IV.—On finding the Ionization of Complex Solutions of given Concentration, and the Converse Problem: *By* Prof. J. G. MacGregor, *Dalhousie College, Halifax, N. S.*

In a paper communicated to this Institute in 1895,[1] I described a method of determining the ionization coefficients of two electrolytes, with one ion in common, in the same dilute aqueous solution. The method described was developed in the study of complex solutions which had been formed by the mixture of simple solutions of known concentration, and involves a knowledge of their concentrations. Even if the complex solutions have not been formed in this way, but have been prepared, say, by the addition of known quantities of the electrolytes to a known quantity of water, they may always be imagined to have been formed by mixture of simple solutions; and in the usual case in which the solutions are so dilute that no change of volume would have occurred in forming them by mixture, the concentrations of the simple solutions by the mixing of which the given complex solution might be formed, can readily be determined. But a simple modification of the method renders it applicable in such cases directly; and when so modified, its application is found both to require fewer data with respect to the conductivity of simple solutions of the electrolytes involved, and to be subject to fewer sources of error, than in its old form. As modified also, it is found to be readily applicable conversely to the determination of the concentration which such complex solutions must have in order that they may have any given possible state of ionization.

In the present paper, I wish to describe this modified form of the method, and to point out how it may be used in deter-

[1]Trans. N. S. Inst. Sci., 9, 101, 1895-96: See also Phil. Mag. (5), 41, 276, 1896, and Trans. Roy. Soc. Can., (2), 2, sec. 3, 65, 1896-7.

mining concentration when state of ionization is given. And I take this opportunity also, of comparing it with two other methods which have recently been employed, of determining the ionization coefficients for solutions of the same degree of complexity.

Determination of the ionization, concentrations being given.

It was shown in the papers cited above, that if the two electrolytes in a complex solution may be supposed to occupy distinct portions or regions of the solution, if the law of kinetic equilibrium may be supposed to be applicable both to these regions singly and to the whole volume of the solution, and if the concentration of ions of each electrolyte in its own region may be supposed to depend at a given temperature on the dilution of the electrolyte in its region, merely, and to depend on dilution in the same way as in the case of a simple solution of the same electrolyte, the relations between the ionization coefficients, the amounts of the electrolytes present, and the dilutions which they must be supposed to have in their fictitious regions, may be expressed by four equations. If we denote the electrolytes by 1 and 2, the concentrations (in gramme-equivalents per litre) of the solution with respect to them by N_1 and N_2 respectively, their ionization coefficients by a_1 and a_2 and their regional dilutions (in litres per gramme-equivalent) by V_1 and V_2 respectively, these equations take the form :

$$\frac{a_1}{V_1} = \frac{a_2}{V_2}, \qquad . \qquad . \qquad . \qquad . \quad (1)$$

$$N_1 V_1 + N_2 V_2 = 1, \qquad . \qquad . \qquad . \qquad . \quad (2)$$

$$\frac{a_1}{V_1} = f_1(V_1), \qquad . \qquad . \qquad . \quad (3)$$

$$\frac{a_2}{V_2} = f_2(V_2), \qquad . \qquad . \qquad . \quad (4)$$

the functions f_1 and f_2 being determinable by means of sufficiently extended observations of the conductivity of simple solutions of 1 and 2 respectively.

The first equation is given by the law of kinetic equilibrium. It may be expressed as follows: The regional ionic concentrations of the two electrolytes, $i.\ e$, the numbers of their free gramme-ions per unit volume of their respective regions, are equal. The second states that the volume of the solution is equal to the sum of the volumes of the regions of the respective electrolytes. The third and fourth assert that the regional ionic concentrations are functions of the respective regional dilutions.

As f_1 and f_2 are very complex functions, these equations could not be solved algebraically even if the functions were known. They can be solved graphically, however, without actually determining what the functions are.

For this purpose we first find, from conductivity observations made on simple solutions of 1 and 2 respectively, corresponding values of dilution and ionic concentration for a sufficient number of solutions of each, and plot dilution-ionic-concentration curves, $i.\ e.$, curves with dilutions as ordinates and ionic-concentrations as abscissæ. To get precise values of the ionization coefficients for the complex solutions, these curves must be accurately drawn. They have, very roughly speaking, the shape of rectangular hyperbolas, and thus, both at great dilution and at great concentration, have but slight curvature, while at moderate dilution they have very rapid curvature. In working with solutions at moderate dilution therefore, it is necessary to have a considerable number of corresponding values of dilution and ionic concentration, in order to plot the curves accurately. When but few are available, it is helpful to plot first a concentration-ionic-concentration curve, $i.\ e.$, one having concentrations of solutions as ordinates and ionic-concentrations as abscissæ. As the dilution-ionic-concentration curves are something like rectangular hyperbolas, the concentration-ionic-concentration curves have comparatively slight curvature, and thus lend themselves readily to interpolation. Corresponding values of concentration and ionic concentration obtained from these curves, when the concentrations are transformed into dilutions, may be used to eke out the values

obtained from the few available observations. In some cases also Kohlrausch's[1] observation may be utilised, viz., that the curves obtained by plotting equivalent conductivity against linear concentration (*i. e.*, the cube root of the concentration), are for univalent salts, through considerable ranges, practically rectilinear.

The dilution-ionic-concentration curves, having been drawn for the simple solutions (curve A for electrolyte 1, and B for 2, in the figures below), the problem resolve itself into finding two points, one on each curve, having, according to equation (1), the same abscissa, and having ordinates which satisfy the condition of equation (2). This may be done of course by inspection, but more accurately, and usually more quickly, by one or other of several graphical processes.
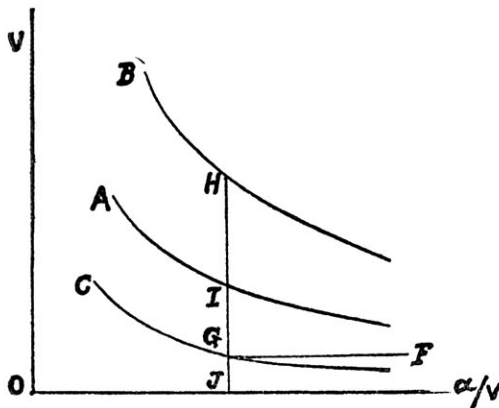

Fig. 1.

(1.) Plot a new curve C (Fig. 1) with the same abscissæ as A and B, but with ordinates equal to the sum of N_1 times the ordinates of A and N_2 times the ordinates of B. Then draw the straight line F G parallel to the axis of ionic concentrations and at a distance unity from it (I assume for simplicity that the dilutions and ionic concentrations have been plotted to the scale unity). Let F G cut C in G; and through G draw the straight line G J parallel to the axis of dilutions and cutting A and B in I and H respectively. I and H are the two points required. For they have the same abscissa O J, and their ordinates, I J and H J, are such that

$$N_1 . IJ + N_2 . HJ = GJ = 1.$$

Then $a_1 = OJ . IJ$, and $a_2 = OJ . HJ.$

[1]Wied. Ann., 26, 201, 1885.

(2.) As equation (2) may be written :

$$V_1 + \frac{N_2}{N_1} V_2 = \frac{1}{N_1},$$

we may proceed as follows :—

Fig. 2.

Plot a new curve D (Fig. 2) with the same abscissæ as A and B, but with ordinates equal to the sum of the ordinates of A and N_2/N_1 times the ordinates of B. Draw K L parallel to the ionic-concentration axis and at a distance $1/N_1$ from it, and let it cut D in L. Draw
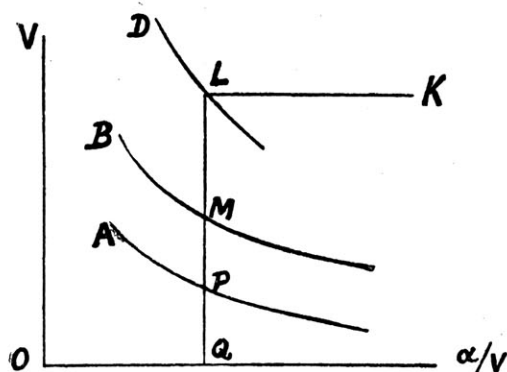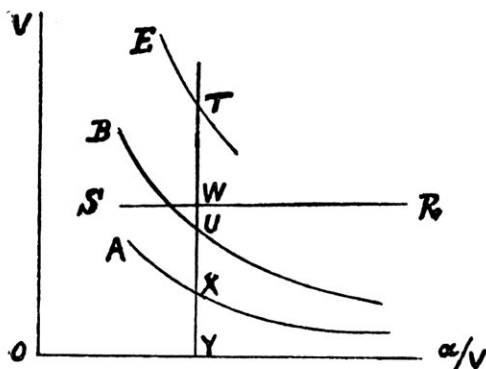
L Q parallel to the dilution axis and cutting A and B in P and M respectively. P and M are the two points required. For they have the same abscissa O Q, and their ordinates, P Q and M Q, are such that

$$PQ + \frac{N_2}{N_1} MQ = LQ = \frac{1}{N_1}.$$

Then $a_1 = OQ \cdot PQ$, and $a_2 = OQ \cdot MQ$.

Fig. 3.

(3) Plot a new curve E (Fig 3), having the same abscissæ as A and B, but with ordinates equal to N_2/N_1 times the ordinates of B. Draw R S parallel to the axis of ionic concentrations and at a distance from it of $1/(2 N_1)$. Find, by inspection, the line T Y parallel to the axis of

dilutions, of which the intercept T X, between the curves A and
E, is bisected by R S, W being the point of bi-section. Let T Y
cut B in U. X and U are the points required. For they have
the same abscissa O Y, and their ordinates, X Y and U Y, are
such that

$$X Y + \frac{N_2}{N_1} U Y = 2 W Y = \frac{1}{N_1}.$$

Then $a_1 = O Y. X Y$, and $a_2 = O Y. U Y$.

The second and third of these methods involve less arith-
metical work, and are less liable to error, than the first, and the
second does not require the procedure by inspection which is
required by the third. The second is therefore the most satis-
factory. But the limited area of co-ordinate paper frequently
gives the third a practical advantage.

Only such portions of the curves A, B, C, D, E, need be drawn
of course as may be seen by inspection to be required for the
purpose in hand.

Determination of the concentration, when the required ionization is given.

The determination of the concentration which must be given
a complex solution in order that it may have any required state
of ionization, is of importance as facilitating the conducting
of research based on the dissociation theory of electrolysis.

It is not sufficient for the determination of the concentra-
tion which the solution must have with respect to the two
electrolytes, that the required ionization coefficients a_1 and a_2
should be given, because they are not independent. For a given
value of a_1 the regional ionic concentration of electrolyte 1 has
a determinate value, which may be found by plotting a curve
for simple solutions of 1, with ionization coefficients as ordinates
and ionic concentrations as abscissæ. The regional ionic con-
centration of electrolyte 2, must by equation (1) be the same as
that of electrolyte 1 ; and since it is thus determined, the ioniza-
tion coefficient, a_2, can have but one value which may be found
by the aid of an ionization-coefficient-ionic-concentration curve

for electrolyte 2. Thus any one of the quantities a_1, a_2, and the common regional ionic concentration, which is of course equal to the total ionic concentration of the whole solution, being given, the others may be found, if we have sufficient data as to the conductivity of the simple solutions.

Even if the ratio only of the ionization coefficients is given, the state of ionization is in many cases completely determined. For as

$$\frac{a_1}{V_1} = \frac{a_2}{V_2},$$

we have

$$\frac{a_1}{a_2} = \frac{V_1}{V_2},$$

and the dilution-ionic-concentration curves are frequently of such forms that a given value of V_1/V_2 corresponds to a definite value of V_1 and V_2, which may be found by inspection of the curves.

Some datum in addition to the state of ionization is therefore requisite, if the concentration of the solution is to be fully determined. It may be the concentration with respect to one of the electrolytes, or the ratio of the concentrations with respect to the two, or the total concentration, or any such function (the conductivity for example) of the concentrations with respect to the two. If the state of ionization is not fully given, an additional datum is obviously required.

(1.) Given the required state of ionization and the concentration with respect to one electrolyte : to find the concentration with respect to the other.—A and B (Fig. 3) being the dilution-ionic-concentration curves, O Y is given ; and N_1 being also given, we have only to find N_2/N_1 in order to determine N_2. From Y draw Y T parallel to the dilution-axis, cutting A and B in X and U respectively. Draw the line R S parallel to the axis of ionic concentrations and distant from it by $1/(2 N_1)$. Let R S cut Y T in W. Cut off W T equal to X W. Then T Y/U Y will be the value of N_2/N_1. (The curve E in Fig. 3 is of course not required.)

(2.) Given the required state of ionization and the ratio of

the concentrations with respect to the two electrolytes : to find the concentrations.—As before, O Y (Fig. 3) is given. From Y draw Y T parallel to the dilution axis, making it of such length that $T Y/U Y$ is equal to the given ratio of the concentrations N_2/N_1. Bisect X T in W. Then

$$W Y = \frac{1}{2 N_1}, \text{ and } N_1 = \frac{1}{2 \, WY}.$$

N_2 also may therefore be found.

(3.) Given the required state of ionization and the total concentration $(N_1 + N_2)$ or the difference of the concentrations $(N_1 - N_2)$: to find N_1 and N_2.—The state of ionization being given, not only are a_1 and a_2 known, but also the total ionic concentration, $a_1 N_1 + a_2 N_2$, which is equal to the regional ionic concentration common to the two electrolytes. N_1 and N_2 may therefore be determined.

(4.) Given the required state of ionization in a solution which is to have a given conductivity : to find the concentrations N_1 and N_2.—As in (3), a_1, a_2, and $a_1 N_1 + a_2 N_2$ are known. The conductivity is expressed by the equation :

$$k = a_1 N_1 \mu_{\infty 1} + a_2 N_2 \mu_{\infty 2},$$

the μ_∞'s being the equivalent conductivities, at infinite dilution, of simple solutions of 1 and 2, and being thus known. N_1 and N_2 may therefore be determined.

Other methods of determining the ionization for complex solutions.

(1.) Schrader[1] has attempted to determine the ionization coefficients for solutions containing two electrolytes with a common ion, by a combination of observations of their conductivity and their electrolysis. The expression of the dissociation theory for the conductivity of such a solution may be put into the form :

$$k = a_1 N_1 \mu_{\infty 1} \left(1 + \frac{a_2}{a_1} \frac{N_2 \mu_{\infty 2}}{N_1 \mu_{\infty 1}}\right) = a_2 N_2 \mu_{\infty 2} \left(1 + \frac{a_1}{a_2} \frac{N_1 \mu_{\infty 1}}{N_2 \mu_{\infty 2}}\right).$$

[1] Zur Elektrolyse von Gemischen, Inaug. Diss., Berlin, 1897.

As $a_1 N_1$ and $a_2 N_2$ are the numbers of gramme-equivalents of dissociated molecules of (1) and (2) respectively in unit volume of the solution, and as $\mu_{\infty 1}$ and $\mu_{\infty 2}$, the respective equivalent conductivities at infinite dilution, of simple solutions of 1 and 2, may in sufficiently dilute solutions, whether simple or complex, be regarded as equal to the velocity of either ion, relative to the other, of 1 and 2 respectively, the quantity $a_2 N_2 \mu_{\infty 2} / a_1 N_1 \mu_{\infty 1}$ may be taken to be the ratio of the number of gramme-ions of 2 and 1 separating out primarily at the appropriate electrode, during electrolysis. This ratio Schrader determined by electrolytic observations. Calling it x, we have :

$$a_1 = \frac{k}{N_1 u_{\infty 1} (1 + x)},$$

$$a_2 = \frac{kx}{N_2 \mu_{\infty 2} (1 + x)}.$$

The values of the ionization coefficients obtained in this way are affected not only by the error involved in the measurement of conductivity, but by the more serious error involved in electrolytic determinations. They cannot be expected therefore to have any high degree of precision.

While Schrader determined the ionization coefficients for solutions containing potassium chloride and iodide, and hydrogen and copper sulphates, and drew certain conclusions from their relative magnitudes in each case, he made no attempt to test the values obtained. They cannot of course be tested by applying them to the calculation of the conductivity of the solutions or the results of their electrolysis ; for these have been used as data in their determination. But they may be tested by being compared with the values given by the method described above. For the values given by this method have stood the test of application to the calculation of the conductivity[1], results of

[1] MacGregor: Trans. N. S Inst. Sci., 9, 101, 1895-6.
McIntosh : Ibid. 9, 120, 1895-96.
Archibald : Ibid. 9, 291 and 307, 1897-98 ; and Trans. Roy. Soc. Can., (2), 3, sec. 3, 69, 1897-98.
McKay : Trans. N. S. Inst. Sci., 9, 321 and 343, 1897-98.
Barnes : Ibid., 10, 49, 1898-99.

electrolysis[1], lowering of the freezing point[2], specific gravity and other physical[3] properties, of complex solutions, in all cases in which the attempt has been made, except in the case of Schrader's solutions containing copper sulphate and sulphuric acid, in which there can be little doubt that the acid sulphate had formed. In the case of Schrader's solutions of potassium iodide and chloride, his observations of conductivity and his electrolytic observations have been shown to be consistent with calculability though they are not sufficiently precise to demonstrate it. We may thus fairly test Schrader's electrolytically determined ionization coefficients by comparing them with those obtained by the above method.

I have accordingly determined the coefficients for the four solutions examined by him, and they are given in the following table. In determining them I have used Kohlrausch's observations of the conductivity of simple solutions, and as the equivalent conductivities at infinite dilution, not Kohlrausch's most recent determinations, but those employed by Schrader. As Schrader does not state at what temperature he made his observations, he may be supposed to have made them at ordinary laboratory temperature, which is not far removed from Kohlrausch's temperature, 18° C.

Concentration (gr.-eq. per litre) with respect to		IONIZATION COEFFICIENTS.					
		SCHRADER'S.		MINE.		Difference per cent.	
K I.	K Cl.	K I.	K Cl.	K I.	K Cl.	K I.	K Cl.
.02595	.02571	.857	.868	.915	.897	− 6.3	− 3.2
.03442	.04748	.866	.892	.886	.866	− 2.3	+ 3.0
.03074	.06176	.861	.857	.879	.860	− 2.0	− 0.3
.01992	.03720	.819	.901	.907	.890	− 9.7	+ 1.2

[1] MacGregor: Trans. Roy. Soc. Can., (2). 4, sec. 3, 117, 1898-99.
[2] Archibald: Trans. N. S. Inst. Sci , 10, 33, 1898-99.
[3] MacGregor: *Ibid.* 9, 219, 1896-97.
   Archibald: *Ibid.*, 9, 335, 1897-98.
   Barnes: *loc. cit.*

It will thus be seen that Schrader's coefficients differ from mine by various amounts up to about 10 per cent., being in most cases smaller, but in some greater. It should be noted also, that while my coefficients are in all cases greater for the iodide than for the chloride, Schrader's are in three out of four cases greater for the chloride than the iodide.

(2) Kay[1] has recently employed an approximation method based upon one previously used by Arrhenius. As a first approximation the ionization coefficients of the two electrolytes in a complex solution were assumed to be the same as they would be in simple solutions of concentration equal to the total concentration of the complex solution. The total concentration of ions of the complex solution (equal to the regional ionic concentrations of the respective electrolytes) was then calculated, and gave a first approximation to the value of the regional ionic concentration. From curves plotted with ionization coefficients of simple solutions as ordinates and ionic concentrations of the same solutions as abscissæ, the values of the ionization coefficients corresponding to the first approximation to the regional ionic concentrations were read off and formed second approximations to the ionization coefficients required. Calculation of the second approximation to the total ionic concentration and a repetition of the above procedure gave a third approximation to the ionization coefficients. In dealing with solutions containing sulphuric acid and a neutral sulphate, he found that in general the second approximation was so close to the first that a third was not necessary ; and he seems to have found that the third in no case differed appreciably from the second.

As, in the case of electrolytes with a common ion, the variation of ionization with dilution is in general not very different, this method may be expected to give very closely approximate results. By way of a test I have made a few determinations for solutions containing zinc and potassium sulphates, using Kohlrausch's conductivity data. The result is shown in the following table in which zinc sulphate is indicated by 1 and

[1] Proc. R. S. Edin., 22, 502, 1898-99.

potassium sulphate by 2, concentration in gramme-equivalents per litre by N, and ionization coefficient by a.

N_1	N_2	By Kay's Method.								By My Method.	
		1st Approx.		2nd Approx.		3rd Approx.		4th Approx.			
		a_1	a_2	a_1	a_2	a_1	a_2	a_1	a_2	a_1	a_2
.01	.03	.509	.799	.469	.807	.470	.808	....	....	.469	.807
.01	.04	.457	.759	.407	.766	.408	.767	....	....	.404	.777
.002	.2	.342	.658	.281	.658	.282	.658	....	....	.280	.659
.2	.002	.342	.658	.341	.712	.341	.712	....	....	.341	.712
.4	.1	.276	.583	.259	.636	.260	.637	.260	.636	.256	.639

The above table shows that for the solutions to which it applies, the ionization coefficients given by Kay's method agree closely with those given by mine, the differences being in no case greater than a little over 1 per cent., and in most cases a small fraction of 1 per cent. It is worth noting that in the cases in which a difference exists, the second approximation values of Kay's method are in general less divergent from mine than those given by higher approximations.

If Kay's method involved considerably less labour than mine it would be worth while to carry out a more extensive comparison in order to determine its general trustworthiness. But the saving of labour, after a little practice with my method, is so slight, that such a comparison is uncalled for. In cases in which either the available data do not admit of the determination of precise values of the ionization coefficients or only approximate values are desired, sufficiently good values may be obtained, with somewhat less trouble, by the use of Kay's method. But in cases in which precise values are desired, and the data are sufficiently exact to give them, the more exact method is to be preferred, notwithstanding the slightly greater labour which it involves.