Forty to fifty points were plotted to establish the slope of each curve. In the range of concentrations given in the tables, there are no apparent irregularities. A change of concentration of telluric acid corresponding to 0.1 of a unit in scale divisions is equivalent to about 0.037 g. per 100 cc. of solution. Likewise for selenious acid, a change of concentration corresponding to 0.1 of a unit in scale divisions is equivalent to 0.029 g. of selenium dioxide per 100 cc. of solution. For potassium ferrocyanide, 0.1 of a unit in scale divisions is equivalent to 0.019 g. of the salt per 100 cc. of solution. As has been previously noted, two individuals can obtain readings whose mean values are within a range of ±0.025. It is therefore believed that a proper control of the method assures rapid analysis with reasonable precision for solutions of the materials mentioned.

The writers wish to acknowledge the kindness of Bausch and Lomb in providing one of their new instruments for this work.

Summary

1. The results in Table I correlate the scale readings of an immersion refractometer and the concentration of aqueous solutions of telluric acid thus making possible a rapid and reasonably accurate determination of the concentration of telluric acid solutions of unknown strength.
2. The results in Table II for selenious acid and those in Table III for potassium ferrocyanide also afford a rapid and accurate means of determining the concentration of these solutions.

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THE INCOMPATIBILITY BETWEEN ANY THEORY OF COMPLETE DISSOCIATION AND MIGRATION DATA FOR DIVALENT IONS

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In 1814 Porrett electrolyzed solutions of mixtures of "prussides" and observed that the potassium and the iron moved in opposite directions, the iron going toward the anode. Ever since, the ferrocyanide ion has been the model of a complex anion. The use of migration is, on account of its simplicity and unambiguity, one of the most powerful tools of the physical chemist in the cases where it can be applied. We wish to adduce it in deciding the rival claims of incomplete and complete dissociation in solutions containing divalent ions.

The object of this communication is to present experimental data which show that all divalent ions take part to a certain extent in such phenomena as those illustrated in extreme form by the prussides above, and familiar to us since Hittorf in the behavior of cadmium iodide. The new data show that all divalent ions, even the simplest, such as magnesium ion and sulfate ion, can form complex anions in such appreciable amount that the ordinary migration of the cation is completely submerged.

When to a 0.05 *M* solution containing a divalent ion sufficient quantity of anion is added, the divalent ion forms a complex anion, and we have the striking and highly significant result that the usual movement of the cation toward the cathode is suppressed or even reversed. Thus when an excess of sulfate ion is added to a 0.05 *M* solution of magnesium or cadmium sulfate, the magnesium or cadmium migrates toward the anode. Such facts constitute a disproof of the applicability of any hundred per cent. dissociation hypothesis to solutions containing divalent ions.

The almost non-conducting mercuric cyanide has never been included in the hundred per cent. hypothesis, and the same remark applies to the mercuric halides and cadmium iodide. The cadmium of cadmium iodide exhibits a migration to the cathode in dilute solution of +0.45 equivalents per faraday of current, but upon the addition of sufficient iodine ions, or indeed upon merely concentrating the cadmium iodide, the cadmium reverses the direction of its movement and now goes to the anode. Thus the migration of cadmium in a molar solution of cadmium iodide is −0.22. This has always been taken as incontrovertible evidence of the formation of complex ions such as CdI_3^-, whose movement carries more cadmium toward the anode than is simultaneously being carried by cadmium ions proper toward the cathode.[1] Since solutions of cadmium iodide are poor conductors, even in such dilutions as 0.1 *M*, and since their activity is correspondingly small, it is evident that much of the cadmium iodide is undissociated and that the undissociated molecules are capable of uniting with iodine ion to form complex anions.

The present communication shows that all of the divalent salts differ only in degree. Thus in a 0.05 *M* solution of magnesium chloride to which a sufficient concentration of chlorine ions has been added, the magnesium goes to the anode just like the cadmium and presumably for the same reason—certainly not because it is hundred per cent. dissociated into simple magnesium ions. The two ions, magnesium ion and sulfate ion, have been specially chosen for study because they are the simplest known divalent cation and anion, respectively, and if even they must be regarded as forming appreciable amounts of undissociated molecules and of complex anions, it is futile to extend any hypothesis of hundred per cent. dissociation to polyvalent ions. The result is not in conflict with the conception of interionic attraction but it is at once a disproof of the unwarranted assumption of hundred per cent. dissociation and a recognition of the molecules and ions really present.

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[1] See, for example, McBain. *Z. Elektrochem.*, **11**, 215–223 (1905); THIS JOURNAL, **34**, 1134–1137 (1912).

Experimental

The results here communicated consist of measurements of migration of cadmium, magnesium, lithium, potassium and calcium in 0.05 M solutions of one of their salts containing at least one divalent ion. In each case there is added a large amount, usually 0.95 M, of a sulfate or chloride. The movement of the element present to the extent of 0.05 M in the mixture is measured. The analysis gives the actual direction, whether toward anode or cathode, unequivocally. A calculation of the distribution of the current between the two salts from known conductivity data gives an approximate value for the migration number. The important fact is that the movement is usually toward the anode. The actual numerical value is of far less interest.

The apparatus was that used and described by McBain and Coleman.[2] It is made of borosilicate glass, has an internal diameter of about 2 cm. and a capacity of 190 cc. The anode is of copper and the cathode of platinum. A very large hollow tap in the middle serves to separate the anode and cathode compartments; the solution just on the anode side of the tap served as middle portion. The current was measured with a silver coulometer.

The first experiment was carried out on 0.05 M cadmium sulfate in the presence of 0.95 M magnesium sulfate. This particular mixture is of interest because Brönsted[3] showed that the e.m.f. of the cell

$$\text{Cd amalgam} \left| \begin{array}{cc} \text{CdSO}_4, & \text{MgSO}_4 \\ c_1 & 2 - c_1 \end{array} \right| \begin{array}{cc} \text{CdSO}_4, & \text{MgSO}_4 \\ c_2 & 2 - c_2 \end{array} \left| \text{Cd amalgam} \right.$$

could be calculated by the ordinary Nernst formula $E = k \ln c_1/c_2$, where c_1 and c_2 represent various dilute solutions of cadmium sulfate, the total concentration being 2 M. This was adduced as evidence in support of the 100% dissociation theory.[4]

In these experiments the solutions taken for analysis were not weighed (the only strictly correct method) but were measured by volume, making the assumption that the total volume in the cathode compartment was the same as that originally measured in. Cadmium deposited on the cathode was dissolved with a little sulfuric acid before the analysis, which was made by titration with $N/10$ ferrocyanide. There was less total cadmium in the cathode compartment after the experiment than before, showing that the net movement was toward the anode and that the cadmium was largely in other forms than positively charged cadmium ion. A previous experiment determining cadmium as cadmium sulfide, not quoted in the tables, gave a migration value of -0.34, that is, again toward the anode.

Having determined that the net movement toward the anode amounted to 1.22 mg. during the passage of 198.5 coulombs of current it is necessary to decide what fraction of the current has been carried by the cadmium sulfate in the mixture. We have done this as a first approximation by assuming that the amount of current carried by each constituent is proportional to its concentration multiplied by the specific conductivity which it exhibits when alone in 1.0 M solution. For the present mixture this fraction is $(19.8 \times 0.05)/[(19.8 \times 0.05) + (21.4 \times 0.95)] = 0.0464$. The final migration number is therefore $(96500 \times 0.00122)/(198.5 \times 0.0464 \times 56.2) = -0.227$, where 56.2 is the equivalent weight of cadmium.

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[2] McBain and Coleman, *Trans. Faraday Soc.*, **15**, Part I, 27–47 (1919).

[3] Brönsted, *Medd. Vetensksakad. Nobelinst.*, No. 25, 1–19 (1919).

[4] Ebert, "Jahrbuch Radioakt. Elektronik," **18**, 134–196 (1921).

Since the vital consideration was not the accurate determination of the migration but the demonstration of the movement of these supposed cations in the wrong direction, a direct comparison was made in most of the other experiments between the amounts of the element in question contained in a definite volume of the original compared with the same volume of solution drawn from the anode or cathode compartment after thorough mixing within that compartment. A diminution in the analytical value in the cathode compartment and a similar increase in the analytical value in the anode compartment meant movement away from the cathode toward the anode. Finally, experiments were carried out in which the solutions were all determined by weight and based upon the amount of water actually present before and after electrolysis. Kahlbaum's or Baker's purest chemicals were used throughout. The current was passed for between three and four hours.

The experimental data are collected in Table I. Magnesium was determined as pyrophosphate, potassium as cobaltinitrite, lithium as sulfate (after evaporation of the ammonium sulfate present in the mixture) and calcium as oxalate. Cadmium and copper are not precipitated in the phosphate method on account of the solubility of their phosphates in ammonia. The phosphate precipitates were allowed to settle for from four to twelve hours before filtration and the filter was put into the crucible when wet, before calcination. The cobaltinitrite method for potassium could be used in the presence of magnesium and copper sulfates and it was always carried out under strictly comparable conditions. The reagent was prepared by dissolving 220 g. of sodium nitrite in 440 cc. of water, then dissolving 113 g. of cobalt acetate in 300 cc. of water and 100 cc. of glacial acetic acid. The two solutions were mixed just before using

TABLE I

ANALYTICAL DATA FOR MIGRATION OF THE CATION OF A SALT CONTAINING DIVALENT ION IN 0.05 *M* SOLUTION IN THE PRESENCE OF A LARGE AMOUNT OF ADDED SULFATE OR CHLORIDE

Concn. of mixture, moles per liter	Change		
	Middle, %	Cathode, mg.	Anode, mg.
0.05 $CdSO_4$ + 0.95 $MgSO_4$	+0.6	−1.22 Cd	....
0.05 $CdSO_4$ + 0.95 $MgSO_4$	+0.1	−0.83 Cd	....
0.05 $MgSO_4$ + 0.95 $(NH_4)_2SO_4$	+0.5	−1.71 Mg	+1.88 Mg
0.05 $MgSO_4$ + 0.95 K_2SO_4[a]	<+0.1	−1.88 Mg	+1.68 Mg
0.05 $MgSO_4$ + 0.95 $CdSO_4$	....	...	Approx. +0.74 Mg
0.05 $MgSO_4$ + 0.95 $CuSO_4$	<+0.2	−0.86 Mg	(+0.23) Mg
0.05 $MgSO_4$ + 0.95 $CuSO_4$ by wt.	<+0.8	−0.55 Mg	+0.84 Mg
0.05 Li_2SO_4 + 0.95 $(NH_4)_2SO_4$	−0.2	+0.19 Li	....
0.05 K_2SO_4 + 0.95 $MgSO_4$	<−0.5	...	−18.6 K
0.05 K_2SO_4 + 1.95 $MgSO_4$	<−0.7	+4.72 K	−4.25 K
0.05 K_2SO_4 + 2.95 $MgSO_4$	+1.0	+7.25 K	−5.09 K
0.05 $MgCl_2$ + 1.9 NH_4Cl	−0.6	+0.677 Mg	−0.535 Mg
0.05 $MgCl_2$ + 3.9 NH_4Cl	−0.3	−0.76 Mg	+1.15 Mg
0.05 $MgCl_2$ + 3.9 NH_4Cl	+0.2	...	+0.46 Mg
0.05 $CaCl_2$ + 4NH_4Cl	+0.4	0.00 Ca	0.00 Ca

[a] Plus a few drops of H_2SO_4 to dissolve the K_2SO_4 hence the sign but not the numerical value of the migration number can be found.

the reagent and the nitrogen peroxide was removed by thorough stirring The reagent was used in large excess, the precipitate allowed to settle for over an hour before filtering on a weighed filter, washed with aqueous acetic acid, dried and weighed by difference.

Discussion

The results of the migration determinations are collected in Table II and the more they are studied the less compatible do they appear with any assumption of 100% dissociation into simple independent ions.

TABLE II

MIGRATION DATA TO SHOW THE PRESENCE OF MOLECULES AND COMPLEX IONS IN SOLUTIONS CONTAINING DIVALENT IONS

Concn. of mixture, moles per liter	Element	Obs.[a] migration, n	Remarks
0.05 $CdSO_4$ + 0.95 $MgSO_4$	Cd	−0.23	Cd to anode
0.05 $CdSO_4$ + 0.95 $MgSO_4$	Cd	− .20	Cd to anode
0.05 $MgSO_4$ + 0.95 $(NH_4)_2SO_4$	Mg	− .60	Mg to anode
0.05 $MgSO_4$ + 0.95 K_2SO_4[b]	Mg	Negative	Mg to anode
0.05 $MgSO_4$ + 0.95 $CdSO_4$	Mg	−0.25	Mg to anode
0.05 $MgSO_4$ + 0.95 $CuSO_4$	Mg	− .20	Mg to anode
0.05 $MgSO_4$ + 0.95 $CuSO_4$	Mg[c]	− .13	Mg to anode
0.05 Li_2SO_4 + 0.95 $(NH_4)_2SO_4$	Li	+ .06	Li to cathode
0.05 K_2SO_4 + 0.95 $MgSO_4$	K	+ .36	K to cathode
0.05 K_2SO_4 + 1.95 $MgSO_4$	K	+ .11	K to cathode
0.05 K_2SO_4 + 2.44 $MgSO_4$	K	+ .12	K to cathode
0.05 $MgCl_2$ + 1.9 NH_4Cl	Mg	+ .1	Mg to cathode
0.05 $MgCl_2$ + 3.9 NH_4Cl	Mg	− .36	Mg to anode
0.05 $MgCl_2$ + 3.9 NH_4Cl	Mg	− .38	Mg to anode
0.05 $CaCl_2$ + 4NH_4Cl	Ca	± .00	Ca neither

[a] 0.05 salts when alone give $CdSO_4$ +0.37; $MgSO_4$ +0.36; Li_2SO_4 +0.39; K_2SO_4 +0.49; $MgCl_2$ +0.39; $CaCl_2$ +0.40.

[b] Plus a few drops of H_2SO_4 to dissolve the K_2SO; 0.0017 g. moved to the anode.

[c] Complete measurements of all constituents results based upon absolute amount of water.

The result is to show that in the majority of cases more of the metal studied is being carried to the anode than is migrating as simple ion to the cathode. This proves the presence of complex anions in relatively large amount. The complex anions have been formed by adding to such a solution as 0.05 *M* $MgSO_4$ or 0.05 *M* $MgCl_2$ a large excess of sulfate ions or chlorine ions, respectively. Thereupon these ions have combined with the $MgSO_4$ or $MgCl_2$ to produce the complex ions, showing the presence of the undissociated molecules with which they are thus combining.

For the last five or six years the complete dissociation of strong electrolytes has been generally assumed, and a fundamental separation has thus been made between strong and weak electrolytes. The weak electrolytes consist of weak acids and bases and a few individual salts such as mercuric chloride and cyanide. Acids of every degree of strength up to hydrochloric acid are, however, still recognized. In concentrated solution of sulfuric acid it is customary to explain formation of persulfuric acid on electrolysis as due to combination of two of the incompletely dissociated ions, HSO_4^-. All hypotheses, including that of Arrhenius, agree that in sufficiently dilute solution the dissociation is complete. In the development of the Debye and Hückel theory[5] of interionic attraction, the degree of dissociation α was, for lack of definite evidence, assumed to be unity. The present results indicate that the real value of α is less than unity and that the numerical values of the coefficients must be altered accordingly. Indeed, a sound physical explanation of the different coefficients introduced in that theory for higher concentrations is lacking.

The recent widespread use of activity coefficients has induced many scientists to leave the problem of the true degree of dissociation of strong electrolytes completely unsolved, although activity coefficients are completely empirical and their numerical values depend upon arbitrary conventions. It must remain a primary aim to determine the actual molecular species present and their real concentrations.

Recently Nernst[6] has rightly argued that some strong electrolytes must be incompletely dissociated because their heats of dilution are of the opposite sign to that predicted from interionic attraction alone. He even suggests a degree of dissociation for strong electrolytes which agrees with the mass law. His hypothesis, however, is not yet completely developed. Fajans[7] deduces from optical measurements that neutral molecules and complex ions are present in solutions of strong electrolytes. Several writers[8] have adduced migration data to show that 100% dissociation, even if it occurs for some salts, cannot be general. For solutions of different salts with a common ion at any definite molality, the product of the conductivity (μ) and the transference number of the common ion (n) must be the same for all the salts if they are completely dissociated. In this way MacInnes and Cowperthwaite showed that even if alkali chlorides are assumed to be completely dissociated in 0.1 N solution, such nitrates as those of sodium, potassium and silver must be incompletely dissociated or at least their ions must be partly paired or associated in Bjerrum's sense. Tables III and IV show similar calculations for the sulfate and chlorine ions, using the data of Landolt-Börnstein.

Deficient conductivity might be explained in terms of "associated ions"

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[5] Debye and Hückel, *Physik. Z.*, **24**, 185, 305, 334 (1923); **25**, 97 (1924).

[6] Nernst, *Z. Elektrochem.*, **33**, 428 (1927); Naude, *ibid.*, —; Nernst and Orthmann, *Ergebnisse der exakten Naturwissenschaften*, **6**, 155 (1927).

[7] Fajans, *Trans. Faraday Soc.*, **23**, 357 (1927).

[8] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 321; MacInnes and Cowperthwaite, *Trans. Faraday Soc.*, **23**, 400–404 (1927).

TABLE III

"100%" MOBILITIES $n\text{Cl}^-$

Salt	In 0.01 *M*	In 0.05 *M*	Salt	In 0.01 *M*	In 0.05 *M*
NaCl	60.0	56.0	$BaCl_2$	58.5	52.6
KCl	60.4	56.6	$MgCl_2$	57.5	51.6
LiCl	61.0	57.4	$CaCl_2$	57.1	48.4
$(NH_4)Cl$	60.7	56.3	$SrCl_2$	57.9	52.2
HCl	61.4	57.9	$CdCl_2$	41.6	28.5

TABLE IV

"100%" MOBILITIES, $n\text{SO}_4^{--}$

Salt	In 0.01 *M*	In 0.05 *M*	Salt	In 0.01 *M*	In 0.05 *M*
Na_2SO_4	55.8	48.4	$MgSO_4$	41.6	31.2
K_2SO_4	56.0	48.4	$ZnSO_4$	42.8	28.2
Li_2SO_4	..	42.2	$CuSO_4$	..	27.4
H_2SO_4	51.25	40.0	$CdSO_4$	37.2	26.4

if one desired to deny the existence of undissociated molecules, but this does not appear to be adequate to explain the new migration data of Tables I and II, where the outstanding effect is the ready movement toward the wrong electrode. A new kind of "association" of ions in clusters containing one kind of ion in excess might be assumed, but this new assumption is of little value until, firstly, it is proved to be a legitimate possibility; secondly, the further consequences have been faced; and, thirdly, it has been shown capable of explaining the migration data.

The first thing is to demonstrate that it does not contradict existing knowledge of solutions and the laws of electricity. In other words, it has to be shown that such clusters of ions can be formed stably in relatively large amount and remain in stable units when placed in an electric field in which the constituent ions will travel together although pulled in opposite directions. Further, there is no reason apparent for explaining why clusters merely of three ions should occur. If ternary clusters can form in large amount, then larger ones would seem to be possible up to indefinite sizes, up through colloidal dimensions to complete crystals, in solution far from saturation. Indeed the conception is difficult to harmonize with solubility data (compare, for example, $ZnSO_4$, $MgSO_4$ and $BaSO_4$).

The second thing is to realize the consequences of denying undissociated molecules and true complex anions in favor of clusters of ions. It is obvious that since by hypothesis such clusters are largely broken down into independent ions by thermal vibration, they are less stable in an electric field where the components are pulled in opposite directions. The strain must increase with the slope of potential. Hence we must deduce that the transference numbers should change with the voltage applied—a possibility, although not yet recorded. If the voltage were high enough this conception would therefore seem to predict a reversal of direction of the movements observed, and a return to migration data such as are characteristic of ordinary dilute solutions A similar influence of voltage would be expected in conductivity measurements, which might afford an easier method of testing the existence of such an effect.

A third consequence of the conception, which shows that the occurrence or non-occurrence of ionic "association" is in general irrelevant to our main inquiry, is the fact that it predicts almost equal numbers of positively and negatively charged clusters. This is because the same Coulomb's Law and the same ionic radii or distances are used alike in calculating the electrostatic forces acting in a cluster of two positive with one negative as in a cluster of two negative with one positive ion.[9] The attractive forces and the repulsive forces are substantially identical in the two cases, thus giving cationic and anionic clusters in equal numbers—whose effects on migration would almost cancel each other, whereas the proportion of anionic clusters would have to be overwhelmingly greater than that of the cationic clusters if the observed data are to be accounted for.

Professors Parks, Bray and Latimer in conversation have suggested to us the possibility that the assumption of excessive hydration of all the cations might explain our results, and save recourse to recognizing complex anions.[10] Usually hydration has an almost negligible effect, but here its effect is multiplied about 19-fold, since 0.05 M salt is studied in presence of a 19-fold higher concentration of the other salt. For this purpose it is necessary to assume that each cation is much more hydrated than the sulfate or chloride ion; that is, that the cations actually take along with them large quantities of water during migration. Suppose, for example, a divalent cation carries ten molecules of bound water more than the anion. During migration this water is carried to the cathode, thus displacing the whole solution bodily toward the anode. Hence for each faraday of current carried by the divalent cation, there would be an apparent movement toward the anode of the amount of each constituent contained in one-half of 10 moles or 90 g. of water. For the 0.05 M salt (divalent) this would be $2 \times 0.09 \times 0.05$ equivalents = only 0.009 equivalents change

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[9] This becomes evident for ions whose charges are central or symmetrical when one draws three circles in contact, with centers lying on a straight line, the two outer circles representing ions of charge opposite to that of the ion between them. The opposite ions need not be of the same size.

[10] Such large movement would be readily tested by experiments such as those of Nernst, Washburn and others. One of us (J. W. M.) carried out such measurements at the University of Toronto in 1904 with cadmium sulfate, using acetone as reference substance [see McBain, *Z. Elektrochem.*, **11**, 216 (1905), also *Proc. Wash. Acad. Sci.*, **9**, 7 (1905)], where the general formulation is discussed. Unfortunately the result was to show that the sulfate ion is *more* hydrated than cadmium ion, an experimental finding in the opposite direction from that required for the hydration explanation. If necessary one can arbitrarily discount this by saying that acetone cannot have been a suitable reference substance but must have combined with the cadmium ion, and that the uncombined acetone may have been moving in the opposite direction, of course to a less extent.

in apparent migration. But this is reduced in proportion to the migration number of the 0.95 molar cation, and then increased by the approximate 19-fold, because the whole movement of the 0.05 *M* cation is referred to the current carried by the 0.05 *M* salt. For 0.95 *M* $CuSO_4$ the migration number of the copper is 0.30. Hence the approximate effect on 0.05 *M* $MgSO_4$ in its presence would be $19 \times 0.30 \times 0.009 = 0.05$. This is wholly inadequate to explain our results, where a ten times larger correction would be required to explain them away. This cannot be done, for we have already assigned nearly one-fifth of the total water to the excess hydration of copper ion (and similarly for Mg^{++}, Cd^{++}, Cu^{++}; K^+ and NH_4^+) above that of SO_4^{--} or Cl^-. Hence even if *all* the water in the aqueous solution were combined with the cation, the effect on the migration observed would be only half that required to explain away our results.

It is less forced to admit that we are here dealing with complex ions, particularly when it is universally admitted that numerous complex ions such as the silver cyanide ion $Ag(CN)_2^-$, are to be taken for granted.

Lastly, if undissociated molecules and complex ions are present in such large amounts under the conditions obtaining in our experiments, it must be admitted that they cannot be considered as negligible in much more dilute solutions. A similar conclusion follows from an inspection of graphs of migration numbers of divalent cations plotted against the logarithm of the concentration. This will be illustrated in a further communication dealing with cadmium salts.

Summary

It is shown that when a sufficient excess of chlorine ions or sulfate ions is added to 0.05 *M* solutions of salts containing a divalent ion, the migration of the anion is suppressed or often reversed, showing that the sulfate or chlorine ions have combined with undissociated molecules to form complex ions. Such migration is incompatible with the assumption that salts containing polyvalent ions are completely dissociated, except in extreme dilution.

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