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THE POTENTIAL OF THE THALLIUM ELECTRODE.

By Gilbert N. Lewis and Carl L. von Ende.

Received March 25, 1910.

The first determination of the electrode potential of thallium was made by Neumann[1] who obtained the following values:

			Volt.
Tl, Tl_2SO_4	(saturated),	N. E.;[2]	$E = +0.674$
Tl, $TlNO_3$	(saturated),	N. E.;	$E = +0.671$
Tl, TlCl	(saturated),	N. E.;	$E = +0.711$
Tl, TlA	(0.1 N),	N. E.;	$E = +0.677$
Tl, TlA	(0.02N),	N. E.;	$E = +0.705$
Tl, TlA	(0.01N).	N. E.;	$E = +0.715$

The last three values are averages obtained from the study of 23 thallous salts, chiefly of organic acids, at the three concentrations given. Neumann believed his results to be entirely reproducible. In fact he found the potential of thallium in the twenty-three salts at hundredth-normal concentration to be the same within one millivolt. This agreement must have been purely accidental for we shall see that all of Neumann's measurements of the thallium potential were attended by a very large error of entirely fortuitous character.

The doubtful character of Neumann's determinations is apparent when the above values of the thallium potentials are plotted against the logarithms of the ion concentrations, as in Fig. 1. The continuous straight line shows the way the potential would change with the ion concentration according to the Nernst equation; the points enclosed in circles show the values obtained by Neumann. These obviously neither follow the

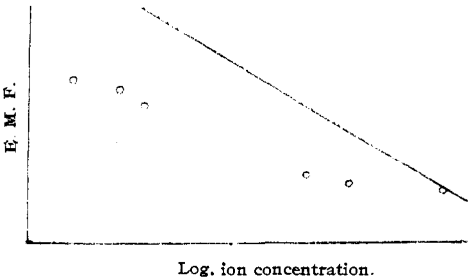

Fig. 1.

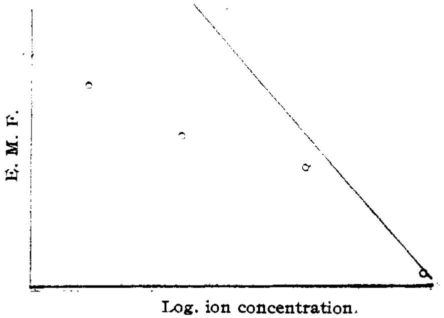

Fig. 2.

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[1] Z. *physik. Chem.*, 14, 193 (1894).

[2] N. E. stands for normal electrode. A positive electromotive force, E, indicates always that the current tends to pass in the cell from left to right.

theoretical curve nor show any great regularity in their deviation therefrom.

The dependence of the thallium potential upon the concentration of thallous ion has ben recently studied by Abegg and Spencer[1] with various concentrations of thallous nitrate, chloride, sulphate and hydroxide. Their results for the potentials in different concentrations of thallous chloride are reproduced in Fig. 2, where the continuous line again represents the theoretical change of potential with the concentration. The authors conclude that the Nernst formula is not even approximately true for the thallium electrode. This conclusion is also reached by Shukow.[2]

In all cases studied the potential changes less rapidly with the concentration than theory requires, and in all cases the deviations are greater the more dilute the solutions. This could readily be explained by assuming that the thallium electrode is oxidized by the oxygen contained in the solution, thus increasing the concentration of thallous ion next the electrode. The percentage change of concentration thus produced would obviously be greater in the more dilute solutions. This possibility, however, was considered both by Zhukov and by Abegg and Spencer, and in both cases precautions were taken which seemed adequate to preclude it.

Any other explanation must depend upon the assumption of some abnormality in thallous ion. In fact Denham[3] has claimed that metallic thallium in the presence of thallous ion forms sub-thallous ion. Kohlrausch and von Steinwehr[4] have suggested that a somewhat anomalous trend in the conductivity of thallous chloride indicates the tendency on the part of thallium to form complex ions. Finally we might surmise the formation of a double ion Tl_2^{++} analogous to the one which is supposed to exist in the case of univalent mercury. On account of these various possibilities it seemed desirable to investigate the subject more closely from the experimental side.

The Effect of Thallous Ion Concentration upon the Potential of Thallium.

The solutions used in this investigation were made from salts carefully purified by suitable recrystallizations, and from doubly distilled water. The metallic thallium employed came from two independent sources (Kahlbaum, Eimer and Amend) and both varieties proved to be identical in electromotive behavior. In determining the effect of the various solutions upon the potential, the kind of thallium electrode used was unimportant provided that it be constant and reproducible. A concentrated but

[1] *Z. anorg. Chem.*, **46**, 406 (1905).

[2] *Ber.*, **38**, 2691 (1905).

[3] *Proc. Chem. Soc.*, **24**, 76 (1908).

[4] *Ber. Berlin. Akad.*, **1902**, 581.

unsaturated thallium amalgam, prepared with doubly distilled mercury, proved most satisfactory. The amalgam used contained 20 per cent. thallium and was kept in a pipette provided with stopcocks, where it was protected from atmospheric moisture and could be withdrawn as needed. All measurements were made in a thermostat maintained at 25.00°.

The solutions were prepared by dissolving known weights of the dried salts, or from saturated solutions obtained by shaking the salt and water together in the thermostat for 24 hours. These solutions were introduced into electrode vessels of the ordinary "half-cell" type together with the 20 per cent. amalgam. These half cells could then be measured against one another or against a single one chosen arbitrarily. The one so chosen contained a saturated thallous chloride solution with an excess of the solid salt lying above the amalgam.

The first series of experiments was made with solutions of thallous chloride and nitrate. On account of the almost equal mobility of thallous ion and chloride ion the liquid potential between different solutions of thallous chloride may be entirely neglected. Between electrodes in chloride and nitrate of the same concentration a small difference was observed corresponding as nearly as could be observed to the calculated potential[1] between the liquids. It was found possible to eliminate this difference by interposing a normal potassium chloride solution between the two liquids, and this was done in the succeeding experiments.

The results of this series are given in Table I where the first column shows the salt used and its concentration (*S* denotes a saturated solution). The third column gives the potential between the electrode in question and the one in saturated thallous chloride. Each value is the mean of several determinations, which, in the concentrated solutions, were very concordant.

TABLE I.

	Volt.		Volt.
$TlNO_3$ 1/10 *N*...........	—0.0414	$TlCl$ 1/200 *N*...............	+0.0240
$TlNO_3$ 1/30 *N*...........	—0.0175	$TlNO_3$ 1/200 *N*.............	+0.0228
$TlNO_3$ 1/40 *N*...........	—0.0112	$TlCl$ 1/5 *S*.................	+0.0301
$TlCl$ *S*..................	0.0	$TlCl$ 1/400 *N*...............	+0.0356
$TlCl$ 1/100 *N*............	+0.0104	$TlNO_3$ 1/400 *N*.............	+0.0339
$TlCl$ 1/2 *S*..............	+0.0144		

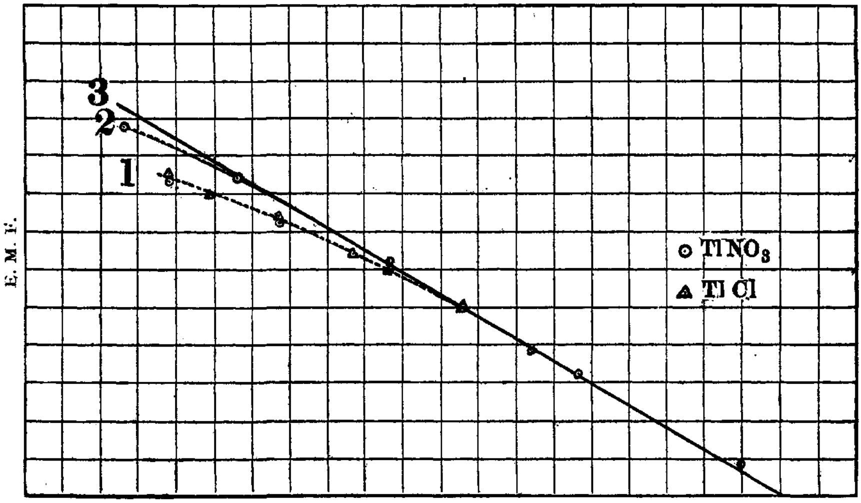
These values are plotted in Fig. 3 against the concentrations of thallous ion, the latter values being obtained with the aid of degrees of dissociation calculated from Kohlrausch's conductivity data. The solubility of thallous chloride at 25° is taken as 0.0161 *N*. This is the value obtained in perfect agreement both by Noyes[2] and by Kohlrausch.[3]

[1] See Lewis and Sargent, THIS JOURNAL, 31, 363 (1909).

[2] *Z. physik. Chem.*, 49, 296 (1904).

[3] *Ibid.*, 64, 149 (1908).

In the dilute solutions there is obviously an increasing divergence from the straight line (3) demanded by the Nernst equation. However, this divergence, although in the same direction, is so much smaller than that found by previous investigators, and the potentials measured were so much less certain in the dilute solutions than in the concentrated, that we were inclined to believe the apparently anomalous behavior of the dilute solutions to be due to some cause latent in the experimental method. This suspicion was confirmed when the solutions which had been used with the thallium electrodes were tested with phenolphthalein and found to be decidedly alkaline.



Log. ion concentration.
Fig. 3.

This alkalinity must obviously be due to the oxidation of metallic thallium by dissolved oxygen. The small amount of thallous hydroxide thus produced is insufficient to produce an appreciable percentage increase in thallous ion concentration in the concentrated solutions, but evidently might be sufficient in the dilute solution to cause the low potentials observed. For this reason several dilute solutions were investigated further with two additional precautions. The first consisted in exhausting the solutions of air as far as possible,[1] the second in filling the electrode vessel first with solution and then introducing the amalgam through a capillary dipping below the surface of the solution. These changes resulted in an increase of 0.0008 volt in the potential of the electrode with saturated thallous chloride. The other new electrodes measured against this new thallous chloride electrode gave the values in Table II.

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[1] It was found possible to exhaust a solution without appreciably changing its concentration, by boiling it for a minute or two under reduced pressure at a temperature of 25° to 30° C.

TABLE II.

	Volt.		Volt.
TlCl *S*	0	$TlNO_3$ 1/262 *N*	+0.0346
$TlNO_3$ 1/100 *N*	+0.0121	$TlNO_3$ 1/515 *N*	+0.0480

These data are shown also in Fig. 3, and are represented by the points lying on the second dotted curve (2). These points approach very close to the theoretical except at the highest dilution. Moreover, the solutions still gave a faint coloration with phenolphthalein, showing the presence of amounts of thallous hydroxide which, though very small, might affect the potential at high dilutions. Of the values thus far obtained those least likely to be affected by the oxidation of the electrode are undoubtedly those for the two most concentrated solutions, tenth- and thirtieth-normal $TlNO_3$, and the two most concentrated of the diluter solutions in which special precautions were taken, namely, saturated thallous chloride and hundredth-normal thallous nitrate. These values agree very closely with the Nernst formula and it seemed particularly desirable to obtain an equally reliable value for a more dilute solution, in order to test the formula over as wide a range as possible.

We had already observed that an electrode under saturated thallous chloride, with excess of solid thallous chloride, was more reproducible than one containing the same concentration of an unsaturated thallous salt. This was to be expected since a small amount of thallous ion accidentally added to saturated thallous chloride would be largely removed from the solution as solid thallous chloride. For this reason we decided to use for the most dilute solution a saturated solution of thallous bromide. This has a solubility at 25° of 0.00199 *N* according to the recent work of Kohlrausch,[1] whose measurements moreover agree perfectly with those of several other observers.

A saturated solution of this salt and an excess of the solid were placed in a specially designed electrode receptacle through which very pure hydrogen could be passed continuously, so as to bubble through the solution. When this process had been continued long enough to insure the removal of all the oxygen from the solution and the gas above it, by turning a stopcock the thallium amalgam was allowed to enter through a fine capillary. The electrode thus prepared gave, against the saturated TlCl electrode, a very constant potential of +0.0521 volt and the solution after long standing in contact with the electrode gave no coloration with phenolphthalein. We may therefore consider this potential as reliable as the four mentioned above. We reproduce these five values in Table III, which gives the concentration, *C*, of the salt used, the degree of dissociation, α, as obtained from conductivity measurements, the ion concentration, C', the potential, *E*, against the saturated thallous chloride

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[1] *Z. physik. Chem.*, 64, 149 (1908).

electrode, and the values of *E* calculated from the Nernst equation. These data are also plotted in Fig. 4.

TABLE III.

	C.	α.	*C'*.	*E*.	*E* (calc.).
$TlNO_3$	0.100	0.79	0.0790	-0.0422	-0.0438
$TlNO_3$	0.0333	0.88	0.0293	-0.0183	-0.0182
$TlCl(S)$	0.0161	0.89	0.0143	0	(standard)
$TlNO_3$	0.0100	0.93	0.00930	+0.0113	+0.0113
$TlBr(S)$	0.00199	0.97	0.00193	+0.0513	+0.0516

The deviation of one and a half millivolts between the observed and calculated values for tenth-normal thallous nitrate is undoubtedly real, and not to be attributed to experimental error. Moreover such a real deviation from the Nernst equation in the direction found is to be expected in the case of a solution as concentrated as tenth-normal. There is much experimental evidence to show that if conductivity is taken as a measure of ion concentration, the ions (although much less abnormal in behavior than the undissociated substance) do not quite obey the laws of a perfect solution. The ratio of their activity[1] to their concentration, which should be constant, diminishes somewhat at the higher concentrations.[2]

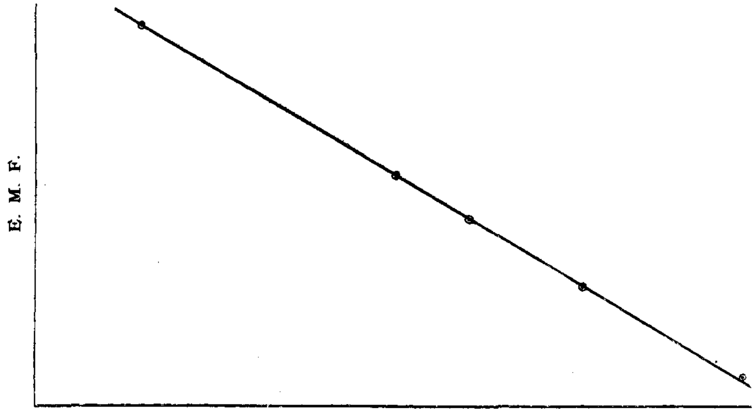

Fig. 4.

The remaining values agree remarkably with the Nernst equation, the deviations being irregular, and amounting in no case to more than 0.0003 volt. This agreement, and the constancy of the potential when the solutions in the electrode vessels are stirred, we regard as strong evidence against the existence of the subthallous ion assumed by Denham.[3]

Instead then of finding any anomaly in the electromotive behavior of thallous ion, we may assert that the Nernst equation holds for the thallium

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[1] See Lewis, *Proc. Am. Acad.*, 43, 259 (1907); *Z. physik. Chem.*, 61, 129 (1907).

[2] In an article about to appear in THIS JOURNAL, Bray and Mackay point out an interesting case in which this rule is confirmed.

[3] *Loc. cit.*

electrode over a large range of concentration with greater accuracy than it has as yet been shown to do in the case of any other electrode.

The Thallium Electrode Potential.

In order to determine the absolute electrode potential of thallium, we must use an electrode of pure metallic thallium or some electrode that is its equivalent. It was shown by Kurnakov and Puschkin[1] that thallium and mercury form no solid compound above 15°. Sucheni[2] showed that mercury does not dissolve to any extent in solid thallium, and that a saturated solution of thallium in mercury therefore has the same potential as pure thallium. This fact, which we have also corroborated, enables us to use a paste of thallium and thallium amalgam in place of solid thallium, which like all solid metals gives an inconstant potential owing to uncontrollable surface variations.

A mixture of 55 parts thallium and 45 parts mercury was warmed until liquid in the electrode vessels. After cooling, the electrodes were rinsed with the solution to be used and the vessels then filled. After this rinsing, electrodes prepared without special precautions gave the same results as those prepared in the total absence of oxygen. The first experiments, with three electrodes of this type (in two of which the amalgams were made from samples of thallium of different origin) were made with saturated solutions of thallous chloride containing an excess of the solid chloride. In the first case no special precautions were taken, in the second the solution was freed from air by exhaustion, in the third by a stream of hydrogen. Against the normal electrode the electromotive forces were 0.7258, 0.7256, 0.7257, respectively. We may write, therefore,

$$\mathrm{Tl, TlCl\ (sat.)\ N.\ E.};\ E = 0.7257\ \text{volt}.$$

The ion concentration of thallium in the saturated chloride solution is 0.0143 N. From the Nernst equation,

$$\mathrm{Tl, Tl^{+}}(N),\ \mathrm{Tl^{+}}(0.0143\ N),\ \mathrm{Tl};\ E = 0.1087\ \text{volt}.$$

Adding these equations gives

$$\mathrm{Tl, Tl^{+}}(N),\ \mathrm{N.\ E.};\ E = \underline{0.6170\ \text{volt}}.$$

On account of the almost equal mobility of thallous and potassium ions, the liquid potential is here negligible. Therefore, the potential of the thallium electrode, when the normal electrode is taken as zero, is 0.6170 volt at 25°.[3]

We also investigated electrodes of saturated thallium amalgam under tenth-normal and normal potassium chloride saturated with thallous

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[1] *Z. anorg. Chem.*, 30, 86 (1902).

[2] *Z. Elektrochemie*, 12, 726 (1906).

[3] As in other cases, this is not the potential against a real normal solution of thallous ion, but against a sort of hypothetical normal solution, between which and a dilute solution the Nernst formula would hold. This potential would in any case be more useful in calculation than that against the real normal solution, even if the latter value could be obtained.

chloride. Electrodes of this type were used successfully by Sucheni and we find them, as was to be expected, much less affected by any oxidation of the electrode than the other types that have been used. The electrodes with tenth-normal potassium chloride gave against the normal electrode the following potentials in four experiments, the last one being made with a new potassium chloride solution prepared from salt of a different origin. (1) 0.7707, (2) 0.7704, (3) 0.7705, (4) 0.7708. The average is therefore,

$$\text{Tl, TlCl (solid), KCl } (1/10\ N)\text{, N. E.; } E = 0.7706 \text{ volt.}$$

From this value also it is possible to calculate the normal potential of thallium, although this calculation is less justifiable than the one above, since it assumes the validity of the laws of the perfect solution up to a higher concentration. The solubility product of TlCl is $(0.0143)^2$, and the concentration of Cl^- due to the potassium chloride may be taken as 0.085, allowing for the degree of dissociation, in the presence of thallous chloride; then, if x is the concentration of thallous ion, we obtain from the solubility-product rule,

$$(0.085 + x)\, x = (0.0143)^2.$$

Hence $x = 0.00234$ and the above equation for electromotive force may be written

$$\text{Tl, Tl}^+ \ (0.00234\ N)\text{, N. E.; } E = 0.7706 \text{ volt.}$$

From the Nernst formula,

$$\text{Tl, Tl}^+ \ (N)\text{, Tl}^+(0.00234\ N)\text{, Tl; } E = -0.1555 \text{ volt.}$$

Hence,

$$\text{Tl, Tl}^+(N)\text{, N. E.; } E = 0.6151 \text{ volt.}$$

The difference of nearly two millivolts between this value and the one obtained above is not to be ascribed to experimental error, but was to have been predicted from the principle stated above, namely that when we calculate concentrations in the ordinary way the activity of an ion in tenth-normal solution is always lower than that calculated from the behavior of more dilute solutions. The chloride ion from the tenth-normal potassium chloride has really then a smaller effect on the solubility of thallous chloride than we have ascribed to it when we assumed the complete validity of the ideal laws upon which the solubility-product rule is based. We shall adhere therefore to the first value, 0.6170 v., as the potential of the thallium electrode.

We also investigated saturated thallium amalgam in normal potassium chloride saturated with thallous chloride, and this furnished the most constant electrode of all those that we measured. With reasonable care it should give fully as reproducible a potential as the normal calomel electrode. Against the latter it has the following potential:[1]

$$\text{Tl, TlCl (solid), KCl } N\text{, N. E.; } E = 0.8227 \text{ volt.}$$

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[1] It is worth noting that the difference of 0.0521 v. between the electrodes in N and $1/10\ N$ KCl is almost identical with the difference of about 0.0526 v. between the normal and tenth-normal calomel electrodes.

This electrode, although it gives entirely reproducible potentials, shows a gradual increase of potential on long standing. This phenomenon had been observed to a greater degree with the other electrodes. Electrodes in saturated solutions of thallous chloride in water, 1/10 *N* KCl and *N* KCl respectively, increased in potential after four months' standing by 0.0038 volt, 0.0014 volt, and 0.0004 volt. We have not ascertained the cause of this increase. It is not due to any change in the amalgam, since in every case the original potential is obtained when the electrode vessel is refilled with a fresh solution.

Summary.

Contrary to some views previously published, there is nothing anomalous in the electromotive behavior of thallous ion, nor do we find any evidence of the existence of a sub-thallous ion.

Previous measurements of the thallium potential have been vitiated by the oxidation of the electrode and the consequent increase in thallous ion concentration. When such oxidation is avoided the Nernst formula is obeyed more closely than has been shown to be the case with any other electrode.

The assumption of the validity of the Nernst formula and the solubility-product rule (ion concentration being measured by conductivity) leads to measurable errors when the concentration is as high as tenth-normal, and the direction of these errors can be predicted.

The potential of pure thallium in saturated solutions of thallous chloride in water, in 1/10 *N* KCl and in *N* KCl were measured. The potential of pure thallium against (hypothetical) normal thallous ion is 0.6170 volt at 25° when the normal calomel electrode is taken as zero.

This work was completed in the summer of 1908.

Note.—Since this paper was written our attention has been called to an article by Brislee[1] who has investigated thallium potentials with precautions against the oxidation of the electrodes. He also finds no striking deviation from the Nernst equation although the variations which he observes are much larger than ours. This is doubtless because electrodes of solid thallium were used and because the work was not done in a thermostat. His value for the thallium electrode potential differs considerably from ours. We give below a table of values for the e. m. f. of Tl, $Tl^{+}N$, N. E. calculated from the results of the various observers whose work has been mentioned above. All the values are based on experiments with saturated thallous chloride.

	E. M. F.
Neumann	0.605
Abegg and Spencer	0.614
Brislee	0.602
Lewis and von Ende	0.6170

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[1] *Trans. Faraday Soc.*, **4**, 157 (1909).

Our value, obtained at 25°, we regard as undoubtedly accurate within a few tenths of a millivolt. Brislee's value was obtained in the neighborhood of 17° and the wide difference between the two values may be in part due to the difference in temperature, which would indicate, however, an exceptionally large temperature coefficient for the thallium electrode.

BOSTON, MASS.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 48.]

THE IONIZATION OF SALTS IN MIXTURES WITH NO COMMON ION.

BY MILES S. SHERRILL.

Received April 14, 1910.

Contents.

1. Purpose of the Investigation.—The general purpose of this investigation was to determine what modification must be made of the empirical principles which have been found to express the ionization of salts in mixtures with a common ion, in order that they may be applicable also to mixtures with no common ion; in other words, to determine the *general* law governing the ionization relations of salts.

Although many researches have been carried out on the conductance of mixtures with a common ion, few data exist upon mixtures with no common ion suitable for the purpose just mentioned.[1] At the suggestion of Professor A. A. Noyes, this investigation was therefore undertaken, the plan being to measure the conductance of mixtures of two salts with no common ion, and to compare the results with the conductance calculated by the principle discussed in the following section. The salts chosen were potassium chloride and sodium sulphate, and sodium chloride and potassium sulphate. Thus mixtures of salts of two ionic types could be prepared, whereby a more satisfactory test of the theory would be afforded.

2. Principles Relating to the Ionization of Salts in Mixtures.—The principles already established may be first briefly reviewed.

The mass-action law requires that the ionization γ of any salt vary with the concentration C, in accordance with the equation:

$$\frac{(\gamma C)^n}{(1-\gamma)C} = K. \qquad (1)$$

where K is the ionization constant for the salt, and n is the number of ions produced by the ionization of 1 molecule of the salt. The numerical

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[1] The only measurements that exist seem to be those of Barmwater (*Z. physik. Chem.*, **28**, 427 (1899)), on certain mixtures of uni-univalent salts.