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THE EFFECT OF CONCENTRATION AND IONIZATION
ON THE RATES OF DIFFUSION OF SALTS
IN AQUEOUS SOLUTION.¹

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I. INTRODUCTION.

ACCORDING to the modern theory of solutions the osmotic pressure in a solution is proportional to the concentration of the solute. If now there is a difference of osmotic pressure between two points, there is a tendency for the solute to move from the region of higher to that of lower pressure, and the rate of this movement is proportional directly to the difference in pressure or concentration and inversely to the resistance of the medium. If the amount of the solvent is large in comparison with that of the solute this resistance is independent of the concentration of the substance. In the case where an ordinary inorganic salt is the solute the simplicity of this relation may be influenced by the change

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taking place with change of concentration in the character of the solute due to ionization. The ions in a solution act osmotically in a manner similar to the undissociated molecules, exerting a pressure proportional to their concentration ; but the frictional resistance which they encounter is different from that of the undissociated substance. Although any difference in the resistance to the motion of the separate ions would tend to cause the faster one to diffuse more rapidly and thus separate it from the others, yet it is held back by the great electrostatic charge which would thus be generated, so that a positive and negative ion of the substance must move together ; but the resultant effect will in general be to produce a rate of diffusion different from that of the undissociated part.

Assuming that the salt was totally ionized Nernst in 1888¹ derived an expression for the rate of diffusion based upon values of the equivalent conductance of the ions as determined by transference and conductivity measurements at great dilution. These calculated values checked very well with experimentally found ones when the experiments were carried on at great dilutions but deviated more and more as the concentration increased. This variation is probably due to the increasing part taken in the diffusion by the undissociated substance as the concentration increases ; and it is the purpose of this investigation to determine the difference in mobility existing between the dissociated and undissociated portions of the solute.

In order to simplify the calculations, the work was restricted to the case of diffusion in one direction only. This was accomplished by using a cylindrical tube filled with pure water at the start, but having a saturated solution at the bottom, thus allowing the diffusion to take place against gravity. The concentration changes were determined by measurement of the electrical conductivity at different points along the tube after various intervals of time. These values substituted in the proper formula allowed the separate diffusion constants of the ions and of the undissociated substance to be calculated. The salts thallium sulphate and barium nitrate were selected as they are to a large extent undissociated in 0.100 normal solutions.

¹Z. Phys. Chem., 2, 613, 1888.

2. THEORETICAL PRINCIPLES RELATING TO DIFFUSION.

General Law of Diffusion.—Although osmotic phenomena as such were not recognized until a later date, its principles were first applied to diffusion by Fick, who in 1854,¹ expressed the law that the quantity of salt which diffuses through a given area is proportional to the difference between the concentrations of two areas infinitely near to each other. That is, if we take two points in a solution at an infinitesimal distance apart dx , the difference in concentration at these two points will be dc and hence the concentration gradient in the direction x will be $\partial c/\partial x$. Fick's law states that, for the case when the diffusion is in one direction only, as occurs when it is allowed to take place in a cylinder, the amount of solute dS which will cross a given cross-section a in a time dt is expressed by

$$dS = -Da \frac{\partial c}{\partial x} dt \quad (1)$$

or the rate of change by

$$\frac{dS}{dt} = -Da \frac{\partial c}{\partial x}. \quad (2)$$

The minus sign here denotes that the solute diffuses in the direction of decreasing concentration. D is the so-called diffusion-constant or specific diffusion-rate; it is equal to the amount of solute which would diffuse across unit area under a concentration gradient of unity in unit time if the rate were constant during that time. In this work the time is expressed in days, the concentration in equivalents per liter, and the distance in centimeters.

In the above equation we have two independent variables x and t , and two dependent ones S and c . By the following considerations we can reduce the dependent variables to one. Consider an infinitesimal volume in a cylinder bounded by planes at the distance x and $x+dx$. The amount of solute which will accumulate in this volume in time dt will be the difference in the amount which will cross the planes at x and at $x+dx$. This may be written $-\partial(dS)/\partial x \cdot dx$ since the amount which will cross at $(x+dx)$ equals

$$\left(dS + \frac{\partial(dS)}{\partial x} dx \right).$$

¹Pogg. Ann., 94, 59, 1855.

The increase in concentration of the solute in time dt in this volume then is the total accumulation divided by the volume or

$$\frac{-\frac{\partial(dS)}{\partial x} dx}{a dx}.$$

As this may also be expressed by the quantity $\partial c/\partial t \cdot dt$ we get

$$\frac{\partial c}{\partial t} dt = -\frac{1}{a} \frac{\partial(dS)}{\partial x}.$$

Substituting for dS its value $-Da \cdot \partial c/\partial x \cdot dt$ given by Fick's law, carrying out the differentiation, and eliminating dt we get as our reduced equation for the case the cross-section is uniform

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}. \quad (3)$$

This equation is analogous to that of Fourier for the flow of heat, and has different solutions according to the conditions imposed by the methods of carrying out the diffusion. If in a tube so long as to be practically infinite, so far as the time of an ordinary experiment is concerned, the concentration is held constant at one end and is zero at the other, and if at the start the concentration is zero throughout the tube, we may obtain by solving the differential equation under the assumption that D is constant the following expression for the concentration c at any point x after any time t .

$$c = c_0 \left(1 - \frac{2}{\sqrt{\pi}} \int_0^u e^{-u^2} \right) \quad (4)$$

where c_0 is the constant concentration at the lower end, and

$$u = \frac{x}{2\sqrt{Dt}}.$$

Knowing the value c for any point we can inversely calculate D the diffusion constant. If D is not constant for all values of c , as is the case if the assumption of the different rates of diffusion of the dissociated and undissociated substances is true, another formula must be developed which will take this fact into consideration.

Diffusion of Completely Ionized Substances. — Assuming the solute to be totally dissociated Nernst in 1888¹ derived theoretically an expression for D in terms of the ionic velocities as computed from transference and conductivity data for the case of a salt splitting into two univalent ions. For the more general case in which the salt is completely dissociated into any number of ions of any valence, an expression may be similarly derived,² as follows :

Let us take an electrolyte whose formula weight yields on complete dissociation n_c mols of cations of valence v_c and n_a mols of anions of valence v_a . The product of the number of mols of each ion by its valence is necessarily the same for both the positive and negative ions ; or $n_c v_c = n_a v_a$. If C is the concentration in formula weights per liter, the number of ions having the same electrical sign is $n_c C$ for the cation and $n_a C$ for the anion ; and correspondingly, the concentration-gradients for the cation and anion are $n_c dC/dx$ and $n_a dC/dx$, respectively. As the osmotic pressure of the ions is expressed by $P = nCRT$, the force acting across unit area through the distance dx in the positive direction of x is the difference between the force P at x and $P + dP$ at $x + dx$ or is

$$- n_a RT \frac{dC}{dx} dx \quad \text{and} \quad - n_c RT \frac{dC}{dx} dx$$

for the anions and cations respectively. This is the force that acts upon the ions in the volume dx that is upon $n_a C dx$ and $n_c C dx$ mols of anions and cations so that the force acting upon one mol will be

$$\frac{- n_a RT \frac{dC}{dx} dx}{n_a C dx} = \frac{- n_c RT \frac{dC}{dx} dx}{n_c C dx} = - \frac{RT}{C} \frac{dC}{dx} \quad (5)$$

it being therefore identical for both the anion and cation.

Now, since the friction against the solvent is different for the different ions one ion would tend to get ahead of the other. This, however, would generate an electrostatic field between the positive and negative ions, which field in turn would accelerate the slower ion and retard the more rapidly moving one. Let us consider the

¹ Loc. cit.

² For this derivation I am indebted to Professor A. A. Noyes.

electric potential generated to be E , then the electric force acting upon one mol of cation or anion is $-v_c F \cdot dE/dx$ or $+v_a F \cdot dE/dx$ respectively, where F is one faraday of electricity. The total force acting upon one mol, therefore is:

$$-RT \frac{1}{C} \frac{dC}{dx} - v_c F \frac{dE}{dx} \text{ for the cations,} \quad (6)$$

$$-RT \frac{1}{C} \frac{dC}{dx} + v_a F \frac{dE}{dx} \text{ for the anions.} \quad (7)$$

Let u_c and u_a be the velocities of each ion when the force acting upon one mol is unity, and let dN_c and dN_a be the number of mols of each ion passing a cross-section a in the time dt , then under the above force

$$dN_c = u_c a n_c C \left(-RT \frac{1}{C} \frac{dC}{dx} - v_c F \frac{dE}{dx} \right) dt, \quad (8)$$

$$dN_a = u_a a n_a C \left(-RT \frac{1}{C} \frac{dC}{dx} + v_a F \frac{dE}{dx} \right) dt. \quad (9)$$

But

$$\frac{dN_c}{n_c} = \frac{dN_a}{n_a}, \quad (10)$$

since equivalent quantities of the two ions must pass through any section in the same time, therefore

$$u_c \left(RT \frac{1}{C} \frac{dC}{dx} + v_c F \frac{dE}{dx} \right) = u_a \left(RT \frac{1}{C} \frac{dC}{dx} - v_a F \frac{dE}{dx} \right) \quad (11)$$

or

$$F \frac{dE}{dx} = - \left(\frac{u_c - u_a}{u_c v_c + u_a v_a} \right) \frac{RT dC}{C dx}. \quad (12)$$

If this value and equation (8) or (9) is substituted in equation (10) above we have

$$\frac{dN_c}{n_c} = dN = -aRT \frac{dC}{dx} \left(\frac{u_a u_c (v_a + v_c)}{u_c v_c + u_a v_a} \right) dt, \quad (13)$$

where dN is the number of formula weights passing cross-section in time dt . If instead of formula weights we use equivalent weights, since one formula weight equals $n_c v_c$ or $n_a v_a$ equivalents, and

$U_c = u_c v_c$ and $U_a = u_a v_a$ represent the velocities when unit-force acts on one equivalent weight of ions we obtain by substitution and reduction

$$dS = -aRT \frac{dc}{dx} \frac{U_a U_c}{U_a + U_c} \left(\frac{1}{v_c} + \frac{1}{v_a} \right) dt, \quad (14)$$

where dS is the number of equivalents crossing in time dt , and where dc/dx represents the concentration-gradient in equivalents.

By a comparison of this formula with the expression of Fick's law (equation 1) we see that we can express D in terms of quantities derived from electrical measurements or

$$D = RT \frac{U_a U_c}{U_a + U_c} \left(\frac{1}{v_c} + \frac{1}{v_a} \right), \quad (15)$$

provided, of course, we assume that the solute is totally dissociated, and hence all diffusion is done by the ions only. This condition is approached only in very dilute solutions and hence D is the limiting value at infinite dilution. At other concentrations the value of D as found from Fick's formula will be greater or less according as the undissociated substance diffuses faster or slower than the ions. As a general rule the diffusion constant has been shown to become larger as the dilution is increased and hence we believe that the ions move more rapidly than the undissociated portion.

Diffusion of Partly Ionized Substances.—As shown above, in the case of diffusion of a simple substance, the amount of solute which will diffuse across any plane of cross-section a in the time dt may be expressed by the equation

$$dS = -Da \frac{\partial c}{\partial x} dt.$$

A dissociated solute diffuses in two parts, the dissociated and undissociated, and during an infinitesimal time the parts may be considered as moving independently, each having its own diffusion coefficient.¹ Hence we can say that the total amount crossing the area is equal to the sum of the two parts, that is,

$$dS = dS_1 + dS_2, \quad (16)$$

¹ Nernst, Z. Phys. Chem., 2, 634, 1888

where dS_1 and dS_2 represent the number of equivalents of un-ionized substance and of ionized substance, respectively.

$$dS = -D_1 a \frac{\partial c_1}{\partial x} dt - D_2 a \frac{\partial c_2}{\partial x} dt, \quad (17)$$

where c_1 and D_1 refer to the undissociated portions and c_2 and D_2 to the dissociated. As the ions must move together they will not have separate diffusion constants and D_2 will be the constant corresponding to the whole dissociated portion. By reasoning similar to that applied to the general equation we get

$$\frac{\partial c}{\partial t} = \frac{-\frac{\partial(dS)}{\partial x} dx}{adx} = -\frac{1}{a} \frac{\partial(dS)}{\partial x} = \frac{\partial^2 c_1}{\partial x^2} D_1 + \frac{\partial^2 c_2}{\partial x^2} D_2 + \left(\frac{\partial c_1}{\partial x} D_1 + \frac{\partial c_2}{\partial x} D_2 \right) \frac{\partial a}{\partial x}. \quad (18)$$

If the tube is uniform, $\partial a / \partial x = 0$, and we obtain

$$\frac{\partial c}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} + D_2 \frac{\partial^2 c_2}{\partial x^2}. \quad (19)$$

Equation (19) is an expression in five variables, of which x and t are independent. It can be considerably simplified with the help of the relation between the concentrations c , c_1 and c_2 . Storch¹ and others have found that this relation can be almost exactly expressed between 0.100 normal and zero concentration by an equation of the form $c_1 = Kc_2^n$ (20) where n varies somewhat with the salt but has always approximately the value 1.5. We have also of course $c = c_1 + c_2$.

From these functions we get

$$\begin{aligned} \frac{\partial c}{\partial t} &= \frac{\partial}{\partial t}(c_2 + Kc_2^n) = \frac{\partial c_2}{\partial t}(1 + Kn c_2^{(n-1)}), \\ \frac{\partial c_1}{\partial x} &= Kn c_2^{(n-1)} \frac{\partial c_2}{\partial x}, \\ \frac{\partial^2 c_1}{\partial x^2} &= Kn \left[c_2^{(n-1)} \frac{\partial^2 c_2}{\partial x^2} + (n-1)c_2^{(n-2)} \left(\frac{\partial c_2}{\partial x} \right)^2 \right]. \end{aligned}$$

¹Z. Phys. Chem., 19, 13, 1896.

Substituting these ratios in equation (19) we obtain an expression in c_2 , t , and x .

$$\begin{aligned} (1 + Kn c_2^{(n-1)}) \frac{\partial c_2}{\partial t^2} = D_2 \frac{\partial^2 c_2}{\partial x^2} \\ + D_1 \left\{ Kn \left[c_2^{(n-1)} \frac{\partial^2 c_2}{\partial x^2} + (n-1) c_2^{(n-2)} \left(\frac{\partial c_2}{\partial x} \right)^2 \right] \right\}. \quad (21) \end{aligned}$$

If a suitable solution can be found for this equation which will satisfy the conditions of the experiment, the constants D_1 and D_2 could be determined provided we measure the concentrations at various points along the tube at definite times. As yet a method of integrating this equation has not been found, and the equation has therefore been used in its differential form. Empirical expressions can be determined which express the concentration as a function of the distance at the time of each measurement, and also other expressions which express the concentration as a function of the time at the distance of each electrode in the tube. By differentiating these expressions with respect to the distance and time respectively we can obtain differential coefficients which when substituted in the differential equation (21), will give a series of simultaneous equations containing as unknowns D_1 and D_2 , the diffusion constants.

Since the concentrations were determined from conductances, as will be described in section 4, it was found more convenient in the experiments to change the dependent variable from c_2 to L , where L is the specific conductance and is equal to the product of c_2 into A_0 , the equivalent conductance at zero concentration. Making this substitution we obtain as our equation

$$\begin{aligned} \left[1 + Kn \left(\frac{L}{A_0} \right)^{n-1} \right] \frac{1}{A_0} \frac{\partial L}{\partial t} = D_2 \frac{1}{A_0} \frac{\partial^2 L}{\partial x^2} \\ + D_1 \left[Kn \left\{ \left(\frac{L}{A_0} \right)^{(n-1)} \frac{1}{A_0} \frac{\partial^2 L}{\partial x^2} + (n-1) \left(\frac{L}{A_0} \right)^{(n-2)} \frac{1}{A_0^2} \left(\frac{\partial L}{\partial x} \right)^2 \right\} \right]. \quad (22) \end{aligned}$$

This can be reduced to

$$(1 + K_2 L^{n-1}) \frac{\partial L}{\partial t} = D_2 \frac{\partial^2 L}{\partial x^2} + D_1 \left[K_2 L^{n-1} \left\{ \frac{\partial^2 L}{\partial x^2} + (n-1) \frac{1}{L} \left(\frac{\partial L}{\partial x} \right)^2 \right\} \right]$$

(23)

where

$$K_2 = \frac{Kn}{A_0^{n-1}}.$$

With this equation if the law expressing the relation between the conductance and concentration of the substance is known and the specific conductances at different points along the tube are measured, the partial derivatives in respect to time and distance at each point and time can be found. Substituting these in the equation above (23) an expression is obtained in which D_2 and D_1 are the only unknowns.

$$P = QD_2 + RD_1. \quad (24)$$

A number of these expressions found for different times and distances can be combined by applying the method of least squares and the most probable values of D_1 and D_2 , the specific diffusion rates can be thereby obtained.

3. WORK OF PREVIOUS INVESTIGATORS.

A large number of articles have been published dealing with the theory of diffusion or with rough quantitative measurements of it. References to these will be found in the footnote.¹ A fuller mention of the recent more exact work of Öholm² is however appropriate, since his results for the first time show with some degree of accuracy the effect of integrated concentration intervals on the values of the specific diffusion rates.

His apparatus consisted of a cylindrical tube about 25 cm. long and 3.5 cm. in diameter. Pure water was run in until it filled three fourths of the tube, and under this was run a layer of salt solution of known content. After standing for a time the solution was drawn off at the bottom in four portions and analyzed. By means of the tables of Stefan³ and Kawalki⁴ he calculated the diffusion-constants for varying initial concentrations of his diffusing

¹Graham, Phil. Trans., 1, 805, 1850; 483, 1851. Fick, Pogg. Ann., 94, 59, 1855. Simmler and Wild, Pogg. Ann., 100, 217, 1857. Graham, Phil. Trans., 151, 183, 1861. Weber, Wied. Ann., 7, 469, 536, 1879. Stefan, Wien. Akad., 79, 161, 1879. Schaffer, Berichte, 15, 788, 1882; 16, 1903, 1883. Nernst, Z. Phys. Chem., 2, 613, 1888. Voigtlander, Z. Phys. Chem., 3, 316, 1889. Wiedeburg, Wied. Ann., 41, 675, 1890. Wiedeburg, Z. Phys. Chem., 10, 512, 1892. Arrhenius, Z. Phys. Chem., 10, 51, 1892. Bose, Z. Phys. Chem., 29, 658, 1899. Wiedeburg, Z. Phys. Chem., 30, 586, 1899. Graham, Z. Phys. Chem., 50, 257, 1904. Öholm, Z. Phys. Chem., 50, 309, 1904.

²Öholm, Z. Phys. Chem., 50, 309, 1904.

³Stefan, Wien. Akad., 79, 161, 1879.

⁴Kawalki, Wied. Ann., 52, 166, 1894.

solution. He found the same gradation in their values that others had found, and believed it to be mainly due to the change in dissociation, but not entirely, since he found that after a certain concentration was reached the value of the diffusion-constant increased with increasing concentration. This could be accounted for by consideration of Van der Waals' equations. He also came to the conclusion that the temperature-coefficient was equal to the sum of the coefficients of osmotic pressure and electric conductivity, as the kinetic theory requires. By considering measurements of internal friction he came to the conclusion that the internal friction of the molecule was greater than that of the ion, but slightly less than that of the sum of the ions. He also checked Nernst's formula almost exactly.

4. EXPERIMENTAL METHOD USED IN THE INVESTIGATION.

In order to approach the ideal conditions of diffusion in one direction only, these experiments were carried on in a cylindrical tube held in a vertical position so that the direction of motion of the solute was opposite to the force of gravity. It was found by calculation from known values of diffusion that the force exerted by gravity is negligibly small compared with that exerted by osmotic pressure, and hence as a direct force it would not enter;¹ but if the tube were not perpendicular, as the solute diffused there would be produced by gravity a density-gradient in a direction different from that along the axis of the tube, making measurement uncertain.

¹ As seen in equation (7) the osmotic force acting upon one formula weight of salt is equal to $RT/c \cdot dc/dx$. Assuming the general solution

$$c = c_0 \left[1 - \frac{2}{\sqrt{\pi}} \int_0^u e^{-u^2} du \right] \quad \text{where} \quad u = \frac{x}{2\sqrt{Kt}}$$

and assuming values of K , x and t which will make dc/dx smaller than that found at any place used in our measurements, that is, $K=1$, $t=49$, $x=8$, we obtain

$$\text{Osmotic force} = RT \frac{-\frac{1}{4} \cdot \frac{2}{\sqrt{\pi}} e^{-(.57)^2}}{\left[1 - \frac{2}{\sqrt{\pi}} \int_0^{.57} e^{-u^2} du \right]} = 0.12RT = 3 \times 10^9 \text{ dynes.}$$

The force of gravity on one formula weight or 504 grams of Tl_2SO_4 is $504 \times 980 = 4.94 \times 10^5$ dynes; and taking into account the buoyancy of the water the effective force would become considerably less than this.

From the values of the diffusion-constants already determined by other investigators, it was found by calculation, assuming equations (3) and (4), that after three months' time the concentration of solute at a distance of 50 cm. from the foot of the tube would be less than 0.1 per cent. of that at the bottom. Hence within the limits of error of the experiment a tube 50 cm. high would act as if it were infinite in length. The lower end of the tube contained solid salt so that the concentration there was that of the saturated solution, while, by starting with pure water throughout the whole length of the tube, the other end was practically held at zero concentration. To determine the concentrations at different points, pairs of platinized wire electrodes were inserted at definite intervals along the tube and the electrical conductivity between the electrodes of each pair was measured. Each pair was in a plane perpendicular to the axis of diffusion; and the separate wires were near enough together so that the conductivity measured was that corresponding to the concentration at the mean distance of the electrode pair from the lower end of the tube, or from the plane of the solid salt. If the two electrode wires had not been placed near together, as there was a concentration-gradient across each pair which was not linear, the reading would have corresponded to a concentration higher than that present at the mean distance of the wires. In order to ascertain what error was introduced into the calculation by the assumption that the mean distance of the electrode pair was that corresponding to the conductance or concentration measured, an experiment was made in which the upper level of a column of uniformly conducting solution within the tube was lowered until the electrode pair was nearly uncovered. It was found when the upper level of the solution was one millimeter above a pair of wires 4 mm. apart, that the conductance between the wires was about thirty per cent. less than that found when the tube was full. By a calculation assuming formula (4) we see, if $x = 10$, $K = 1$, $t = 25$, and therefore $u = 1.00$ that $c = 0.1574c_0$. If $x = 10.3$ and 9.7 the values of c at those points are $0.1452c_0$ and $0.1701c_0$, respectively. As for such a small change in concentration the rate of change of dissociation with the concentration can be considered a constant, the average of the conductances at the points 10.3 and 9.7 will correspond to the average of their concentrations. This

latter will be $0.1576c_0$ or will correspond to point $x = 9.994$ instead of $x = 10.000$. This would make an error of 0.06 of a millimeter; but, as the distances between the electrodes at the best cannot be determined closer than 0.1 millimeter, this error is negligible. This deviation moreover would be in the same direction for all the electrodes and would in this way tend to eliminate itself in the calculations after the experiment has proceeded for a considerable time, and even more so if the wires were placed nearer together.

It was decided to carry on the experiments in a tube about 50 cm. long and 5 cm. in diameter; but, as it was thought impracticable to insert the electrodes through such a large tube, a smaller one, 1.5 cm. in external diameter, was placed at the axis of the large tube holding the electrodes and containing the lead wires within it. To seal in such large wires as it would be necessary to use would result in protuberances that would cause large deviations in the cross-section of the tube; so holes 3 mm. apart and 1 mm. in diameter, just large enough to pass the wire through, were bored in the small tube by means of a diamond and the whole held firmly in place by filling the small tube with a mixture consisting of 95 per cent. shellac and 5 per cent. ceresin.

This mixture was found the most suitable of several which were tried. Paraffin although the best insulator was not firm enough at 30° to keep the electrodes in place and at that temperature it slowly flowed out between the glass and the electrodes, so covering the latter as to change the cell-constants. No other pure hydrocarbon seemed satisfactory, as none would stick sufficiently to the glass to prevent the formation of an annular space between the glass and the body of the filling material, when the tubes were allowed to cool. Rosin in itself is too brittle; but when mixed with a little paraffin it is still firm and adheres to glass very well, giving fair results. It, however, is slowly attacked by water, thus allowing the solution to work its way into the small tube and around the electrodes and lead wires. Gum shellac seemed to have the best adhesive properties; and, when mixed with about 5 per cent. of a high melting paraffin like ceresin, it sticks firmly to the glass, does not flow, and is attacked very slightly by boiling water. This shellac was prepared from the commercial gum shellac by first dis-

solving it in alcohol, filtering, and then precipitating by adding water to the alcoholic solution. This it was believed would throw down only that portion very insoluble in water. To further obviate, as far as possible, any error which might result from the solubility of the shellac, the precipitate from the alcohol-water solution was boiled repeatedly with conductivity water until a water solution, containing one fourth of its volume of shellac, showed a rise in specific conductance of only 2 or 3×10^{-6} reciprocal ohms after heating for about two or three hours upon a steam bath. As the only shellac surface exposed during a diffusion experiment was that between the wires and the glass, and as, by way of further precaution this space was filled as far as practicable with ceresin, it is believed that very little contamination came from this source.

The electrode wires were one millimeter in diameter and extended about one centimeter beyond the outer surface of the inner tube. The distance between the two wires of a single pair was made about 3.0 mm. The distances between the successive electrode pairs were measured by a cathetometer to 0.1 mm. Although the attempt was made to bore the two holes for a single pair of electrodes in a plane perpendicular to the axis of the tube, this was not always fully successful, so the distance of an electrode pair was taken as the mean distance of upper and lower points of both ends of both wires. This allowed for all deviations in the position of the wires provided they were approximately parallel to each other and perpendicular to the tube. The large outer tubes were calibrated with mercury to determine any deviations in cross-sections; but the variation was so small that it gave rise to an error of less than 0.2 per cent. and was therefore neglected. This small variation was secured by selecting tubes that showed less than 0.1 mm. variation in diameter in 10 cm. length. All tubes were of Jena glass.

For fear that a definite line of saturated solution would not be maintained at the bottom of the tube, holes were bored through the outer tube so that their tops were level with the lowest pair of electrodes. The lower end of the tube was then placed in a beaker containing a saturated solution and a large excess of solid salt above the line of holes, thus keeping by gravity a saturated solution at the line of the lowest electrodes, from which line the distances along

the tube were measured. The top of the beaker was closed airtight by melting into it a mixture of rosin and paraffin.

The elevation of one of the tubes is shown in Fig. 1.

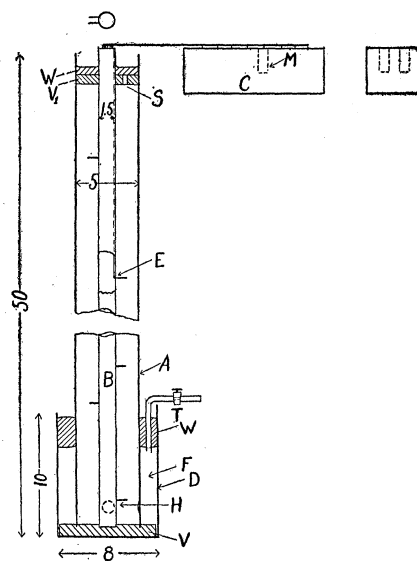


Fig. 1.

A is the outer tube, *B* the inner one containing the electrodes *E*, and *C* a slate block serving as commutator and containing the mercury cups *M* to which the wires lead from the platinum electrodes. *D* is the outside beaker containing the solid salt *F* and saturated solution into which the large outer tube *A* is placed. *H* shows the holes through which the saturated solution flows by gravity keeping a constant concentration at the plane of their tops. *V* and *V*₁ are vulcanite blocks which hold the two tubes and beaker in their proper positions. *T* is a tube for drawing off the solution at the start, *W* is a filling mixture of shellac or rosin and paraffin, and *S* is a hole in the vulcanite top for the introduction of pure water.

In making up an inner tube the method of procedure is as follows: A Jena glass tube of very uniform diameter equal to about 1.5 cm. and having comparatively thin walls (about 1 mm.) is selected. Pairs of holes 1 mm. in diameter and 3 mm. apart are

bored with a diamond drill at distances approximately 2, 10, 13, 16, 19, 22, 25, and 32 cm. from the end. These distances are purely arbitrary; but the aim is to have them about 3 cm. apart after the second electrode. The last electrode should be so placed that it is in the upper part of the diffusion apparatus, and is used only as a means of determining the extent of any stirring and contamination, because no appreciable amount of salt can reach there by diffusion until about six weeks have elapsed. Platinum wires 1 mm. in diameter and about 2 cm. long are bent at right angles about the middle or a little beyond, and insulated copper wires are soldered to the shorter end. These electrodes and leads are then put in place beginning with the upper pair, by putting the free end of the lead wire through the inner tube until the electrode comes opposite to the hole into which it is desired to place it. It is advisable before cutting the platinum wire to platinize it several times, burning in the black each time in a blast lamp flame. This gives a rough surface and makes the final platinization more satisfactory.

After all the pairs of electrodes are fastened in their proper position on the outside by means of screw clamps, a thick hot alcoholic solution of pure shellac (without ceresin) is run into the tube until the inside of the glass is thus coated with a thin layer of the solution. A current of air is then passed through the tube, evaporating the alcohol and leaving a thin layer of shellac on the inside of the glass and lead wires. This is baked on in a hot closet with frequent passage of air and then the process is repeated several times. By this means a layer of shellac is formed on the glass which does not break away when the tube is cooled. Finally the tube is filled solid with the melted mixture of shellac and ceresin.

The clamps can now be removed and the wires cleaned and platinized. In one of the tubes a coating of iridium black was put on instead of platinum, as it was found to give a much better minimum in making the conductivity measurements; but it is very hard to make the iridium black stick satisfactorily and therefore platinum is preferable.

The wires from the electrodes are led to a commutator block consisting of eight pairs of mercury cups in a block of slate.

The outer tube is ground flat on one end and four holes 1 cm. in

diameter are cut through it in such a manner that when the two tubes are fitted to the vulcanite base, the tops of the holes will be in the same plane as the lower electrode pair of the small tube. The vulcanite top V_1 is also fitted and a hole large enough to pass a glass tube is cut through it.

The two tubes are then put together temporarily, corking the large holes H , and the cell constants of the electrode pairs are determined at 30° with a 0.02 normal solution of potassium chloride or some other solution of known conductance.

In starting an experiment the two tubes are fitted into the block V and into the beaker D as shown in Fig. 1. The lower end of the outer tube up to the lowest electrodes and the beaker about half way up are filled with solid salt. The tube T is put in place and some form of packing, such as a rubber ring, is fitted down upon the salt, then a melted mixture of shellac or rosin and paraffin is poured on top of the packing in order to make the whole airtight and rigid. Water is added by means of a long tube through S very slowly in order to diminish stirring; and as soon as a point along the tube is reached where the added water shows very low conductance, the solution is drawn off at the tube T , at the same time adding water at the top at an equal speed until the lowest electrodes show only slight conductance. The tube T is then closed, the hole S is corked and a shellac mixture run on top of V_1 to make it tight. The time of starting is taken when the tube T is shut off. The whole is then placed in a thermostat held at 30° and measurements of the conductance at each electrode pair are made every few days. It is better if possible to place the apparatus in the thermostat before completing the drawing off and to have the pure entering water at a little above 30° .

The form and arrangement of the thermostat needs explanation. The first experiment was made with the diffusion apparatus immersed in a large water bath kept at constant temperature by an electric heater and regulator which was easily able to keep the water constant to within 0.02 or 0.03° C. The water level of the bath was kept about 5 cm. below the top of the outer tube, which made it at least 5 cm. above the level of the liquid within the tube. The upper part of the tube B led out through the cover of the

thermostat and the commutator block was placed on top of the cover where it would be dry. The experiment was started; but it was found after a few days that the upper electrodes showed a large conductance and also that they all seemed to have about the same conductance. The first inference was that the solution was being contaminated by the dissolving of the glass, shellac, etc., and much time was spent trying to find some way of making tubes made out of or coated with ceresin work successfully. But these seemed to give the same results and about to the same degree. It was finally discovered that by keeping the lead wires at the same temperature as the thermostat the trouble almost ceased, and therefore that the contamination was due to stirring caused by the conduction of heat by the copper-lead wires from around the inner tube to the outside of the bath, thus producing a denser solution in the region close to the electrodes and causing stirring by gravity. This was obviated by enclosing the lead wires and commutator block in an air space which was also kept at a constant temperature by a regulator and heater. Two successful experiments were carried on in this way, but in the last experiment another form of thermostat was used. This consisted of an air space $60 \times 40 \times 30$ cm. surrounded on five sides with a water jacket 8 cm. in thickness which was kept at constant temperature. The tubes, wires, and block were all placed in this air space and the sixth side was closed with double glass plates separated by 2 cm. of asbestos feathers, and outside of all by two heavy asbestos boards. The air within the space was stirred by a small motor which ran intermittently and the temperature of the surrounding water was kept just enough above 30° (about 30.15°) so that the temperature within was $30.00^{\circ} + .05$. The commutator block was reached by a rod carrying properly spaced lead wires so that after the experiment was started the thermostat did not have to be opened. In this form of thermostat it is to be noted that changes of temperature of the outer bath are taken up so slowly by the air and by the diffusion tubes, since the air has such a low heat-capacity, that large changes of temperature in the outer bath produce no error by stirring in the tubes. On one occasion the heating apparatus failed during the night and the temperature fell about 10° ; but no stirring was apparent even after the temperature had been brought back to 30° again.

5. EXPERIMENTAL DATA.

Four series of experiments or runs were carried out according to the procedure described in the preceding section. In two of these thallium sulphate and in two barium nitrate was used as the diffusing electrolyte. These salts were chosen because their solubilities were between normal and tenth normal, thus giving concentrations at the electrodes which not only were measurable by means of conductivity, but which also followed the law of Storch.¹ Two runs were started on each substance in order to test the ability of the method to give concordant results. In the second run on each substance the air bath form of thermostat was used in order to eliminate if possible the stirring which was evident in the first experiments. On account of a slight leak in the second tube with barium nitrate the results with it were not satisfactory and are not given below.

In Table I. are given the distances of each pair of electrodes from the bottom and their cell-constants determined both before and after each run. These cell-constants were determined by measuring in the tube at 30° a 0.02000 normal potassium chloride solution made up at 18°. The value of the specific conductance of potassium chloride was taken as 0.003036 reciprocal ohms.

In Tables II., III. and IV. are given the actual conductances during the diffusion experiments measured at the different electrodes at the times indicated. The times are expressed in days and fractions of a day. The electrode distances are in centimeters.

In order to determine what correction must be applied to the actual conductance on account of the contamination to the solution from the glass, electrodes, shellac, etc., a blank run was made for two months using conductivity water. The increase in specific conductance in 30 days was found to be about 6 to 8×10^{-6} reciprocal ohms. This value did not seem to increase much for the next 30 days. In the first thallium sulphate run no attempt was made to correct for the slight stirring which apparently occurred because it was impossible to tell how far down the tube it extended. In the second run between the times 4.29 and 7.25 the thermostat had to be opened and some stirring resulted. In this case it was

¹Loc. cit.

corrected for because it seemed to be uniform along the whole tube. In Table V. the corrections applied to the specific conductance are given and in Tables VI., VII. and VIII. are given the final corrected values of specific conductance used in the calculations.

In order to determine the constants in the concentration law $c_1 = Kc_2^n$, series of measurements of conductance were made upon the two salts at 30°.

If for c_1 and c_2 are substituted their values,

$$c_1 = L \left(\frac{1}{A} - \frac{1}{A_0} \right) \quad \text{and} \quad c_2 = \frac{L}{A},$$

the above expression changes to

$$\frac{1}{A} - \frac{1}{A_0} = \frac{K}{A_0^n} (L)^{n-1}$$

in which L and A are the specific and equivalent conductances at corresponding concentrations, A_0 the equivalent conductance at zero concentration and K and n empirical constants. By applying the following conductance values to this equation and solving several simultaneously not only were K and n calculated but also A_0 . This seems to be the best method to determine A_0 as the solutions used are dilute and the law holds to as great dilution as measurements can be made accurately.

Concentration.	Ti ₂ SO ₄ .		Ba(NO ₃) ₂	
	Δ Found.	Δ Calc.	Δ Found.	Δ Calc.
0.8550 ¹			61.8	67.1
0.2458 ²	90.7	87.7		
0.1000	104.8	104.6	100.6	100.6
0.0500	116.9	117.3	110.3	110.4
0.02000	132.4	132.4	121.6	121.7
0.01000	142.3	142.2	128.0	128.6
0.004000	152.4	152.4	135.8	135.6
0.002000	158.4	158.2	139.4	139.4
Δ ₀		173.4		149.8
n		1.55		1.53
K		3.079		2.052

¹Sat. Sol. Ba(NO₃)₂.

²Sat. Sol. Ti₂SO₄.

TABLE I.

Values of Cell Constants. Thallium Sulphate. Run No. 1.

Electrode Distance.	8.28	11.40	14.25	17.31	20.29	23.21	33.25
Cell Constant before Run	1.092	0.9738	1.044	0.8774	0.9137	0.9007	0.7504
After Run	1.101	0.9795	1.043	0.8788	0.9124	0.9000	0.7511

Thallium Sulphate. Run No. 2.

Electrode Distance.	11.13	13.98	17.04	20.02	22.94	32.98
Cell Constant before Run	0.9694	1.035	0.8718	0.9097	0.9001	0.7501
After Run	0.9743	1.038	0.8748	0.9099	0.8991	0.7543

Barium Nitrate. Run No 1.

Electrode Distance.	8.52	11.63	14.69	17.80	20.78	30.80
Cell Constant before Run	1.003	0.9160	0.9162	0.7554	0.8778	0.9346
After Run	1.007	0.9111	0.9166	0.7571	0.8758	0.9404

TABLE II.

Thallium Sulphate. Run No. 1. Values of Actual Conductance. Reciprocal Ohms $\times 10^6$.

Time.	Electrode Distance.						
	8.28	11.40	14.25	17.31	20.29	23.21	33.25
0.00	12	14	10	6	4	4	3
2.00	30	15	11	7	5	6	4
4.88	641	80	12	7	5	6	5
8.00	1,882	476	82	15	8	8	7
14.00	4,454	1,821	585	181	24	19	17
17.67	5,186	2,702	1,064	432	115	27	22
20.84	5,998	3,427	1,509	711	223	41	41
24.87	6,798	4,251	2,080	1,119	429	140	58
27.72	7,340	4,817	2,493	1,433	594	217	74
30.75	7,796	5,334	2,896	1,739	799	353	87
33.61	8,206	5,795	3,273	2,107	1,009	471	132
36.11	8,513	6,169	3,587	2,405	1,199	583	149
38.89	8,890	6,594	3,936	2,726	1,418	729	169
42.06	9,219	6,988	4,296	3,080	1,672	912	209
45.07	9,515	7,358	4,625	3,409	1,914	1,083	250
48.13	9,811	7,725	4,952	3,745	2,168	1,268	342
51.07	10,010	8,004	5,222	4,033	2,392	1,431	365
52.71	10,210	8,230	5,406	4,219	2,533	1,536	390

TABLE III.

*Thallium Sulphate. Run No. 2. Values of Actual Conductances.
Reciprocal Ohms $\times 10^6$.*

Time, Days.	Electrode Distance.					
	11.13	13.98	17.04	20.02	22.94	32.98
0.00	23	13	10	5	7	5
4.29	81	16	15	10	13	12
7.25	314	30	34	27	29	32
10.24	942	206	48	31	32	35
16.25	2,393	873	346	88	38	43
22.08	3,730	1,693	863	306	116	50
27.26	4,798	2,444	1,435	599	262	59
31.02	5,448	2,954	1,864	852	405	68
36.07	6,258	3,624	2,471	1,237	644	80
41.32	6,977	4,232	3,061	1,646	920	97
46.38	7,593	4,809	3,633	2,063	1,223	149
50.00	7,986	5,176	4,022	2,357	1,445	205

TABLE IV.

*Barium Nitrate. Run No. 1. Values of Actual Conductance.
Reciprocal Ohms $\times 10^6$.*

Time.	Electrode Distance.					
	8.52	11.63	14.69	17.80	20.78	30.80
0.00	18	22	8	7	6	4
3.06	225	37	23	26	13	10
6.75	2,716	446	72	41	22	17
9.91	5,825	1,552	312	48	29	23
13.95	9,450	3,695	1,022	267	55	35
17.19	11,960	5,391	1,859	593	122	47
19.83	13,820	6,913	2,711	1,041	259	56
22.75	15,610	8,482	3,687	1,622	443	81
25.15	16,850	9,694	4,522	2,171	664	92
27.93	18,230	11,080	5,495	2,867	977	108
30.90	19,530	12,430	6,539	3,659	1,352	135
34.00	20,690	13,750	7,602	4,533	1,793	169
37.06	21,850	14,990	8,644	5,428	2,273	256

The unit of concentration was taken one equivalent per liter. The values of A must therefore be divided by 1,000 when used in the equations. The values given in columns 2 and 4 are the means of several independent determinations which agreed among them-

TABLE V.

*Correction to Specific Conductances for Initial Conductance and Contamination.
Reciprocal Ohm $\times 10^6$. Thallium Sulphate. Run No. 1.*

Electrode Distance.	8.28	11.40	14.25	17.31	20.29	23.21	33.25
After 25 days	15	16	13	10	8	8	7
After 50 days	19	20	17	14	12	12	12

Thallium Sulphate. Run No. 2.

Electrode Distance.	11.13	13.98	17.04	20.02	22.94	32.98
After 20 days	31	27	28	26	27	25
After 50 days	33	29	30	28	29	27

Barium Nitrate. Run No. 1.

Electrode Distance.	8.52	11.63	14.69	17.80	20.78	30.80
After 20 days	36	32	16	10	8	6
After 40 days	45	34	18	12	10	8

TABLE VI.

*Thallium Sulphate. Run No. 1. Corrected Values of Specific Conductances.
Reciprocal Ohms $\times 10^6$.*

Time.	Electrode Distance.						
	8.28	11.40	14.25	17.31	20.29	23.21	33.25
0.00	0	0	0	0	0	0	0
2.00	20	11	0	0	0	0	0
4.88	688	64	2	0	0	0	0
8.00	2,043	448	74	6	1	0	0
14.00	4,853	1,758	598	11	9	6	5
17.67	5,652	2,616	1,100	370	98	23	9
20.84	6,540	3,322	1,563	615	197	30	25
24.87	7,439	4,136	2,158	972	383	118	37
27.72	8,037	4,690	2,589	1,249	535	188	49
30.75	8,542	5,196	3,010	1,517	722	310	58
33.61	8,996	5,648	3,403	1,839	913	415	92
36.11	9,334	6,015	3,730	2,101	1,086	516	104
38.89	9,750	6,431	4,094	2,383	1,286	647	119
42.06	10,118	6,819	4,469	2,693	1,517	811	148
45.07	10,446	7,183	4,812	2,981	1,739	965	179
48.13	10,770	7,542	5,153	3,277	1,969	1,130	247
51.07	11,000	7,819	5,434	3,529	2,174	1,277	264
52.71	11,220	8,041	5,626	3,691	2,301	1,377	281

TABLE VII.

*Thallium Sulphate. Run No. 2. Corrected Value of Specific Conductance.
Reciprocal Ohms $\times 10^6$.*

Time.	Electrode Distance.					
	11.13	13.98	17.04	20.02	22.94	32.98
0.00	0	0	0	0	0	0
4.29	52	0	0	0	0	0
7.25	274	5	2	2	2	2
10.24	883	186	15	3	3	3
16.25	2,290	878	274	56	8	8
22.08	3,595	1,728	726	252	78	13
27.26	4,635	2,505	1,224	519	209	20
31.02	5,265	3,032	1,599	748	336	25
36.07	6,052	3,727	2,128	1,099	551	34
41.32	6,751	4,354	2,643	1,470	799	46
46.38	7,349	4,953	3,141	1,849	1,071	85
50.00	7,731	5,333	3,481	2,117	1,281	128

TABLE VIII.

*Barium Nitrate. Run No. 1. Corrected Values of Specific Conductance.
Reciprocal Ohms $\times 10^6$.*

Time.	Electrode Distance.					
	8.52	11.63	14.69	17.80	20.78	30.80
0.00	0	0	0	0	0	0
3.06	203	10	7	2	2	2
6.75	2,706	374	54	20	9	8
9.91	5,832	1,390	271	27	17	14
13.95	9,510	3,254	921	192	40	27
17.19	12,040	4,893	1,687	438	99	39
19.83	13,880	6,284	2,468	778	219	49
22.75	15,670	7,713	3,363	1,217	380	71
25.15	16,920	8,814	4,127	1,632	573	80
27.93	18,310	10,067	5,020	2,158	847	95
30.90	19,620	11,296	5,976	2,757	1,174	119
34.00	20,800	12,526	6,950	3,420	1,560	151
37.06	21,970	13,630	7,905	4,098	1,980	233

selves to 0.1 per cent. The values in columns 3 and 5 are those calculated from the values of A_0 , n , and K given and are seen to correspond closely to those found for all values between 0.10 normal and zero concentration but do not correspond for the saturated solution. As the equation is used only in its differential form, and

the diffusion values are computed by means of concentrations between 0.2 and 0.01 normal, it is not necessary that the formula should hold beyond that range; but as the value of L_0 serves to determine the dissociation we have made our formula correspond more exactly to the values for the dilute solutions than to those for the more concentrated ones.

6. CALCULATION OF DIFFUSION CONSTANTS.

In equation (23) the unknown quantities are the two constants D_1 and D_2 and the three variables $\partial L/\partial t$, $\partial L/\partial x$, $\partial^2 L/\partial x^2$. These variables are to be determined empirically from our measurements for each time at each electrode along the tube. An attempt was made to do this graphically, but the errors that would arise in getting a second derivative by plotting were too great; so they were determined analytically. In doing this, it was found most convenient to obtain empirical expressions for each time of measurement which would include all electrode-distances, and expressions for each electrode-distance which would include all times. By differentiating these expressions the derivatives $\partial L/\partial t$, $\partial L/\partial x$, $\partial^2 L/\partial x^2$ for each time at each electrode were obtained. The form of expression found to be most satisfactory was

$$L = L_0 \left[1 - \frac{2}{\sqrt{\pi}} \int_0^u e^{-u^2} du \right], \quad (25)$$

where

L = specific conductance at any point x and any time t ,

L_0 = specific conductance calculated to correspond to the point $x = 0$, which is nearly that of the saturated solution.

$$u = \gamma + \frac{\alpha + \beta x}{t}. \quad (26)$$

α , β , and γ are empirical constants found by trial to satisfy equation (25)

x = distance above the level of the saturated solution.

t = time of diffusion.

In the equation (25) the value of L_0 is not the actual value of the specific conductance in the saturated solution, but is the conductance which a saturated solution would have if the formula $c_1 = Kc_2^n$

held over the whole range. It is therefore in reality nothing more than an additional empirical constant.

When the separate expressions were computed for thallium sulphate, it was found that a general expression of similar form could be made which would satisfy all the conductance values. In fact this expression could be reduced to equation (25) where

$$u = \frac{\beta x}{\sqrt{t}} \quad (27)$$

or

$$u = \gamma + \frac{\beta x'}{\sqrt{t}}, \quad (28)$$

and the values of L computed from this formula checked those measured with an average deviation less than 0.2 per cent. In the second run on thallium sulphate (27) was used, while in the first run (28)¹ was used, although an expression similar to (27) satisfied the values of L almost as closely. In the barium nitrate run the check was not so good and deviations as much as 0.8 per cent. were apparent at the electrode at the distance 8.52. This is not surprising because the conductance values of barium nitrate may have some doubt cast upon them from the fact that on some of the electrodes after the diffusion there was found to be some plant growth. This may have influenced the cell constant values, as it would naturally have become dislodged when the tube was cleaned and the cell constants redetermined. Yet the values of diffusion-constants cannot be effected more than a few per cent. when a mean of all the values is taken.

The values of γ and β are as follows :

	Tl ₂ SO ₄		BaNO ₃	
	γ	β	γ	β
First Run	0.0181	0.4129	0	0.4358
Second Run	0	0.4128		
L_0	0.02155		0.05735	

By the help of equation (25), our general differential equation (25) can be somewhat simplified by finding expressions for

¹ Equation (28) is the same as (26) as the expression $a + \beta x$ can be put in the form x' by adding a constant quantity to each value of x .

$$\frac{\partial L}{\partial t}, \quad \frac{\partial L}{\partial x}, \quad \frac{\partial^2 L}{\partial x^2},$$

$$\frac{\partial L}{\partial t} = L_0 \left[-\frac{2}{\sqrt{\pi}} e^{-u} \frac{\partial u}{\partial t} \right] = L_0 \left[-\frac{2}{\sqrt{\pi}} e^{-u^2} \frac{\beta x}{t^{\frac{3}{2}}} \left(-\frac{1}{2}\right) \right] = \frac{L_0}{\sqrt{\pi}} e^{-u^2} \frac{\beta x}{t^{\frac{3}{2}}},$$

$$\frac{\partial L}{\partial x} = L_0 \left[-\frac{2}{\sqrt{\pi}} e^{-u} \frac{\partial u}{\partial x} \right] = L_0 \left[-\frac{2}{\sqrt{\pi}} e^{-u^2} \frac{\beta}{\sqrt{t}} \right],$$

$$\frac{\partial^2 L}{\partial x^2} = L_0 \left[-\frac{2}{\sqrt{\pi}} \frac{\beta}{\sqrt{t}} e^{-u^2} (-2u) \frac{\partial u}{\partial x} \right] = L_0 \left[\frac{4}{\sqrt{\pi}} \frac{\beta^2}{t} e^{-u^2} u \right].$$

Substituting these values in equation (25) we obtain as our working equation

$$\frac{(K_2 L^{n-1} + 1)x}{4\beta\sqrt{t}} = uD_2 + D_1(K_2 L^{n-1}) \left[u + \frac{(n-1)}{\sqrt{\pi}} \left(\frac{L_0}{L} e^{-u^2} \right) \right]. \quad (31)$$

All the quantities in this equation are either known or can be computed from the data except D_1 and D_2 ; hence we can write

$$P = QD_2 + RD_1, \quad (26)$$

$$P = \frac{(K_2 L^{n-1} + 1)x}{4\beta\sqrt{t}},$$

TABLE IX.

Values of P , Q and R for Thallium Sulphate. Run No. 1.

Values of P .

Time, Days.	Electrode Distance.				
	8.28	11.40	14.25	17.31	20.29
24.87	1.854	2.230	2.469	2.680	
27.72	1.789	2.168	2.411	2.617	
30.75	1.726	2.106	2.353	2.554	
33.61	1.674	2.053	2.303	2.513	2.685
36.11	1.632	2.010	2.264	2.477	2.645
38.89	1.592	1.969	2.223	2.438	2.605
42.06	1.545	1.920	2.178	2.395	2.563
45.07	1.505	1.878	2.137	2.356	2.525
48.13	1.469	1.840	2.100	2.320	2.491
51.07	1.435	1.803	2.064	2.287	2.459
52.71	1.421	1.787	2.047	2.271	2.443

Values of $Q=n$.

24.87	0.6675	0.9226	1.1627	1.4169	
27.72	0.6299	0.8717	1.0991	1.3408	
30.75	0.5995	0.8287	1.0444	1.2793	
33.61	0.5732	0.7930	0.9984	1.2166	1.4350
36.11	0.5542	0.7652	0.9633	1.1718	1.3834
38.89	0.5312	0.7352	0.9267	1.1282	1.3317
42.06	0.5115	0.7085	0.8915	1.0848	1.2793
45.07	0.4940	0.6839	0.8612	1.0481	1.2351
48.13	0.4770	0.6609	0.8323	1.0127	1.1935
51.07	0.4653	0.6433	0.8097	0.9846	1.1600
52.71	0.4541	0.6295	0.7947	0.9674	1.1404

Values of R .

24.87	1.0500	0.9858	0.8399	0.6430	
27.72	1.0480	0.9979	0.8835	0.7052	
30.75	1.0440	1.0230	0.9191	0.7525	
33.61	1.0390	1.0330	0.9462	0.8002	0.6311
36.11	1.0340	1.0400	0.9658	0.8332	0.6713
38.89	1.0270	1.0450	0.9847	0.8644	0.7122
42.06	1.0210	1.0470	1.0000	0.8958	0.7526
45.07	1.0140	1.0500	1.0120	0.9175	0.7865
48.13	1.0060	1.0500	1.0220	0.9389	0.8175
51.07	0.9998	1.0490	1.0280	0.9541	0.8416
52.71	0.9917	1.0480	1.0330	0.9638	0.8553

$$Q = n,$$

$$R = (K_2 L^{n-1}) \left(n + \frac{n-1}{\sqrt{\pi}} \frac{L_0}{L} e^{-\pi z} \right),$$

$$K_2 = \frac{Kn}{\sqrt{0}^{n-1}}.$$

TABLE X.

Values of P , Q and R . Thallium Sulphate. Run No. 2.
Values of P .

Time, Days.	Electrode Distance.			
	11.13	13.98	17.04	20.02
22.08	2.246	2.484	2.711	2.918
27.26	2.131	2.374	2.595	2.775
31.02	2.054	2.303	2.523	2.696
36.07	1.967	2.224	2.446	2.614
41.32	1.888	2.146	2.372	2.538
46.38	1.820	2.083	2.311	2.478
50.00	1.775	2.039	2.271	2.440

Values of Q = u.

22.08	0.9777	1.2370	1.5018	1.7830
27.26	0.8766	1.1108	1.3470	1.5952
31.02	0.8233	1.0417	1.2625	1.4933
36.07	0.7626	0.9636	1.1674	1.3800
41.32	0.7130	0.9022	1.0915	1.2896
46.38	0.6733	0.8490	1.0288	1.2149
50.00	0.6489	0.8178	0.9895	1.1692

Values of R.

22.08	0.9583	0.7850	0.5794	0.3791
27.26	1.006	0.8754	0.7001	0.5087
31.02	1.025	0.9208	0.7658	0.5859
36.07	1.040	0.9656	0.8362	0.6683
41.32	1.047	0.9954	0.8892	0.8720
46.38	1.050	1.0160	0.9292	0.8015
50.00	1.049	1.0270	0.9517	0.8349

An equation of the form of the above was found for each time at each electrode and the values of *P*, *Q*, and *R* computed are given in Tables IX., X. and XI.

TABLE XI.

Values of P, Q and R for Barium Nitrate. Run No. 1.

Values of P.

Time, Days.	Electrode Distance.			
	8.52	11.63	14.69	17.80
19.83	2.074	2.374	2.565	
22.75	1.996	2.311	2.508	
25.15	1.937	2.260	2.466	
27.93	1.877	2.210	2.422	2.572
30.90	1.819	2.158	2.379	2.530
34.00	1.762	2.108	2.335	2.492
37.06	1.714	2.062	2.298	2.459

Values of Q = u.

19.83	0.8272	1.1314	1.4308	
22.75	0.7746	1.0583	1.3372	
25.15	0.7405	1.0087	1.2724	
27.93	0.7042	0.9580	1.2082	1.4697
30.90	0.6716	0.9123	1.1490	1.3980
34.00	0.6436	0.8703	1.0958	1.3319
37.06	0.6168	0.8349	1.0493	1.2745

Values of R .

19.83	1.290	1.105	0.8297	
22.75	1.305	1.162	0.9194	
25.15	1.311	1.198	0.9804	
27.93	1.313	1.229	1.0390	0.7916
30.90	1.313	1.260	1.0900	0.8606
34.00	1.310	1.275	1.133	0.9243
37.06	1.302	1.288	1.169	0.9781

The large number of equations of form (24) corresponding to these values of P , Q and R were then solved for D_1 and D_2 by combining them in accordance with the method of least squares.

In this treatment our equations would be as follows, where V is the probable deviation :

$$P - QD_2 - RD_1 = V,$$

$$V_1 \frac{\partial V_1}{\partial D_2} + V_2 \frac{\partial V_2}{\partial D_2} = \Sigma V \frac{\partial V}{\partial D_2} = 0. \quad (30)$$

Similarly

$$\Sigma V \frac{\partial V}{\partial D_1} = 0. \quad (31)$$

Solving these

$$\Sigma PQ - D_2 \Sigma Q^2 - D_1 \Sigma QR = 0, \quad (32)$$

$$\Sigma PR - D_2 \Sigma QR - D_1 \Sigma R^2 = 0. \quad (33)$$

The numerical values of these two latter expressions are

$$\begin{aligned} & \text{Ti}_2\text{SO}_4 \quad \text{Run 1.} \\ & 106.606 = 47.250D_2 + 42.725D_1 \\ & 102.187 = 42.725D_2 + 46.200D_1 \\ & \quad \quad \quad D_1 = 0.765 \\ & \quad \quad \quad D_2 = 1.563 \end{aligned}$$

$$\begin{aligned} & \text{Ti}_2\text{SO}_4 \quad \text{Run 2.} \\ & 73.825 = 35.967D_2 + 24.844D_1 \\ & 54.382 = 24.844D_2 + 27.412D_1 \\ & \quad \quad \quad D_1 = 0.797 \\ & \quad \quad \quad D_2 = 1.503 \end{aligned}$$

$$\begin{aligned} & \text{Ba}(\text{NO}_3)_2 \quad \text{Run 1.} \\ & 59.045 = 28.244D_2 + 28.184D_1 \\ & 62.223 = 28.184D_2 + 32.923D_1 \\ & \quad \quad \quad D_1 = 0.688 \\ & \quad \quad \quad D_2 = 1.404 \end{aligned}$$

7. DISCUSSION OF THE RESULTS.

The probable error of D_1 and D_2 as determined from the preceding equations by the method of least squares assuming equal weights for all values is 0.5 per cent. This low value, however, cannot be cited as a measure of the accuracy of the two constants for it does not take into account any constant errors or those that may be caused by inexact assumptions.

In order to give an idea as to the direction and magnitude of the possible variations in the diffusion constants, combinations have been made of some of the different single equations (24) from which the final mean was derived. For this purpose Tl_2SO_4 , run no. 2 was taken and values calculated for different pairs of electrode distances and at different times. In the following table are shown the values of D_1 and D_2 calculated, using the same intervals of electrode distances and changing the time and also using the same time interval but taking values at different distances.

Times.	Distance Interval, 11.13 to 17.04.		Distance Interval, 13.98 to 20.02.		Electrode Distance.	Time Interval, 27.26 to 50.00.	
	D_1	D_2	D_1	D_2		D_1	D_2
27.26	1.508	0.804	1.470	0.846	11.13	1.690	0.647
36.07	1.562	0.750	1.507	0.801	13.98	1.535	0.762
50.00	1.646	0.673	1.552	0.752	17.04	1.492	0.835
					20.02	1.461	0.879

From the above values it is seen that the variations in values of D_1 and D_2 are regular and not of such a character as could be claimed to be due to accidental errors. In this connection it is also noticeable that D_1 and D_2 computed from the two different runs of Tl_2SO_4 differ by about 4 per cent. and yet the values of conductance at the corresponding electrodes differ but very little from each other. If in the first run the values at the first electrode are not considered it is found that the values of the diffusion-constants fall near to those in run no. 2. This is practically reducing the calculation to electrodes at the same distances from the end and would seem to indicate that the trouble is theoretical in the assumptions. This is also indicated by the fact that when the first

electrode of the barium nitrate tube is not used, the values of the constant of the ion is reduced to about 1.37.

What the cause of these variations may be is uncertain, but there are many possibilities. The salts may dissociate in steps into intermediate ions like TlSO_4 and Tl . The mobilities of the ions may change with dilution. The ions and undissociated portion may not diffuse independently having a dragging influence one upon the other. But in any case the effect is not large, amounting to a few per cent. only.

Another fact worthy of mention is that no matter whether the diffusion constants are calculated using a few electrode distances and times or all of them, it is always true of the different pairs of values that the sum of the two diffusion constants of any one salt is a constant. No explanation of this presents itself.

It is of interest to see what values are obtained for the different diffusion constants of the ions alone by the consideration of formula (15) derived on page 151. When numerical values are inserted in this formula¹ we obtain for thallium sulphate and barium nitrate, respectively,

$$D_2 = 0.02243 \frac{84.9 \times 88.4}{173.3} \frac{3}{2} (1.041) = 1.517,$$

$$D_2 = 0.02243 \frac{72.42 \times 77.38}{149.8} \frac{3}{2} (1.041) = 1.310.$$

These are seen to be lower than the experimentally found ones for the first thallium sulphate run and for the barium nitrate one but about the same for the second thallium sulphate run. This is probably due to the fact that this latter run was calculated using more dilute solutions than the first and would in consequence come nearer to satisfying the theory than the first in which the fairly concentrated solutions at the electrode distance 8.28 were brought into the calculations.

Another calculation seems worthy of mention. It was found that the values of L in formulas (27) and (29) are very nearly satisfied when $\beta = 0.4129$ and $\beta = 0.4358$ for thallium sulphate and barium

¹ See Nernst, Theoret. Chemie, 4th ed., p. 367.

nitrate, respectively. Now according to equations (5) and (6) if there were no undissociated portion

$$\beta = \frac{1}{2\sqrt{D_2}}.$$

This would also hold true provided ions are never transformed into or produced out of un-ionized molecules, since in that case the total concentration of the ions at any point is simply determined by the quantity of them that have diffused as such to that point. If a calculation is made in this way the values of D_2 are found to be 1.468 and 1.316 for thallium sulphate and barium nitrate respectively. These, it is seen, are very close to the value calculated from the equivalent conductances of the ions by Nernst equation (16) which were 1.517 and 1.310 respectively. This agreement shows that the assumption just stated in regard to the non-transformation of ionized and un-ionized substance is at least approximately fulfilled, and therefore that the ions and un-ionized molecules must diffuse at such relative rates as will make transformation unnecessary. Namely, between the quantities dN_1 and dN_2 of un-ionized and ionized substance passing a given cross-section in time dt , there must evidently exist the relation $dN_1/dN_2 = C_1/C_2$, if there is to be no transformation in the adjoining cross-section. Now under the assumption of the independent diffusion of the two forms of the salt, which has been made throughout this article, it is easy to determine the corresponding relation which must exist between the specific diffusion-rates D_1 and D_2 of the un-ionized and ionized substance. Namely, since

$$dN_1 = -D_1 \frac{\partial c_1}{\partial x} dt \quad \text{and} \quad dN_2 = -D_2 \frac{\partial c_2}{\partial x} dt,$$

it follows by division of the first of these equations by the second and combination of the result with the preceding equation that

$$\frac{D_1}{D_2} \frac{(\partial c_1 / \partial x)}{(\partial c_2 / \partial x)} = \frac{c_1}{c_2} \quad \text{or} \quad \frac{D_1}{D_2} = \frac{\partial \log c_2 / \partial x}{\partial \log c_1 / \partial x}.$$

Combining this result with the concentration-function expressed by the equation $c_1 = Kc_2^n$ from which follows :

$$\log c_1 = n \log c_2 + \log K \quad \text{and} \quad d \log c_1 = n d \log c_2,$$

we get $D_1 = D_2/n$. And in fact this relation is not very far from being fulfilled.

So far the probability of theoretical errors existing in the method has been discussed, but before concluding that the deviations must be principally due to that source it will be well to examine into the possibility of experimental errors. The fact that a low "probable error" of 0.5 per cent. was obtained only indicates that equation (25) satisfies the data and that such accidental errors as our likely to occur would make small deviations in the final mean. This takes no account however of the constant errors which would not tend to eliminate each other in the computation of the mean and would thus give incorrect values to it.

Five classes of quantities were measured during the experiments: the distances between the electrodes, the cell-constants, the conductances at each electrode, the time of each measurement of conductance, and the temperatures both at these times and during the rest of the experiment. Besides these, measurements were made by which the concentration-function of each electrolyte was determined; but these were carried on according to the usual Kohlrausch methods for determining conductance, and the checks that were obtained showed a precision of 0.1 to 0.2 per cent. in the values of conductance. Moreover, the values of conductance computed by the concentration-function checked those experimentally found within 0.1 per cent.

Without entering here into a discussion of the effect of errors in these measured quantities on the values of the diffusion constants, it may be stated that such a consideration shows that the possible error in each of these measured quantities can hardly give rise to an error of more than 0.2-0.3 per cent. in the final values of D_2 , the diffusion-constant for the ions, so that the combined effect of all these errors is not likely to exceed 0.5 per cent. A far more important source of error is that arising from a slight convection which seems to have been due to minute temperature differences, such as were caused in one run by the fact that the lead wires were sometimes under a slightly different temperature from that of the bath, and in another by the fact that one side of the air bath was not kept at exactly the same temperature as the rest of it. This

stirring was indicated by the fact that more salt reached the upper part of the tube as shown greater conductances, when such changes of temperature were known to exist than when the temperature was known to be constant throughout. A comparison of the two runs with thallium sulphate made under dissimilar conditions and showing quite different concentrations at the upper electrode leads to the belief that there may be an error of 2 or 3 per cent. from this source ; but, as it is not known whether it is positive or negative and there are indications that it may have a different sign at different points, the probabilities are that the final mean values will be in error by a smaller per cent. In view of this experimental error it is believed that the precision of final values of D_2 , so far as the experimental part of the determination is concerned, can be placed at 2 per cent. If the trouble from stirring can be eliminated a precision of 0.5 per cent. in the method can be expected so far as experimental errors are concerned.

8. SUMMARY AND CONCLUSION.

In the foregoing pages has been described a method for the direct determination of the specific diffusion rates or diffusion constants of both the undissociated and the dissociated portion of partly ionized substances. The method consists in allowing the salt to diffuse upwards into a long cylindrical tube initially filled with pure water, keeping the concentration constant at the lower end. The concentration of the electrolyte is determined at different times and at different points along the tube by measuring the electrical conductance between platinum wires arranged in pairs and placed at different distances along the tube. Three runs were made, two in which thallium sulphate and one in which barium nitrate was used as the diffusing substance.

The principles involved in the calculations are as follows : Assuming that Fick's law of diffusion

$$dS = - Da \frac{\partial c}{\partial x} dt$$

applies both for the ionized and un-ionized portions, that is, assuming that the diffusion of the ions and undissociated portions takes place independently, the following differential equation has been derived

which expresses the changes in the concentrations in this tube with respect to the time and the distance along the tube.

$$\frac{\partial c}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} + D_2 \frac{\partial^2 c_2}{\partial x^2},$$

where

- c = total concentration in equivalents per cubic centimeter,
 c_1 = concentration of undissociated portion,
 c_2 = " " dissociated "
 x = distance in centimeters along the tube from the plane of constant concentration.
 t = time in days during which the diffusion has been progressing.
 D_1 and D_2 = diffusion constants for the undissociated and dissociated portion respectively.

By means of the empirical relations which exist between the total concentration and those of the ionized and un-ionized portions

$$c = c_1 + c_2, \quad c_1 = Kc_2^n,$$

in which K and n are empirical constants, the above equation is simplified to the following one involving only one independent variable c_2 ,

$$(1 + Knc_2^{n-1}) \frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial x^2} + D_1 \left[(Knc_2^{n-1}) \left\{ \frac{\partial^2 c_2}{\partial x^2} + (n-1)c_2^{n-2} \left(\frac{\partial c_2}{\partial x} \right)^2 \right\} \right].$$

As it was found impossible to integrate this equation it was necessary to determine c_2 and the differential coefficient $\partial c_2/\partial t$, $\partial c_2/\partial x$, $\partial^2 c_2/\partial x^2$ for different points along the tube at different times and thus to obtain expressions containing only D_1 and D_2 . In order to facilitate the calculations, advantage was taken of the fact that the concentration c_2 is proportional to the specific conductance L and that the ratio of the equivalent conductance at any concentration to that at zero concentration is a measure of the dissociation. This enables the last equation to be changed into one in which the only variable quantities are the values of L and those of the three differential

coefficients $\partial L/\partial t$, $\partial L/\partial x$, $\partial^2 L/\partial x^2$. These values of L and those of the differential coefficients were determined from the conductance measurements and equations were thus obtained for various times and distances in which the only unknowns are D_1 and D_2 . By solving the large number of these equations simultaneously by the method of least squares, the best values of D_1 and D_2 were calculated. These were found for thallium sulphate and barium nitrate to be

Salt.	Run.	D_1	D_2
Tl ₂ SO ₄	1	0.77	1.56
	2	0.80	1.50
Ba(NO ₃) ₂	1	0.69	1.40

From these values it is seen that the rate of diffusion of the undissociated substance is one half that of the ionized portion. This shows that the friction encountered by the molecule is twice the average of that encountered by the two ions which is in all probability due to the larger size of the former.

In a manner similar to that used by Nernst¹ an equation has been derived in which D_2 , the diffusion constant of the ionized portion for any salt dissociated into more than two ions of any valence, can be calculated from the equivalent conductance values of the ions at great dilution. This equation is

$$D_2 = KRT \frac{U_a U_c}{U_a + U_c} \left(\frac{1}{V_a} + \frac{1}{V_c} \right).$$

U_a and U_c = equivalent conductances in reciprocal ohms of anion and cation at great dilution.

V_a and V_c = valences of anion and cation.

K = constant depending on units used which has the value $9.854 + 10^{-13}$ when R is expressed in ergs per centigrade degree, and D_2 in equivalents per day.

The values of D_2 calculated by means of this latter formula are 1.52 and 1.31 for thallium sulphate and barium nitrate, respectively. These values are seen to correspond closely to those found by means of our measurements and are a confirmation of the results

¹Z. Phys. Chem., 2, 613, 1888.

of the diffusion experiments and of the assumptions involved in the calculations, especially that the ions and un-ionized molecules diffuse independently and that the ionization is given at least approximately by the conductance ratio.

If instead of using the differential equation

$$\frac{\partial c}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} + D_2 \frac{\partial^2 c_2}{\partial x^2}$$

it is assumed that the equation

$$\frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial x^2}$$

is applicable, the value of D_2 can be found from the solution of this latter equation, that is, by Fourier's integral,

$$c_2 = (c_2)_0 \left[1 - \frac{2}{\sqrt{\pi}} \int_0^u u^2 du \right],$$

$$u = \frac{x}{2\sqrt{D_2 t}}.$$

The values of D_2 found when this assumption is made are fairly constant for different values of x , t and c_2 and average 1.47 and 1.32 for thallium sulphate and barium nitrate, respectively. The agreement between these values and those calculated from the Nernst formula (1.52 and 1.31) seems to indicate that the assumption inherent in the above formula is approximately true, that is, that the concentration of ions at any point is determined only by the number of ions that diffuse and that there is no formation of new ions from the undissociated molecules. This evidently requires that the mols of ions and of undissociated substance that diffuse through any cross-section be proportional to their respective concentrations, that is, that $dN_1/dN_2 = c_1/c_2$ and therefore, that $D_1 = D_2/n$, where n is the constant in the empirical concentration law $c_1 = Kc_2^n$. The relation $D_1 = D_2/n$ is not very far from true; which explains why the simple formula involving only the ionic concentration and diffusion-constant gives a close method of measuring the rate of diffusion of salts.

In this connection I wish to express my gratitude to Dr. A. A. Noyes at whose suggestion the work was undertaken and by whose constant interest and counsel it was enabled to be successfully carried on.