tures from 110 to −210°. The apparatus employed involves no stopcocks that are required to remain under vacuum more than momentarily.

At a given pressure the adsorption is relatively large at the lowest temperatures, decreases to a minimum at −200 to −175° depending on the pressure, then rises to a maximum in the neighborhood of −100°, and finally decreases again at higher temperatures. The fact that at 600 mm. the adsorption is independent of the temperature from −110 to 0° is taken as evidence that here a completely saturated single layer is formed.

It is shown that the values obtained are reproducible, and readily reversible with respect to changes of pressure, particularly at the lower temperatures. However, on cooling to about −190° a sample previously brought to equilibrium at 0°, the adsorption does not decrease to the value obtained isothermally at −190°, but reaches a new reversible equilibrium at which larger quantities of gas are adsorbed than at 0°.

At −191 and −183° the adsorption increases with pressure in a discontinuous manner, an observation whose explanation is somewhat obscure.

The major results of the work are interpreted on the hypothesis that at the lowest temperatures the adsorption is of the "secondary," or ordinary molecular type, while at higher temperatures a progressively larger fraction of the nickel surface is capable of holding the hydrogen by adsorption of the "primary" type, involving a marked activation of the gas.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

THE INCOMPATIBILITY BETWEEN ANY THEORY OF COMPLETE DISSOCIATION AND MIGRATION DATA

BY JAMES W. McBAIN AND PIERRE J. VAN RYSSELBERGE

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Inspection of the migration data for solutions of pure single electrolytes cannot, in general, give very conclusive evidence for or against the existence of any but the simplest ions in such solutions. In general, migration ratios are not constant throughout a range of concentrations, but it is a matter of rather arbitrary interpretation as to whether this is due to the ions being unequally affected by increase of concentration or whether the appearance of new (complex or intermediate) ions is assumed to account for the change in the gross transport number. It is only in the few rare instances, such as the well-known case of cadmium iodide where the change in transport number becomes so great that the sign of the migration is actually changed, that this method yields any conclusive proof of the existence or presence of complex ions.

It is evident that, if the migration number of a salt such as potassium chloride changes somewhat upon concentration, the change would most readily be ascribed to unequal change in the mobilities of the K^+ and Cl^- ions, whichever of the various explanations for such behavior might be adopted. The same would be true for the case of such a salt as sodium chloride, the constitution of whose solution might be expected to be very similar to that of potassium chloride. Moreover, a point which has escaped adequate appreciation, the same would be true of an examination of the movement of the common ion such as the chloride ion in a mixture of sodium and potassium chlorides. The results would be just as inconclusive as if either salt alone had been employed. The measurements of MacInnes[1] and Miss Dewey[2] are, therefore, necessarily inconclusive.

It is otherwise when the two salts are mixed in very unequal proportions, and the movement of the cation present in smaller quantity is directly measured. Here the excess of the salt present in larger proportion has the effect of largely increasing the relative concentration of any complex ions which can be formed from the lesser constituent, and, if so, the migration of the single dilute ion is greatly affected.

In our previous communication[3] we took advantage of this circumstance to test for the presence of complex ions in mixtures of such salts as magnesium and ammonium sulfates or magnesium and ammonium chlorides. For example, in a mixture of 0.05 M $MgSO_4$ with 0.95 M K_2SO_4 the magnesium actually migrates in the direction of the anode instead of going toward the cathode. This affords the most unequivocal proof possible that a negative charge appertains to most of the magnesium present. In other words, there is more transport of magnesium in negatively charged form (complex anion) than there is of ordinary magnesium ion itself. This negative movement of the material of the dilute ion (ignoring the movement of the concentrated cation or the common anion) serves, therefore, as a remarkable and trustworthy indicator for the presence of complex ions in considerable amounts in those mixtures.

Hence we must further conclude that in a solution of one of the salts

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[1] D. A. MacInnes, THIS JOURNAL, **47**, 1922 (1925); D. A. MacInnes, I. A. Cowperthwaite and T. Shedlovsky, *ibid.*, 51, 2671 (1929). In this connection it may be noted that MacInnes' formula appears to contain an assumption which renders it not strictly applicable to mixtures above a total concentration of 0.2 equivalent per liter, such as the higher concentrations studied by Schneider and Braley, *ibid.*, **45**, 1121 (1923). Moreover, this formula presupposes that potassium and sodium chlorides are dissociated to the same extent, an assumption which, for example, is rejected by Nernst [*Z. physik. Chem.*, **135**, 237 (1928); Orthmann, *Ergebnisse der exakten Naturwiss.*, **6**, 189 (1927)].

[2] J. Dewey, THIS JOURNAL, **47**, 1931 (1925).

[3] J. W. McBain and P. J. Van Rysselberge, *ibid.*, **50**, 3009 (1928). Through inadvertence, the total amount of current passed was omitted from Table I. The coulometer readings in grams of silver deposited were, in order of the experiments listed: 0.22205, 0.16945, 1.48005, not measured, 0.3853, 0.72065, 0.93975, 1.7300, 1.0212, 0.9476, 1.0318, 1.8467, 1.7912, 0.8277, 0.7202.

alone, if complex ions are present in these mixtures in such significant amounts that they overshadow the ordinary migration of the dilute ion, we have to recognize the presence of such complexes in the solutions of the corresponding single electrolytes of the same total concentration as the mixture. Indeed, as is evident from the principle of mass action, the concentration of the complexes will be even greater in absolute amount, but, of course, the proportion relative to the total concentration is correspondingly lowered and the considerations deduced in the first two paragraphs will apply. What such measurements of transport in mixed solutions achieve is, therefore, to prove the existence of important amounts of complex ions, and that only if the migration of the single dilute ion is actually measured. Evaluation of the exact amounts of the complexes present requires the combination of supplementary methods, such as determinations of e. m. f. of the single constituents and total freezing-point lowering, conductivity, etc.[4]

The measurements communicated in the previous paper showed that the formation of complex ions is general throughout all solutions containing polyvalent ions. This, of course, would render futile any attempt to apply hypotheses of complete dissociation to solutions containing such ions save in extreme dilution, where all theories agree in assuming complete dissociation. The complex ions are probably formed by combination of ordinary undissociated molecules with ions. Mere clustering of ions through the operation of electrostatic forces (Bjerrum's term "association") appeared inadequate as an explanation of the migration effects observed, because it should result in comparable amounts of complex cations and anions being formed and leave the migration essentially unaffected.[5] Hence the results point not only to the presence of complex ions but to ordinary undissociated molecules as well. Hydration of ions as ordinarily recognized is quite inadequate to explain away these results.

The present investigation shows that the negative migration of magnesium in a mixture of magnesium sulfate with the sulfate of one of the

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[4] We have attempted such a complete evaluation for solutions of cadmium iodide and cadmium sulfate, to be published elsewhere.

[5] An experiment was carried out on the movement of chlorine in the mixture 0.05 M $MgCl_2$ + 1.95 M $MgSO_4$. For a total current corresponding to 0.4631 g. of silver, the changes observed were: middle, +0.6%; cathode, 0.968 mg. Calculated by the usual approximation of the isohydric principle, the migration of the chlorine in the magnesium chloride is 0.95, which is about what would be expected for a highly concentrated solution of magnesium chloride. Its chief significance is to show that there is no anomalous movement toward the cathode, whereas in all the other mixtures that have common anion instead of common cation there is a large movement of the dilute ion toward the "wrong" electrode. Hence we arrive at the important result that the effects are not symmetrical; complex anions have to be assumed in large amount, but not complex cations. This does not accord with purely physical explanations.

least hydrated ions, rubidium, is just as pronounced as before. The measurements are also extended to solutions containing only univalent ions such as mixtures of sodium and potassium chlorides.

Experimental

The migration apparatus was that used in the previous work[3] except for the chloride experiments.[6] The current of average strength, 0.05 ampere, was measured in a silver coulometer. The electrodes were of platinum except in the case of the mixture of sulfates when a copper anode was used. The solution, whose weight and composition by volume were known, was introduced into the cleaned and weighed apparatus. After the experiment about 50 cc. was withdrawn from the middle portion; 11 cc. was locked in the tap and served as a second middle portion. The anode and cathode portions were then closed with rubber stoppers and weighed. The weights of the solution in the two portions were thus known. In most experiments samples were then taken from the anode, cathode, middle and original solutions, weighed in weighed pyrex beakers and analyzed. The experiments were carried out at room temperature.

Magnesium was estimated as phosphate after precipitation with ammonium phosphate. In the first recorded experiment the precipitates obtained by the phosphate method were much heavier than expected from the composition of the pyrophosphate and the concentration of the solution. It was found that these precipitates contained rubidium, their probable formula being $3P_2O_5 \cdot 4MgO \cdot 2Rb_2O$. In the second experiment carried out on the same mixture, the first precipitates were dissolved in hot hydrochloric acid and then reprecipitated. The usual ammonium magnesium phosphate was obtained.

Rubidium was precipitated and weighed as rubidium sodium cobalt nitrite. Analysis of the anode portions, however, gave irregular results, probably due to the presence of copper from the anode, so that the cathode results alone are recorded.

The transference numbers are calculated as in the previous paper on the approximate assumption that the current is distributed between the two constituents of the mixture in proportion to their respective concentrations and to the specific conductivities of the salts separately in concentrations equal to the total concentration of the mixture. The total current is indicated in the second column of the tables in terms of the silver deposited in the coulometers.

TABLE I

MIGRATION DATA IN MIXTURES OF RUBIDIUM AND MAGNESIUM SULFATES, SHOWING THAT EITHER MAGNESIUM OR RUBIDIUM IN THE PRESENCE OF EXCESS OF THE OTHER SULFATE MIGRATES TO THE ANODE

Concn. of mixture, moles per liter	Ag, g.	Change			Observed migration
		Middle, %	Cathode, mg.	Anode, mg.	
0.05 $MgSO_4$ + 0.95 Rb_2SO_4	0.3113		Mg negative		
0.05 $MgSO_4$ + 0.95 Rb_2SO_4	.3867	0.02		+0.00128	−1.87 −0.65
0.025 Rb_2SO_4 + 1.975 $MgSO_4$	(.9118)	2	−0.0082		− .19
0.025 Rb_2SO_4 + 1.975 $MgSO_4$	.619	0.1	− .0038		− .13
0.025 Rb_2SO_4 + 1.975 $MgSO_4$	(.9719)		Rb negative		

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[6] J. W. McBain and R. C. Bowden, *J. Chem. Soc.*, **123**, 2417 (1923).

Mixtures of Ammonium and Potassium Iodide

Potassium iodide containing 2% equivalent ammonium iodide was chosen because of the convenient analytical method for the determination of the (NH_4) constituent. The solution is neutralized, then treated with excess of neutral, filtered formaldehyde. The ammonium salt is quantitatively decomposed, forming hexamethylenetetramine with the formation of an equivalent amount of hydriodic acid, which is directly estimated by titration. The systematic error of 2% in this method does not affect the conclusions, since the results are all obtained by difference. However, at times the reaction appears more complicated, probably due to hydrolysis or reactions at the electrodes, for duplicated points were sometimes not reproducible. Even so, though irregular, the results show qualitatively that the transference of the ammonium constituent is decreased or almost suppressed by the presence of a large excess of iodine ions due to complexes containing NH_4^+ ion. Iodine was liberated at the anode and formed a solution which diffused in the whole anode portion and to a slight extent in the middle portion. Four samples were taken of each portion, cathode, middle and anode, and directly compared with the original solution. Table II contains the migration data for the mixtures of ammonium and potassium iodides of total concentration from 0.5 to 2.0 equivalents per liter.

TABLE II

MIGRATION DATA FOR MIXTURES OF POTASSIUM AND AMMONIUM IODIDES, SHOWING THAT MOVEMENT OF AMMONIUM IS LARGELY SUPPRESSED BY EXCESS OF POTASSIUM IODIDE[a]

Concn. of mixture, moles per liter	Ag, g.	Change in NH_4 content			Migration, n_{NH_4}
		Middle, %	Cathode, mg.	Anode, mg.	
0.1 NH_4I	0.1730	...	+14.46	− 7.96	+0.501
.1 NH_4I	.1330	−0.9	+10.42	−11.23	+ .531
.01 NH_4I + 0.49 KI	.4043	+ .4	.....	− 0.16	+ .11
.012 NH_4I + .588 KI	.3490	+ .7	+ 0.3	− .31	+ .26
.015 NH_4I + .735 KI	.5860	+ .1	+ .38	− .45	+ .21
.016 NH_4I + .784 KI	.5980	+ .2	+ .09	− .28	+ .14
.018 NH_4I + .882 KI	.3953	+ .66	.00	.00	.00[b]
.02 NH_4I + .98 KI	.3930	+ .3	.....	− .04	+ .03
.04 NH_4I + 1.96 KI	.5650	+ .5	.....	− .11	+ .06

[a] Other experiments by Mrs. M. E. McBain (née M. E. Laing) showed a decreased migration number of the same order of magnitude. 0.01 NH_4I + 0.49 KI gave a transport number of +0.4, and 0.02 NH_4I + 0.98 KI gave transport numbers of +0.17 and +0.13 (instead of 0.5). [b] The change in the middle portion is greater than the change in the anode and cathode portions.

Mixtures of Potassium and Sodium Chlorides

The experiments of others on mixtures of chlorides have already been referred to, but it is to be noted further that all their work has been carried out with a ratio of the two salts under 4 to 1 and a total concentration of chiefly 0.1 or 0.2 *N*, respectively. The ratios of sodium to potassium in this work are 49, 24 or 9, to 1, the total concentration being either 2.0 or 5.0 *N*. The data refer to the movement of the potassium.

The apparatus used in these experiments consisted of three U-tubes connected by ground joints. These tubes were provided with ground stoppers which allowed an easy removal of three middle portions; namely, a central middle portion, an anode middle portion and a cathode middle portion, the two latter being contained in the horizontal tubes connecting the U-tubes. Both anode and cathode were made of platinum.

Potassium was precipitated and weighed as sodium potassium cobalt nitrite. It was found that potassium may be precipitated from these solutions in many different forms, corresponding to different degrees of hydration of the complex nitrite. It was also found that the composition of the precipitate increases with the time of settling, probably on account of gradual hydration. In order to obtain directly comparable results, it is necessary to carry out all the analyses under strictly identical conditions: the total volumes of the samples before precipitation must be the same; the same amount of sodium cobalt nitrite must be added to each of them; the time of settling must be the same for all the samples and should be at least twelve hours; the washing and drying of the precipitates should be carried out under constant conditions. In spite of all these precautions, a difference of about 1.3% is sometimes found between samples which should give identical weights of precipitates. This seems to be due to a difference in composition corresponding to one-third of a molecule of water.

Table III

Migration Data for Mixtures of Potassium and Sodium Chlorides, Showing that the Migration Number of Potassium Chloride is Greatly Altered by Presence of Excess of Sodium Chloride

Concn. of mixture, moles per liter	Ratio, $\frac{\text{NaCl}}{\text{KCl}}$	Ag, g.	Change in K content			Migration,[a] n_K
			Middle, %	Cathode, mg.	Anode, mg.	
0.2 KCl + 1.8 NaCl	9	0.7121	<0.4	+14.39	−14.71	+0.407
				+15.90	−12.45	
				+ 5.68		
.08 KCl + 1.92 NaCl	24	.6963	<.2	+ 4.59	− 4.31	+ .352
				+ 5.35	− 4.34	
.04 KCl + 1.96 NaCl	49	.8922	...	+ 3.20	− 2.71	+ .352
				+ 3.73		
.5 KCl + 4.5 NaCl	9	1.3479	<.2	+31.13	−18.02	+ .287
				+30.98	−22.62	
				+17.65		
.2 KCl + 4.8 NaCl	24	1.6336	<.3	+19.85	− 8.52	+ .344
				+14.47		

[a] The values of the transport number of potassium given in Table III are those calculated from the observed data according to the isohydric principle; they should be compared with that for potassium chloride alone, namely, 0.5.

The changes in content of potassium at the electrodes are calculated by comparing the amounts of complex nitrite given by weighed samples with the amounts of complex given by weighed samples of the original solution.

Nernst's recent modification of the theory of strong electrolytes leads to unequal degrees of dissociation for potassium and sodium chlorides, sodium chloride being more dissociated than potassium chloride. Nernst's theory affords values for the degrees of dissociation, and it was found that these degrees of dissociation obey the law of mass action.

It is interesting to see if the low values found for the movement of potassium cannot be accounted for by the decrease of the degree of dissociation of potassium chloride, due to the presence of the large amount of sodium chloride. Table IV gives the values of the (Nernst) degrees of dissociation of potassium and sodium chlorides for the concentrations used in our experiments. In the calculations it has been assumed that the dissociation of sodium chloride is not affected by the presence of the small amount of potassium chloride. The modified values of the degree of dissociation of potassium chloride, combined with the fractions of the current carried by potassium chloride on the assumption that the two salts are independent of each other, allow us to predict the transport number of potassium. It can be seen in Table IV that the predicted and measured values agree quite well.

TABLE IV

COMPARISON OF OUR OBSERVED DATA WITH THOSE PREDICTED FROM THE NERNST FORM OF THE DISSOCIATION THEORY

Concn. of mixture, moles per liter	Degree of dissociation of KCl in pure solution	KCl in mixture	NaCl	Predicted migration	Measured migration
0.2 KCl + 1.8 NaCl	0.950	0.700	0.834	0.357	0.366
0.08 KCl + 1.92 NaCl	.998	.625	.825	.308	.294
0.04 KCl + 1.96 NaCl	1.000	.605	.827	.299	.281
0.5 KCl + 4.5 NaCl	0.890	.526	.704	.287	.265
0.2 KCl + 4.8 NaCl	.950	.525	.694	.268	.268

It remains an open question whether the decrease in the degree of dissociation of potassium chloride, due to the presence of the large excess of sodium chloride, is the real explanation for the low values found for the movement of potassium or whether the agreement between the predictions of Nernst's theory and our experimental values is the result of a mere coincidence, complex ion formation having been neglected.

Mixtures of Potassium and Sodium Nitrates

One experiment was carried out on the following mixture: 0.08 *N* KNO_3 + 1.92 *N* $NaNO_3$, and the same procedure as for the mixtures of potassium chlorides was followed. Table V gives the results of this experiment.

The degrees of dissociation of pure 0.08 *N* KNO_3 and of pure 1.92 *N*

TABLE V

MIGRATION DATA SHOWING THAT PRESENCE OF SODIUM NITRATE LOWERS THE MIGRATION NUMBER OF POTASSIUM IN POTASSIUM NITRATE

Concn. of mixture, moles per liter	Ratio, $\frac{NaNO_3}{KNO_3}$	Ag, g.	Middle, %	Cathode, mg.	Anode, mg.	Migration[a] n_K
				+7.08		
0.08 KNO_3 + 1.92 $NaNO_3$	24	0.9678	<0.7	+8.87	−5.26	+0.396
				+7.69	−6.27	

[a] This number is that calculated on the assumption that the amount of current carried by the potassium nitrate is that calculated on the isohydric principle; it should be compared with that for pure potassium nitrate, namely, 0.513.

$NaNO_3$, according to Nernst,[7] are 96.4 and 69.9%, respectively. In the mixture, the degree of dissociation of potassium nitrate should, therefore, be 0.562. The movement of potassium should then be 0.5 × (0.562/0.964) or 0.292, when, in the calculation of the amount of current carried by potassium nitrate, the salts are considered as independent. The corresponding experimental value is 0.270.

Discussion

The migration data in Tables I–V, like those in our previous communication, show that in the majority of cases the presence of a large excess of anion reduces, suppresses or even reverses the movement of the supposed cation of a dilute solution of a strong electrolyte. These results are evidently incompatible with any assumption of complete dissociation into simple, independent ions.

Whenever the movement is reversed, more of the metal studied is being carried toward the anode than is migrating as simple ion toward the cathode. This is definite proof of the existence of complex anions, and in relatively large amount. For the reasons adduced in the previous communication these complex anions must be regarded as being formed by chemical combination of the ions with undissociated molecules present in the solution. The proportion of complex ions should increase rapidly with the concentration of the simple common anion of the mixture and, therefore, should also depend upon the degree of dissociation of the salt added in excess. Thus the addition of an ammonium or an alkali metal sulfate should cause a much greater change in migration number of a given salt than addition of such salts as copper or cadmium sulfates, as is illustrated by the experimental data. Furthermore, divalent ions show a larger tendency to complex formation than do monovalent ions.

Taking first the experiments of Table I for mixtures of sulfates, we see that excess of rubidium sulfate drives magnesium to the anode, whilst excess of magnesium drives rubidium to the anode. This shows that both magnesium sulfate and rubidium sulfate contain complex anions. The

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[7] See Orthmann, *Ergebnisse der exakten Naturwiss.*, **6**, 193 (1927).

simplest assumption is that they are represented by the formulas $Mg(SO_4)_2^=$ and $Rb(SO_4)^-$, respectively, the latter being analogous to the HSO_4^- ion of sulfuric acid, which was usually held responsible for the formation of persulfuric acid in electrolysis. It is clear from these and all the other data so far available that divalent ions much more readily form complex ions than do monovalent ions.

Rubidium sulfate was chosen for study because the rubidium ion is recognized to be nearly anhydrous so that it is incapable of displacing large amounts of solution toward the anode by carrying along with it corresponding amounts of water toward the cathode. Hence the effect cannot be explained away as being due to hydration of the cation present in excess.

The numerical values of the migrations in these mixtures possess only semi-quantitative significance owing to the mode of calculation from the actual movements observed. Quantitative evaluation would require a knowledge of the formulas and actual mobilities of each of the ions present in the mixture, and the greater the formation of complex ions the more would such a result depart from the rule of simple mixtures on the principle of isohydrism. This may account for such an extreme number as −1.87, but the possibility of still higher complexes has to be borne in mind.

It may be worth noting here that C. W. Davies[8] has shown that the change in conductivity of magnesium sulfate with change in concentration is incompatible with the assumption of the complete dissociation of magnesium sulfate into single ions. Onsager's[9] conductivity equation, based on the hypothesis of 100% dissociation, fails completely for magnesium and cadmium sulfates, and Davies modified the equation by taking the incomplete dissociation into consideration.

Complex anions containing copper have been detected by Rieger[10] in solutions of the double sulfate $K_2Cu(SO_4)_2$. He found that here the migration of the copper ion was much smaller than in solutions of pure copper sulfate of the same concentration and that the transference number decreases when the concentration of the double sulfate increases. This is due presumably to the presence of complex anions, $Cu(SO_4)_2^=$, analogous to $Mg(SO_4)_2^=$.

Pfanhauser[11] found that in a saturated solution of nickel ammonium sulfate, the nickel moves entirely to the anode in the form of the complex ion $Ni(SO_4)_2^=$. Some incomplete data relating to a 0.1 molar solution of the double sulfate show that, even at this low concentration, the nickel is largely in the form of complex ions.

Tables II and III are especially interesting in that only uni-univalent

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[8] C. W. Davies, *Trans. Faraday Soc.*, **23**, 351 (1927).

[9] L. Onsager, *ibid.*, **23**, 341 (1927).

[10] E. Rieger, *Z. Elektrochem.*, **7**, 863, 871 (1901).

[11] W. Pfanhauser, *ibid.*, **7**, 698 (1901).

salts are concerned. Table III refers to potassium chloride, the typical strong electrolyte. The experiments show that the presence of a large excess of Cl^- can decrease the transference of potassium ion to about 55% of its value in a solution of potassium chloride alone. Similarly, excess of potassium iodide practically suppresses the movement of ammonium ion toward the cathode. Nernst's form of the dissociation theory would predict that the transference number of potassium chloride should tend toward a definite limit as the excess of sodium chloride present is increased. It is easily shown that the relative hydrations of sodium and chlorine ion as measured in such investigations as those of Washburn[12] and Miss Taylor and Sawyer[13] could not account for more than a very small fraction of the effects here observed.

Familiar examples of complex anions derived from uni-univalent salts are the $Ag(CN)_2^-$ of double cyanides and the mixtures[10] of potassium and silver iodides in which the silver likewise migrates toward the anode.

Measurements of activity coefficients in mixtures of electrolytes afford at least qualitative information as to the possibility of incomplete dissociation. Results obtained for hydrochloric acid in presence of alkali chlorides, such as those of Harned,[14] recalculated by Lewis and Randall,[15] show that in concentrated solutions "the activity coefficient of the hydrochloric acid depends upon the specific nature of the added chloride." This would indicate that a complete dissociation does not hold in these mixtures. The results obtained by Loomis, Essex and Meacham[16] with 0.1 molar mixtures of potassium chloride and hydrochloric acid are not exactly constant when the ratio of the concentrations of the two constituents varies. In general, if Lewis and Randall's ionic strength principle can be considered as closely verified for moderate concentrations, the deviations occurring at high concentrations can be accounted for by recognizing incomplete dissociation and, at least in the case of polyvalent salts, by taking into account the existence of complex ions.

Brönsted has published two experimental papers on electromotive force[17] which are most frequently quoted in support of the hypothesis of 100% dissociation. The first paper deals with cadmium electrodes dipping into two solutions containing two different concentrations of cadmium sulfate, the total concentration in each case, however, being made up to 2.0 molar by addition of magnesium sulfate. The electromotive forces were in substantial agreement with those calculated by using the gross concentration

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[12] E. W. Washburn, THIS JOURNAL, **31**, 322 (1909).

[13] M. Taylor and E. W. Sawyer, *J. Chem. Soc.*, 2095 (1929).

[14] H. S. Harned, THIS JOURNAL, **42**, 1808 (1920).

[15] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," The McGraw-Hill Book Co., New York, 1923, p. 367.

[16] N. E. Loomis, J. L. Essex and M. R. Meacham, THIS JOURNAL, **39**, 1133 (1917).

[17] J. N. Brönsted, *Medd. Vetenskapsakad. Nobelinst.*, **5**, No. 25, 1 (1919).

of cadmium sulfate in the usual Nernst formula. His very doubtfully valid procedure of correcting his results by means of the thermodynamically unpredictable cell where one of the cadmium electrodes dipped into a solution of magnesium sulfate containing no cadmium salt is only a minor objection. The chief point is that his results, according to the mass law, are equally in accord with the hypothesis of complete dissociation, or of partial dissociation, or of formation of any suggested proportion of complex ions, the last possibility being that which was shown in our previous communication to be true for these mixtures from the fact that the cadmium migrates toward the anode and is, therefore, not predominantly in the form of the positively charged cadmium ion.

Brönsted himself recognized this complete inconclusiveness or ambiguity and proceeded to make the experiments of his second paper[18] in which the chlorine electrode was dipped in two solutions of magnesium chloride of different concentration, the total concentration being made up to 4.0 *N* with magnesium sulfate in every case. Here Brönsted relied upon the fact that magnesium chloride is a ternary electrolyte and, therefore, would become completely dissociated at infinite dilution of magnesium chloride even in presence of the concentrated magnesium sulfate. To this standpoint no exception can be taken because more complicated modes of dissociation would merely obscure but not invalidate the final effect. However, Brönsted's numerical evaluation of his results is based upon the implicit assumption that a 0.0032 *N* magnesium chloride in 4.0 *N* solution of magnesium sulfate is 100% dissociated, and, if so, 0.1 *N* magnesium chloride is 99.3% dissociated. The assumption, however, begs the whole question, which is therefore seen to be one of opinion and not of experimental evidence. Migration data such as we adduce show, on the contrary, that magnesium, whether in chloride or sulfate, can be carried to the anode and, therefore, in such mixtures more of it bears a negative than a positive charge, a result fatal to any assumption of complete dissociation into simple ions.

Summary

1. In 0.05 *M* solutions of magnesium or rubidium sulfates, addition of a large proportion of the other sulfate causes the magnesium or rubidium to migrate away from the cathode toward the anode. In mixtures of ammonium iodide with excess of potassium iodide the movement of the ammonium may be practically suppressed. In mixtures of potassium chloride with excess of sodium chloride or of potassium nitrate with excess of sodium nitrate, the movement of the potassium may be considerably decreased.

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[18] J. N. Brönsted, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, **3**, No. 9, 14 (1920); *Trans. Faraday Soc.*, **44**, 727 (1928).

2. The general conclusion is that strong electrolytes form undissociated molecules and complex anions; they differ only in degree from such an extreme case as that of cadmium iodide. Electrolytes would all seem to fall within a triangle whose corners represent extreme dissociation, extremely weak electrolytes and complete formation of complex ions, respectively.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. VIII. USE OF METHYL RED, ERIO GLAUCINE AND ERIO GREEN INDICATORS IN THE REACTION BETWEEN CERIC AND FERROUS IONS

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Introduction

A number of applications of ceric sulfate in volumetric analysis have been described recently.[1] The use of various organic substances, for example, methyl red, methylene blue and methyl orange, as irreversible oxidation-reduction indicators in the titration of trivalent antimony with ceric sulfate was proposed by Rathsberg.[2] We have shown that methyl red may be used as an indicator in the titration of hydroquinone with ceric sulfate.[3]

We have found that methyl red is an excellent indicator in the titration of ferrous salt with ceric sulfate or *vice versa.* Upon titration of a ferrous solution with ceric sulfate, the ferrous salt is oxidized first; a slight excess of ceric sulfate oxidizes the methyl red to a substance that is brownish in concentrated solution and yellow in very dilute solution. The oxidation product is destroyed upon standing in contact with an excess of ceric sulfate.

When ceric sulfate is being titrated with ferrous sulfate solution, the latter is added rapidly until the color of the ceric ion has almost disappeared. Methyl red is added, and is oxidized to the yellowish product. Upon further addition of ferrous salt, there is a transition from yellow to violet when a slight excess of ferrous salt is present. If phosphoric acid be added, the color change agrees well with the potentiometric end-point. The color change of methyl red is much more rapid than that of diphenylamine under the same conditions. In agreement with Willard and Young[4]

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[1] A bibliography is given in the preceding paper of this series, THIS JOURNAL, **52**, 1443 (1930); reference to the older literature is given by Willard and Young, *ibid.*, **50**, 1322 (1928), and by Furman, *ibid.*, **50**, 755 (1928).

[2] Rathsberg, *Ber.*, **61**, 1664 (1928).

[3] Furman and Wallace, THIS JOURNAL, **52**, 1443 (1930).

[4] Willard and Young, THIS JOURNAL, **50**, 1336 (1928).