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THE ACTIVITY OF THE IONS AND THE DEGREE OF DISSOCIATION OF STRONG ELECTROLYTES.

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Some four years ago through a study of all the available data concerning the conductance, the transference number, and the activity of the constituents, of dilute salt solutions, I was led to somewhat unorthodox views regarding the degree of dissociation of electrolytes. Since then, some additional data have become available, all of a corroborative character. There is still a dearth of suitable experimental measurements; but, since those which are now at hand are sufficient to demonstrate conclusively the correctness of some of the previous conclusions, and since it has become necessary to use the results in the free energy calculations which are now being published, it seems advisable to put forth in a preliminary form a résumé of some of the facts which have already been ascertained, together with a brief discussion of their probable theoretical significance.

In this paper attention will be called especially to the properties of strong uni-univalent electrolytes, not because these possess any greater interest than the electrolytes of higher type, but because this is the only case in which existing data enable us to draw even qualitative conclusions unambiguously. Salts of a mixed type offer an especially difficult problem, owing to the possible existence, in considerable amount, of intermediate ions.

According to the ionic theory, the conductance of an electrolyte depends upon two factors only, the concentration of the ions and their mobility. Kohlrausch assumed that the mobility of an ion is at a given temperature independent of the concentration, and therefore that if Λ is the equivalent conductance at a given concentration, and Λ_0 is the equivalent conductance at infinit dilution, $\Lambda/\Lambda_0 = \alpha$, the degree of dissociation. If then c is the total concentration of a salt such as KCl, αc is the concentration of either K^+ or Cl^-, and $(1 - \alpha)c$ is the concentration of the undissociated salt. If this method actually gives the concentrations in question, then we should expect that the application of the mass law would give an approximately constant value of the ratio $(c\alpha)^2/c(1 - \alpha)$. As a matter of fact, it is well known that in the case of the so called strong electrolytes this ratio varies enormously with the concentration. We must therefore assume either that the method of Kohlrausch does not give a true measure of the actual concentrations, or that the ions or undissociated substances, or both, form very far from perfect solutions; in other words, that for one or more of the substances the activity is by no means proportional to the concentration. If then we assume that the law of Kohlrausch is correct, we must inquire whether it is the ions or the undissociated substance or both to which we must attribute the abnormality.

The Activity of the Ions and of the Un-ionized Salt.

Let us first assume that the principle of Kohlrausch is correct and that the concentration of ion and un-ionized salt can be calculated exactly from the conductivities. It is then possible merely from a thermodynamic discussion of experimental data to determin how the activity of each constituent of an electrolyte varies with its concentration. It has been shown elsewhere[1] that (as a first approximation) the activity of the ions (at least in solutions of typical uni-univalent salts) is proportional to their concentration, but that the activity of the un-ionized part increases much more rapidly than its concentration, as the salt concentration increases. This is shown by the fact that in all cases which do not directly involve the un-ionized salt, approximately correct results are obtained by the application of the simple laws of the perfect solution. Thus we have the principle of the solubility product, the Nernst equation for the electromotive force of a concentration cell (which is not even approximately valid when applied to the un-ionized part), and the work of Rothmund[2] in which he studied the equilibrium between the ions of picric acid in water and the undissociated acid in another solvent. So also the various methods which have been used for the determination

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[1] Lewis, "Outlines of a New System of Thermodynamic Chemistry," *Proc. Am. Acad.*, **43**, 259 (1907); *Z. physik. Chem.*, 61, 129 (1907). Lewis, "The Use and Abuse of the Ionic Theory," *Ibid.*, **70**, 212 (1909). From another point of view James Walker, *Chem. News*, **104**, 104 (1911), has recently been led to similar conclusions.

[2] Rothmund, *Z. physik. Chem.*, **46**, 827 (1904).

of the degree of dissociation of water would not yield concordant results if the ions were not approximately normal in their behavior.

When, however, we examin the problem more carefully, we find that even the behavior of the ions is not strictly normal, and that the activity actually increases somewhat less rapidly than the concentration. Thus the ions and the un-ionized salt deviate from the perfect solution in opposit directions. This view, which was first put forward in the early paper already cited, has since been corroborated in numerous instances, and no univalent ion has been studied for which the ratio a/c of activity to concentration is not somewhat less in tenth molal solution than at infinit dilution. Thus Lewis and von Ende[1] found the potential of the thalium electrode to be 0.0018 volts higher in 0.1 M solution than was calculated from the potential in 0.01 M solution, thus showing a diminution of about 7% in a/c between 0.01 M and 0.1 M. Similar results have been obtained by Mr. Faragher, in an investigation about to be published, on the potential of the iodine electrode. Another case of different character which shows the same effect has been pointed out by Bray and MacKay.[2]

Another illustration is furnished by a study of the equilibrium in the reaction $H^+ + NO_3^- + 2NO + H_2O = 3HNO_2$. Assuming that the weak electrolyte HNO_2 is normal, a lack of constancy of a/c for H^+ and NO_3^- should lead to a change in the equilibrium constant with the concentration in the direction actually observed by Saposhnikov[3] and by Lewis and Edgar.[4] More extensive data for the calculation of a/c at different concentrations is furnished by the papers of Bray[5] on the influence of one salt upon the solubility of another, and of Tolman and Ferguson[6] on the free energy of dilution of hydrochloric acid, as well as from a few exact measurements of the freezing-point lowering of dilute aqueous solutions, which will presently be discussed.

Let us consider first the solubility measurements. If a solid salt such as thallous chloride is in equilibrium with its ions, then if a_1 is the activity of one ion and a_2 that of the other, it is thermodynamically necessary that the product a_1a_2 should always remain constant at a given temperature. Now it is shown in the paper of Bray that the product of the concentrations c_1c_2 does not remain constant, but increases with increasing ion concentration in every case studied. This was shown to be true for thallous chloride and potassium perchlorate in the presence of other uni-univalent salts. This shows that for at least one of the ions the ratio

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[1] Lewis and von Ende, THIS JOURNAL, 32, 737 (1910).

[2] Bray and MacKay, *Ibid.*, 32, 930 (1910).

[3] Saposhnikov, *J. Russ. Phys. Chem. Soc.*, 32, 375 (1900).

[4] Lewis and Edgar, THIS JOURNAL, 33, 292 (1911).

[5] Bray, *Ibid.*, 33 1673 (1911).

[6] Tolman and Ferguson, *Ibid.*, 34, 232 (1912).

a/c falls off with increasing ion concentration. The product a_1a_2 is constant, and therefore between any two solutions it is evident that $c_1c_2/c'_1c'_2$ is equal to $(a'_1/c'_1 \times a'_2/c'_2) \div (a_1/c_1 \times a_2/c_2)$. Now introducing the assumption that both ions behave alike, we have $c_1c_2/c'_1c'_2 = (a'_1/c'_1)^2 \div (a_1/c_1)^2 = (a'_2/c'_2)^2 \div (a_2/c_2)^2$. Thus, from the change in the solubility product we can find the way in which the ratio a/c varies for each ion. The following table contains a summary of some of the results thus obtained and includes a number of data obtained from an early paper of Noyes.[1] In each case $c'_1c'_2$ is taken as the extrapolated value for infinit dilution of the solubility product. This extrapolation is performed by plotting the solubility product against the total ion concentration, which seems to be the predominant factor which causes the variation. This extrapolation in the case of thallous chloride is entirely reliable. In the case of the much more soluble salt, potassium perchlorate, it is very rough and is only made to render the results for this salt comparable with those for thallous chloride.

TABLE I.

		Per cent diminution in a/c at			
Solid salt.	Added salt.	0.02 *M*.	0.05 *M*.	0.1 *M*.	0.2 *M*.
$TlCl$	KCl	4	8	13	18
$TlCl$	$NaCl$	4	8	13	19
$TlCl$	NH_4Cl	4	8	..	20
$TlCl$	HCl	4	7	9	12
$TlCl$	$TlNO_3$	4	8	13	..
$TlCl$	KNO_3	4	7	10	..
$KClO_4$	KCl	.	.	9	12

The last four columns of this table show the percentage diminution in the ratio a/c for the ions, between zero salt concentration and the concentration given at the head of each column. The results are very striking and show the generality of the lowering of the ratio of a/c with increasing salt or ion concentration. In the case of hydrochloric acid the concentrations employed in the calculation are not strictly speaking those derived from the conductivity; but, in accordance with the view which has now become very general, the degree of dissociation is assumed to be the same as that of potassium chloride at each concentration.

We may next consider the results of Tolman and Ferguson on the free energy of dilution of hydrochloric acid. Their results give immediately the variation of a/c assuming, again, that the two ions behave alike. Once more calculating the concentration on the assumption of a dissociation equal to that of potassium chloride, we find for the percentage diminution of a/c from the value at infinit dilution, 3% at 0.02 *M* and 6% at 0.1 *M*.

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[1] Noyes, *Z. physik. Chem.*, 9, 603 (1892).

Any other data, from which we may calculate the free energy change accompanying the dilution of a salt, would furnish material for similar calculations. A search through the literature relating to the freezing points of dilute aqueous solutions showed that several investigations were of sufficient accuracy to warrant their use in this connection.

The thermodynamic use of freezing-point data is not as simple as it is usually assumed to be. Let us consider the problem of determining the change in free energy when a mol of salt is carried from a large amount of a solution of one concentration into a solution of another concentration. We will choose for convenience the two concentrations, 0.1 *M* and 0.02 *M*. We must in the first place construct from the experimental data a smooth curve relating freezing-point lowering and concentration. This may best be done by plotting θ/c, the ratio of freezing-point lowering to concentration, against the concentration. The best smooth curve being drawn, the value of θ at any concentration can be taken from this curve. We next plot several values of θ as abscissas against the corresponding values of $1/c$ as ordinates, and measure the area under this curve between the ordinates corresponding to 0.1 *M* and 0.02 *M*. This gives the definit integral between these two limits, $\int(1/c)d\theta$. The reason for this particular construction may readily be seen. If $\overline{F}_1$ is the partial molal free energy of the salt in the solution, and N_1 its mol fraction, and if $\overline{F}_2$ is the partial molal free energy of the water whose mol fraction is N_2, then by the law of Duhem, any change in composition at constant temperature changes the free energies according to the equation

$$N_1 d\overline{F}_1 + N_2 d\overline{F}_2 = 0 \quad \text{or} \quad d\overline{F}_1 = -N_2/N_1\, d\overline{F}_2.$$

Now the integration of this equation, which is ordinarily somewhat complicated, can be simplified in this case (owing to the fact that the solutions are dilute) by making certain approximations, none of which lead to appreciable numerical error. Thus we may take each partial free energy at the freezing point equal to that at the same concentration at the centigrade zero. Moreover, we may call N_2 equal to unity. We may replace N_1 by $c_1/55.5$ where the denominator is the number of mols in 1000 grams of water. We have then[1]

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[1] The relation between the partial free energy of the water and the lowering of the freezing point may be obtained as follows: Let $\overline{F}_2$ for convenience be referred to the free energy of liquid water as zero, but $\overline{F}_2$ at the freezing point is equal to the free energy of the ice. We have then to consider the reaction $H_2O(l) = H_2O(s)$ and since $\overline{F}_2$ is the free energy change in this reaction, then $\overline{F}_2 - \Delta H = T\, d\overline{F}_2/dT$. Now at 0° C., $\overline{F}_2$ is zero, and we may write, $d\overline{F}_2 = -(\Delta H/T)\, dT$ and for small values of θ $\overline{F}_2 = (\Delta H/T)\theta$. The heat of fusion of one mol of ice, namely 1438 cal., is equal to $-\Delta H$, and writing, $T = 273.1$, $\overline{F}_2 = -5.27\,\theta$.

The notation here employed, and the use of such free energy equations, will be explained more fully in a paper to appear in the next number of THIS JOURNAL.

$$d\overline{F}_1 = -(55.5/c_1)\, d\overline{F}_2 = (55.5 \times 5.27/c_1)\, d\theta.$$

Hence

$$\int d\overline{F}_1 = 292.2 \int 1/c\, d\theta.$$

Now $\int d\overline{F}_1$ between the limits of integration is equal to RT ln a/a', where a and a' represent the activity of the salt at the two concentrations. If, instead of the activity of the salt itself, we wish to consider that of the ions, then we may replace the activity of the salt by the product of the activities of the ions, which is proportional to it. Assuming, as before, that the two ions behave alike, then if the a's now refer to the ions, we have

$$\mathrm{RT} \ln a_1/a_1' = (292.2/2) \int 1/c_1\, d\theta.$$

This method has been applied to the salts given in the following table. The last column shows the diminution in the ratio a/c between 0.02 and 0.1 M.

TABLE II.

Salt.	Observer.	$\int_{0.02\,M}^{0.1\,M} d\overline{F}_1$ Cal.	Ratio of ion activity $a(0.1M)$: $a(0.02\,M)$.	Ratio of ion concentrations $c(0.1\,M)$: $c(0.02\,M)$.	Per cent diminution[5] in a/c 0.02 M to 0.1 M.
KCl	Flügel[1]	1566	4.23	4.72	10.3
NaCl	Flügel, Barnes[2]	1578	4.28	4.67	8.3
HCl	Barnes	1598	4.36	4.72	7.6
$NaClO_3$	Flügel	1547	4.16	4.44	6.2
$NaBrO_3$	Flügel	1545	4.15	(4.44)	6.5
$NaNO_3$	Roth[3]	1547	4.16	4.55	8.6
$CsNO_3$	Washburn and MacInnes[4], Roth	1466	3.87	4.58	15.5

All these results show conclusively that the ratio a/c for the univalent ions diminishes with increasing total ion concentration. Furthermore, it appears to be true that this diminution is the same for all the ions in all the salts investigated at small concentrations, but that certain specific effects begin to appear even below 0.1 M, and doubtless are greatly exaggerated at still higher concentrations. In concentrated solutions it would not therefore be correct to assume that the two ions of a salt behave alike or that the ratio a/c for an ion depends solely upon the total ion concentration, regardless of how this total concentration is made up. It seems, however, that both these assumptions are approximately correct up to a concentration of about 0.05 M.

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[1] Flügel, *Z. Physik. Chem.*, **79**, 577 (1912).

[2] Barnes, *Trans. Nova Scotian Inst. Science*, 10, 153; *Trans. Roy. Soc., Canada*, II, [3] 6, 37 (1900).

[3] Roth, *Z. physik. Chem.*, **79**, 599 (1912).

[4] Washburn and MacInnes, THIS JOURNAL, **33**, 1686 (1911).

[5] The concentrations were obtained from the conductivities at 0° C. The values for $NaClO_3$ and $NaBrO_3$ were estimated, those for HCl were as before taken equal to those of KCl.

All of this discussion is based on the assumption that the principle of Kohlrausch is valid. If we should abandon this assumption, we might suppose that the true ion concentration, instead of being measured by the conductivity, is really proportional to the activity. Then, in accordance with the tables given above, we should regard the degree of dissociation of potassium chloride as about 4% less than that given by the conductivity at 0.02 *M*; 8% less at 0.05 *M*; and about 14% less at 0.1 *M*. We should then have $\alpha = 0.89$ at 0.02 *M*, $\alpha = 0.82$ at 0.05 *M*, and $\alpha = 0.74$ at 0.1 *M*.

If we adopt such new values for the degree of dissociation, not only do the ions become normal, but the un-ionized part becomes much more nearly so, and in at least one case (cesium nitrate)[1] the mass law actually holds between 0.02 *M* and 0.1 *M*.

Since the degree of dissociation and the concentrations obtained by this method not only will prove convenient, but probably are, as we shall see in the following sections, nearer to the true values than those obtained through the assumption of Kohlrausch, we may call the new values provisionally the *corrected degree of dissociation* and the *corrected concentration*.

The Degree of Dissociation Obtained by Combining Conductivity and Transference Data.

When we make a systematic tabulation of the values of Λ and Λ_0 for a large number of uni-univalent electrolytes, we find a striking relation at any chosen concentration between the values of Λ/Λ_0 and Λ_0 itself. Bredig[2] determined the conductivity of 78 unhydrolyzed organic salts. I have calculated the values of Λ/Λ_0 at the concentration 1/32 *M* and arranged the salts in the order of the Λ_0 values. The results are synopsized in the following table. The salts are grouped, all those whose Λ_0 lies between 140 and 130 constituting the first group, etc. The last column gives the average value of Λ/Λ_0 for each group.

TABLE III.

No. of salts.	Λ_0.	Λ/Λ_0.
4	140–130	0.900
3	130–120	0.885
11	120–110	0.871
40	110–100	0.861
20	100–90	0.849
1	90–80	0.833

It is evident that the values of Λ/Λ_0 diminish with diminishing Λ_0. Now it might be suspected, since these are for the most part salts of high molecular weight, that even at such a low concentration as 1/32 *M* viscosity

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[1] Cf. Biltz, *Z. physik. Chem.*; 40, 218 (1902); Washburn and MacInnes, THIS JOURNAL, **33**, 1686 (1911).

[2] Bredig, *Z. physik. Chem.*, 13, 191 (1894).

effects might be responsible for the variation in Λ/Λ_0. For this reason I have tabulated all the available data for the inorganic uni-univalent salts for the most of which the viscosity effects have been determined and shown to be negligible up to the concentration 0.1 M, which will be chosen for this tabulation. The full data are contained in Table V and are synopsized in Table IV. Here again the last column shows the average value of Λ/Λ_0 at 0.1 M for the group of salts whose Λ_0 values lie between the limits shown in the second column.

TABLE IV.—(18° C.)

No. of salts.	Λ_0.	Λ/Λ_0.
2	390–370	0.923
2	220–200	0.895
12	140–130	0.860
4	130–120	0.831
10	120–100	0.833
5	100–90	0.819
2	80–70	0.779
3	70–60	0.761

Here again we see a very marked decrease in the average value of Λ/Λ_0 as we pass from electrolytes of higher Λ_0 to electrolytes of lower Λ_0. There is nothing in the present theory of electrolytic dissociation which would enable us to predict this result, and the question arises as to whether this variation in Λ/Λ_0 means a real variation in α, the degree of dissociation.

The highest values of Λ/Λ_0 are those of hydrochloric and nitric acid, 0.925 and 0.921. Now it was shown by Noyes and Sammet[1] and Noyes and Kato[2] that the transference number of these acids changes very materially between zero concentration and 0.1 M, and this has been corroborated in the case of hydrochloric acid by the work of Jahn, Joachim and Wolff[3] and of Riesenfeld and Reinhold.[4] Any change in the transference number shows that at least one of the ion mobilities is varying. But the principle of Kohlrausch rests upon the assumption that both ion mobilities are constant. If for any salt there is a change in the transference number with change in concentration, this proves conclusively that, for that salt at least, Λ/Λ_0 cannot be a measure of the true degree of dissociation.

If we write $\Lambda_0 = u_0 + v_0$ where u_0 and v_0 are the mobilities at infinit dilution of the cation and anion, respectively, then we must write for the degree of dissociation not $\alpha = \Lambda/(u_0 + v_0)$, but $\alpha = \Lambda/(u + v)$ where

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[1] Noyes and Sammet, THIS JOURNAL, **24,** 944 (1902); **25,** 165 (1903).

[2] Noyes and Kato, *Z. physik. Chem.*, **62,** 420 (1908).

[3] Jahn, Joachim and Wolff, *Ibid.*, **58,** 641 (1907).

[4] Riesenfeld and Reinhold, *Ibid.*, **68,** 440 (1909). This paper contains an interesting summary of the work of previous investigators.

u and v are the ion mobilities at the concentration in question. Noyes and Kato, assuming the mobility of the chloride ion to be constant, calculated the change in mobility in the hydrogen ion, and thus showed the degree of dissociation of hydrochloric acid to be equal to that of potassium chloride. This conclusion has been very generally adopted, the degree of dissociation of 0.1 *M* HCl being taken as 0.86.

But now we must ask whether indeed the hydrogen ion is the only one whose mobility changes with the concentration, or whether all of the ions show similar variation to a greater or less degree. After a careful survey of all the existing transference data, a very important generalization was reached, one which has also been pointed out recently by Riesenfeld and Reinhold, namely, that all transference numbers change in general with the concentration and in such a direction that the transference number departs more from the number 0.5, the higher the concentration. An inspection of any collection of transference data will show the very general, although probably not universal, validity of this principle. The reason that it has not been more obvious is that the great majority of substances of which the transference number has been measured are composed of ions which move with nearly the same speeds. It seems that any attempt to determin the degree of dissociation from the conductivities, without the consideration of transference data as well, must lead to false conclusions.

Instead of assuming with Kohlrausch that the mobility of each ion is constant, let us make the much more limited assumption that one ion has the same mobility in different salts, provided that these are all at the same concentration. Thus chloride ion will be assumed to have the same mobility in 0.1 *M* HCl and in 0.1 *M* KCl. This assumption is alone sufficient to prove from the experimental data that these two electrolytes are equally dissociated. For the proof of this and for the derivation of the following formula, I am indebted to Prof. R. C. Tolman.

If at a given concentration we have two salts with the same anion, then we may write

$$\alpha_1 = \Lambda_1/(u_1 + v_1) \quad \text{and} \quad \alpha_2 = \Lambda_2/(u_2 + v_2).$$

Now if n_1 and n_2 are the two anion transference numbers, we may write

$$n_1 = v_1/(u_1 + u_2) \quad \text{and} \quad n_2 = v_2/(u_2 + v_2).$$

Now introducing the assumption that $v_1 = v_2$, we find[1]

$$\alpha_1/\alpha_2 = \Lambda_1 n_1/\Lambda_2 n_2.$$

This gives us a means of calculating the relative degree of dissociation

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[1] This same formula was obtained by Denison and Steele, *Z. physik. Chem.*, **57**, 110 (1906), and used by them for the calculation of the degrees of dissociation, but they do not comment upon the difference in the results obtained by this method and the common method.

of two salts with a common ion, without the aid of any assumption except that in both solutions at the same concentration the common ion has the same mobility. All the data available for this calculation have been collected in Table V. Let us select first for consideration the four chlorides, HCl, KCl, NaCl and LiCl. The Λ/Λ_0 values show wide variation. They are, respectively, 0.925, 0.860, 0.844 and 0.833, but when we apply the above formula we find for the ratio αHCl/αKCl 0.996, αNaCl/αKCl 0.998 and αLiCl/αKCl 0.992. In other words, all these salts have within the limits of experimental error the same degree of dissociation. So we may proceed to find the degree of dissociation of all the other chlorides. We may now compare by means of a similar calculation all the salts with a common cation, and thus we may compare the degree of dissociation in each of the tenth molal solutions to that of one chosen salt.[1] Potassium chloride has been selected for this purpose. The results are given in Table V. The values under Λ are the molecular conductivities at 0.1 *M*, and n_a and n_c denote the anion and cation transference numbers, respectively. All of the transference data are taken from the excellent work of Denison and Steele,[2] and of Denison[3] except as otherwise indicated. The five values marked *P* are taken from a very kind personal communication of Prof. Denison. He regards these values as only preliminary. One value obtained by Riesenfeld and Reinhold is marked *R*, and *K* denotes values taken from the book of Kohlrausch and Holborn. The value for lithium chloride is the mean of those given by Denison and by Kohlrausch. The values marked *C* have not been determined experimentally, but were calculated by a method which will be discussed presently. Of the conductivity data some were determined by Kohlrausch, others in this laboratory, and the majority by Denison and Steele.

The conclusions to be drawn from this table are too obvious to require further emphasis. We may conclude with much confidence that the chlorides, bromides, and iodides of hydrogen, lithium, sodium, potassium, rubidium, cesium, and ammonium are all dissociated in tenth molal solution to practically the same extent; furthermore, that nitrates, bromates and chlorates are several per cent less dissociated than the corresponding halides, and that thalium and silver salts are less dissociated than salts of the alkali metals.

Now what is the true degree of dissociation of these salts? The table

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[1] It is obviously possible to compare a salt such as CsI with potassium chloride by a number of different paths. Thus we might compare NH_4I with KCl, and CsI with NH_4I, or KI with KCl and CsI with KI, and so on. As a matter of fact, I have related all the potassium salts with KCl and then all the chlorides with KCl. Any other salt was then related to KCl through both these paths, and the average taken.

[2] Denison and Steele, *loc. cit.*

[3] Denison, *Trans. Faraday Soc.*, 5, 165 (1909).

TABLE V.—(18° C.).

	Λ_0.	Λ.	Λ/Λ_0.	N_a.	$N_a\Lambda$.	$N_c\Lambda$.	a/aKCl.
HCl	380.0	351.4	0.925	R 0.1612	56.7	294.7	0.996
HNO_3	376.3	346.4	0.921	0.145	50.2	296.2	0.982
KOH	238.6	213.0	0.893	0.738	157.2	55.8	1.012
NaOH	217.5	195.0	0.897	K 0.82	159.8	35.2	1.013
CsBr	135.7	115.8	0.854	0.507	58.7	57.1	0.995
RbBr	135.2	115.6	0.855	0.508	58.8	56.8	1.005
CsI	134.6	115.2	0.856	0.503	57.9	57.3	1.000
RbI	134.1	116.0	0.865	0.503	58.4	57.6	1.018
CsCl	133.5	113.4	0.850	0.500	56.7	56.7	0.996
RbCl	133.0	113.9	0.857	0.506	57.6	56.3	1.012
NH_4Br	132.4	114.3	0.864	0.519	59.3	55.0	1.004
KBr	132.2	114.1	0.863	0.519	59.2	54.9	0.996
NH_4I	131.3	113.5	0.865	0.516	58.6	54.9	1.006
KI	131.1	114.0	0.869	0.514	58.6	55.4	1.005
NH_4Cl	130.2	112.0	0.860	0.511	57.2	54.8	1.005
KCl	130.0	112.0	0.862	0.508	56.9	55.1	1.000
$CsNO_3$	129.8	105.0	0.810	P 0.476	50.0	55.0	0.941
$RbNO_3$	129.3	...	...	P 0.478	...	...	....
$TlNO_3$	127.7	101.2	0.792	P 0.496	50.2	51.0	0.920
NH_4NO_3	126.5	106.6	0.843	C 0.500	53.3	53.3	0.977
KNO_3	126.3	104.7	0.829	0.498	52.1	52.6	0.954
KSCN	121.2	104.3	0.860	....	...	...	....
$KClO_3$	119.6	99.2	0.829	0.464	46.0	53.2	0.966
$AgNO_3$	115.8	94.3	0.814	K 0.528	49.8	44.5	0.913
TlF	112.6	92.6	0.823	....	...	...	....
$KBrO_3$	112.1	93.0	0.830	0.430	40.0	53.0	0.962
KF	111.2	94.0	0.845	....	...	...	....
NaBr	111.1	93.0	0.837	0.624	58.0	35.0	0.984
NaI	110.0	92.5	0.841	0.624	57.7	34.8	0.988
NaCl	108.9	92.0	0.844	0.617	56.8.	35.2	0.998
$NaNO_3$	105.2	87.2	0.829	K 0.615	53.6	33.6	0.968
LiBr	101.0	...	...	P 0.692	...	...	....
$KC_2H_3O_2$	100.0	83.8	0.838	0.33	27.6	56.2	1.019?
LiI	99.9	...	...	P 0.692	...	...	....
LiCl	98.8	82.3	0.833	KP 0.685	56.4	25.9	0.992
KIO_3	98.5	79.7	0.810	....	...	...	....
$LiNO_3$	95.1	79.1	0.832	C 0.676?	53.5?	25.6?	0.979?
KH_2PO_4	91.0	74.0	0.81	....	...	...	....
NaF	90.1	73.1	0.812	....	...	...	....
$NaC_2H_3O_2$	78.9	61.1	0.775	0.44?	26.9	34.2	0.983?
$NaIO_3$	77.4	60.5	0.782	....	...	...	....
NaH_2PO_4	69.9	54.4	0.778	....	...	...	....
$LiIO_3$	67.3	51.5	0.765	....	...	...	....
$NaH_3P_2O_7$	63.9	47.0	0.74	....	...	...	....

only shows us the relative value. In order to go further we must interpret in some way the change in transference number with the concentration. Two simple hypotheses are at hand; (1) that all the ions increase in mobility[1] with increasing ion concentration, the increase being relatively greater the greater the original mobility, (2) that all ions decrease in mobility with increasing ion concentration, the decrease being greater the smaller the original mobility. Of these the first is much more likely, for, although it is impossible as yet to form any exact theory of the change in mobility, there are two possible causes for an increase in mobility with increasing concentration. The first is a gradual dehydration of the ions. The second can only be vaguely suggested. If we assume that in a concentrated solution there is superposed upon the ordinary mechanism of conduction another kind of conduction analogous to that supposed in the Grotthus theory, involving the undissociated salt, this additional conduction would account for the assumed increase in mobility. Of these two causes, the first, although undoubtedly present, does not in all probability play a dominant part.

Admitting that this interpretation of the facts is hypothetical in character, it is nevertheless interesting to observe that it leads to a degree of dissociation approaching the "corrected degree of dissociation" obtained thermodynamically in the preceding section.

Before proceeding to the further discussion of this problem, I will call attention parenthetically to an interesting consequence of the assumption that in solutions of the same concentration a given ion has the same mobility. Let us consider the four salts (1) KCl, (2) KNO_3, (3) NH_4NO_3, (4) NH_4Cl. Now if x represents the ratio of the cation transference number to the anion transference number, then

$$x_1 = u_K/v_{Cl},\ x_2 = u_K/v_{NO_3},\ x_3 = u_{NH_4}/v_{NO_3},\ x_4 = u_{NH_4}/v_{Cl}$$

hence

$$x_1x_3 = x_2x_4$$

and if we know the transference number for three of the salts, that of the fourth can be obtained. This was in fact the way that the values for NH_4NO_3 and $LiNO_3$ were calculated for Table V. Considering the difficulty of determining transference numbers experimentally, this method of calculating and checking such numbers is important.

Conclusions.

If we admit that the mobilities of the ions all increase with increasing concentration, then it is evident from Table V that the degree of dissocia-

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[1] Jahn (*Z. physik. Chem.*, 33, 545 (1900)) was the first to consider the possibility of an increase in ion mobility with increase of concentration as an explanation of the deviation of strong electrolytes from the mass law. He took it for granted that the concentration of the ions could be obtained from the Nernst formula for the electromotive force of a concentration cell. Arrhenius (*Ibid.*, 36, 28 (1901)) showed that neither Jahn's theoretical work, nor his experimental data were as reliable as the latter supposed. Nevertheless, the results of the present investigation substantiate the correctness of Jahn's fundamental assumption.

tion of no uni-univalent compound at 0.1 *M* concentration can be more than about 0.75, but this is about the value of the corrected degree of dissociation obtained thermodynamically. Supposing that we assume arbitrarily the degree of dissociation of 0.1 *M* potassium chloride as 0.74. Having made this assumption, we may calculate from Table V the degree of dissociation of the other salts. This is done in Table VI for those salts which are common to Tables II and V. The second column gives α, the degrees of dissociation, as computed from Table V, the third column gives α', the corrected degree of dissociation calculated from Table II (on the assumption that between zero concentration and 0.02 *M* the ratio a/c diminishes 4%, as indicated in Table I).

TABLE VI.

	α.	α'.
KCl	0.74	0.74
NaCl	0.74	0.74
HCl	0.74	0.79
$NaNO_3$	0.72	0.75
$CsNO_3$	0.69	0.68

The agreement between α and α' in case of KCl, NaCl, and $CsNO_3$ is quite satisfactory. In the case of $NaNO_3$ the discrepancy may well be due to experimental error, for the measurements with this salt are not very reliable. This, however, is not the case with HCl, for while the degree of dissociation is shown by the combination of conductivity and transference numbers to be identical with that of KCl, the corrected degree of dissociation is shown to be more than that of KCl in three different ways, namely, by Table I, by Table II, and by the experiments of Tolman and Ferguson. The agreement between α and α' would doubtless be much more exact at 0.05 than at 0.1 *M*. At the latter concentration, the true degree of dissociation is, as we have seen, very nearly the same for the four salts KCl, NaCl, LiCl, HCl; while α' undoubtedly increases somewhat, in the order given. At still higher concentrations the discrepancies will doubtless be found to be very great and to depend upon the specific nature of the salt and the ion investigated.

Probably, however, hydrochloric acid represents a pretty extreme case and we shall be safe in regarding the true degree of dissociation and the corrected degree of dissociation, as equal up to a few hundredths molal, and approximately equal up to tenth molal. As a further illustration of the truth of this statement, we may consider thallous nitrate, whose degree of dissociation is shown by Table V, to be 8% less than potassium chloride. Now the effect of thallous nitrate on the solubility of thallous chloride is less than that of potassium chloride by just this percentage.

The conclusion then to which all of these facts lead may be summarized as follows: A very large number of chlorides, bromides, and iodides are equally dissociated, while nitrates, chlorates, and bromates, and salts of silver and thallium are somewhat less dissociated. The degree of dissociation of uni-univalent salts is probably much smaller than commonly supposed. If we assume that potassium chloride is 74% dissociated at 0.1 *M*, 82% at 0.05 *M* and 89% at 0.02 *M*, then in all cases up to a few hundredths molal, and probably in most cases up to tenth molal, the activity of the ions is proportional to the concentrations thus calculated.

The familiar deviation of strong electrolytes from the mass law is, according to this view, as in the theory of Jahn, to be attributed largely to a general increase in mobility of ions with the total ion concentration. This view differs essentially from the theory advanced by Franklin and Kraus[1] and by Lewis and Wheeler.[2] According to that theory, the abnormalities of the conductivity curves for electrolytes were attributed to a change in the dissociating power of the solvent due to the addition of a stronger electrophile as solute. According to the one explanation, it is the speed of the ions which does not obey the laws announced by the founders of the ionic theory; according to the other, it is the degree of dissociation. It is probable that neither of these explanations alone suffices, but the evidence which has been here adduced in support of the view that the ions in aqueous solution have a variable mobility makes it extremely desirable that further investigations should be made of the mobility of ions in non-aqueous solvents. Especially it should be noted whether in such cases there is a change of transference number over a wide range of concentration.

In conclusion I wish to express my thanks to Dr. Merle Randall for valuable assistance in the collection of the data used in this paper.

BOSTON, June 14, 1912.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF PHOSPHORUS.[3]

[THIRD PAPER.]

THE ANALYSIS OF PHOSPHORUS TRICHLORIDE.

BY GREGORY PAUL BAXTER AND CHARLES JAMES MOORE.

Received October 17, 1912.

In two recent investigations in this laboratory, tri-silver phosphate[4] and phosphorus tribromide[5] have been analyzed with the following results for the atomic weight of phosphorus:

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[1] Franklin and Kraus, THIS JOURNAL, **27**, 216 (1905).

[2] Lewis and Wheeler, *Z. physik. Chem.*, **56**, 179 (1906).

[3] Reprinted from *Original Communications, Eighth International Congress of Applied Chemistry*, **2**, 21 (1912).

[4] Baxter and Jones, *Proc. Am. Acad.*, **45**, 137 (1910); THIS JOURNAL, **32**, 268; *Z. anorg. Chem.*, **66**, 97.

[5] Baxter, Moore and Boylston, *Proc. Am. Acad.*, **47**, 385 (1912); THIS JOURNAL, **34**, 259; *Z. anorg. Chem.*, **74**, 365.