89. *The Extent of Dissociation of Salts in Water. Part VII.*
The Conductivity of Mixtures.

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The available data for the conductivities of binary mixtures of salt solutions in water have been examined in the light of the dissociation constants derived in previous parts of this series. The large departures from additivity found with certain mixtures are always in the direction, and of the approximate magnitude, to be expected on account of mass-action effects, and therefore confirm in a semi-quantitative way the previous work on the incomplete dissociation of aqueous salt solutions. It is shown, on the other hand, that the absence of such deviations cannot be interpreted as evidence of complete dissociation.

THE conductivity of mixtures of two electrolytes has been the subject of several recent studies (Smith and Gortner, *J. Physical Chem.*, 1933, **37**, 79; Van Rysselberghe and Nutting, *J. Amer. Chem. Soc.*, 1934, **56**, 1435; 1937, **59**, 333; Van Rysselberghe, Grinnell, and Carlson, *ibid.*, 1937, **59**, 336; O'Connor, *Nature*, 1937, **139**, 151), and more than one investigator has commented on effects that might be attributable to the incomplete dissociation of one or both of the electrolytes present. It seemed worth while to examine this aspect of the problem more closely, and in this paper the available data are used to test dissociation constants already derived for aqueous salt solutions, and to estimate the probable value of the method as a means of studying dissociation equilibria. Attention is confined to the type of system usually studied, in which the total electrolyte concentration is unaltered by mixing.

When two electrolyte solutions of the same equivalent concentration are mixed, the conductivity will in general differ from that calculated by the simple additive formula on account of two effects : changes in the mobilities of the ions, and, if dissociation is not complete, changes in the concentrations of the ions. The mobilities change because the rate of formation or dissipation of an ionic atmosphere is determined by the mobilities (and relative concentrations) of the ions present, so that the retardation suffered by a migrating ion on account of the " relaxation time " effect is diminished by the presence of an ion of higher mobility and increased by an ion of lower mobility. For two cations, or anions, present in approximately equal concentration, the greater absolute change will be that suffered by the ion of higher mobility, so that the net result of mixing will be a conductivity decrease which will be greater the greater the mobility difference. The quantitative theory of these mobility changes has been given by Onsager and Fuoss (*J. Physical Chem.*, 1932, **36**, 2689), but their general equation is valid only for very dilute solutions, in which the further changes attributable to incomplete dissociation effects will usually be extremely small. At higher concentrations information must be sought from the experimental data; these have been reviewed and supplemented by Van Rysselberghe and Nutting (*loc. cit.*), who quote seven mixtures of alkali-metal halides of 1-molal total concentration. In each of these mixtures dissociation can be taken as complete, and the whole conductivity change can therefore be attributed to the mobility changes. The effect at this high concentration may amount to as much as 1 % of the total conductivity, but is usually less than this. In accordance with theoretical predictions, the conductivity of the mixture is always less than that given by the mixture rule, and Van Rysselberghe and Nutting find, further, that there is a rough parallelism between the maximum conductivity decrease ($\Delta\Lambda$) and the difference between the conductivities of the pure salts (λ). Though such a relation can be only very approximate, we find that the equation $\Delta\Lambda = 0.021\lambda$ satisfies the results for these seven mixtures with an average deviation of 0.07, and a maximum deviation of 0.16 unit, and there is not much doubt that so long as the equation is not applied to mixtures containing the hydrogen ion or other ion of abnormal mobility, or to mixtures containing ions of different valency, it enables the conductivity decrease due to mobility changes to be estimated to within 0.2 unit.

Our object is now to consider mixtures in which dissociation may not be complete, and to ascertain whether the residual conductivity change, after allowance has been made for the mobility effect, is in accordance with the predictions of the incomplete dissociation theory. Van Rysselberghe and Nutting have studied five such mixtures : potassium nitrate and chloride; sodium nitrate and chloride; potassium and sodium nitrates; potassium nitrate and sodium chloride; and sodium nitrate and potassium chloride; and the requisite dissociation constants have been derived (Part I, *Trans. Faraday Soc.*, 1927, **23**, 351) : for potassium nitrate $K = 1.3$, for sodium nitrate $K = 3.8$, and the chlorides are completely dissociated. We shall expect that on mixing potassium nitrate and chloride in equimolecular amount there will occur a slight decrease in the extent of dissociation of the potassium nitrate, on account of the higher concentration of the common (potassium) ion in the added potassium chloride solution. A conductivity decrease slightly greater than would be expected from the very small mobility effect should therefore occur, and this is what is found; Van Rysselberghe and Nutting report a decrease of 0.3 unit, whilst the decrease predicted, on the basis of calculations outlined later, is 0.6 unit. The same arguments apply to the sodium nitrate–chloride mixture, but the effect should be smaller, as sodium nitrate is more fully dissociated than potassium nitrate; here the experimental decrease is 0.2 unit and the calculated decrease 0.2 unit. With potassium and sodium nitrates the adjustment on mixing is again small; the experimental decrease is 0.4, the calculated decrease 0.7.

With the remaining two mixtures much larger effects are to be anticipated owing to the absence of a common ion; moreover, they should be in opposite directions in the two cases, and therefore provide a good test of the theory of mass-action effects. On mixing potassium nitrate and sodium chloride solutions, adjustment to the new concentrations will involve the breaking up of a number of potassium nitrate ion-pairs with a consequent increase of conductivity; this will be only partly offset by the formation of sodium nitrate

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ion-pairs, since sodium nitrate is the stronger salt, so that the net effect will be a marked increase in conductivity. With sodium nitrate and potassium chloride, on the other hand, the change will be a decrease in conductivity, since the association of potassium with nitrate ions will more than counterbalance the dissociation of sodium nitrate ion-pairs. These predictions are in complete agreement with Van Rysselberghe and Nutting's results, as will be seen from the following table, in which the experimental and calculated values of the deviations from additivity are compared :

KNO₃ + NaCl.			NaNO₃ + KCl.		
Molality.	$\Delta\Lambda$, expt.	$\Delta\Lambda$, calc.	Molality.	$\Delta\Lambda$, expt.	$\Delta\Lambda$, calc.
0·9NaCl,0·1KNO₃	+0·5	+0·7	0·9KCl,0·1NaNO₃	−1·0	−1·3
0·75NaCl,0·25KNO₃	+1·2	+1·5	0·75KCl,0·25NaNO₃	−2·4	−2·6
0·5NaCl,0·5KNO₃	+1·8	+1·8	0·5KCl,0·5NaNO₃	−2·9	−3·5
0·25NaCl,0·75KNO₃	+1·2	+1·3	0·25KCl,0·75NaNO₃	−2·3	−2·5
0·1NaCl,0·9KNO₃	+0·6	+0·6	0·1KCl,0·9NaNO₃	−1·1	−1·2

The calculations at such high concentrations must necessarily involve a number of uncertainties. The most serious approximation made was to assume that the mean ionic activity coefficients remain constant throughout each series of mixtures, and the probable errors involved in this approximation are sufficient to cover the differences between $\Delta\Lambda$, expt. and $\Delta\Lambda$, calc. shown in the table. With this approximation the dissociation of potassium nitrate can be written $[K^{\cdot}][NO_3']/[KNO_3] = K_0/f_{\pm}^2 = K'$, where K' has a constant value for all mixtures of 1-molal total concentration, and similarly for sodium nitrate. K' is determined as follows. Combination of MacInnes and Longsworth's value (*Chem. Reviews*, 1932, **11**, 210) for the transport number of 1N-potassium chloride with Van Rysselberghe and Nutting's conductivities gives the following ionic conductivities at 1N : $l_{K^{\cdot}} = 54\cdot7$, $l_{Na^{\cdot}} = 28\cdot8$, $l_{Cl'} = 57\cdot4$; Shedlovsky's mobilities at zero concentration for chloride, potassium, and nitrate ions are respectively : 76·3, 73·5, 71·4, and for the nitrate ion at 1N the value 52·7 may accordingly be taken. Curves of ionic conductivity against the square root of the concentration can now be constructed, Shedlovsky's figures up to 0·1N being combined with the values just derived, and a comparison between these and Van Rysselberghe and Nutting's experimental conductivities for 1-molal potassium and sodium nitrates enables the degree of dissociation in these two solutions to be calculated in the usual way by successive approximations. The values obtained are : KNO₃, $\alpha = 0\cdot855$, $K' = 4\cdot8$; NaNO₃, $\alpha = 0\cdot926$, $K' = 11\cdot5$. Some check on these values is obtained by comparing them with the K_0 values previously determined at low ionic strengths and so calculating $f_{\pm}$. This procedure gives, for potassium nitrate, $f_{\pm} = 0\cdot58$, which may be compared with the experimental value for potassium chloride, $f_{\pm} = 0\cdot61$; similarly for sodium nitrate, $f_{\pm} = 0\cdot64$, the experimental value for sodium chloride being 0·65. The values are therefore reasonable ones. The actual ionic composition of the mixtures can now be obtained by successive approximations, and the conductivity calculated on this basis can be compared with that calculated from the mixture rule to give $\Delta\Lambda$, calc. The following figures illustrate the process for 0·5-molal potassium chloride plus 0·5-molal sodium nitrate. The density of the solution is 1·0456, and therefore 1 l. contains 0·4842 equiv. of each component. $K'_{KNO_3} = 4\cdot8$, $K'_{NaNO_3} = 11\cdot5$, and by successive approximations the composition of the solution is given by : [NaNO₃] = 0·0174, [KNO₃] = 0·0395, [Na⁺] = 0·4668, [K⁺] = 0·4447, [Cl'] = 0·4842, [NO₃'] = 0·4273 mol./l. The specific conductivity is therefore given by : $1000 \kappa_{calc.} = 0\cdot4668\ l_{Na^{\cdot}} + 0\cdot4447\ l_{K^{\cdot}} + 0\cdot4273\ l_{NO_3^{\cdot}} + 0\cdot4842\ l_{Cl'}$. The 1-molal sodium nitrate is 92·6% dissociated, and so the simple mixture rule would give : $1000 \kappa_{mixt.} = 0\cdot4842 \times 0\cdot926$ $(l_{Na^{\cdot}} + l_{NO_3^{\cdot}}) + 0\cdot4842\ (l_{K^{\cdot}} + l_{Cl'})$. Subtracting, $1000 \Delta\kappa = 0\cdot0176\ l_{Na^{\cdot}} - 0\cdot0395\ l_{K^{\cdot}} - 0\cdot0219$ $l_{NO_3^{\cdot}} = -2\cdot81$, and $\Delta\Lambda = -2\cdot81/0\cdot97 = -2\cdot9$. In addition, a conductivity decrease of approximately 0·6 unit is to be expected on account of the mobility effect, giving a total decrease of 3·5 units.

In a second paper, Van Rysselberghe, Grinnell, and Carlson (*loc. cit.*) report measurements on a number of mixtures containing bivalent ions. The majority of these are mixtures of an alkali metal halide with the corresponding halide of zinc or cadmium, and the authors are undoubtedly correct in attributing the large conductivity decreases to the formation of complex anions; the absence of the effect when the bivalent metal is magnesium is also what would be expected from the fact that magnesium chloride is completely dissociated (Righellato and Davies, *Trans. Faraday Soc.*, 1930, **26**, 592). With mixtures of cadmium sulphate and potassium sulphate, however, there is no necessity to

postulate the existence of complex ions to explain the conductivity decrease; potassium sulphate ($K = 0.15$) is a much stronger electrolyte than cadmium sulphate ($K = 0.0038$), and the decrease in conductivity will follow from the partial suppression of the dissociation of the cadmium sulphate, just as in the parallel cases of the chloride–nitrate mixtures already discussed.

Some further data suitable for the present discussion have been obtained by Smith and Gortner (*loc. cit.*), who investigated a large number of mixtures at 30.17°. For the binary combinations hydrochloric acid plus potassium chloride, and magnesium chloride plus sodium chloride, only small deviations from additivity were found, and this is in accordance with expectations, since the electrolytes are completely dissociated; for mixtures of copper and zinc sulphates the deviations were also small, which is explained (see below) by the fact that these salts, though weak, have identical dissociation constants (Part I, *loc. cit.*); these examples do not require further consideration. The remaining five combinations of salts showed large deviations, sometimes positive, sometimes negative, and in three cases changing sign with changes in the total concentration. The authors offered no explanation for "the apparently erratic behaviour of these conductivity measurements." These results will be considered in turn.

For sodium chloride–sodium sulphate mixtures the measured conductivities are 0.3 unit higher than the calculated (additive) values at total concentrations of 0.01 and 0.1N, but about 1.5 units lower than those calculated at 1.0 and 2.0N. The explanation is that two influences are at work, the one predominating in the more dilute solutions being a mobility effect that we have not previously had to consider. At 0.01N total concentration the ionic strength of the sodium chloride is 0.01, but that of the sodium sulphate is approximately 0.015. Here, therefore, as with every mixture of salts of different valency types, mixing will cause a large alteration of ionic strength, with a resulting change in the mobilities of all four ions. The largest of these changes will be that of the bivalent sulphate ion, and for this reason there will be a significant increase in the conductivity of the mixture. An approximate calculation based on Onsager's equation gives $\Delta\Lambda = + 0.4$ for the increase at 0.01N; at higher concentrations the value will be smaller. In addition to this mobility effect there is a small mass-action effect due to a depression of the dissociation of the $NaSO_4'$ ion; this amounts to only -0.06 unit at 0.01N, but at higher concentrations will be greater. At 0.01N, therefore, the net calculated effect is $\Delta\Lambda = + 0.3$, in agreement with the experimental result. The calculations have not been taken to higher concentrations, where the inevitable approximations would lead to uncertainties of the order of magnitude of the small changes observed, but clearly the effects described are sufficient to explain the result at 0.01N and to account for the change of sign observed at higher concentrations.

In mixtures of magnesium chloride and sodium sulphate large decreases of conductivity are observed, the deviation from the mixture rule amounting to as much as 10% of the total conductivity in some cases. This is due to the formation of magnesium sulphate ion-pairs. In the following table observed and calculated values for the conductivity decrease at a total concentration of 0.00465M are compared. The calculated values are low by about 0.6 unit, or 0.5% of the total conductivity, a discrepancy probably covered by the experimental error, and by the fact that no correction was made by Smith and Gortner for the volume change on mixing.

Ratio $MgCl_2/Na_2SO_4$	80 : 20	50 : 50	20 : 80
$\Delta\Lambda$, obs.	-5.0	-7.5	-4.6
$\Delta\Lambda$, calc.	-4.3	-6.8	-4.3

At 0.005M the calculations involve no undue approximations. The composition of each mixture is first calculated from the equations derived in previous papers (*loc. cit.*) : $\log [Na^\cdot][SO_4''] / [NaSO_4'] = \log 0.20 + 2\sqrt{I} - 1.3I$, and $\log [Mg^{\cdot\cdot}][SO_4''] / [MgSO_4] = \log 0.0061 + 4\sqrt{I} - 4I$; the conductivity is then calculated by means of ionic mobilities obtained from Smith and Gortner's data for the pure salt solutions, the cation transport number of potassium chloride being assumed to be the same at 30.17° as at 25°. No allowance has been made for the mobility effect, which at this concentration will be small.

With mixtures of magnesium chloride and magnesium sulphate a decrease in conductivity is again to be expected, since the dissociation of the magnesium sulphate will be depressed on account of the higher concentration of magnesium ions in the added solution. This is what is found, the observed and calculated changes at 0·005M being as follows :

Ratio MgCl$_2$/MgSO$_4$	80 : 20	50 : 50	20 : 80
ΔΛ, obs.	−1·7	−1·7	−1·1
ΔΛ, calc.	−0·9	−1·3	−0·8

The other two combinations studied by Smith and Gortner were mixtures of sodium chloride with the sulphates of zinc and copper. Calculations regarding these mixtures must involve the dissociation constants of zinc and copper chlorides, which are not yet known with certainty. Conductivity measurements at 0·5N indicate (Banks, Righellato, and Davies, *Trans. Faraday Soc.*, 1931, **27**, 621) that both are highly dissociated, and unpublished calculations based on some solubility measurements of Peterson and Meyers (*J. Amer. Chem. Soc.*, 1930, **52**, 4853) support this conclusion for copper chloride. On the other hand, Riley and Smith (*J.*, 1934, 1448) consider copper chloride to be one of the weakest of inorganic salts, and by a potentiometric method obtain for it the approximate dissociation constant $K = 0·0016$. The great discrepancy between these conclusions prompted a reconsideration of Riley and Smith's measurements, as a result of which it is believed that the effects observed by them were primarily due to the difference in ionic strength in the two sides of their concentration cell, and that this, together with the influence of various experimental difficulties, makes their estimate of the dissociation constant an unreliable one. In considering Smith and Gortner's results it has therefore been assumed that the dissociation of copper and zinc chlorides at 0·005N is complete, an approximation that is not likely to cause very serious errors. The main result of mixing copper or zinc sulphate with sodium chloride will then be an increase in conductivity due to the dilution of the metal sulphate and the resulting increase in its degree of dissociation, and this will be only slightly offset by the much smaller interaction between the sodium and sulphate ions. The calculated increase is the same for zinc as for copper sulphate, since the dissociation constants of the two are identical. The observed and calculated values at 0·01N concentration are as follows :

Ratio NaCl/XSO$_4$	80 : 20	50 : 50	20 : 80
ΔΛ, obs. (ZnSO$_4$)	+4·5	+5·1	+3·3
ΔΛ, obs. (CuSO$_4$)	+4·0	+5·6	+2·6
ΔΛ, calc.	+3·7	+5·3	+2·7

It may be noticed that with this type of mixture, unlike those previously considered, the magnitude of the measured change depends markedly upon which constituent is in excess ; and that this peculiarity also is faithfully reproduced by the calculated figures.

With these two salt mixtures Smith and Gortner found that at higher concentrations the conductivity increase diminishes, and at 2N is replaced by a decrease. This is most probably due to the formation of complex anions by the chloride ion and the bivalent metal (compare Van Rysselberghe, Grinnell, and Carlson's results for zinc iodide–potassium iodide mixtures). At 0·01N this will be quite negligible, and the conductivity change, as we have seen, is mainly due to the dissociation of the bivalent metal sulphate ; but it follows from the mass-action law that as the concentration is increased the latter effect becomes less, whereas the formation of complex anions becomes more and more, important. The net effect will therefore be a change in the sign of ΔΛ such as is actually observed.

To summarise this discussion : in every recorded case where the conductivity change on mixing two salt solutions cannot be explained by mobility changes, the results are in the direction and, within the limits imposed by the uncertainties of the calculations, are of the magnitude to be predicted on the basis of the known dissociation constants. The conductivity change is greatest when an incompletely dissociated electrolyte is mixed with a highly dissociated electrolyte not containing a common ion, and experiments with such mixtures may well prove valuable in detecting incomplete dissociation or in providing

approximate confirmation of dissociation constants found by other methods. In such measurements the change observed in the equivalent conductivity will of course depend on the concentration range employed, but the choice of concentration is not critical. For instance, the bivalent metal sulphates ($K = ca.$ 0·005) will exhibit the maximum conductivity increase at $\text{M} = 0\cdot01$, approximately, but the increase will still be 75% of the maximum at concentrations of 0·0025 or 0·04M.

Finally, there is a general case which calls for treatment. When equimolecular solutions of two electrolytes of the same valency type, and with identical, or almost identical, dissociation constants are mixed, there will be no measurable departure from the mixture rule, provided they possess an ion in common. This statement is easily justified by an extension of the isohydric principle. For both salts before mixing we can write $\alpha^2 m/(1 - \alpha) = K/f_{\pm}^2$, where $f_{\pm}$ is the mean ion activity coefficient. Now it has been shown in previous papers (compare Banks, Righellato, and Davies, *loc. cit.*) that the deviations observed amongst the stoicheiometric activity coefficients of salts of any given valency type can, in dilute solution, be attributed entirely to the mass-action effects, and that the mean ion activity coefficients at a given ionic concentration are identical. If K, in the equation just given, is also the same for the two salt solutions, these must before mixing have the same degree of dissociation. After the two salts have been mixed in the ratio $x : (1 - x)$, the equations for them become $x\alpha^2 m/x(1 - \alpha) = K/f_{\pm}^2$ and $(1 - x)\alpha^2 m/(1 - x)(1 - \alpha) = K/f_{\pm}^2$; clearly no change is demanded in the degree of dissociation or the ionic strength, and there will be no departure of the conductivity from additivity except in so far as there is a mobility effect. Two examples of this kind have been studied by O'Connor (*loc. cit.*), who measured the conductivities of very dilute solutions of the sulphates and dithionates of calcium and strontium. He found that the conductivities of all four salts, when plotted against the square root of the concentration, give slopes far greater than those derived from Onsager's equation; that calcium and strontium sulphate show identical conductivities throughout the range of concentrations examined, and that the same is true of the dithionates. He then investigated mixtures of the two sulphates, and also of the two dithionates, and found the conductivities of these to be additive, which result, he states, indicates complete dissociation of the salts. It will be seen, however, that if we attribute the deviations from Onsager's equation to incomplete dissociation we must assign identical dissociation constants to calcium and strontium sulphates, since their conductivity curves are identical throughout, and that therefore there can be no alteration in the degree of dissociation on mixing solutions of the same concentration. Furthermore, since the mobilities of calcium and strontium are found to be the same, there will be no mobility effect. The conductivities of all mixtures of the two salts will necessarily be additive therefore, and the fact can afford no evidence for complete dissociation. The same is true of the dithionates.

If the two salts, say CA and KS, have identical dissociation constants but no common ion, the mixed conductivity will clearly depend on the dissociation constants of the salts formed, CS and KA, and on the mobilities of the ions no longer free to conduct. If all four salts have identical dissociation constants, however, it is easy to show that the mixed conductivity is once more additive. Though this condition is not likely to be exactly fulfilled in any actual mixture, it will quite commonly be approximately fulfilled, and the conductivity changes to be looked for in such cases will be very small.

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