here is very marked and in dilute solutions is almost equal to 2. The association increases rapidly with concentration, having a value of nearly 5 at a concentration of 3%. Until this concentration is attained there seems to be no tendency for the dissociation to exceed

the association. Acetic acid forms a compound[1] with hydrobromic acid, but the ratio of the two acids has not been obtained with certainty.

TABLE VII.—ACETONE. K = 103.1.
M. W. = 58.
G = 71.6 grams.

g.	Δ.	M.	M'.
0.172	0.340	72.9	72.9
0.362	0.540	96.7	137.1
0.570	0.683	120.2	208.8
0.944	0.937	145.2	212.2
1.127	1.056	153.9	221.7
1.497	1.230	175.5	306.0
1.891	1.551	175.5	176.7
2.208	1.908	166.8	127.7

G = 63.1 grams.

g.	Δ.	M.	M'.
0.190	0.301	100.3	100.3
0.466	0.580	131.4	167.3
0.844	0.853	161.9	226.3
1.182	1.079	178.2	244.2
1.383	1.246	181.4	197.3
1.681	1.565	175.5	153.1
1.958	1.886	170.0	141.0
2.186	2.259	158.4	99.9
2.374	2.598	149.2	90.7
2.760	3.377	133.3	80.3

TABLE VIII.—ACETIC ACID. K = 103.1.
M. W. = 60.
G = 72.8 grams.

g.	Δ.	M.	M'.
0.286	0.321	126.4	126.4
0.659	0.484	192.9	324.1
1.230	0.643	270.6	511.5
1.825	0.828	311.4	453.2

G = 70.0 grams.

g.	Δ.	M.	M'.
0.222	0.314	104.2	104.2
0.455	0.597	114.5	126.1
0.745	0.724	154.4	337.8
1.137	0.851	199.7	456.9
1.477	0.940	234.2	563.0
1.862	1.050	264.2	516.2
2.152	1.146	280.0	446.0

The molecular weights of paraldehyde and acetaldehyde are shown in Table IX.

The paraldehyde compound even in dilute solutions seems to be dissociated to a considerable extent and the dissociation increases with concentration. There seems to be no tendency to association, which is to be expected as the paraldehyde is already associated.

The results with acetaldehyde are interesting since the molecular weights found agree well enough with those obtained for the paraldehyde to show that the acetaldehyde is at once polymerized to paraldehyde by the hydrogen bromide.

Table X shows the results obtained with bromine as the solute.

They prove that bromine is soluble in liquid hydrobromic acid, and that the bromine behaves normally, showing no tendency to association or dissociation. It seems to be a simple case of solution, the bromine existing as Br_2 and probably not uniting with the solvent.[2]

Maass and McIntosh[3] found bromine to be insoluble in liquid hydrogen bromide, probably on account of the frozen bromine taking a measurable time to dissolve. Beckmann and Waentig[3] also found bromine only

[1] THIS JOURNAL, **30**, 1103 (1908).
[2] Compare chlorine and hydrochloric acid, *Loc. cit.*
[3] *Loc. cit.*

TABLE IX.—PARALDEHYDE. K = 103.1.

M. W. = 132.

G = 83.5 grams.

g.	Δ.	M.	M'.
0.174	0.209	103.0	103.0
0.350	0.415	104.2	105.3
0.599	0.769	95.8	86.1
0.737	0.983	92.3	79.6
1.083	1.451	91.9	91.5
1.462	2.141	84.2	67.8
1.916	2.967	79.6	67.9

G = 76.2 grams.

0.174	0.266	88.4	88.4
0.524	0.790	89.7	90.5
0.782	1.203	88.0	84.6
1.133	1.719	89.0	92.0
1.501	2.402	84.6	73.0
1.850	3.092	81.0	68.4
2.118	3.587	79.9	73.3

ACETALDEHYDE. M. W. = 44.

G = 73.3 grams.

0.173	0.250	97.3	97.3
0.382	0.566	94.8	92.9
0.568	0.866	92.5	87.4
0.854	1.339	89.8	85.2
1.130	1.800	88.3	84.3
1.584	2.489	89.6	92.7
1.892	3.013	88.3	82.1

TABLE X.—BROMINE. K = 103.1.

M. W. = 160.

G = 66.9 grams.

g.	Δ.	M.	M'.
0.217	0.225	148.5	148.5
0.347	0.360	148.0	147.7
0.493	0.504	150.3	155.6
0.814	0.777	161.0	181.0
1.123	1.023	168.7	193.0

G = 68.0 grams.

0.195	0.185	159.5	159.5
0.397	0.374	161.0	162.4
0.628	0.576	165.3	173.4
0.807	0.754	162.4	152.9

very slightly soluble in liquid hydrobromic acid, and to give it a light brown color. On the other hand two Dutch investigators, whose paper we have unfortunately misplaced, have plotted the freezing-point curve, bromine—hydrogen bromide, and have found the bromine readily soluble in the liquefied acid. We found it quite soluble and also that the color of the solution changed from light brown to deep red with increasing concentration.

TABLE XI.

	Dilution.	Asso-ciation.	Mol. conduc-tivity × 10⁴.		Dilution.	Asso-ciation.	Mol. conduc-tivity × 10⁴.
C₂H₅OH	5.00	2.35	0.502	C₂H₆O	5.00	2.26	0.34
	3.33	2.35	0.605		3.33	2.50	0.77
	2.00	2.47	1.002		2.00	3.07	1.40
	1.66	2.44	1.310		1.66	3.13	2.32
	1.25	2.30	2.464		1.35	3.03	3.24
	1.00	2.22	4.650		1.07	2.90	4.30
CH₃OH	5.00	3.38	0.685	CH₃COOH	5.00	2.00	18.4
	3.33	3.38	0.820		3.33	2.50	44.8
	2.00	3.39	1.660		2.00	3.30	123.0
	1.66	3.50	2.385		1.66	4.00	171.0
	1.25	3.45	4.710		1.25	5.00	252.0
	1.00	3.53	9.250				

Summary.

We have learned something of the molecular complexity of the substances used when dissolved in liquid hydrogen bromide. With the exception of paraldehyde, which is already associated, all the substances forming compounds with the solvent were found to be both associated and dissociated, the amount of association varying very much according to the substances used. Up to the present, no method has been devised for measuring the amount of dissociation of these substances in solution, so that the true amount of association cannot be found. In dilute solutions, however, the amount of association as found will be very nearly correct because of the low value of the molecular conductivity in these solutions.

The relationship between the amount of association and the molecular conductivity seems to agree with the theory enunciated. Figures for the molecular conductivities of ethyl and methyl alcohol,[1] acetic acid,[2] and acetone[3] in liquid hydrogen bromide alone are available, and, as shown by Table XI, the solutes showing the greatest amount of association in solution have the greatest molecular conductivity. Acetic acid has an abnormally high conductivity. This may be due to the presence of hydrogen ions as well as the complex ions. Except in dilute solutions it also shows the greatest tendency to association.

A comparison of the properties of ether, alcohol, etc., dissolved in liquid chlorine with the same compounds in hydrobromic acid can now be made. Oxonium compounds are formed in both cases, and a study of the slopes of the freezing curves in systems such as hydrobromic acid—ether and chlorine—ether shows that in solution these compounds are largely broken down into their constituents. Solutions in chlorine, however, are non-conductors, i. e., exhibit no electrolytic dissociation. The determination of molecular weights in this solvent made recently by P. Waentig and one of us[4] show normal results for ether over a considerable concentration, while methyl and ethyl alcohol are greatly polymerized. We have, then, complex systems where the compounds are partially broken down into their constituents further complicated by association and in some cases, electrolytic dissociation. It seems impossible at present to assign these three factors their proper proportion, and to give formulae to the oxonium compounds.

The increase in complexity in solution shown by the increasing values of the molecular weights and the rapid increase in molecular conductivity, points to the correctness of the view previously expressed,

[1] THIS JOURNAL, **29**, 665 (1907).

[2] *Ibid.*, **29**, 1415 (1907).

[3] *Loc. cit.*

[4] *Trans. Roy. Soc.*, Canada, **1915**.

that the ions are much more complex than would be expected from the oxonium theory.

UNIVERSITY OF BRITISH COLUMBIA,
VANCOUVER, CANADA.

THE DECOMPOSITION OF TETRATHIONATES IN ALKALINE SOLUTION AS A SOURCE OF ERROR IN CERTAIN IODINE TITRATIONS.[1]

BY ROBERT M. CHAPIN.

It has long been known that tetrathionates are not stable. Particularly has Gutmann[2] shown that sodium tetrathionate rapidly reacts with moderately concentrated hot caustic soda to form sodium thiosulfate and sodium sulfite. But that the reaction might progress with significant rapidity in cold and dilute solutions seems to have remained unsuspected; at any rate, no allowance is made for such a possibility in certain methods of quantitative analysis. For example, it is a very common procedure to determine arsenic in a variety of materials by some modification of the process described by Williamson.[3] Iodine resulting from the use of hydriodic acid as a reducing agent is removed by sodium thiosulfate, following which the solution is in practice frequently rendered decidedly alkaline before being brought to the proper condition for titration.

Some time ago, following the official directions of the Assoc. Offic. Agr. Chemists[4] for the estimation of "total arsenious oxide" in insecticides and fungicides, the writer became impressed with the fact that the method, as laid down, did not afford the uniformly accurate results promised by the theory of the process. He found that substitution of sodium sulfite for thiosulfate as a discharging agent for iodine produced a distinct improvement in results and acted accordingly in work[5] in which accuracy was particularly necessary. Later, incidental to other work,[6] he showed that tetrathionates are in fact rather rapidly affected by exposure at room temperature to comparatively low concentrations of hydroxyl ions. The purpose of the present paper is to extend these observations sufficiently to form a guide to correct procedure in iodometric methods, etc., involving the conditions outlined.

Tetrathionate solution (0.0519 N) was prepared by titrating iodine

[1] Published by permission of the Secretary of Agriculture.
[2] *Ber.*, **40**, 3614 (1907).
[3] Sutton, "Volumetric Analysis," 10th Edition, p. 156.
[4] Bur. of Chemistry, *Bull.* **107** (Revised), Reprint January 18, 1912, p. 25.
[5] *J. Ind. Eng. Chem.*, **6**, 1002 (1914).
[6] *Ibid.*, **8**, 151 (1916).