

LXIX.—*The Electrical Conductivity of Acids and Bases in Aqueous Solutions.*

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IN previous papers (this vol., pp. 449, 627, 707), it has been shown that the variation of equivalent conductivity with dilution, in the case of all binary univalent salts, is represented by the equation

$$\frac{N \cdot E^2 \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} = 2RT \log_e \frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad (1)$$

where N is Avogadro's number, E the absolute charge on an ion, D the dielectric constant of the solvent, and V the dilution.

Abnormally High Values of Activity-coefficients of Acids and Bases.—Aqueous solutions of strong acids like hydrochloric or nitric acids, and of strong bases like sodium or potassium hydroxides, however, prove exceptions to the above rule. This irregular behaviour will be at once evident from table I, where the values of the activity-coefficients calculated from equation (1) are com-

pared with the observed values (Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 474).

TABLE I.

	$V =$	10.	20.	50.	100.	200.	500.
$\frac{\mu_v}{\mu_\infty}$ calc.		0.844	0.875	0.906	0.924	0.940	0.955
$\frac{\mu_v}{\mu_\infty}$ obs. for HCl.....		0.925	0.944	0.962	0.972	0.981	0.988
$\frac{\mu_v}{\mu_\infty}$ obs. for KOH ...		0.887	0.910	0.933	0.945	—	0.970

This irregularity disappears as we pass from the aqueous to non-aqueous solutions of strong acids. In alcoholic solutions, for example, equation (1) is exactly followed. In table II, the observed values of the molecular conductivity of hydrochloric acid in methyl alcohol are taken from the work of Goldschmidt and Thuesen (*Zeitsch. physikal. Chem.*, 1912, **81**, 32). For dilute solutions, the agreement between observed and calculated values is always within 1 per cent., and the validity of equation (1) is therefore proved beyond doubt.

TABLE II. $T = 25^\circ$.

	$V =$	40.	80.	160.	320.	640.
μ_∞ calc. from $\mu_{80} = 192.2$	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	142.5	151.8	159.5	166.7	170.9
μ_∞ obtained by extrapolation = 192.1		141.0	151.8	160.5	167.2	171.9

Abnormally High Values of the Electrical Conductivity of Acids and Bases.—It has always appeared remarkable that the values of the equivalent conductivity of acids and bases in aqueous solutions are not of the same order of magnitude as those of other salts. Thus the conductivities of hydrogen and hydroxyl ions in aqueous solutions are 318 and 175 respectively at 18° , whilst those of the other ions never exceed 70. In non-aqueous solutions, again, this abnormality is not observed. Thus in ethyl alcohol, the conductivities of hydrogen and hydroxyl ions are 32.1 and 16.5, whilst those of potassium and ammonium ions are 21.5 and 20 respectively (Godlewski, *Zeitsch. physikal. Chem.*, 1905, **51**, 751; Hägglund, *Arkiv. Kem. Min. Geol.*, 1911, **4**, No. 11). Here the values are of the same order. This is also true for solutions in other solvents, for example, methyl alcohol or acetone.

The Conductivity of Aqueous Solutions of Acids and Bases—not entirely a Convection Process.—It is thus evident that the abnormal conductivities of hydrogen and hydroxyl ions, in aqueous solutions,

are somehow related to the high values of the activity-coefficients of acids and bases, both these abnormalities disappearing when the solvent medium is other than water. Equation (1) has a good theoretical basis, and it appears more reasonable to assume that the observed ratio $\frac{\mu_{\nu}}{\mu_{\infty}}$ for acids and bases in aqueous solutions is not a real expression for the activity-coefficient, than to impugn its validity. It appears to the author that the observed conductivity of hydrogen and hydroxyl ions in water is the additive effect of two separate and independent processes, namely, (1) the transference of electricity by the convection of charged bodies, and (2) the transference of electric charge through molecules of water by the alternate processes of dissociation and recombination during impact with hydrogen or hydroxyl ion.

The first process is, of course, the ordinary method of electrolytic conduction met with in salt solutions. Here, only the free ions take part in the transference of electricity, and their number is given by the equation

$$N' = 2N \cdot e^{-\frac{A}{2kT}} \dots \dots \dots (2)$$

The mechanism of transport of electricity through molecules of water may be conceived as follows.

A molecule of water is capable of dissociating into hydrogen and hydroxyl ions, the only ions that possess abnormal conductivity. Now, in a dilute solution of hydrochloric acid the hydrogen ion is surrounded by water molecules on all sides. It appears probable that when a hydrogen ion strikes against a molecule of water, the latter in some cases undergoes dissociation. The hydrogen ion thus produced carries away the electric charge by convection, whilst the hydroxyl ion of the water molecule combines with the impinging hydrogen ion to generate a molecule of water. The conception of the process is similar to that imagined by Grotthuss to explain the phenomenon of electrolytic conduction. It may well be that the hydrogen atom of the water molecule, which is farthest from the point of impact, shoots off as a charged particle, and if the process of dissociation and recombination is instantaneous, the electric charge (+ E) appears to be carried instantaneously through a distance proportional to the diameter S of the water molecule. Thus at each impact attended with dissociation a distance $K_1 S$ is saved, where K_1 is always a fractional quantity. The result is that the hydrogen ion appears to move with a velocity much greater than its true characteristic velocity. Now let U_H be the real velocity of the hydrogen ion. The total number of impacts with water molecules per second is $K_2 N \cdot \pi \cdot S_1^2 U_H \cdot n$, where n is the

number of water molecules in a c.c. and S_1 the diameter of the hydrogen ion. The number of impacts attended with dissociation is $K_3 \cdot K_2 \cdot N \cdot \pi \cdot S_1^2 U_H \cdot n$, and the distance saved per second = $K_1 \cdot S \cdot K_3 \cdot K_2 \cdot N \cdot \pi \cdot S_1^2 \cdot U_H \cdot n = C$ at a constant temperature, since K_1, K_2, K_3, U_H , have always the same value at constant temperature. C also does not vary with dilution if n and N do not vary. Now in the case of dilute solutions, the number of solvent molecules in a c.c. may always be regarded as constant, independent of concentration, without introducing much error. Since, according to the theory developed before, strong electrolytes are completely dissociated in dilute solutions, the number of hydrogen ions in a solution containing a gram-molecule is always constant. Whilst in the first process—the transference of electric charge by convection—only the free hydrogen ions take part, this is not the case in the second process. Here it stands more to reason to assume that all the hydrogen ions are equally efficient, for, considering that some of the hydrogen ions are stationary, there is nothing to prevent their collision with water molecules, for the latter are always free to move. In fact, the inactive hydrogen ions are always capable of vibratory motion. The distance C saved per second is thus independent of dilution.

Hence, for solutions of hydrochloric acid, on the basis that the activity-coefficient α at any dilution is the same as that of univalent binary salts, we get

$$\mu_v = \alpha(U_{H^+} + U_{Cl^-}) + C_1 \dots \dots \dots (3)$$

where α is the activity-coefficient at dilution v , and C_1 a constant independent of dilution. α can always be calculated from equation (1).

Again,

$$\mu_\infty = U_{H^+} + U_{Cl^-} + C_1 \dots \dots \dots (4)$$

From equations (3) and (4),

$$U_{H^+} = \frac{\mu_\infty - \mu_v - (1 - \alpha)U_{Cl^-}}{1 - \alpha} \dots \dots \dots (5)$$

and

$$C_1 = \mu_\infty - U_{H^+} - U_{Cl^-} \dots \dots \dots (6)$$

U_{H^+} , the real ionic mobility of the hydrogen ion, and C_1 , the conductivity due to the second process, can thus at once be calculated from available data.

Experimental Confirmation of the above Hypothesis.—The experimental data on the conductivity of acids must always yield the same value of C_1 and U_{H^+} provided the acid is a strong electrolyte. This expectation has been fully realised. Thus, for a solution of

hydrochloric acid at dilution 10 and temperature 25° , $\mu_v = 390.4$, $\mu_{\alpha} = 426$, $U_{cr} = 75.8$, and $\alpha = 0.844$, whence $U_{H.} = 152.4$ and $C_1 = 197.8$.

Again, for solutions of nitric acid, at dilution 10, the available data give for $U_{H.}$ 151.3 and 198.8 for C_1 (Noyes and Falk, *loc. cit.*). The values of $U_{H.}$ and C_1 obtained from the data on the conductivity of hydrochloric and nitric acids therefore agree within 1 per cent. We may take 152 as the mean value of $U_{H.}$ and 198.5 as that of C_1 . The real mobility of hydrogen ion is therefore of the same order of magnitude as those of the other ions. The second process is thus responsible for the transference of about half the electric current in acid solutions.

The values of $U_{H.}$ and C_1 having once been determined, it is possible to calculate the molecular conductivity of any strong acid at any dilution from equation (3). Tables III and IV show how the calculated values agree with the observed ones.

In table III, the observed values are taken from the work of Noyes and Falk (*loc. cit.*), whilst the data in table IV are obtained from a paper by Wegscheider and Lux (*Monatsh.*, 1909, **30**, 436).

TABLE III.

	$V =$	20.	100.	500.	1000.	2000.
HCl	$\int \mu_v$ calc.	397.6	408.9	416.5	418.4	—
	$\int \mu_v$ obs.	398.4	410.5	418.5	420.4	—
HNO ₃	$\int \mu_v$ calc.	393.1	404.5	411.0	—	415.0
	$\int \mu_v$ obs.	393.3	406.0	413.0	—	417.0

TABLE IV.

	$V =$	100.	400.	111.	1600.
Naphthalene- β - sulphonic acid	$\int \mu_v$ calc.	637.2	372.4	375.3	376.3
	$\int \mu_v$ obs.	367.4	374.9	376.9	377.4
Toluene- p - sulphonic acid.....	$\int \mu_v$ calc.	369.9	375.0	377.6	378.5
	$\int \mu_v$ obs.	368.4	375.3	378.2	379.0

The agreement between the observed and calculated values is always within 0.5 per cent.

The real values of $U_{OH.}$ and C_1 for bases can also be obtained in the same way. Thus, at dilution 10, μ_v for potassium hydroxide is 213; μ_{α} is 240.2. From these data, the value of $U_{OH.}$ is 109 and of C_1 for bases 66. Table V shows how exactly the observed values of the molecular conductivity of potassium hydroxide agree with those calculated from equation (3).

TABLE V.

	$V =$	20.	50	100.	500.
KOH.....	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	218.4	224.0	227.1	232.5
		219.0	225.0	228.0	233.0

Arrhenius has already suggested "that the exceptionally great conductivity of these ions (H^+ and OH') in water is probably due only to the fact that they are the two ions into which water is electrolytically decomposed" ("Theories of Solution," p. 138). In the foregoing pages, an attempt has been made to develop a quantitative explanation of the abnormal mobility of hydrogen and hydroxyl ions by assuming that an electric charge can be transferred almost instantaneously through water molecules during impact with these ions by the converse processes of dissociation and recombination taking place alternately.

A General Hypothesis for all Electrolytes.—The electrolytes can be classified into three groups, namely, (1) consisting of strong electrolytes, (2) containing acids of intermediate strength, "transition electrolytes," and (3) consisting of weak acids and bases where Ostwald's dilution law holds good.

For the first group we have the following empirical laws:

$$\mu_v = \mu_\infty - a \sqrt[3]{C} \quad (\text{Kohlrausch, } Ann. Phys. Chem., 1885, [iii], 26, 161) \quad (7)$$

and

$$i = 2 - b - \sqrt[3]{C} \quad (\text{Noyes and Falk, } J. Amer. Chem. Soc., 1910, 32, 101) \quad (8)$$

Equation (1) becomes identical with Kohlrausch's empirical law in the case of dilute solutions where μ_v is only slightly less than μ_∞ . Thus, equation (1) may be put in the form

$$\frac{K}{\sqrt[3]{V}} = \log_e \frac{\mu_\infty}{\mu_v}$$

or

$$K \sqrt[3]{C} = \frac{\mu_\infty - \mu_v}{\mu_\infty} = 1 - \frac{\mu_v}{\mu_\infty} \quad (9)$$

or

$$\mu_v = \mu_\infty (1 - K \sqrt[3]{C}) = \mu_\infty - a \sqrt[3]{C},$$

Again, the activity-coefficient

$$a = \frac{\mu_v}{\mu_\infty} = 1 - K \sqrt[3]{C} \quad (10)$$

Noyes and Falk's empirical law can easily be derived by apply-

ing Clausius's virial theorem to salt solutions. It has already been shown that

$$\begin{aligned}
 i &= n \left\{ 1 - \frac{1}{3} \log_e \frac{\mu_\alpha}{\mu_v} \right\} \dots \dots \dots (11) \\
 &= n \left\{ 1 - \frac{1}{3} K \sqrt{C} \right\} \\
 &= n - \frac{1}{3} n \cdot K \cdot \sqrt[3]{C} \\
 &= 2 - b\sqrt[3]{C}, \text{ for binary salts where } n=2.
 \end{aligned}$$

Whilst the strong electrolytes of group 1 belong to the limiting case, we have, for the other two groups, as in Arrhenius's original theory, both undissociated molecules and ions in solution. The law of mass action in its original form is, however, not applicable to electrically charged bodies. It requires modification in the sense that only the free ions take part in the equilibrium. It is only the fraction of the total number of ions which, by virtue of their kinetic energy, can overcome the force of electrostatic attraction, that really matter. They only are free to move, and hence have the chance of colliding with one another. From the kinetic point of view, therefore, only these free ions are to be taken into consideration in applying the law of mass action to the process of electrolytic dissociation. Thus, if x is the fraction of a gram-molecule of acid, which has undergone dissociation into ions, the law of mass action is not expressed by the equation

$$\frac{x^2}{(1-x)V} = K,$$

but by the equation

$$\frac{(\alpha x)^2}{(1-x)V} = K \dots \dots \dots (12)$$

where α is the activity-coefficient at the ionic concentration $\frac{x}{V}$

Now, α for any dilution can be calculated from equation (1) or (10). In the case of weak acids belonging to the third group, X is generally very small; $\frac{x}{V}$ becomes always negligibly small, and hence α is very nearly equal to one at all dilutions. For very weak acids, therefore, equation (12) becomes identical with Ostwald's dilution law.

A Dilution Formula for Transition Electrolytes.—Here the activity-coefficient α is not always equal to one, and the equation

$$\frac{(\alpha x)^2}{(1-x)V} = K,$$

must be applied as such. According to the ideas developed before,

the equivalent conductivity of an acid of intermediate strength may be equated thus:

$$\mu_v = x \cdot 198.5 + \alpha x (U_{H^+} + U_{Anion}) \dots (13)$$

where x is the gram-equivalent of total hydrogen ion and $U_{H^+} = 152$ at 25° , or

$$\mu_v = x \cdot 198.5 + (1 - K^3/C)x \cdot (U_{H^+} + U_{Anion}) \text{ from equation (10)}$$

$$= x(198.5 + U_{H^+} + U_{Anion}) - K \left(\frac{x}{V} \right)^3 \cdot x \cdot (U_{H^+} + U_{Anion})$$

$$\text{or since } c = \frac{x}{V}$$

$$= x \cdot \mu_\infty - \frac{K}{\sqrt[3]{V}} \cdot x^4 \cdot (U_{H^+} + U_{Anion}).$$

The equation contains only one unknown quantity, x , and hence it admits of a solution. The real value of x can, however, be easily obtained with great accuracy by the method of successive approximation. x having thus been determined, it is easy to calculate α at concentration $\frac{x}{V}$. Hence all the factors for verifying the equation

$$\frac{(\alpha x)^2}{(1-x)V} = K,$$

can be had from the conductivity data. In tables VI, VII, VIII, and IX four acids have been chosen in the order of increasing strength to illustrate the validity of the above equation. The values of molecular conductivity have been taken from the very accurate work of Kendall (*loc. cit.*). According to this author, M for the hydrogen ion at 25° is 347, whilst the value obtained by Noyes and Falk as the mean of the data given by various workers is 350. In the following tables, the latter value has been accepted as true.

TABLE VI.

Cyanoacetic Acid. $\mu_\infty = 389.1$ at 25° .

V .	μ_v .	x .	α .	K .
16.82	88.0	0.2370	0.9158	0.00365
33.64	117.0	0.3120	0.9260	0.00361
67.28	152.5	0.4050	0.9352	0.00358
134.56	193.9	0.5125	0.9442	0.00357
269.10	238.7	0.6283	0.9524	0.00358
538.20	282.6	0.7409	0.9606	0.00363
1076.40	320.0	0.8361	0.9673	0.00368

TABLE VII.

o-Nitrobenzoic Acid. $\mu_{\infty} = 382.2$ at 25° .

V.	μ_p .	x .	α .	K.
32.0	139.7	0.3810	0.9204	0.00621
64.0	179.0	0.4854	0.9310	0.00620
128.0	221.9	0.5984	0.9407	0.00617
256.0	265.0	0.7106	0.9497	0.00616
512.0	303.6	0.8108	0.9588	0.00622
1024.0	333.5	0.8861	0.9664	0.00627

TABLE VIII.

Dichloroacetic Acid. $\mu_{\infty} = 388.6$ at 25° .

V.	μ_p .	x .	α .	K.
16.0	231.4	0.6337	0.8835	0.0535
32.0	273.2	0.7400	0.9009	0.0534
64.0	309.8	0.8318	0.9174	0.0540
128.0	338.7	0.9020	0.9319	0.0550

TABLE IX.

Trichlorobutyric Acid. $\mu_{\infty} = 379.0$ at 25° .

V.	μ_p .	x .	α .	K.
23.6	308.8	0.8616	0.8861	0.1783
47.2	331.7	0.9149	0.9068	0.1720
77.26	343.9	0.9434	0.9195	0.1720
108.0	350.4	0.9566	0.9273	0.1800

A comparison of the numbers in column five at once shows that for each acid a constant value of K is obtained. The degree of dissociation in the case of cyanoacetic acid has been varied from 0.23 to 0.83, but the equation holds good exactly throughout this interval.

The applicability of the formula has also been demonstrated for the entire range of transition electrolytes, beginning with cyanoacetic acid, which borders on the type of electrolytes included in the third group, and ending with trichlorobutyric acid, the strength of which is comparable with that of mineral acids.

Summary.

The abnormally high mobility of the hydrogen and hydroxyl ions in aqueous solutions has been explained on the assumption that electricity is partly carried by the ordinary process of convection and partly propagated through water molecules undergoing alternate dissociation and recombination. The apparently high activity-coefficients of strong acids and bases in aqueous solutions

has also been traced to this cause. A modified Ostwald equation, $\frac{(\alpha x)^2}{(1-x)V} = K$, based on the consideration that only free ions have the capacity of regenerating undissociated molecules, has been developed for weaker electrolytes, where the degree of dissociation is less than one. It has been shown that this equation becomes identical with Ostwald's dilution law in the case of very weak electrolytes where α is always very nearly equal to one, and also gives very concordant values for the equilibrium constant in the case of "transition electrolytes" where Ostwald's equation is not applicable.

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