375. *The Interaction of Metal Chlorides with Organic Chlorides. Part II.* Electrochemical Studies on Solutions of Titanium Tetrachloride in Some Alkyl Chlorides.*

By W. R. Longworth and P. H. Plesch.

The specific conductivity κ of titanium tetrachloride and of its solutions in benzene and various alkyl chlorides was measured by using a high-vacuum technique. For solutions in methylene dichloride and ethyl chloride at 0° κ is of the order of 10^{-7} mho cm.$^{-1}$ and goes through a marked maximum near $[TiCl_4] = 0{\cdot}4$M. The conductivity is ascribed to a self-ionisation $2TiCl_4 \rightleftharpoons TiCl_3^+ + TiCl_5^-$, of which the equilibrium constant in both solvents at 0° is of the order of 10^{-16}—10^{-18}, and falls approximately exponentially with increasing concentration of titanium tetrachloride. Our interpretation is supported by electrolyses in which titanium trichloride was deposited on the cathode. The decrease in κ with increasing concentration of titanium tetrachloride is ascribed to the concurrent decrease in the dielectric constant of the solutions.

The results of other authors on the conductivity of solutions of aluminium bromide and of the methylaluminium bromides in alkyl bromides have been reinterpreted in terms of self-ionisation.

The interaction of metal halides with alkyl halides is of wide interest, not least because of the possible formation of ions in such systems. This feature is of particular interest in connection with Friedel–Crafts reactions and cationic polymerisations. The evidence most frequently quoted in support of the ionisation of alkyl halides by metal halides is the work of Wertyporoch [1] on the conductivity of solutions of aluminium bromide in ethyl bromide. However, a re-examination of this system by Fairbrother and Scott [2] under rigorously dry conditions showed that the electrical conductivity is due to a self-ionisation of the aluminium bromide; our re-interpretation of their results supports this conclusion. Further support for the idea of a general ionogenic reaction between metal halides and alkyl halides appeared

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* Part I, *J.*, 1958, 451.

[1] Wertyporoch, *Ber.*, 1931, **64**, 1369, and others.

[2] Fairbrother and Scott, *J.*, 1955, 452.

to be provided by the formation of triphenylmethyl cations from triphenylmethyl halides and metal halides.[3,4,5]

The reactions in question can be represented by the equilibrium

$$\mathrm{RX} + \mathrm{MX}_n \rightleftharpoons \mathrm{R^+MX}_{n+1}{}^-$$

Since the position of the equilibrium is governed by the free-energy change, and the entropy changes will be relatively small, we can consider the matter in terms of the enthalpy change. Thus,

$$\Delta H = D(\mathrm{R{-}X}) - I(\mathrm{R}) + E(\mathrm{X}) - D(\mathrm{MX}_n\mathrm{{-}X^-}) - \Delta H_s(\mathrm{R^+MX}_{n+1}{}^-) + \Delta H_s(\mathrm{RX}) + \Delta H_s(\mathrm{MX}_n) - e^2/r$$

The *D*'s are bond-dissociation energies, *I*(R) is the ionisation potential of radical R, *E*(X) the electron-affinity of atom X, and the ΔH_s's are heats of solvation; the term e^2/r represents the Coulombic energy of the ion-pair. The first three terms can conveniently be represented by the heterolytic bond-dissociation energy

$$\theta(\mathrm{R^+{-}X^-}) = D(\mathrm{R{-}X}) - I(\mathrm{R}) + E(\mathrm{X}).$$

Variations in the nature of the alkyl halide RX will affect all the ingredients of ΔH, but especially θ, which ranges from 230 kcal./mole for methyl chloride to about 115 kcal./mole for triphenylmethyl bromide. It is, therefore, evident that the extent of ionogenesis will vary widely and that argument by qualitative analogy may be very misleading.[6] One can understand in these terms the apparent absence of ionisation which H. C. Brown and his collaborators found in various metal halide–alkyl halide systems.[7] Our own results [8] on the binary freezing-point phase diagrams of titanium tetrachloride with various alkyl chlorides also gave no evidence for any such interaction. In the present work we studied the conductivity of titanium tetrachloride in a number of alkyl chlorides and in benzene, in a further attempt to detect and, if possible, to identify any ions present. This is of particular interest to us in connection with current theories of cationic polymerisation, especially in relation to the cocatalytic activity of alkyl halides with metal halide catalysts.[9,10,11]

EXPERIMENTAL

Materials.—Alkyl chlorides and titanium tetrachloride were purified as described.[8] Benzene was purified and dried by conventional methods and then over calcium hydride, fractionally distilled, fractionally crystallised twice, and fractionated once in the vacuum system by bulb-to-bulb distillation.

Apparatus.—The conductivity cell of Pyrex glass, closely similar to Fairbrother and Scott's,[2] was fitted with bright platinum electrodes, 1·5 × 1·5 cm., 1·5 mm. apart, sealed through soda-glass and graded seals, and contained a glass-enclosed magnet for stirring. The cell constant (by KCl calibration) was 0·053. The resistance of the solution did not vary with the quantity of solution in the cell provided this exceeded 12 ml.

Operation.—The cell was fused to a high-vacuum system without joints or greased taps, thoroughly flamed, pumped, flushed with titanium tetrachloride vapour, and pumped again, before each series of measurements. The titanium tetrachloride and the alkyl chloride or benzene were distilled into the cell, and the concentrations computed as described.[8] When the required mixture had been distilled in, the cell was brought to constant temperature in melting ice, and the resistance measured; the contents were stirred magnetically.

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[3] Fairbrother and Wright, *J.*, 1949, 1058.
[4] Evans *et al.*, *J.*, 1955, 206, 3104; 1957, 1020.
[5] Porter and Baughan, *J.*, 1958, 744.
[6] Burton and Praill, *Quart. Rev.*, 1952, **6**, 302.
[7] Brown *et al.*, *Ind. Eng. Chem.*, 1953, **45**, 1462.
[8] Longworth, Plesch, and Rigbi, *J.*, 1958, 451.
[9] Pepper, *Trans. Faraday Soc.*, 1949, **45**, 397.
[10] Plesch, *J.*, 1953, 1662.
[11] Colclough and Dainton, *Trans. Faraday Soc.*, 1958, **54**, 901.

Resistance measurements were made, at 1000 c./sec., by a Wheatstone bridge using a cathode ray oscilloscope as visual null-point indicator, as described by Haszeldine and Woolf.[12] Both resistance and capacity out-of-balance were indicated separately. The discrimination for resistances of the order of 100,000 ohms was 1 part in 1000. The smallest measurable conductivity was 10^{-8} mho cm.$^{-1}$. Each reading was checked over a period of 15 min. and, if constant, was recorded; if the resistance drifted, further readings were taken until it was constant.

RESULTS

Conductivity Experiments.—All the recorded observations except those with benzene were made on colourless solutions of titanium tetrachloride, and colour was used as a criterion of purity, because a faint yellow colour was found to indicate a leak in the vacuum system. All benzene solutions of titanium tetrachloride were yellow because of the binary complex which is formed.[13]

Pure Materials.—The conductivities of pure titanium tetrachloride, carbon tetrachloride, chloroform, methylene dichloride, ethyl chloride, and benzene were not detectable.

Titanium tetrachloride in carbon tetrachloride, chloroform, and benzene. The conductivities of solutions of titanium tetrachloride in carbon tetrachloride, chloroform, and benzene at 0°, containing up to 1 mole/l. of titanium tetrachloride, could not be detected, and there was no change after several hours at ambient temperatures.

TABLE 1. *Specific conductivity (in mho cm.$^{-1}$) of titanium tetrachloride solutions at* 0° *(molar concns.).*

In methylene dichloride				In ethyl chloride					
Series 1		Series 2		Series 1		Series 2		Series 3	
[$TiCl_4$]	$10^8\kappa$	[$TiCl_4$]	$10^8\kappa$	[$TiCl_4$]	$10^7\kappa$	[$TiCl_4$]	$10^7\kappa$	[$TiCl_4$]	$10^7\kappa$
0·19	5·26	0·06	6·20	0·30	4·48	0·10	0·84	0·63	4·30
0·62	7·64	0·13	7·12	0·37	4·68	0·23	3·46	0·88	3·40
1·20	6·74	0·23	7·75	0·47	4·76	0·38	4·64	1·06	2·54
1·63	5·84	0·37	8·00	0·57	4·48	0·50	4·72		
2·03	4·78	0·64	8·23	0·66	3·72	0·63	4·16		
2·48	3·68	1·15	7·12						

Methylene dichlorides. All solutions of titanium tetrachloride in methylene dichloride were stable for up to 6 hr. Two separate series of experiments gave the results shown in Table 1 and plotted in Fig. 1 (curve *A*).

Ethyl chloride. All solutions of titanium tetrachloride in ethyl chloride were stable; during 6 hr., the approximate duration of the experiments, the conductivity changed by less than 10%. The results obtained in three series of experiments with different batches of materials are shown in Table 1 and plotted in Fig. 1 (curve *B*).

Ethyl chloride–carbon tetrachloride mixtures. In order to examine the effect of dielectric constant on conductivity, measurements were made on mixtures of titanium tetrachloride, ethyl chloride, and carbon tetrachloride in which the concentration of titanium tetrachloride was kept constant and that of carbon tetrachloride increased. The results are shown in Table 2.

TABLE 2. *Specific conductivity of titanium tetrachloride in mixtures of ethyl chloride and carbon tetrachloride at* 0°.

			A				B	
[$TiCl_4$] (mole/l.)	0·33	0·33	0·44	0·44	0·44	0·44	0·42	0·406
Volume (%) of CCl_4	4·80	7·00	0	4·76	6·92	6·92	10·00	12·92
Volume (%) of total tetrachlorides	8·45	10·50	4·76	9·53	11·60	11·60	14·50	17·30
$10^7\kappa$ (mho cm.$^{-1}$)	4·20	3·87	5·00	4·31	3·74	3·74	2·78	2·28

A further series in which the concentration of titanium tetrachloride was reduced by successive additions of carbon tetrachloride is shown in Table 2 and Fig. 1*C*.

Electrolyses.—These were carried out at ambient temperatures with a cell of Pyrex glass fitted with two bright platinum electrodes, 1 cm. in diameter and 2·5 cm. apart, with a potential

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[12] Haszeldine and Woolf, *Chem. and Ind.*, 1950, 544.

[13] Cullinane, Chard, and Leyshon, *J.*, 1952, 4106.

difference of 1000 v. During the electrolysis the cell was kept in the dark because of the reported effect of light on the solutions.[8] The cell was fused to the high-vacuum system and filled as described for the conductivity cell. The current was measured by a microammeter with 20 μA divisions.

With 20 ml. of a 0·4M-solution of titanium tetrachloride in methylene dichloride, the current started at 60 μA and had fallen to approximately 10 μA after 1 hr. After 4 hr. a bronze-coloured deposit was formed on the cathode while the anode remained bright and clean. After 30 hr. the current had dropped to less than 1 μA; the colour of the deposit had darkened and dark violet crystals could be seen growing from the cathode; the anode remained clean but became slightly pitted. This growth of crystals on the cathode continued as long as the current was passed, which was 20 days. The progressive fall in the current was presumably due to the coating on the cathode. Because of the small current, a chemical analysis of the fluid cell contents did not appear promising. A comparative mass-spectrometric analysis of the washed and dried fluid and of a fresh specimen of the same batch of methylene dichloride showed them to be identical and to contain no impurities in quantities greater than a few parts per 100,000. Analysis of the deposit on the cathode showed it to be titanium trichloride.

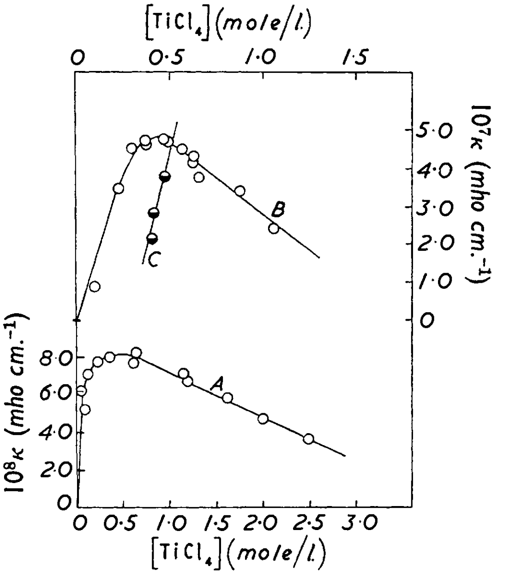

FIG. 1. *Specific conductivity* κ *of solutions of* $TiCl_4$ *in:* A, CH_2Cl_2; B, EtCl; C, *a mixture of* EtCl *and* CCl_4.

A similar experiment was carried out with 20 ml. of a 0·47M-solution of titanium tetrachloride in ethyl chloride. The current started at 550 μA and had fallen to about 90 μA after 1 hr. The electrolysis was continued for 12 days, at the end of which the current had fallen to about 2 μA. The appearance of the brownish-purple deposit on the cathode was similar to that formed in the experiment with methylene dichloride. Analysis of the deposit showed it to consist of 0·048 mole of titanium trichloride. The fluid cell contents were not analysed. Integration of the current–time curve showed that a quantity of electricity equivalent to 0·054 mole had been passed through the cell. However, because of the relative crudeness of the microammeter this figure cannot be regarded as very reliable.

DISCUSSION

Conductivity Curves.—The absence of any measurable conductivity in pure titanium tetrachloride and in its solutions in benzene and carbon tetrachloride was to be expected and requires no comment; the absence of conductivity in the chloroform solutions will be discussed below. The very marked maximum in the specific conductivity curves for the methylene dichloride and ethyl chloride solutions appears to be a new phenomenon for which we have found no close analogue in the literature.

The explanation of these curves requires the answering of two questions: what is the ionogenic reaction, and what are the influences which produce the variation of specific conductivity with concentration of titanium tetrachloride?

The hypothetical ionogenic reaction of the metal chloride with the solvent

$$\mathrm{TiCl_4 + RCl \rightleftharpoons R^+ + TiCl_5^-} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad \text{(i)}$$

cannot account for the observations, since it implies that the total concentration of ions, and therefore also the specific conductivity, varies with the square-root of the titanium tetrachloride concentration, which is not in agreement with our results. Nor does the combination of equilibrium (i) with others involving ion-pairs and -triplets, and complex ions, such as $\mathrm{Ti_2Cl_9^-}$, lead to the required results.

The only other plausible ionogenic reaction is a self-ionisation, such as *

$$\mathrm{2TiCl_4 \rightleftharpoons TiCl_3^+ + TiCl_5^-} \quad (K) \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad \text{(ii)}$$

This implies a linear relationship between specific conductivity and concentration and thus represents the initial parts of our curves, but by itself it cannot account for the maximum. We have examined combinations of equilibrium (ii) with a large number of others without finding any plausible system of equilibria which would give a maximum in the conductivity curve, even taking into consideration the smaller ionic conductivities of large complex ions.

We are thus driven to seek the origin of the phenomenon in effects other than the existence of a multiplicity of equilibria. The most obvious feature is the reduction in the dielectric constant (D.C.) of the systems with increasing concentration of titanium tetrachloride. We are aware of the fact that the macroscopic D.C. of a liquid—and even more so of a mixture of liquids—is not an adequate measure of its solvating properties, and thus of its influence on ionogenic and ionic equilibria. However, it is the only simple and readily available property which can be used at present. The effect of varying D.C. on the conductivity can be separated into two components: in view of the low D.C. of all our solutions, the equilibrium (ii) must be the net result of an ionogenic equilibrium

$$\mathrm{2TiCl_4 \rightleftharpoons TiCl_3^+TiCl_5^-} \quad (K_1) \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad \text{(iii)}$$

giving ion-pairs, and a dissociation equilibrium of the ion pairs:

$$\mathrm{TiCl_3^+TiCl_5^- \rightleftharpoons TiCl_3^+ + TiCl_5^-} \quad (K_2) \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad \text{(iv)}$$

The influence on K_1 and K_2 of the change in D.C. with changing concentration of titanium tetrachloride can be analysed as follows:

From the equilibria (iii) and (iv) it follows that

$$\begin{aligned}\kappa &= \lambda_3[\mathrm{TiCl_3^+}] + \lambda_5[\mathrm{TiCl_5^-}]\\ &= (\lambda_3 + \lambda_5)K_1^{\frac{1}{2}}K_2^{\frac{1}{2}}[\mathrm{TiCl_4}]\end{aligned}$$

The *true* ionic conductivity is

$$\Lambda_T = (\lambda_3 + \lambda_5) = 2\kappa/c$$

where c is the *total* concentration of *free* ions. Denoting $[\mathrm{TiCl_4}]$ by a, we obtain

$$\kappa = \Lambda_T K_1^{\frac{1}{2}}K_2^{\frac{1}{2}}a \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

Hence

$$\frac{\mathrm{d}\ln\kappa}{\mathrm{d}a} = \frac{\mathrm{d}\ln\Lambda_T}{\mathrm{d}a} + \frac{1}{2}\frac{\mathrm{d}\ln K_1K_2}{\mathrm{d}a} + \frac{1}{a}$$

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* Another, and perhaps more plausible, equilibrium is $\mathrm{3TiCl_4 \rightleftharpoons 2TiCl_3^+ + TiCl_6^{2-}}$. This also yields a linear relationship between κ and the concentration of titanium tetrachloride, analogous to eqn. (1), so that the available information does not enable us to discriminate between the two modes of ionisation; for simplicity we shall interpret our results in terms of equilibrium (ii): the matter could be decided by transport experiments.

The Λ_T depends on a principally through the viscosity η, and K_1 and K_2 depend on a through the D.C. (ε). If we express the variation of η and of ε with a by the linear relationships

$$\eta = \eta_0 + \gamma a \quad \text{and} \quad \varepsilon = \varepsilon_0 - \beta a \qquad (2)$$

we obtain

$$\mathrm{d}\eta/\mathrm{d}a = \gamma \quad \text{and} \quad \mathrm{d}\varepsilon/\mathrm{d}a = -\beta$$

Thus

$$\frac{\mathrm{d}\ln\kappa}{\mathrm{d}a} = \frac{1}{a} + \gamma\frac{\mathrm{d}\ln\Lambda_T}{\mathrm{d}\eta} - \frac{\beta}{2}\frac{\mathrm{d}\ln K_1K_2}{\mathrm{d}\varepsilon} \qquad (3)$$

Since Walden's rule holds to a good approximation in most systems of the kind which are under consideration here,

$$\mathrm{d}\ln\Lambda_T/\mathrm{d}\eta = -1/\eta = -1/(\eta_0 + \gamma a) \qquad (4)$$

Thus

$$\frac{\mathrm{d}\ln\kappa}{\mathrm{d}a} = \frac{1}{a} - \frac{\gamma}{\eta_0 + \gamma a} - \frac{\beta}{2}\left(\frac{\mathrm{d}\ln K_1}{\mathrm{d}\varepsilon} + \frac{\mathrm{d}\ln K_2}{\mathrm{d}\varepsilon}\right) \qquad (5)$$

The second term on the right of equation (5) can be written as $1/(a + \eta_0/\gamma)$ and is thus seen to be positive and smaller than the first term, so that the sum of the first two terms is positive. Regarding the third term, both theory and experiment show that equilibrium constants of the type of K_1 and K_2 fall very rapidly with decreasing D.C., and that, moreover, the rate of change increases with falling D.C. The third term is, therefore, positive, and it is an increasing function of a since the D.C. ε decreases with increasing a. Thus eqn. (5), and, therefore, also the κ–a curves, must have a maximum, and eqn. (5) is, therefore, at any rate in qualitative accord with our observations.

The effect of D.C. on conductivity is perhaps most strikingly illustrated by the results in Table 2*A*, and Fig. 2*C*. The addition of carbon tetrachloride at constant titanium tetrachloride concentration produces a drastic reduction in the conductivity. Moreover, as shown by the results of Table 2*B* and Fig. 1*C*, when the titanium tetrachloride concentration is reduced progressively by the addition of carbon tetrachloride the fall in the conductivity is far steeper than can be accounted for by the simple dilution effect in the binary system.

The variation of conductivity with D.C. can be evaluated from equations (1), (2), and (4), and is conveniently represented by

$$\frac{\mathrm{d}\ln(\kappa/a)}{\mathrm{d}\varepsilon} = \frac{\mathrm{d}\ln\Lambda_T}{\mathrm{d}\varepsilon} + \tfrac{1}{2}\frac{\mathrm{d}\ln K}{\mathrm{d}\varepsilon}$$

$$= \frac{1}{\beta(a + \eta_0/\gamma)} + \tfrac{1}{2}\frac{\mathrm{d}\ln K}{\mathrm{d}\varepsilon} \qquad (6a)$$

$$= \frac{1}{\varepsilon_0 - \varepsilon + \beta\eta_0/\gamma} + \tfrac{1}{2}\frac{\mathrm{d}\ln K}{\mathrm{d}\varepsilon}, \qquad (6b)$$

where $K = K_1K_2$. Our results are shown as plots of log (κ/a)against $1/\varepsilon$ in Fig. 2. The D.C. of the solutions were computed by assuming a linear dependence on concentration, and using the following values for the D.C. of the pure substance at 0°: CH_2Cl_2 9·93,[14] C_2H_5Cl 12·25,[15] $TiCl_4$ 2·80,[14] CCl_4 2·28.[14] Since the first term of eqn. (6) varies only very slowly with ε, the very rapid variation of κ with D.C. is evident.

[14] National Bureau of Standards, Circular 514.

[15] Longworth and Plesch, *J.*, 1959, 1618.

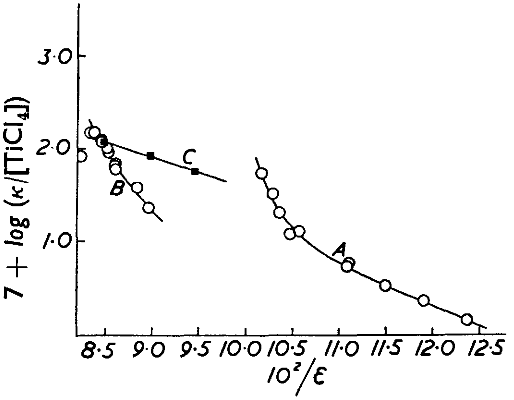
Since the D.C. of chloroform at 0° is relatively low (5·21), our inability to detect a measurable conductivity for solutions of titanium tetrachloride in this solvent is in conformity with our other results.

The composite equilibrium constant of equilibrium (ii), $K = K_1K_2$, can be estimated as follows: Λ_T can be estimated to be of the order of 100 for both solvents. If $\kappa/a = 10^{-6}$, it follows from eqn. (1) that K is of the order of 10^{-16}. The limiting value of K at $a = 0$ is of the order of 10^{-18} for methylene dichloride and 10^{-16} for ethyl chloride.

It should be noted that in these systems Λ_T *cannot* be derived from the limiting value of κ/a unless K is measured by an independent method.

Electrolysis.—Our theory of self-ionisation suggests that, if the solutions are electrolysed, titanium trichloride should be deposited at the cathode. This has been confirmed qualitatively, and a semi-quantitative experiment has shown that at any rate the major portion of the current is carried in this manner. The fate of the chlorine which must be liberated at the anode is unknown. It is noteworthy that our electrolytic preparation of titanium trichloride provides one of the very few examples of a polyatomic ion being deposited intact upon discharge at an electrode.

FIG. 2. *Plot of* log (κ/[$TiCl_4$]) *against the reciprocal of the dielectric constant* ε. *Curve* A, *in* CH_2Cl_2; *curve* B, *in* EtCl; *curve* C, *in mixtures of* EtCl *and* CCl_4. (For curve *C*, [$TiCl_4$] = 0·44 mole/l.)



Conclusion.—The results give no indication of an ionogenic reaction between titanium tetrachloride and methylene dichloride or ethyl chloride. The observed conductivities can be interpreted by a self-ionisation of the titanium tetrachloride, the extent of which depends strongly on the dielectric constant of the solution.

Ionisation of Aluminium Bromide.—Only very few studies have been made of simple systems analogous to ours, *i.e.*, consisting of metal halide and alkyl halide only, and most of these are vitiated by failure adequately to exclude moisture. Fairbrother and Scott's results [2] on the system aluminium bromide–ethyl bromide promised to provide an interesting comparison with our work. We re-examined their conductivity data and found that the specific conductivity is accurately proportional to the square of the concentration of aluminium bromide. If it be assumed that there is only one type of cation and of anion, and these be represented by A^+ and A^- in order not to prejudice the question of their nature, and if c is the *total* concentration of free ions, then

$$\kappa = \lambda_+[A^+] + \lambda_-[A^-] = \tfrac{1}{2}\Lambda_T c$$

Λ_T is the *true* ionic conductivity, and not the quantity $\Lambda = \kappa/[AlBr_3]$ used by the original authors which—in view of the very low degree of ionisation—has little, if any, significance. Since κ is proportional to c, it follows that for this system c must be proportional to the square of the aluminium bromide concentration. An examination of all plausible equilibria, including those favoured by the original authors, showed that the only one which would yield this relationship is

$$4\mathrm{AlBr_3} \rightleftharpoons (\mathrm{AlBr_3})_x\mathrm{AlBr_2}^+ + (\mathrm{AlBr_3})_{2-x}\mathrm{AlBr_4}^-$$

If $x = 1$

$$4\mathrm{AlBr_3} \rightleftharpoons \mathrm{Al_2Br_5}^+ + \mathrm{Al_2Br_7}^-$$

and

$$K = \frac{[\mathrm{Al_2Br_5}^+][\mathrm{Al_2Br_7}^-]}{[\mathrm{AlBr_3}]^4} \approx \frac{c^2}{4[\mathrm{AlBr_3}]^4}$$

It follows that

$$\kappa = \tfrac{1}{2}\Lambda_T c = \Lambda_T K^{\frac{1}{2}}[\mathrm{AlBr_3}]^2$$

and from the slope of the plot of κ against $[\mathrm{AlBr_3}]^2$, we find $\Lambda_T K^{\frac{1}{2}} = 1{\cdot}44 \times 10^{-4}$. If we assume that Λ_T is of the order of 100 mho cm.^{2} mole^{-1}, we obtain $K = 2 \times 10^{-18}$ l.^{2} mole^{-2} at 25°. The greater mobility of the anion reported by Fairbrother and Scott may be due to the cation's being more strongly solvated than the anion, or x may be greater than unity. Thus Fairbrother and Scott's conclusion, that the conductivity of aluminium bromide in ethyl bromide is due to self-ionisation, is valid but this self-ionisation probably occurs in a manner different from that originally suggested. Dr. Fairbrother has authorised us to state that he concurs with our views as preferable to his original interpretation.

An analysis of Jacober and Kraus's results [16] along the same lines shows that at 0° in methyl bromide solution the specific conductivities of aluminium bromide and of methylaluminium dibromide are accurately proportional to the square of the concentration, and that for dimethylaluminium bromide the specific conductivity is proportional to the fourth power of the concentration. The specific conductivities found by Jacober and Kraus are much higher than those of Fairbrother and Scott, and the plots of their results make relatively large intercepts on the conductivity axis; this indicates that their work may have been strongly affected by impurities, so that an evaluation of equilibrium constants from it is probably not warranted. The very high degree of complexity of the ions formed from the dimethylaluminium bromide which is suggested by these results is noteworthy.

The absence of any obvious dielectric effect in these systems, in contrast to our own, is most probably due to the fact that they cover a smaller concentration range and, more important, that the D.C. of aluminium bromide is appreciably greater than that of titanium tetrachloride; extrapolation indicates a D.C. of about 3·7 for the hypothetical supercooled liquid at 0°.

[*Added, April* 1*st*, 1959.—Conductivity maxima similar to those in Fig. 1 were obtained by Greenwood and Martin (*J.*, 1953, 757) with the system boron fluoride–methanol, and by Payne (Proc. International Conference on Co-ordination Compounds, Amsterdam, 1953, p. 75) with the system titanium tetrachloride–phosphoryl chloride. These authors did not attempt to explain the maxima, but it is evident that the dielectric constant effect suggested by us will also explain their results.]

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UNIVERSITY COLLEGE OF NORTH STAFFORDSHIRE,
KEELE, STAFFORDSHIRE.

[*Received, December* 8*th*, 1958.]

[16] Jacober and Kraus, *J. Amer. Chem. Soc.*, 1949, **71**, 2405.