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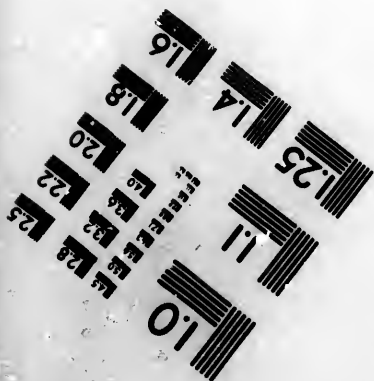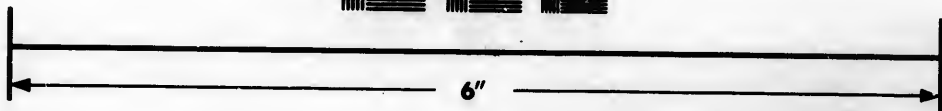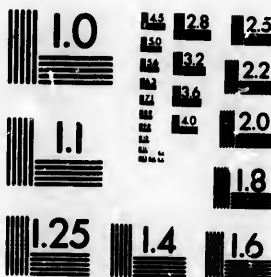
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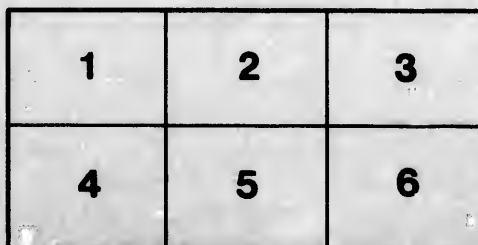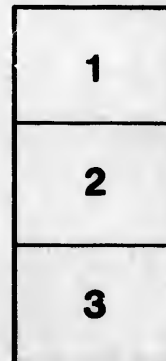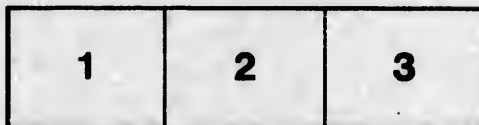
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V.—*On the Calculation of the Conductivity of Electrolytes.*

By Prof. J. G. MacGregor, D.Sc., Dalhousie College, Halifax, N.S.

(Read May 20, 1896.)

According to the dissociation theory of electrolysis, it is possible to calculate the conductivity of complex solutions of electrolytes, provided we know the quantities of the electrolytes present in a given volume of the solution, their states of dissociation, and their specific molecular conductivities at infinite dilution. If v is the volume of a solution which contains N_1, N_2, N_3, etc., gramme-equivalents of the respective electrolytes present, if α_1, α_2, α_3, etc., are their coefficients of dissociation or ionisation, and if $\mu_{\infty 1}$, $\mu_{\infty 2}$, $\mu_{\infty 3}$, etc., are their specific conductivities per gramme-equivalent at infinite dilution, then, according to the above theory, the specific conductivity of the solution is equal to

$$\frac{1}{v}\left(\alpha_1 N_1 \mu_{\infty_1} + \alpha_2 N_2 \mu_{\infty_2} + \alpha_3 N_3 \mu_{\infty_3} + \text{etc.}\right).$$

In order, therefore, to effect a calculation we must be able to determine (1) the numbers of gramme-equivalents of the various electrolytes present, (2) their ionisation coefficients, and (3) the specific molecular conductivities of the electrolytes at infinite dilution in the circumstances in which they exist in the complex solution.

With regard to (3), as but little change in the ionic velocities of one electrolyte in a solution can be produced by the presence of small quantities of others, the value of the conductivity, at infinite dilution, of an electrolyte in a complex solution, may be taken to be the same as in a simple solution, provided the complex solution is sufficiently dilute. Hence, in calculating the conductivity of complex solutions which are dilute, the values of $\mu_{\infty 1}$, $\mu_{\infty 2}$, etc., determined by experiments with simple solutions, may be employed. The error involved in employing such values, however, may be expected to increase with the concentration of the solutions.

With regard to (1) and (2), it is the object of this paper to show how the numbers of gramme-equivalents of the electrolytes present in a solution, and their coefficients of ionisation, may in all cases be determined, ideally at least, by the aid of observations on the conductivity of simple solutions only.

According to the dissociation theory, any electrolyte in a solution is partially dissociated into its constituent ions, the state of dissociation being one of equilibrium, provided the frequency with which mole-

cules undergo dissociation is equal to the frequency with which free ions re-combine. The amount of an electrolyte which is dissociated when the equilibrium condition has been attained is, therefore, to be determined by the application of the law of chemical equilibrium, which expresses the equality of the two frequencies just mentioned.

As any electrolyte which is in dissociational equilibrium is to be regarded as being in this state not only throughout the whole volume of the solution, but also throughout any finite part of it, the law of equilibrium may be applied to any such part.

As each electrolyte in a complex solution, with its undissociated and dissociated parts, though disseminated throughout the whole volume, may be regarded as occupying a definite portion of the volume, which we may speak of as its region, the law of equilibrium may be applied either to one such region or to the regions of two or more electrolytes which have ions in common.

We shall consider, first, solutions containing electrolytes which have all a common ion, and, next, the more complex cases of solutions containing two or more electrolytes having no common ion.

CASE I.—SOLUTIONS CONTAINING TWO ELECTROLYTES WITH A COMMON ION.

In such a case the two electrolytes added to the solvent, in preparing the solution, are the only electrolytes present. The numbers of gramme-equivalents (N_1 and N_2) in any given volume of the solution are thus known. Call the electrolytes 1 and 2, respectively. Let b_1, b_2 be the numbers of undissociated, and β_1, β_2 the numbers of dissociated gramme-equivalents of 1 and 2 in the given volume v of the solution, and let v_1, v_2 be the volumes of the regions occupied by them, respectively.

Applying the law of equilibrium to electrolytes 1 and 2 throughout their own regions, respectively, we obtain :

$$(1) \quad \cdots \quad c_1 \frac{b_1}{v_1} = \frac{\beta_1}{v_1} \cdot \frac{\beta_1}{v_1}$$

$$(2) \quad \cdots \quad c_2 \frac{b_2}{v_2} = \frac{\beta_2}{v_2} \cdot \frac{\beta_2}{v_2},$$

where c_1 and c_2 are constants. Applying the law throughout the whole volume, we have :

$$(3) \quad \cdots \quad c_1 \frac{b_1}{v_1 + v_2} = \frac{\beta_1 + \beta_2}{v_1 + v_2} \cdot \frac{\beta_1}{v_1 + v_2},$$

$$(4) \quad \cdots \quad c_2 \frac{b_2}{v_1 + v_2} = \frac{\beta_1 + \beta_2}{v_1 + v_2} \cdot \frac{\beta_2}{v_1 + v_2}.$$

From (1) and (3) we obtain :

$$c_1 \frac{b_1}{\beta_1} = \frac{\beta_1}{v_1},$$

$$c_1 \frac{b_1}{\beta_1} = \frac{\beta_1 + \beta_2}{v_1 + v_2}.$$

Hence

$$\frac{\beta_1}{v_1} = \frac{\beta_1 + \beta_2}{v_1 + v_2},$$

and

$$\frac{\beta_1}{v_1} = \frac{\beta_2}{v_2}.$$

If we combine (2) and (4), we obtain the same result. Hence the sole condition of equilibrium is that the numbers of dissociated gramme-equivalents of the two electrolytes, per unit volume of the regions occupied by them, or the concentrations of the ions of the two electrolytes, shall be equal.

Arrhenius has shown[1] (and the above is but a slightly modified form of his reasoning) that two simple solutions of electrolytes, having a common ion, which undergo no change of volume on being mixed, will also undergo no change in their state of dissociation, provided the concentrations of ions of the simple solutions were equal.

The equations necessary for the determination of the ionisation coefficients, α_1 and α_2, may now be obtained, as follows :—From the definition of a coefficient of ionisation we have :

$$\frac{\beta_1}{v_1} = \frac{\alpha_1 N_1}{v_1} = \frac{\alpha_1}{v_1/N_1} = \frac{\alpha_1}{V_1},$$

if the dilution of an electrolyte in the solution, i.e., the volume per gramme-equivalent, of the region occupied by it, be indicated by V. Similarly,

$$\frac{\beta_2}{v_2} = \frac{\alpha_2}{V_2}.$$

Hence we have

(a) from the condition of equilibrium,

$$\frac{\alpha_1}{V_1} = \frac{\alpha_2}{V_2}.$$

A second equation is obtained from the equality of the volume of the solution to the sum of the volumes of the regions occupied by the electrolytes it contains. Hence, since $v_1 = N_1 V_1$ and $v_2 = N_2 V_2$, we have

(b) from the volume relation,

$$N_1 V_1 + N_2 V_2 = v.$$

Other two equations are furnished by our knowledge that, at a definite temperature, the ionisation coefficients depend upon dilution alone, and

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[1] Ztschr. f. physikal. Chemie, vol. ii., p. 284 (1888).

that, therefore, the concentrations of ions are functions of the dilution
only. Hence we have

(*c*) from the relation of dissociation to dilution,

$$\frac{\alpha_1}{V_1} = f_1 (V_1),$$

$$\frac{\alpha_2}{V_2} = f_2 (V_2).$$

What the functions involved in these equations are, may be determined
from measurements of the specific molecular conductivity of sufficiently
extended series of simple solutions of the respective electrolytes.

We have thus four equations for determining the four unknown
quantities involved, viz., α_1, α_2, V_1, V_2.

These equations may be most conveniently solved by a graphical
process. Draw curves from the experimental data just referred to, having
as abscissæ the concentrations of ions for simple solutions of 1 and 2,
respectively, and as ordinates N_1 and N_2 times the corresponding values
of the respective dilutions. Then select two points, one on each curve,
which have the same abscissa, and which have ordinates the sum of
which is equal to v. Multiply the values of the ordinates of these points,
read off on the scale on which they would represent dilutions, by the
common value of the abscissa, and we have the values of α_1 and α_2.

If the solution have been formed by the mixing of two simple solutions,
and especially if the constituent solutions had equal volumes and were so
dilute as to undergo no appreciable change of volume on mixing, the
graphical process is very easily carried out.[1]

Arrhenius[2] has shown that the conductivity of a complex solution,
containing two electrolytes with one ion in common, may be calculated
by, first, making sufficiently extended series of observations to determine
what simple solutions of the two electrolytes are isohydric with one an-
other (*i.e.*, do not change in their state of dissociation on being mixed),
and, secondly, finding by the aid of these observations, and by a series
of approximations, of what two isohydric solutions the complex solution
might be formed by mixture. Isohydric solutions were recognized as
such by the equality of the specific conductivity of a mixture of equal
volumes of them, to the mean of their specific conductivities. The iso-
hydric constituents of the complex solution having been determined, its
conductivity was the mean of their conductivities. The method was ap-
plicable only to solutions so dilute that there was no appreciable change
of volume on mixing.

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[1] For a detailed account of this graphical process see **Trans. Nova Scotian Inst.
Sci.**, vol. ix., p. 107.

[2] Wied. Ann., xxx., p. 73 (1887).

CASE II.—SOLUTIONS CONTAINING ANY NUMBER OF ELECTROLYTES HAVING A COMMON ION.

In this case also the electrolytes added to the solvent in the preparation of the solution are the only ones present in it, and the N's are thus known. We may indicate the electrolytes in the solution by the numerals $1, 2, \ldots . p$.

Applying the law of equilibrium to the different electrolytes throughout the regions occupied by themselves only, and using the same symbols as above, we obtain a set of equations similar to (1) and (2) of Case I. Applying the law to the various electrolytes throughout the regions occupied by themselves and one other electrolyte, we obtain a set of equations similar to (3) and (4) of Case I. Combining these equations, as in that case, we find that they reduce to

$$(5) \qquad \frac{\beta_1}{c_1} = \frac{\beta_2}{c_2} = \frac{\beta_3}{c_3} = \ldots . = \frac{\beta_p}{v_p}.$$

If we now apply the law to each electrolyte throughout the region occupied by it and two other electrolytes, we obtain a series of equations, such as

$$c_1 \frac{b_1}{v_1 + v_2 + v_3} = \frac{\beta_1 + \beta_2 + \beta_3}{c_1 + c_2 + v_3} \cdot \frac{\beta_1}{c_1 + c_2 + v_3}.$$

These equations, however, are not independent of those already obtained. For from (1) and (5) we have

$$c_1 \frac{b_1}{\beta_1} = \frac{\beta_1}{c_1} = \frac{\beta_1 + \beta_2 + \beta_3}{c_1 + c_2 + c_3}.$$

Hence

$$c_1 \frac{b_1}{v_1 + v_2 + c_3} = \frac{\beta_1 + \beta_2 + \beta_3}{c_1 + c_2 + c_3} \cdot \frac{\beta_1}{c_1 + c_2 + c_3}.$$

Similarly the equations obtained by applying the law to the various electrolytes throughout the regions occupied by themselves and other three, four, etc., electrolytes, may be deduced from such equations as those given above. Hence the sole condition of equilibrium is expressed in equations (5).

For the determination of the coefficients of ionisation we have thus :
(a) from the conditions of equilibrium,

$$\frac{\alpha_1}{V_1} = \frac{\alpha_2}{V_2} = \cdots = \frac{\alpha_p}{V_p} \ldots \ldots . . p - 1 \text{ equations,}$$

(b) from the volume relation,

$$N_1 V_1 + N_2 V_2 + \ldots + N_p V_p = v \ldots . . 1 \text{ equation,}$$

(c) from the relation of dissociation to dilution,

$$
\left.
\begin{aligned}
\frac{\alpha_1}{V_1} &= f_1\,(\,V_1), \\
\frac{\alpha_2}{V_2} &= f_2\,(\,V_2), \\
&\text{etc.}
\end{aligned}
\right\} \quad \cdots \cdots \cdots \cdots \; p \text{ equations,}
$$

in all $2p$ equations, for the determination of p α's, and p V's.

As in the former case, these equations may be most readily solved by a graphical method, curves representing the relation between the concentrations of ions, and N_1, N_2, ... N_p, times the dilutions, being drawn for the respective electrolytes from experimental data with regard to the conductivities of their simple solutions, and points being found on these curves, by inspection, having the same abscissa and having ordinates whose sum is equal to the volume of the solution. The common value of α/V and the values of the dilution, V_1, V_2, etc., of the various electrolytes in the complex solution are thus determined, and the values of the α's may then be found by multiplication.

CASE III.—SOLUTIONS CONTAINING TWO ELECTROLYTES HAVING NO COMMON ION.

In this case there will in general be other electrolytes in the solution besides those added to the solvent in its preparation, these being formed by the process of double decomposition. Thus a solution prepared by the addition of sodium chloride and potassium bromide to water will contain also sodium bromide and potassium chloride. Let 1 and 2 be the electrolytes, with no common ion, from which the solution was prepared;

NaCl (1)	KCl (3)
NaBr (4)	KBr (2)

and let 3 and 4 be those formed by double decomposition. Then one ion of 1 will be common to it and 3, its other ion being common to it and 4; and similarly 2 will have one ion in common with 3 and the other in common with 4. It may assist the imagination to represent the constitution of the solution by the diagram in the margin.

The application of the law of equilibrium to electrolyte 1 throughout its own region gives :

$$
(6) \quad \cdots \quad \cdots \quad c_1\,\frac{b_1}{v_1} = \frac{\beta_1}{v_1}\,.\,\frac{\beta_1}{v_1},
$$

as in Case I. A similar application to the other electrolytes gives three other similar equations. The application of the law to electrolyte 1

throughout the regions occupied by it and 3, and by it and 4, respectively, gives the equations,

$$c_1 \frac{b_1}{c_1 + c_3} = \frac{\beta_1 + \beta_3}{c_1 + c_3} \cdot \frac{\beta_1}{r_1 + c_3},$$

$$c_1 \frac{b_1}{v_1 + c_4} = \frac{\beta_1 + \beta_4}{c_1 + c_4} \cdot \frac{\beta_1}{v_1 + c_4};$$

and a similar application to the other electrolytes gives six other similar equations. These twelve equations may be reduced, as in Case I., to the three independent equations,

$$(7) \quad \cdots \quad \frac{\beta_1}{r_1} = \frac{\beta_2}{c_2} = \frac{\beta_3}{c_3} = \frac{\beta_4}{c_4}.$$

It is, therefore, a necessary condition of equilibrium that the concentrations of ions, in the regions occupied by the four electrolytes, respectively, shall be equal.

We may obtain other equations of equilibrium by expressing the fact that each electrolyte is in equilibrium throughout the whole solution. Thus we obtain for electrolyte 1,

$$(8) \quad \cdots \quad c_1 \frac{b_1}{v} = \frac{\beta_1 + \beta_3}{v} \cdot \frac{\beta_1 + \beta_4}{v},$$

and similar equations for 2, 3 and 4. From (6) we have,

$$c_1 b_1 = \frac{\beta_1}{c_1} \beta_1.$$

and from (8),

$$c_1 b_1 = \frac{(\beta_1 + \beta_3)(\beta_1 + \beta_4)}{v}.$$

Hence

$$\frac{\beta_1}{v_1} = \frac{(\beta_1 + \beta_3)(\beta_1 + \beta_4)}{\beta_1 v}.$$

From the other equations similar to (6) and (8) we obtain :

$$\frac{\beta_2}{c_2} = \frac{(\beta_2 + \beta_3)(\beta_2 + \beta_4)}{\beta_2 c},$$

$$\frac{\beta_3}{v_3} = \frac{(\beta_3 + \beta_1)(\beta_3 + \beta_2)}{\beta_3 c},$$

$$\frac{\beta_4}{v_4} = \frac{(\beta_4 + \beta_1)(\beta_4 + \beta_2)}{\beta_4 c}.$$

From these four equations and (7), we obtain :

$$\beta_2 (\beta_1 + \beta_3)(\beta_1 + \beta_4) = \beta_1 (\beta_2 + \beta_3)(\beta_2 + \beta_4),$$
$$\beta_3 (\beta_1 + \beta_3)(\beta_1 + \beta_4) = \beta_1 (\beta_3 + \beta_1)(\beta_3 + \beta_2),$$
$$\beta_4 (\beta_1 + \beta_3)(\beta_1 + \beta_4) = \beta_1 (\beta_4 + \beta_1)(\beta_4 + \beta_2);$$

and these three, when combined, reduce to

$$\beta_1\beta_2 = \beta_3\beta_4.$$

It is, therefore, also a necessary condition of equilibrium that the products of the numbers of the dissociated gramme-equivalents of the two pairs of electrolytes having no common ion, shall be equal.

This condition may be otherwise expressed. For, by (7),

$$\frac{\beta_1}{c_1}\frac{\beta_2}{c_2} = \frac{\beta_3}{c_3}\frac{\beta_4}{c_4}.$$

Hence,

$$(9) \quad . \quad . \quad . \quad . \quad c_1c_2 = c_3c_4;$$

i.e., for equilibrium, the products of the volumes of the regions occupied by the two pairs of electrolytes having no common ion, must be equal. In the case of a solution containing two electrolytes with no common ion, there are, therefore, four necessary conditions of equilibrium, expressed in equations (7) and (9).

Arrhenius [1] has shown that if a solution containing two electrolytes with no common ion have been prepared as a mixture of four simple solutions of these electrolytes and of the products of their double decomposition, if the simple solutions before mixture had equal concentrations of ions, had such volumes that the products of the volumes of the solutions containing electrolytes with no common ion were equal, and were so dilute that no change of volume occurs on mixing, and if no change occur in the state of dissociation on mixing, the mixture will satisfy the conditions of the equilibrium.

For the determination of the coefficients of ionisation and the numbers of gramme-equivalents of the four electrolytes in any volume v of the solution, we have, therefore, the following equations:

(*a*) from the conditions of equilibrium,

$$\frac{\alpha_1}{V_1} = \frac{\alpha_2}{V_2} = \frac{\alpha_3}{V_3} = \frac{\alpha_4}{V_4} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot 3 \text{ equations;}$$

$$N_1V_1 \cdot N_2V_2 = N_3V_3 \cdot N_4V_4 \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot 1 \text{ equation;}$$

(*b*) from the volume relation,

$$N_1V_1 + N_2V_2 + N_3V_3 + N_4V_4 = v \cdot \cdot \cdot \cdot 1 \text{ equation;}$$

(*c*) from the relation of ionisation to dilution,

$$\left.\begin{array}{l}\dfrac{\alpha_1}{V_1} = f_1(V_1), \\ \text{etc.,}\end{array}\right\} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot 4 \text{ equations.}$$

Although in this case we do not know the values of N_1, N_2, N_3, N_4, we do know the numbers of gramme-equivalents of 1 and 2 added to volume

[1] Ztschr. f. physikal. Chemie, vol. ii., p. 284, (1888).

r of the solution in its preparation. Let these be n_1 and n_2. Then it is obvious that we have,

(d) from the law of the conservation of mass, applied to the process of double decomposition,

$$\left.\begin{array}{l} n_1 = N_1 + N_3 \\ n_1 = N_1 + N_4 \\ n_2 = N_2 + N_3 \\ n_2 = N_2 + N_4 \end{array}\right\} \quad \cdots\cdots\cdots, 3 \text{ independent equations.}$$

since each of these four equations is deducible from the other three.

We have thus in all 12 equations for the determination of 12 unknown quantities, viz., 4 a's, 4 N's, and 4 V's.

To solve these equations by a graphical method, we may first reduce the second, third and last three to two, by eliminating all but one of the N's. We thus obtain:

$$N_3 = \frac{r - V_1 n_1 - V_2 n_2}{V_3 + V_4 - (V_1 + V_2)},$$

and

$$N_3^2 \left(\frac{V_3 V_4}{V_1 V_2} - 1 \right) + N_3 (n_1 + n_2) = n_1 n_2.$$

Now draw curves for all four electrolytes, from experimental data obtained from observations on their simple solutions, with values of the concentration of ions as abscissæ and the corresponding values of the dilution as ordinates. Select what seems a probable value of the common concentration of ions in the complex solution, and read off from the curves the corresponding values of V_1, V_2, V_3, V_4. Determine N_3 from the first of the last two equations by substituting these values in it, and see whether this value of N_3 is, first, a possible value, and, secondly, one that will satisfy the last equation. If not we must make another shot at the common value of the concentration of ions; and so on until a value of N_3 is obtained which does satisfy the last equation. Such a value having been found, the common value of a/V, and the values of V_1, V_2, V_3, V_4, become known, and a_1, a_2, a_3, a_4 may be determined by multiplication. Also n_1, n_2 and N_3 being known, N_1, N_2 and N_4 may be determined from equations (d) above. And thus all the data are available for calculating the conductivity. The application of this method would require that the curves based on the observations on simple solutions should be very accurately drawn. For the denominator of the above expression for N_3 is the difference between the sums of two dilutions, and this difference may be small. Hence even a small error in their determination may lead to a great error in the value of N_3 which is found.

If we wish not to calculate the conductivity of a given solution, but merely to test the dissociation theory by comparing the observed and

calculated values of any solution, it might be better to proceed other-
wise, viz., by determining the constitution of a complex solution of the
electrolytes 1, 2, 3, 4 with a known common concentration of ions. For
this purpose select any value of the concentration of ions and read off
from the experimental curves referred to above the corresponding values
of the dilutions V_1, V_2, V_3, V_4, of simple solutions of 1, 2, 3, 4, selecting
a concentration of ions characteristic of dilute solutions so as to avoid the
complication which would be introduced by change of volume on mixing.
If simple solutions of these dilutions are mixed in proper proportions as
to volume, there will be no change of ionisation on mixing. To find the
proper proportions, select arbitrarily any value of v_4 the volume of the
solution of 4 which is to be mixed with the others. It will contain
$N_4 = v_4/V_4$ gramme-equivalents of 4. From equations (d) above we
must have $N_3 = N_4$. Hence the volume of 3 to be mixed with the others
will be $v_3 = V_3 v_4/V_4$. Next select arbitrarily any value of v_2. Then in
order that there may be no change of ionisation on mixing we must have

$$v_1 = v_3 v_4/v_2 = V_3 v_4^2/V_4 v_2$$

The volumes of the simple solutions of dilutions V_1, V_2, V_3, V_4, which must
be mixed in order to form a complex solution with the selected concen-
tration of ions, are thus known. The solution may therefore be prepared
and its conductivity experimentally determined. The conductivity may
also be calculated. For the concentrations of the simple solutions and the
volumes of them which are mixed being known, the N's may be found;
and the common concentration of ions and the dilutions being known, the
a's may be found. If the densities of the simple solutions are known.
either from the data of published tables or from preliminary experiments,
the numbers, n_1, n_2, of gramme-equivalents of 1 and 2 which must be
added, say, to a kilogramme of water in order to produce the required
complex solution, may be calculated, and the solution may thus be pre-
pared by three weighings, the errors due to measurements of volume
being thus avoided.

Case IV.—Solutions containing Three Electrolytes having no Common Ion.

In this case there will in general be nine electrolytes in the solution,
as illustrated in the diagram, in which the
numbers are given by which we shall indicate
the various electrolytes.

NaCl (1)	HCl (4)	KCl (6)
NaI (5)	HI (2)	KI (8)
NaBr (7)	HBr (9)	KBr (3)

The application of the law of equilibrium
to each electrolyte throughout its own region
gives nine equations, such as,

$$c_1 \frac{b_1}{v_1} = \frac{\beta_1}{v_1} \cdot \frac{\beta_1}{v_1}.$$

Applied to each electrolyte throughout the

region occupied by itself and one other electrolyte having a common ion, it gives thirty-six equations such as,

$$c_1 \frac{b_1}{v_1 + v_4} = \frac{\beta_1 + \beta_4}{v_1 + v_4} \cdot \frac{\beta_1}{v_1 + v_4}.$$

These forty-five equations, however, are not independent, but may be reduced to eight, viz. :

$$(10) \quad \cdots \quad \frac{\beta_1}{v_1} = \frac{\beta_2}{v_2} = \cdots = \frac{\beta_9}{v_9},$$

which are thus necessary conditions of equilibrium.

Applied to each electrolyte throughout the region occupied by itself and two other electrolytes having a common ion, we obtain 18 equations, such as,

$$c_1 \frac{b_1}{v_1 + v_4 + v_6} = \frac{\beta_1 + \beta_4 + \beta_6}{v_1 + v_4 + v_6} \cdot \frac{\beta_1}{v_1 + v_4 + v_6}.$$

These, however, as in Case III., may be deduced from those given above.

Applied to each electrolyte throughout the region occupied by it, another electrolyte having no ion in common with it, and the products of their double decomposition, the equilibrium law gives 36 equations, such as,

$$c_1 \frac{b_1}{v_1 + v_2 + v_4 + v_5} = \frac{(\beta_1 + \beta_4)\,(\beta_1 + \beta_5)}{(v_1 + v_2 + v_4 + v_5)^2}.$$

These equations, when combined, give 9 equations, such as,

$$v_1 v_2 = v_4 v_5,$$

which, however, are not independent, but reduce to four, say,

$$(11) \quad \cdots \quad \begin{cases} v_1 v_2 = v_4 v_5, \\ v_2 v_3 = v_8 v_9, \\ v_5 v_9 = v_2 v_7, \\ v_4 v_8 = v_2 v_6, \end{cases}$$

which thus form additional necessary conditions of equilibrium.

Applied to each electrolyte throughout the whole volume of the solution, the equilibrium law gives 9 equations, such as

$$c_1 \frac{b_1}{v} = \frac{\beta_1 + \beta_4 + \beta_6}{v} \cdot \frac{\beta_1 + \beta_5 + \beta_7}{v},$$

which, however, may be deduced from the twelve equations (10) and (11). These twelve equations thus express the necessary conditions of equilibrium.

For the determination of the ionisation coefficients and the numbers of gramme-equivalents of the nine electrolytes in a solution of this complexity, we have, therefore, the following equations :

(a) from the conditions of equilibrium,

$$\frac{\alpha_1}{V_1} = \frac{\alpha_2}{V_2} = \cdots = \frac{\alpha_9}{V_9} \ldots \ldots \ldots \text{ 8 equations,}$$

$$\left.\begin{array}{l} N_1 V_1 \cdot N_2 V_2 = N_4 V_4 \cdot N_5 V_6, \\ N_2 V_2 \cdot N_3 V_3 = N_8 V_8 \cdot N_9 V_9, \\ \qquad \text{etc.,} \end{array}\right\} \cdots \text{ 4 equations,}$$

(b) from the volume relation,

$$N_1 V_1 + N_2 V_2 + \ldots + N_9 V_9 = v \ldots \text{ 1 equation,}$$

(c) from the relation of ionisation to dilution,

$$\left.\begin{array}{l} \dfrac{\alpha_1}{V_1} = f_1 \, (V_1), \\ \qquad \text{etc.,} \end{array}\right\} \ldots \ldots \ldots \ldots \text{ 9 equations,}$$

(d) from the conservation of mass,

$$\left.\begin{array}{l} n_1 = N_1 + N_5 + N_7, \\ n_1 = N_1 + N_4 + N_6, \\ n_2 = N_2 + N_5 + N_8, \\ n_2 = N_2 + N_4 + N_9, \\ n_3 = N_3 + N_7 + N_9, \\ n_3 = N_3 + N_6 + N_8, \end{array}\right\} \ldots \ldots \ldots \text{ 5 equations,}$$

since each of these last equations may be deduced from the other five. We have thus in all twenty-seven equations for the determination of nine α's, nine N's, and nine V's.

The solution of these equations by the aid of the graphical process referred to above would, of course, be ideally possible; but it would probably be found impossible, with the data as to the conductivity of simple solutions at present at our disposal, to draw the requisite curves, showing the relation of concentration of ions to dilution, with sufficient accuracy for the purpose.

CASE V.—SOLUTIONS CONTAINING ANY NUMBER OF ELECTROLYTES WITH
NO COMMON ION.

If the solution is formed by the addition of p such electrolytes to the solvent, there will be p^2 electrolytes in the solution, as is illustrated in the diagram.

$NaCl$ (1)	HCl (4)	KCl (6)		
NaI (5)	HI (2)	KI (8)		
$NaBr$ (7)	HBr (9)	KBr (3)		

It is unnecessary to write down the equations which may be obtained from the application of the law of equilibrium to the various electrolytes throughout different regions of the solution For, as each electrolyte is in equilibrium in its own region, and each also in the region occupied by it and every other electrolyte having one ion in common with it, we have, as in former cases,

$$\frac{\beta_1}{v_1} = \frac{\beta_2}{v_2} = \cdots \cdot \frac{\beta_p}{v_p},$$

forming a set of $p^2 - 1$ conditions of equilibrium. Also, as each electrolyte is in equilibrium in the region occupied by itself, any other electrolyte having no ion in common with it, and the products of their double decomposition, we have,

$$v_1 v_2 = v_4 v_5,$$
$$v_2 v_3 = v_8 v_9,$$
$$\text{etc.,}$$

forming a set of $(p-1)^2$ conditions of equilibrium. These $2p(p-1)$ conditions are also the only conditions. For if we apply the law of equilibrium to each electrolyte through the whole volume of the solution, we obtain p^2 equations, such as,

$$c_1 \frac{b_1}{v} = \frac{\beta_1 + \beta_4 + \beta_6 + \text{etc.}}{v} \cdot \frac{\beta_1 + \beta_5 + \beta_7 + \text{etc.}}{v},$$

which, as in Case IV., will be found to be deducible from the equations given above.

For determining the ionisation coefficients, and the numbers of gramme-equivalents of the various electrolytes present in the solution, we have therefore:

(a) from the conditions of equilibrium,

$$\frac{\alpha_1}{V_1} = \frac{\alpha_2}{V_2} = \text{etc.}, \cdots \cdots \cdots \cdots \cdots p^2 - 1 \text{ equations,}$$
$$\left. \begin{array}{l} N_1 V_1 \cdot N_2 V_2 = N_4 V_4 \cdot N_5 V_5, \\ \text{etc.} \end{array} \right\} \cdots \cdot (p-1)^2 \text{ equations,}$$

(b) from the volume relation,

$$N_1 V_1 + N_2 V_2 + \text{etc.} = v \ldots\ldots\ldots\ldots \text{1 equation,}$$

(c) from the relation of ionisation to dilution,

$$\left. \begin{aligned} \frac{\alpha_1}{V_1} &= f_1\,(V_1), \\ \text{etc.}, & \end{aligned} \right\} \ldots\ldots\ldots\ldots\ldots p^2 \text{ equations,}$$

(d) from the conservation of mass,

$$\left. \begin{aligned} n_1 &= N_1 + N_5 + N_7 + \text{etc.}, \\ n_1 &= N_1 + N_4 + N_6 + \text{etc.}, \\ \text{etc.}, & \end{aligned} \right\} \ldots\ldots\ldots 2p-1 \text{ equations,}$$

in all, therefore, $3p^2$ equations for determining p^2 α's, p^2 N's, and p^2 V's.

CASE VI.—SOLUTIONS CONTAINING ANY NUMBER OF ELECTROLYTES WITH NO COMMON ION, THE PRODUCTS OF THEIR DOUBLE DECOMPOSITION, AND ANY OTHER ELECTROLYTES.

It is obvious that if in preparing such a solution there are added to the solvent, p electrolytes with no common ion and q other electrolytes, having each, therefore, one ion in common with one of the p electrolytes, there will be $p\,(p+q)$ electrolytes in the solution. Thus, if sodium chloride, hydrogen iodide, potassium bromide and mag-

$NaCl$ (1)	HCl (4)	KCl (6)	$\frac{1}{2}MgCl_2$ (10)	
NaI (5)	HI (2)	KI (8)	$\frac{1}{2}MgI_2$ (11)	
$NaBr$ (7)	HBr (9)	KBr (3)	$\frac{1}{2}MgBr_2$ (12)	

nesium chloride be dissolved in water, the solution will contain the electrolytes specified in the diagram.

As in the last case, it is unnecessary to obtain the conditions of equilibrium. It will be obvious, on the grounds there specified, that we have, as such conditions,

$$\frac{\beta_1}{v_1} = \frac{\beta_2}{v_2} = \frac{\beta_3}{v_3} = \text{etc.},$$

forming a set of $(p\,(p+q) - 1)$ equations, and

$$\begin{aligned} v_1 v_2 &= v_4 v_5, \\ v_6 v_{11} &= v_8 v_{10}, \\ \text{etc.}, & \end{aligned}$$

forming a set of $(p - 1)\,(p + q - 1)$ equations. That the equations of this set are $(p - 1)\,(p + q - 1)$ in number is obvious from the fact that if such equations be written down for each group of four electrolytes represented in the above diagram as occupying contiguous squares, of

which there are $(p-1)$ $(p+q-1)$, similar equations may then be deduced from them for all groups of the electrolytes consisting of two with no common ion and the products of their double decomposition.

That the above $2p$ $(p+q-1) - q$ equations form the only conditions may be shown by deducing from them the equations obtained by applying the law of equilibrium to each electrolyte throughout the whole volume, as, for example,

$$c_1 \frac{b_1}{v} = \frac{\beta_1 + \beta_4 + \beta_6 + \beta_{10} + \text{etc.}}{v} \cdot \frac{\beta_1 + \beta_3 + \beta_7 + \text{etc.}}{v},$$

or, without this trouble, by showing, as is done below, that these equations are sufficient to determine the state of dissociation.

Arrhenius [1] says with regard to this general case : " It is easy to see that if we mix any number mn of combinations of m positive and n negative ions, equilibrium will not be disturbed, provided these mn electrolytes formed isohydric solutions among one another before the mixing, and the product of the active masses [*i.e.*, quantities of dissociated ions] of two electrolytes $I_m J_n$, $I_o J_p$ is equal to the product of the active masses of $I_m J_p$ and $I_o J_n$. This will be the case if the volumes of the isohydric solutions are related to one another as the surfaces in the annexed diagram," in which diagram the surfaces, so far as the eye can judge, are equal. It is obvious that if the volumes occupied by the various electrolytes in the solutions were equal, the second set of equilibrium conditions would be satisfied ; but equality of volumes is not necessary for their satisfaction.

For determining the quantities of the various electrolytes present in the solution, and their ionisation coefficients, we have the following equations :

(*a*) from the equilibrium conditions,

$$\frac{\alpha_1}{V_1} = \frac{\alpha_2}{V_2} = \text{etc.}, \quad \dots \dots \dots \dots \dots \dots \quad p\,(p+q) - 1 \text{ equations.}$$

$$\left. \begin{array}{l} N_1 V_1 \cdot N_2 V_2 = N_4 V_4 \cdot N_5 V_5 \\ \qquad\qquad \text{etc.} \end{array} \right\} \dots \dots (p+q-1)\,(p-1) \text{ equations,}$$

(*b*) from the volume relation,

$$N_1 V_1 + N_2 V_2 + \text{etc.} = v \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \text{1 equation,}$$

(*c*) from the relation of ionisation to dilution,

$$\left. \begin{array}{l} \frac{\alpha_1}{V_1} = f_1\,(V_1), \\ \qquad \text{etc.,} \end{array} \right\} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \quad p\,(p+q) \text{ equations,}$$

(*d*) from the conservation of mass,

$$\left. \begin{array}{l} n_1 + n_{10} + \text{etc.} = N_1 + N_4 + \text{etc.} + N_{10} + \text{etc.} \\ \qquad n_{10} = N_{10} + N_{11} + N_{12} + \text{etc.,} \\ \qquad\qquad \text{etc.,} \end{array} \right\} \dots (2p+q-1) \text{ equs.,}$$

in all $3p\,(p+q)$ equations for determining $p\,(p+q)$ α's, $p\,(p+q)$ N's, and $p\,(p+q)$ V's.

[1] Ztschr. f. physikal. Chemie, vol. ii., p. 284 (1888).

V's.

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The possibility of calculating the conductivity of complex solutions of electrolytes is probably of no practical value; but it affords a means of subjecting the dissociation theory of electrolytes to severe tests, the greater the complexity of the solution the greater being the severity of the test.

With the object of testing this theory, I have calculated[1] the conductivities of a series of solutions containing sodium and potassium chlorides, the conductivities of which had been observed by Bender. The following table gives the results:

Constituent solutions. Gramme-equivalents per litre.		Conductivity of Mixture.		
NaCl.	KCl.	Bender's observed values (corrected).	Calculated values.	Difference per cent.
0·5	0·1875	291	289·5	— 0·52
0·5	0·375	370	373·1	+ 0·84
0·5	0·5	430	426·1	— 0·90
0·5	0·75	540	537·6	— 0·44
0·5	1·5	863	858·3	— 0·54
1·0	0·1875	459	461·4	+ 0·52
1·0	0·375	541	540·6	— 0·07
1·0	0·75	703	701·1	— 0·27
1·0	1·0	808	809·2	+ 0·15
1·0	1·5	1015	1015·2	+ 0·02
1·0	2·0	1209	1200·6	— 0·69
2·0	0·1875	773	773·9	+ 0·12
2·0	1·0	1079	1086·3	+ 0·68
2·0	2·0	1445	1458	+ 0·90
2·0	3·0	1823	1808·6	— 0·79
3·0	1·0	1321	1324	+ 0·23
3·0	2·0	1664	1660	— 0·24
3·0	3·0	2007	1988·7	— 0·91
4·0	0·375	1345	1350·4	+ 0·40
4·0	2·0	1858	1849·3	— 0·47
4·0	3·5	2303	2239·2	— 2·77
4·0	4·0	2432	2345·3	— 3·56

[1] Trans. Nova Scotian Inst. Sci., vol. ix., p. 101: and Phil. Mag. [5], 41, p. 276 (1896).

Mr. D. McIntosh has made a series of observations, in my laboratory, of the conductivity of mixtures of solutions of sodium chloride and hydrochloric acid, and has also calculated their conductivities by the method given above. The following table gives the results :

Constituent solutions. Gramme-equivalents per litre.		Conductivity of mixture.		
HCl.	*NaCl.*	Calculated.	Observed.	Difference per cent.
2	2·02	3020	3008	+ 0·4
2·5	2·02	3489·5	3456	+ 1·0
3·0	2·02	3885	3888	— 0·08
3·5	2·02	4233·5	4260	— 0·6
4·0	2·02	4622·3	4580	+ .1·0
4·5	2·02	4944	4880	+ 1·3
1	1·04	1751	1752	— 0·005
1·5	1·04	2373	2332	+ 1·7
2·0	1·04	2928·3	2900	+ 0·9
2·5	1·04	3428·5	3398	+ 0·9
3·0	1·04	3906	3872	+ 0·9
3·5	1·04	4340·7	4316	+ 0·6
4·0	1·04	4715	4700	+ 0·3
4·5	1·04	5055	5036	+ 0·4
·4	·607	829·8	838	— 1·0
·5	·607	983·4	976	+ 0·8
·6	·607	1125·5	1116	+ 0·8
·7	·607	1255	1250	+ 0·4
·8	·607	1384·7	1388	— 0·2
·9	·607	1524·6	1525	— 0·025
1·0	·607	1658·6	1656	+ 0·16
1·1	·607	1787·6	1784	+ 0·2
1·2	·607	1917·1	1913	+ 0·2

[1] Trans. Nova Scotian Inst. Sci., vol. ix., p. 120 ; and Phil. Mag. [5]. 41, p. 510 (1896).

It will be observed that in both the above series of comparisons the agreement between the observed and the calculated values is very satisfactory for the more dilute solutions. As pointed out above, the more concentrated the solutions. the more must the ionic velocities of each electrolyte be modified by the presence of other electrolytes in the solution, and the greater, therefore, must be the error involved in taking the specific molecular conductivity at infinite dilution, determined by experiments on simple solutions as being its value when the electrolyte exists in a complex solution.

I am engaged at present, with the assistance of students in my laboratory, on a series of observations and calculations of the conductivity of solutions containing two electrolytes with no common ion. We hoped to have them ready in time to include the results in the present paper, but have been prevented from completing them at a sufficiently early date.