431. *The Conductances of Some Chlorides in Ethanol. Part I. Hydrochloric Acid, Cæsium Chloride, Magnesium Chloride, and Lanthanum Chloride.*

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The conductances of very dilute solutions of hydrochloric acid, cæsium chloride, magnesium chloride, and lanthanum chloride have been measured in anhydrous ethanol at 25°. Some measurements on magnesium chloride solutions at 20° were also obtained. The effects of traces of water on the conductances of cæsium chloride and magnesium chloride were determined. Hydrochloric acid and cæsium chloride behave as strong electrolytes exhibiting ion-association in accordance with theory. The behaviour of magnesium chloride or lanthanum chloride is not unambiguously determined by conductance measurements because of the possibility of solvolysis but they are not strong electrolytes.

In preparation for studies on the solvolysis of the chlorides of Group IV metals it was necessary to obtain molecular conductances of the chlorides of uni-, bi-, and ter-valent metals in anhydrous ethanol. For comparison with the behaviour of thorium chloride it was preferable to obtain data on chlorides of the heavier metals and to this end the chlorides of cæsium, barium, and lanthanum were chosen. Unfortunately, the very low solubility of barium chloride precluded its measurement and magnesium chloride was studied instead. In view of the possible solvolysis of Group IV chlorides to form hydrochloric acid and the discrepancies among recorded values for the conductance of the latter we included it in this work.

EXPERIMENTAL

The magnitude of interionic effects with a solvent of low dielectric constant requires that measurements be made at the lowest concentrations possible. This can only be achieved under extremely rigorous conditions of purity of solvent and solutes. In particular, ethyl alcohol is very hygroscopic and although water has only a small effect on the conductivity of pure alcohol we have found that the conductivities of some electrolytes are very sensitive to water. Consequently most attention was given to producing " conductivity alcohol " and to avoiding the inclusion of water during the making up and transference of solutions.

Conductivity Alcohol.—After trial of several recorded methods for purifying alcohol an improved method was devised which readily furnished large quantities having consistently the second lowest recorded specific conductance. Absolute alcohol (5 l.) was given a preliminary azeotropic drying by fractional distillation (100 cm. column, packed with 4 mm. Fenske glass helices) with benzene (100 c.c.). After removal of the benzene, sodium (5 g., clean cut) was dissolved in the alcohol, followed by diethyl phthalate (20 c.c.), and the solution was boiled under reflux for 4 hr. The water content of the distillate was estimated by the Karl Fischer method to be *ca.* 0·002% and the specific conductivity was $3 \cdot 94 \times 10^{-9}$ mho. The only lower value reported is $1 \cdot 25 \times 10^{-9}$ mho obtained by Danner and Hildebrand [1] using a more complicated procedure in which the alcohol was finally distilled *in vacuo* into a sealed-on glass conductivity cell. In our method a large stock (4·5 l.) of conductivity alcohol was prepared and could be drawn on over a period of time during which frequent checks showed that its conductivity was unchanged. However, it was essential to purify the diethyl phthalate carefully and to pass purified nitrogen through the stillhead. Distillation of this " conductivity " alcohol from anhydrous copper sulphate or 2 : 4 : 6-trinitrobenzoic acid did not lower the specific conductivity.

Cæsium Chloride.—Commercial " pure " cæsium chloride (4·5 g.) was azeotropically dried, conductivity alcohol (100 c.c.) and benzene (80 c.c.) being used. Most of the cæsium salt appeared to remain insoluble and was separated from the final solution (70 c.c.) by decantation. The residue (4 g.) was dried *in vacuo* and analysed for chloride (gravimetrically as AgCl) and water (Karl Fischer method) (Found: Cl, 21·08; H_2O, 0·008. Calc. for CsCl: Cl, 21·05%).

Magnesium Chloride.—Hydrated magnesium chloride (5 g.; " AnalaR ") was azeotropically dried with conductivity alcohol (200 c.c.) and benzene (15 c.c.). When the clear solution had been concentrated to 100 c.c. it was allowed to cool and deposit magnesium chloride alcoholate. The crystals were separated and subjected to the foregoing treatment which was again repeated on the second crop and finally the third crop was thrice recrystallised from conductivity alcohol. The dried product was analysed for magnesium (oxine method), chloride (AgCl, gravimetric), ethoxide (method of Bradley *et al.*[2]) and water (Karl Fischer method) (Found: Mg, 6·61; Cl, 19·12; EtO, 73·42; H_2O, 0·008. Calc. for $MgCl_2,6EtOH$: Mg, 6·54; Cl, 19·08; EtO, 73·55%).

Lanthanum Chloride.—Commercial " pure " lanthanum chloride hydrate (5 g.) was azeotropically dried with conductivity alcohol (300 c.c.) and benzene (190 c.c.), and the solution evaporated to dryness since it did not crystallise. The lanthanum chloride ethyl alcoholate was then converted into the *iso*propyl alcoholate by alcohol interchange and twice recrystallised from *iso*propyl alcohol. The dried solid (6 g.) was analysed for lanthanum (precipitation as hydroxide and ignition to La_2O_3), chloride (AgCl, gravimetric), *iso*propoxide (method of Bradley *et al.*[2]) and water (Karl Fischer method) (Found: La, 32·55; Cl, 25·07; Pr^iO, 42·4; H_2O, 0·007. Calc. for $LaCl_3,3Pr^iOH$: La, 32·64; Cl, 24·99; Pr^iO, 42·4%).

Alcoholic Hydrochloric Acid.—Hydrogen chloride was generated in an all-glass apparatus by running concentrated hydrochloric acid (" AnalaR ") into concentrated sulphuric acid (" AnalaR "). The gas was passed first through concentrated sulphuric acid (" AnalaR "),

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[1] Danner and Hildebrand, *J. Amer. Chem. Soc.*, 1922, **44**, 4824.

[2] Bradley, Halim, and Wardlaw, *J.*, 1950, 3450.

then through a cold-trap packed with purified glass wool at *ca.* −78°. The latter device served both to remove spray and to effect final drying. The hydrogen chloride was finally led into conductivity alcohol which was vigorously stirred (magnetically) and cooled to minimise esterification. All connections were poly(vinyl chloride) tubing. When the solution was judged to be *ca.* 0·1N the absorption of hydrogen chloride was discontinued and the solution immediately analysed and then accurately diluted with conductivity alcohol.

Potassium Chloride.—" AnalaR " reagent was crystallised four times from distilled water in Pyrex apparatus and finally from conductivity water in a platinum dish. The crystals were dried at 130° for one day, then taken to dull red heat, transferred to an agate mortar, and ground. The powder was dried for 2 days at 180° and allowed to cool in the presence of phosphoric oxide. Qualitative tests showed no magnesium, sodium, or sulphate and the product gave a neutral solution.

Benzoic Acid.—Benzoic acid (" AnalaR ") was crystallised thrice from hot conductivity water then dried at 110°. It melted at 121·7°.

Nitrogen.—Since nitrogen was continuously passed through the refluxing conductivity alcohol it was essential that the gas be highly purified. After considerable research the following procedure was judged to be most efficient. Commercial " oxygen-free " nitrogen was passed through (*a*) a cotton-wool dust-trap, (*b*) a tube of soda-lime to remove carbon dioxide, (*c*) a Kraus and Parker [3] scrubber containing dilute potassium hydroxide solution, (*d*) a spray trap, (*e*) a second scrubber containing dilute phosphoric acid to remove ammonia, (*f*) another spray trap, (*g*) a wash-bottle containing concentrated sulphuric acid for preliminary drying, (*h*) a spray trap containing a glass-wool filter, (*i*) a column of silica gel, (*j*) a column packed with phosphoric oxide suspended on glass-wool, and finally another glass-wool filter. Connections were made as before. Nitrogen purified in this manner was used exclusively in all operations.

FIG. 1.

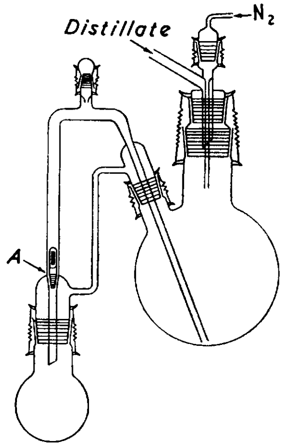
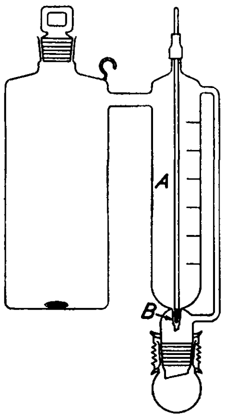


FIG. 2.



Conductivity Still.—The fractionating column described above was fitted to a total-condensation variable-take-off still-head in which the reflux ratio was controlled by the inclination of a crescent-shaped glass rod placed beneath the returning condensate. This device was externally operated by a glass lever acting through a standard ground-glass joint arranged so that the conductivity alcohol did not pass through taps or joints on leaving the still-head. The collected condensate passed through a dripper on to another crescent-shaped divider which allowed the alcohol to pass into either a built-in conductivity cell or the storage flask (2 l.) shown in Fig. 1. The conductivity cell (capacity 40 c.c.) was of the siphon type and contained a thermometer well and it allowed frequent checks on the specific conductivity of the alcohol. The alcohol was siphoned as required from the storage vessel through a magnetically operated ground-glass valve (*A* in Fig. 1) directly into the other conductivity cell, a counter-current of nitrogen excluding air during the attachment or detachment of the cell.

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[3] Kraus and Parker, *J. Amer. Chem. Soc.*, 1922, **44**, 2429.

Conductivity Cell.—The cell was of approx. 750 c.c. capacity and was constructed in Pyrex glass. The dipping electrodes were of bright platinum with an area approx. 7 cm.^{2} and separated by about 7 mm. The electrodes were welded to strips of thin platinum foil which made contact *via* pinched glass seals to the mercury wells. The electrode assembly was held rigidly by glass pillars. Solution in the cell could be magnetically stirred.

Preparation of Solution.—A relatively concentrated solution was made up in a weight burette (Fig. 2) by weighing in a sample of solute, then collecting pure solvent, and using a magnetic stirrer to speed dissolution. The burette could be weighed to determine the total weight of solution. The solution was transferred to the roughly graduated limb *A* by tilting and then dispensed through the ground glass valve *B* into the main conductivity cell. The conductance of the concentrated solution was also measured directly in a small cell and its purity and stability could thus be frequently checked. Instead of using the Ostwald–Arrhenius dilution procedure we adopted Whetham's method.[4] First the cell was filled with a known weight of pure solvent (approx. 450 c.c.) and its conductance was measured. Then small successive additions of concentrated solution were made from the weight burette, and the conductance was remeasured. In this manner the errors due to contamination of the solution, which must accumulate during a dilution procedure, are made least in the most dilute solutions. The advantage of the Ostwald–Arrhenius method is the elimination of errors due to adsorption but experiments in which powdered glass was added to dilute solutions showed that adsorption errors were negligible in our work whereas the sensitivity of the solvent to contamination was very high.

Determination of the Cell Constant.—The cell constant was determined by measuring the conductance of freshly prepared potassium chloride solutions using Davies's data. The following values for the cell constant obtained at approximately 8-monthly intervals reflect the stability of the cell: 0·078849, 0·078853, and 0·078842. These determinations were confirmed by the method recommended by Ives and Sames [6] using benzoic acid solutions.

Density Determinations.—Measurements on alcohol and some of the more concentrated electrolyte solutions were made at various temperatures, by using an all-glass dilatometer containing two vertical " Veridia " capillaries (2·0 mm. bore) as described previously.[7] The value for pure alcohol at 25·00° was d_4^{25} 0·78479 (lit.,[8] 0·78506).

Cleaning Procedure.—Experiments showed that repeated treatment of the conductivity cell with chromic acid cleaning mixtures gave erratic results and the following method was adopted instead. The apparatus was cleaned with chromic–nitric acid mixture, then rinsed with distilled water, and subjected to prolonged steaming. In the latter stage we found that steam generated from alkaline potassium permanganate solution was unsuitable (cf. Ives *et al.*[9]) and conductivity water was used instead. After steaming, the apparatus was dried at 140° for several hours and allowed to cool in a stream of nitrogen. After this initial treatment the apparatus was no longer treated with chromic acid and at the end of each experiment it was rinsed thoroughly with conductivity water, steamed, and dried. This procedure was applied to all apparatus and gave reproducible results.

Electrical Measurements.—A Doran conductivity bridge was suitably adapted for this work and the usual precautions required for a.c. measurements were observed. For determining the specific resistance of the alcohol and of dilute solutions the " shunt " method was used. An 80,000 ohm Sullivan non-inductive resistance was first measured alone and then with the conductivity cell in parallel. The cell was kept at 25° ± 0·01° in a thermostat, the temperature being checked with a standard thermometer. Weights were corrected for buoyancy when necessary. The solvent conductance was subtracted from the conductance of the solution and this correction did not exceed 1—2% for the most dilute solutions.

RESULTS AND DISCUSSION

Hydrochloric Acid.—The results are given in Table 1 in which *C* is the concentration in equivs./l. and Λ_c is the corresponding equivalent conductance. The results conformed

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[4] Whetham, *Phil. Trans.*, 1900, **194**, 321.
[5] Davies, *J.*, 1937, 434.
[6] Ives and Sames, *J.*, 1943, 512.
[7] Bradley, Kay, and Wardlaw, *J.*, 1956, 4916.
[8] International Critical Tables.
[9] Ives and Riley, *J.*, 1931, 1999; Feates, Ives, and Pryor, *J. Electrochem. Soc.*, 1956, **103**, 580.

to the equation $\Lambda_c = 83{\cdot}60 - 395\sqrt{C}$ as is shown by the calculated values. The Kohlrausch slope is practically double the theoretical value (199·6) calculated from the Onsager

TABLE 1. *Hydrochloric acid in ethanol.*

10^4C	Λ_c	$83{\cdot}60—395\sqrt{C}$	10^3K	10^4C	Λ_c	$83{\cdot}60—395\sqrt{C}$	10^3K
0·9120	79·80	79·83	8·36	8·311	72·22	72·21	8·25
1·3805	78·99	78·96	7·99	13·995	68·87	68·82	8·37
3·4351	76·28	76·28	7·83	18·320	66·81	66·70	8·39
4·556	75·16	75·17	7·84				

equation and ion-association evidently occurs. The method of Fuoss[10] was used to determine the thermodynamic dissociation constant K. The mean ionic activity coefficient $f_{\pm}$ was determined from the Debye–Hückel equation which for ethanol at 25° takes the form

$$-\log f_{\pm}^2 = (5{\cdot}954\sqrt{\alpha C})/(1 + 0{\cdot}5921a_i\sqrt{\alpha C})$$

where α is the degree of dissociation of ion-pairs and a_i is the average effective diameter (Å) of the ions. However, trial computations showed that best agreement was obtained by ignoring a_i and using the simplified equation $-\log f_{\pm}^2 = 5{\cdot}954\sqrt{\alpha C}$. The limiting equivalent conductance and the dissociation constant were then found to be $\Lambda_0 = 82{\cdot}46$ and $K = 8{\cdot}23 \times 10^{-3}$. K is extremely sensitive to error as shown in the calculated values of K in Table 1. Λ_0 is significantly lower than the value (83·60) obtained by extrapolation of the Kohlrausch equation. Other values have been reported for Λ_0, *viz.*, 81·8 (ref. 12), 83·8 (ref. 13), and 84·25 (ref. 14). In particular the work of Bezman and Verhoek[14] showed that the conductance of ethanolic hydrochloric acid is sensitive to water and, in the region $[H_2O] = 0—1{\cdot}4$M, Λ_0 decreases with increase in water content. Our value for Λ_0 corresponds to the feasible water content of 0·0025% according to their results, although their conductivity alcohol was less pure than ours.

Cæsium Chloride.—The data for cæsium chloride are given in Table 2 and represent three completely independent runs arranged in order of ascending concentration irrespective of the number of the run. The conductances conform to the equation:

$$\Lambda_c = 48{\cdot}55 - 268{\cdot}9\sqrt{C}$$

as shown in Table 2.

TABLE 2. *Cæsium chloride in ethanol.*

10^4C	Λ_c	$\Lambda_{\text{calc.}}$	10^3K	10^4C	Λ_c	$\Lambda_{\text{calc.}}$	10^3K	10^4C	Λ_c	$\Lambda_{\text{calc.}}$	10^3K
0·9698	45·85	45·91	6·0	1·396	45·34	45·24	6·0	1·742	44·95	45·00	6·1
0·9803	45·93	45·89	6·8	1·497	45·26	45·26	6·0	1·823	44·94	44·94	6·6
1·0145	45·85	45·84	6·5	1·506	45·30	45·25	6·7	1·837	45·00	44·90	7·1
1·0857	45·79	45·75	6·8	1·577	45·19	45·17	6·5	1·975	44·86	44·77	7·1
1·1109	45·75	45·72	6·6	1·607	45·11	45·14	6·2	1·997	44·77	44·76	6·6
1·179	45·67	45·67	6·7	1·654	45·13	45·12	6·7	2·198	44·56	44·57	6·6
1·341	45·50	45·47	6·9	1·712	45·07	45·03	6·6				

The abnormally high Kohlrausch slope (theory 152·4) suggested the occurrence of ion-association and this was confirmed by application of Fuoss's method which gave $\Lambda_0 = 48{\cdot}01$ and $K = 6{\cdot}61 \times 10^{-3}$. The complete Debye–Hückel expression for the activity coefficient was used for several values of a_i and any value between 5·0—8·0 Å gave satisfactory calculations. The individual values of K in Table 2 were based on $a_i = 5{\cdot}0$ Å. In the Bjerrum theory[11] for ion-association the dissociation constant K may be calculated as a

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[10] Fuoss, *J. Amer. Chem. Soc.*, 1935, **57**, 488.

[11] Bjerrum, *Kgl. danske Videnskab. Selskab*, 1926, **7**, 9.

[12] Goldschmidt and Dahl, *Z. phys. Chem.*, 1925, *A*, **114**, 1.

[13] Murray-Rust and Hartley, *Proc. Roy. Soc.*, 1929, *A*, **126**, 84.

[14] Bezman and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1330.

function of the distance of closest approach a of the ions. It is interesting that a value of $a = 3{\cdot}46$ Å, the sum of the *unsolvated* ionic radii,[15] would require a value of K of the right order. Addition of water to alcoholic cæsium chloride caused a decrease in conductance as shown by the data in Table 3 in which the initial concentration of cæsium chloride was 10^{-4} mole/l. This behaviour can be ascribed mainly to the increase in viscosity caused by the addition of water. For example, a 0·1% aqueous alcohol solution has a viscosity 0·3% higher than pure alcohol whilst the cæsium chloride solution with 0·1% of water has a conductance *ca.* 0·5% lower than that of the anhydrous solution.

TABLE 3.

Water (%)	0	0·022	0·056	0·183	0·286	0·465	0·700	0·948
$10^6\kappa$ (mhos)	4·662	4·650	4·642	4·631	4·627	4·618	4·607	4·596

Magnesium Chloride.—In view of the ion-association found with the uni-univalent electrolytes the measurements on magnesium chloride were taken to extremely low concentrations. Preliminary Kohlrausch plots, based on complete ionisation of magnesium chloride as a bi-univalent electrolyte ($\frac{1}{2}\text{MgCl}_2 \longrightarrow \frac{1}{2}\text{Mg}^{2+} + \text{Cl}^-$), suggested that dissociation was incomplete whilst an Ostwald plot ($c\Lambda_c$ *versus* $1/\Lambda_c$, where c = normality and Λ_c = equivalent conductance) was linear. The data are presented in Table 4 in which the values of $\Lambda_{\text{calc.}}$ were obtained at each concentration by using the values of the apparent limiting equivalent conductance ($\Lambda'_0 = 38{\cdot}98$) and the " dissociation constant " ($K_c = 1{\cdot}876 \times 10^{-4}$) obtained by application of the least-squares method to the Ostwald plot.

TABLE 4.

10^5C	Λ_c	$\Lambda_{\text{calc.}}$	10^5C	Λ_c	$\Lambda_{\text{calc.}}$	10^5C	Λ_c	$\Lambda_{\text{calc.}}$
1·0420	36·98	36·84	2·9725	34·09	34·25	5·2348	31·63	31·73
1·4435	36·42	36·28	3·5129	33·78	33·56	5·9446	31·00	31·12
1·5218	36·27	36·20	3·5436	33·49	33·49	5·9952	31·04	31·07
1·9244	35·44	35·62	4·0911	33·05	32·92	6·7512	30·48	30·45
2·0634	35·54	35·43	4·3566	32·67	32·61	6·7541	30·35	30·45
2·4690	34·75	34·85	4·6014	32·56	32·41	7·5279	29·76	29·82
2·4910	34·98	34·82	5·2094	31·94	31·77	7·6414	29·77	29·73
2·9334	34·14	34·27						

These results involve two separate runs and are given in ascending order of concentration irrespective of the run. Although the Ostwald relation obviously applied very well to the results this must be fortuitous because on the one hand interionic effects are ignored whilst on the other the proposed ionisation would require a linear plot of $(c\Lambda_c)^2$ against $1/\Lambda_c$. Alternatively, if the magnesium chloride functions as a weak uni-univalent electrolyte (*viz.*, $\text{MgCl}_2 \rightleftharpoons \text{MgCl}^+ + \text{Cl}^-$) then the limiting equivalent conductance deduced from the Ostwald plot (using molar concentration of MgCl_2 instead of equivalent concentration) would be 77·96 which is impossibly high (cf. Λ_0 for hydrochloric acid = 82·46). Whilst our work was in progress Dawson and Golben[16] reported their results for the conductances of magnesium halides in alcohol at 20°. They showed that the variation of conductance with concentration was consistent with the magnesium chloride's behaving as a strong electrolyte in its first ionisation (*i.e.*, $\text{MgCl}_2 \longrightarrow \text{MgCl}^+ + \text{Cl}^-$) and as a weak electrolyte in the secondary ionisation (*i.e.*, $\text{MgCl}^+ \rightleftharpoons \text{Mg}^{2+} + \text{Cl}^-$). Moreover, they applied the appropriate corrections for interionic effects and used activities instead of concentrations although some assumptions were made. Thus it was assumed that the activity coefficients for the univalent ions MgX^+ and Cl^- were equal over the concentration

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[15] Sidgwick, " The Chemical Elements and Their Compounds," Oxford Univ. Press, 1950, Vol. I, p. xxix.

[16] Dawson and Golben, *J. Amer. Chem. Soc.*, 1952, **74**, 4134.

range studied and it is not clear how they deduced the limiting equivalent conductance for MgX^+. Moreover, they pointed out that the activity coefficient for magnesium ions was one of the two decisive factors in their computation but in order to deduce this coefficient from the Debye–Hückel equation it was necessary to estimate the " minimum distance of approach " for solvated magnesium ions (a_i) and this may well be an important source of error (*e.g.*, omission of the term involving (a_i) would incur an error of *ca.* 0·4% in $-\log f_i$ at a normality of 10^{-6} but about 4% at a normality of 10^{-4}). It is also noteworthy that these authors showed that a simple mass-law plot using concentrations instead of activities and ignoring interionic effects gave the required linear relation and a value of Λ_0 (41·08) close to that obtained (41·75) by the refined method. In addition, they obtained a value of 40·64 by using an Ostwald plot (assuming a uni-univalent ionisation with normality as concentration) and 39·57 from a plot of $(C\Lambda)^2$ against $1/\Lambda$ (*i.e.*, applications of mass law to simultaneous binary dissociation $MgCl_2 \rightleftharpoons Mg^{2+} + Cl^-$) although in the latter the linearity of the plot was less extensive than for the former. In view of these computations we feel that there is some ambiguity concerning the ionisation of magnesium chloride in ethanol and that there is a possibility of solvolysis occurring {*i.e.*, either (1) $MgCl_2 + EtOH \rightleftharpoons MgCl(OEt) + H^+ + Cl^-$, or (2*a*) $MgCl_2 \longrightarrow MgCl^+ + Cl^-$, or (2*b*) $MgCl^+ + EtOH \rightleftharpoons MgCl(OEt) + H^+ + Cl^-$}. It is clear that irrespective of the precise relation between conductance and concentration the value of the molar conductance extrapolated to infinite dilution would in these cases approximate to the limiting equivalent conductance for hydrochloric acid. We have already mentioned that the limiting molar conductance obtained by using the Ostwald plot on our results was close to the limiting equivalent conductance for hydrochloric acid. It is evident that the problem will only be resolved by carrying out some independent experiments such as the measurement of hydrogen-ion concentrations and the examination of solutions of magnesium chloride ethoxide. Before leaving magnesium chloride we report some results for the conductance at 20°. These experiments were carried out as a check on Dawson and Golben's data since their values for Λ at 20° seemed high compared with ours at 25°. Our results for 20° (Table 5) are considerably lower than Dawson and Golben's. It is possible that the discrepancy is due to our solutions' having a lower water content than theirs because the conductance of ethanolic magnesium chloride is very sensitive to traces of water, as shown in Table 6 (the concentration of magnesium chloride was $2·5 \times 10^{-4}$ equiv./l.). It is clear that even a low concentration of water causes a marked increase in conductance (cf. with the decrease for strong electrolytes) and emphasizes the difficulties in obtaining accurate results at low concentration in this solvent.

TABLE 5.

10^6C_M	4·859	7·210	10·044	14·252	18·637	23·317	28·592	36·639
Λ_M	68·69	66·22	63·685	61·55	58·73	56·27	54·03	51·80

TABLE 6.

Water (%)	0	0·083	0·207	0·285	0·317	0·411	0·518
$10^6\kappa$	5·376	5·857	6·133	6·323	6·401	6·531	6·665

Lanthanum Chloride.—The variation of conductance with concentration of lanthanum chloride showed typical weak electrolytic behaviour. A plot of $\Lambda_M C_M$ against $1/\Lambda_M$ took the form of two intersecting straight lines. In the most dilute region extrapolation of the line to infinite dilution gave $(\Lambda'_0)_1 = 70·57$ and $(K_c)_1 = 2·468 \times 10^{-5}$. The results in this region are given in Table 7 and represent three separate runs arranged in order of ascending concentration irrespective of the number of the run. The results for concentrations above $2·8 \times 10^{-5}$ mole/l. fall on another straight line which gave on extrapolation to infinite dilutions: $(\Lambda'_0)_2 = 50{\cdot}55$; $(K_c)_2 = 1{\cdot}293 \times 10^{-4}$. The data for this region are given in Table 8. The two values of $\Lambda_{\text{calc.}}$ in parentheses were calculated from the equation of the first straight line and although these two points are the nearest to that line it is evident that they are not on it.

TABLE 7.

10^6C_M	Λ_M	$\Lambda_{\text{calc.}}$	10^6C_M	Λ_M	$\Lambda_{\text{calc.}}$	10^6C_M	Λ_M	$\Lambda_{\text{calc.}}$
6·524	58·01	58·06	11·479	52·20	52·42	15·503	49·08	49·10
6·571	57·59	57·96	11·853	51·89	52·10	18·132	47·40	47·29
8·383	55·97	55·67	12·485	51·47	51·53	18·575	47·12	47·00
8·478	55·80	55·55	15·049	49·78	49·46	19·101	46·23	46·66
8·582	55·59	55·44	15·382	48·70	49·20	20·850	45·95	45·65
9·790	53·56	54·10						

TABLE 8.

10^5C_M	Λ_M	$\Lambda_{\text{calc.}}$	10^5C_M	Λ_M	$\Lambda_{\text{calc.}}$
2·8405	42·75	42·65 (41·91)	3·7721	40·97	40·90
2·8965	42·47	42·55 (41·68)	4·0161	40·25	40·46
2·9190	42·41	42·48	4·1250	40·33	40·30
3·2489	41·99	41·86	4·1836	40·24	40·21
3·3289	41·69	41·69	4·6239	39·90	39·48
3·4168	41·42	41·56	4·6965	39·20	39·43
3·6350	41·21	41·15	4·7129	39·32	39·37

Let us consider first the value of 70·57 for the limiting molecular conductance of lanthanum chloride. Obviously the possibility of complete ionisation (*viz.*, $LaCl_3 \longrightarrow La^{3+} + 3Cl^-$) may be ruled out because the chloride ions alone would contribute 72·9 (if Barak and Hartley's value[17] of 24·3 is accepted for the equivalent conductance of the chloride ion), making the conductance of the La^{3+} ion −2·6. It is very interesting that at such a low concentration the lanthanum chloride does not appear to behave as a ter-univalent electrolyte. In view of the difficulties encountered in interpreting the conductance data for magnesium chloride it is not profitable to theorise deeply on those for lanthanum chloride. However, the existence of two intersecting straight lines in the Ostwald plot is noteworthy and puzzling. Thus the straight line covering the higher concentration range gave an apparent limiting molecular conductance of 50·55 which suggests the presence of a weak uni-univalent electrolyte (cf. CsCl 48·01) and might correspond to the first stage of ionisation as follows: $LaCl_3 \rightleftharpoons LaCl_2^+ + Cl^-$. The second straight line, which gave a limiting molecular conductance of 70·57 (cf. $MgCl_2$ 77·96), presumably corresponds to the secondary ionisation: $LaCl_2^+ \rightleftharpoons LaCl^{2+} + Cl^-$.

It is clear that more work on the electrochemistry of ethanolic solutions is needed before the electrolytic behaviour of these salts can be understood. In particular the determination of transport numbers and activity coefficients would be invaluable.

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[17] Barak and Hartley, *Z. physikal. Chem.*, 1933, **165**, 273.