

XCV.—*Molecular Association and its Relationship to Electrolytic Dissociation. The Molecular Complexity of Halogen-containing Compounds.*

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DURING recent years, largely as the outcome of the study of molecular compounds, theories of valency have undergone considerable changes. The former views, which assigned a definite valency to a particular element, and saw in the combination between molecules, alike or different, the action only of a modified form of valency possessed by the molecule as a whole, have been substituted by others which seek to assign to each separate element, not only a definite power of combination within a distinct molecular unit, but a certain residual, latent, or changing valency. They assert, in other words, that molecular compounds are not due to the valency of each molecule, as a whole, but to the presence within them of such elements as are possessed of latent valencies.

These views have been applied, not only to cases of definite compound formation, but to assist also in the classification of physical phenomena, especially in connexion with the problems in which either electrolytic dissociation or molecular association is

concerned. As regards the latter, Guye, for example, has suggested that the association of certain organic liquids containing unsaturated nitrogen or oxygen is due to chemical forces (Guye and Baud, *Compt. rend.*, 1901, **132**, 1555). Abegg, whose theory of valency is generally recognised as a valuable means of classification, took the view that association, either of similar or dissimilar molecules,\* could be attributed to the latent or contra-valencies of elements, as distinct from the so-called normal valencies. After showing that the number of these contra-valencies possessed by an element increases as we pass from left to right in the Periodic table, Abegg states (*Zeitsch. anorg. Chem.*, 1904, **39**, 330): “. . . wir können nun weiter alle assoziierten Molekeln als durch chemische zwischen Atomen wirkende Kräfte verbunden erklären, sofern es gelingt nachzuweisen, dass in ihren Komponenten Elemente vorhanden sind, deren Maximalvalenz in nicht assoziierter Form noch nicht ausgenutzt ist.” And, again, “Je weiter ein solches Element im periodischen System nach recht steht, um so grösser wird seine Fähigkeit, sich mit sich selbst oder anderen Atomen . . . zusammenzulagern. . . .”

Then are mentioned as illustrations certain oxides, organic hydroxylic compounds, and, further, all of them salts or electrolytes, a number of chlorine compounds.

We are thus led to expect the occurrence of molecular association among the halogen compounds to at least the same extent as among those of oxygen. A consideration of certain of the illustrations leads to this position. And, at any rate, recent interpretations of the function of latent valencies make it clear that the deduction has good foundation. Thus, according to the later theory of Friend (*Trans.*, 1908, **93**, 260; “Theory of Valency,” 1909, p. 100), the fact that *o*-chlorophenol is non-associated, whereas both the *m*- and *p*-compounds undergo association, is explained on the supposition that the latent valencies of the oxygen atom are neutralised by those of the chlorine atom. This suggestion, which has been repeated recently by Thole (*Trans.*, 1910, **97**, 2603), appears to be entirely consistent with the statement of the theories, both of Abegg and of Friend. The view involves the assumption, however, that these forces acting within the molecule to restrain association are just as capable, when either of the conjugate groups is removed, of external activity to bring about association. That is to say, chloro- or iodo-benzene should be capable of association.

\* The present communication is intended to deal only with association of similar molecules. The author hopes in another paper to make reference to association of dissimilar molecules.

It was the object of this investigation to test, in the first place, how far the theory that molecular association is due to the latent valencies of individual elements within the molecule is capable of experimental realisation. At first, the research was confined to carbon compounds containing halogens, but it was soon expanded into a review of all types of compounds containing these elements.

Of the various classes of substances dealt with, the most important is that of salts. The metallic compounds of the halogens have received more thorough investigation than any other salts, whether at high temperature, as vapour, or at lower temperatures, in solution. All the vapour density determinations, as, for example, those of Deville and Troost (*Compt. rend.*, 1857, **45**, 821; *Ann. Chim. Phys.*, 1860, [iii], **58**, 557), Friedel and Crafts (*Compt. rend.*, 1888, **106**, 1764), Nilson and Pettersson (*Zeitsch. physikal. Chem.*, 1887, **1**, 459; 1889, **4**, 206), V. Meyer and C. Meyer (*Ber.*, 1879, **12**, 609, 1112, 1185, and 1292), and Biltz and V. Meyer (*Ber.*, 1889, **22**, 725), on the halogen compounds of aluminium, and on ferric and cuprous chlorides were undertaken in order to test whether a simple or a double formula should be assigned. Less attention was paid to the fact that molecular association varied with the temperature. This communication emphasises the fact that molecular association, like electrolytic dissociation, is progressive, and varies both with concentration and temperature. On this view, it is best to assign the simple or unimolecular formulæ to most salts, just as fractional values are not assigned to a salt from the molecular-weight results obtained in aqueous solution. We should, in fact, adopt for general use the limiting value of the molecular formula, not simply because of the measurements quoted on p. 900, but because any other formula is dependent on the circumstances of the measurement, on the temperature, on the nature of the medium, and on the concentration. Only cuprous chloride appears to have a strong claim to the double formula, since its molecules resist dissociation, even at 1600°. In certain other cases it is known that dissociation into simple molecules occurs on rise of temperature. The substances still found to be associated in the state of vapour, the aluminium haloids, for example, can be regarded as having a very small temperature-coefficient of association, just as in the solutions investigated by the author, several salts have only a small concentration-coefficient of association. It is to be noted that these substances of small coefficient are not, in most cases, of high degree of association initially.

One effect of the study of the few metallic haloids still associated in the gaseous state has been, the author believes, to increase the difficulty of accepting the assertions variously made of the associa-

tion of all metallic salts. The tendency has been to think of association, where it has been found to exist, as concerning double molecules, rather than as being progressive.

Further, much of the previously existing evidence of the molecular condition of salts in solution has also encouraged the view that salt molecules in most cases exist as single units.

The supreme difficulty of obtaining information about the molecular size of salts lies in their lack of solubility in indifferent solvents. One method of dealing with the problem which suggested itself to the author was to make an investigation of the salts of organic bases, and then to apply the results to test such other evidence as could be obtained concerning the metallic salts. For since these bases contain alkyl groups, or, in general, organic radicles, the solution of their salts in the common indifferent solvents is more likely to be achieved than in the case of metallic haloids. Hantzsch found that dimethylamine hydrochloride was soluble in chloroform, and was able to measure its molecular complexity (*Ber.*, 1905, **38**, 1045). He found it strongly associated. Chloroform would fulfil every requirement. It belongs to the class of indifferent solvents, has a low dielectric constant (five at 20°), and, as Hantzsch showed with dimethylamine hydrochloride, gives a non-conducting solution. A test with chloroform showed that it has marked solvent power on a large number of halogen, and, indeed, on other salts of organic bases, although these same salts are, like metallic salts, either insoluble or only very slightly soluble in benzene, ether, carbon disulphide, and similar solvents. The cause of the solubility in chloroform cannot be suggested. In no case observed did combination occur with the separation of an additive product, although solutions have been kept for many months; and no separation of chloroform with the solute was observed. Tetrapropylammonium iodide, which is very soluble, was recovered from chloroform solution by evaporation at the ordinary temperature, and the product dried in the air. It gave the same results on analysis as the original substance. Supposing, however, that combination in solution occurred, the results would be lowered thereby, and tend, therefore, to mask association.

There was found available for the investigation a number of salts corresponding closely with the salts of ammonium and the alkalis. The tetraethyl- and tetrapropyl-ammonium, and the triethylsulphonium bases have been proved by Bredig (*Zeitsch. physikal. Chem.*, 1894, **13**, 288) to be strong bases like the hydroxides of the alkali metals. Moreover, tetraethylammonium iodide resembles closely the corresponding salts of the alkali metals, and has been used as a normal electrolyte by Walden in numerous

investigations. The bromide and chloride have also been used, although less frequently. The data obtained, therefore, by the examination of these substances then opened up the possibility of collecting for discussion evidence concerning the molecular state of metallic salts, particularly of the alkalis, and of drawing up certain definite conclusions, not only on their molecular condition, but also on the relation of molecular association to the phenomenon of electrolytic dissociation.

The author also hoped to be able to make a comparison of the salts of bases derived from nitrogen, oxygen, sulphur, selenium, and iodine. Triethylselenium iodide was prepared, but found to undergo too easy decomposition in boiling chloroform, and its solubility in bromoform appeared to take place only at the expense of decomposition. Diphenyliodonium iodide, and the chlorides, bromides, and iodides of *o*-, *m*-, and *p*-ditolyliodonium were also prepared, but found insoluble in all reagents tested save water and alcohol.\*

In addition to the substances already mentioned, the following were tested and found to be too insoluble in boiling chloroform to allow of use; ethylamine hydrochloride, tetramethylammonium chloride, bromide and iodide, aniline hydrochloride, benzylamine hydrochloride, and tetraethylammonium iodide. Aluminium and ferric chlorides are slightly soluble in chloroform, but no other metallic chloride was found to dissolve in this solvent. A number of other solvents, including bromoform, *p*-toluidine, diphenylamine, and ethylene dibromide yielded no better success.

*Notes on Materials and on the Behaviour of Certain Substances  
in Chloroform Solution.*

The methyl iodide, ethyl bromide and iodide, propyl chloride, isopropyl iodide, allyl chloride, allyl iodide, bromobenzene, benzyl chloride and iodide, *p*-dibromobenzene, and *p*-iodoaniline were obtained by purchase, mainly from Kahlbaum, and were all subjected to purification. Benzyl iodide was repeatedly frozen until the melting point was constant at 23°; *p*-dibromobenzene and *p*-iodo-

\* The iodonium compounds dissolve to a very slight extent in chloroform, the chlorides being most soluble, but the process of solution appears to be accompanied in all cases by decomposition. Slow evaporation yielded some solid residue with a considerable quantity of decomposition product, probably the aryl iodide. The melting points given by McCrae (*Ber.*, 1895, 23, 97) and Heilbronner (*ibid.*, p. 1814) appear to be decomposition points pure and simple, since they could be varied over a considerable range according as heating was slow or rapid.

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aniline were crystallised from alcohol. The other substances named were fractionally distilled.

Chlorobenzene and iodobenzene were prepared from aniline, and *o*-, *m*-, and *p*-iodotoluene from the corresponding toluidines.

Ortho-, meta-, and para-iodonitrobenzenes were prepared from the corresponding nitroanilines, and purified by steam distillation in slightly acid solution (a very slow process with the *m*- and *p*-compounds), and subsequent crystallisation from alcohol. Melting points: ortho-, 49–50°; meta-, 36°; para-, 172–173°.

A few of the salts were obtained by purchase, but the majority were prepared as below.

The following salts were obtained by passing dried hydrogen chloride, bromide, or iodide into a solution of the base, chloroform being the solvent used in the preparation of the first two substances below, a mixture of chloroform and benzene for dimethylpyrone, and benzene in all other cases: Triethylamine, dipropylamine, and *n*-propylamine hydrochlorides; *isobutylamine* hydrochloride and hydriodide; *isoamylamine* and methylaniline hydrochlorides; ethylaniline hydrochloride and hydriodide; diethylaniline hydrochloride and hydriodide; diphenylamine, dibenzylamine, tribenzylamine, and phenylethylhydrazine hydrochlorides; quinoline hydrochloride, hydrobromide, and hydriodide; and dimethylpyrone hydrochloride.

Ethylaniline hydriodide separates from benzene first as an oil. White tablets appear after a time, and crystallisation is then rapid.

With regard to dimethylpyrone hydrochloride, Collie and Tickle (Trans., 1889, 75, 711) found that the crystalline form with two molecular proportions of water lost hydrogen chloride on keeping, and, when desiccated for a month over sulphuric acid, lost, not only water, but an appreciable quantity of hydrogen chloride as well. The anhydrous specimen prepared as above does not suffer this loss. After keeping in a desiccator over sulphuric acid, analysis at the end of two months gave Cl=22.04, and at the end of six months 22.07, against the calculated value of 22.09 per cent.; so that no trace of decomposition was evident.

The following substances were prepared by the action of silver oxide on the iodide and neutralisation of the base: Tetrapropylammonium chloride, bromide, and nitrate; triethylsulphonium chloride and bromide. They contained no trace of iodide.

Tetraisoamylammonium iodide was prepared from triamylamine and amyl iodide at 150°, the periodide being reduced with hydrogen sulphide. It was crystallised from aqueous alcohol.

Quinoline ethiodide was also obtained from the base and ethyl iodide. In aqueous solution it can be titrated with silver nitrate

solution, just as in the case of the tetraethylammonium and triethylsulphonium salts.

All the salts were subjected to careful purification, either by repeated precipitation from chloroform solution by pure ether, or by crystallisation. Antimony trichloride was dried in a vacuum over sulphuric acid, then distilled, and afterwards desiccated in a vacuum over phosphoric oxide. Notwithstanding this treatment it still appeared to contain a trace of moisture, and gave a slight turbidity in chloroform. The amount was very small, and was neglected. Arsenic and antimony tri-iodides were crystallised from carbon disulphide. It may be noted, further, that acetone is a very good crystallising medium for triethylsulphonium iodide, whilst chloroform is particularly useful as a medium from which to crystallise antimony tribromide, quinoline ethiodide and hydriodide, and tetraethylammonium chloride.

Before use the salts were dried by heating at some suitable temperature, followed by desiccation in a vacuum over phosphoric oxide until constant weight was obtained. This treatment was necessary owing to the deliquescent nature of many of the substances. As a further check on their purity, the salts, with the exception of those of arsenic and antimony, were analysed immediately before the molecular-weight determinations. In drying by heat, it was found that the chlorides were always most stable, and the iodides least. The chlorides are also the most, and the iodides the least, deliquescent of the salts. Two substances, namely, triethylsulphonium bromide and iodide, were found to be more readily decomposed by heat than is generally supposed. The former suffers appreciable decomposition above  $90^{\circ}$ , whilst the latter rapidly decomposes at about  $100^{\circ}$ .

Three of the substances, diphenylamine and dimethylpyrone hydrochlorides and triethylsulphonium iodide, suffer decomposition in boiling chloroform. The two hydrochlorides emit copious fumes of hydrogen chloride, and the temperature of the solution gradually rises, so that the molecular weights recorded have no quantitative value, although they afford sure proof of strong association. It was proved, in the case of diphenylamine hydrochloride, that the decomposition is not due to traces of moisture. Triethylsulphonium iodide is more stable than the hydrochlorides named. A solution in chloroform of 2.332 grams of the substance was boiled for about twenty minutes, then carefully evaporated, and kept under diminished pressure until constant in weight. The residue weighed 1.992 grams. The actual loss during a molecular-weight determination, therefore, could not have been very great, although with such a highly associated substance the presence of small quantities of



the decomposition products, which are themselves non-associated, must reduce considerably the molecular-weight values. It would be interesting to examine the substance at a lower temperature if a suitable solvent could be found. In cold bromoform it is soluble only to a very slight extent, and is insoluble in carbon disulphide, ether, or ethylene dibromide.

The solvents used in the molecular-weight determinations were carefully purified, and the chloroform was always tested before use for traces of decomposition products. The carbon sulphide, distilled over mercury, twice over litharge, and then fractionated, and the benzene were of constant boiling point.

In calculating results, the following values of molecular elevation of boiling point or depression of freezing point were used. The boiling-point constant of carbon disulphide was tested with anthracene, and found to agree well with that of Beckmann (Beckmann, Fuchs, and Gernhardt, *Zeitsch. physikal. Chem.*, 1895, **18**, 511).

Benzene (freezing point),  $C=5000$ .

Chloroform (boiling point),  $C=3900$ .

Carbon disulphide (boiling point),  $C=2350$ .

#### *The Conditions Necessary for Molecular Association.*

The data necessary for a solution of this question is recorded in the series of tables below. Table I embodies the results of the author's own measurements with benzene solutions of alkyl and aryl halogen compounds. As in no single instance was molecular association discovered, the results are given only in a summarised form with the values at the limits of concentration employed.

TABLE I.

#### *Molecular Weights in Benzene of Alkyl and Aryl Halogen Compounds.*

##### **Cryoscopic Experiments.**

Substance.	M. W. {(calcd.).}	Wt. substance per 100 grams solvent.	M. W. (obs.).
Methyl iodide .....	142.0	2.07—11.76	142.4—140.4
Ethyl bromide .....	109.0	0.96—4.87	102.5—104.2
Ethyl iodide .....	156.0	1.39—8.08	157.3—161.2
<i>n</i> -Propyl chloride .....	78.5	1.26—3.47	76.2—76.8
<i>iso</i> Propyl iodide .....	170.0	1.36—8.87	168.0—170.2
Allyl chloride .....	76.5	1.27—3.44	74.8—76.8
Allyl iodide .....	168.0	1.28—4.21	160.3—168.0
Chlorobenzene .....	112.5	1.75—7.55	110.6—114.2
Bromobenzene .....	157.0	1.50—6.63	154.4—157.3
Iodobenzene .....	204.0	2.85—12.63	200.8—205.0
Benzyl chloride.....	126.5	1.57—6.34	127.0—127.8



TABLE I (*continued*).

Substance.	M.W. (calcd.).	Wt. substance per 100 grams solvent.	M.W. (obs.).
Benzyl iodide.....	218.0	1.95—7.03	205.9—212.5
<i>o</i> -Iodotoluene.....	218.0	1.80—8.46	218.6—221.0
<i>m</i> -Iodotoluene ..	218.0	1.59—7.10	215.7—215.5
<i>p</i> -Iodotoluene.....	218.0	1.77—6.14	222.0—218.0
<i>o</i> -Iodonitrobenzene .....	249.0	2.29—6.88	253.4—261.9
<i>m</i> -Iodonitrobenzene .....	249.0	1.25—11.25	233.3—254.1
* <i>p</i> -Iodonitrobenzene .....	249.0	2.06	241.9
<i>p</i> -Iodoaniline.....	217.0	1.57—6.53	217.6—223.5
<i>p</i> -Dibromobenzene .....	236.0	2.20—7.40	213.5—233.6
Iodobenzene dichloride...	275.0	1.72	291.0

\* Sparingly soluble only in cold benzene.

There is no evidence in any case of molecular association, and substitution in the benzene nucleus of groups which of themselves appear to have little or no associating power do not induce this power in the halogen atom. Iodobenzene is capable of combining with chlorine to form a dichloride, but so far as the formation of molecular aggregates is concerned, multiple valency on the part of the iodine is not exerted. Hence, in this class of compound the possession by the halogen element of latent valencies does not lead to molecular association.

In the next table, embodying the results of measurements, made by various workers, of molecular weights in solution, the review is extended to compounds of the halogens with other elements than carbon. The important point when making the selection of data was to consider the influence of the solvent in so far as it allows or hinders molecular association. A knowledge of the dielectric constant of the solvent is one guide, associating solvents having, as a rule, low values of this constant. The molecular condition of the solvent itself gives further help. Where these properties of the solvent are unknown, or where one of the rules breaks down, as in the case of nitrobenzene, which has a dielectric constant of 36.4 \* and yet permits association, a fairly safe guide is afforded by the practical test. Thus, Beckmann and Junker (*Zeitsch. anorg. Chem.*, 1907, **55**, 371) found the dissociating power of carbonyl chloride to be very small, since it permitted very strong association of acetic and benzoic acids; and these same acids were also found to be very decidedly associated in nitrobenzene (Beckmann and Lockemann, *Zeitsch. physikal. Chem.*, 1907, **60**, 385). The validity of the measurements in liquid chlorine and bromine is substantiated by the results obtained in other solvents.

\* Possibly this value is too high. Beckmann and Lockemann point out that the hygroscopic nature of nitrobenzene probably accounts for the variations found in the values of the physical constants of nitrobenzene.

TABLE II.

*Molecular Weights in Indifferent Solvents.*

Substance.	M. W. (calc.)	Solvent.	Per cent. concn.	M. W. (obs.)
Phosphorus trichloride <sup>1</sup> ...	—	Benzene	—	Normal
Phosphorus pentachloride <sup>2</sup>	—	Carbon tetrachloride	—	„
Arsenic trichloride <sup>3</sup> .....	181.4	Benzene	—	„
—	—	Carbonyl chloride	3.39—11.1	189—194
Sulphur monochloride <sup>4</sup> ...	134.9	Bromine	0.52—2.31	131—129
„ „ .....	134.9	Chlorine	0.60—1.87	127—126
Sulphur dichloride <sup>5</sup> .....	103.0	Benzene	—	Normal
„ „ .....	103.0	Chlorine	1.75—3.66	108—105
„ „ .....	103.0	Xylene	—	Normal
—	—	Ethylene dibromide	—	Normal
Iodine monochloride- $\alpha$ <sup>6</sup> ...	162.4	Bromoform	0.18—0.32	166—167
Iodine monochloride- $\beta$ <sup>6</sup> ...	162.4	Bromoform	0.62—0.95	173—182
Iodine trichloride <sup>7</sup> .....	233.4	Carbonyl chloride	0.50—0.80	205—229
Tin tetraiodide <sup>8</sup> .....	625.9	Benzene	3.03—19.71	613—566
Hydrochloric acid <sup>9</sup> .....	36.46	Nitrobenzene	0.29—2.43	148.1—61.2
„ „ .....	—	Benzene	0.036—1.74	101.8—63.8

<sup>1</sup> Raoult (*Compt. rend.*, 1885, **101**, 1056).<sup>2</sup> Oddo and Serra (*Gazzetta*, 1899, **29**, ii, 243).<sup>3</sup> Raoult (*loc. cit.*); Beckmann and Junker (*Zeitsch. anorg. Chem.*, 1907, **55**, 371).<sup>4</sup> Beckmann (*Zeitsch. anorg. Chem.*, 1906, **51**, 96).<sup>5</sup> Costa (*Gazzetta*, 1890, **20**, 367); Beckmann (*loc. cit.*); Beckmann, Junker, and Klopfer (*Zeitsch. physikal. Chem.*, 1909, **65**, 289).<sup>6</sup> Walden (*Zeitsch. anorg. Chem.*, 1910, **68**, 307).<sup>7</sup> Beckmann and Junker (*loc. cit.*).<sup>6</sup> Beckmann (*loc. cit.*).<sup>9</sup> Beckmann and Lockemann (*Zeitsch. physikal. Chem.*, 1907, **60**, 385).

Reference should also be made to table IX.

In addition to the compounds tabulated in this list, there are several others, namely, phosphoryl chloride and bromide, sulphuryl, thionyl, and chromyl chlorides, which might be inserted. The primary objection to their inclusion is that they contain oxygen, an element the presence of which in certain compounds gives rise to molecular association. The general rule relating to the condition required for molecular association, which is drawn up at the end of this section, applies equally well to those oxyhalogen compounds for which there is definite proof of association. Oddo and Serra (*loc. cit.*) found that all of them gave normal molecular weights in freezing benzene, but that in boiling benzene, carbon tetrachloride, and, where examined, also in carbon disulphide and chloroform, results showing distinct association were obtained. One would naturally be inclined at first to give preference to the determinations in cold benzene, but the general agreement among the values at the boiling point receives additional support in the case of sulphuryl and thionyl chlorides from measurements made on these substances in the liquid state.

The iodine monochlorides have not yet been sufficiently characterised to decide whether they are capable of association. In dilute solution the numbers do not show any marked tendency to association. Other than the oxyhalogen compounds, only one substance, hydrochloric acid, is definitely associated. It is an electrolyte.

Table III summarises our present knowledge of the molecular condition in the liquid state, as tested by well-tried methods, of a number of halogen compounds, and entirely confirms the rule, laid down at the end of this section, to which associated substances conform. Column *A* consists of the values of the degree of association calculated by Ramsay and Shields (Trans., 1893, **63**, 1099) from their own measurements, except in the case of the liquefied hydrogen haloids, the molecular state of which was ascertained by Steele, McIntosh, and Archibald (*Zeitsch. physikal. Chem.*, 1906, **55**, 145) on the basis of the Ramsay and Shields method. In column *B* are the values calculated by Walden (*Zeitsch. physikal. Chem.*, 1909, **65**, 129). The values of the degree of association of silver and of lead chlorides have been calculated from the experimental record of Lorenz and Kaufler (*Zeitsch. anorg. Chem.*, 1906, **51**, 71).

TABLE III.

*Molecular Complexity in the Liquid State.*

Substance.	Degree of association.		Substance.	Degree of association.	
	<i>A.</i>	<i>B.</i>		<i>A.</i>	<i>B.</i>
Methyl iodide .....	—	1·02	Phosphorus trichloride	1·02	0·99
Ethyl iodide .....	1·01—0·96	1·00	Sulphur monochloride	0·95—1·04	—
Ethyl bromide .....	—	1·05	Phosphoryl chloride ...	1·00	—
Ethylene dichloride ...	—	1·05	Sulphuryl chloride ...	0·97	1·02
Ethylene dibromide ...	—	1·00	Thionyl chloride .....	1·08	1·10
Chloroform .....	—	1·04	Hydrogen chloride.....	1·72	1·55
Carbon tetrachloride	1·01	0·99	Hydrogen bromide ...	1·07	1·21
Acetyl chloride .....	1·06	1·00	Hydrogen iodide .....	1·10	1·09
Chlorobenzene .....	1·03	—	Silver chloride .....	3·29	—
Silicon tetrachloride ...	1·06	1·03	Lead chloride.....	3·60	—
Tin tetrachloride .....	—	0·98			

Too much emphasis is not to be laid on small departures of the values of the degree of association from unity, for the results, as is known, afford only an approximate value of the molecular association. There is a consensus of evidence, however, that thionyl chloride is distinctly associated, and sulphuryl chloride is regarded by Walden also as belonging to this class. Besides these substances, there are five others, in which molecular association exists, namely, the hydrogen haloids and the salts silver chloride and lead chloride. Although there is no experimental evidence of the condition of hydrobromic and hydriodic acids in neutral solvents, there can be

little doubt from the author's measurements on salts of these acids that the acids themselves would be found, like hydrochloric, to be extensively associated. All the five associated substances, be it noted, are electrolytes.

The final table of data consists of measurements by the author of the molecular complexity of a large number of chlorides, bromides, and iodides of organic bases in chloroform solutions. The boiling-point apparatus in which the experiments were conducted has already been described (Trans., 1910, **97**, 1184). To prevent entrance of any trace of moisture it was kept closed during many of the experiments.

In the tables, the symbol *N* represents the number of milligram-molecules of the substance, calculated on the basis of the simple molecule, dissolved in 100 grams of the solvent.

In some cases the tables contain two or more series of experiments. Where this is so, the figures in italics mark the end of the series.

TABLE IV.

*Molecular Weights of Halogen Salts of Organic Bases.**Ebullioscopic Experiments in Chloroform.**n-Propylamine Hydrochloride*  
(M. W. = 95.5).

<i>N</i> .	$\Delta^\circ$ .	M. W.
16.6	0.105	588
12.7	0.079	601
15.2	0.108	524
12.8	0.094	506
10.5	0.083	474
9.2	0.077	443

*isoAmylamine Hydrochloride*  
(M. W. = 123.6).

43.4	0.298	703
33.6	0.229	707
27.0	0.175	728
22.4	0.146	739

*Diethylamine Hydrochloride*  
(M. W. = 109.5).

57.4	0.665	369
41.5	0.538	330
30.3	0.433	299
30.3	0.418	310
23.0	0.348	282
17.1	0.265	275

*Triethylamine Hydrochloride*  
(M. W. = 137.6).

52.0	1.105	233
40.2	0.904	220
31.1	0.725	212
26.0	0.655	196

*isoButylamine Hydrochloride*  
(M. W. = 109.6).

<i>N</i> .	$\Delta^\circ$ .	M. W.
53.7	0.430	533
40.4	0.333	518
31.1	0.260	511
25.7	0.210	522

*isoButylamine Hydriodide*  
(M. W. = 201.1).

47.6	0.259	1442
36.3	0.230	1238
28.9	0.199	1140
44.9	0.265	1328
34.3	0.227	1184
27.6	0.194	1115
23.2	0.184	990

*Dipropylamine Hydrochloride*  
(M. W. = 137.5).

49.0	0.823	320
36.2	0.632	308
37.4	0.665	302
26.8	0.490	294
19.8	0.377	282

*Triethylamine Hydrobromide*  
(M. W. = 182.0).

51.3	0.904	403
37.0	0.709	363
23.5	0.598	339
20.6	0.487	300
14.7	0.356	294

TABLE IV (continued).

<i>Triethylamine Hydriodide</i> (M. W. = 229.0).			<i>Tetraethylammonium Chloride</i> (M. W. = 165.6).		
N.	$\Delta^\circ$ .	M. W.	N.	$\Delta^\circ$ .	M. W.
34.5	0.449	686	38.8	0.257	976
27.9	0.405	616	29.5	0.210	906
22.8	0.366	555	23.6	0.183	835
19.7	0.353	498	19.4	0.157	798
23.2	0.365	571	23.5	0.172	884
17.0	0.310	491	16.0	0.145	713
12.5	0.253	440	12.1	0.121	646
<i>Tetraethylammonium Bromide</i> (M. W. = 210.1).			<i>Tetrapropylammonium Chloride</i> (M. W. = 221.7).		
37.9	0.172	1808	47.1	0.718	567
30.5	0.149	1677	33.5	0.482	601
24.7	0.138	1465	26.2	0.368	614
20.3	0.118	1410	20.3	0.271	647
			21.2	0.280	654
			17.0	0.206	716
<i>Tetrapropylammonium Bromide</i> (M. W. = 266.1).			<i>Tetrapropylammonium Iodide</i> (M. W. = 313.1).		
41.2	0.443	965	42.9	0.376	1393
30.2	0.318	985	30.4	0.267	1389
22.3	0.227	1021	22.5	0.201	1368
17.6	0.181	1011	18.0	0.164	1337
			13.6	0.131	1272
			10.3	0.100	1254
<i>Tetraisoamylammonium Iodide</i> (M. W. = 427.3).			<i>Methylaniline Hydrochloride</i> (M. W. = 143.5).		
12.2	0.319	636	38.3	0.610	351
9.28	0.270	573	28.8	0.479	336
7.39	0.233	528	23.5	0.398	330
			19.1	0.345	310
			16.3	0.296	308
<i>Ethylaniline Hydrochloride</i> (M. W. = 157.6).			<i>Ethylaniline Hydriodide</i> (M. W. = 249.1).		
28.5	0.494	354	29.1	0.498	569
21.7	0.384	346	22.8	0.413	536
18.4	0.325	348	17.6	0.327	523
15.3	0.271	346	15.0	0.289	504
<i>Diethylaniline Hydrochloride</i> (M. W. = 185.6).			<i>Diethylaniline Hydriodide</i> (M. W. = 277.0).		
42.5	1.046	294	37.0	0.649	616
31.6	0.816	280	27.4	0.516	575
22.6	0.629	261	20.3	0.415	528
17.6	0.510	256			
<i>Diphenylamine Hydrochloride</i> (M. W. = 204.5).			<i>Dibenzylamine Hydrochloride</i> (M. W. = 233.5).		
14.1	0.291	487	3.78	0.064	481
11.5	0.185	496	2.85	0.048	478
			2.31	0.038	487
<i>Phenylethyldiazine Hydrochloride</i> (M. W. = 172.6).					
49.4	0.621	535			
37.6	0.522	484			
23.5	0.333	476			
20.3	0.318	430			

TABLE IV (*continued*).

<i>Quinoline Hydrochloride</i> (M. W. = 165.5).			<i>Tribenzylamine Hydrochloride</i> (M. W. = 323.6).		
<i>N.</i>	$\Delta^\circ$ .	M. W.	<i>N.</i>	$\Delta^\circ$ .	M. W.
74.7	1.102	438	14.5	0.460	397
55.5	0.869	413	12.3	0.387	401
41.8	0.699	386	10.5	0.338	393
44.5	0.741	388	9.2	0.296	392
32.4	0.560	373	<i>Quinoline Hydrobromide</i> (M. W. = 210.0).		
26.1	0.501	336	52.0	0.641	664
21.9	0.431	328	37.8	0.522	593
<i>Quinoline Hydriodide</i> (M. W. = 258.0).			29.9	0.436	561
5.24	0.127	414	38.1	0.525	595
4.24	0.115	369	26.9	0.415	530
3.60	0.115	315	20.3	0.347	480
3.01	0.102	297	<i>Quinoline Ethliodide</i> (M. W. = 285.0).		
<i>Triethylsulphonium Chloride</i> (M. W. = 154.6).			4.69	0.076	687
36.7	0.310	714	3.41	0.069	550
27.8	0.264	636	2.84	0.066	479
21.7	0.212	617	2.39	0.056	474
17.6	0.177	599	2.09	0.051	456
<i>Triethylsulphonium Iodide</i> (M. W. = 246.1).			<i>Triethylsulphonium Bromide</i> (M. W. = 199.1).		
50.7	0.165	2951	42.7	0.244	1359
37.6	0.160	2258	31.7	0.212	1161
40.3	0.142	2735	24.9	0.199	972
30.9	0.142	2089	31.3	0.207	1172
23.5	0.128	1765	25.0	0.192	1010
			20.2	0.165	949
			<i>Dimethylpyrone Hydrochloride</i> (M. W. = 160.5).		
			30.1	0.609	310

It is not proposed in this section to enter into a close analysis of the results just given. It is sufficient for the present purpose to emphasise what is readily obvious, that molecular association of a very pronounced type is shown by these halogen salts. In the majority of instances, the most concentrated solution does not reach 10 per cent., and in a number of cases it is less than 5 per cent., yet the association in the dilute solutions is much greater than that which substances such as organic acids, alcohols, phenols, amides, etc., show in concentrated solution.

At the foot of tables II and III it has been pointed out that the substances which give evidence of molecular association are either electrolytes or conducting media. Combine now the whole of the results detailed in this paper, and this statement will be found a rule without exception. Even the oxychlorides already alluded to in table II afford no exception to the rule, and at once are associated substances and capable of transmitting a current of electricity.

The fact that associated liquids form good conducting media is well known. It was pointed out by Crompton in 1897 (*Trans.*, 1897, **71**, 945), and re-stated in modified form by Dutoit (with Aston, *Compt. rend.*, 1897, **125**, 240; with Friderich, *Bull. Soc. chim.*, 1898, [iii], **19**, 321). As will be evident by the results now brought forward, conducting solutes, or electrolytes, must also be capable of association; at any rate, when in the free state. And it may be pointed out in this connexion that even acetamide, ethyl alcohol, and other organic compounds capable of association, although they are not electrolytes in the ordinary sense of the term, considerably augment the conductivity of the liquid halogen haloids when dissolved in the latter (Steele, McIntosh, and Archibald, *loc. cit.*; Beckmann and Waentig, *Zeitsch. anorg. Chem.*, 1910, **67**, 17).

The conductivity and the degree of association of organic liquids do not always run in the same order (Walden, *Zeitsch. physikal. Chem.*, 1903, **46**, 103). The connexion between the two is best displayed in series of similar substances. Again, the conductivity of organic substances, however highly associated, bears no comparison with that of fused salts. The halogen-containing compounds do afford an excellent example, perhaps better than any other at present known, of the frequently found relationship between conductivity and molecular association. Table V, which follows, supplies the illustration, and helps to prove, what it is the purpose of this section to show, that molecular association among halogen-containing compounds only occurs when the substance is a conductor of electricity.

Two of the substances mentioned in the table, namely, arsenic trichloride and antimony trichloride, have not previously been mentioned, but data concerning their molecular state are quoted in tables VII and VIII. As to the conductivities, most of the values were measured by Walden (*Zeitsch. anorg. Chem.*, 1902, **29**, 371). In addition, the ionising power of the solvents, measured by their effect on tetraethylammonium iodide, was also tested by him, and found in perfect agreement with the measurements on the medium alone.

In the table,  $x$  is the degree of association in the liquid state,  $\lambda$  the conductivity in reciprocal ohms.



TABLE V.

*Comparison of Conductivity and Degree of Association.*

A. Non-associated substances.		B. Associated substances.		
Substance.	$\lambda$ .	Substance.	$\alpha$ .	$\lambda$ .
PCl <sub>3</sub> .....	0	SO <sub>2</sub> Cl <sub>2</sub> .....	1·02	$0·18 \times 10^{-6}$
S <sub>2</sub> Cl <sub>2</sub> .....	0	SOCl <sub>2</sub> .....	1·10	$2·0 \times 10^{-6}$
SiCl <sub>4</sub> .....	0	POCl <sub>3</sub> .....	— <sup>1</sup>	$2·2 \times 10^{-6}$ <sup>2</sup>
SbCl <sub>5</sub> .....	0	SbCl <sub>3</sub> .....	— <sup>3</sup>	$109 \times 10^{-6}$ (80°)
SnCl <sub>4</sub> .....	0	AgCl.....	2·25 <sup>4</sup>	1·83 <sup>5</sup> (500°)
AsCl <sub>3</sub> .....	$1·24 \times 10^{-6}$	PbCl <sub>2</sub> .....	2·3 <sup>4</sup>	2·39 <sup>5</sup> (520°)
		KCl.....	8 <sup>4</sup>	1·91 <sup>5</sup> (750°)
		NaCl.....	10 <sup>4</sup>	3·34 <sup>5</sup> (750°)

<sup>1</sup> Oddo and Serra (*loc. cit.*); Walden (*Zeitsch. Elektrochem.*, 1909, **14**, 715).<sup>2</sup> See also Oddo (*Atti R. Accad. Lincei*, 1901, [v], **10**, i, 452); Walden (*Zeitsch. anorg. Chem.*, 1910, **68**, 307).<sup>3</sup> See Table VII.<sup>4</sup> Table IX.<sup>5</sup> Landolt-Börnstein, *Tabellen*, 1905.

The above table, it will be seen, is entirely of inorganic liquids. The non-associated halogen compounds of carbon are generally recognised as non-conductors.

In the table, the only non-associated substance showing conductivity is arsenic trichloride. Although small, the conductivity is quite definite. It may be remarked, however, that the detection of conductivity is infinitely easier than the decision, whether a substance is or is not associated.\* All associated substances are however, conductors, and the best conductors are the substances which are most associated.

Other examples can be quoted of this connexion between conductivity and association. One will suffice. The liquid hydrogen haloids are comparatively but poor conductors (Steele, McIntosh, and Archibald, *loc. cit.*; Beckmann and Waentig (*loc. cit.*). In accordance with this, their degree of association is also small. The parallelism between the two properties can be traced still further with hydrogen chloride; for, when dissolved in nitrobenzene, both conductivity and degree of association decrease as the concentration is increased (Beckmann and Lockemann, *loc. cit.*). Thus, there is here perfect agreement between conductivity and molecular association.

All the preceding evidence points, therefore, to the fact that a halogen-containing substance, to be capable of molecular association, must be electrically active: either a conducting medium or an electrolyte. Further, the expectation of finding molecular association among the halogen-containing substances, based on the view

\* Although arsenic trichloride is called a non-associated substance, the molecular weight values found by Beckmann and Junker are somewhat above the normal.

that the halogen elements have latent valencies capable of chemical activity, have not been realised, except on the condition named. The electrical behaviour of a substance is the only single criterion by which the possibility of molecular association can be safely predicted.

Of equal importance to the establishment of the conditions necessary for association is the fact which now comes to light that molecular association appears as the inverse of electrolytic dissociation or ionisation. Salts which, in solvents of low dielectric constant (for example, chloroform) are associated, display the phenomenon of electrolytic dissociation when dissolved in liquids of high dielectric constant. Using the terms in their commonly accepted sense, we may say, with the knowledge that the converse is also true, no ionisation, no association.

*The Molecular Size of Haloid Salts of Organic Bases.*

In order to ascertain, so far as the data allow, the factors that govern the extent of the molecular association of these salts, a closer examination will here be made of the experimental values already recorded. Immediately following is a table summarising these results, the concentrations being expressed in terms of grams of solute per 100 grams of solvent. Under *A* are given the association factors calculated for the extremes of concentration. The salts have also been more accurately compared at a common molecular concentration of 25 milligram molecules per 100 grams of solvent. The symbol  $A_{25}$  represents the degree of association at this concentration. For a substance of formula weight 200, this strength of solution corresponds approximately with 5 per cent., and is therefore covered by the term "dilute."

In order to afford comparison with diethyl and dipropylamine hydrochlorides, there has been added to the table, after recalculation to the author's standards, the results of Hantzsch's measurements on dimethylamine hydrochloride.

The two substances, diphenylamine hydrochloride and dimethylpyrone hydrochloride, which undergo decomposition in boiling chloroform are not included.

The numbers enclosed in brackets must be considered as approximate only. Propylamine hydrochloride is so slightly soluble, and the elevation of boiling point is consequently so small, that a small experimental error in the measurement of temperature will have a large effect on the molecular weight calculated. In the case of tetra-amyllumonium iodide, lack of material prevented determinations at higher molecular concentrations.

TABLE VI.

*Molecular Size in Chloroform of Halogen Salts of Organic Bases.*

Substance.	M. W. (calc.)	Concentration.	M. W. (obs.).	<i>A.</i>	<i>A</i> <sub>25</sub> .
<i>n</i> -C <sub>3</sub> H <sub>7</sub> ·NH <sub>2</sub> , HCl ...	95·5	0·88—1·58	443—588	4·6—6·2	(8)
<i>iso</i> -C <sub>4</sub> H <sub>9</sub> ·NH <sub>2</sub> , HCl ...	109·6	2·81—5·88	522—533	4·77—4·87	4·63
<i>iso</i> -C <sub>4</sub> H <sub>9</sub> ·NH <sub>2</sub> , HI .....	201·1	4·67—9·58	990—1443	4·93—7·17	5·37
<i>iso</i> -C <sub>5</sub> H <sub>11</sub> ·NH <sub>2</sub> , HCl ...	123·6	2·77—5·37	739—703	5·98—5·67	5·92
NHMe <sub>2</sub> , HCl .....	81·5	0·47—3·18	227—333	2·78—4·09	3·92
NHEt <sub>2</sub> , HCl .....	109·5	1·87—6·29	275—369	2·51—3·37	2·63
NHPr <sub>2</sub> , HCl .....	137·5	2·72—6·75	282—320	2·05—2·35	2·11
NEt <sub>3</sub> , HCl .....	137·6	3·58—7·11	213—253	1·55—1·84	1·62
NEt <sub>3</sub> , HBr .....	182·0	3·74—9·34	294—403	1·64—2·22	1·78
NEt <sub>3</sub> , HI .....	229·0	4·51—7·90	498—686	2·17—3·00	2·52
NEt <sub>4</sub> Cl .....	165·6	2·00—6·43	646—976	3·90—5·90	5·12
NEt <sub>4</sub> Br .....	210·1	4·26—7·97	1410—1794	6·71—8·60	7·2
NPr <sub>4</sub> Cl .....	221·7	3·78—10·43	716—517	3·23—2·56	2·78
NPr <sub>4</sub> Br .....	266·1	4·70—10·95	1011—965	3·80—3·63	3·76
NPr <sub>4</sub> I .....	313·1	3·21—13·42	1254—1393	4·00—4·45	4·40
N(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> I .....	427·3	3·15—5·17	523—636	1·24—1·49	(2·17)
NHPhMe, HCl ...	143·5	2·33—5·50	308—351	2·15—2·45	2·31
NHPhEt, HCl .....	157·6	2·40—4·49	346—353	2·20—2·25	2·22
NHPhEt, HI .....	249·1	3·73—7·51	504—569	2·19—2·46	2·19
NPhEt <sub>2</sub> , HCl .....	185·6	3·35—7·88	256—294	1·38—1·58	1·43
NPhEt <sub>2</sub> , HI .....	277·0	5·62—10·25	528—616	1·91—2·22	2·04
NH(CH <sub>2</sub> Ph) <sub>2</sub> , HCl ...	233·5	0·48—0·79	487—481	2·06	(?)
N(CH <sub>2</sub> Ph) <sub>3</sub> , HCl .....	323·6	2·98—4·68	392—397	1·21—1·23	1·26
NHPh·NHEt, HCl ...	172·6	3·50—8·52	430—535	2·49—3·10	2·57
C <sub>9</sub> H <sub>7</sub> N, HCl .....	165·5	3·62—12·37	328—437	1·98—2·64	2·07
C <sub>9</sub> H <sub>7</sub> N, HBr .....	210·0	4·27—10·92	480—664	2·29—3·16	2·48
C <sub>9</sub> H <sub>7</sub> N, HI .....	257·0	0·78—1·35	297—414	1·44—1·61	(?)
C <sub>9</sub> H <sub>7</sub> N, EtI .....	285·0	0·60—1·34	456—687	1·6—2·4	(?)
SEt <sub>3</sub> Cl .....	154·6	2·72—5·68	599—714	3·87—4·62	4·0
SEt <sub>3</sub> Br .....	199·1	4·02—8·50	949—1359	4·77—6·83	5·0
SEt <sub>3</sub> I .....	246·1	5·73—12·48	1765—2951	6·7—12·0	7·6

Comparing the different salts with one another it will be seen that in nearly all cases the degree of association increases with the concentration. Exceptions to the rule are *iso*amylamine hydrochloride and tetrapropylammonium chloride. The behaviour of these substances, although somewhat unusual, resembles that of hydrochloric acid in benzene and in nitrobenzene solutions (Beckmann and Lockemann, *loc. cit.*).

The coefficient of increase of association with concentration is also subject to variation from substance to substance. Tetrapropylammonium iodide has a comparatively small coefficient, and two or three of the hydrochlorides (notably ethylaniline hydrochloride) have coefficients of still smaller value. Allowing for experimental error, it is found in many cases that the curve connecting the molecular weight with the concentration is a straight line; or, the association is a linear function of the concentration.

As to the factors determining the extent of association, an inspection of the degree of association of the different salts shows that

the association is dependent on two factors, the one for the acid, the other for the base. Turning first to the question of the effect of the acid it will be seen throughout that the chlorides are least associated, the iodides most. The list of association factors at the comparison concentration contains one case which does not appear to bear out this rule, for the degree of association of ethylaniline hydrochloride is slightly greater than that of the hydriodide. A closer inspection will reveal the fact that the association of the hydrochloride alters but slightly with the concentration, whilst that of the hydriodide is subject to much greater variation, so that at a higher concentration than the one chosen for comparison the order is reversed.

The ratios between the values of  $A$  for the chloride, bromide, and iodide vary from salt to salt, and no general rule is observable. It has to be remembered, however, that the comparison concentration is chosen quite arbitrarily.

The predominating factor in the association of salts appears to be the base. As regards the basic tendencies of nitrogen, oxygen, sulphur, etc., experimental difficulties have prevented a comparison, except of nitrogen and sulphur bases. Here we find, from the comparison of the tetraethylammonium and the triethylsulphonium salts, that the nitrogen bases produce the more strongly associated salts.

Of nitrogen bases alone there is a long list available for comparison, and when these are studied it is found that the mass of the base has a very marked effect on the association of the salt. The salts derived from the monoalkylamines are most strongly associated, then follow the salts from the dialkyl-, and last, in degree of association, those derived from the trialkyl-amines. Further illustration may be had by a study of dimethyl-, diethyl-, and dipropyl-amine hydrochlorides; di- and tri-benzylamine hydrochlorides; and tetraethyl- and tetrapropyl-ammonium chlorides. Again, tetra-*iso*amylammonium iodide, the base of which has a high molecular weight, is not very strongly associated as compared with other iodides.

The effect of the base on the association of the salt is not proportionate to its mass, as will be observed by comparing the salts of the aliphatic and aromatic amines. It depends both on the size and the number of the groups which have substituted hydrogen in the amine. In passing, however, from the tri-substituted amine to tetra-substituted ammonium, the association of the salt shows a decided increase instead of a decrease. Quinoline ethiodide in the same way is more associated than quinoline hydriodide.

We might reasonably expect to find, therefore, that the effect

of the base on the association of its salts would run parallel with its strength. So far as the tetra-substituted ammonium and the trialkylsulphonium bases are concerned, this expectation is realised, these bases being strong, like the alkaline hydroxides. As regards the other salts, however, there appears to be no connexion between the degree of association of the salt and the strength of the base as measured by the dissociation constant in aqueous solution (Bredig, *loc. cit.*). The monoalkylamines, for example, are considerably weaker than the dialkyl, but their effect on the association of salts derived from them is in the reverse order.

There does appear, however, to be an approximate agreement between the degree of association of the salt and the dielectric constant of the base, assuming the latter to be of the  $NX_3$  type. The ammonium salts also would probably be capable of classification in this way. Whether the agreement is more than accidental it is not possible to decide, the data concerning the dielectric constants being too incomplete.

The rules which it may be said with certainty are obeyed by the halogen salts of organic bases are:

- (1) Molecular association always occurs.
- (2) The degree of association depends on two factors, one for the acid, the other for the base.
- (3) The extent of association increases in the order

Chloride  $\rightarrow$  Bromide  $\rightarrow$  Iodide,

that is, with increase in the mass of the halogen; and,

- (4) Decreases, when salts from similarly constituted bases are concerned, with the mass of the base.

#### *The Molecular Condition of Metallic Halogen Salts.*

Since some of the most important questions in theoretical chemistry are centred in the problem of the molecular complexity of metallic salts, many attempts have been made to settle their actual molecular condition. All the systematic investigations on this subject have dealt with the problem as presented by the chlorides, bromides, and iodides, and the present inquiry is also limited to this class of salt.

This present section resolves itself into three parts: (*a*) a critical examination of previous investigations, which appear at first sight to disfavour the conclusion that metallic salts are associated; (*b*) a review of indirect evidence, which most strongly points to association occurring; (*c*) an endeavour both to discover the rules concerning the association of these salts and to establish the relationship between molecular association and electrolytic dissociation.

Much of the evidence on the molecular condition of metallic salts appears undoubtedly to ascribe to them the simple unimolecular formulæ by which, as a rule, they are represented. The determinations of the molecular weight of metallic chlorides, however, in boiling piperidine, pyridine, methyl and ethyl sulphides, etc., by Werner and his pupils (*Zeitsch. anorg. Chem.*, 1897, **15**, 1); in boiling quinoline (Beckmann, *ibid.*, 1907, **55**, 236), and in freezing mercuric chloride (Beckmann, *ibid.*, 1907, **55**, 175); in boiling bismuth chloride by Rügheimer (*Ber.*, 1903, **36**, 3030) and Rügheimer and Rudolfi\* (*Annalen*, 1905, **339**, 311); in fused salt hydrates by Morgan and Benson (*Zeitsch. anorg. Chem.*, 1907, **55**, 261); in urethane by Castoro (*Gazzetta*, 1898, **28**, [ii], 317), one and all have not only led to the present adoption of the unimolecular formulæ for the salts investigated: they have, in the author's opinion, gone further than this in masking the association of salts which other evidence declares to exist. The results of the above investigations do not make it necessary, however, to assume the physical indifference to one another of salt molecules, and the following suggestions, whilst they do not pretend to solve all the difficulties involved, do indicate, nevertheless, that the bulk of the evidence cited above should not be taken as evidence that salts are non-associated substances.

The results of a molecular-weight determination must depend on two factors: on the medium and on the temperature. The third factor, the concentration, need not be considered here. As regards the medium, the Neinst-Thomson rule (J. J. Thomson, *Phil. Mag.*, 1893, [v], **36**, 313; Nernst, *Zeitsch. physikal. Chem.*, 1894, **13**, 535) asserts that dissociation of the solute will be allowed or restricted according as the dielectric constant of the solvent is high or low, and, conversely, association is allowed to the fullest extent by a medium of low dielectric constant. This rule can be shown to represent the general experience. So far as association is concerned, it was tested by Meldrum and Turner (*Trans.*, 1908, **93**, 876; 1910, **97**, 1605) in connexion with the amides, and found to hold for five solvents used. Other examples of the operation of this rule can be furnished where the solutes concerned are salts. Thus, according to the author's measurements, tetraethylammonium iodide should be very highly associated in chloroform, the dielectric constant of which is 5 (at 22°); in pyridine, of dielectric constant 20 (at 20°), this salt is very much less associated (Walden and Centnerszwer, *Zeitsch. physikal. Chem.*, 1906, **55**, 321). Again, in ethyl alcohol, of dielectric constant 26, lithium chloride appears to

\* Although all the chlorides used had normal molecular weight in bismuth chloride solution, Rügheimer, on other considerations, expresses the view that many metallic chlorides are really associated.

be dissociated (Beckmann, *Zeitsch. physikal. Chem.*, 1890, **6**, 460), but in amyl alcohol, of dielectric constant 15.9, Andrews and Ende (*Zeitsch. physikal. Chem.*, 1895, **17**, 144) found pronounced association. A comparison of certain of the author's values in chloroform with those in liquid sulphur dioxide obtained by Walden and Centnerszwer (*Zeitsch. physikal. Chem.*, 1901, **39**, 578) bears out the rule. Finally, the principle is established by the very fact that the salts of organic bases investigated by the author are readily ionised by water, and strongly associated in chloroform. We might, in fact, use the principle thus established to prove that the substances which are electrolytically dissociated in solvents of high dielectric constant must be associated in those of low dielectric constant, although the original rule probably did not intend this interpretation.

Another factor besides that of dielectric constant must be considered. The solvent should also be indifferent towards the solute in the sense that chemical action should not occur. Wherever chemical combination in solution takes place, the molecular-weight results are lowered.

If we examine in the light of these arguments the investigations cited above, we find that piperidine and pyridine both have somewhat high dielectric constants. No electrolytic dissociation was found by Werner, but the dissociating power of pyridine on molecular complexes has already been shown in connexion with tetraethylammonium iodide. Moreover, resorcinol and organic acids, which are strongly associated in naphthalene and in benzene, have the normal molecular-weight values in pyridine (Innes, *Trans.*, 1901, **79**, 265). Further, Werner found that the solvents he used formed, in many cases, definite compounds with the solutes, which must lead, as Kohler proved (*Amer. Chem. J.*, 1900, **24**, 385), to low values of the molecular weight. Thus, aluminium bromide in carbon disulphide had the formula  $\text{Al}_2\text{Br}_6$ ; but in nitrobenzene, with which it forms a definite compound, its molecule corresponds with  $\text{AlBr}_3$ . In spite of chemical combination, it may be noted that, like tetraethylammonium iodide in pyridine, the haloids of silver, which belongs to the first group in the periodic table, show pronounced association in piperidine (Werner, *loc. cit.*).

Some of the arguments raised against the use of pyridine probably also apply to quinoline (Beckmann, *loc. cit.*). As regards the use of mercuric chloride and bismuth chloride as solvents, we have no knowledge of their dielectric constants. From evidence given below, however, it is certain that both are to some extent associated substances, and, according to general experience, associated substances do not appear to be associated in associated solvents.



Again, like the chlorides of mercury and bismuth, urethane, used by Castoro as a solvent, is decidedly associated; and salt hydrates exert a dissociating influence, glycerol and glycol, for example, having normal molecular weights in the solvents used by Morgan and Benson.

Finally, in connexion with the fact that Nernst (*Zeitsch. Elektrochem.*, 1903, **9**, 622) found the vapours of sodium chloride and potassium chloride at temperatures approaching 2000° to consist mainly of simple molecules, it may be urged that such evidence does not deny the possibility of association at lower temperatures. Whether a substance, associated when liquid, will still be found associated in the state of vapour depends on the temperature-coefficient of association, and less on the initial degree of association. The molecular aggregates of liquid formamide, which is highly associated, break up rapidly with increasing temperature. Water is strongly associated as a liquid, but not when vaporised. On the other hand, acetic acid, the degree of association of which is much less susceptible to change of temperature, is still associated in the state of vapour, provided the temperature is not too high.

Certain indirect evidence which strongly points to the association of metallic salts is now brought forward.

1. *Evidence from Solubility*.—The fact that most metallic salts do not dissolve in indifferent solvents, whilst preventing accumulation of direct evidence, does, in itself, afford certain indirect evidence of the molecular state of these substances. Crompton pointed out (*Trans.*, 1897, **71**, 939) that unimolecular liquids mixed readily, but the solubility of unimolecular and associated substances one in the other appeared to be limited. Although molecular complexity may not be the only factor determining solubility—the influence of mass, for example, quite apart from its effect on association, cannot be neglected—it appears to be one of the main factors, and the rule is a fairly trustworthy guide where other evidence is wanting. It has been abundantly verified during the course of investigations in which the author has been engaged. In the light of the association factors of salts quoted in this paper, additional support can be obtained from Walden's investigations on solubility (*Zeitsch. physikal. Chem.*, 1906, **55**, 683; 1908, **61**, 633).

Associated substances, it will be found, do not readily dissolve in the solvents which make that association manifest. This rule holds, both for ordinary association and for association in water (Meldrum and Turner, *Trans.*, 1910, **97**, 1805; Peddle and Turner, this vol., p. 685). So far as organic substances are concerned, it will suffice, although there are many examples, to quote the

immiscibility of formamide, acetamide, sulphuric acid, water, glycol, glycerol, and the sugars, with liquids such as benzene, chloroform, carbon disulphide, etc. With respect to association in water, examples have been pointed out recently (Peddle and Turner, *loc. cit.*). Passing on to the salts of organic bases which have been examined in connexion with the present investigation, the same rules hold. All are soluble in water; generally speaking, the more associated the substance the more soluble in water. On the other hand, the salts are insoluble, or but very sparingly soluble, in benzene, carbon disulphide, ether, etc. Tetra-amyllumonium iodide, which is not strongly associated, is much less soluble in water, but much more soluble in benzene, than the strongly associated salts. Even solubility in chloroform does not, in one sense, depart from the rule, for here it is found, especially if similar substances are compared, that the more associated the salt the smaller its solubility. Thus, solubility increases in the order ethylamine-, propylamine-, butylamine hydrochloride; dibenzylamine-, tribenzylamine hydrochloride; again, tetraethylammonium iodide is not soluble to the extent of 0.5 per cent. in boiling chloroform, whereas tetrapropylammonium iodide is readily soluble; and finally, among other examples, iodides are much less soluble than chlorides. In all these cases, the least soluble substance is the most strongly associated.

If we apply these rules now to the metallic haloids, the ready solubility of these substances in water and their insolubility in the indifferent solvents, renders it highly probable that the haloid salts are associated. Leaving out of consideration those solvents which it has been proved owe their solvent power to combination with the solute, metallic salts dissolve most readily in water and in formamide (compare Turner and Merry, *Trans.*, 1910, **97**, 2069). From tables VII, VIII, and IX an idea of the relative degree of association of the different salts can be obtained, and it will be found, on the whole, that the most associated salts are most easily soluble in water (alkali haloids), and are insoluble in indifferent solvents. Less associated substances are more soluble in ethyl alcohol than the alkali chlorides; such substances, for example, as the haloids of iron, aluminium, mercury ( $Hg^{++}$ ). Aluminium bromide and iodide are even soluble in carbon disulphide, and so, also, to some extent are the mercuric haloids. Prideaux concluded from measurements of Trouton's constant (*Trans.*, 1910, **97**, 2039) that of the mercuric haloids the chloride is most, and the iodide least associated. This conclusion accords with solubility data as interpreted here, for mercuric chloride is most soluble in water and the iodide least, the order being reversed when carbon disulphide is the solvent.

Finally, the non-associated or only slightly associated haloids of the metalloids arsenic and antimony are hydrolysed by water, but are soluble in a number of indifferent solvents, such as benzene and carbon disulphide.

Solubility data may, therefore, be interpreted in such a way as to give some indication of the degree of association of a salt.

2. *Evidence from Molecular-weight Determinations in Water.*—Molecular-weight determinations of organic substances in water yield, where the substance is readily soluble, normal results, supposing only dilute solutions to be considered. More recently it has been shown (Meldrum and Turner, *loc. cit.*; Peddle and Turner, *loc. cit.*) that the more nearly normal a substance is when in the free state or when dissolved in indifferent solvents, the more does it appear to be associated in water. We can apply this fact to mercuric chloride, which is a non-electrolyte. Practically all salts give abnormally small molecular weights in water, but Beckmann (*Zeitsch. physikal. Chem.*, 1890, **6**, 460) and Kahlenberg (*J. Physical Chem.*, 1901, **5**, 367) have found that mercuric chloride is distinctly associated in water, a result which proves that in the free state, as also in indifferent solvents, this substance must be considerably less associated than most metallic salts. This conclusion is in agreement with that of Prideaux formed on other evidence.

3. *Evidence from the Results with the Salts of Organic Bases.*—The resemblance between the salts of the alkalis and those of the nitrogen bases discussed in the earlier sections of this paper, need not be emphasised. Whether we regard the ammonium salts as being at the head of the series of amine salts, or most like the tetra-substituted ammonium salts, the evidence admits of no other conclusion than that ammonium chloride, bromide, and iodide must be strongly associated. And if the ammonium salts are associated, then we may expect the corresponding salts of the alkalis to be likewise associated.

Again, it is possible to prepare periodides of the types  $MI_3$ ,  $MI_5$ ,  $MI_7$ ,  $MI_9$  in nitrobenzene solution (Dawson and Goodson, *Trans.*, 1904, **85**, 796; Dawson and Jackson, *ibid.*, 1908, **93**, 2063), where M represents the alkali metals, ammonium, tetraethyl- and tetrapropyl-ammonium. Evidence will be brought forward in another communication to show that this kind of association, namely, association with iodine, is a measure of the power of the individual salt molecules to unite with one another. As also the property of forming periodides is greatest with the most strongly electropositive metals (Abegg and Hamburger, *Zeitsch. anorg. Chem.*, 1906, **50**, 403; Olivari, *Atti R. Accad. Lincei*, 1908, [v], **17**, ii, 584, 717),

it is not unreasonable to conclude that the haloid salts of the alkalis are more strongly associated than those of any other metals. Mercuric iodide, according to Olivari, forms no periodide.

Such direct evidence will now be cited as will suffice to prove that metallic haloids are associated, and allow one to test whether the rules drawn up for the salts of organic bases hold also for metallic salts.

Table VII contains the results of the limited measurements which the author found it possible to make in indifferent solvents. The determinations were carried out at the boiling point of the solvent.

TABLE VII.

*Molecular Weights in Carbon Disulphide.*

<i>Arsenic Tri-iodide</i> (M. W. = 455.7).			<i>Antimony Tri-iodide</i> (M. W. = 501).		
N.	$\Delta^\circ$ .	M. W.	N.	$\Delta^\circ$ .	M. W.
21.7	0.499	466	7.06	0.168	495
19.1	0.442	462	6.17	0.148	497
17.5	0.413	452	5.50	0.129	502
15.7	0.369	455	4.90	0.125	462
13.8	0.334	443			
12.4	0.300	442			

*Molecular Weights in Chloroform.*

<i>Antimony Trichloride</i> (M. W. = 226.6).			<i>Antimony Tribromide</i> (M. W. = 380).		
N.	$\Delta^\circ$ .	M. W.	N.	$\Delta^\circ$ .	M. W.
49.0	1.527	284	27.5	0.921	420
39.9	1.297	272	23.0	0.790	408
33.0	1.084	269	19.2	0.669	402
28.2	0.951	262	16.3	0.581	393
			14.2	0.520	383

Arsenic tri-iodide is not associated. Antimony trichloride and tribromide are both somewhat associated. At a concentration of 25 milligram-molecules per 100 grams of solvent, the association factor of the chloride is 1.14, that of the bromide 1.15, so that there is little difference between them. The tri-iodide does not appear to be associated, although concentrated solutions could not be obtained.

Tables VIII and IX summarise data drawn from various sources, and allow a number of conclusions to be drawn. In table VIII the solvents selected are those which do not possess very high dielectric constants. The actual values of this constant are given side by side with the solvent. Objections might be raised against the solvent sulphur dioxide on the score that Walden and Centnerszwer (*Zeitsch.*

*physikal. Chem.*, 1903, **42**, 432) had reason to suspect, in certain cases, that sulphur dioxide was capable of combining with the solute. When all has been said, however, this circumstance strengthens the proof of association, since, if association be evident at all, it must be considered only as a reduced value of the true association.

TABLE VIII.

*Molecular Weights in Solution of Metallic Haloids.*

## A.—Non-associated Substances.

Substance.	Solvent.	Dielect. constant.	Observer.
AsCl <sub>3</sub> .....	Benzene	2.3	Raoult (see table II.)
—	Carbonyl chloride	?	Beckmann and Junker
AsI <sub>3</sub> .....	Carbon disulphide	2.6	Turner
SbI <sub>3</sub> .....	Carbon disulphide		
SbCl <sub>5</sub> .....	Carbonyl chloride	?	Beckmann and Junker
SnI <sub>4</sub> .....	Benzene	2.3	Beckmann

## B.—Associated Substances.

Sub- stance.	Solvent.	D.C.	Concn.	A.	Observer.
SbCl <sub>3</sub>	Chloroform	5.0	6.4 — 11.1	1.16—1.25	Turner
—	Carbonyl chloride	?	0.60—3.04	1.07—1.12	Beckmann & Junker
—	Ether	4.4	?	1.01—1.19	Lespieau
SbBr <sub>3</sub>	Chloroform	5.0	5.1 — 9.9	1.06—1.19	Turner
HgCl <sub>2</sub>	Ether	4.4	?	1.13—1.31	Lespieau <sup>1</sup>
ZnCl <sub>2</sub>				1.66—3.91	„
FeCl <sub>3</sub>				1.0 — 1.11	„ <sup>2</sup>
AlBr <sub>3</sub>	Carbon disulphide	2.6	1.5 — 10.9	2.0 (approx.)	Kohler
AlI <sub>3</sub> ...			2.5 — 10.7	2.0 (approx.)	
LiCl...	Amyl alcohol	15.9	0.66—6.0	0.94—1.7	Andrews & Ende
NH <sub>4</sub> I	Sulphur dioxide	13.75	Normal solutions	2.44	Walden and Centnerszwer
KI ...				2.38	
RbI ...				1.92	

<sup>1</sup> *Compt. rend.*, 1897, **125**, 1094.<sup>2</sup> See also Muller, *Compt. rend.*, 1894, **118**, 644.

From table VIII it is evident that the salts of the alkali metals must be strongly associated, especially when we take into account the considerable dielectric constants of amyl alcohol and sulphur dioxide. Probably, also, the degree of association of mercuric chloride is somewhat greater than indicated by the measurements in ether.

Table IX summarises a number of values of the molecular complexity in the liquid state. Column I contains numbers given by Lorenz and Kaufer (*loc. cit.*) calculated by the Ramsay and Shields' formula. The values in column II were calculated by Walden (*Zeitsch. Elektrochem.*, 1908, **14**, 715) from the experiments of

various workers, on the basis of the formula  $\frac{Ma_{\phi}^2}{T_{\phi}} = \text{constant}$ , repre-

senting the relationship between the molecular cohesion and the melting point on the absolute scale. Walden found that the equation gave results for a large number of organic and non-metallic compounds in fair agreement with those calculated by other means, and that it was free from the objections which have been raised against the Ramsay and Shields' formula (compare Walden, *Zeitsch. physikal. Chem.*, 1909, **65**, 129; *ibid.*, 1910, **75**, 555; Turner and Merry, *Trans.*, 1910, **97**, 2069). The results in the case of salts received confirmation from measurements of the latent heat of fusion.

TABLE IX.

*Molecular Complexity of Fused Salts.*

Substance.	Degree of association.		Substance.	Degree of association.	
	I.	II.		I.	II.
NaCl .....	—	{ 10·0 8·0	KI .....	—	{ 6·0 4·0
NaBr .....	—	8·0	CdCl <sub>2</sub> .....	—	5·0
NaI .....	—	6·2	PbCl <sub>2</sub> .....	3·60	2·3
KCl .....	—	{ 8·0 6·0	PbBr <sub>2</sub> .....	—	2·2
KBr .....	—	7·0	AgCl .....	3·29	2·25
			SbBr <sub>3</sub> .....	—	1·3

Tin tetrachloride, quoted in table III, may also be taken into account here.

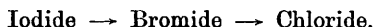
Without further detailed criticism of these tables, all the evidence contained in this section leads, the author believes, to the following conclusions.

## 1. Metallic haloid salts are associated substances.

The evidence appears to indicate that as we pass from left to right in the periodic table, the power of association of the haloids diminishes. On the one hand, we have the alkali chlorides as the most strongly associated substances; on the other, the chlorides of carbon, silicon, phosphorus, sulphur, and iodine are non-associated. Zinc and cadmium chlorides are less associated than those of the alkalis, but more than the aluminium halides.

As the metallic character of the element grows, the tendency of the salt to associate also increases. (Compare the haloids of phosphorus, arsenic, and antimony.)

## 2. The degree of association depends on both the acid and the base. It rises in the order



In this respect the metallic halides do not appear to behave like the salts of organic bases. All available evidence, however, points to the metallic chlorides being most associated, and the iodides least. (Compare salts of sodium, potassium, lead, mercury (Hg<sup>++</sup>), and antimony.)

3. In a series of similar salts the degree of association decreases with increase in the atomic weight of the metal. (Compare the salts of the alkalis, zinc, and mercury.)

Here there is close agreement with the salts of organic bases.

All these conclusions are in agreement with previously disclosed evidence that molecular association is complementary to electrolytic dissociation. Thus, Abegg and Bodländer (*Zeitsch. anorg. Chem.*, 1899, **20**, 453) drew the conclusion that the power of ionisation possessed by the metals in salts of a common acid decreases as we pass from left to right in the periodic table. The evidence in the case of molecular association is much less complete, but what there is presents a close parallel with the tendency to become ionised. Further, if we accept conclusion (2) as correct, it also falls into line in that Abegg and Bodländer state that chlorides have the strongest and iodides the least tendency to become ionised. Again, in the series of the alkali salts, ionisation diminishes with increase in the atomic weight of the metal; the same order, therefore, as for molecular association.

One further test of this parallelism is revealed by a study of the results of hydrolysis. In regard either to conductivity or to ionisation, a substance is less active the more easily it suffers hydrolysis. All the data given in this paper show that non-associated or only slightly associated substances, whether metallic or non-metallic, are hydrolysed or decomposed by water. Referring to metallic compounds only, the alkali chlorides are not appreciably hydrolysed; but metallic tetrachlorides, such as stannic chloride, suffer either complete or very extensive hydrolysis (Bruner, *Zeitsch. physikal. Chem.*, 1900, **32**, 133; Kowalewsky, *Zeitsch. anorg. Chem.*, 1900, **23**, 1; **25**, 189). The result of hydrolysis is, moreover, to transform an electrically inactive into an electrically active substance or substances.

#### *The Cause of the Molecular Association of Salts.*

So far it has been demonstrated that the power of forming molecular aggregates rests only with those halogen compounds which are electrically active. Certain considerations suggested that molecular association was not traceable to single elements to which definite residual valencies can, according to modern theories, be assigned; and that substances other than chlorides, bromides, and iodides would be found capable of association in indifferent solvents. The establishment of a connexion between the phenomena of electrolytic dissociation and molecular association necessarily urged this view, to which also certain observations of other workers gave countenance. Thus, Bottomley found that in the fused state

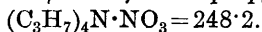


sodium and potassium nitrates are both highly associated (Trans., 1903, **83**, 1422), and Lorenz and Kaufler (*loc. cit.*) have confirmed this discovery. Again, sulphuric acid is highly associated, although the presence of hydroxyl groups has generally been regarded as the cause of association.

In order to test whether salts other than those of the halogens are associated in solution, several such salts have been prepared. Of these, tetrapropylammonium nitrate best fulfilled the required conditions, being easily soluble in chloroform, and being also not very hygroscopic. The following numbers give the result of the test made with this substance.

TABLE X.

*Molecular Size in Chloroform of Tetrapropylammonium Nitrate.*



Wt. Solute = 1·689 grams.

<i>W</i> (grams).	$\Delta^\circ$ .	<i>N</i> .	M. W.	<i>A</i> .
17·74	0·288	38·3	1289	5·2
24·57	0·219	27·7	1224	—
33·02	0·155	20·6	1258	—
39·87	0·136	17·5	1243	5·0

The nitrate is somewhat more associated than the iodide. At a molecular concentration of 25 milligram-molecules per 100 grams of solvent, the association factor (*A*) of the iodide is 4·40, that of the nitrate 5·07. It is of interest to note that among the metallic salts, Bruner (*loc. cit.*) found hydrolysis greater with chlorides than nitrates.

From the results recorded in this paper, including the proof that nitrates are associated, it appears to the author that the theory which considers molecular association as due to the presence of an element of high residual valency is not capable of predicting association, and does very little to explain the cause of association. True it is that in all compounds capable of association there are present elements which may be said to possess unsaturated chemical valencies. The electronegative radicles of salts are composed of such elements. To this extent there is no escape from the theory. But clear demonstration has not yet been made of decided molecular association which can be regarded as due directly to unsaturated elements. Recently it has been shown (Turner and Merry, *loc. cit.*) that the association of tervalent nitrogen compounds only exists when this element is present in distinct electronegative groups; and this condition in at least a considerable measure applies to oxygen compounds. Since also proof exists of the molecular association of acids and of salts, of the association of salts containing

either compound or simple electronegative radicles, it is clear that this association must be assigned to a particular constitution of the substance as a whole. And any theory of the cause of the association must state clearly the function of each of the component parts of the molecule. It is also clear that the association must be due to electrical rather than to the chemical forces such as act between the atoms of a molecule.

So far as electrolytic dissociation is concerned, Abegg (*loc. cit.*) did recognise that the power of ionisation of a salt depended on each component part; and Abegg and Bodländer (*loc. cit.*) stated that an electrochemical theory based on the property of electro-affinity of the component parts of an electrolyte afforded a more satisfactory account of the phenomena of electrolytic dissociation than the chemical valency theory. In this respect their conclusions very largely agree with those to which this paper leads. The difficulty arises, it appears to the author, in attempting to combine the two modes of explanation, electro-affinity and a fixed system of chemical valency.

Two points which are the outcome of this work have a bearing on the theory of electrolytic dissociation, and are very briefly referred to. In the state of vapour, it is known, molecules of salts tend to become simple. In the fused state the complexity is much greater, and increases as the temperature falls. We must suppose, therefore, that marked association exists in the solid state. The various explanations based on the electrolytic dissociation theory of the behaviour of salts in ionising media assume that the molecules which are dissociated into ions are simple (compare Walden, *Zeitsch. physikal. Chem.*, 1907, **59**, 209). If, however, the salts before solution in water are associated, and the process of solution is one of simplification, even to the formation of ions, part of the energy changes must be due to a breakdown of the originally associated molecules.

Further, the theory of electrolytic dissociation assumes that electrical forces are called into existence only when ionisation occurs, due to solution in water. The original molecules are considered neutral. But molecular association, due to electrical forces, is so strong in the case of salts that it is not easy to see how the molecules can be regarded as neutral.

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