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The Halogen Hydrides as Conducting Solvents. Part I. The Vapour Pressures, Densities, Surface Energies and Viscosities of the Pure Solvents. Part II. The Conductivity and Molecular Weights of Dissolved Substances. Part III. The Transport Numbers of Certain Dissolved Substances. Part IV. The Abnormal Variation of Molecular Conductivity, etc.

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IV. *The Halogen Hydrides as Conducting Solvents. Part I.—The Vapour Pressures, Densities, Surface Energies and Viscosities of the Pure Solvents. Part II.—The Conductivity and Molecular Weights of Dissolved Substances. Part III.—The Transport Numbers of Certain Dissolved Substances. Part IV.—The Abnormal Variation of Molecular Conductivity, etc.*

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PART I.

The Vapour Pressures, Densities, Surface Energies and Viscosities of the Pure Solvents. *By* D. McIntosh *and* B. D. Steele.

Although our knowledge of the ionising power of non-aqueous solvents has been considerably increased during recent years by the investigations of Walden, Franklin, Kahlenberg, and others, the liquefied halogen hydrides and sulphuretted hydrogen have received little or no attention.

Gore ('Phil. Mag.' (4), 29, p. 54), who experimented at ordinary temperatures, found that the hydrides of chlorine, bromine, and iodine were very feeble conductors. Bleckrode ('Pog. Ann.' (2), 23, p. 101) stated that hydrogen bromide conducts slightly; while Hittorf ('Pog. Ann.' (2), 3, p. 161, 4, p. 374, considered these substances to be non-conductors.

With regard to their behaviour as solvents, Skilling ('Amer. Ch. Jl.,' 1901, 26, p. 383) found that at ordinary temperatures sulphuretted hydrogen dissolves potassium chloride freely; but that the solution is a non-conductor of electricity. Helbig and Fausti ('Zeit. für angewandte Chemie,' 1904, 17) state that stannic chloride is soluble in hydrogen chloride, but that this solution also is a non-conductor.

As it seemed highly improbable to us that sulphuretted hydrogen, which is analogous to water in so many ways, should be devoid of dissociating power, we decided to investigate its solvent action systematically, and at the same time to examine the hydrides of chlorine, bromine, iodine, and phosphorus.

Preliminary Experiments.

It has been found, as a result of our preliminary experiments, that water and all the ordinary metallic salts which were tried are insoluble, or very sparingly soluble, in any of the solvents.

Hydrogen chloride and bromide are freely soluble in hydrogen sulphide, and hydrogen sulphide in hydrogen bromide.

The salts of the organic ammonium bases are soluble in hydrogen chloride, bromide, iodide, and sulphide, and the resulting solutions conduct the current. Certain ammonium salts also yield very feebly conducting solutions. Two metallic salts, namely, sodium acetate and potassium cyanide, were, at first, thought to be soluble, as their addition to the solvent greatly increased its conductivity. This has since been found to be due to decomposition of these salts into acetic acid and hydrocyanic acid respectively. Both of these acids are soluble in the foregoing solvents.

No substance has yet been found which will dissolve in phosphine and yield a conducting solution.

A few preliminary measurements of the conductivity were made, and in every case the molecular conductivity diminished considerably with dilution, instead of increasing as it does in aqueous solutions. The results of these measurements are given in Part II., which contains a detailed account of the measurements of solubility and of conductivity.

After we had ascertained that the hydrides of chlorine, bromine, iodine, and sulphur can act as conducting solvents, we proceeded to the measurement of the following physical constants of each of the pure substances :—

(1) The vapour-pressure curve ;
(2) The density and its temperature coefficient ;
(3) The surface energy and its temperature coefficient ;
(4) The viscosity and its temperature coefficient.

The results of these measurements are described in the following pages.

Preparation of Liquefied Gases.

Hydrogen chloride was prepared by the action of sulphuric acid on pure sodium chloride. The gas was dried by passing it through two wash bottles containing sulphuric acid, and afterwards through a tube containing phosphoric anhydride. It was then led into a receiver which was maintained at −100°, by means of carbon dioxide and ether, under diminished pressure. At this temperature the gas liquefied rapidly, forming a colourless mobile liquid. This was re-distilled before being used for the measurements.

The hydrogen bromide was prepared by the action of bromine on red phosphorus suspended in water. Traces of bromine were removed by passing the gas through a thin paste of amorphous phosphorus and a saturated solution of hydrogen bromide. The gas was then dried by passing it over about 40 centims. of phosphoric anhydride, and, in order to remove impurities other than water-vapour, it was passed through two U-tubes surrounded by solid carbon dioxide, in each of which a small quantity of liquefied gas soon collected. The gas bubbled through this liquid, which was thus submitted to a process of fractional distillation. It was finally condensed in a vessel surrounded by a mixture of carbon dioxide and ether.

The hydrogen iodide was made by the action of iodine and water on amorphous phosphorus, in a similar manner to that employed for the preparation of hydrogen bromide, and similar means were used to purify it. The liquid was invariably coloured, and it could not be obtained quite colourless even by repeated distillation.

The hydrogen sulphide was prepared by the action of dilute sulphuric acid on ferrous sulphide. The gas was washed by passing it through water, dried by passage over phosphoric anhydride, and condensed by means of carbon dioxide and ether. It was purified by distillation.

Phosphuretted hydrogen was prepared by the action of a solution of potassium hydroxide on phosphonium iodide. It was dried by means of phosphoric anhydride and condensed in a receiver which was immersed in liquid air.

The Constant-temperature Bath.

The constant-temperature bath consisted of ether which was contained in a vacuum vessel and cooled by liquid air. The temperature was measured by a constant-volume hydrogen thermometer, similar to that described by TRAVERS, SENTER, and JAQUEROD ('Phil. Trans.,' 1902, A, 200, pp. 105–180). The arrangement of the apparatus is shown in fig. 1, in which C represents the hydrogen thermometer, A the large vacuum vessel containing the ether, and B a large vacuum flask containing liquid air. The bulb, *a*, of the thermometer was connected to the dead space of the manometer by a fine capillary tube. A mercury reservoir was attached to the stop-cock *k* by rubber tubing, and by raising or lowering this reservoir the mercury in the dead space could be adjusted to the level of the glass point *c*.

The volume of the thermometer bulb and dead space was carefully determined by calibration with mercury. The constants were volume of—

(1) Bulb and portion of stem within the liquid = 17·480 cub. centims. at 0°;
(2) Stem from *s* to surface of ether = 0·1358 cub. centim.;
(3) Dead space and stem to mark *s* = 0·5719 cub. centim.

It has been assumed, in making our calculations, that the average temperature of the section (2) was midway between that of the bath and that of the atmosphere; an error of a few degrees in the temperature of this section is without influence on the bath temperatures, which are given only to the nearest tenth of a degree.

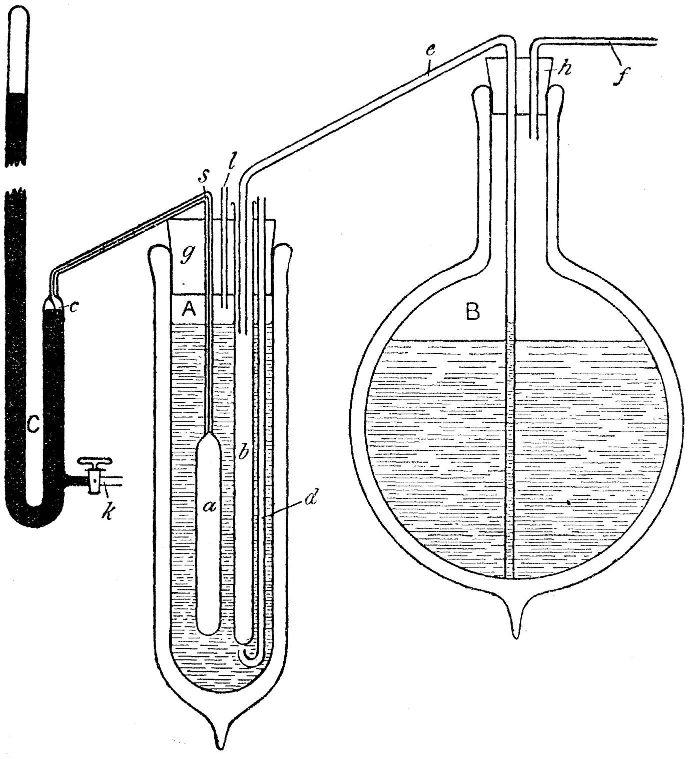

Fig. 1.

The vacuum vessel A was closed by a large indiarubber stopper, through which holes had been cut to allow the passage of the stem of the thermometer, the apparatus containing the liquefied gas, and the tubes *b*, *d*, and *l*.

The closed tube *b* was about 7 millims. in diameter and long enough to reach nearly to the bottom of the vessel. The tube *d* was placed so that its open end came immediately under the tube *b*.

The large vacuum flask B was fitted with tubes as shown in the diagram, so that by blowing into *f* liquid air could be forced into the tube *b*.

In order to obtain any desired temperature between that of the room and the melting-point of ether (−117°) the vessel A was filled with ether, and the tube *d* connected to an air blast, by means of which the liquid was continuously and uniformly stirred, the air escaping through the tube *l*, which was provided for the purpose.

After mercury had been taken out of the manometer through *k*, the ether was cooled by blowing liquid air from B into *b*, where it rapidly boiled away. When the temperature of the bath had been adjusted, it could be kept constant for as long as was desired by blowing liquid air in very small quantities into *b*.

The deposition of dew on the walls of the vacuum vessel A was prevented by placing it inside a wider cylindrical glass vessel containing phosphoric anhydride.

The Vapour-pressure Curves.

In order to measure the vapour-pressure, a tube containing the liquid was immersed in the bath and simultaneous observations of the temperature and corresponding vapour-pressure were taken.

This simple arrangement could not be used with hydrogen bromide and iodide on account of the action of these gases on the mercury of the manometer. The errors due to this action were avoided by the use of a special form of apparatus which is shown in fig. 2.

To use this apparatus, the tube *m* was attached to the pump, and the bulb *a* placed in the low-temperature bath, after which the whole apparatus was exhausted to a pressure of about 60 millims. and the stop-cock *h* closed.

The outer portion of the apparatus was completely exhausted and the stop-cock *g* closed. A vessel containing the liquefied gas was then attached to *n* by rubber tubing, the point *l* broken within the tube, and as soon as a sufficient quantity of liquid had distilled into the bulb *a* the apparatus was sealed off at *k*.

Before making any measurements the stop-cock *g* was opened for a few moments, and all traces of air were displaced from the tube by allowing a small quantity of liquid to evaporate into the pump.

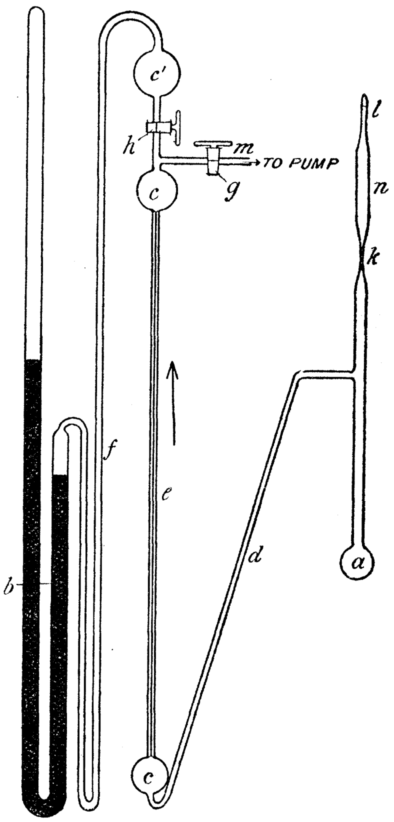

Fig. 2.

The bath was cooled to the lowest temperature at which observations were to be taken, and the stop-cock *h* opened. As the vapour-pressure of hydrogen bromide and of hydrogen iodide, even at the lowest temperatures employed, was greater than 60 millims., a flow of gas from *c* into *c*′ followed, and continued until the pressure in the manometer became equal to the vapour-pressure of the liquid. As soon as the pressure ceased to rise, the temperature and pressure were read and the stop-cock *h* was immediately closed. The temperature was then raised to the next point of observation, and the stop-cock *h* again opened, until the pressure in the manometer became constant, when readings were again taken and the stop-cock closed.

In this way a succession of readings was obtained without the hydrogen generated by the action of the gas on the mercury of the manometer finding its way into the bulb *a*. As a precaution against diffusion, the bulbs *c*, *c* and the capillary tube *e* were introduced, the stop-cock *g* being opened after each observation and the contents of the bulbs *c* and *c* withdrawn through the pump.

The formation of hydrogen was reduced to a minimum by the device of leaving in the manometer a small quantity of air, which prevented the hydrogen bromide (or iodide) from reaching the surface of the mercury until a considerable time had elapsed.

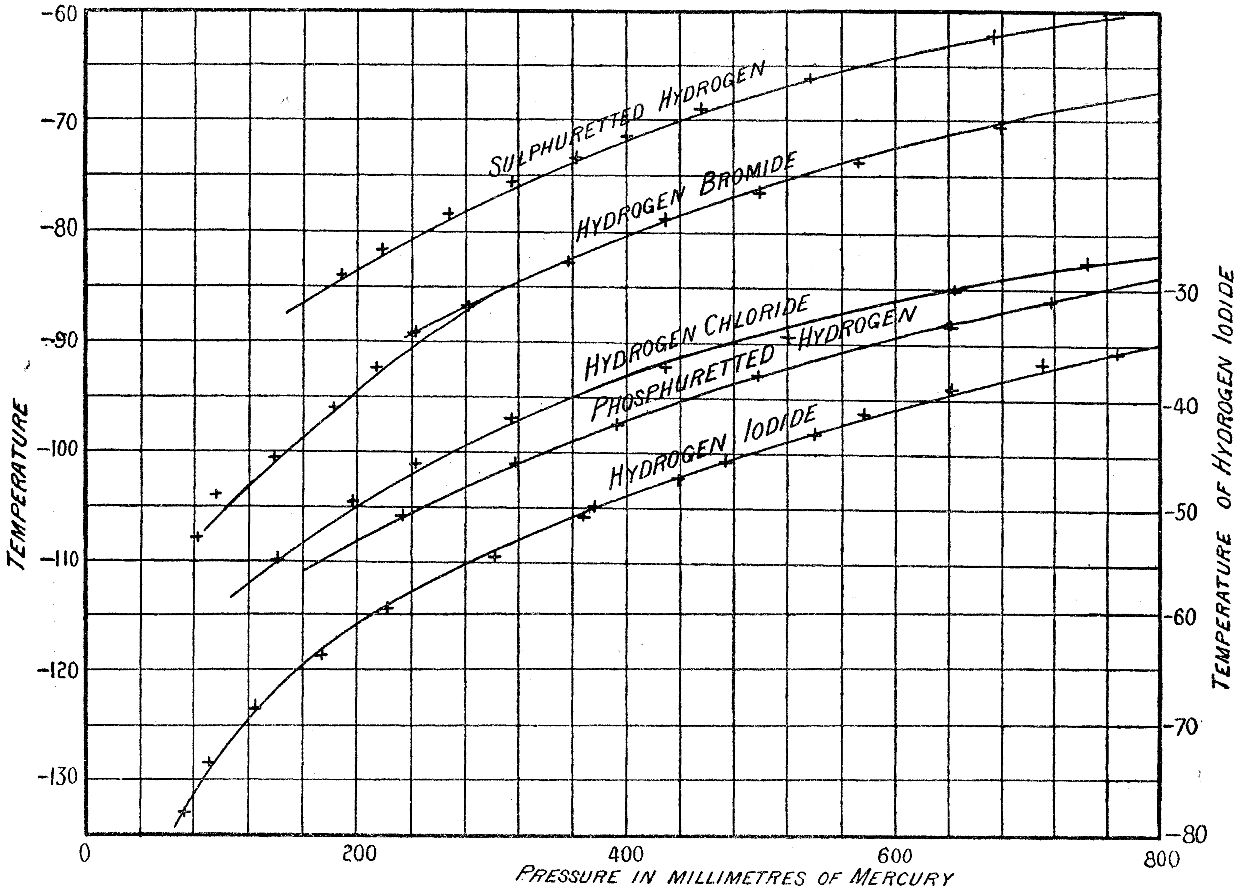

Fig. 3.

The results of the measurements are collected in Table I., which contains the experimental (a) and smoothed (b) values of the vapour-pressure for each of the liquefied gases.

In the case of hydrogen bromide and iodide the measurements have been continued considerably below the melting-point, and the vapour-pressure curve both for solid and for liquid are given in fig. 3. It will be noticed that the change in curvature at the melting-point is very slight both for hydrogen bromide and for hydrogen iodide.

The melting- and boiling-points found by us for the pure substances are given in Table II., together with recent measurements by other observers.

TABLE I.

Temperature.	Vapour pressure.		Temperature.	Vapour pressure.	
	a.	*b.*		*a.*	*b.*
° C.	millims.	millims.	° C.	millims.	millims.
HYDROGEN CHLORIDE.					
−80·0	—	896	−95	—	363
−80·5	868	—	−96	—	343
−81	—	851	−97	—	323
−82	—	808	−97·2	316	—
−83	—	764	−98	—	304
−83·2	748	—	−99	—	287
−84	—	718	−100	—	270
−85	—	673	−101	—	254
−85·9	648	—	−101·3	245	—
−86	—	632	−102	—	238
−87	—	594	−103	—	225
−88	—	557	−104	—	210
−89	—	552	−104·5	198	—
−89·8	522	—	−105	—	196
−90	—	493	−106	—	184
−91	—	463	−107	—	173
−92	—	435	−108	—	162
−92·9	430	—	−109	—	149
−93	—	410	−109·9	141	—
−94	—	385	−110	—	138
HYDROGEN IODIDE.					
−35	—	783	−56	—	274
−35·9	769	—	−57	—	258
−36	—	750	−58	—	244
−36·9	713	—	−59	—	230
−37	—	718	−59·5	224	—
−38	—	686	−60	—	218
−39	—	657	−61	—	206
−39·4	644	—	−62	—	194
−40	—	628	−63	—	183
−41	—	600	−63·5	185	—
−41·7	578	—	−64	—	173
−42	—	573	−65	—	162
−43	—	547	−66	—	152
−43·5	530	—	−67	—	143
−44	—	519	−68	—	134
−45	—	494	−68·4	126	—
−46	—	471	−69	—	126
−47	—	448	−70	—	118
−47·7	438	—	−71	—	111
−48	—	425	−72	—	103
−49	—	404	−73	—	97
−50	376	—	−73·5	92	—
−51	—	364	−74	—	90
−52	—	343	−75	—	84
−53	—	325	−76	—	79
−54	—	307	−77	—	73
−54·8	303	—	−77·9	74	—
−55	—	289	−78	—	70

Table I. (continued).

Temperature.	Vapour pressure.		Temperature.	Vapour pressure.	
	a.	b.		a.	b.
° C.	millims.	millims.	° C.	millims.	millims.
			Hydrogen Bromide.		
–65	—	—	–87	—	283
–66	—	891	–87·1	284	—
–67	—	835	–88	—	266
–68	—	785	–89	—	259
–68·4	775	—	–89·3	245	—
–69	—	743	–90	—	247
–70	—	704	–91	—	239
–70·7	682	—	–92	—	222
–71	—	671	–92·8	214	—
–72	—	635	–93	—	214
–73	—	609	–94	—	204
–74	575	—	–95	—	195
–75	—	546	–96	—	187
–76	—	519	–96·3	185	—
–76·7	501	—	–97	—	177
–77	—	483	–98	—	167
–78	—	468	–99	—	157
–79	—	445	–100	—	147
–79·3	431·5	—	–100·7	142	—
–80	—	423	–101	—	136
–81	—	402	–102	—	125
–82	—	381	–103	—	114
–83	357	—	–104	—	102
–84	—	340	–104·2	96	—
–85	—	321	–105	—	90
–86	—	302			
			Sulphuretted Hydrogen.		
–60	—	770	–74	—	345
–61	—	724	–75	—	326
–62	—	682	–75·6	314	—
–62·2	676	—	–76	—	309
–63	—	644	–77	—	292
–64	—	607	–78	—	276
–65	—	573	–78·4	270	—
–66	—	541	–79	—	261
–66·1	538	—	–80	—	246
–67	—	513	–81	—	232
–68	—	484	–81·7	220	—
–69	—	458	–82	—	218
–69·1	456	—	–83	—	205
–70	—	432	–84	193	—
–71	—	409	–85	—	181
–71·6	400	—	–86	—	169
–72	—	384	–87	—	158
–73	—	364	–88	—	148

TABLE I. (continued).

Temperature.	Vapour pressure.		Temperature.	Vapour pressure.	
	a.	b.		a.	b.
° C.	millims.	millims.	° C.	millims.	millims.
		PHOSPHURETTED HYDROGEN.			
−86	—	770	− 97	—	403
−86·6	719	—	− 97·7	393	—
−87	—	716	− 98	—	382
−88	—	668	− 99	—	362
−88·6	644	—	−100	—	342
−89	—	630	−101	—	324
−90	—	595	−101·2	319	—
−91	—	563	−102	—	305
−92	—	531	−103	—	287
−93	—	503	−104	—	269
−93·1	498	—	−105	—	253
−94	—	473	−105·9	237	—
−95	—	448	−106	—	235
−96	—	425			

TABLE II.

		HCl.	HBr.	HI.	H_2S.	PH_3.
Melting-point	*	—	−86	−50·8	—	—
	†	−111·1	−88·5	−50·8	—	—
	‡	−111·3	−86·1	−51·5	−82·9	—
	§	—	—	—	—	—
Boiling-point	*	− 82·9	−68·7	−35·7	−60·2	86·4
	†	− 83·7	−64·9	34·1	—	—
	‡	− 83·1	−68·1	36·7	60·4	—
	§	—	—	—	—	−85

* McINTOSH and STEELE.

† ESTREICHER, 'Zeit. Phys. Chem.,' 1896, 20, p. 605.

‡ LADENBERG and KRÜGEL, 'B. B.,' 1900, 33, p. 637.

§ OLSZEWSKI, 'Monatshefte für Chemie,' 7, p. 371.

Heats of Evaporation.

CLAUSIUS has shown that the heat of vaporisation of a liquid can be calculated from the equation

$$\frac{dp}{dT} = \frac{PW}{RT^2},$$

in which $\frac{dp}{dT}$ represents the change of vapour-pressure with temperature, P the pressure, T the absolute temperature, R the constant of the gas equation, and W the latent heat of evaporation of one gram-molecule of the liquid.

The values of W at a pressure of 760 millims., as calculated from our vapour-pressure curves, are

for hydrogen chloride,	$14 \cdot 8 \times 10^{10}$ ergs,
,, ,, bromide,	$17 \cdot 4 \times 10^{10}$,,
,, ,, iodide,	$20 \cdot 7 \times 10^{10}$,,
,, ,, sulphide,	$19 \cdot 3 \times 10^{10}$,,
,, phosphuretted hydrogen,	$17 \cdot 2 \times 10^{10}$,,

We can find no account of any direct determination of W for these substances.

The Measurement of Density.

The apparatus (fig. 4) employed for these measurements consisted of a bulb with a graduated capillary stem, to which a two-way stop-cock *c* was attached.

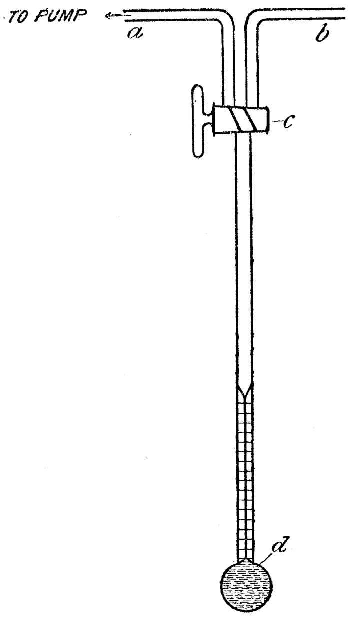

Fig. 4.

The bulb had a capacity of about 1·5 cub. centim., and its volume and that of each division of the stem was accurately determined by calibration with mercury. After the tube *a* had been sealed to the pump, and the apparatus exhausted, it was immersed in the constant-temperature bath. The tube *b* was then connected to a vessel containing the liquefied gas, which was distilled into the bulb until both bulb and stem were completely filled. The stop-cock was turned and the liquid allowed to evaporate into the pump until the meniscus had come to a definite position on the stem, when the stop-cock was turned so as to disconnect all the tubes. To obtain the volumes occupied by a constant weight of liquid, it was only necessary to read the position of the meniscus at different temperatures.

The weight of liquid was obtained by attaching to the tube *b* a weighed set of Geissler's bulbs containing potassium hydrate solution.

On opening the stop-cock and raising the temperature of the bath the liquid evaporated and the gas was absorbed in the bulbs and weighed.

To prevent the potash solution sucking back, a little mercury was placed in the first bulb. The small amount of gas remaining in the apparatus was finally pumped out through *a* and measured.

The numbers obtained by the foregoing method have been checked in the case of hydrogen chloride, hydrogen bromide, and hydrogen iodide by distilling each of them into a thick-walled bulb of known volume, and sealing it. After the bulb containing the liquid had been weighed it was cooled, the stem broken, and the empty bulb and stem again weighed.

The densities so obtained agreed to the 3rd decimal place with those obtained at the same temperature by the first method.

In the case of phosphine the density was determined by the second method and the temperature coefficient by the first method.

The results of the measurements are given in Table III., in which D′ represents the experimental and D the smoothed value of the density. The density in each case is a linear function of the temperature and is given by the relation

$$D_{T'} = D_T[1+\alpha(T-T')],$$

where T and T′ represent the boiling-point and the temperature of observation respectively, both on the absolute scale; D_T and $D_{T'}$ being the corresponding densities.

The values of the coefficient α for the different substances are contained in the following table :—

HCl	$D_{T'} = 1\cdot187\,[1+\cdot000268\,(T-T')]$
HBr	$D_{T'} = 2\cdot157\,[1+0\cdot0041\,(T-T')]$
HI	$D_{T'} = 2\cdot799\,[1+0\cdot0043\,(T-T')]$
H_2S	$D_{T'} = 0\cdot964\,[1+0\cdot00169\,(T-T')]$
PH_3	$D_{T'} = 0\cdot744\,[1+0\cdot0008\,(T-T')]$

TABLE III.—Densities.

T (abs.).	D.	D′.	T (abs.).	D.	D.
° abs.			° abs.		
		HYDROGEN CHLORIDE.			
164·0	1·257	—	180	1·213	—
166	1·251	—	180·1	—	1·2127
168	1·246	—	182	1·207	—
168·5	—	1·2438	183·2	—	1·2038
170	1·240	—	184	1·201	—
171·8	—	1·2347	186	1·196	—
172	1·234	—	187·2	—	1·1937
174	1·229	—	188	1·190	—
175·8	—	1·2242	189·9	—	1·1842
176	1·224	—	190	1·185	—
178	1·218	—	192	1·179	—

TABLE III.—Densities (continued).

T (abs.).	D.	D′.	T (abs.).	D.	D′.
° abs.			° abs.		
		HYDROGEN BROMIDE.			
182	2·245	—	195·3	—	2·1932
184	2·237	—	196	2·191	—
184·7	—	2·2337	198	2·183	—
186·0	—	2·2286	198·2	—	2·1823
186	2·229	—	200	2·176	—
188	2·222	—	200·4	—	2·1742
190	2·214	—	202	2·168	—
192	2·206	—	203·8	—	2·1600
193·3	—	2·2047	204	2·160	—
194	2·199	—			
		HYDROGEN IODIDE.			
222	2·863	—	232	2·822	—
223·3	—	2·8600	232·9	—	2·819
224	2·855	—	234	2·813	—
224·9	—	2·8496	236	2·805	—
226	2·847	—	236·3	—	2·8034
227·0	—	2·8412	238	2·796	—
228	2·838	—	240	2·787	—
229·3	—	2·8330	240·4	—	2·7862
230	2·830	—	242	2·779	—
		HYDROGEN SULPHIDE.			
190	1·004	—	201·5	—	0·9846
191·3	—	1·0019	202	0·984	—
192	1·001	—	203·9	—	0·9806
194	0·998	—	204	0·980	—
194·6	—	0·9968	206	0·976	—
196	0·994	—	206·9	—	0·9759
197·4	—	0·9925	208	0·973	—
198	0·991	—	210	0·970	—
199·7	—	0·9875	210·8	—	0·9692
200	0·987	—	212	0·967	—
		PHOSPHURETTED HYDROGEN.			
166	0·761	—	180	0·750	—
167·1	—	0·7604	182	0·748	—
168	0·760	—	184	0·747	—
170	0·758	—	184·4	—	0·7465
171·8	—	0·7560	186	0·745	—
172	0·756	—	186·5	—	0·7448
174	0·755	—	188	0·743	—
175	—	0·7534	190	0·742	—
176	0·753	—	192	0·740	—
178	0·751	—	192·8	—	0·7392
179·9	—	0·7504	194	0·739	—

Kopp has shown that the molecular volume of a liquid at its boiling-point is an additive property, being equal to the sum of the atomic volumes of the component elements. Certain elements, however, such as oxygen, appear to possess two values for the atomic volume, depending on the nature of the linking of the oxygen to the other atoms in the molecule.

It has also been shown that, in the case of the elements chlorine, bromine, and sulphur, the atomic volumes calculated from the density of compounds containing them are the same as those obtained from the densities of the pure elements. We have calculated the atomic volumes of the elements chlorine, bromine, iodine, sulphur, and phosphorus from the densities of their respective hydrides, in order to see how the values so obtained agree with those given by Kopp and others.

The results of these calculations are given in Table IV., which contains D, the densities of the compounds at their respective boiling-points, the molecular volume M/D, and the atomic volume A′ of the halogen elements.

The values of these are invariably higher than those of Kopp, which are given under A, in the fifth column. It is possible that this discrepancy is due to a variation in the atomic volume of hydrogen, which has accordingly been calculated from each compound by subtracting the figures in the fifth column from those in the third.

The values for A, so obtained, are given in the last column, and are uniformly higher than 5·5, which is the number found from the study of organic compounds.

Table IV.—Molecular Volumes at Boiling-point.

Substance.	D.	M/D.	A′.	A, Kopp, &c.	A_h.
HCl	1·185	30·8	25·3	22·8	8·0
HBr	2·158	37·4	31·9	27·9	9·5
HI	2·799	45·7	40·2	37·8	7·9
H_2S	0·964	35·2	24·2	22·6	6·3
H_3P	0·743	45·7	29·2	21·9* 26·0†	8·0 6·6

* Masson. † Thorpe.

The Molecular Surface Energies.

The molecular surface energies were measured by Ramsay and Shields' method, slightly modified in order that the measurements might be made at low temperatures. The apparatus (fig. 5) consisted of a tube *b*, 6 centims. long and 1·3 centims. in diameter, which was provided with a small side tube *d*, and joined to a two-way stop-cock by a long tube *a*.

A small glass scale *s*, which had been very carefully calibrated, was securely fixed inside *b*. The capillary *c* was sealed to a long tube *g*, in the manner described by

Ramsay and Shields. The tube *g*, which enclosed a piece of soft iron, *i*, was selected so as to slide easily and smoothly in *a*. It was held in position by the two glass hooks *e* and *f*, which were placed so that when *f* was resting on *e* the bottom of the capillary was a few millimetres below the scale.

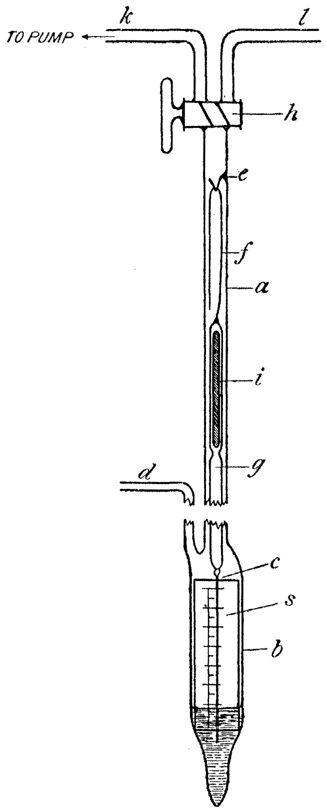

Fig. 5.

A mark had been previously etched on the capillary, and when making the measurements the position of the tube *g* was adjusted by means of an electro-magnet, so that this mark always coincided with the meniscus inside the capillary. The radius of the capillary near the etched mark was determined by introducing a quantity of pure ether into the apparatus, and measuring the height of the column of liquid when the capillary was in different positions. The radius could then be calculated from Ramsay and Shields' values for the surface energy of ether. The following values were found :—

Position of meniscus.	Height of ether column.	Radius.
	millims.	
At the mark	34·28	·013767
1·9 millims. below mark . .	34·29	·013763
0·4 ” ” ” . .	34·32	·013751
1·1 ” above ” . .	34·31	·013755
7·5 ” ” ” . .	34·57	·013652

To carry out the experiments, the apparatus was placed in the constant-temperature bath and exhausted through the tube *k*. The stop-cock *h* was then turned, and an excess of the liquid to be measured was introduced through the tube *l* by distillation. The stop-cock was again turned, and all traces of air were displaced from the apparatus by allowing some of the liquid to evaporate into the pump, after which the stop-cock was closed. The bath was then maintained successively at different temperatures, and the mark on the capillary having first been brought into coincidence with the meniscus, the height of the column of liquid was accurately measured.

The tube *d* was attached to a manometer, and measurements of the vapour-pressure of the liquid were made during the experiment. This tube was removed during the measurements of hydrogen bromide and hydrogen iodide.

The results of the measurements are given in Tables V. to IX., in which the letters employed have the following meaning:—

T = the absolute temperature;
D = the density of the liquid;
σ = the density of the vapour;
V = the specific volume of the liquid;
V.P. = the vapour-pressure of the liquid;
h = the height of the column of the liquid;
γ = surface tension in dynes per centimetre $= \frac{1}{2} rgh (D-\sigma)$;
$\gamma (MV)^{\frac{2}{3}}$ = the molecular surface energy in ergs;
g = the constant of gravity;
M = the molecular weight of the liquid.

Table V.—Hydrochloric Acid.

T (abs.).	D.	σ.	$D-\sigma$.	V.P.	h.	γ.	$(MV)^{\frac{2}{3}}$.	$\gamma (MV)^{\frac{2}{3}}$.
				millims.	centims.			
163·1	[1·2530]	0·00051	1·2525	141	3·303	27·874	9·4600	263·68
168·5	1·2438	0·00069	1·2431	198	3·214	26·912	9·5073	255·87
171·7	1·2347	0·00083	1·2339	245	3·152	26·251	9·5537	250·80
175·8	1·2242	0·00105	1·2232	316	3·094	25·477	9·6080	244·78
180·1	1·2127	0·00139	1·2113	430	3·033	24·718	9·6690	239·00
183·2	1·2038	0·00167	1·2021	522	2·974	24·046	9·7167	233·65
187·2	1·1937	0·00202	1·1917	648	2·936	23·467	9·7725	229·30
189·9	1·1842	0·00230	1·1819	748	2·866	22·760	9·8233	223·57
192·6	1·1770	0·00263	1·1744	868	2·838	22·409	9·8634	221·03

TABLE VI.—Hydrobromic Acid.

T (abs.).	D.	σ.	D $-$ σ.	V.P.	h.	γ.	$(MV)^{\frac{2}{3}}$.	$\gamma\,(MV)^{\frac{2}{3}}$.
				millims.	centims.			
181·8	[2·2400]	0·0015	2·2385	210	2·015	30·191	10·932	330·1
184·7	2·2337	0·0018	2·2319	250	1·990	29·728	10·953	325·6
186·1	2·2286	0·0019	2·2267	275	1·958	29·182	10·970	320·1
188·9	[2·2185]	0·0023	2·2158	327	1·926	28·570	11·014	314·6
193·4	2·2047	0·0028	2·2019	410	1·887	27·812	11·049	307·30
195·3	2·1932	0·0031	2·1901	430	1·830	27·019	11·087	299·6
198·2	2·1823	0·0035	2·1788	525	1·800	26·440	11·124	294·8
200·5	2·1742	0·0039	2·1703	600	1·790	26·201	11·152	292·2
203·9	2·1600	0·0047	2·1553	730	1·740	25·399	11·201	284·5

TABLE VII.—Hydriodic Acid.

T (abs.).	D.	σ.	D $-$ σ.	V.P.	h.	γ.	$(MV)^{\frac{2}{3}}$.	$\gamma\,(MV)^{\frac{2}{3}}$.
				millims.	centims.			
225·3	2·8523	0·0039	2·849	420	1·511	29·06	12·63	367·0
227·1	2·8401	0·0042	2·836	460	1·496	28·64	12·67	362·8
229·3	2·835	0·0045	2·831	503	1·479	28·26	12·69	358·6
230·9	2·829	0·0048	2·824	558	1·467	27·97	12·71	355·5
232·9	2·820	0·0053	2·815	595	1·451	27·57	12·73	351·0
235·0	2·812	0·0057	2·806	655	1·440	27·27	12·76	348·0
236·5	2·806	0·0061	2·800	700	1·427	26·96	12·78	344·6

TABLE VIII.—Sulphuretted Hydrogen.

T (abs.).	D.	σ.	D $-$ σ.	V.P.	h.	γ.	$(MV)^{\frac{2}{3}}$.	$\gamma\,(MV)^{\frac{2}{3}}$.
				millims.	centims.			
189·0	[1·006]	0·00055	1·006	192	4·962	33·418	10·458	349·5
191·3	1·002	0·00063	1·001	219	4·906	32·902	10·495	345·3
194·6	0·997	0·00076	0·996	269	4·816	32·126	10·522	338·0
197·4	0·992	0·00086	0·992	313	4·765	31·645	10·557	334·1
199·7	0·987	0·00098	0·986	363	4·695	31·020	10·584	328·3
201·5	0·985	0·00107	0·984	399	4·676	30·813	10·604	326·6
203·9	0·9806	0·00122	0·979	454	4·642	30·448	10·639	324·7
206·9	0·9759	0·00142	0·975	536	4·540	29·631	10·669	316·7
210·8	0·9692	0·00175	0·968	674	4·442	28·783	10·720	308·6

TABLE IX.—Phosphuretted Hydrogen.

T (abs.).	D.	σ.	D $-$ σ.	V.P.	h.	γ.	$(MV)^{\frac{2}{3}}$.	$\gamma\,(MV)^{\frac{2}{3}}$.
				millims.	centims.			
167·1	0·760	0·00079	0·7592	237	4·484	22·783	12·605	287·2
171·8	0·756	0·00101	0·7550	319	4·372	22·095	12·654	279·6
175·4	0·753	0·00122	0·7522	393	4·282	21·553	12·683	273·4
179·9	0·746	0·00151	0·7450	498	4·171	20·798	12·761	265·4

The foregoing results are represented graphically in fig. 6, in which the molecular surface energies are plotted against the absolute temperature.

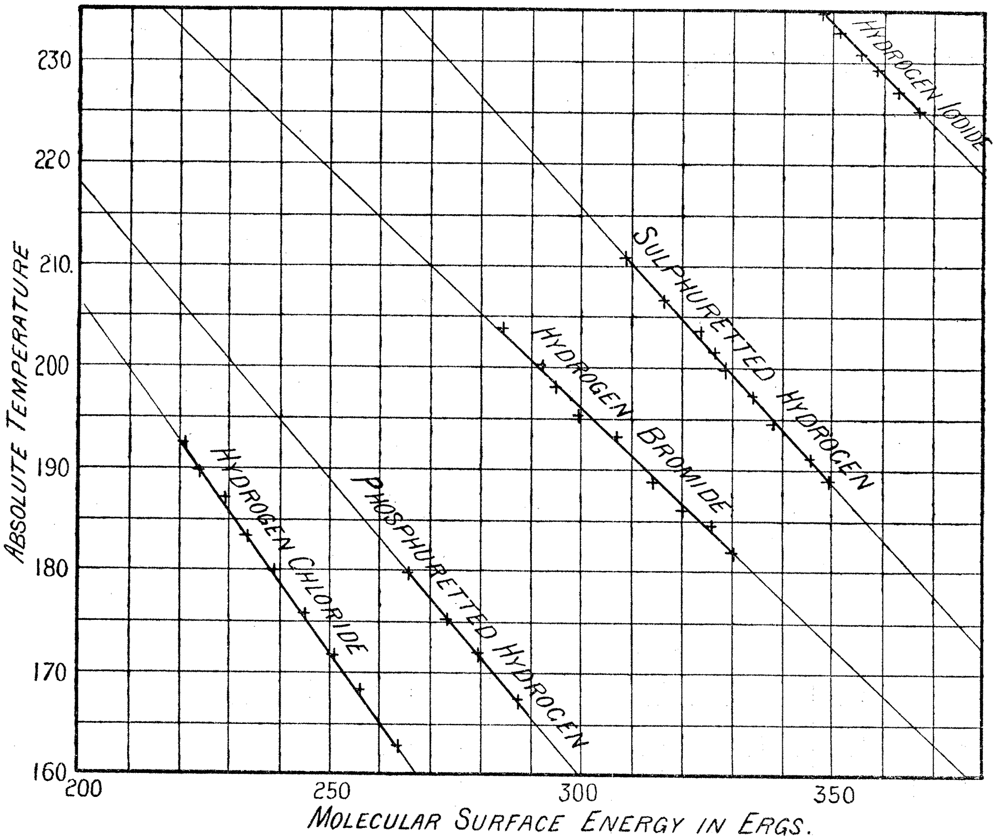

Fig. 6.

The range of temperature over which measurements were made was small, and in the case of each substance the curve appears to be a straight line.

The temperature coefficients $\frac{d}{dt}\gamma(\mathrm{MV})^{\frac{2}{3}}$ are given in Table X.

TABLE X.

Substance.	Temperature range.	$\frac{d}{dt}\gamma(\mathrm{MV})^{\frac{2}{3}}$.
Hydrogen iodide	225–236	1·99
" bromide . . .	181–204	2·03
" sulphide . . .	189–211	1·91
" phosphide . .	167–180	1·70
" chloride . . .	159–192	1·47

The average value of this coefficient is, according to Eötvös, 2·27. From the experiments of Ramsay and Shields it is 2·12, while Baly and Donnan have found that the liquefied gases oxygen, nitrogen and carbon monoxide give values very near to 2, and this number has also been found by us for the three substances hydrogen bromide, iodide and sulphide.

Ramsay and Shields have shown that for normal liquids the relation between molecular surface energy and temperature is given by the equation

$$\gamma(\mathrm{MV})^{\frac{2}{3}} = 2{\cdot}12(t-d),$$

in which t represents the temperature measured from the critical point and d is a small constant.

From this equation it follows that the surface energy disappears at a temperature d degrees below the critical point, and therefore the curve for a normal liquid, if produced, should cut the temperature axis at this point.

This is the case for hydrogen bromide, iodide and sulphide, for which, as will be seen from Table XI., the value of d is 16·3, 15·7 and 0·2 respectively.

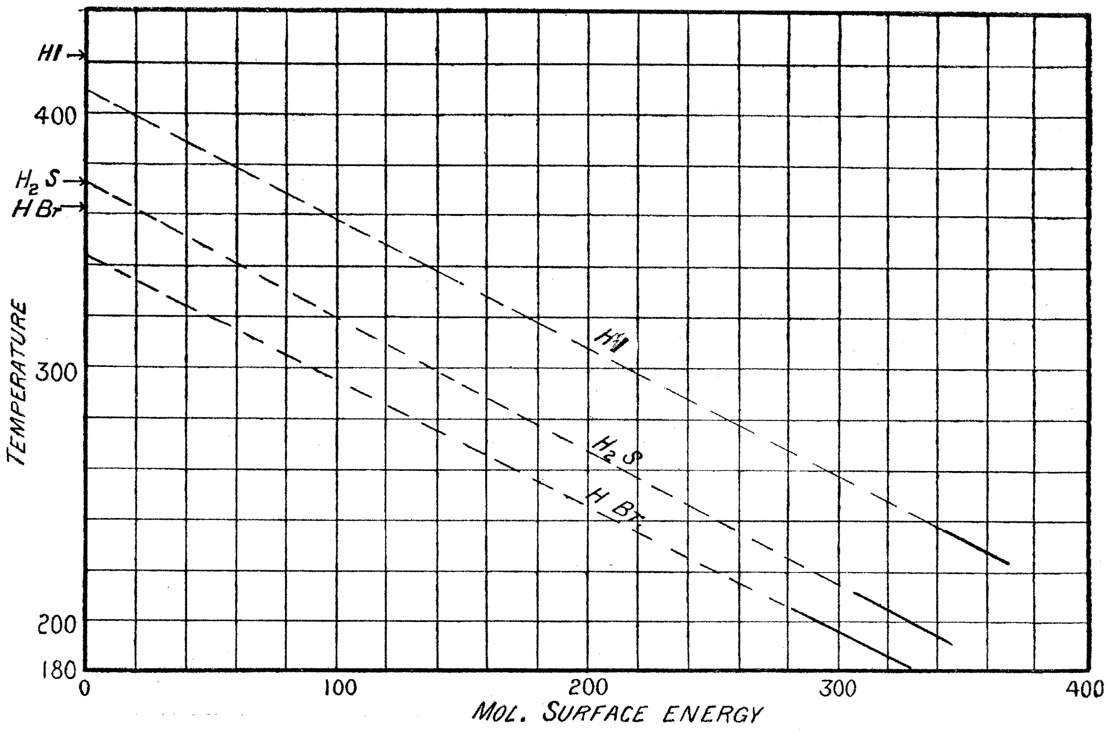

Fig. 7.

The curves are shown in fig. 7, in which the critical temperature of each liquid is indicated by an arrow.

TABLE XI.

	Critical temp.	Temp. at which curve cuts T axis.	*d.*
	° C.	° C.	
Hydrogen chloride	52·3	65·2	+11·9
„ bromide	91·3	75·0	−16·3
„ iodide	150·7	134·0	−15·7
„ sulphide	100·2	100·0	− 0·2
Phosphuretted hydrogen . . .	—	61·6	—

RAMSAY and SHIELDS also showed that another class of liquid exists, for which the above relation does not hold, inasmuch as the coefficient not only was less than 2·12, but also varied with the temperature. If a tangent is drawn to the curve, for a liquid of this class, it will cut the temperature axis at a point above the critical temperature.

This abnormal behaviour is explained by the assumption that the molecules of such liquids are associated to form larger molecular complexes; in other words, that their molecular weights are abnormally high. Hydrogen chloride and phosphide, from the magnitude of their temperature coefficients, must be classed with the abnormal or associated liquids, but the curves which we have obtained are too short to be distinguished from straight lines. These curves have, however, been produced and the results are shown in fig. 8 and Table XI.

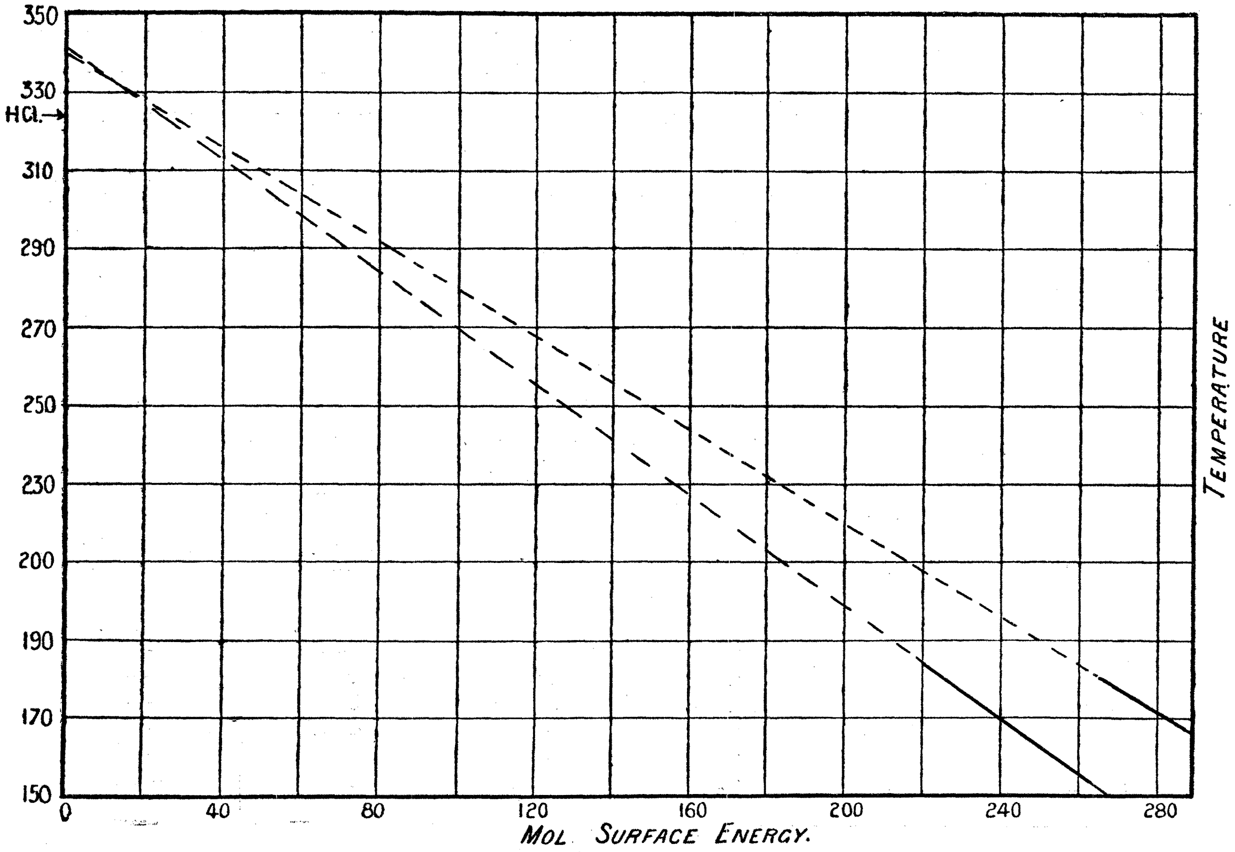

Fig. 8.

It will be seen that the curve for hydrogen chloride cuts the temperature axis at 65·2°, or 11·9° above the critical point.

We have not been able to find any record of measurements of the critical temperature of phosphuretted hydrogen.

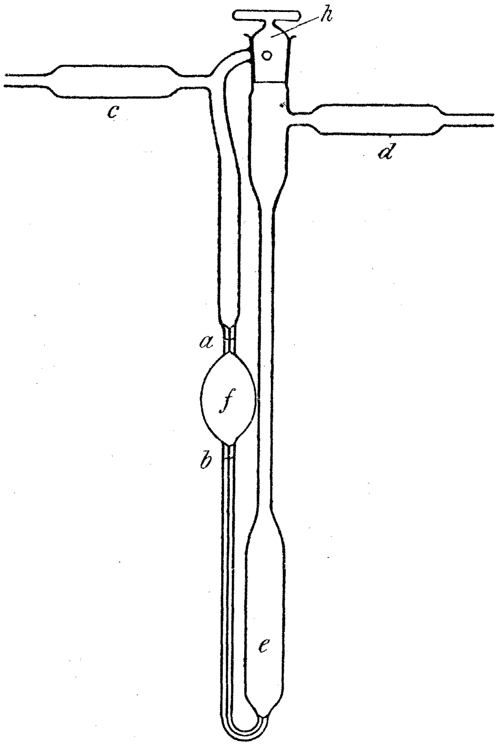

Fig. 9.

The Measurement of Viscosity.

The viscosity apparatus (fig. 9) was of the usual form, but with some slight additions, which were designed to prevent access of water vapour. For this purpose the two ends of the apparatus were joined to the stop-cock *h*, and the two tubes *c* and *d*, containing phosphoric anhydride, were attached. After the apparatus had been placed in the bath, a definite quantity of the liquid was distilled into it through *d*.

In order to make the measurements, the stop-cock was closed and, by blowing into *d*, the liquid was forced into *f* until it reached a position about one centimetre above the mark *a*. The stop-cock was then opened and the time required for the liquid to fall from *a* to *b* measured with a stop-watch. The apparatus was calibrated with distilled water at 22°.

In the tables, D refers to the density of the liquefied gas; η is the viscosity compared with that of water at 22°, and $\frac{d\eta}{dt}$ is the temperature coefficient of viscosity.

TABLE XII.—Hydrogen Chloride.

Apparatus B. Time of flow for water = 75·3 seconds at 22°.

T (abs.).	Time.	D.	η.	$\frac{d\eta}{dt}$.	Smoothed $\frac{d\eta}{dt}$.
				per cent.	per cent.
160·8	35·1	1·265	0·590	—	—
166·7	34·3	1·249	0·569	0·61	—
171·7	32·3	1·236	0·530	0·03	—
177·0	31·7	1·221	0·514	0·91	—
183·2	30·8	1·204	0·493	0·88	—
188·2	30·2	1·189	0·477	0·86	0·88

TABLE XIII.—Hydrogen Bromide. Apparatus B.

T (abs.).	Time.	D.	η.	$\frac{d\eta}{dt}$.	Smoothed $\frac{d\eta}{dt}$.
				per cent.	per cent.
186·8	30·8	2·227	0·911	—	—
188·8	30·6	2·219	0·902	0·50	—
190·8	30·3	2·212	0·890	0·59	—
193·7	30·0	2·200	0·877	0·57	—
197·3	29·5	2·186	0·857	0·60	—
199·4	29·4	2·178	0·851	0·56	0·57

TABLE XIV.—Hydrogen Sulphide. Apparatus B.

T (abs.).	Time.	D.	η.	$\frac{d\eta}{dt}$.	Smoothed $\frac{d\eta}{dt}$.
				per cent.	per cent.
191·0	40·3	1·002	0·547	—	—
193·3	39·8	0·998	0·528	1·6	—
198·2	38·8	0·990	0·510	1·0	—
201·2	37·3	0·985	0·488	1·19	—
206·1	36·2	0·977	0·470	1·09	—
209·8	35·2	0·972	0·454	1·08	1·1

TABLE XV.—Hydrogen Iodide. Apparatus A. Time of flow for Water = 43 seconds at 22°.

T (abs.).	Time.	D.	η.	$\frac{d\eta}{dt}$.	Mean.
				per cent.	per cent.
223·3	22·3	2·858	1·479	—	—
225·6	22·0	2·849	1·454	0·75	—
227·2	21·8	2·842	1·437	0·75	—
229·6	21·7	2·832	1·426	0·59	—
231·5	21·4	2·824	1·402	0·67	—
233·9	21·1	2·813	1·377	0·70	—
236·4	20·8	2·802	1·353	0·71	0·70

SUMMARY of Tables XII. to XV.

Substance.	η at B.P.	$\frac{d\eta}{dt}$.
HCl	0·47	0·90
HBr	0·83	0·58
HI	1·35	0·70
H_2S	0·45	1·10

PART II.

The Conductivity and Molecular Weights of Dissolved Substances. *By* D. McIntosh *and* E. H. Archibald.

The second part of this investigation deals with the solubilities of substances in the liquefied halogen hydrides and sulphuretted hydrogen, and with the conductivities of the resulting solutions; the molecular weights of a few substances, when dissolved in each of these solvents, have also been determined.

The Temperature Bath.

As liquid air was not available in sufficient quantities to make use of the bath described in Part I., a mixture of carbon dioxide and ether, which under atmospheric pressure gives a very constant temperature of −81°, was used for the measurements of solutions in hydrogen bromide and sulphide.

The same mixture, under reduced pressure, was used for the measurement of solutions in hydrogen chloride. By carefully regulating the pressure over the mixture the temperature was maintained at −100°.

For the hydrogen iodide solutions a temperature of −50° was obtained by slowly running cold ether into the vacuum vessel and syphoning off the warmer upper layer.

The Determination of Solubilities.

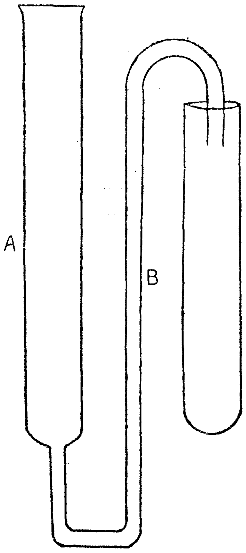

Fig. 1.

The solubilities were measured by means of an apparatus (fig. 1) which consisted of a test-tube A, to the bottom of which a delivery tube B was sealed. The bottom of A was covered with a thick layer of asbestos which acted as a filter, and the whole was immersed in the constant-temperature bath.

The liquefied gas and the substance of which the solubility was under investigation were introduced into A, where they were vigorously stirred with a platinum rod. A portion of the liquid was then blown through the delivery tube into a weighed and graduated test-tube. The volume of liquid in the test-tube was observed, the liquid allowed to evaporate, and the residue weighed. The solubility was calculated from the data thus obtained.

The results of the measurements may be summarised as follows:—

(1) Inorganic substances insoluble, or soluble only in traces, in any of the solvents—

The chlorides, bromides, and iodides of the alkalis and alkaline earths: salts of nickel, iron, lead, and mercury; stannous chloride, potassium permanganate, and potassium bichromate.

(2) Inorganic substances soluble—in some cases with decomposition:—

(*a*) In hydrogen chloride—

*Stannic chloride, phosphorus pentabromide, phosphorus pentachloride, and phosphorus oxychloride;

(*b*) In hydrogen bromide—

Phosphorus oxychloride, bromide, and sulphuretted hydrogen;

(*c*) In hydrogen iodide—

Iodine and phosphorus oxychloride;

(*d*) In sulphuretted hydrogen—

Sulphur, phosphorus oxychloride, hydrogen bromide, and hydrogen chloride.

(3) Inorganic substances soluble with decomposition in hydrogen chloride, potassium cyanide, ammonium sulpho-cyanate, sodium acetate.

(4) Organic substances. In addition to the organic ammonium bases, which, as stated in Part I., dissolve somewhat freely in all the solvents, we have found that a very large number of organic compounds are soluble, as, for example, the aldehydes, ketones, alcohols, ethereal salts of fatty and of aromatic acids, cyanides, and sulpho-cyanates, hydrocarbons, and nitro-compounds. Hydrogen sulphide is an excellent solvent for such bodies, but the solutions, as a rule, are non-conductors. The solutions in the halogen hydrides, on the other hand, usually conduct the current.

The Measurement of Conductivity.

Although the investigation of the solubility of inorganic salts failed to indicate that these were soluble in more than traces in any of the solvents, we have tested the conductivity of the different solvents after the addition of certain inorganic substances. We find that an increase of conductivity was produced by adding the following substances to:—

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* HELBIG and FAUSTI ('Atti R. Accad. Lincei,' 1904 (V), 13, p. 30) found that stannic chloride was soluble in hydrogen chloride. We regret that by an oversight we contradicted this statement in our Preliminary Note ('Roy. Soc. Proc.,' 1904, 73, p. 554), and we wish now to make the necessary correction.

(*a*) Hydrogen chloride—

Bromine, potassium iodide, thionyl chloride, sulphuryl chloride, and uranium nitrate (very slight increase), phosphorus pentachloride, pentabromide, and oxychloride (considerable increase);

(*b*) Hydrogen bromide—

Phosphorus oxychloride (considerable increase);

(*c*) Hydrogen iodide—

Iodine, sulphuric acid, carbon disulphide, and phosphorus oxychloride (slight increase);

(*d*) Sulphuretted hydrogen—

Phosphorus pentachloride, and sulphuryl chloride (slight increase).

The following substances did not cause an increase in the conductivity of either of the solvents:—

Sodium, sodium sulphide, sodium biborate, sodium acid phosphate, sodium nitrate, sodium sulphide, sodium thiosulphate, sodium arsenate, chromic acid, the following salts of potassium: the nitrate, hydroxide, chromate, sulphide, acid sulphate, ferrocyanide, ferricyanide; ammonium fluoride and carbonate; rubidium and cæsium chlorides;

Magnesium sulphate, calcium fluoride, strontium chloride, barium chloride, oxide, nitrate and chromate; copper sulphate, mercuric chloride, zinc sulphate, boron trichloride, aluminium chloride, and sulphate; carbon dioxide, stannous chloride, lead peroxide, nitrate, and cyanide; phosphorus tribromide, bismuth nitrate, tartar emetic, manganese chloride, ferric chloride, ferrous sulphate, nickel sulphate, and cadmium sulphate.

In addition to the organic ammonium bases, we have, in conjunction with Dr. J. W. Walker,[*] examined the conductivity of solutions of about 80 organic substances in each of the foregoing solvents.

The only substances which form conducting solutions in H_2S are the ammonium bases and a few alkaloids such as nicotine and pyridine. On the other hand, many ethers, ketones, esters, nitrites, and, generally speaking, substances containing oxygen or nitrogen, form conducting solutions in hydrogen chloride, bromide, and iodide. The hydrocarbons, although in some cases soluble in all proportions, do not conduct. We have noticed that the solution of those substances which conduct is accompanied by a considerable evolution of heat, while little or no heat is evolved in the case of other substances.

This indicates chemical interaction between the conducting solute and the solvent, and many of the resulting compounds have been isolated and analysed.[†] It has been

---

[*] 'Journal of the Chemical Society,' 1904, 85, p. 1098.

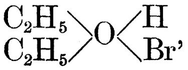
[†] Archibald and McIntosh, 'J. C. S.,' 1904, 85, p. 919.

found, for example, that ether enters into combination with the three halogen acids, forming compounds which have the following formulæ:

$$(C_2H_5)_2O,\ 5HCl,\ \text{M.P.} = -120,$$
$$(C_2H_5)_2O,\ HBr,\ \text{M.P.} = -\ 42,$$
$$(C_2H_5)_2O,\ HI,\ \text{M.P.} = -\ 18.$$

We have explained the formation of these and similar compounds by assuming the existence of tetrad oxygen at these low temperatures.

The compound of ether and hydrogen bromide would thus have the formula



$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!O\!<\!\!\begin{matrix}H\\Br\end{matrix}$, and might be expected to undergo electrolytic dissociation.

Quantitative Measurements of Conductivity.

The pure solvents are extremely poor conductors of electricity, their specific conductivity being as follows:

Hydrogen	chloride	about	$0{\cdot}2 \times 10^{-6}$,
,,	bromide	,,	$0{\cdot}05 \times 10^{-6}$,
,,	iodide	,,	$0{\cdot}2 \times 10^{-6}$,
,,	sulphide	,,	$0{\cdot}1 \times 10^{-6}$,
that of the purest water being			$0{\cdot}04 \times 10^{-6}$.

The resistances are thus much greater than that of an ordinary sample of distilled water.

The majority of the measurements of conductivity were made in an apparatus (fig. 2) consisting of a graduated test-tube with fixed electrodes.

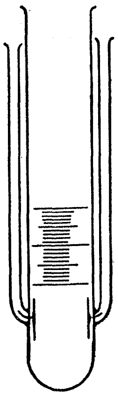


Fig. 2.

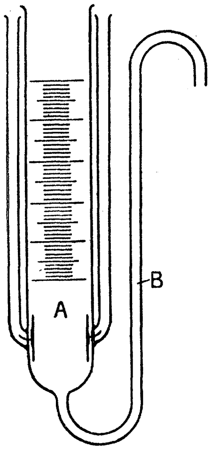


Fig. 3.

A sufficient quantity of the solvent was first placed in the conductivity vessel and a weighed quantity of the substance under investigation introduced by means of a cooled platinum spoon. The mixture was then stirred until the conductivity remained constant, after which the volume of the solution was observed. A further weighed quantity of the substance was then introduced and dissolved, and the conductivity again measured. The same series of operations was frequently repeated until a sufficient number of measurements had been made.

Other measurements were made in the apparatus shown in fig. 3. This consisted of a graduated test-tube A, provided with fixed electrodes, and with a delivery tube B attached.

A saturated solution of the substance was made in the apparatus shown in fig. 1, a portion removed for analysis, and a sufficient amount put into the conductivity vessel, where its conductivity was measured and the volume noted. More of the solvent was then added, and the liquids were well mixed by blowing air through the delivery tube B. The volume was again read and the conductivity measured.

This succession of operations was repeated until the vessel became full of liquid, after which a measured volume of the solution was removed, and the operations were continued until a sufficient number of measurements had been obtained.

In all the measurements the electrodes were sufficiently immersed to give the maximum conductivity of the apparatus.

Our results are given in the following tables, which also contain the temperature coefficient of conductivity for those solutions which are marked with an asterisk.

The dilutions, which are given under V, represent the number of litres of solution which contain 1 gram-molecule of solute, and the molecular conductivities in reciprocal ohms × 10^{-3} are given under μ. The numbers are thus expressed in the same units as the molecular conductivity of aqueous solutions as given by KOHLRAUSCH and HOLBORN (' Leitvermögen der Elektrolyte ').

TABLE I.—Solvent : Hydrochloric Acid.

HYDROCYANIC ACID.

V.	μ.	V.	μ.
41·4	0·51	4·90	2·09
21·3	0·91	4·08	2·83
14·1	0·98	3·12	3·65
10·2	1·08	*2·56	4·47
9·2	1·34	1·79	5·81
7·35	1·48	1·23	7·70

Temperature coefficient between − 99° and − 95° = − 2·0 per cent.
" " " − 99° " − 90° = − 1·8 "
" " " − 99° " − 85° = − 1·3 "

Table I.—Solvent: Hydrochloric Acid (continued).

V.	μ.	V.	μ.
Triethylammonium Chloride.			
71·4	1·80	7·69	4·37
37·0	1·80	6·13	5·18
20·4	2·28	5·00	6·05
16·1	2·71	4·25	6·73
11·6	3·15	3·64	7·72
9·43	3·67	*2·99	8·51
Temperature coefficient between −98° and −89° = 0·39 per cent. ,, ,, ,, −98° ,, −86° = 0·67 ,,			
Ethyl Oxide.			
12·50	0·14	1·09	2·03
5·00	0·23	0·88	2·20
3·12	0·39	0·72	2·90
1·92	0·95	0·61	3·09
1·45	1·41	—	—
Temperature coefficient between −99° and −95° = 1·9 per cent. ,, ,, ,, −99° ,, −90° = 1·8 ,, ,, ,, ,, −99° ,, −85° = 1·7 ,,			
Acetamide.			
29·4	1·59	2·86	8·20
12·8	3·12	2·13	9·41
8·62	4·27	1·54	10·8
4·65	6·39	0·95	12·1
4·15	6·92	0·51	12·3
Temperature coefficient between −97° and −92° = 1·4 per cent. ,, ,, ,, −97° ,, −86° = 1·2 ,, ,, ,, ,, −97° ,, −83° = 1·2 ,,			
Acetonitrile.			
21·7	1·51	2·17	6·82
8·33	2·44	1·54	6·25
4·76	3·89	1·09	8·08
3·22	5·25	0·81	9·64

TABLE II.—Solvent: Hydrobromic Acid.†

V.	μ.	V.	μ.
TRIETHYLAMMONIUM CHLORIDE.			
143	0·19	5·26	3·29
50	0·22	3·33	4·90
27·7	0·50	2·17	6·20
15·6	0·83	1·61	8·19
8·33	2·00	—	—
ETHYL OXIDE.			
16·6	0·005	1·23	0·152
5·55	0·014	1·03	0·164
4·00	0·024	0·68	0·182
2·00	0·106	0·47	0·726
1·54	0·129	—	—
ACETONE.			
8·33	0·10	1·64	2·32
5·00	0·34	1 35	3·24
3·23	0·77	1·07	4·30
2·00	1·40	0·75	5·63
ACETAMIDE.			
90·9	0·06	6·66	0·94
58·8	0·10	3·85	1·47
23·3	0·27	3·03	1·80
14·5	0·42	*2·08	2·37
10·2	0·57	1·41	3·15
Temperature coefficient between −83° and −77° = 0·94 per cent.			
„ „ „ −83° „ −74° = 0·94 „			
ACETONITRILE.			
33·3	0·14	1·47	4·62
4·76	1·08	1·22	5·43
3·70	1·32	0·96	6·99
2·50	2·48	0·72	10·01
1·85	3·46	—	—
ETHYL PROPIONATE.			
12·5	0·05	2·63	0·82
7·14	0·16	1·92	1·19
5·26	0·38	1·39	1·69
3·45	0·49	—	—
ORTHO-NITROTOLUENE.			
25	0·04	3·85	0·21
16·6	0·07	2·38	0·45
12·5	0·07	1·50	0·67
11·1	0·10	0·92	1·02
8·33	0·11	0·66	1·28

---

† The solutions marked thus † were measured by McINTOSH and STEELE.

TABLE II.—Solvent : Hydrobromic Acid (continued).

V.	μ.	V.	μ.
†TETRAMETHYLAMMONIUM CHLORIDE.			
200	5·40	10·5	12·53
21·3	8·94	9·42	13·30
14·1	10·56	—	—
†TETRAMETHYLAMMONIUM BROMIDE.			
166	[12·6]	34·5	7·25
62·5	7·0	11·8	12·6
†TETRAMETHYLAMMONIUM IODIDE.			
62·5	8·75	22·2	13·10
34·5	10·35	—	—

TABLE III.—Solvent : Hydriodic Acid.

V.	μ.	V.	μ.
TRIETHYLAMMONIUM CHLORIDE.			
27·8	0·07	5·55	1·15
21·7	0·11	4·50	1·48
15·4	0·23	3·85	1·91
10·4	0·43	3·13	2·37
8·55	0·65	2·50	2·97
7·14	0·80	2·17	3·58
ETHYL OXIDE.			
10·0	0·02	1·49	1·11
5·88	0·07	1·25	1·40
3·33	0·22	1·06	1·79
2·46	0·61	*0·88	2·21
1·79	0·84	—	—
Temperature coefficient between −50° and −45° = 1·9 per cent.			
„ „ „ −50° „ −40° = 1·8 „			
ETHYL BENZOATE.			
16·6	0·014	2·56	1·65
7·14	0·170	2·04	2·30
4·76	0·47	1·66	2·98
3·45	1·02	1·37	3·60

TABLE IV.—Solvent: Sulphuretted Hydrogen.

TRIETHYLAMMONIUM CHLORIDE.

V.	μ.	V.	μ.
71·4	0·12	4·00	0·87
12·8	0·21	3·13	1·17
8·33	0·33	*2·50	1·58

Temperature coefficient between − 80° and − 75° = 0·88 per cent.
" " " − 80° " − 70° = 0·90 "
" " " − 80° " − 65° = 0·85 "

NICOTINE.

V.	μ.	V.	μ.
66·7	0·03	2·27	0·38
14·3	0·04	1·92	0·50
6·67	0·06	1·03	0·76
4·00	0·16	—	—

PIPERIDINE.

V.	μ.	V.	μ.
9·09	0·02	0·75	0·46
1·18	0·29	0·64	0·48
0·90	0·39	*0·55	0·50

Temperature coefficient between − 80° and − 66° = 1·82 per cent.
" " " − 80° and − 63° = 1·84 "

TETRAMETHYLAMMONIUM CHLORIDE.

V.	μ.	V.	μ.
34·5	1·71	3·33	4·02
11·0	3·41	2·93	3·85
4·35	3·85	—	—

Temperature coefficient between − 70° and − 64·7° = 0·95 per cent.
" " " − 70° " − 62·6° = 1·07 "
" " " − 70° " − 60·8° = 1·09 "

The foregoing results are shown graphically in the figs. 4 to 7, in which the molecular conductivities are plotted against the dilutions. It will be seen that in every case μ decreases enormously with dilution, a variation which is exactly opposite to that which might be expected from analogy with aqueous solutions. These results indicate that, if conduction is due to ionisation, the degree of dissociation decreases with dilution, a result which is in opposition to the law of mass action.

This subject will be discussed fully in Part IV.

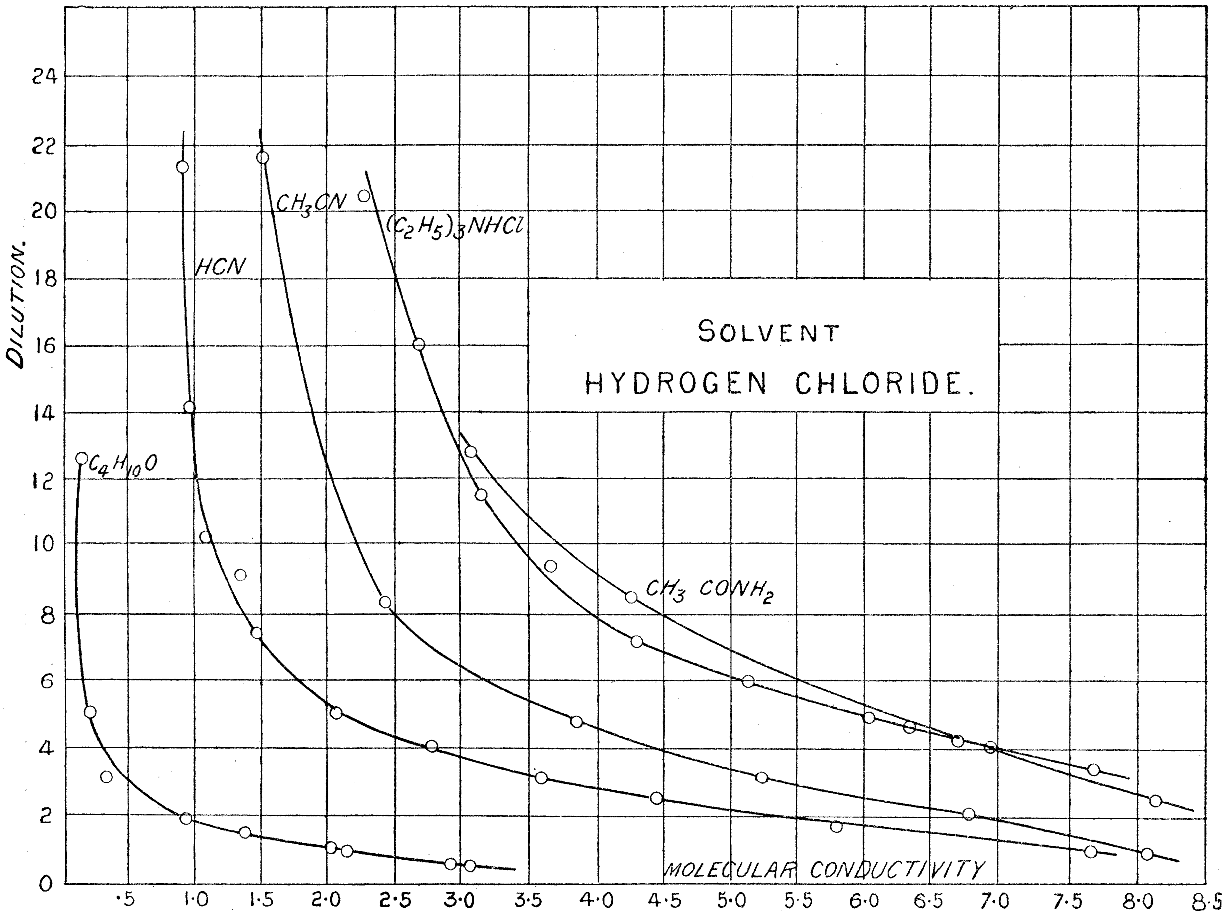

DILUTION.
24
22
20
18
16
14
12
10
8
6
4
2
0
HCN
CH3CN
(C2H5)3NHCl
C4H10O
CH3 CONH2
SOLVENT
HYDROGEN CHLORIDE.
MOLECULAR CONDUCTIVITY
·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5
5·0
5·5
6·0
6·5
7·0
7·5
8·0
8·5

Fig. 4.

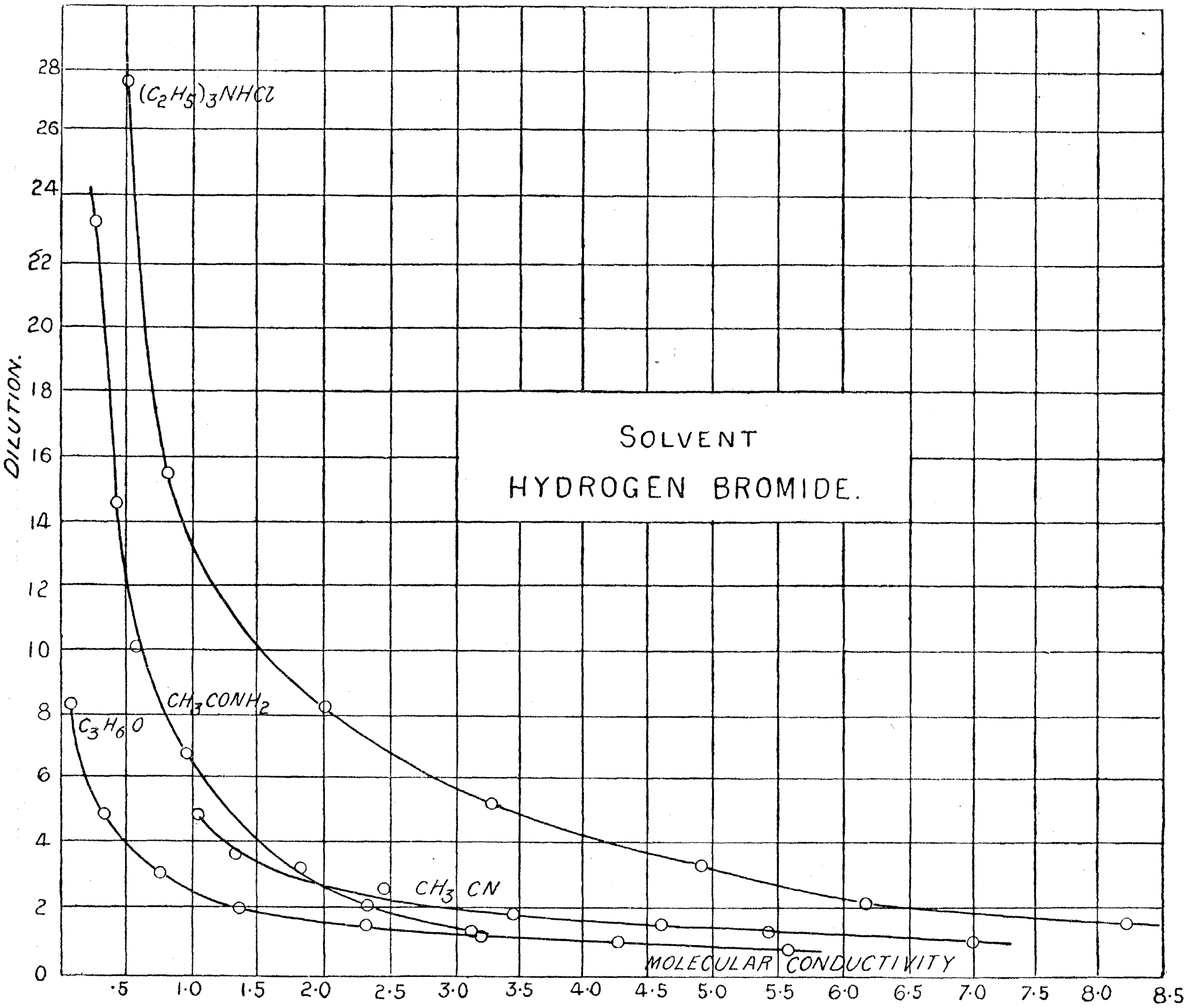

SOLVENT
HYDROGEN BROMIDE.
DILUTION.
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
(C2H5)3NHCl
CH3CONH2
C3H6O
CH3 CN
MOLECULAR CONDUCTIVITY
·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5
5·0
5·5
6·0
6·5
7·0
7·5
8·0
8·5

Fig. 5.

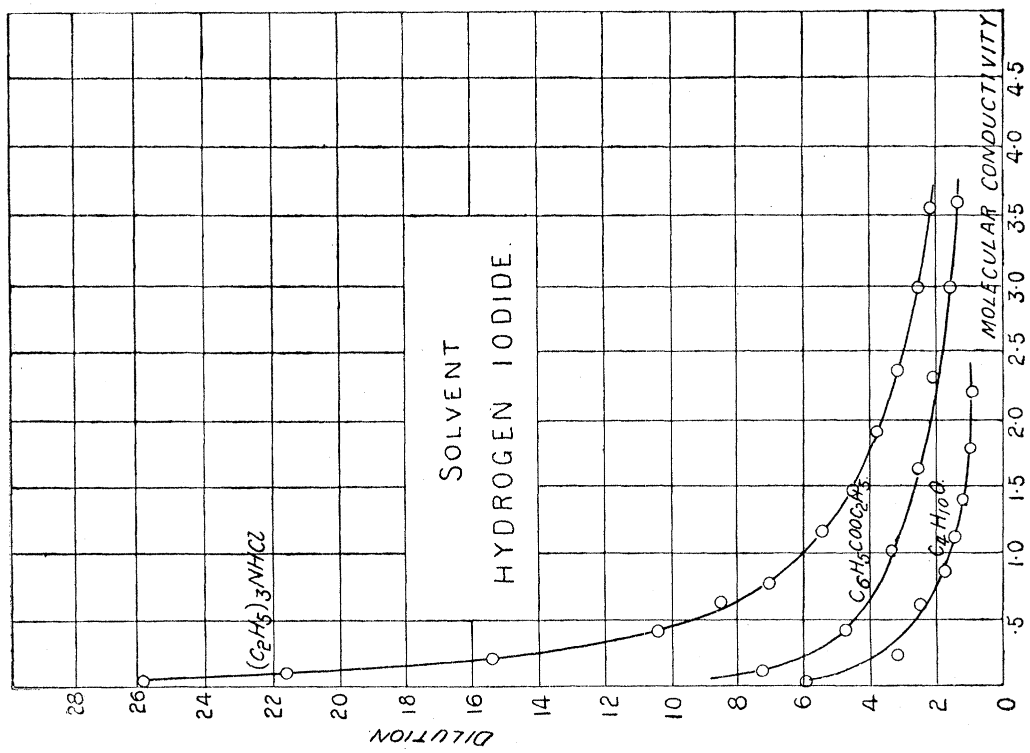

SOLVENT
HYDROGEN IODIDE.
$(C_2H_5)_3NHCl$
$C_6H_5COOC_2H_5$
$C_4H_{10}O$
DILUTION
MOLECULAR CONDUCTIVITY
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5

Fig. 6.

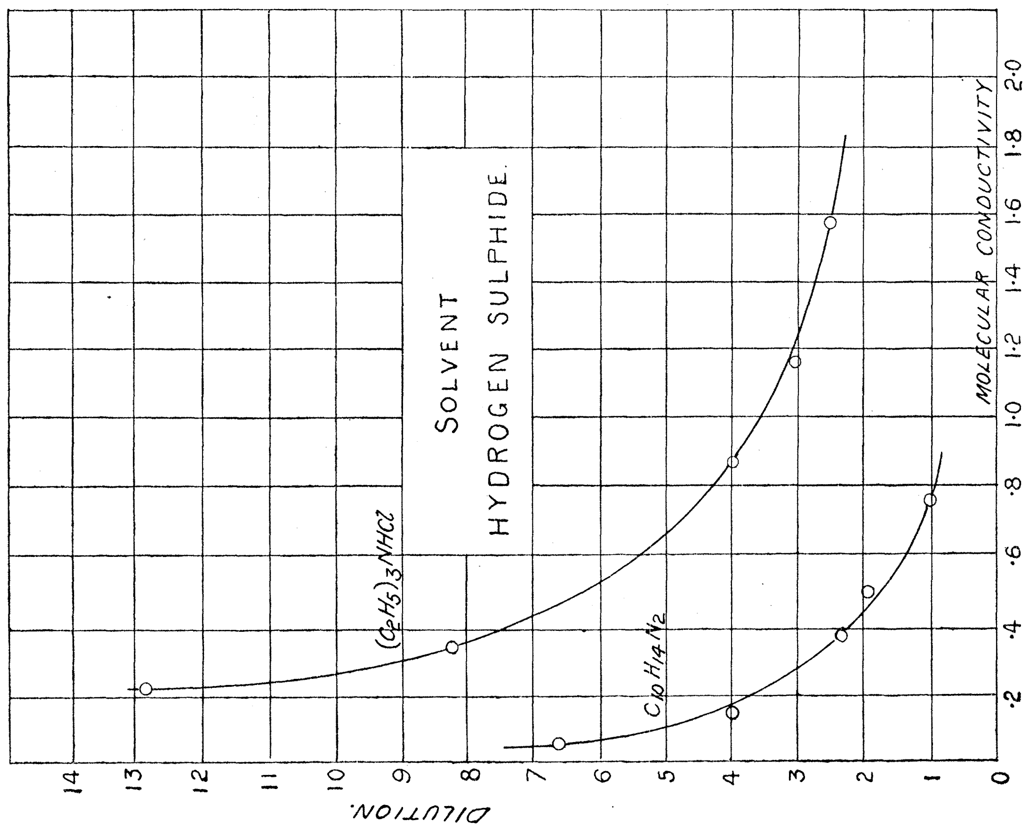

SOLVENT
HYDROGEN SULPHIDE.
$(C_2H_5)_3NHCl$
$C_{10}H_{14}N_2$
DILUTION.
MOLECULAR CONDUCTIVITY
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
·2
·4
·6
·8
1·0
1·2
1·4
1·6
1·8
2·0

Fig. 7.

As a general rule, the same substances conduct better when dissolved in hydrogen chloride than in the other solvents. Next, in the order given, come solutions in hydrogen bromide, iodide, and sulphide. An exception to this rule is found in the case of ether, which conducts best in hydrogen chloride, and worst in hydrogen bromide.

The conductivity temperature coefficients do not appear to have anything in common with the viscosity temperature coefficient, so that the ions cannot be looked upon as being surrounded with an atmosphere of the solvent (KOHLRAUSCH, 'Roy. Soc. Proc.,' 71, 338, 1903).

The coefficients are for the most part positive, the conductivity increasing with rise of temperature, an exception occurring in the case of hydrocyanic acid dissolved in hydrochloric acid.

The Determination of Molecular Weights.

The molecular weights were determined by measuring the rise in boiling-point which was brought about by the addition of known quantities of the dissolved substance.

Considerable experimental difficulty has been experienced during the progress of the work, which has also proved expensive on account of the very large quantities of carbon dioxide which were required, and consequently only a few determinations have been made.

The accurate measurement of small differences of temperature at low temperatures has been successfully accomplished by the use of a differential method, in which two platinum resistance thermometers were employed to measure the temperatures, one of the thermometers being immersed in the pure boiling solvent and the other in the boiling solution.*

The thermometers were each made from about 2 metres of 6 mil wire, and had exactly the same resistance, which was of such a magnitude that a difference of 1° in the temperature of the two coils produced a displacement of 16·7 millims. in the balance point on the bridge. The thermometers were supplied with compensation leads in the usual way. The bridge was of the Carey-Foster type. With the galvanometer used a difference in temperature of 0·03° could be detected with certainty.

The apparatus was tested by immersing the two coils in (*a*) boiling water, (*b*) melting ice, (*c*) boiling hydrogen sulphide, (*d*) boiling hydrogen bromide, and (*e*) boiling hydrogen chloride; the same balance point was obtained in each case.

The measurements were made in the two pieces of apparatus shown in fig. 8,

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* The bridge and resistance thermometers were lent to us by Dr. H. L. BARNES, through whose advice and assistance many difficulties have been avoided. We take this opportunity of expressing our thanks to him for his kindness and help.

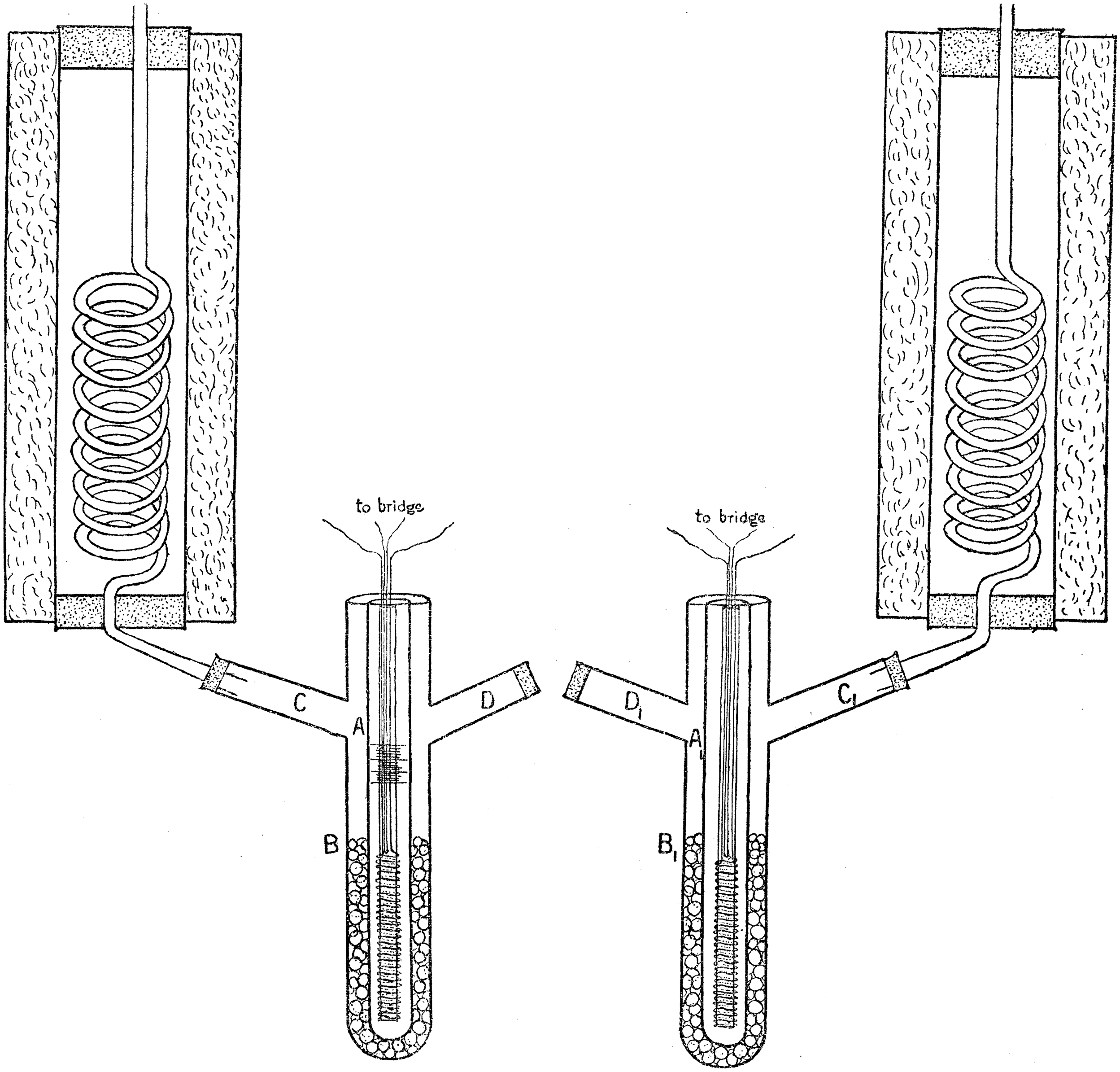

Fig. 8.

each of which consisted of two concentric tubes, A and B, which were sealed together at the top. The outer tube B was provided with the two side tubes C and D, to one of which, C, the condenser was attached, the other being closed by a well-fitting cork. The two thermometers were placed in A and A′, and were held in position by waxed corks.

To carry out an experiment, a sufficient quantity of the liquefied gas was introduced through the side tubes D and D′ into the vessels B and B′, both of which contained beads to ensure steady boiling. In order to determine the quantity of solvent used in making the solutions, the volume of liquid in one of the vessels was measured at a definite temperature, or, if liquid air was available, the liquid was frozen and the vessel containing it weighed. The condensers were then filled with a mixture of solid carbon dioxide and ether, maintained at atmospheric pressure for the experiments with hydrogen bromide and sulphide, and at reduced pressure for the experiments with hydrogen chloride.

After the liquid in the vessels had commenced to boil, the vessels were wrapped in natural wool, and the balance point on the bridge was determined. Weighed quantities of the substances whose molecular weight was to be determined were then successively introduced, and the displacement of the balance point was determined after each addition. From these displacements the corresponding rise in boiling-point was calculated. The loss by evaporation, due to the high vapour pressure of the solvents at the temperature of the condenser, was corrected for by means of a blank experiment.

Evaporation also occurred when the substances were introduced into the apparatus, but as this evaporation was proportional to the amount of substance added, a correction was easily applied. As a check on these corrections, the boiling-point apparatus was removed after each two or three determinations, and when liquid air was available, the apparatus was cooled and weighed. When liquid air could not be obtained, the tube was cooled to a definite temperature, the volume of solution measured, and the amount of solvent calculated on the assumption that no volume change occurred on mixing.

From the data thus obtained the molecular weight constant was calculated by means of the formula

$$M = \frac{Kg}{G\,\Delta},$$

in which the molecular weight of the dissolved substance is expressed in terms of g, its weight in grammes dissolved in G-gramme of the solvent, and of the corresponding rise in boiling-point Δ, K being a constant in the case of a solute which is neither associated nor dissociated. The values of g, G, Δ, and K for the various substances investigated are given in the first four columns of Tables V, VI, and VII.

The following example will show the method of making the calculations :—

Toluene in Hydrochloric Acid.

Apparent volume of liquid + 0·39g toluene	38·3 cub. centims.
,, ,, ,, beads	17·0 ,,
Real volume of liquid	21·3 ,,
Volume of toluene	0·4 ,,
,, ,, hydrochloric acid	20·9 ,,
Weight (Part I.)	25·0g.
Rise of boiling-point	0·42°.
Constant	= 2480.

VAN 'T HOFF has shown that the molecular rise of boiling-point can be calculated by means of the formula

$$dT = \frac{0{\cdot}02T^2}{W},$$

where T is the absolute temperature and W is the latent heat of evaporation of 1 gramme of the solvent.

We have calculated the values for the molecular rise of boiling-point of the various solvents by means of the latent heats which are given in Part I.

The molecular weight of the dissolved substance has been calculated from the values so obtained for the molecular rise.

The molecular weights are given under M′ in the sixth column of the tables, and in the fifth column the concentrations of the solutions are expressed in grammes of solute dissolved in 100 grammes of solvent.

TABLE V.—Molecular Weights in Hydrogen Chloride, $\frac{0{\cdot}02T^2}{W} = 720$.

g.	G.	Δ.	K.	C.	M′.
TOLUENE.					
0·39	25·0	0·42	2480	1·56	26·6
0·88	24·5	0·93	2380	3·59	27·8
2·25	24·5	2·25	2250	9·18	29·4
3·25	23·9	3·35	2270	13·60	29·2
4·28	23·9	4·31	2210	17·91	29·9
ETHER.					
1·54	38·4	0·27	500	4·01	107
2·99	36·3	0·96	860	8·24	61·8
3·62	33·9	1·56	1080	10·68	49·3
3·62	30·4	1·98	1230	11·91	43·3
4·29	29·2	2·95	1485	14·69	35·9
4·69	28·4	3·63	1630	16·02	32·8
4·69	25·5	4·82	1940	18·40	27·5

TABLE VI.—Hydrogen Bromide, $\frac{0 \cdot 02 T^2}{W} = 1770$.

g.	G.	Δ.	K.	C.	M′.
TOLUENE.					
1·82	51·3	0·77	2000	3·54	81·4
2·15	50·3	1·02	2200	4·27	74·1
2·71	49·3	1·27	2120	5·50	76·7
3·45	48·3	1·62	2090	7·14	78·1
ETHER.					
0·39	38·8	0·24	1745	1·02	75·1
0·79	38·1	0·48	1700	2·09	77·0
1·15	37·4	0·78	1870	3·08	69·9
1·69	36·7	1·27	2045	4·60	64·1
2·18	35·5	1·95	2350	6·14	53·7
2·64	34·0	2·94	2800	7·76	46·7
3·05	32·6	4·18	3300	9·37	39·7
ACETONE.					
0·55	45·4	0·22	1060	1·21	97·1
1·23	42·4	0·53	1060	2·91	97·1
1·89	39·4	1·20	1450	4·80	70·7
2·76	37·4	2·94	2310	7·38	4·44

TABLE VII.—Sulphuretted Hydrogen, $\frac{0 \cdot 02 T^2}{W} = 620$.

g.	G.	Δ.	K.	C.	M′.
TOLUENE.					
1·25	22·1	0·44	670	5·64	79·5
2·25	22·1	0·72	650	11·51	87·8
3·29	22·1	1·01	625	14·89	91·4
4·22	22·1	1·16	560	19·10	102·1
TRIETHYLAMMONIUM CHLORIDE.					
0·76	22·6	0·23	940	3·36	90·7
1·30	22·3	0·44	1040	5·83	82·2
1·62	21·9	0·60	1115	7·40	76·5
1·98	21·6	0·69	1035	9·17	82·4

These results may be briefly summarised as follows:—

Toluene, which is a non-conductor in each of the solvents, has an average molecular weight of about 30 in hydrogen chloride, 78 in hydrogen bromide, and about 90 in sulphuretted hydrogen, and therefore appears to be dissociated when dissolved in hydrogen chloride and hydrogen bromide and to a greater extent in the former solvent.

Kahlenberg ('Jour. of Phys. Chem.,' 1901, v., 344; 1902, vi., 48) has noticed a similar anomaly in the case of a solution of diphenylamine in methyl cyanide.

Ether in hydrogen chloride and hydrogen bromide, and acetone in hydrogen bromide have molecular weights which indicate association in the more dilute solvents and dissociation in the more concentrated.

Triethylamine hydrochloride appears to be dissociated when dissolved in sulphuretted hydrogen, the dissociation being greater in the more concentrated solutions.

PART III.

The Transport Numbers of Certain Dissolved Substances. *By* B. D. Steele.

The strikingly abnormal variation of molecular conductivity with dilution that we have found to occur in solutions in the liquefied halogen hydrides finds a possible explanation in the assumption that it is the solvent and not the solute which is ionised. As the transport number of the dissolved substance might be expected to yield information not only as to the correctness of this assumption, but also as to the constitution of the electrolyte, the transport numbers of a few substances have been measured, and the results are given in the following pages.

The only measurements of the migration ratio which have hitherto been made in solvents other than water are those of a few salts in methyl and ethyl alcohol, and of silver nitrate in pyridine and in acetonitrile.

Direct measurements of the velocities of certain ions in liquefied ammonia have recently been made by Franklin and Cady ('Journal of Amer. Chem. Soc.,' 1904, vol. 26, p. 499), who used a modification of Masson's method ('Phil. Trans.,' A, 1902, vol. 192, p. 331).

Method of Measurement.

It has been shown by the author (Steele, 'Phil. Trans.,' 1902, A, vol. 198, p. 105) that the direct method of measurement gives trustworthy results only when the salt under examination is of the simplest type. Now Hittorf has shown that in alcoholic solution cadmium iodide and certain other salts are dissociated into ions which are much more complicated than those occurring in aqueous solutions of the same concentration.

The only substances which we have found to be capable of forming conducting solutions in any of the solvents which we have been investigating are certain organic compounds, and although the nature of the ions into which these dissociate is entirely unknown, it is probable that the ionisation is even more complicated than that of cadmium iodide dissolved in alcoholic solution.

From these considerations it was decided to use Hittorf's method, notwithstanding the fact that it is much more tedious and presents greater experimental difficulties than the alternative method of direct measurement.

Hittorf's method consists in the analysis, after electrolysis, of the solution which surrounds one of the electrodes. The original concentration being known, the actual amount of substance which has been carried to the electrode by the current can then be calculated. The current is usually measured by a silver voltameter placed in the same circuit as the electrolytic cell. The calculation, neglecting certain small corrections, is as follows:—

If x grammes of the substance, whose equivalent weight is n, be transported by the current which deposits y grammes of silver on the cathode of the voltameter, then the transport number of the cation is given by $p = \frac{x \times 10}{y \times n}$. p represents the fraction of the total current which is carried by the cation, on the assumption that one unit charge of electricity is associated with one equivalent of the dissolved substance. It is probable that this condition is fulfilled only in solutions of salts of the simplest type (STEELE, *loc. cit.*).

Preparation of Solutions.

The most convenient refrigerant which was available was a mixture of carbon dioxide and acetone, and as at the temperature of this mixture hydrogen chloride is a gas and hydrogen iodide a solid, the choice of solvent was limited to hydrogen sulphide and hydrogen bromide. Solutions in the former solvent are very much more difficult to analyse than those in the latter, and accordingly hydrogen bromide only has been used as solvent during the investigation.

The hydrogen bromide was prepared and purified by the method described in Part I. In order to make the solutions for electrolysis, the gas was condensed in a graduated vessel in which a sufficient quantity of the substance under examination had been placed, the condensation being stopped as soon as the desired volume of solution had accumulated.

A quantity was usually made sufficient for two experiments, and by placing the receiver in a good silvered vacuum vessel with a stiff paste of the carbon dioxide and ether, the solution could be kept for a period of twenty hours without renewal of the refrigerant. The apparatus in which the electrolysis was carried out was immersed in a bath of solid carbon dioxide and acetone contained in a large cylindrical silvered vacuum vessel. This mixture can be maintained at a practically constant temperature by blowing a steady stream of air through it; the temperature, moreover, may be varied within certain limits by altering the rapidity of the air current.

The Validity of FARADAY'S *Law.*

The measurement of the transport number depends on FARADAY'S law, and although this is known to hold rigidly for aqueous solutions, there is no evidence as to its validity for solutions such as those under investigation. Experiments were therefore undertaken with the object of testing the law.

This was accomplished by comparing the weight of silver deposited in a voltameter with the volume of the hydrogen evolved at the cathode during the electrolysis of solutions in hydrogen bromide. The apparatus used (fig. 1) consisted of a tube A with a coiled platinum wire *p* sealed through the bottom and projecting about an inch into the tube, the stem of the projecting part being covered with blue enamel glass. Electrical contact with this electrode, which was used as cathode, was made by means of mercury contained in the tube *b*. The inner cell C was provided with a long capillary *d*, which passed through the rubber cork *e*, and served for delivering the hydrogen into a measuring tube. The anode *g* consisted of a ring of platinum wire, which was attached to the tube *f*.

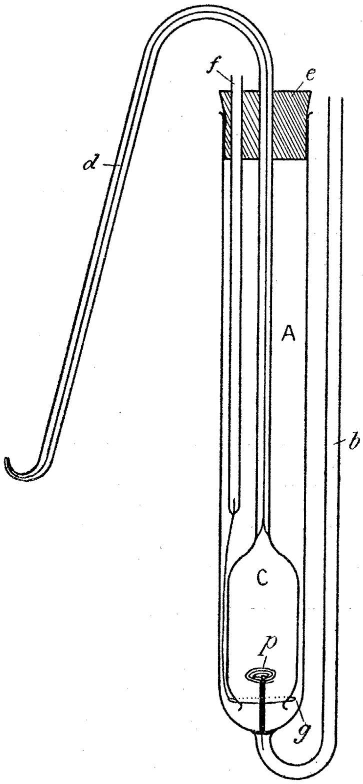

Fig. 1.

In carrying out the experiments the tube A was first immersed in a bath of carbon dioxide and ether; the solution to be electrolysed was then run in, and C, which had been previously cooled, placed in position. A silver voltameter was then placed in the circuit, and current from a battery of about 60 volts was passed through the cell. The hydrogen evolved in A escaped through *d*, and was collected and measured.

Two experiments of this nature were carried out, the details of which are as follows:—

Experiment 1. Solution of diethylamine in hydrogen bromide. E.M.F. = 50 volts. Current = 0·091 ampère. Silver deposited in voltameter = 0·1894 gramme, equivalent to 19·8 cub. centims. hydrogen at 0° and 760 millims. Hydrogen evolved = 19·7 cub. centims. at 0° and 760 millims.

Experiment 2. Solution of acetophenone in hydrogen bromide. E.M.F. = 60 volts. Current = 0·190 ampère. Silver deposited in voltameter = 0·1661 gramme. Hydrogen equivalent = 17·31 cub. centims. at 0° and 760 millims. Hydrogen evolved = 17·38 cub. centims. at 0° and 760 millims.

These experiments were considered sufficient to show that Faraday's law is valid for solutions of organic substances in hydrogen bromide.

The Method of Analysis.

As the total increase in concentration which had to be measured amounted to only a few centigrammes, it was necessary to carry out the analysis with a high degree of accuracy. This was found to be extremely difficult on account of the very high vapour-pressure of hydrogen bromide even at temperatures near its freezing-point, and it was only after months of failure that an apparatus was designed, by means of which sufficiently accurate analyses were obtained.

The apparatus consisted of two parts, the transferrer and the absorber.

The transferrer (T, fig. 5, see p. 144) consisted of a wide H-shaped tube, with a capillary tube *a* passing through three of its branches, the two tubes being sealed together at *b* and *b'*, as shown in the figure. By filling the space between the tubes with a mixture of carbon dioxide and ether, the capillary between *b* and *b'* could be cooled to −81°. In fig. 5 the transferrer is shown when placed in the electrolytic cell.

The absorber (fig. 2) consisted of a stoppered tube A, connected by C with the bubbler B; this bubbler was so constructed that it was impossible for water to be either ejected from the apparatus or sucked back into A. A smaller vessel *b* of the same type was contained within the apparatus. The calcium chloride tube *d*, which was provided with a stop-cock, was attached to B by a ground joint.

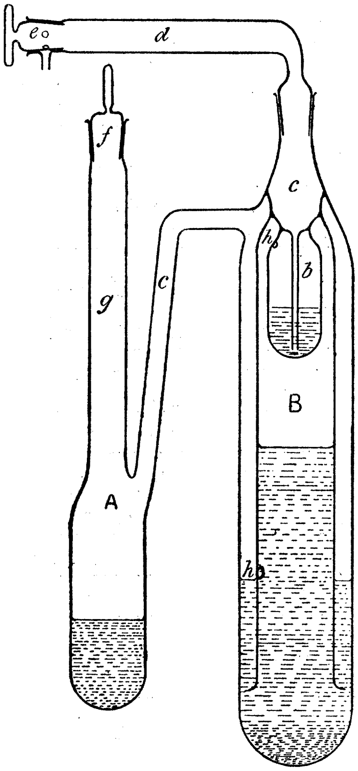

Fig. 2.

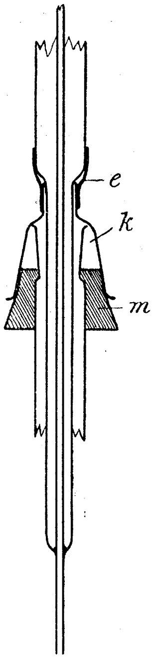

Fig. 3.

The method of using the apparatus was as follows:—A quantity of moist garnets were first placed in the tube A, and a quantity of glass beads in the section *c* of the absorber. The requisite amount of distilled water was then placed in the bubblers B and *b*, and the tube *d* and stop-cock *f* were replaced. The apparatus was then weighed, a glass counterpoise of approximately the same size, shape, and weight being used. The tube A was next immersed in a mixture of solid carbon dioxide and ether, and after the cap *k*, fig. 3, had been placed in position by means of the rubber cork *m*, the limb of a transferrer was passed through *k*, and the whole apparatus made air-tight by means of a piece of rubber tubing, *e*.

The object of the cap *k* was to prevent the limb of the transferrer from coming into contact with the rubber grease, with which the stoppers were lubricated, and it was constructed so that when in position its narrow portion was exactly in the axis of the tube *g*.

The transferrer was then packed with the carbon dioxide and ether mixture, and the hydrogen bromide blown into A by means of a small indiarubber bellows. The rubber tube *e* was then cut away, after which the transferrer and then the cap *k* were removed, and the stop-cock *f* was re-inserted.

The tube A was finally removed from the cold bath and the hydrogen bromide allowed to boil off. This always took place steadily, provided the vessel contained moist beads or garnets; in the absence of these, or if they were dry, the violent bumping which resulted was liable to blow out one or other of the stoppers. The hydrogen bromide as it boiled off passed through C, and was almost completely absorbed at the surface of the water in the outer portion of B; a small quantity of gas bubbled through the hole *h* and was absorbed inside; very occasionally a few bubbles passed through *b*, where any traces of acid which might have passed through the larger portion of the apparatus were absorbed. After all the hydrogen bromide had evaporated the stop-cock *e* was closed, the apparatus immersed in distilled water, carefully wiped and again weighed, the necessary correction being made for the increase of volume of the liquid contained in it. The increase in weight gave the amount of solution that had been used. The contents of the absorber were next washed into a large beaker and the hydrogen bromide determined by titration with a twice normal alkali solution, which had been carefully standardised and was free from carbonate. The difference between the amount of acid found in this manner and the amount of solution actually weighed gave the weight of the dissolved substance. The alkali was contained in a weighing burette of the pattern shown in fig. 4. In order to deliver from this burette, the cap *b* was removed and the stop-cock opened, when by blowing through the side tube *d* the liquid was forced through the tube *c*. The burette was weighed to 0·002 gramme, a glass counterpoise of approximately the same volume being used.

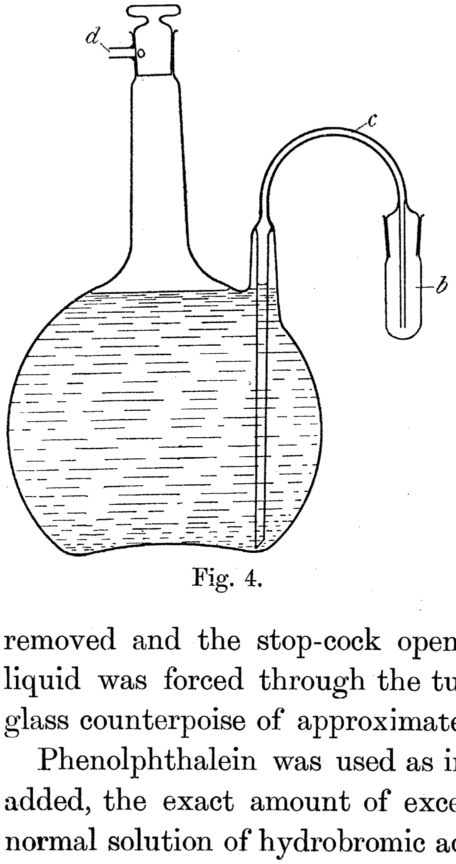

Fig. 4.

Phenolphthalein was used as indicator, and an excess of one or two drops of alkali added, the exact amount of excess being determined by titration with a twentieth normal solution of hydrobromic acid.

In order that the determination of acid by titration should be strictly comparable with the weighing of the solution, the alkali was standardised by direct comparison with about 60 grammes of pure hydrogen bromide which was weighed in the absorber. Duplicate standardisations of the same alkali solution gave the following figures for the amount of hydrobromic acid equivalent to 1 gramme of alkali solution:

(1) 1 gramme solution = 0·149293 HBr,
(2) 1 ,, ,, = 0·149301 HBr.

The Electrolysis.

In designing an electrolytic cell it was necessary to consider the changes of density which were brought about during electrolysis, and to construct an apparatus in which the lighter solution would be formed at the top and the heavier at the bottom. Preliminary experiments were undertaken to ascertain the influence of an increase in concentration of the dissolved substance on the density of the solution, and it was found that in all the cases examined the less concentrated solution was the heavier.

The experiments which had been conducted to test FARADAY'S law having shown that the bromine is carried to the anode, the apparatus was designed to enable the cathode solution to be analysed. The anode solution was neglected, as its analysis was complicated by the presence of bromine.

The apparatus which has been employed is shown diagrammatically in fig. 5. It consisted of a U-tube, both arms of which were provided with side tubes. The anode *a* consisted of a platinum wire, which was sealed through the bottom of the side tube O, the other end of the wire projecting into the glass tube *h*, by means of which connection with the battery could be made. A small side tube *n* was also attached to the same arm of the U-tube, and there was a constriction at *r* into which the hollow stopper *s* was ground to fit tightly. The stopper *s* was sealed to a branch of the transferrer T′, and a hole was bored in its shoulder to allow the free passage of liquid through the transferrer.

It was found in the preliminary experiments that a considerable amount of mixing was occasioned by the escape of hydrogen at the cathode, and in order to reduce this to a minimum, the side tube P was attached to the apparatus. In the centre of P a narrow tube *u* was fastened, inside which the cathode was placed, so that the escaping bubbles of hydrogen were confined to this tube and very little mixing took place outside P. A small hole had been blown in the wall of the tube *u* so that the pressure should be equal at all parts of the surface of the liquid. The tube P was made long enough to be held in the clamp outside the vacuum vessel in which the apparatus was placed and its end was closed by a stopper *w*, through which passed the platinum wire which was used as cathode. One end of the transferrer T was made long enough and bent so as to reach to the bottom of the U-tube, and both the transferrers were attached to the open ends of the main apparatus by pieces of india-rubber tubing, *t* and *t′*.

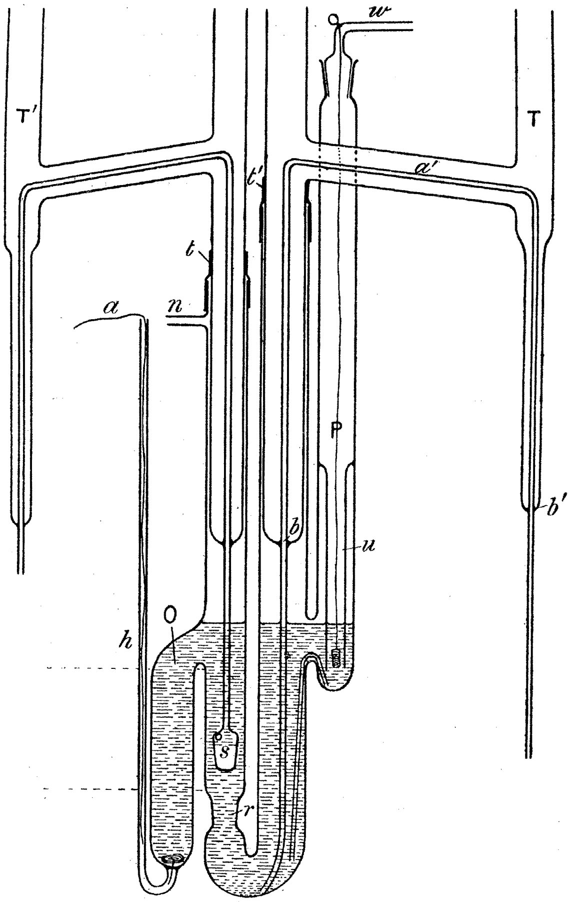

Fig. 5.

In carrying out an experiment the method of procedure was as follows:—The apparatus was placed in the vacuum vessel and held rigidly by a clamp which grasped the tube P. The open ends of the transferrers T and T′ were then closed by rubber tubing and glass plugs, and a tube filled with phosphoric oxide was attached to *n*. The stop-cock *w* with the cathode attached was then removed and a third transferrer (not shown in the figure) inserted in the tube P. The acetone was then placed in the vacuum vessel and solid carbon dioxide added till the temperature had fallen to the desired point. The outside arm of the third transferrer was provided with a filter of glass wool and reached to the bottom of a vessel containing 10 cub. centims. more of the solution than was necessary for the electrolysis. After the whole of this liquid had been forced into the apparatus by blowing air from a rubber bellows into the vessel containing the liquid, the transferrer was removed and the stopper *w* replaced.

Before commencing the experiment three absorbers had been filled with distilled water and weighed. The transferrer T was next attached to one of these in the manner previously described and 10 cub. centims. of the solution were taken out and analysed. This analysis gave the concentration of the solution before electrolysis. A silver voltameter and a milliampermeter having been placed in the circuit, the electrolysis was started by connecting the electrodes to the terminals of a battery, the voltage of which could be varied within wide limits, and the voltage was adjusted so as to give a current of not more than 12 or 14 milliampères. If a larger current than this was employed, the heating effect was found to cause mixing of the liquid by convection. After the electrolysis had been continued for about two hours it was stopped by removing the cathode from the voltameter, and the liquid in the cell was separated into two portions by inserting the stop-cock *s* into its socket. An absorber was then attached to the transferrer T′ and the column of liquid contained within the dotted lines was blown into the absorber, which was then removed. The third absorber was next attached to the transferrer T and the solution contained in the apparatus forced into it by blowing through *w*, the tube *v* acting as a syphon to remove the liquid contained in P, and finally the third absorber was removed and weighed. Three solutions were thus obtained for analysis, namely: (1) the 10 cub. centims. which had been removed before electrolysis and gave the original concentration; (2) the small quantity taken out in the second absorber (which should be of the same concentration as (1)); and (3) the solution surrounding the cathode, which gave the change of concentration brought about by the electrolysis.

In order that an experiment should be successful it was necessary that the foregoing procedure should be strictly followed. Identical values for the original concentration and that of the middle portion have never been obtained unless the whole solution was first placed in the apparatus and all three portions were taken from it.

At least half-a-dozen other methods have been tried without success. Fortunately it is easy at the close of an experiment to see if any mixing has taken place, from the fact that bromine is liberated at the anode, where it forms a deep red solution in the hydrogen bromide. If the experiment has been successful, this solution remains as a very clearly defined layer surrounding the anode, and the coloration does not extend more than about 1·5 centims. up the tube. On the other hand, if mixing has taken place, as may happen either if the current is too large or if the temperature of the bath is allowed to vary, the bromine is distributed throughout the solution and no clearly defined layer is seen at the anode.

Experimental Results.

The results of the experiments are contained in the following table, in which the concentration of the various solutions is expressed under N, which gives the number of gramme equivalents of dissolved substance per litre of solution, the percentage also being given in the 3rd column. The 4th column contains the weight of silver deposited on the cathode of the silver voltameter, the 5th column gives the weight of substance transported, the 6th column the cation transport numbers.

Number of experiment.	N.	Percentage of composition.	Deposited in cathode.	Transported.	p.
SERIES 1. ETHER. N = 1·0 approximately.					
2	1·07	3·96	·0995	·0567	·83
3	1·14	4·26	·0918	·0530	·82
7	1·06	3·92	·1120	·0607	·79
				Mean =	·82
SERIES 2. ETHER. N = 1·7 to 2·04.					
6	1·72	6·61	·0988	·0489	·73
8	1·80	6·85	·0997	·0212	·31
17	2·04	8·03	·0918	·0366	·58
SERIES 3. TRIETHYLAMMONIUM BROMIDE. N = ·5 to ·75.					
5	·75	6·54	·1064	0·382	·21
9	·515	4·47	·0921	0·288	·18
10	·622	5·37	·0817	0·300	·22
				Mean =	·20
SERIES 4. TRIETHYLAMMONIUM BROMIDE. N = 1·04.					
11	1·04	8·98	·0907	·0473	·31
12	1·05	9·01	·1051	·0700	·39
				Mean =	·35
SERIES 5. ACETONE. N = 1·0.					
15	1·05	2·98	·0863	·0151	·41
16	1·01	2·87	·0938	·0141	·36
				Mean =	·38
SERIES 6. ACETONE. N = 1·8.					
13	1·83	5·37	·0931	·0361	·91
14	1·82	5·32	·0878	·0372	·99
				Mean =	·95
SERIES 7. METHYLHEXYLKETONE.					
18	·90	5·34	·0965	·0398	·38
19	·90	5·36	·0880	·0384	·41
				Mean =	·39
SERIES 8. METHYLHEXYLKETONE.					
20	1·80	11·83	·1015	·0815	·75
21	1·80	11·87	·0943	·0830	·82
				Mean =	·77

SUMMARY.

Substance.	N.	Mean value of p.
Ether	1·0	·82
Triethylammonium bromide	0·5	·18
,, ,,	0·62 – 0·75	·22
,, ,,	1·04	·35
Acetone	1·0	·38
,,	1·82	·95
Methylhexylketone	0·9	·39
,,	1·8	·77

With the exception of Nos. 1 and 4, which unfortunately were lost, all the experiments which have been made are given in the tables. The transport number of each substance has been measured at two concentrations, the more concentrated solution usually containing about twice as much solute as the other. It will be seen that the cation transport number is always increased by increase of concentration and that the amount of disagreement between parallel experiments, although in some cases approaching 10 per cent., is never sufficient to leave any doubt as to the influence of change of concentration. This change from analogy with aqueous solutions indicates an increase in the complexity of the cation as the solution becomes stronger, but the measurements of conductivity and of the molecular weight, which are given in Part II., do not appear to confirm this conclusion. The significance of the change will be discussed in Part IV.

A special significance is to be attached to the results of Series 2, for the following reasons :—In the foregoing description of the method of analysis it has been explained that after the solution was transferred to the absorber the hydrogen bromide was allowed to evaporate and to become dissolved in the water. During the evaporation the temperature of the liquid in A gradually rose until finally it reached that of the atmosphere, when the liquid which remained was a saturated solution of hydrogen bromide in ether.

At this stage little or no decomposition occurred in a solution which had not been electrolysed, or in a dilute solution which had, but in the case of the cathode portion of a concentrated electrolysed solution the decomposition which occurred was sufficient to give results so discordant as those tabulated in Series 2. This behaviour seems to indicate the formation at the cathode of some extremely unstable substance during the electrolysis of these solutions, and it is possible that a compound is formed by the union of two or more discharged cations by a reaction similar to that by which persulphuric acid results from the electrolysis of sulphuric acid.

PART IV.

The Abnormal Variation of Molecular Conductivity, etc.

By B. D. Steele, D. McIntosh *and* E. H. Archibald.

In discussing the nature of those inorganic liquids which are able to act as "ionising" solvents, Walden ('Zeit. für anorg. Chemie,' 1900, 25, p. 209) states that "a measurable dissociation (ionisation) occurs only in combinations of the elements of the 5th and 6th groups of the periodic table and in compounds of these elements with hydrogen and the halogens." We have shown in Part I. of this investigation that the hydrides of the halogen elements and of sulphur belong to the class of "ionising" solvents, so that this class consists of compounds of the elements of the 5th, 6th, and 7th groups amongst themselves and with hydrogen. Attempts have been frequently made to arrive at some generalisation connecting the so-called "ionising" power with certain physical constants of the pure solvents.

Thus, according to Nernst and Thomson, a close relationship exists between the dissociating power and the dielectric constant. These investigators were led to look for this relation by the consideration that the force with which two electrically charged bodies attract or repel each other depends on the magnitude of the dielectric constant of the separating medium, and as the ions are to be regarded as electrically charged bodies, the force attracting two unlike ions will be more weakened, and dissociation aided, in a solvent of high than in one of low dielectric constant.

This expectation is only partially realised in the parallelism which exists for a great number of solvents between the two properties in question; thus liquefied ammonia which possesses a low dielectric constant is a better dissociating solvent for some substances than water which has a high dielectric constant; moreover, the majority of electrolytes are far more dissociated in water than in hydrocyanic acid or in hydrogen peroxide, although the dielectric constant of water is less than that of either of these liquids. No measurements of the dielectric constant of the halogen hydrides or of sulphuretted hydrogen have yet been made.

Dutoit and Aston ('C. R.,' 1897, 125, p. 240) have attempted to show that ionic dissociation occurs only in solvents in which the molecules are associated, but, although numerous instances occur in which this parallelism obtains, it is by no means a general rule. Thus, although both ammonia and sulphur dioxide are unassociated liquids, both are able to form conducting solutions; and although the hydrides of bromine, iodine, and sulphur are unassociated, and hydrogen chloride is associated, all four compounds are equally able to act as conducting solvents, whilst this property is not possessed by hydrogen phosphide, which is associated.

Brühl ('Zeit. Phys. Chem.,' 1898, 27, p. 319) has pointed out that unsaturated compounds, as a rule, are good conducting solvents. A consideration of the non-conducting unsaturated solvents phosphorus hydride and trichloride, and of the conducting saturated solvent phosphorus oxychloride, is sufficient to show that this is not a general rule.

The heat of vaporisation (Obach, 'Phil. Mag.,' 1891, (5), 32, p. 113) is a fourth property which has been suggested as being intimately connected with the dissociating power of the solvent. In this case, as in that of the others considered, the connection is very obscure and many exceptions occur.

The temperature coefficients of conductivity and of viscosity are approximately equal in the case of aqueous solutions. This is not so in solutions in the solvents examined by us, although in these, also, a rise of temperature conditions an increase of conductivity and a decrease of viscosity. It is interesting to note that the increase of conductivity is, in nearly all cases, *greater* than the decrease of viscosity.

The foregoing summary shows that failure has attended every attempt which has been made to express the power of forming conducting solutions as a function of the solvent only.

As a matter of fact, every solvent exhibits a very marked selective action as regards the nature of the conducting solute. Thus water dissolves the majority of salts to form solutions which conduct the current; organic bodies also, other than salts, are in many cases soluble, but the solutions are not conductors. Hydrocyanic acid behaves similarly to water, but only a few salts are appreciably soluble in this solvent. Ammonia, sulphur dioxide, and some other solvents form conducting solutions, not only with many salts, but also with a few organic substances not usually classed as electrolytes. The halogen hydrides, on the other hand, form conducting solutions with non-saline organic substances, as well as with salts of the ammonium bases, but such solutions are not formed with metallic salts.

It is evident, therefore, that the ability to form a conducting solution is a function of both the solute and the solvent, and this has been recognised in the various attempts that have been made to connect the ionising power of a solvent with its tendency to form compounds with the solute. Indeed Cady ('Jour. Phys. Chem.,' 1897, 1, p. 707) was led to investigate the conductivity of solutions of substances in ammonia from the analogy between the water and the ammonia compounds of copper sulphate.

Kahlenberg and Schlundt ('Jour. Phys. Chem.,' 1902, 6, p. 447) express the opinion that conductivity is due to mutual action between the solute and the solvent; and an attempt to obtain experimental evidence in support of this view has been made by Patten ('Jour. Phys. Chem.,' 1902, 6, p. 554).

For many solvents the substances which dissolve to form conducting solutions may be broadly designated as those which enter into combination with the solvent.

Thus the metallic salts as a class are characterised by their tendency to form compounds with water, while non-saline organic bodies as a class are not able to form such compounds.* Many, but not all, salts which form ammonia compounds dissolve in ammonia to form conducting solutions.

Compounds of the solute with the solvent are also clearly indicated in the case of many conducting solutions in sulphur dioxide, and WALDEN and CENTNERSZWER ('Zeit. Phys. Chem.,' 1903, 42, p. 432) have isolated and investigated two such compounds containing potassium iodide and sulphur dioxide.

In the halogen hydrides we find that the only substances which conduct are the amines, alcohols, ethers, ketones, &c., all of which are able to enter into combination with the solvents. Many similar cases have been observed amongst organic solvents, and as an example of these reference may be made to solutions in amylamine (KAHLENBERG and RUHOFF, 'Journ. Phys. Ch.,' 1903, 7, p. 254).

The study of the behaviour of aqueous solutions has led to ARRHENIUS' theory of ionic dissociation and to VAN 'T HOFF'S theory of solutions; and numerous investigations have been undertaken with the object of testing these theories, when applied to solutions in non-aqueous solvents.

As a result it has been found that, as required by the theory, most substances, when dissolved in ammonia, sulphur dioxide, hydrocyanic acid, and some other solvents, show an increase of the molecular conductivity, μ, with dilution, but that the opposite change occurs in solutions of a few substances in the same solvents. This difference in behaviour cannot therefore be conditioned by the nature of the solvent only, although if we consider the inorganic hydrides as solvents, we find that μ varies normally, that is to say, increases with dilution, in solutions in water and ammonia, hydrides, namely, of elements in the first series of the periodic table, whereas μ decreases with dilution in solutions in the remaining hydrides, the variation therefore being abnormal.†

The results of the molecular weight determinations in non-aqueous solvents are, as a general rule, not concordant with the conductivity results, many conducting solutions being known in which, contrary to expectations, the dissolved substance appears to be associated.

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* The view that compounds of the solute and the solvent exist also in solutions appears to be steadily gaining ground, see MORGAN and KANOLT ('Jour. Amer. Chem. Soc.,' 1904, 26, p. 635) and JONES and GETMAN ('Zeit. Phys. Chem.,' 1904, 49, p. 390).

† Amongst others the following cases have been observed of solutions in which the molecular conductivity decreases with dilution: Silver nitrate, cadmium iodide, and ferric chloride in amylamine (KAHLENBERG and RUHOFF, 'Jour. Phys. Chem.,' 1903, 1, p. 284); Antimony bromide and phosphorus pentabromine in bromine (PLOTNIKOFF, 'Jour. Russ. Phys. Chem. Soc.,' 1902, 34, p. 466; 1903, 35, p. 794); Hydrogen chloride in ether and in amyl alcohol (KABLUKOFF, 'Zeit. Phys. Chem.,' 1889, 4, p. 429); Hydrogen chloride in cineol (SACKUR, 'Ber. D. Chem. Ges.,' 1902, 35, p. 1242), &c.

The consideration of these abnormalities has led KAHLENBERG to conclude that the theory of ionic dissociation is not applicable to the majority of conducting solutions.

It is our object to show that the abnormal behaviour of solutions in the solvents examined by us can be simply and consistently explained in terms of the theory of ARRHENIUS, if the assumption is made that the original dissolved substance, being itself incapable of undergoing ionic dissociation, either polymerises or combines with the solvent to form a compound containing more than one molecule of the solute, and that the polymer, or compound, as the case may be, then acts as the electrolyte.

Those non-saline organic substances which are able to conduct the current when dissolved in certain solvents are considered by WALDEN ('Zeit. Phys. Chem.,' 1903, 43, p. 385) to be abnormal, in view of their usually well-known constitutions and their behaviour in aqueous solutions, but if the foregoing assumption of the formation of compounds be made, these substances are not more abnormal electrolytes than ammonia, which with water forms the compound ammonium hydroxide.

It has been suggested that the existence of compounds of the solute with the solvent is proved by the abnormal variation of the molecular conductivity, to which reference has been made; but the following considerations will show that an increase of μ with dilution furnishes no evidence for or against the occurrence of such compounds.

Let us suppose that a reaction between the solute, AB, and the solvent, CD, takes place according to the equation

$$\mathrm{AB+CD} \rightleftarrows \mathrm{AB, CD},$$

and let

$$a \qquad b \qquad\qquad c$$

be the active masses of the three substances.

Now, provided that moderate dilutions are used, we are justified in regarding b as constant, when from the law of mass action $\frac{c}{a} = \text{constant}$.

Now if conduction is due to the dissociation of the compound ABCD, the number of dissociated molecules is given by αc, where α is the degree of ionic dissociation; but $c = \mathrm{K}a$; therefore the concentration of the ions is equal to $p\alpha\mathrm{K}a$ if p is the number of ions formed from one molecule of solute.

But the specific conductivity κ of the solution is proportional to the ionic concentration, and therefore

$$\kappa = p\alpha k\mathrm{K}a = \alpha\mathrm{K}'a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

and since the molecular conductivity

$$\mu = \frac{\kappa}{a} = \alpha\mathrm{K}',$$

it must vary with α, that is to say, it must increase with dilution even when a compound of the solute with the solvent is formed.

This is the case, for example, in an aqueous solution of ammonia, to which reference will be made later.

If, however, we assume that two or more molecules of AB unite to form a compound which undergoes ionic dissociation, AB itself being unable to conduct the current, then the molecular conductivity may *decrease* with dilution whether the solvent enters into the composition of the electrolytic compound or not.

If we consider the two cases :—

(1) A compound of n molecules of solute with m molecules of solvent is formed according to the equation

the active masses being

$$\underset{a}{n\,(\mathrm{AB})} + \underset{b}{m\,(\mathrm{CD})} \rightleftarrows \underset{\text{and } c.}{(\mathrm{AB})_n\,(\mathrm{CD})_m},$$

Then, if we again consider sufficiently dilute solutions, b may be regarded as constant, and

$$ka^n = k'c \quad \text{or} \quad c = \mathrm{K}a^n.$$

If ionic dissociation occurs so that α* of the compound is ionised, then, as before, the ionic concentration $= p\alpha c = p\alpha \mathrm{K} a^n$.

The specific conductivity

$$\kappa = pk'\alpha \mathrm{K} a^n = \alpha \mathrm{K}' a^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

The molecular conductivity

$$\mu = \frac{\kappa}{a} = \alpha \mathrm{K}' a^{n-1},$$

and since the dilution

$$\mathrm{V} = \frac{1}{a},$$

$$\kappa = \alpha \mathrm{K}' \mathrm{V}^{-n},$$

or

$$\kappa \mathrm{V}^n = \alpha \mathrm{K}'.$$

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* In the development of this relation no assumption has been made as to the nature of the ionisation of the electrolyte.

If we consider the second case, for example, there are a number of ways in which the compound A_nB_n can ionise.

Thus

$$(1) \quad \mathrm{A}_n\mathrm{B}_n \rightleftarrows \overset{\oplus}{\mathrm{A}_n\mathrm{B}_{n-1}} + \overset{\ominus}{\mathrm{B}},$$

$$(2) \quad \mathrm{A}_n\mathrm{B}_n \rightleftarrows \overset{nx\oplus}{\mathrm{A}_n} + n\overset{\ominus}{\mathrm{B}},$$

and generally

$$(3) \quad \mathrm{A}_n\mathrm{B}_n \rightleftarrows \overset{rx\oplus}{\mathrm{A}_n\mathrm{B}_{n-r}} + r\overset{\ominus}{\mathrm{B}}.$$

If dissociation takes place according to the first of these equations, 2 ions result from the dissociation of 1 molecule of the electrolyte.

If according to the second equation, the number of ions is $(n+1)$, and, generally, the number is $(r+1)$.

Now whatever value r may have, the number of ions present is given by $\alpha\,(r+1)$ and is therefore proportional to α.

(2) Combination between the solute and the solvent does not occur, but an ionising polymer of the solute is formed. In this case the equation is

$$n\mathrm{AB} \rightleftarrows \mathrm{A}_n\mathrm{B}_n,$$

the active masses are

$$a \quad \text{and} \quad c,$$

and from the law of mass action

$$ka^n = k'c \quad \text{and} \quad c = \mathrm{K}a^n,$$

which leads to the same expression as before, namely

$$\kappa = \alpha\mathrm{K}'a^n, \quad \mu = \alpha\mathrm{K}'a^{n-1}, \quad \text{and} \quad \kappa\mathrm{V}^n = \alpha\mathrm{K}'.$$

Now, since the number of molecules always increases with dissociation, α must increase with dilution in whatever manner dissociation takes place; but unless the increase in α is greater than the diminution in a^{n-1} which is brought about by dilution, the sum of the effects due to the variation of α and of a^{n-1} in the equation

$$\mu = \alpha\mathrm{K}'a^{n-1}$$

must produce a diminution in μ with increasing dilution.

It follows, therefore, that the molecular conductivity may decrease with dilution in the case of any conducting solution in which the electrolyte is a compound of two or more molecules of the dissolved substance, whether it is a simple polymer or a compound containing one or more molecules of the solvent.

It follows, also, from the equation

$$\kappa = \alpha\mathrm{K}'a^n$$

that in the case of a solution in which the ionic dissociation was approaching completion, in which α therefore varied but slightly, the specific conductivity of the solution should be very nearly proportional to the n^{th} power of the concentration of the dissolved substance; for such solutions we therefore have the relation

$$\frac{\kappa}{a^n} = \kappa\mathrm{V}^n = \mathrm{K}'.$$

Although we have shown that it is not necessary that union with the solvent should occur in order to bring about an abnormal variation of μ, we nevertheless consider that the formation of such compounds* affords the best explanation of the behaviour of solutions of organic substances in the halogen hydrides and in sulphuretted hydrogen.

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* See also WALKER, 'J. C. S.,' 1904, vol. 85, p. 1082, and WALKER, MCINTOSH, and ARCHIBALD, 'J. C. S.,' 1904, vol. 85, p. 1098.

We are led to this conclusion by a consideration of the following facts:—

(1) Large quantities of heat are evolved when conducting solutes are added to either of these solvents. This heat evolution we take to indicate chemical union.

(2) Compounds containing a varying number of molecules of solvent have been isolated (ARCHIBALD and McINTOSH, 'Jour. Chem. Soc.,' 1904, vol. 85, p. 919).

(3) The ionisation of a compound such as $((CH_3)_2CO)_nHBr$ is much easier to understand than that of a simple polymer such as $((CH_3)_2CO)_n$.

In order to apply the foregoing conclusions to a specific case, we will consider a solution of acetone in hydrogen bromide.

According to our hypothesis, such a solution contains a compound of acetone and hydrogen bromide, the formula of which we will assume to be $Ac_3(HBr)_m$.

This compound dissociates simultaneously in two different ways, a certain number of molecules being dissociated into acetone and hydrogen bromide, other molecules being dissociated into ions, and the ratio of the number of molecules undergoing each dissociation will be constant.

Applying the equation $\mu = \alpha K' a^2$, we see that the molecular conductivity will increase with increasing concentration of the acetone, the increase—neglecting variation of α—being proportional to the square of the concentration. Similarly, we see that if α is nearly constant, the specific conductivity will be proportional to the cube of the acetone concentration. If, however, α is not constant, then κ/α will be proportional to the cube of the acetone concentration.

This conception of an intermediate compound which is able to break up in different ways is by no means new to chemists, and the solution of ammonia, which we have already referred to, furnishes an example of such a case, which, in many ways, is analogous to the preceding.

The compound that is formed in this solution is ammonium hydroxide, and the dissociations are

$$(1)\ NH_4OH \rightleftharpoons NH_3 + H_2O\,;$$

$$(2)\ NH_4OH \rightleftharpoons \overset{+}{N}H_4 + \overset{-}{O}H.$$

The relation between specific conductity and concentration for such a solution has been already developed in equation (1) $\kappa = \alpha K' a$, which is a special case of equation (2). Here again

$$\mu = \frac{\kappa}{a} = \alpha K',$$

so that

$$\alpha = \frac{\mu}{K}; \quad \text{but} \quad \alpha = \frac{\mu}{\mu_\infty},$$

so that K′ is simply the molecular conductivity at infinite dilution.

In order to test the conclusions that have been arrived at, we require to know the concentration of the unassociated solute for each dilution.

If A gram-molecules of the solute are dissolved in one litre of solvent, and if there are formed c gram-molecules of the electrolytic compound, then, if n molecules are required to form one molecule of the compound, nc molecules of solute will have been used, when equilibrium is established, so that the equilibrium equation is

$$k\,(\mathrm{A}-nc)^n = k'c,$$

or

$$c = \mathrm{K}\,(\mathrm{A}-nc)^n,$$

and the general expression for the specific conductivity becomes

$$\kappa = \alpha\mathrm{K}'\,(\mathrm{A}-nc)^n.$$

No solution of any substance in any one of the halogen hydrides has yet been found with high value for the conductivity, a fact which may be assigned to one of three causes, namely, either (1) the concentration, or (2) the coefficient of ionisation of the electrolyte is small, or (3) the ionic velocities may be very small. If we assume the first to be the most probable cause, $\mathrm{A}-nc$ will not differ much from A, and we may without sensible error make use of the values for the total concentration in applying the above equation to our results.

This has been done, the equation being used in the form of $\kappa\mathrm{V}^n = \alpha\mathrm{K}'$, and the results of the calculations are given in Tables I. and II.

Table I. contains the values of V and of $\kappa\mathrm{V}^n$ (or $\alpha\mathrm{K}'$) for those solutions in which $n = 2$, that is, in which two molecules of solute combine with the solvent to form one molecule of the electrolyte. Table II. contains the similar value for those solutions for which $n = 3$.

It will be noticed that in some cases the figures exhibit considerable irregular variation. This is to be expected from the fact that the measurements of conductivity and of concentration are subject to considerable experimental error. These errors were not specially guarded against, as our object was to establish beyond question the nature of the variation of μ with V rather than to obtain accurate measurements, which, in the present state of our knowledge, would not possess any special value.

The figures for K at very high dilution are, in some cases, quite valueless as a test of our hypothesis, on account of the enormous influence of very slight errors of observation at these dilutions.

The results contained in Tables I. and II. are shown graphically in figs. 1 and 2 respectively.

Table I.

Acetonitrile in Hydrogen Chloride.

V	21·7	8·33	4·73	3·22	2·17	1·09	0·81
$\alpha\kappa = \kappa V^2$	32·8	20·3	18·5	17·0	14·8	8·8	8·3

Acetamide in Hydrogen Chloride.

V	29·4	12·8	8·62	4·65	4·15	2·86	2·13	1·54	0·95	0·51
$\alpha\kappa = \kappa V^2$	46·7	40·0	36·8	29·6	28·7	23·4	20·0	16·6	11·5	6·42

Triethylammonium Chloride in Hydrogen Chloride.

V	71·4	37·0	20·4	16·1	11·6	9·43	7·69	6·13	5·00	4·25	3·64	2·99
$\alpha\kappa = \kappa V^2$	128·6	667	465	437	365	343	334	316	302	285	281	254

Hydrocyanic Acid in Hydrogen Chloride.

V	41·4	21·3	14·1	10·2	9·2	7·35	4·90	4·10	3·12	2·56	1·79	1·23
$\alpha\kappa = \kappa V^2$	21·6	19·6	14·0	11·0	12·0	10·9	10·3	11·5	11·5	11·5	10·4	9·4

Ether in Hydrogen Chloride.

V	12·5	5·0	3·12	1·92	1·45	1·09	0·88	0·72	0·61
$\alpha\kappa = \kappa V^2$	1·75	1·15	1·22	1·82	2·05	2·22	1·93	2·08	1·88

Tetramethylammonium Chloride in Hydrogen Bromide.

V	200	21·3	14·1	10·5	9·4
$\alpha\kappa = \kappa V^2$	1080	190·0	149·0	131·0	125·0

Tetramethylammonium Bromide in Hydrogen Bromide.

V	62·3	34·5	11·8
$\alpha\kappa = \kappa V^2$	43·7	25·0	14·8

Tetramethylammonium Iodide in Hydrogen Bromide.

V	62·5	34·5	22·1
$\alpha\kappa = \kappa V^2$	546	360	290

Triethylammonium Chloride in Hydrogen Bromide.

V	143·0	50·0	27·7	15·6	8·33	5·26	3·33	2·17	16·1
$\alpha\kappa = \kappa V^2$	27·4	11·0	13·8	12·9	16·6	17·3	16·4	13·5	13·3

Ether in Hydrogen Bromide.

V	16·6	5·55	4·00	2·00	1·54	1·23	1·03	0·68	0·47
$\alpha\kappa = \kappa V^2$	·083	·078	·096	·212	·199	·187	·170	·124	·341

TABLE I. (continued).

ACETAMIDE IN HYDROGEN BROMIDE.

V	90·9	58·8	23·3	14·5	10·2	6·66	3·85	3·03	2·08	1·41
$\alpha\kappa = \kappa V^2$	5·94	5·88	6·3	6·1	5·8	6·25	5·65	5·45	4·92	4·45

ACETONITRILE IN HYDROGEN BROMIDE.

V	33·3	4·76	3·70	2·50	1·85	1·47	1·22	0·96	0·72
$\alpha\kappa = \kappa V^2$	4·61	5·15	4·80	6·2	6·4	6·8	6·7	6·7	7·2

ETHYL PROPIONATE IN HYDROGEN BROMIDE.

V	12·15	7·14	5·26	3·45	2·63	1·92	1·39
$\alpha\kappa = \kappa V^2$	·62	1·14	2·00	1·7	2·16	2·30	2·28

ORTHO-NITROTOLUENE IN HYDROGEN BROMIDE.

V	25	16·6	12·5	11·1	8·33	3·85	2·38	1·50	0·92	0·66
$\alpha\kappa = \kappa V^2$	1·00	1·16	0·87	1·11	0·92	0·71	1·06	1·00	0·94	0·845

PIPERIDINE IN SULPHURETTED HYDROGEN.

V	9·09	1·18	0·90	0·75	0·64	0·55
$\alpha\kappa = \kappa V^2$	·18	·34	·35	·34	·31	·28

TETRAETHYLAMMONIUM CHLORIDE IN SULPHURETTED HYDROGEN.

V	34·5	11·0	4·25	3·32	2·93
$\alpha\kappa = \kappa V^2$	59·4	37·6	16·4	13·4	11·3

TABLE II.

V.	κV^3.	V.	κV^3.
ACETONE IN HYDROGEN BROMIDE.			
8·33	6·94	1·64	6·2
5·00	8·50	1·35	5·9
3·23	8·03	1·07	4·9
2·00	5·6	0·75	3·2

V.	κV^2.	$\alpha K = \kappa V^3$.	V.	κV^2.	$\alpha K = \kappa V^3$.
TRIETHYLAMMONIUM CHLORIDE IN HYDROGEN IODIDE.					
27·8	1·95	54	5·55	6·38	35·4
21·7	2·4	52	4·50	6·16	30·0
15·4	3·56	55	3·85	7·35	28·3
10·4	4·47	47	3·13	7·42	23·4
8·55	5·56	47·5	2·50	7·42	18·6
7·14	5·71	41	2·17	7·77	16·9
ETHER IN HYDROGEN IODIDE.					
10·0	·2	2·0	1·49	1·65	2·46
5·88	·41	2·42	1·25	1·75	2·19
3·33	·73	2·44	1·06	1·90	2·01
2·46	1·50	3·69	0·88	1·94	1·70
1·79	1·50	2·69			
ETHYL BENZOATE IN HYDROGEN IODIDE.					
16·6	·233	3·86	2·56	4·22	10·8
7·14	1·22	8·67	2·04	4·69	9·6
4·76	2·23	10·6	1·66	4·94	8·2
3·45	3·54	12·1	1·37	4·93	0·68
TRIETHYLAMMONIUM CHLORIDE IN SULPHURETTED HYDROGEN.					
71·4	8·6	61·3	4·00	3·48	13·9
12·8	2·69	34·4	3·13	3·66	11·5
8·33	2·75	22·9	2·50	3·95	9·88
NICOTINE IN SULPHURETTED HYDROGEN.					
66·7	2·0	—	2·27	·86	1·96
14·3	·57	—	1·92	·96	1·84
6·67	·40	2·67	1·03	·79	0·81
4·00	·64	2·56			

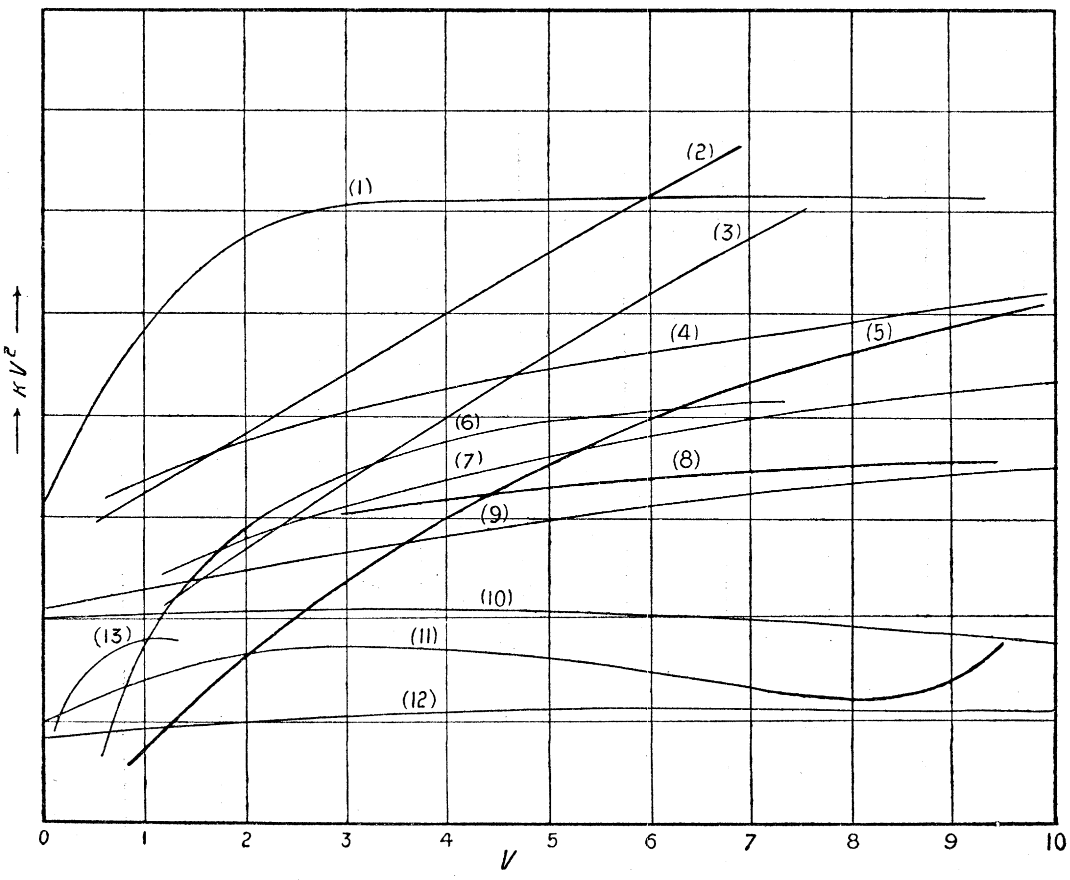

Fig. 1.

(1) Acetamide in hydrogen bromide.
(2) Tetramethylammonium bromide in hydrogen bromide.
(3) ,, iodide ,, ,,
(4) Acetonitrile in hydrogen chloride.
(5) Tetramethylammonium chloride in hydrogen sulphide.
(6) Acetamide in hydrogen chloride.
(7) Triethylammonium chloride in hydrogen chloride.
(8) Tetramethylammonium chloride in hydrogen bromide.
(9) Hydrocyanic acid in hydrogen chloride.
(10) Ether in hydrogen chloride.
(11) Triethylammonium bromide in hydrogen bromide.
(12) Orthonitrotoluol in hydrogen bromide.
(13) Piperidine in hydrogen sulphide.

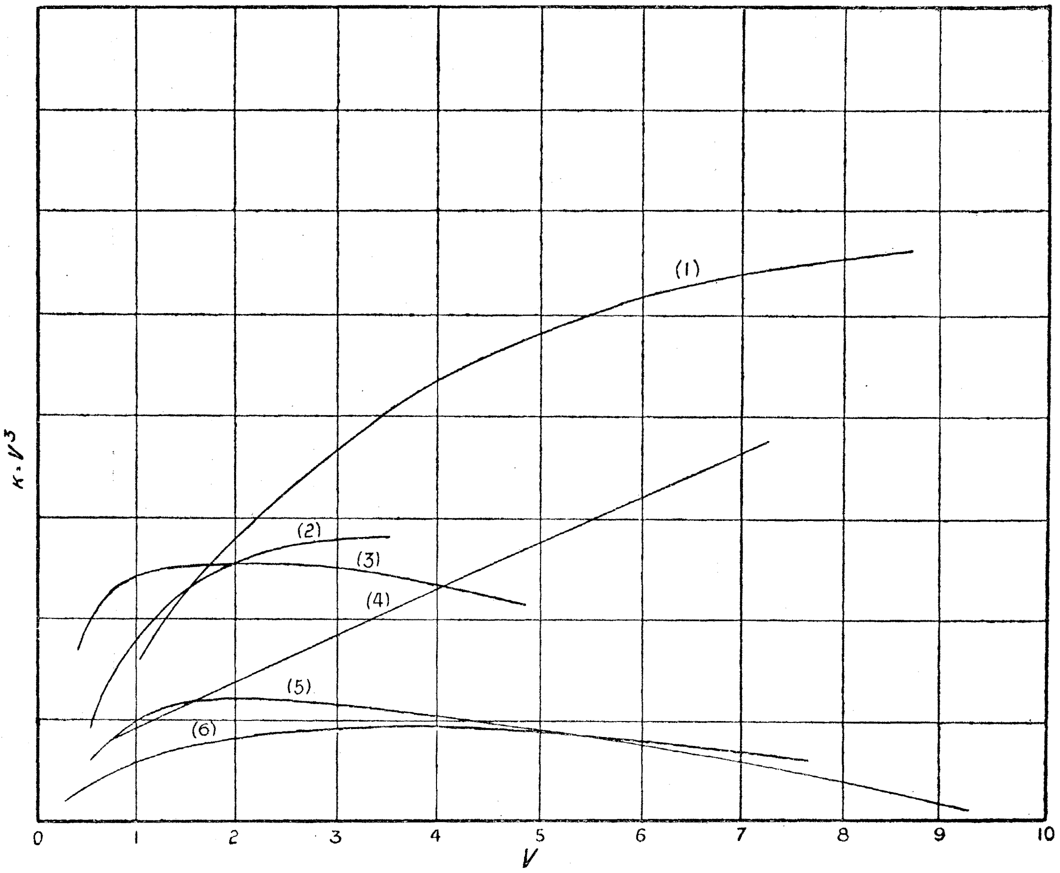

Fig. 2.

(1) Triethylammonium chloride in hydrogen iodide.
(2) Nicotine in hydrogen sulphide.
(3) Ether in hydrogen iodide.
(4) Triethylammonium chloride in hydrogen sulphide.
(5) Ethyl benzoate in hydrogen iodide.
(6) Acetone in hydrogen bromide.

Fig. 3 contains typical curves showing the variation of $\kappa V = \mu$ with V for

(1) Substances dissolved in halogen hydrides ;
(2) Potassium chloride in water ;
(3) Sodium carbonate in water ;
(4) A solution of ammonia in water.

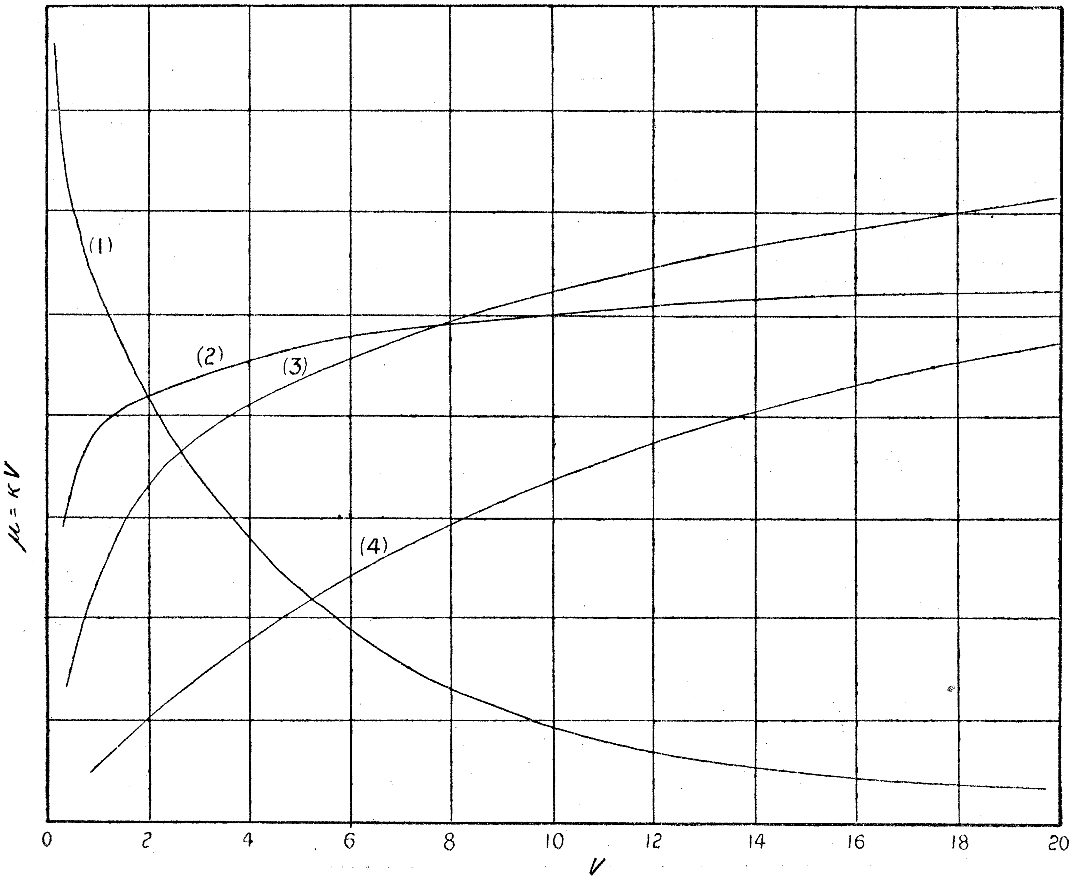

Fig. 3.

The similarity between the variation with dilution of κV^2 (or κV^3) for solutions in the halogen hydrides and that of $\kappa V = \mu$ for aqueous solutions is at once apparent.

Since in the former case $\kappa V^2 = \alpha K'$, and in the latter $\mu = \kappa V = \alpha \mu$, and since both μ_∞ and K′ are constants, it is evident that both sets of curves represent a variation in α and that K′ represents the value of the molecular conductivity at infinite dilution of the *electrolytic compound.*

Although the majority of the curves in figs. 1 and 2 are analogous to those for water solutions, some of them exhibit a maximum value for κV^n, whilst others are extremely steep, thus indicating a very rapid increase in the value of α.

These irregularities are to be expected, since, as already stated, we have been compelled to use, in the calculation of κV^n, the total concentration instead of that of the unassociated substance.

It is also possible that more than one type of electrolytic compound is formed in a given solution, as, for example, the compounds ABCD and $(AB)_2CD$; in which case the total conductivity will be the sum of the conductivities due to the ionisation of each of these compounds. In such a case as this extremely complicated curves might result. Moreover, we cannot strictly apply the equation to the concentrated solutions, since for these the active mass (b) of the solvent is no longer constant.

The fact that the curves, as a whole, are so analogous to those for a simple electrolyte in aqueous solution appears to indicate that, as a general rule, the main effect is due to the ionisation of a single substance.

The equation $\kappa V^n = \alpha K'$ should also be applicable to abnormal solutions in other solvents. This is the case for the solutions investigated by PLOTNIKOFF ('Zeit. Phys. Chem.,' 1904, 48, p. 224), who found very abnormal variations of μ for antimony tribromide and phosphorus pentabromide in bromine. The experimental figures for antimony tribromide lead to the following values for V and κV^n :—

V	251,	312,	356,	418,	445,	552,	918
κV^3	154,	178,	171,	174,	164,	98,	168

The molecular conductivity of phosphorus pentabromide in bromine varies so irregularly as to suggest that some disturbing effect is at work rendering the figures valueless.

Another solvent in which μ increases with concentration is amylamine (KAHLENBERG and RUHOFF, 'Jour. Phys. Chem.,' 1903, 7, p. 254), and the equation has been applied to the measurements of conductivity for cadmium iodide, ferric chloride and silver nitrate dissolved in this solvent. The results of the calculations when $n = 2$, 3 and 4 are given in Table III. It will be noticed that maxima are shown in each case.

Passing on now to the consideration of the molecular weight determinations which are recorded in Part II., we find that some of these afford confirmation of our hypothesis, inasmuch as ether and acetone in dilute solutions possess a greater molecular weight than the theoretical.

TABLE III.

V.	κV.	κV^2.	κV^3.
	SILVER NITRATE IN AMYLAMINE.		
·4001	·530	·212	0·085
·4351	·639	·278	0·121
·5096	·870	·443	0·226
·6206	1·128	·700	0·434
·8629	1·402	1·21	0·021
1·158	1·476	1·71	1·98
1·685	1·376	2·32	3·91
2·302	1·144	2·63	6·06
2·850	0·908	2·59	7·37
3·261	0·744	2·43	7·91
6·330	0·168	1·06	6·73
11·45	0·038	0·44	4·98
31·07	0·008	0·24	7·72
81·63	0·002	0·16	1·33
	CADMIUM IODIDE IN AMYLAMINE.		
0·7810	·465	·363	·284
·8909	·534	·476	·424
1·095	·542	·594	·650
1·237	·480	·594	·735
1·450	·346	·502	·728
1·738	0·187	·325	·565
2·473	0·034	·084	·208
5·482	0·002	·011	·055

V.	Δ.	ΔV.
	FERRIC CHLORIDE IN AMYLAMINE.	
5·021	0·217	1·09
13·43	0·158	2·12
18·34	0·138	2·53
27·05	0·086	2·32

We have been unable to ascertain whether the molecular weight reaches a limiting value with dilution, as the experimental errors incidental to measurements at the low temperatures involved prevented the examination of the more dilute solutions.

KAHLENBERG, WALDEN, and others have called attention to many solutions in which, although μ varies normally, the solute is associated.

Thus WALDEN and CENTNERSZWER ('Zeit. Phys. Chem.,' 1902, 39, p. 513) found that the molecular weight of potassium iodide dissolved in hydrocyanic acid is twice as large as the normal. ABEGG ('Die Theorie der electrolytischen Dissociation,' p. 103) has pointed out that this can be explained by the assumption that the undissociated substance is polymerised; in which case a high average molecular weight might occur even with considerable ionisation.

A compound such as $(KI)_4$, for example, if it were completely dissociated into two ions, would have an average molecular weight of 332. We find that in most cases the molecular weight increases with increasing concentration, and although the opposite change occurs in dilute aqueous solution, this variation is the same as that which takes place in more concentrated aqueous solutions.

This will be seen from the following comparison of the figures for acetone dissolved in hydrogen bromide with those for lithium bromide dissolved in water, the latter figures being taken from a recent paper by JONES and GETMAN ('Zeit. Phys. Chem.,' 1904, 49, p. 390).

(*a*) Acetone in hydrogen bromide—

c = concentration in gram-molecules per litre = 0·51, 1·17, 1·85, 2·56;

$\frac{\Delta}{c}$ = molecular depression = 4·5, 4·5, 6·5, 11·5.

(*b*) Lithium bromide in water—

c = 0·48, 0·97, 1·94, 3·88; $\frac{\Delta}{c}$ = 4·07, 4·41, 5·31, 7·86.

JONES and GETMAN attribute the apparent increase in the number of molecules in more concentrated solution to the formation of hydrates in solution.

The low molecular weight which we have found for triethylammoniam chloride in sulphuretted hydrogen, although at first sight difficult to reconcile with the hypothesis of association, is not inconsistent with it.

Thus if the compound formation and subsequent dissociation takes place according to the general scheme

$$n\mathrm{AB}+m\mathrm{CD} \rightleftharpoons (\mathrm{AB})_n\,(\mathrm{CD})_m$$

and

$$(\mathrm{AB})_n\,(\mathrm{CD})_m \rightleftharpoons \overset{mx\oplus}{(\mathrm{AB})_n\,(\mathrm{CD})_m}+m\overset{-}{\mathrm{D}},$$

and if dissociation were nearly complete, it is evident that if m is equal to or greater than n, a larger number of molecules than n would be formed, and therefore the average would be less than the theoretical molecular weight.

We can offer no suggestion as to why toluene, when dissolved in hydrogen chloride, although it absolutely fails to conduct the current, possesses such an extremely low molecular weight. Similar cases have been observed by KAHLENBERG, but no explanation has been suggested.

A possible explanation of the abnormal variation of molecular conductivity might be found in the hypothesis that when acetone or ether is added to hydrogen bromide the acetone or ether acts as an ionising solvent, and the hydrogen bromide is ionised. When looked at from this point of view, the variation of μ which actually occurs appears as a normal one. This explanation is, however, shown to be incorrect when we come to consider the transport number experiments.

Thus, during the electrolysis of ether in hydrogen bromide, the deposition of 1 gram-molecule of silver by the current is accompanied by a transport of ·8 gram-molecule of ether to the cathode. But, if the ether did not take part in the electrolysis, the same result would be obtained by the transport of a sufficient quantity of bromine as anion from the cathode to the anode.

A simple calculation, however, shows that in order to bring this about no less than 23 gram-molecules of bromine must be transported for every gram-molecule of silver.

Now we have shown that Faraday's law is valid for solutions in hydrogen bromide, and accordingly we conclude that ether takes part in the carriage of the current, and that conduction is not due to ionisation of the hydrogen bromide.

Information regarding the constitution of the electrolyte is also afforded by the transport number. If we again consider the case of ether dissolved in hydrogen bromide, there is in solution an electrolyte of the formula $((C_2H_5)_2O)_2(HBr)_n$, which can ionise either

(1) into $\overset{+}{H}$ ions and a complex anion $((C_2H_5)_2O)_2Br_n$

or (2) ,, $\overset{-}{Br}$,, ,, cation $((C_2H_5)_2O)_2H$.

If the former, the ether will be transported to the anode as a component of a complex anion; if the latter, it will be carried to the cathode as a component of a complex cation. Experiment has proved that the latter is the case not only for ether but also for the other substances which have been examined.

It has been found that the cation transport number increases considerably with concentration. This increase can be easily explained if we assume, with Jones and Getman (*loc. cit.*), that the number of molecules of solvent in combination with one molecule of solute is greater in the more dilute solution.

According to the theory of Abegg and Bodländer ('Zeit. für Anorg. Chem.,' 1899, 20, p. 453), the resulting change of constitution of the electrolyte would be conditioned as follows:

Any salt in which one ion is much weaker than the other manifests a tendency to form complex ions by the addition of a neutral molecule to the weaker ion. In the solutions under discussion the weaker ion would undoubtedly be the complex cation, which, when the active mass of the solvent (neutral molecules) was increased by dilution, would tend to become still more complex by the addition of more solvent molecules.

The effect of this increased complexity would be that the velocity of the ion would be diminished without altering the ionic change, and also that the concentration change at the cathode would be lessened, owing to the carriage of extra solvent molecules to the cathode. Both of these effects would cause a diminution of the cation transport number as the solution was diluted.

It will be noticed that this explanation involves a change in the active mass of the solvent, and, as a matter of fact, it was not possible to measure the transport number except in solutions which were so concentrated, that the assumption of a constant active mass for the solvent was no longer justified.

We have not been able to calculate, even approximately, the velocity of the various ions, as we had no means of determining the actual nature, concentration, or degree of dissociation of the corresponding electrolytes.

Summary.

The foregoing pages contain an account of measurements of the vapour pressures, densities, surface energies, and viscosities of the liquefied hydrides of chlorine, bromine, iodine, sulphur, and phosphorus.

The solvent action of these substances has also been investigated, and we have shown that, with the exception of phosphuretted hydrogen, they are all able to act as ionising solvents, and the conductivity, molecular weight, and transport number of certain dissolved substances have been measured.

The results of the measurements, although abnormal, are not inconsistent with the ionic theory; since we have shown that—

(1) If in a given solution the electrolyte is a compound containing n molecules of the dissolved substance, the concentration of this compound will be proportional to the n^{th} power of the concentration of the dissolved substance, and therefore the expression for the molecular conductivity of the *electrolyte* becomes κV^n instead of κV. We have also shown that $\kappa V^n = \alpha K'$, and therefore the molecular conductivity of the *electrolyte* increases with dilution in these solutions in the same manner as in aqueous solutions.

The variation of the molecular conductivity of the electrolyte with dilution is probably complicated by the occurrence of compounds which contain a different number of solvent molecules at different dilutions.

(2) The want of agreement between conductivity and cryoscopic measurements is a necessary consequence of the occurrence of polymers or compounds in solution, and may be taken as evidence of the existence of such compounds.

(3) The conduction of organic substances when dissolved in the halogen hydrides is best explained by the occurrence of electrolytic compounds of the organic substance with the solvent. Transport number measurements have shown that the organic substance is carried to the cathode as a component of the complex cation.

In conclusion, we wish to express our thanks to Professor B. J. Harrington, Director of the McGill University Chemical Laboratory, and to Professor John Gibson, of the Heriot Watt College, for placing facilities at our disposal and for kindly interest taken in the work. Our thanks are also due to Professor John Cox, Director of the McGill Physical Laboratory, for the use of apparatus, and for kindly supplying us with large quantities of liquid air. We also wish to express our thanks to the Research Grant Committee of the Chemical Society for a grant made to one of us, by means of which a large portion of the expense of the work of Part III. has been met.