195. *Electrolytic Dissociation Processes. Part I. The Dipole Moment of Iodine Monochloride in Solution.*

By Fred Fairbrother.

Two extreme types of valency bond have been generally recognised : the homopolar or covalent bond, and the ionic bond. Further consideration has required the subdivision of these types of bond, and has postulated the existence of bonds of " mixed " type, intermediate between the two extremes. It nevertheless remains a fact that, in the pure state, most molecules are held together by bonds which are either mainly covalent or mainly ionic (compare Sidgwick, " The Co-valent Link in Chemistry," Cornell, 1933). There is, however, an important class of compounds which, although essentially covalent in the gaseous state, yet are known to undergo a transition into ionically bound molecules in suitable

* (Note added in proof). The value of *b* has been found to depend to some extent on the composition of the paraffin wax used. The effect is being investigated.

solvents. This transition may be partial or complete. Such transitions from a mainly covalent bond to an ionic bond in solution are of considerable importance, since they probably lie at the root of many chemical reactions. It is with such changes that this work is mainly concerned.

It has previously been shown (Fairbrother, J., 1932, 43; 1933, 1541; *Trans. Faraday Soc.*, 1934, **30**, 862) that the dipole moments of hydrogen chloride, bromide, and iodide are greater in solution in non-polar solvents than in the gaseous state. This effect was ascribed (*ibid.*) to an increase in the ionic character of the valency bond, brought about by the forces of solvation—a kind of incipient ionisation.

The influence of solvation in determining the type of solute bond was discussed at the same time by Rodebush (*ibid.*, p. 778), and the dissociation into free ions in solution, of an initially homopolar molecule, has been discussed in more detail by Ogg and Polanyi (*ibid.*, 1935, **31**, 604) as part of their theory of ionogenic reactions.

The present work is concerned, not only with the process of complete ionisation (as distinct from the simultaneous or subsequent electrolytic dissociation), but also with the intermediate stage between the gaseous covalent molecule and the ionically bound pair.

For hydrogen chloride dissolved in benzene the conception of an increase in the ionic nature of the valency bond is supported by the recent experiments of Plyler and Williams (*Physical Rev.*, 1936, **49**, 215), who have measured the infra-red absorption spectrum of such solutions. They find that the band, the centre of which is at $3·46\mu$ in the gaseous hydrogen chloride, shows a slight shift to the longer wave-lengths when the substance is dissolved in benzene. This shift indicates a diminution in the vibrational frequency of the molecule, and hence a slight decrease in the binding energy between the hydrogen and chlorine nuclei. They also find that the absorption coefficient of hydrogen chloride in benzene is about 3—4 times greater than in the gaseous state, indicating that the change of electric moment in the act of absorption is greater in solution than in the gaseous state.

It may be argued that the case of the hydrogen halides, taken alone, is a special one, and not typical of such processes in general, but that it is brought about by the unique nature of the cation. For example, there is good evidence to show that the electrolytic dissociation of these compounds takes place only when the solvent molecules can enter into chemical combination with the proton (Lowry, *Chem. and Ind.*, 1923, **42**, 1048; Brønsted, *Rec. trav. chim.*, 1926, **30**, 777). It is therefore desirable to examine other cases, in which the atoms are more nearly alike in size and the electrolytic dissociation follows a more normal course. A good example of this has now been found in iodine monochloride, of which the dipole moment in solution in carbon tetrachloride and *cyclo*hexane is about twice as large as in the gaseous state. On dissolution in a polar solvent, the bond between the chlorine and iodine nuclei may become so weak that some of the molecules pass into solution as separated ions.

EXPERIMENTAL.

The choice of non-polar solvent in which to dissolve the iodine monochloride is very restricted owing to the great reactivity of the solute towards many organic compounds. When it dissolves in dry benzene, it does so with a hissing sound and the development of some heat. There is usually a small amount of immediate reaction, probably caused by local heating, but the subsequent disappearance of " available halogen " (estimated with aqueous potassium iodide and sodium thiosulphate) is very slow at room temperature. Also, the reaction between dry benzene and a solution of the chloride in carbon tetrachloride is detectable only after the lapse of several hours. The solution in benzene looks just like a solution in the tetrachloride, but a spectroscopic examination shows that the molar extinction coefficient in the visible region of the spectrum is much larger, and also that there is a large general absorption in the near ultra-violet. For these reasons, it was deemed that benzene was not a suitable solvent for the measurement of the dipole moment of iodine chloride.

Measurements were also attempted in decane (di*iso*amyl), but although the iodine chloride dissolved slowly, as would be expected from the low polarisability of the solvent, it was clear that a reaction was taking place : on standing even for a few hours, the solution became violet and a gas (probably hydrogen chloride) was evolved.

Measurements of the dipole moment were therefore made in carbon tetrachloride and *cyclo*-

hexane. Iodine chloride is probably unassociated both as a pure liquid and in solution : where cryoscopic measurements are available, they indicate a normal molecular weight in solution [compare Gmelin–Kraut, " Handb. d. anorg. Chem.," (8), 1933, Jod, p. 609 ff.]. Gillam and Morton's spectrographic measurements (*Proc. Roy. Soc.*, *A*, 1931, **132**, 152) show that iodine chloride exists in carbon tetrachloride solution as a definite undissociated compound. It also dissolves slowly and to a limited extent in *cyclo*hexane. Some spectrographic measurements of such solutions were kindly made by Mr. A. E. M. Gillam, using a Hilger E3 quartz spectrograph with a Spekker photometer; the results are in Fig. 1, together with the curve (broken line) obtained by Gillam and Morton for carbon tetra-

chloride solutions. They show that the molar extinction coefficient of 145 in *cyclo*hexane solution is in excellent agreement with that of 150 in carbon tetrachloride. The absorption maximum, however, is at about 505 $\mu\mu$ whereas in carbon tetrachloride solutions it is at 460 $\mu\mu$. On standing at room temperature, iodine chloride slowly reacts with *cyclo*hexane. This is most noticeable in very dilute solutions, which gradually acquire a violet tinge after a few days. The reaction, however, is very slow, and does not affect the results given below.


FIG. 1.

The carbon tetrachloride (Kahlbaum) was freed from residual traces of sulphur compounds by repeated treatment with alcoholic potash (Schmitz-Dumont, *Chem.-Ztg.*, 1897, **21**, 510). The *cyclo*hexane, a commercial product, was shaken with 100% sulphuric acid to remove benzene, and then fractionated several times : spectrographic examination showed that it was free from benzene. Both solvents were kept in contact with phosphoric oxide for several weeks prior to the final distillation.

Since iodine monochloride reacts instantly with water and fumes when exposed to the air, it was necessary to minimise the latter exposure; the chloride was therefore manipulated in the following manner. The commercial substance was first fractionally frozen several times :

FIG. 2.
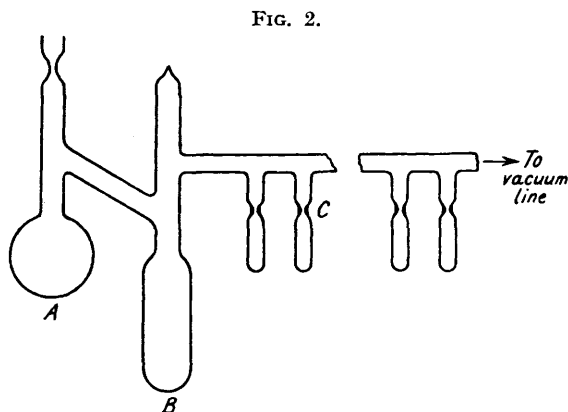
Stortenbeker (*Rec. trav. chim.*, 1888, **7**, 152) recommended this method of purification in preference to fractional distillation on account of dissociation, which occurs more readily when the substance is not dry (Curtis and Patkowski, *Phil. Trans.*, 1934, **232**, *A*, 395). The monochloride was then melted, kept in contact with phosphoric oxide at 30° for several days, and decanted into the flask *A* (Fig. 2), which was then sealed off. The pressure in the system was reduced, and the iodine chloride subjected to a rough fractionation at room temperature, the first fraction passing through the apparatus to a liquid-air trap, the middle fraction being condensed on fresh phosphoric oxide in *B*, which

was cooled in solid carbon dioxide–acetone, and the remainder left in *A* ; *A* was then sealed off from *B*. The pressure in the system was now further reduced, and the chloride fractionally sublimed from the phosphoric oxide in *B* into the little side tubes. During this process, *B* was kept at 0° or slightly above, and the side tube in liquid air. The pressure of permanent gas in the system during this sublimation was never greater than 10⁻⁴ mm., and for most of the time was below 10⁻⁶ mm. : iodine chloride possesses sufficient vapour pressure for a fairly rapid sublimation under these conditions. During this process much of it passed through the apparatus and was caught by the liquid-air traps. When sufficient had been condensed in one of the little tubes, it was sealed off in a vacuum, the glass having been thickened at *C* for this purpose. Owing to the absence of air in the tubes, the monochloride readily sublimed from one part of the tube to another and formed magnificent crystals on standing. It was then condensed, by cooling in solid carbon dioxide, to one end of the tube, where it remained when the tube
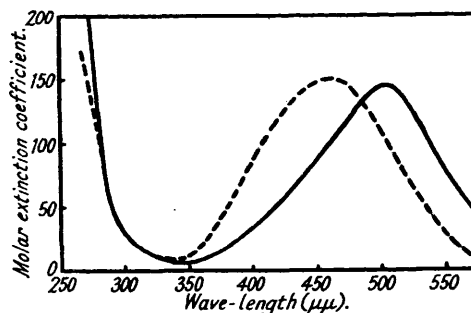
was allowed to regain room temperature. A scratch was made near the empty end of the tube, and the latter and its contents weighed. The tube was then cracked by a hot rod, the pieces separated, and the monochloride quickly slipped into a weighed quantity of solvent contained in a 100-c.c. stoppered flask. In this way contact with the air was reduced to a minimum. The tube was usually broken cleanly into two pieces, which were subsequently washed and dried, and the weight of chloride was obtained by difference with due allowance for vacuum corrections.

The dielectric constants were measured in a platinum plate condenser, of about 215 $\mu\mu$F capacity when filled with dry air, by a resonance method which was essentially as previously described (*Proc. Roy. Soc., A*, 1933, **142**, 173). The chief modifications to this method were the use of a frequency of 200 kc. instead of 1000 kc., in order to decrease the inductance corrections, and the use of a steady current to balance part of the rectified resonance current so as to use a higher portion of the resonance curve and a more sensitive galvanometer. The standard variable condenser was a Muirhead Type II condenser of 1250 $\mu\mu$F maximum capacity, with quartz insulation. The frequency of 200 kc. was obtained by a Dynatron oscillator with a buffer-amplifier valve between the Dynatron valve and the coupling to the resonance circuit. The power factors of the solutions (as shown by the shape of the resonance curve) were not detectably different from those of the pure solvents, which indicated the absence of free ions.

The densities were measured in a capped glass pyknometer of the Sprengel type. The mol.-fractions of solute f_2, dielectric constants ε, densities d, and polarisations are given in the table.

	Iodine in carbon tetrachloride.					*Iodine chloride in* cyclohexane.			
f_2.	ϵ.	d.	P_{12} (c.c.).	P_2 (c.c.).	f_2.	ϵ.	d.	P_{12} (c.c.).	P_2 (c.c.).
0·000	2·236	1·5939	28·16	—	0·000	2·021	0·7786	27·42	—
0·007366	2·261	1·5998	28·47	69·9	0·01126	2·049	0·7909	27·84	63·9
0·01028	2·270	1·6021	28·57	68·4	0·01397	2·0555	0·7940	27·92	63·1
0·01684	2·292	1·6068	28·85	68·9	0·01601	2·059	0·7959	27·98	62·0
0·03036	2·336	1·6184	29·34	66·9	0·01787	2·064	0·7982	28·04	62·0
0·05559	2·402	1·6304	30·14	63·8					

$_\infty P_2 = 71$ c.c. (left) $_\infty P_2 = 69.5$ c.c. (right)

DISCUSSION.

The absorption band-spectrum of the vapour of iodine chloride has been much studied (for references, see Jevons, " Report on the Band-spectra of Diatomic Molecules," Cambridge, 1932). In the ground state it is a $^1\Sigma$ molecule, with a valency bond that is essentially homopolar or covalent. The dielectric polarisation of the gaseous substance at 61·1—161·1° has been measured by Luft (*Z. Physik*, 1933, **84**, 767), whose results may be expressed in the form $P = 31 + 1700/T$ c.c., indicating a dipole moment of 0·5 D. This corresponds to a total molar polarisation of 37 c.c. as compared with the present value of about 70 c.c. in solution. It is clear, therefore, that a considerable increase in the dipole moment of iodine chloride occurs when it is dissolved in carbon tetrachloride or cyclohexane.

Some measurements of the polarisation of iodine chloride in carbon tetrachloride solution have also been made by Malone and Ferguson (*J. Chem. Physics*, 1934, **2**, 99), who found $_\infty P_2 = 60$ c.c. which is less than the present values. They state that their solutions tarnished the gold plating of the cell. In the present work there was no detectable action whatever on the platinum plates of the cell, which remained bright throughout the measurements. Their results, however, agree with the author's in that the polarisation in carbon tetrachloride is considerably greater than that in the gaseous state.

There do not appear to be any recorded measurements of the refractive index of iodine chloride, either in the pure state or in solution. Moreover, the calculation of the electronic polarisation from refractive-index measurements in the visible region of the spectrum is uncertain on account of the strong absorption bands in the spectrum. We may, however, obtain a rough estimate of P_E for the homopolar molecule from the mean of the molar refractivities of gaseous iodine and chlorine. From Cuthbertson's figures for these (*Phil. Trans.*, 1914, *A*, **213**, 1) at 6708 A., the molar volume being taken as 22·4 l., this mean is 20·5 c.c. The sum of the refractivities of the separated ions will be slightly less than the sum of the refractivities of Cl′ and atomic iodine. Fajans and Joos (*Z. Physik*, 1924, **23**, 1) give the former as 9 c.c., and half the refractivity of molecular iodine, calculated from Cuthbertson's data (*loc. cit.*) at 6708 A., is 14·7 c.c. : the sum is 23·7 c.c. We may reason-

ably assume, therefore, an upper limit of 24 c.c. for P_{E+A}, whence it seems that Luft's value of 31 c.c., obtained by extrapolation, is too high and may arise from the well-known experience that small individual errors in such measurements are greatly magnified when the polarisation is extrapolated to $1/T = 0$. His total molar polarisation figures at 60° and a value of 24 c.c. for P_{E+A} indicate a moment of 0·8 D. In the same way the present results show, for solution in carbon tetrachloride, $\mu = 1·49$ D, and in *cyclo*hexane $\mu = 1·47$ D.

It is suggested that this increase in dipole moment is caused by an increase in the ionic character of the valency bond. It is probably accompanied by a slight increase in the nuclear separation. Pauling and Yost (*Proc. Nat. Acad. Sci.*, 1932, **18**, 414) and Pauling (*J. Amer. Chem. Soc.*, 1932, **54**, 3570) have pointed out that the actual bond energy of pure iodine chloride, *viz.*, 2·143 e.v., is 0·142 e.v. higher than the mean of the bond energies of iodine and chlorine, which indicates that the wave function representing the bond may contain ionic terms, even when we are dealing with the gaseous state.

The polarising influence of solvation will then increase the relative probability of the configuration I^+Cl^-, this probability increasing as the polarisability of the solvent (and hence the solvation energy) increases. In solvents such as carbon tetrachloride and *cyclo*hexane, we are concerned only with a partial " ionisation." As the dielectric constant of the solvent increases, the ionic character of the bond becomes more marked, until the ionic terms greatly exceed the covalent terms.

Some idea of the energy necessary for the various steps in the electrolytic dissociation of iodine chloride may be gained from a consideration of the approximate potential-energy curves relating to the respective states. These are given in Fig. 3. The curve A for the gaseous molecule, which is essentially a homopolar molecule, has been

FIG. 3.

calculated by the well-known Morse expression (*Physical Rev.*, 1929, **34**, 37), *viz.*, $E = D[2e^{-a(r-r_0)}) - e^{-2a(r-r_0)}]$ by using the following data (Jevons, *loc. cit.*): $D = 2·143$ e.v., $\omega_e = 384·6$ cm.$^{-1}$, $r_e = 2·310$ A., $\alpha = 1·875$. The effect of the solvent atmosphere on this curve is small, so that it can be taken to refer to the homopolar molecule either in the gaseous state or in solution.

The curve B, which represents the potential energy of the unsolvated ions I^+ and Cl^- as a function of nuclear separation, has been calculated by the expression $E = -e^2/r + b/r^9$. The value of the coefficient b is obtained by equating the first derivative to zero and putting r equal to the equilibrium distance in the lowest state. For this purpose, and for the subsequent estimation of the solvation energies, it is necessary to assign an ionic radius to the positive iodine ion. This can only be done indirectly, for no direct evidence is available. There seems no doubt, however, that iodine can exist separately as a positive ion : *e.g.*, it forms a number of other stable compounds with electronegative atoms and radicals (compare Gmelin–Kraut, *op. cit.*, p. 454). From a consideration of the radii of the isoelectronic tellurium atom, the neutral iodine atom, and of a number of other atoms and ions down to I^{+5} and I^{+7} (Smithsonian Physical Tables, 1934, 491), all of which lie near a straight line when plotted against the effective atomic number (the total number of extra-nuclear electrons), it appears that a very probable radius for I^+ is 1·30 A. The radius of Cl^- is taken as 1·81 A. (Pauling, *J. Amer. Chem. Soc.*, 1927, **49**, 765), and the equilibrium nuclear separation of the ion pair as the sum of these, *viz.*, 3·11 A. In this, no account has been taken of the compressibilities of the ions, which will affect both the equilibrium separation and the shape of the left-hand branch of the curve : but this will not affect the present argument.
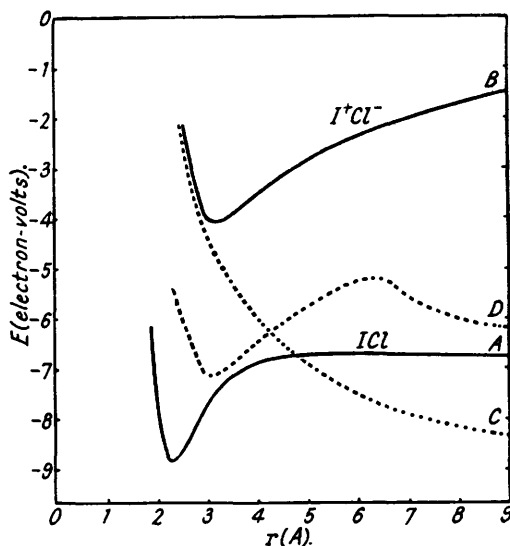
The ionisation potential of iodine I $\longrightarrow$ I$^+$$+$ e is 10·44 e.v. (Evans, *Proc. Roy. Soc.*, *A*, 1931, **133**, 417), and the electron affinity of chlorine is 3·75 e.v.   The asymptotic value of the potential energy of the separated ions must therefore lie 10·44 $-$ 3·75 $=$ 6·69 e.v. above the asymptote of the homopolar curve.

If the ions be solvated, their potential energies will be reduced accordingly, and therefore the potential-energy curve relating to the solvated ions will lie below B.   When the solvent is such that actual dissociation of the homopolar molecule occurs, the form of the curve will be as shown at C, the position depending both on the solvation energy and on the size of the solvent molecules.

The change in potential energy when an ion of radius a and charge e is immersed in a homogeneous medium of dielectric constant ε is given by $- \Delta E = e^2(1 - 1/\varepsilon)/2a$.   The actual energy of solvation of an ion will generally be somewhat less than this, since, first, the medium surrounding the ion is not homogeneous but consists of discrete solvent molecules, and secondly, the use of the macroscopic dielectric constant is not strictly justifiable since it is measured at low field strengths whereas the field strength in the neighbourhood of an ion may be very large.   For example, the decrease in potential energy of a chlorine ion of radius 1·81 A., when immersed in a homogeneous medium of $\varepsilon = 81$, as calculated by the above expression is 3·9 e.v.; on the other hand, Webb (*J. Amer. Chem. Soc.*, 1926, **48**, 2589) has calculated the free energy of hydration of the chlorine ion to be 70·1 kg.-cals. = 3·16 e.v.

Nevertheless, we may use this expression to calculate to a first approximation the energy of solvation of the ions with which we are concerned.   Such a calculation shows that the total energy of solvation of I$^+$ ($a = 1·30$ A.) and Cl$^-$ ($a = 1·81$ A.), when completely separated from one another and immersed in a medium of $\varepsilon = 2$, is 4·7 e.v.   The energy of solvation of the ion-pair in contact will be less than this, of the order of 75%, since the ions will be surrounded by fewer solvent molecules.   The potential-energy curve of the ion-pair in a medium of low dielectric constant, though it cannot be completely represented on a two-dimensional diagram, will be somewhat of the form shown at D (Fig. 3).

It is clear, therefore, that the solvation energy is sufficient to permit of a greatly increased interaction between the covalent and the ionic state of iodine chloride when dissolved in a medium, even of low dielectric constant.

A closer approximation to the actual energy of solvation may perhaps be made in the case of small solvent molecules, by assuming, say, a four-fold co-ordination of solvent molecules around the ion and calculating the energy of interaction between the ion and the solvent molecule by the expression $E = \alpha e^2/2r^4$, in which α is the polarisability of the solvent molecule and r is the distance between its centre and the ion nucleus.   For large solvent molecules this becomes less approximate as the binding force is mainly exerted between the ion and the atoms of the solvent molecule which are closest to it ; moreover, in this we must again calculate α from macroscopic measurements.   It may be added also that, when dealing with *polar* solvents, we must include in the polarisability which is effective in solvation, not only the optical or electron polarisability, but also the orientation polarisability arising from the dipole moment of the solvent ; otherwise, the ionising power of solvents would not run parallel with the dielectric constant.

In the case of iodine chloride, a total ionic solvation energy of 7 e.v., corresponding to immersion in a medium of $\varepsilon = 3·9$, would bring the potential-energy curve of the solvated ions at infinite separation below that of the homopolar molecule, which it would then cross at a moderate separation.   The ionic curve would then be almost wholly repulsive, and we should expect electrolytic dissociation to occur.   This, in fact, is what happens.   Preliminary measurements made at 20° show that iodine chloride dissolved in chlorobenzene ($\varepsilon = 5·8$) is an extremely weak electrolyte, but conducts sufficiently well to preclude the measurement of its dielectric constant by a resonance method.   In ethylene dichloride ($\varepsilon = 10$) it conducts very much better, but is still a very weak electrolyte.   Walden (*Z. physikal. Chem.*, 1903, **43**, 385) has measured its conductivity in arsenic trichloride, sulphuryl chloride, and liquid sulphur dioxide, and Solly (*Phil. Mag.*, 1836, **8**, 400) observed that the liquid substance itself conducted electricity.

Although, in the above, the electrolytic dissociation has been discussed on the basis of

curves A and C (Fig. 3), the homopolar curve A being taken as relating to the initial state of the system in solution, it should be remarked that this is not strictly so in fact, since the dissolution of iodine chloride in the solvent is accompanied by an increase in the dipole moment. Hence it follows that the lowest state of the molecule in the undissociated form will be one which is lower than A by reason of the ionic terms introduced into the bond energy.

Whether or not any given molecule will undergo an increase of dipole moment as compared with the gaseous state, on dissolution in a non-polar solvent, and electrolytic dissociation in a suitably polar solvent, appears to depend chiefly on two factors, providing that the solvent molecules do not enter into chemical combination with part of the solute molecule to form another kind of ion, *viz.*, (*a*) on the solvation energy available, which in turn depends on the ionic radii and the polarisability of the solvent molecules, and (*b*) on the energy difference between the wholly ionic and the wholly covalent state, *i.e.*, on the difference between the energy required to remove an electron from the positive radical and the electron affinity of the negative radical.

SUMMARY.

The dipole moment of iodine monochloride has been measured in solution in carbon tetrachloride and in *cyclo*hexane, and in these solutions it is about twice as large as in the gaseous state. The results are interpreted as being due to an increase in the ionic character of the valency bond of the substance. The approximate potential-energy curves of the homopolar and the ionic state have been calculated, and also the approximate energy of solvation of the ions. It is shown that the latter is sufficient to account for the observed results. The results are also discussed in relation to the process of electrolytic dissociation into free ions, of an initially covalent molecule. Preliminary results are mentioned to confirm the conclusion that, in a medium of dielectric constant slightly higher than those of the solvents used, the iodine chloride would give rise to free ions.