203. *The Electrical Conductivity of Iodine Monochloride and Iodine Trichloride.*

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The electrical conductivity of molten iodine monochloride passes through a maximum at 40°. The conductivity of solid and liquid iodine trichloride has been measured in the range 70—150°. That of the solid increased rapidly with increasing temperature. There was no marked discontinuity at the melting point. In the molten state there was a maximum in the conductivity–temperature curve at 111°. It was shown that the maximum in the case of the monochloride was probably due to a decrease with rising temperature in the number of ions present. The degree of ionisation in molten iodine monochloride was of the order of 1%. For neither compound was there any indication of a decomposition potential. On prolonged electrolysis of molten iodine monochloride a small back e.m.f. was observed.

Both iodine monochloride and iodine trichloride dissolve in a variety of solvents and in many cases such solutions are found to conduct electricity. For instance, iodine monochloride is a conductor when dissolved in acetic acid, nitrobenzene, arsenic trichloride, sulphur dioxide, sulphuryl chloride, or water, and the trichloride conducts in all of these solvents, as well as in dichloroacetic acid and liquid bromine. Solutions of iodine trichloride in carbon tetrachloride, silicon tetrachloride, and chloroform are, however, non-conducting (Plotnikov and Rokotyan, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 723). Evidence for the nature of the ions in the molten iodine chlorides cannot readily be obtained directly but in the above solutions fairly definite deductions may be made. In the case of solutions of iodine monochloride dissociation into I^+ and $[ICl_2]^-$ appears most likely. This explains why electrolysis results in the deposition of iodine at both the cathode and the anode since, at the latter, a disproportionation of ICl_2 into I and ICl_3 (or I and Cl) could occur. This also explains why the concentration of both halogens (either free or in combined form) increases at the anode although the ratio of iodine to chlorine decreases (Sandonnini and Borgello, *Atti Accad. Lincei*, 1937, **25**, 46).

The nature of the ions formed by iodine trichloride in solution is less clear. Bruns (*Z. physikal. Chem.*, 1925, **118**, 89) claimed that, when an acetic acid solution was electrolysed, the whole of the iodine trichloride migrated to the anode. To explain this and also certain dilution effects the equilibrium $ICl_3,nCH_3{\cdot}CO_2H \rightleftharpoons ICl_3^{--} + (CH_3{\cdot}CO_2H)_n^{++}$ was postulated. Other equilbria which have been suggested are : $ICl_3 \rightleftharpoons I^{+++} + 3Cl^-$ and $ICl_3 \rightleftharpoons I^+ + Cl_3^-$. Yet another possibility, which is supported by the existence of salts such as $KICl_4$, is : $2ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$. It is not certain that the ions in the molten compound will be identical with those in solution, but for the purposes of calculations of ion concentrations made later, the existence of I^+ and ICl_2^- in molten ICl has been assumed. The conductivity of molten iodine monochloride at 35° was measured by Cornog and Karges (*J. Amer. Chem. Soc.*, 1932, **54**, 1882), who showed that after repeated crystallisation the specific conductivity at this temperature was $4{\cdot}57$—$4{\cdot}59 \times 10^{-3}$ohm^{-1}cm.$^{-1}$. The compound was also shown to behave as an ionising solvent towards potassium chloride and ammonium chloride. Fialkov and Goldman (*J. Gen. Chem. Russia*, 1941, **11**, 910) found a conductivity of $4{\cdot}87$—$5{\cdot}39 \times 10^{-3}$ohm^{-1}cm.$^{-1}$ at 35° after purification by distillation at atmospheric pressure. During the course of the work described below, Fialkov and Shor (*Zhur. Obsch.*, 1948, **18**, 14) showed the existence of an extended maximum in the temperature–conductivity curve for molten iodine monochloride. The existence of this maximum was observed independently in the present work, though the absolute values of the conductivity of iodine monochloride were rather lower than those reported by Fialkov and Shor. No previous observations have been recorded on the conductivity of molten iodine trichloride, which also passes through a maximum. A discussion of these maxima and of the absence of a decomposition potential in either of the iodine chlorides is given later.

Experimental.

Iodine monochloride, prepared by Cornog and Karges's method (*loc. cit.*), was purified by recrystallisation in a static vacuum in an apparatus, shown in Fig. 1, in which a conductivity cell of the conventional type with sealed-in platinum electrodes was incorporated. About 100 g. of the monochloride were melted in the right-hand bulb, about 80% of the melt was allowed to crystallise, and the supernatant liquid was poured into the left-hand bulb. This process was repeated until the final batch of crystals showed the same m. p. on two successive operations. Usually four or five recrystallisations were found to give extremely pure iodine chloride having m. p. 27·20° as given by Cornog and Karges (*loc. cit.*). These pure crystals were then melted and poured into the cell, which was sealed at the constriction. Conductivities were measured by using the amplified output of a 1000-cycle oscillator in a Wheatstone-type network, and the balance point was detected electronically with a cathode-ray oscilloscope. The thermostat was controlled to ±0·05° by a contact thermometer in a large oil-bath.

The results obtained are shown in Fig. 2. Curve I shows data for impure iodine monochloride between the m. p. (27·2°) and 65°. Curve II represents the results for a purer sample: not only is the conductivity less, but there is a maximum at 45°. In Curve III and Table I the results for highly purified iodine monochloride are summarised. The conductivity is still lower and the maximum has been displaced to 40°. The data in Table I were reproducible, the value of 4·60 × 10^{-3}ohm^{-1}cm.$^{-1}$ for the conductivity at 35° being in close agreement with Cornog and Karges's value (*loc. cit.*). In col. 4 the values of a quantity μ/n are given. This function has been extensively used to compare the conductivities of molten chlorides at their melting points (Biltz and Klemm, *Z. anorg. Chem.*, 1926, **152**, 267). The quantity n is defined to be one less than the number of ions formed by dissociation of one molecule, and has been taken as unity for iodine monochloride.

FIG. 1.

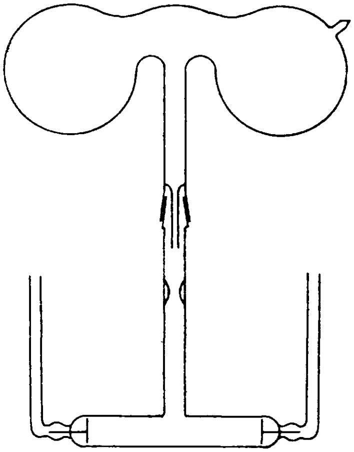
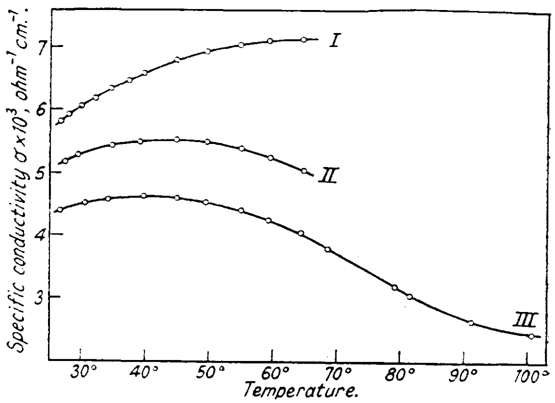


FIG. 2.



Iodine monochloride: I, impure; II, partly purified; III, highly purified.

TABLE I.

Conductivity of molten iodine monochloride between 27° and 120°.

Temp.	$\sigma\times10^3$ (ohm^{-1} cm.$^{-1}$).	Density (d) (g./cm.^{3}).*	$\mu/n = M\sigma/dn$.	Temp.	$\sigma\times10^3$ (ohm^{-1} cm.$^{-1}$).	Density (d) (g./cm.^{3}).*	$\mu/n = M\sigma/dn$.
26·75°	4·403	3·193	0·2217	64·8°	4·057	3·066	0·2149
30·6	4·519	3·180	0·2309	69·0	3·810	3·052	0·2027
34·45	4·593	3·168	0·2355	79·3	3·271	3·017	0·1760
39·9	4·637	3·149	0·2392	81·8	3·068	3·010	0·1655
45·1	4·610	3·131	0·2392	91·4	2·667	2·977	0·1455
49·7	4·541	3·117	0·2366	101·0	2·471	—	—
55·1	4·415	3·098	0·2314	113·0	2·043	—	—
59·8	4·270	3·082	0·2250	122·0	1·817	—	—

* By interpolation from Hannay's data (*J.*, 1873, **26**, 815).

The current–voltage curves obtained in a series of direct-current measurements with iodine monochloride are shown in Fig. 3. Two temperatures were chosen, one above and one below the temperature of maximum conductivity, and in neither case was there any evidence of a decomposition potential. The measurements were extended down to potentials of 1 mv. with the same result. In a parallel experiment, iodine monochloride was electrolysed at 35° in a cell with separate anode and cathode compartments. After a given time the circuit was broken, and the back e.m.f. followed potentiometrically until a steady value had been attained. This having been read, the electrolysis was continued for a further period and the same procedure repeated. Usually, the steady value was attained within 5 minutes of breaking the circuit and was about two thirds of the original value. This back e.m.f. remained constant for one hour. The results are given in Table II. The A.C. resistance of the cell was 24300 ohms, the D.C. voltage 113 v., and the D.C. current 4·65 milliamp. The volume of each electrode compartment was approx. 5 ml. Not only was the back e.m.f. extremely small, but it was also dependent on the amount of electrolysis. An explanation of these effects is presented in the discussion.

TABLE II.

Time of electrolysis (min.)	30	55	178
Faradays passed, $\times10^4$	0·868	1·59	5·15
Back e.m.f. (mv.)	7	8·5	11

Iodine Trichloride.—Pure iodine trichloride was prepared by adding finely powdered resublimed iodine to an excess of liquid chlorine at −78°. The chlorine had been purified by distillation. The excess of chlorine was allowed to evaporate through a silica drying tower. This material was filled directly into the conductivity cell, which was sealed at atmospheric pressure. The cell was made of Pyrex glass with a 3-mm. wall thickness in order to withstand the high pressure of the molten trichloride at and above its m. p. (101°). This pressure is 16 atm. at 101°. The molten trichloride attacked platinum rapidly but tungsten was not corroded even on prolonged heating. Tungsten rods of 5-mm. diameter were used as electrodes and were ground to 2-mm. diameter where they passed through the glass wall of the cell. The electrical circuit and the thermostatic control were the same as in the experiments on iodine monochloride.

TABLE III.

Conductivity of solid and of liquid iodine trichloride between 70° *and* 150°.

Temp.	70·0°	79·9°	84·8°	89·9°	95·0°	96·2°	97·7°	99·4°	100·1°	102·0°	103·7°	
$\sigma \times 10^3$, ohm^{-1} cm.$^{-1}$	0·0190	0·0597	0·175	0·490	2·64	4·68	6·87	8·25	8·35	8·60	9·13	
Temp.	105·3°	107·0°	109·3°	112·5°	115·0°	122·9°	127·0°	131·0°	135·5°	139·0°	142·7°	146·5°
$\sigma \times 10^3$, ohm^{-1} cm.$^{-1}$	9·31	9·40	9·55	9·53	9·34	8·15	6·73	4·52	2·39	1·29	0·69	0·36

The data in Table III show the results of a typical series of measurements made below and above the m. p. of the trichloride on material previously melted and allowed to solidify. These data show that the conductivity of solid iodine trichloride increases rapidly as the temperature is raised and that there is no pronounced discontinuity at the m. p. Above the m. p. the conductivity rises more slowly, passing through a maximum at 111°. Thereafter the value falls and at 145° is equal to that for the solid 10° below the m. p. The existence of the maximum is conveniently represented by plotting the logarithm of the conductivity against the reciprocal of the absolute temperature, as in Fig. 4. As in the case of iodine monochloride, direct-current measurements gave linear current–voltage plots without any indication of the existence of a decomposition potential.

FIG. 3.

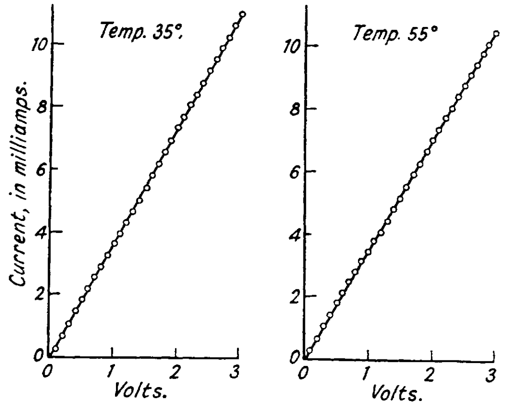
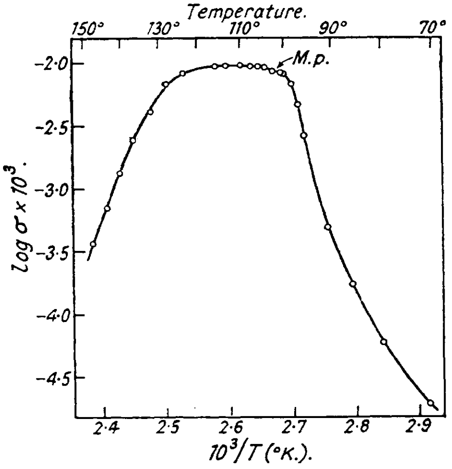


FIG. 4.



DISCUSSION.

The degree of ionisation required to account for the observed conductivity of iodine monochloride may be calculated very approximately, but the necessary data are not available for the trichloride. By extrapolation of Beck's results (*Z. physikal. Chem.*, 1904, **48**, 641) the viscosity (η) of iodine monochloride at 35° is 3·74 centipoises. From the data of Cornog and Karges (*loc. cit.*) the equivalent conductivity at infinite dilution (λ_∞) of potassium chloride in iodine monochloride is 31·7, from which the product $[\eta \cdot \lambda_\infty]_{\text{KCl in ICl}}$ is 118 The corresponding figure, $[\eta \cdot \lambda_\infty]_{\text{KCl in H}_2\text{O}}$, for an aqueous solution of potassium chloride, is 136. It would therefore seem that Walden's rule applies approximately, the conductivity of potassium chloride varying inversely as the solvent viscosity. The applicability of Walden's rule may be fortuitous, but experimentally it does hold for the conductivity of potassium chloride in iodine monochloride and in water, and this fact may be used to estimate the ionic mobilities by the following argument.

Fialkov and Kaganskaya (*J. Gen. Chem. Russia*, 1948, **18**, 289) have shown that the ionic species present in a solution of potassium chloride in iodine monochloride are K^+ and $[ICl_2]^-$ and that the transference number of the $[ICl_2]^-$ ion is 0·504, a value which is very close to that for the Cl^- ion in an aqueous solution of potassium chloride. It is therefore possible to estimate the mobility of $[ICl_2]^-$ from the known mobility of Cl^- in aqueous solution ($7{\cdot}9 \times 10^{-4}$ cm./sec. per volt/cm.), as $v_{ICl_2^-} = 7{\cdot}9 \times 10^{-4} \times (\eta_{H_2O}/\eta_{ICl}) \simeq 2 \times 10^{-4}$ cm.^{2}volt^{-1}sec.$^{-1}$. It being assumed to a first approximation that the mobilities of I^+ and ICl_2^- are equal, the average ionic mobility (v) of iodine monochloride may be taken as 2×10^{-4}cm.^{2}volt^{-1}sec.$^{-1}$, a value which is likely to be correct to within a factor of 2. If $\boldsymbol{m}$ is the number of current carriers per c.c. and $\boldsymbol{e}$ is the electronic charge, then as the conductivity at 35° ($\sigma_{35} = mev$) has a value of $4{\cdot}6 \times 10^{-3}$ohm^{-1}cm.$^{-1}$, a value for m of $1{\cdot}4 \times 10^{20}$ carriers/c.c. is obtained. If the value of the density at 35° is taken as 3·165 g.cm.$^{-3}$, 1 c.c. of iodine monochloride contains $1{\cdot}17 \times 10^{22}$ molecules, and the degree of ionisation is therefore $1{\cdot}2 \times 10^{-2}$. Thus, from this approximate calculation, about one in eighty molecules of iodine monochloride is dissociated into ions at 35°, a value which should be correct, at least as far as order of magnitude is concerned.

The specific conductivity data for iodine monochloride show a maximum at 40°. This maximum might arise from opposing density and viscosity effects. The maximum persists, however, when the quantity $\mu/n(= M\sigma/dn)$ is plotted against temperature. This is shown by the data in the last column of Table I. The quantity μ/n has been used by Biltz and Klemm (*loc. cit.*) to compare the conductivity of molten chlorides at their melting points. It effects a correction for the change in the number of conducting species per c.c. arising from the change of density with temperature, and the persistence of the maximum when this correction has been made shows that the maximum is not due to opposing viscosity and density effects. Increase in temperature lowers the viscosity, so that mobilities will tend to increase. This increase can only be counterbalanced by a decrease in ionisation as the temperature is raised.

The appreciable conductivity of iodine trichloride in the solid state is of great interest. The conductivity is of the same order of magnitude as the ionic conductivity of alkali halide crystals near their melting points (Mott and Gurney, " Electronic Processes in Ionic Crystals," p. 36). In these crystals, the conductivity is governed by the number and mobility of the lattice defects. Expressions derived for a conductivity arising from the migration of these defects show a linear dependence of log σ on $1/T$. Such a dependence was not found for iodine trichloride (Fig. 4). It should be emphasised, though, that the method used to measure the conductivity of the solid is not free from criticism. Accurate measurements on the solid would require a more elaborate circuit; the present results are merely presented to show that iodine trichloride in the solid state has a considerable conductivity. At present, the possibility of semiconduction is not definitely ruled out, even though this also would lead to an exponential dependence of the conductivity on $1/T$ in a range where only one conduction process is occurring. Transport experiments on solid iodine trichloride, or thermoelectric measurements, would distinguish between the two possible conduction mechanisms.

An explanation of the extremely small back e.m.f. generated on electrolysing molten iodine monochloride may be based on the hypothesis that the electrode products are already present in the melt, in thermodynamic equilibrium with iodine monochloride. In this case electrolysis would merely alter the concentration of the products at each electrode and a concentration e.m.f. would be set up on electrolysis. The magnitude of this should depend on the amount of electrolysis, and this effect has been observed (Table II).

If one assumes the electrode products are iodine at the cathode, and iodine trichloride at the anode, then, using the published values of free energy for the reactions concerned, it is possible to show that such a hypothesis does, in fact, reproduce the essential features of the back e.m.f. measurements. In addition, the hypothesis would explain why no decomposition potential is observed when D.C. current–voltage measurements are made. As electrolysis merely alters locally the normal equilibrium concentrations of iodine and iodine trichloride in the melt, and since the amount of electrolysis in the current–voltage measurements is considerably less than that used in the back e.m.f. measurements (see Table II), the back potentials developed would be so small as to be undetectable with the precision of measurement used. It is likely that a similar explanation would account for the absence of a decomposition potential in iodine trichloride and bromine trifluoride, though in these cases the nature of the electrode processes is less certain and the requisite thermodynamic data are not available.

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