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Electrolytic Conductance And the Conductances of the Halogen Acids in Water

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UNITED STATES DEPARTMENT OF COMMERCE
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Electrolytic Conductance and the Conductances of the Halogen Acids in Water

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National Bureau of Standards
Washington, D.C. 20234

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Foreword

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LEWIS M. BRANSCOMB, *Director*

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Preface

This document represents the initial effort in the compilation and critical evaluation of available data on the electrolytic conductance of aqueous solutions of electrolytes. A readily available source of such data is presently needed since the last such compilation and evaluation was made in the early 1930's. Although, for the most part, these data are available in the literature, they have not been brought together in a single volume nor have they been treated in a consistent manner. For example, some data in the literature are given in international ohms, others in absolute ohms. Methods used to obtain limiting equivalent conductances differ widely. Also most of the literature data are expressed on the old atomic weight scale of 16 for naturally occurring oxygen rather than on the ^{12}C scale. All data reported here have been converted to absolute ohms, and the ^{12}C scale of atomic weights; data presented in subsequent reports will be treated in a similar manner.

Modern theories of conductance, especially those developed by Peter J. W. Debye, Lars Onsager, and Raymond M. Fuoss are or will be used in the critical evaluation of the data, in particular for the determination of limiting equivalent conductances. Also when the available data are of sufficient accuracy, modern theories will be used to determine apparent "ion-size" parameters; such determinations will not be made in the present document, however. In general, the data on equivalent conductances will be presented in tables. Equations, based in part on theory, which give equivalent conductances as a function of concentration will also be included. In some cases, empirical equations will be used in the entirety, but these will reproduce the experimental results which are, in essence, the essential product desired by the user. For example, empirical equations are used to express the conductances of HCl at −10 and −20 °C; in the limit of zero concentration the solutions are solid, i.e., in the frozen state.

In the present document, definitions relating to the conductance of electrolytic solutions are first presented. These are followed by some general considerations of the migration of ions and general laws governing the movement of ions under applied potential gradients as are involved in electrolytic conductance. Conductance relations (equations) are then given, and these are followed by a condensed treatment of the Debye-Hückel-Onsager-Fuoss theories of electrolytic conductance, given in general terms (a more detailed treatment is given in Appendix A, but even there the minor details and mathematical complexities are omitted). Values of the parameters, namely B_1, B_2, E_1, and E_2 in the theoretical equations are given for temperatures from 0 to 100 °C for the convenience of those engaged in conductance measurements. They are not needed, however, by those who are interested only in data on the equivalent conductance of an electrolytic solution. Finally, tables of data on the electrolytic conductance of HF, HCl, HBr, and HI are given for various concentrations and temperatures in tables 10 through 19. The constants governing the dissociation of HF from 0 to 25 °C are given in table 9.

For the convenience of the reader a glossary of symbols is given at the end of the document.

In 1968, the Commission on Symbols, Terminology, and Units of the Division of Physical Chemistry of the International Union of Pure and Applied Chemistry in a tentative proposal (IUPAC Bulletin No. 32) did not include "equivalent conductance" among its list of definitions, but replaced it by "molar conductance" and assigned the symbol Λ to the latter. Accordingly, if this proposal is eventually adopted, the term "equivalent" in the present document should be replaced by "molar" and the definitions of "molar conductance" and "limiting molar conductance" given on page 1 eliminated (historically, molar conductivity, as defined on page 1, had use in determining the mode of ionization of salts when it was not possible to determine the equivalent weight of the salt). Under this proposal of IUPAC, the meaning of a mole of salt would need to be clearly specified. Thus, the molar conductance of $MgCl_2$, for example, could be given as

$$\Lambda(\tfrac{1}{2}\,\mathrm{MgCl_2}) = 129\ \Omega^{-1}\ \mathrm{cm^2 mol^{-1}} \text{ or as } \Lambda(\mathrm{MgCl_2}) = 258\ \Omega^{-1}\ \mathrm{cm^2 mol^{-1}}$$

(see IUPAC Bulletin No. 32) depending on how a mole of $MgCl_2$ is specified (of course, Avogadro's constant would apply only to the latter definition).

Acknowledgment

The authors wish to express their appreciation to Professor Raymond M. Fuoss of Yale University for his advice during the course of this work.

Contents

Electrolytic Conductance and the Conductances of the Halogen Acids in Water

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Definitions, symbols, general principles, and general laws related to the electrolytic conductance of aqueous solutions are presented. The general laws considered are Coulomb's law for charged bodies, Poisson's equation relating the electrostatic potential to charge distribution, and the Stokes and Oseen laws for the velocity of a sphere in a fluid medium. The relations between electrical resistance, electrical conductance, specific resistance, specific conductance, and equivalent conductance are set forth. Theoretical expressions for the equivalent conductance as derived by Debye, Onsager, and Fuoss are given in general form and in a somewhat more detailed fashion in an appendix. The general methods of treating the equivalent conductances of ionophores and ionogens, especially in regard to the determination of the limiting equivalent conductance, the degree of ionic association, and the degree of ionic dissociation are discussed. Data on the equivalent conductances of the halogen acids, hydrofluoric, hydrochloric, hydrobromic, and hydriodic acids in water are given for a wide range of concentration and temperature.

Key words: Conductances of HF, HCl, HBr, and HI; electrolytic conductance; theories ot electrolytic conductance.

1. Definitions and Symbols

Conductance, σ—The conductance of a conductor of electricity is the reciprocal of its electrical resistance (R) and its unit is the reciprocal "absolute" ohm, ohm^{-1}, or mho.

Specific conductance, σ_{sp}—The specific conductance, or conductivity, of a conductor of electricity is the conductance of the material between opposite sides of a cube, one centimeter in each direction. The unit of specific conductance is ohm^{-1} cm^{-1} or mho cm^{-1}.

Electrolytic cell constant, J_c—The cell constant of an electrolytic cell is the resistance in ohms of that cell when filled with a liquid of unit resistance.

Equivalent conductance, Λ—The equivalent conductance of an electrolytic solution is the conductance of the amount of solution that contains one gram-equivalent of a solute (or electrolyte) when measured between parallel electrodes which are one centimeter apart and large enough in area to include the necessary volume of solution. Equivalent conductance is numerically equal to the conductivity multiplied by the volume in cubic centimeters containing one gram-equivalent of the electrolyte. The unit of equivalent conductance is ohm^{-1} cm^2 equiv^{-1} (frequently, in the literature the unit is given simply, although incorrectly, as ohm^{-1}, so that it may be comparable to the unit for conductance, in general).

Limiting equivalent conductance, Λ_0—The limiting equivalent conductance of an electrolytic solution, Λ_0, is expressed by $\Lambda_0 \equiv \lim_{c \to 0} (\sigma_{corr}/c)$ where σ_{corr} is solution conductance corrected for solvent conductance and c is the equivalent concentration. Λ_0 is the value which Λ approaches as the solution is diluted so far that the effects of interionic forces become negligible (and dissociation, in the case of ionogens, is essentially complete).

Molar conductance, Λ^m—The molar conductance of an electrolytic solution is the conductance of a solution containing one gram mole of the solute (or electrolyte) when measured in a like manner to equivalent conductance. Seldomly used.

Limiting molar conductance, Λ_0^m—The limiting molar conductance of an electrolytic solution, Λ_0^m, is expressed by $\Lambda_0^m \equiv \lim_{m \to 0} (\sigma_{corr}/m)$ where σ_{corr} is solution conductance corrected for solvent conductance and m is the molar concentration. Λ_0^m is the value which Λ^m approaches as the solution is diluted so far that the effects of interionic forces become negligible. Seldomly used.

Degree of dissociation (or ionization) in general, α—The degree of dissociation (or ionization) of an electrolytic solution is the percentage of solute (or electrolyte) in the dissociated (or ionized) state in solution. Classically this degree is obtained from conductance measurements from the ratio, Λ/Λ_i where Λ_i is the equivalent conductance an electrolytic solution would have at some *finite* concentration if it were completely dissociated into ions at that concentration. (See ionogens). This symbol is also used to denote the fraction of free ions in a solution when simple ions, ion pairs, and clusters higher than ion pairs are present. (See ionophores).

Degree of association, $(1-\alpha)$—The degree of association of an electrolytic solution is the percentage of ions associated into nonconducting species, such as ion-pairs. (See ionophores).

Ionic equivalent conductance, λ—The ionic equivalent conductance is the equivalent conductance of an individual ion constituent of the solute (or electrolyte) of an electrolytic solution. This symbol is also used to designate the equivalent conductance of complex ions, ion pairs, ion clusters, etc., in combination with simple ions.

Limiting ionic equivalent conductance, λ_0—The limiting ionic equivalent conductance of an individual ion constituent of the solute (or electrolyte) of an electrolytic solution is given by $\lambda_0 \equiv \lim_{c \to 0} (\lambda / c)$. This symbol is also used to designate the limiting equivalent conductances of complex ions, ion pairs, ion clusters, etc., in combination with simple ions.

Ionic mobility, u—The mobility of an ion at any finite equivalent concentration is the velocity with which the ion moves under unit potential gradient. Its unit is $\mathrm{cm}^2\ \mathrm{sec}^{-1}\ \mathrm{volt}^{-1}\ \mathrm{equiv}^{-1}$ or $\mathrm{cm}^2\ \mathrm{ohm}^{-1}\ F^{-1}$ where F is the Faraday expressed in coulombs (or ampere seconds) equiv^{-1}.

Limiting ionic mobility, u^0—The limiting mobility of an individual ion of a solute (or electrolyte) is given by $u^\circ \equiv \lim_{c \to 0} u$.

Kohlrausch law of independent migration of ions—The value of the equivalent conductance, as the concentration approaches zero, is equal to the sum of the limiting ionic equivalent conductances of the ions constituting the solute of the electrolytic solution.

Transference (or transport) number, t—The transference number of each ion of a solute (or electrolyte) in an electrolytic solution is the fraction of the total current carried by that ion, and is given by the ratio of the mobility of the ion to the sum of the mobilities of the ions of the solute constituting the electrolytic solution.

Interionic attraction—The electrostatic attraction between ions of unlike charge (sign).

Interionic repulsion—The electrostatic repulsion between ions of like charge (sign).

Ion atmosphere (or continuous charge distribution)—In the electrostatic effects between ions the term ion atmosphere denotes a continuous charge distribution, or charge density, $\rho\ (r)$, which is a continuous function of r, the distance from the reference ion, rather than a discrete or discontinuous charge distribution. The ion atmosphere extends from $r = a$ to $r = 0(V^{1/3}) \approx \infty$, where V is the volume of the system, and acts electrostatically somewhat like a sphere of charge $-e$ at a distance, κ^{-1}, from the reference ion of charge $+e$ (see below for definition of κ^{-1}).

Thickness or average radius of ion atmosphere, κ^{-1}—The average distance of the ion atmosphere from the reference ion in angstrom units. This average distance decreases in magnitude with the square root of the ionic concentration. Mathematically, κ^{-1} is the distance at which the average charge, $d\bar{q}$, in a spherical shell of volume $4\pi r^2 dr$ reaches a maximum using the continuous density, $\rho\ (r)$, approximation.

Ion size or "ion-size" parameter, a (or a_i)—The ion size is formally considered to be the sum of the ionic radii of the oppositely charged ions in contact. The ion size is also called the "distance of closest approach" of the ions, or the "ion-size" parameter. Generally the ion size is greater than the sum of the crystal radii, and the "ion-size" parameter may include several factors which contribute to its numerical value.

Electrophoretic effect—The slowing down, owing to interionic attraction and repulsion, of the movement of an ion with its solvent molecules in the forward direction by ions of opposite charge with their solvent molecules moving in the reverse direction under an applied electrical field (potential gradient).

Relaxation-field effect—The delay in the ion atmosphere in maintaining its symmetry around a central ion as the central ion moves in the forward direction under an applied electrical field (potential gradient).

Osmotic-pressure effect—An enhancement in the velocity of the central ion, in the direction of the applied external field, as a result of more collisions on the central ion from ions behind the central ion than from ions in front of it.

Viscosity effect—An alteration in the velocity of a given ion as a result of the contribution to the bulk viscosity owing to the ions of opposite charge. This effect applies to ions of large size.

Walden's rule, $\Lambda_0 \eta_0$—Walden's rule states that the product of the limiting equivalent conductance of an electrolytic solution, Λ_0, and the viscosity of the solvent, η_0, in which the solute (or electrolyte) is dissolved is a constant at a particular temperature. Walden's rule is an approximation which would be valid only for ions which behave hydrodynamically like Stokes spheres in a continiuum (see later for Stokes Law).

Debye-Falkenhagen effect—The increase in the conductance of an electrolytic solution produced by alternating currents of sufficiently high frequencies over that observed with low frequencies or with direct current.

Wien effect—The increase in the conductance of an electrolytic solution produced by high electrical fields (potential gradients).

Dissociation-field effect—The increased dissociation (or ionization) of the molecules of weak electrolytes under the influence of high electrical fields (potential gradients).

Ionophores—Substances, like sodium chloride, which exist only as ionic lattices in the pure crystalline form, and which when dissolved in an appropriate solvent give conductances which change according to some fractional power of the concentration. Such solutions possess no neutral molecules which can dissociate, but may contain associated ions.

Ionogens—Substances, like acetic acid (HAc), which, although in the pure state are nonelectrolytic neutral molecules, can react with certain solvents to form products which rearrange to ion pairs which then dissociate to give conducting solutions. As an example:

$$HAc + H_2O \rightleftharpoons HAc \cdot H_2O$$
$$\rightleftharpoons H_3O^+ \cdot Ac^- \rightleftharpoons H_3O^+ + Ac^-$$

2. General Considerations

Three factors cause ions to move in a medium in which they may exist. These are (1) thermal motion of a random nature, (2) flow of the medium as a whole, and (3) forces acting on the ions. The last may be internal or external or both. Internal forces may arise from concentration gradients, velocity gradients (which produce tangential stresses in viscous flow), temperature gradients (Soret effect), and electrostatic forces due to the ions themselves. External forces may be produced by pressure changes, gravitational fields, or the application of an electric field. Ions in an electrolytic solution are neither created nor destroyed during their motion under a dc field, i.e., they follow the *equation of continuity*, analogous to the equation of continuity in hydrodynamics which states that matter is conserved in liquid flow. In moving through a medium, ions must overcome friction whatever may be its cause. If an ion has a mobility of u_i, its velocity v_i under a force $\mathscr{F}$ will be $\mathscr{F} u_i$. Since the coefficient of friction of the ion, ρ_i, equals $1/u_i$, the ionic velocity under the force $\mathscr{F}$ is given by $\mathscr{F}/\rho_i$. The "absolute" mobility of a body in the Système International d' Unites (SI) and MKSA systems of units is the velocity in m per s attained under a force of 1 N; in the cgs system of units the "absolute" mobility of a body is the velocity in cm per s attained under a force of 1 dyne. In practice, however, when dealing with ions, the unit of force is taken as a unit potential gradient acting on a unit charge. Letting u_i denote "absolute" mobility of an ion and u_i' "electrical mobility", the velocity attained by an ion under unit potential gradient is:

$$u_i = u_i'/|z_i|e = Nu_i'/|z_i|F \qquad (2.1)$$

where N is Avogadro's constant and F the Faraday. Since the ionic equivalent conductance, denoted by λ_i, is equal to Fu_i' eq (2.1) may be written:

$$u_i = u_i'/|z_i|e = N\lambda_i/|z_i|F^2 \qquad (2.2)$$

The "electric mobility" is directly proportional, therefore, to the "absolute" mobility and the applied potential gradient. Since 1 V = [1/299.7925(1)] esu of potential (cgs system) and the elementary charge $e = 4.80298(7) \times 10^{-10}$ esu of charge, a field of 1 V/cm exerts on an ion a force of 1.60210(3) $\times 10^{-11}|z_i|$dyn. (See appendix C for SI units.) The figures in parentheses give the uncertainty in the last decimal arising from the uncertainties in the physical constants.

In the treatment of electrolytic conductance at any selected constant temperature presented here, it is assumed that internal and external forces acting on the ions are restricted to electrostatic forces between ions, the virtual forces due to local concentration gradients produced by interionic forces, and an applied electrical field.

3. General Laws

In dealing with electrolytic conductance the following must be considered:

(1) *Coulomb's law for charged bodies:* This law states that the force, $\mathscr{F}$, between two charges, e_1 and e_2, directed along a line between the charges, is directly proportional to the magnitude of the charges and inversely proportional to the square of the distance, r, of their separation. If a material medium is present the force is weakened. This law may be represented by

$$\mathscr{F} = (e_1e_2/\epsilon r^2)\mathbf{r}_1 \qquad (3.1)$$

where $\mathbf{r}_1$ is the unit vector in the direction from e_1 to e_2 and ϵ denotes the dielectric constant of the material medium.

(2) *Poisson's equation relating the electrostatic potential to charge distribution:* This law states that for any point (ion) in a medium located by three space coordinates, the divergence of the gradient of the potential, Ψ_0, is proportional to the charge density at that point (ion). This law, in cartesian coordinates, may be represented by

$$\text{div grad } \Psi^0 = \nabla \cdot \nabla \Psi^0 = \nabla^2\Psi^0 = \frac{-4\pi\rho_c}{\epsilon} \qquad (3.2)$$

where ϵ again is the dielectric constant of the medium, and ρ_c is the average charge density.

(3) *Stokes law:* This law states that the velocity, v, of a sphere of radius, r, moving under a force $\mathscr{F}$, in a medium will be inversely proportional to the viscosity, η, of the medium and the radius of the sphere. This law may be represented by

$$v = \mathscr{F}/6\pi\eta r \qquad (3.3)$$

For ions moving under an electrical force, $\mathscr{F}_e$, this equation becomes

$$v_i = \mathscr{F}_e/6\pi\eta r_i = \mathbf{X}z_ie/6\pi\eta r_i \qquad (3.4)$$

where $\mathbf{X}$ is the vector electric field in the x direction, z_i the ionic valence, and e the elementary charge.

(4) *Oseen law:* This law is for a volume force rather than the directional force of Stokes law. This law may be represented by

$$d\mathbf{v} = [d\boldsymbol{\mathscr{F}} + (d\boldsymbol{\mathscr{F}} \cdot \mathbf{r})\mathbf{r}/r^2]/8\pi\eta r \qquad (3.5)$$

which gives the velocity $d\mathbf{v}$ produced by a volume force $d\boldsymbol{\mathscr{F}}$ (acting at the origin), at a point located by the vector $\mathbf{r}$ in a medium whose viscosity is η.

For ions moving under an electric force, $\mathscr{F}_e$, the volume force is replaced by the electrical force, $\mathscr{F}_e$, and the velocity of the ion is taken in the x or field direction.

4. Conductance Relations

Since electrical conductance, σ, is the reciprocal of electrical resistance, R, it may be expressed as

$$\sigma(\Omega^{-1})=\frac{1}{R(\Omega)} \tag{4.1}$$

The resistance of a homogeneous substance of uniform cross-sectional area, A, and length, l, is given by

$$R=R_{\text{sp}}\frac{l}{A}\,\Omega \tag{4.2}$$

where R_{sp} is known as the specific resistance (or resistivity). R_{sp} is a characteristic of a substance under given physical conditions and is numerically equal to the resistance between opposite sides of a cube of the substance, one centimeter in each direction. The unit of R_{sp} is Ω cm. It follows that

$$\sigma=\frac{1}{R}=\frac{A}{R_{\text{sp}}l}=\sigma_{\text{sp}}\frac{A}{l}\,\Omega^{-1}\text{cm}^{-1} \tag{4.3}$$

where σ_{sp} is the specific conductance (or conductivity) in units of Ω^{-1} cm^{-1} or mho cm^{-1}.

In terms of Ohm's law ($E=iR$) the specific conductance is given by

$$\sigma_{\text{sp}}=i/E_a\,\Omega^{-1}\text{ cm}^{-1} \tag{4.4}$$

where i is the electric current and E_a, the potential applied to a centimeter-cube sample of the conductor, the conductance being measured between a pair of opposite faces of the cube.

Since conductance cells are not normally constructed with uniform cross section and length, eq (4.3) cannot be used to compute σ_{sp} from measurements of σ. Instead the cells are calibrated with a conducting solution whose σ_{sp} has been measured when A and l are uniform and accurately known; this σ_{sp} may be represented by $(\sigma_{\text{sp}})_s$ where the subscript s denotes standard. Then eq (4.3) for the calibrating solution becomes:

$$\sigma_s=(\sigma_{\text{sp}})_s\frac{A_s}{l_s} \tag{4.5}$$

and

$$(\sigma_{\text{sp}})_s=\sigma_s\frac{l_s}{A_s}=\sigma_sJ_c \tag{4.6}$$

where J_c is the cell constant. Therefore $(\sigma_{\text{sp}})_e$, the specific conductance of an experimental solution is given by

$$(\sigma_{\text{sp}})_e=\sigma_{\text{sp}}=\sigma_eJ_c=\sigma J_c \tag{4.7}$$

The conductivity data given in this monograph are based on (or referred to) the standards of Jones and Bradshaw [1][1], i.e., their data were used in determining the cell constant of conductance cells. Jones and Bradshaw with great care measured the specific conductance of aqueous solutions of potassium chloride at three different concentrations and three different temperatures. Their specific conductances (reported in international electrical units) are given in table 1[2], corrected to absolute electrical units. The conversion from international to absolute units was made using the relation [2]:

1 international ohm (USA)=1.000495
absolute ohms.

For data obtained outside of the United States the relation:

1 international ohm (mean) = 1.00049
absolute ohms

has been used. Experimental data obtained since January 1, 1949, are presumed to be in absolute units; data obtained prior to January 1, 1949, have been converted from international to absolute units using the above relations. (The conversion from international to absolute units officially took place on January 1, 1948, but it is assumed that approximately one year, from January 1, 1948, to January 1, 1949, was required to put the transition into effect if the authors were not specific about the units they employed.)

Jones and Bradshaw gave their results in terms of a "demal" solution. A "demal" solution is defined as a solution containing a gram mole of salt dissolved in a cubic decimeter of solution at zero degrees Celsius. In calculating the value of "demal" they used the atomic weights of 1933. Fortunately they also gave the grams of KCl added to 1000 g of solution and no change is necessary in their values of the specific conductance as a result of changes in atomic weights to the unified ^{12}C scale of atomic weight (the specific value of their "demal" solutions differs but not the number of grams added to 1000 g of solution).

Although specific conductance is useful in comparing metallic conductors, it has little direct importance in dealing with solutions. As the concentration of solutions may be varied at will, comparisons of the conductances of solutions containing equivalents or fractions therefore are more significant. Equivalent conductance is defined by:

$$\Lambda=\sigma_{\text{sp}}(1000/c)\ \Omega^{-1}cm^2\,\text{equiv}^{-1} \tag{4.8}$$

where c is in equivalents per liter. The factor $1000/c$ replaces A/l in eq (4.3), and, therefore, the equiva-

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[1] Figures in brackets indicate the literature references on p. 13.

[2] All tables are presented in a group beginning on p. 19.

lent conductance is the conductance of that amount of an electrolytic solution which contains one equivalent of solute (or electrolyte) when placed between parallel planes 1 cm apart and of sufficient area to retain the volume expressed in liters of solution; the conductance is measured normal to the planes.

The equivalent conductance may also be expressed in terms of Ohm's law by

$$\Lambda = \frac{1000i}{E_a c}\ \Omega^{-1}\ \text{cm}^2\ \text{equiv}^{-1} \tag{4.9}$$

Accordingly, the equivalent conductance is numerically equal to the current in amperes that would pass through such a solution if a potential gradient of 1 V were applied across the electrodes, all disturbing effects being absent.

If the manner of dissociation (or ionization) of the solute constituting an electrolytic solution is not known, the molar conductance rather than the equivalent conductance is used. It is defined by

$$\Lambda^m = \sigma_{\text{sp}}(1000/m)\Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1} \tag{4.10}$$

where m is the gram moles of solute (or electrolyte) dissolved in 1000 cm^3 of solution.

The equivalent conductance of an individual ion λ_i is given by (+ ion taken for example):

$$\lambda_+ = Fu_+\Omega^{-1}\ \text{cm}^2\ \text{equiv}^{-1} \tag{4.11}$$

where F is the Faraday and u the ionic mobility. The equivalent conductance of a binary electrolyte is equal to the sum of the individual equivalent conductances of the ions, or,

$$\Lambda = \lambda_+ + \lambda_- = F(u_+ + u_-)\Omega^{-1}\ \text{cm}^2\ \text{equiv}^{-1} \tag{4.12}$$

Since the transference number of an ion is given by

$$t_+ = u_+/(u_+ + u_-) \text{ or } t_- = u_-/(u_+ + u_-) \tag{4.13}$$

it follows that

$$\lambda_+ = t_+\Lambda \text{ and } \lambda_- = t_-\Lambda \tag{4.14}$$

5. Theoretical Expressions for Equivalent Conductance

The equivalent conductance, Λ, of an electrolytic solution varies with the concentration, c; for very dilute solutions Λ varies almost linearly with the square root of the concentration but for concentrated solutions the relation between Λ and c is quite complex. Kohlrausch, late in the nineteenth century, found that the equivalent conductance of a large number of electrolytic solutions, in the dilute range, varied with a fractional power of the concentration; he was inclined to favor the square root as the fractional power.

In 1923 Debye and Hückel [3] by considering interionic attraction and repulsion in general and the electrophoretic and relaxation-field effects in particular in a hydrodynamic and electrostatic continuum concluded that Λ should vary linearly with the square root of c in dilute solutions. Somewhat later Onsager [4] improved on their model by including the thermal movement of the reference ion, and considering ions as point charges obtained the relation:

$$\Lambda = \Lambda_0 - \frac{|z_+z_-|e^2\Lambda_0 q}{3\epsilon kT(1+\sqrt{q})}\left(\frac{4\pi \text{N}e^2}{1000\epsilon kT}\right)^{1/2}\sqrt{\sum_1 z_i^2 c_i}$$

$$-\frac{F^2}{6\pi\eta N}(|z_+|+|z_-|)\left(\frac{4\pi \text{N}e^2}{1000\epsilon kT}\right)^{1/2}\sqrt{\sum_i z_i^2 c_i}$$

$$\Omega^{-1}\ \text{cm}^2\ \text{equiv}^{-1} \tag{5.1}$$

where

$$q = \frac{|z_+z_-|(\lambda_0^+ + \lambda_0^-)}{(|z_+|+|z_-|)(|z_+|\lambda_0^+ + |z_-|\lambda_0^-)}$$

and z_+ is the valence of the positively charged ion, z_- the valence of the negatively charged ion, λ_0 the limiting equivalent conductance of the individual + and − ions, ϵ the relative dielectric constant of the solvent, η the viscosity of the solvent, and T = absolute temperature in kelvins, defined in the thermodynamic scale by assigning 273.16 K to the triple point of water (freezing point of water = 273.15 K). The 13th General Conference on Weights and Measures in 1967 changed the unit of temperature and temperature interval from "degrees Kelvin" to simply "kelvin" (symbol K). The constants have the values:

k = Boltzmann constant = 1.38054(18) × 10^{-16} erg K^{-1}
N = Avogadro constant = 6.02252(28) × 10^{23} mol^{-1}
e = elementary charge = 4.80298(20) × 10^{-10} esu
F = 96,487.0(1.6) coulomb (g-equivalent)$^{-1}$,

where the numbers in parenthesis in each case represent established limits of error, namely, three standard errors based on the standard deviations of the data and applied to the last digits in the listed value of the physical constant. These values of the physical constants are those recommended in 1963 by the committee on fundamental constants of the National Academy of Sciences—National Research Council [5]. (See appendix C for SI units.)

The so-called thickness of the ion atmosphere around a central ion, κ^{-1}, appears as its reciprocal in equation 5.1 as

$$\kappa = \left(\frac{4\pi \text{N}e^2}{1000\epsilon kT}\right)^{1/2}\sqrt{\sum_i z_i^2 c_i} = \left(\frac{8\pi \text{N}e^2}{1000\epsilon kT}\right)^{1/2}\sqrt{I}\ \text{cm}^{-1} \tag{5.2}$$

where I, the ionic strength, is equal to $(c/2)$ $(\nu_+z_+^2+\nu_-z_-^2)$ and ν_+ and ν_- are the number of positive and negative ions in one molecule of electrolyte, respectively.

For uni-univalent (or 1–1) electrolytes, eq (5.1) may be simplified to:

$$\Lambda=\Lambda_0-(B_1\Lambda_0+B_2)\ \sqrt{I}\ \Omega^{-1}\,\mathrm{cm}^2\,\mathrm{equiv}^{-1} \qquad (5.3)$$

where

$$B_1=\frac{e^2}{6\epsilon kT(1+\sqrt{1/2})}\,(\kappa/\sqrt{I})\ l^{1/2}\,\mathrm{equiv}^{-1/2} \qquad (5.4)$$

and

$$B_2=\frac{F^2}{3\pi\eta N}\,(\kappa/\sqrt{I})\ \Omega^{-1}\,\mathrm{cm}^2\,l^{1/2}\,\mathrm{equiv}^{-1/2} \qquad (5.5)$$

where B_2 and B_2 are the coefficients of the relaxation and electrophoretic terms, respectively.

Physical properties of water, especially the dielectric constant and viscosity needed to calculate B_1 and B_2 for aqueous solutions are given in table 2. Values of B_1 and B_2 for aqueous solutions, on the volume basis, from 0 to 100 °C, are given in table 3 for 1–1 electrolytes. (Conductivity data are usually reported on the volume basis).

The equation of Onsager is generally referred to as the limiting law for equivalent conductance. It gives the tangent to the conductance curve at zero concentration.

In 1932, Onsager and Fuoss [13] recalculated the electrophoresis term, using charged rigid spheres to represent ions and later Fuoss and Onsager [14] (see also Fuoss and Accascina [15]) by also considering ions as charged spheres rather than point charges and with the retention of higher-order terms in treating the relaxation-field effect obtained for 1–1 electrolytes:

$$\Lambda=\Lambda_0-(B_1\Lambda_0+B_2)\ \sqrt{c}+Ec\ln c$$

$$+J(a)c\ \ \Omega^{-1}\,\mathrm{cm}^2\,\mathrm{equiv}^{-1} \qquad (5.6)$$

where B_1 and B_2 have the same significance as given above, and

$$E=E_1\Lambda_0-E_2 \qquad (5.7)$$

where

$$E_1=2.302585\ \kappa^2a^2b^2/24c \qquad (5.8)$$

and

$$E_2=2.302585\ \kappa abB_2/16c^{1/2} \qquad (5.9)$$

and a function $J(a)$, discussed later, where

$$b=e^2/a\epsilon kT \qquad (5.10)$$

and a is the "ion-size" parameter (actually a cancels in (5.8) and (5.9)). Values of a, according to this theory were calculated from $J(a)$, discussed later.

Values of E_1 and E_2 for temperatures from 0 to 100 °C are given in table 4 for 1–1 electrolytes. Differences in the values of B_1 and B_2 and of E_1 and E_2 from those given if the values of the dielectric constant of water determined by Owen, Miller, Milner, and Cogan [12] are used instead of those of Malmberg and Maryott are given in tables 5 and 6, respectively.

Later, Fuoss [16, 17] extended eq (5.6) to associated electrolytes (associated ionophores) and gave:

$$\Lambda=\Lambda_0-(B_1\Lambda_0+B_2)\sqrt{\alpha c}+E\alpha c\log\alpha c$$

$$+J(a)\alpha c-K_Ac\alpha\gamma_c^2\Lambda\ \Omega^{-1}\,\mathrm{cm}^2\,\mathrm{equiv}^{-1} \qquad (5.11)$$

where $(1-\alpha)$ is the fraction of an ionophore associated in ion pairs and related to the *association* constant by the mass action equation:

$$(1-\alpha)=K_A\alpha^2c\gamma_c^2\ l\,\mathrm{mol}^{-1} \qquad (5.12)$$

where γ_c is the activity coefficient, generally obtained by some theoretical equation [18], such as:

$$\log\gamma_c=-A_c\sqrt{I}/(1+B_ca\sqrt{I}) \qquad (5.13)$$

where I is the ionic strength, a, as before, is the "distance of closest approach of the ions" and A_c and B_c are theoretical constants, the values of which are given from 0 to 100 °C in table 7 (the subscript c means that γ, A, and B are on the volume basis). The Arrhenius hypothesis that

$$\alpha=\Lambda/\Lambda_i \qquad (5.14)$$

where Λ_i is the equivalent conductance of the free ions, is used to calculate α. Equation 5.11 is used to determine approximate values of Λ_i by first taking $\alpha=\Lambda/\Lambda_0$ and then successive arithmetical approximations are carried out until self-consistent values of Λ_i and α are obtained for each concentration.

Fuoss and Kraus [19] using the Bjerrum [20] theory for ion pairs gave

$$K_A=K^{-1}=\frac{4\pi N}{1000}\left(\frac{e^2}{\epsilon kT}\right)^3Q(b)\,l\,\mathrm{mol}^{-1} \qquad (5.15)$$

for the association constant where K^{-1} is the dissociation constant and $Q(b)$ is the definite integral $\int_2^b\exp(x)x^{-4}dx$ where $x=e^2/r\epsilon kT$, and the other symbols have the significance given above. Fuoss and Kraus tabulated values of Q as a function of b. Denison and Ramsey [21] used a Born cycle to show that K_A should be a continuous function of ϵT and for a 1–1 electrolyte obtained:

$$K_A=K_A'\exp(b)\ l\,\mathrm{mol}^{-1} \qquad (5.16)$$

where K'_A was given unit value by neglecting dimensions or taking K'_A as 1 liter per mole. Later, Gilkerson [22] using Kirkwood's [23] partition function obtained:

$$K_A = K_A^0 \exp\ (b)\ l\ \text{mol}^{-1} \qquad (5.17)$$

where K_A^0 included the effect of solute-solvent interaction and the free volume of the solute. In 1958, applying Boltzmann's distribution to the problem and considering the solvent as a continuum, Fuoss [24] obtained:

$$K_A = \frac{4\pi \text{N}a^3}{3(1000)} \exp\ (b)\ l\ \text{mol}^{-1} \qquad (5.18)$$

For the halogen acids in water, considered in this document, it was not necessary to include a consideration of K_A; accordingly, numerical values of K_A as a function of a are not given here.

The method of determining α for ionogens is discussed later.

At a later date Fuoss, Onsager, and Skinner [25] retained the Boltzmann factor explicitly in its exponential form and introduced the dimensionless variable, τ, which is the ratio of the Bjerrum distance, near which most ion-pair distribution functions have a minimum, and the Debye-Hückel distance, $1/\kappa$. This variable is a rational reduced variable for the description of electrolytic solutions; two solutions at different dielectric constants would be equivalent electrostatically; for example, their activity coefficients and relaxation fields would be identical. The variable τ is equal to $[6(0.4342945)E_1c]^{1/2}$. With these changes, Fuoss and Onsager obtained:

$$\Lambda = \Lambda_0 - (B_1\Lambda_0 + B_2)c^{1/2} + Ec\ \log\ \tau^2 + L(a)c - K_A\Lambda_0 c\gamma^2\ \Omega^{-1}\ \text{cm}^2\ \text{equiv}^{-1} \qquad (5.19)$$

for the equivalent conductance of highly dissociated 1–1 electrolytes and

$$\Lambda = \Lambda_0 - (B_1\Lambda_0 + B_2)\ (\alpha c)^{1/2} + E\alpha c\ \log\ \alpha\tau^2 + L(a)\alpha c - K_A\Lambda_0\alpha c\gamma^2\ \Omega^{-1}\ \text{cm}^2\ \text{equiv}^{-1} \qquad (5.20)$$

for associated electrolytes or associated ionophores.

Fuoss, Onsager, and Skinner [25] also pointed out that there are other sources of linear terms in the conductance equation. The volume of the ions, as suggested by Steel, Stokes and Stokes [26] and the $c^{1/2}$ term in the dielectric-constant expression of Debye and Falkenhagen [27] lead to a term linear in c. Accordingly, the coefficient of the c term may be complex consisting of a number of factors. In 1969 Chen [28] considered the interaction between the relaxation field and the electrophoretic flow which Fuoss and Onsager had omitted. Chen found that this consideration lead to an additional term of the order of c log c with the result that the coefficient of c log c term in eqs (5.19) and (5.20) becomes $E_1\Lambda_0 - 2E_2$ and the coefficient $L(a)$ in eqs (5.19) and (5.20) (as well as the $J(a)$ coefficient in eqs (5.6) and (5.11)) acquire a different functional form from that published by Fuoss, Onsager, and Skinner [25] in 1965. Since the $L(a)$ and $J(a)$ functions now have only historical interest, numerical tables for them are not included here.

The final conductance equation then has the form:

$$\Lambda = \Lambda_0 - (B_1\Lambda_0 + B_2)c^{1/2} + (E_1\Lambda_0 - 2E_2)c\ \log\ c + k_e c - K_A\Lambda_0 c\gamma^2\ \Omega^{-1}\ \text{cm}^2\ \text{equiv}^{-1} \qquad (5.21)$$

for highly dissociated electrolytes and

$$\Lambda = \Lambda_0 - (B_1\Lambda_0 + B_2)(\alpha c)^{1/2} + (E_1\Lambda_0 - 2E_2)\ \alpha c\ \log\ \alpha c + k_e\alpha c - K_A\Lambda_0\alpha c\gamma^2\ \Omega^{-1}\ \text{cm}^2\ \text{equiv}^{-1} \qquad (5.22)$$

for associated electrolytes or associated ionophores. As of this date, k_e is considered an empirical constant, although its value will be related to the "ion-size" parameter.

A method [29] of obtaining Λ_i and thus α for ionogens may be illustrated as follows: Λ_i is obtained using the Kohlrausch principle of independent ion migration and the assumption that solutions of alkali salts and inorganic hydrogen acids are totally unassociated into ion aggregates at all concentrations. For acetic acid (HAc), for example, the procedure would be as follows:

(a) Determine the equivalent conductance of acetic acid (HAc) at a series of concentrations,

(b) Determine the equivalent conductance of sodium acetate (NaAc), HCl, and NaCl also at a series of concentrations,

(c) Calculate $\Lambda_{i(\text{HAc})}$ from the relationship:

$$\Lambda_{i(\text{HAc})} = \lambda_\text{H} + \lambda_\text{Cl} + \lambda_\text{Na} + \lambda_\text{Ac} - \lambda_\text{Na} - \lambda_\text{Cl} \qquad (5.23)$$

$$= \lambda_\text{H} + \lambda_\text{Ac} \qquad (5.24)$$

which follows from the Kohlrausch principle and in which λ represents the ionic conductances of the ions denoted by subscripts,

(d) Calculate values of $\Lambda_\text{HAc}/\Lambda_{i(\text{HAc})} = \alpha$ for various values of the stoichiometric concentration which would give values of the degree of dissociation of the acid.

This procedure of obtaining Λ_i entails a short series of approximations since the ionic concentration for which Λ/Λ_i must be calculated cannot be known a priori.

Values of α and Λ_i of ionogens may also be obtained by a series of successive approximations using the procedure discussed for ionophores. For dilute solutions the limiting law of Onsager is used. Values of α at higher concentrations may be obtained if the E and higher coefficients are known. As a start these may be estimated and then iteration is made until values of α, Λ_i, E, and the higher terms are self consistent.

In many cases, complex ionic equilibria exist in aqueous solutions and it is not possible to categorically cover all of these in a general fashion. Instead each case will be considered individually where necessary, as, for example, for HF considered later in this document.

A somewhat more detailed treatment of the Debye-Hückel-Onsager-Fuoss theory of electrolytic conductance is given in appendix A.

6. Determination of Λ_0

The method outlined by Fuoss and Accascina [15] was followed, where possible, in determining Λ_0. As a start the Shedlovsky [30] function Λ_0' given by

$$\Lambda_0' = (\Lambda + B_2 c^{1/2})/(1 - B_1 c^{1/2})\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{equiv}^{-1} \quad (6.1)$$

is calculated from observed values of Λ and the theoretical constants B_1 and B_2. Values of Λ_0' are then plotted against c and a preliminary value of Λ_0 obtained by extrapolation to $c=0$. This preliminary value of Λ_0 is then used to compute $B_1\Lambda_0 + B_2$ and E (or $E_1\Lambda_0 - 2E_2$). Then values of Λ' given by

$$\Lambda' = \Lambda + (B_1\Lambda_0 + B_2)c^{1/2} - Ec = \Lambda_0 + k_e c\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{equiv}^{-1} \quad (6.2)$$

are plotted against c and the intercept at $c=0$ gives Λ_0 with the slope giving the empirical constant, k_e. In some cases the procedure must be iterated until consistent values of Λ_0 (between (6.1) and (6.2)) are obtained. The empirical constant corresponds to the older functions $J(a)$ or $L(a)$ where E was equal to $E_1\Lambda_0 - E_2$. Note here that $E = E_1\Lambda_0 - 2E_2$.

7. Equivalent Conductances of HF, HCl, HBr, HI

Of the four halogen acids HF, HCl, HBr, HI all are unassociated ionogens except HF which is not only incompletely dissociated at finite concentrations, but exhibits association of the fluoride ion and the undissociated molecule. These four acids are considered in order. All data, where necessary, were converted to the Jones-Bradshaw [1] conductance standard, the ^{12}C scale of atomic weights, and the absolute electrical units [2]. All data were programmed for an IBM 7090 computer.

HF

(a) *Equilibria.* Data on the equivalent conductance of HF are available only at 0, 16, 18, 20, and 25 °C. The temperature range has been limited since wax or wax lined cells had to be used owing to the corrosiveness of HF. This situation could be remedied, today, by using polyethylene containers or other containers of plastic. The data in the literature on HF have been reported on various concentration scales, namely, mole percent, weight percent, volume dilution, etc. These data were all converted to the molarity basis using available data on the density of aqueous solutions of HF. The density data were fitted to polynominals, the constants for which are given in appendix B.

The dissociation of HF is controlled by the two equilibria:

$$\mathrm{HF} \rightleftarrows \mathrm{H}^+ + \mathrm{F}^- \quad (7.1)$$

and

$$\mathrm{HF}_2^- \rightleftarrows \mathrm{HF} + \mathrm{F}^- \quad (7.2)$$

with the first one more significant for dilute solutions below 0.001 molar. The equilibrium constants for these equilibria are given, respectively, by:

$$K = \frac{a_{\mathrm{H}^+} a_{\mathrm{F}^-}}{a_{\mathrm{HF}}} = \frac{c_{\mathrm{H}^+} c_{\mathrm{F}^-} \gamma_{\mathrm{H}^+} \gamma_{\mathrm{F}^-}}{c_{\mathrm{HF}} \gamma_{\mathrm{HF}}}\ \mathrm{mol}\ l^{-1} \quad (7.3)$$

and

$$k = \frac{a_{\mathrm{HF}} a_{\mathrm{F}^-}}{a_{\mathrm{HF}_2^-}} = \frac{c_{\mathrm{HF}} c_{\mathrm{F}^-} \gamma_{\mathrm{HF}} \gamma_{\mathrm{F}^-}}{c_{\mathrm{HF}_2^-}\ \gamma_{\mathrm{HF}_2^-}}\ \mathrm{mol}\ l^{-1} \quad (7.4)$$

where a, c, and γ denote, respectively, the activity, concentration, and activity coefficient of the species denoted by the subscripts. If we let y and y_3 be the ratios, respectively, of the concentrations of F^- and HF_2^- to the stoichiometric concentration, C, of HF, and assuming, as a start, that all activity coefficients are unity, we have:

$$K = \frac{Cy(y+y_3)}{1-y-2y_3} \approx Cy(y+y_3)\ \mathrm{mol}\ l^{-1} \quad (7.5)$$

$$k = \frac{Cy(1-y-2y_3)}{y_3} \approx \frac{Cy}{y_3}\ \mathrm{mol}\ l^{-1} \quad (7.6)$$

The approximations given in eqs (7.5) and (7.6) are obtained by setting $1-y-2y_3=1$.

Now the observed conductance of HF is given by:

$$\Lambda = y\lambda_0 + y_3\Lambda_0\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{equiv}^{-1} \quad (7.7)$$

where Λ_0 is the sum of the limiting equivalent conductances of H^+ and F^- and λ_0 is the sum of the limiting equivalent conductances of HF_2^- and H^+. Solving the approximate versions of eqs (7.5) and (7.6) for y and y_3 and substituting in (7.7) gives:

$$\Lambda(1+c/k)^{1/2}=(\Lambda_0\sqrt{K}/\sqrt{c}$$
$$+(\lambda_0\sqrt{K}/k)\sqrt{c}\ \Omega^{-1}\,\mathrm{cm}^2\,\mathrm{equiv}^{-1} \qquad (7.8)$$

This equation may be converted to a linear form [35] by multiplying by $\sqrt{c}$, adding and subtracting $c\Lambda_0\sqrt{K}/k$ to the right side, dividing by $(1+c/k)^{1/2}$, squaring both sides, and simplifying; these steps lead to:

$$c\Lambda^2=\Lambda_0^2K+[2\lambda_0/\Lambda_0-1+(1-\lambda_0/\Lambda_0)^2/(1$$
$$+k/c)]\Lambda_0^2Kc/k\,\Omega^{-2}\,\mathrm{cm}^4\,\mathrm{equiv}^{-2} \qquad (7.9)$$

At low concentrations the term $(1-\lambda_0/\Lambda_0)^2/(1+k/c)$ vanishes while at high concentrations it approaches asymptotically the limit $(1-\lambda_0/\Lambda_0)^2$. Therefore, this may be neglected when λ_0/Λ_0 is sufficiently close to unity to render $(1-\lambda_0/\Lambda_0)^2$ negligible with respect to $(2\lambda_0/\Lambda_0-1)$. Accordingly, equation 7.9 reduces to:

$$c\Lambda^2=\Lambda^2K+c(2\Lambda_0\lambda_0-\Lambda_0^2)K/k\,\Omega^{-2}\ \mathrm{cm}^4\ \mathrm{equiv}^{-2} \qquad (7.10)$$

If we now introduce the ionic activity coefficient, γ, and the ionic mobility coefficient, m', we have:

$$\left(\frac{\gamma}{m'}\Lambda\right)^2\frac{c}{1-\Lambda/\Lambda_0}=\Lambda_0^2K$$
$$+\frac{(2\Lambda_0\lambda_0-\Lambda_0^2)K}{k}\left(1-\frac{\Lambda}{\Lambda_0}\right)c \qquad (7.11)$$

Values of γ and m' are given, respectively, by:

$$\log\gamma=-A_c\sqrt{c\Lambda/\Lambda_0} \qquad (7.12)$$

and

$$m'=1-(B_1\Lambda_0+B_2)\Lambda_0^{-1}\sqrt{c\Lambda/\Lambda_0} \qquad (7.13)$$

where A_c is the Debye-Hückel constant, given by:

$$A_c=\left(\frac{2\pi N}{1000}\right)^{1/2}\frac{e^3}{2.302585k^{3/2}}\left(\frac{1}{T^{3/2}\epsilon^{3/2}}\right)l^{1/2}\ \mathrm{mol}^{-1/2} \qquad (7.14)$$

and B_1 and B_2 are the Debye-Hückel-Onsager constants given, respectively, by eqs (5.4) and (5.5) and A_c is the Debye-Hückel constant in eqs (5.13), values of which are listed from 0 to 100 °C in table 7.

A plot of values of the left side of eq (7.11) against $c(1-\Lambda/\Lambda_0)$ gives a straight line for molarities between 0.004 and 1.0. The intercept when $c(1-\Lambda/\Lambda_0)=0$ gives Λ_0^2K and the slope of the line gives $(2\Lambda_0\lambda_0-\Lambda_0^2)K/k$. Thus, since Λ_0 and λ_0 are known K and k can be evaluated (see below under (b).

(b) *Values for* Λ_0. Values reported for Λ_0 for HF are given in table 8. The limiting equivalent conductances of the ions at 25 °C as compiled by Robinson and Stokes [41] yield 405.0 for Λ_0 for HF (their values were converted to absolute units here). Erdey-Grúz, Majthényi, and Kugler [42] using Shedlovsky's [43] Λ_0 values for HCl and NaCl and their value for NaF obtained 405.04 on the old Parker conductivity standard which becomes 405.09 on the Jones-Bradshaw standard. Using 126.39 for Λ_0 for NaCl [41], 105.43 for Λ_0 for NaF [42], and 426.06 for Λ_0 for HCl (see later in this document) gives 405.10 for Λ_0 for HF; this value was selected here as the most reliable value for Λ_0 for HF at 25 °C.

Wooster [35] gave 255 and 404 for Λ_0 at 0 and 25 °C, respectively. Using the ratio 405.10/404, Λ_0 becomes 255.69 at 0 °C. From a linear plot of Λ_0 against $1/T$ one obtains 354.29, 365.85, 377.26 for Λ_0 at 16, 18, and 20 °C, respectively. Wooster [35] gave 437 and 275.4 for λ_0 at 25 and 0 °C, respectively. On converting to the above basis and using a (λ^0-1/T) plot, λ_0 values of 276.15, 383.08, 395.62, 407.99, and 438.19 are obtained, respectively, at 0, 16, 18, 20, and 25 °C.

(c) *Equivalent conductances of* HF. The available data on HF at 25 °C appear in papers by Deussen [37], Fredenhagen and Wellmann [34], Thomas and Maass [44], Ellis [45], and Erdey-Grúz, Majthényi, and Kugler [42]. Thomas and Maass reported their results to only one decimal place and Erdey-Grúz et al. only for very dilute solutions; the latter's data also appear low on a plot of eq (7.11). The data of Deussen, Fredenhagen, and Wellmann, and of Ellis agree within their experimental uncertainty and were fitted to eq (7.11). Data at 16 and 20 °C were obtained only by Roth [36] while data at 18 °C were obtained both by Roth [36] and Hill and Sirkar [31]. The data of Hill and Sirkar, however, were very much lower than those of Roth and were inconsistent with the data obtained by other experimenters at other temperatures. For 0 °C, data were obtained by Deussen and Hill and Sirkar; the latter data showed erratic changes with concentration and Deussen's data at 0 °C were, therefore, selected as the more reliable.

All of these data were fitted to eq (7.11). From a plot of the values of the left side of eq (7.11) against $c(1-\Lambda/\Lambda_0)$, shown for 25 °C for example in figure 1, the values given in table 9 were obtained for K and k. The s_x values, given in table 9, are the standard deviation with which eq (7.11) was fitted over the concentration range of 0.004 to 1.0 N for 0 °C; of 0.006 to 0.2 N for 16, 18, and 20 °C; and 0.004 to 1.0 N for 25 °C.

Eq 7.11 may be rearranged to give for Λ

$$\Lambda=\left[\Lambda_0^2K\left(\frac{m'}{\gamma}\right)^2(1-\Lambda/\Lambda_0)C+\frac{(2\Lambda_0\lambda_0-\Lambda^2K)}{k}\left(\frac{m'}{\gamma}\right)^2(1-\Lambda/\Lambda_0)^2\right]^{1/2}\ \Omega^{-1}\text{ cm}^2\text{ equiv}^{-1} \qquad (7.15)$$

It was also found that

$$(m'/\gamma)^2(1-\Lambda/\Lambda_0) \text{ and } (m'/\gamma)^2(1-\Lambda/\Lambda_0)^2$$

may be expressed, respectively, by:

$$\left(\frac{m'}{\gamma}\right)^2(1-\Lambda/\Lambda_0)=j_1+j_1'\log C \qquad (7.16)$$

and

$$\left(\frac{m'}{\gamma}\right)^2(1-\Lambda/\Lambda_0)^2=j_2+j_2'\log C \qquad (7.17)$$

Therefore, eq (7.15) may be written:

$$\Lambda=\left[\Lambda_0^2K(j_1+j_1'\log C)C+\frac{(2\Lambda_0\lambda_0-\Lambda_0^2K)}{k}(j_2+j_2'\log C)\right]^{1/2}\ \Omega^{-1}\text{ cm}^2\text{ equiv}^{-1} \qquad (7.18)$$

Values of j_1, j_1', j_2, and j_2' follow:

t	j_1	j_1'	j_2	j_2'	s_x
°C					Ω^{-1} cm² equiv⁻¹
0	1.37	0.307	1.28	0.363	0.7
16	1.28	.230	1.26	.320	1.2
18	1.28	.230	1.26	.320	1.1
20	1.28	.230	1.26	.320	1.1
25	1.34	.268	1.29	.341	0.6

The s_x values are the standard deviations with which eq (7.18) was fitted over the concentration range of 0.004 to 1.0 *M* for 0 and 25 °C and for 0.006 to 0.2 *M* for the other temperatures.

Values of the equivalent conductances of HF for rounded concentrations are given in table 10. Values at other concentrations, within the ranges given, may be calculated from eq (7.18).

HCl

(a) *Data at 25 °C.* The equivalent conductances of HCl at 25 °C have been reported by Ruby and Kwai [46], Hlasko [47], Howell [48], Shedlovsky [43], Saxton and Langer [49], Owen and Sweeton [50], Klochko and Kurbanov [51], Stokes [52], and Murr and Shiner [53]. Of the earlier data given in the

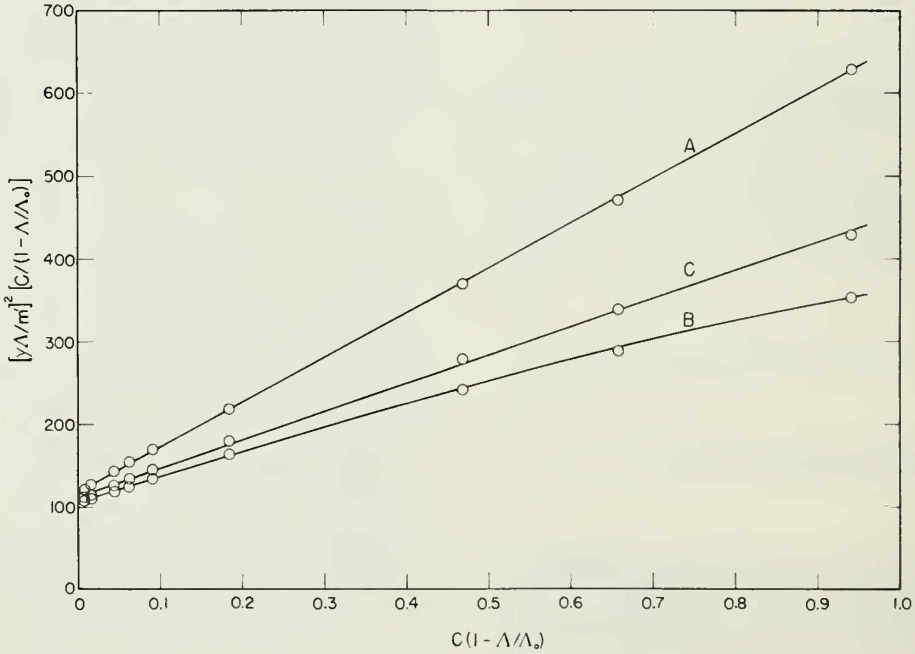

FIGURE 1. *Plots used to obtain values for* K *and* k *governing the dissociation of* HF.

A. No corrections made for activity coefficients or changes in ionic mobilities with concentration.
B. Corrections made for activity coefficients.
C. Corrections made for activity coefficients and changes in ionic mobilities with concentration.

International Critical Tables only the data of Hlasko and Howell are considered here; their data were the most recent and were for higher concentrations where there is a sparsity of data.

It was necessary to divide the data into four concentration ranges to obtain reasonable least square fits to the interpolation equation:

$$\Lambda = \Lambda_0 - (B_1\Lambda_0 + B_2)c^{1/2} + Ec \log c + Ac + Bc^{3/2} + Cc^2 + Dc^{5/2} \ \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1} \qquad (7.19)$$

(This equation is an extension of eq (5.21) which is required for higher concentrations. When higher concentrations are included the coefficient of the c term differs from that obtained when lower concentrations are used). At low concentrations the last two terms on the right were insignificant. The four concentration ranges were as follows:

Concentration range	s_x	References
(molarity)	*Ω^{-1} cm^{2}equiv^{-1}*	
0–0.01	0.05	[43], [49], [50], [52], [53]
0.01–0.1	.14	[43], [46], [47], [49], [50], [52]
0.1–3.0	.10	[50], [51], [52]
3.0–11.6	.15	[47], [48], [50], [51]

The s_x values are the standard deviation with which the following equations fit the experimental data:

0–0.01 *M*

$$\Lambda = 426.06 - 158.63\, c^{1/2} + 185.76\, c \log c + 747.385\, c - 2095.71\, c^{3/2} \ \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1} \qquad (7.20)$$

0.01–0.1*M*

$$\Lambda = 426.06 - 158.63c^{1/2} + 173.11c + 43.515c^{3/2} - 345.46c^2 \ \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1} \qquad (7.21)$$

0.1–3.0*M*

$$\Lambda = 426.06 - 158.63c^{1/2} + 221.501c - 252.771c^{3/2} + 115.606c^2 - 19.5824c^{5/2} \ \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1} \qquad (7.22)$$

3.0–11.6*M*

$$\Lambda = 426.06 - 158.63c^{1/2} + 143.554c - 116.628c^{3/2} + 35.2535c^2 - 3.56231c^{5/2} \ \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1} \qquad (7.23)$$

The coefficient of the $c^{1/2}$ term was obtained from Λ_0 and the B_1 and B_2 coefficients of the Debye-Hückel-Onsager theory. For the dilute range the coefficient of the $c \log c$ term was obtained from Λ_0 and the E_1 and $2E_2$ coefficients given in table 4 (actually 185.767 which was rounded to 185.76). For concentrations above 0.01 *M* it was found that the $c \log c$ term was not needed. It was also found that the value of Λ_0 depended somewhat on the source of the data used in the dilute range. The data of Shedlovsky, Saxton and Langer, Owen and Sweeton, Stokes, and Murr and Shiner below 0.01 *M* were used to obtain Λ_0, according to the procedure outlined by Fuoss and Accascina [15], with the following results:

Experimenters	Number of measurements	Λ_0	s_x
		Ω^{-1} cm^2 equiv^{-1}	*Ω^{-1} cm^2 equiv^{-1}*
Shedlovsky........	11	426.00	0.07
Saxton and Langer..........	10	426.35	.08
Owen and Sweeton........	5	426.55	.07
Stokes.............	9	426.40	.04
Murr and Shiner..........	20	426.06	.02

Since s_x for the Λ_0 value obtained from the data of Murr and Shiner was the lowest their Λ_0 value was selected (evident on reference to eqs (7.20) to (7.23)).

The equivalent conductances of HCl at rounded concentrations at 25 °C, and the experimental range covered, calculated by eqs (7.20) to (7.23), are given in table 11.

(b) *Data at other temperatures.* Values of the equivalent conductance of HCl at −20, −10, 0, 10, 20, 30, 40, and 50 °C, given here, are based on the data of Haase, Sauermann, and Dücker [54], except that at 50 °C the values in the dilute range (0 to 0.01 *M*) were derived from the results of Cook and Stokes [55]. Values at 5, 15, 35, 45, 55, and 65 °C are based on the results of Owen and Sweeton [50]. These results were consistent with those obtained at 25 °C and discussed above.

The equivalent conductances of HCl at rounded concentrations for these temperatures and for the experimental range covered are included in table 11. The data in each case, except below 0 °C, were fitted to the equation:

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \log c + Ac + Bc^{3/2} + Cc^2 + Dc^{5/2} \ \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1} \qquad (7.24)$$

where $S = B_1\Lambda_0 + B_2$ and B_1, B_2 and E are the theoretical Debye-Hückel-Onsager-Fuoss coefficients. Below 0 °C the empirical equation

$$\Lambda = A + Bc + Cc^2 + Dc^3 + Ec^4 + Fc^5 + Gc^6 \; \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1} \qquad (7.25)$$

was used. In this case A obviously doesn't represent Λ_0 as the infinitely dilute solution would be in the solid or frozen state. Nevertheless eq (7.25) may be used for interpolation purposes.

Values of the coefficients of eqs (7.24) and (7.25) and the concentration value over which they apply are given in table 12. The s values given in column 9 are the standard deviations of the fit.

HBr

(a) *Data at 25 °C.* Data on the equivalent conductance of HBr at 25 °C are based on the measurements of Dawson and Crann [56], Hlasko [47], and Haase, Sauermann, and Dücker [54]. Only the last mentioned are recent data. As with HCl the data were divided into concentration ranges (in this case three) to obtain reasonable least square fit of the data with the equation:

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \log c + Ac + Bc^{3/2} + Cc^2 + Dc^{5/2} \; \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1} \qquad (7.26)$$

The $c \ln c$ term was not required above 0.01 M, and for the dilute range the $c^{5/2}$ term was negligible. The concentration ranges with the conductance equations follow (the s values are the standard deviations of the fit):

0.0000 − 0.01M ($s = 0.09$; references [47, 56])

$$\Lambda = 427.74 - 159.02c^{1/2} + 186.65c \log c + 899.72c - 4289.3c^{3/2} + 8912.1c^2 \; \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1} \qquad (7.27)$$

0.01 − 0.10M ($s = 0.09$; references [47, 56])

$$\Lambda = 427.74 - 159.02c^{1/2} + 210.8272c - 209.547c^{3/2} \; \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1} \qquad (7.28)$$

0.10 − 3.0M ($s = 0.08$; references [47, 56])

$$\Lambda = 427.74 - 159.02c^{1/2} + 192.8124c - 177.2474c^{3/2} + 53.93903c^2 - 3.746204c^{5/2} \; \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1} \qquad (7.29)$$

3.0 − 7.5M ($s = 0.09$; references [47, 54])

$$\Lambda = 427.74 - 159.02c^{1/2} + 130.5906c - 101.6916c^{3/2} + 29.49103c^2 - 2.843402c^{5/2} \; \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1} \qquad (7.30)$$

As for HCl the coefficient of the $c^{1/2}$ term was obtained from Λ_0 and the B_1 and B_2 coefficients of the Debye-Hückel-Onsager theory.

The equivalent conductances of HBr at rounded concentrations at 25 °C, calculated by eqs (7.27) to (7.29) for the experimental range covered are given in table 13.

(b) *Data at other temperatures.* Values of the equivalent conductance of HBr at −20, −10, 0, 10, 20, 30, 40, and 50 °C are based on the recent measurements of Haase, Sauermann, and Dücker [54]. The equivalent conductances of HBr at rounded concentrations for these temperatures and for the experimental range covered are given in table 14. The data in each case, except below 0 °C, were fitted to the equation:

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ac + Bc^{3/2} + Cc^2 + Dc^{5/2} \; \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1} \qquad (7.31)$$

with a zero standard deviation. The coefficient S again equals $B_1\Lambda_0 + B_2$. Below 0 °C the empirical equation used for HCl, namely, eq (7.25) was again used. Values of the coefficients of eqs (7.31) and (7.25) (as applied to HBr) are given in table 15 together with the concentration range over which they apply. The coefficients are empirical and the coefficient of the c term is low in terms of modern theory.

HI

Only a few measurements have been made on the electrolytic conductance of HI and, with the exception of those of Haase, Sauermann, and Dücker in [54], these were made over 30 years ago. The International Critical Tables (1929) cited two papers for 18 °C, one by Loomis in 1897 [57] and the other by Heydweiller in 1909 [58]. For 25 °C, the work of Ostwald in 1903 [59], of Washburn and Strachan in 1913 [60], and of Strachan and Chu in 1914 [61] were cited. Ostwald's results were thrown in doubt when Bray and Hunt [62] showed that his data for HCl were in error by about 3 percent and presumably his data on HBr were also questionable. Washburn and Strachan's data were nullified by analytical errors made in establishing the concentration of the solutions: Strachan and Chu corrected their data. Only three references to work on HI were found that had not been listed in ICT. Two of these contained the same data, Hlasko and Wazewski [63] and Hlasko [47]. The third one was by Haase et al. mentioned above [54]. Solutions of HI may also contain traces of iodine although the experimenters made attempts to prevent HI decomposition.

(a) *Data at 25 °C.* The data of Strachan and Chu, Hlasko, and Haase et al. at 25 °C were combined and fitted to a polynomial. The Λ_0 for HI was calculated from the ionic values listed by Robinson and Stokes and converted to absolute units. The equations are from 0.0000 − 0.01M and 0.01 − 7.0M.

respectively, for the equivalent conductance as a function of c at 25 °C

$$\Lambda = 426.45 - 158.72c^{1/2} + 185.96c \log c + 1085.7c - 11678c^{3/2} + 107071c^2 - 394591c^{5/2}\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{equiv}^{-1}, \qquad (7.32)$$

$$\Lambda = 426.45 - 158.72c^{1/2} + 248.885c - 256.566c^{3/2} + 96.2195c^2 - 12.3887c^{5/2}\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{equiv}^{-1} \qquad (7.33)$$

with a standard error of 0.2. The coefficient of the $c^{1/2}$ term is based on the Λ_0 value and the B_1 and B_2 coefficients of the Debye-Hückel-Onsager theory. The coefficient of the $c \log c$ term is based on the Λ_0 value and E_1 and $2E_2$ coefficients of the Debye-Hückel-Onsager-Fuoss theory.

The equivalent conductances of HI at rounded concentrations for 25 °C and for the experimental range covered, as calculated by eq (7.33), are given in table 16.

(b) *Data at other temperatures.* Values of the equivalent conductance of HI at −20, −10, 0, 10, 20, 30, 40, and 50 °C are based on the recent measurements of Haase, Sauermann, and Dücker [54]. The equivalent conductances of HI at rounded concentrations for these temperatures and for the experimental range covered are given in table 17. The data in each case, except below 0 °C, were fitted to eq (7.31). Below 0 °C the empirical equation used for HCl and HBr, namely, eq (7.25) was used except that the c^4, c^5, and c^6 terms were not needed at −20 °C and the c^5 and c^6 terms were not needed at −10 °C. The equations derived for each temperature are listed in table 18; the s values given in the footnote refer to the standard deviation of the fit of the equations.

8. Conclusions

In table 19 the limiting equivalent conductances of HF, HCl, HBr, and HI obtained herein at 25 °C are compared with the best previous data. The agreement is quite good. It is interesting that $\Lambda°$ does not show a consistent trend with the atomic number of the halide.

Except for HF, for very dilute solutions the conductances are in accord with the Debye-Hückel-Onsager limiting law.

9. References

[1] Jones, G., and Bradshaw, B. C., J. Am. Chem. Soc. **55,** 1780 (1933).
[2] NBS Circ. 459, 7 (1947).
[3] Debye, P., and Hückel, E., Physik. Z. **24,** 185, 305 (1923).
[4] Onsager, L., Physik. Z. **27,** 388 (1926); **28,** 277 (1928).
[5] Chem. & Eng. News, p. 39, Nov. 11, 1963.
[6] Thiesen, M., Wiss. Abh. der Physikalisch-Technischen Reichsanstalt **4,** No. 1, 1904.
[7] International Critical Tables **3,** 25 (1928).
[8] Swindells, J. F., Coe, J. R., and Godfrey, T. B., J. Research NBS **48,** 1 (1952) RP2279.
[9] Hardy, R. C., and Cottington, R. L., J. Research NBS **42,** 573 (1949) RP1994.
[10] Coe, J. R., and Godfrey, T. B., J. App. Phys. **15,** 625 (1944).
[11] Malmberg, C. G., and Maryott, A. A., J. Research NBS **56,** 1 (1956) RP2641.
[12] Owen, B. B., Miller, R. C., Milner, C. E., and Cogan, H. L., J. Phys. Chem. **65,** 2065 (1961).
[13] Onsager, L., and Fuoss, R. M., J. Phys. Chem. **36,** 2689 (1932).
[14] Fuoss, R. M., and Onsager, L., Proc. Nat. Acad. Sci. **41,** 283 (1955); Fuoss, R. M., and Onsager, L., J. Phys. Chem. **61,** 668 (1957); Fuoss, R. M., J. Am. Chem. Soc. **79,** 3301 (1957); Fuoss, R. M., and Kraus, C. A., J. Am. Chem. Soc. **79,** 3304 (1957).
[15] Fuoss, R. M., and Accascina, F., Electrolytic Conductance, Ch. XIV and XV (Interscience Publishers, Inc., New York, 1959).
[16] Fuoss, R. M., J. Am. Chem. Soc. **79,** 3301 (1957).
[17] Fuoss, R. M., and Kraus, C. A., J. Am. Chem. Soc. **79,** 3304 (1957).
[18] Hamer, W. J., Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 24, 276 pages (Dec. 1968).
[19] Fuoss, R. M., and Kraus, C. A., J. Am. Chem. Soc. **55,** 1019 (1933).
[20] Bjerrum, N., Kgl. Danske Vidensk. Selskab. Math.-fys. Medd. **7,** No. 9 (1926).
[21] Denison, J. T., and Ramsey, J. B., J. Am. Chem. Soc. **77,** 2615 (1955).
[22] Gilkerson, W. R., J. Chem. Phys. **25,** 1199 (1956).
[23] Kirkwood, J. G., J. Chem. Phys. **18,** 380 (1950).
[24] Fuoss, R. M., J. Am. Chem. Soc. **80,** 5059 (1958).
[25] Fuoss, R. M., Onsager, L., and Skinner, J. F., J. Phys. Chem. **69,** 2581 (1965).
[26] Steel, B. J., Stokes, J. M., and Stokes, R. H., J. Phys. Chem. **62,** 1514 (1958).
[27] Debye, P., and Falkenhagen, H., Physik. Z. **29,** 121, 401 (1928).
[28] Chen, M. S., Dissertation, Yale University, June 1969.
[29] MacInnes, D. A., The Principles of Electrochemistry, Ch. 18 (Reinhold Publishing Corp., New York, 1939).
[30] Shedlovsky, T., J. Am. Chem. Soc. **54,** 1405 (1932).
[31] Hill, E. G., and Sirkar, A. P., Proc. Roy. Soc. **A83,** 140 (1910).
[32] Domange, L., Compt. rend. **198,** 469 (1934).
[33] Winteler, F., Z. angew. Chem. **15,** 33 (1902).
[34] Fredenhagen, K., and Wellmann, M., Z. Phys. Chem. **A162,** 454 (1932).
[35] Wooster, C. B., J. Am. Chem. Soc. **59,** 377 (1937).
[36] Roth, W. A., Ann. Chem. **542,** 35 (1939).
[37] Deussen, E., Z. anorg. Chem. **44,** 310 (1905).
[38] Wegscheider, R., Z. Phys. Chem. **69,** 620 (1909).
[39] Pick, H., Z. Phys. Chem. Nernst-Festschrift, 360 (1912).
[40] Davies, C. W., and Hudleston, L. J., J. Chem. Soc. **125,** 260 (1924).
[41] Robinson, R. A., and Stokes, R. H., Electrolyte Solutions, 2nd. ed., p. 465 (Butterworths Scientific Publications, London, 1959).
[42] Erdey-Grúz, T., Majthényi, L., and Kugler, E., Acta Chim. Acad. Sci. Hung. **37,** 393 (1963).
[43] Shedlovsky, T., J. Am. Chem. Soc. **54,** 1411 (1932).
[44] Thomas, D. K., and Maass, O., Can. J. Chem. **36,** 744 (1958).
[45] Ellis, A. J., J. Chem. Soc. 4300 (1963).
[46] Ruby, C. E., and Kwai, J., J. Am. Chem. Soc. **48,** 1119 (1926).
[47] Hlasko, M., J. Chim. Phys. **26,** 125 (1929).
[48] Howell, O. R., J. Chem. Soc. (1929) 162.
[49] Saxton, B., and Langer, T. W., J. Am. Chem. Soc. **55,** 3638 (1933).
[50] Owen, B. B., and Sweeton, F. H., J. Am. Chem. Soc. **63,** 2811 (1941).

[51] Klochko, M. A., and Kurbanov, M. Sh., Akad. Nauk SSSR, Izvest. sek. Fiz-Khim. analiza **24**, 237 (1954).
[52] Stokes, R. H., J. Phys. Chem. **65**, 1242 (1961).
[53] Murr, B. L., Jr., and Shiner, V. J., Jr., J. Am. Chem. Soc. **84**, 4672 (1962).
[54] Haase, R., Sauermann, P. F., and Dücker, K. H., Z. Phys. Chem. Neue Folge **47**, 224 (1965).
[55] Cook, B. M., and Stokes, R. H., J. Phys. Chem. **67**, 511 (1963).
[56] Dawson, H. M., and Crann, T. W., J. Chem. Soc. **109**, 1262 (1916).
[57] Loomis, E. H., Ann. Physik. und Chemie **296** [3], **60**, 547 (1897).
[58] Heydweiller, A., Ann. Physik. **30**, 873 (1909).
[59] Ostwald, W., Lehrbach der allgemeinen Chemie, (Engelmann, Leipzig, 1903).
[60] Washburn, E. W., and Strachan, E. K., J. Am. Chem. Soc. **35**, 690 (1913).
[61] Strachan, E. K., and Chu, V. G., J. Am. Chem. Soc. **36**, 810 (1914).
[62] Bray, W. C., and Hunt, F. L., J. Am. Chem. Soc. **33**, 781 (1911).
[63] Hlasko, M., and Wazewski, D., Bull. intern. acad. Polonaise, No. **4-5A**, 181 (1928).
[64] Ref. 29, page 342.
[65] Harned, H. S., and Owen, B. B., The Physical Chemistry of Electrolytic Solutions, 3rd ed., p. 231 (Reinhold Publishing Corp., New York, 1958).
[66] Ref. 41, page 465.

10. Appendix A. The Debye-Hückel-Onsager-Fuoss Theory of Electrolytic Conductance

According to the Debye-Hückel theory of electrolytic solutions, in the electrostatic effect between ions, the discrete charge distribution is replaced by a continuous charge distribution, or charge density, $\rho(r)$, or "ion atmosphere" which is a continuous function of r, the distance from a reference ion. The "ion atmosphere" extends from $r=a$ to

$$r=O(V^{1/3}) \approx \infty,$$

where V is the volume of the system, and acts electrostatically somewhat like a sphere of charge $-e$ at a distance κ^{-1} from the reference ion of charge $+e$. The distance κ^{-1} is considered the thickness of the "ion atmosphere".

Thermal or Brownian motion of the ions will tend to disturb this distribution but not entirely so, and Debye and Hückel used the Boltzmann principle to express the ionic distribution as a function of the ratio of the electrical and thermal energies. The localized concentration of a given species of ions is equal to the average or bulk concentration of that species multiplied by the exponential function $\exp(-U/kT)$ where U gives the potential energy at the point under consideration. If we have a solution containing N_i ions of species $i (i=1, 2$ for simple ions and $1, 2 \ldots s$ for electrolyte mixtures) in a volume V, the localized (average) concentration n_{ji} of ionic species i in vicinity of ionic species j is given by

$$n_{ji}=n_i \exp\left(-U_{ji}/kT\right) \tag{A.1}$$

where $n_i=N_i/V$. The potential energy U_{ji} of an i-ion with charge z_ie near a j-ion is given by $z_ie\Psi_j^0$ where e is the elementary charge, z_i the valence of an i-ion, and Ψ_j^0 is the electrostatic potential at the location of the i-ion, stated in terms of a spherical coordinate system with the origin at the location of the j-ion (or reference ion). The thermal energy is given by kT. Since $U=z_ie\Psi_j^0$ eq (A.1) may be written:

$$n_{ji}=n_i \exp\left(-z_ie\Psi_j^0/kT\right) \tag{A.2}$$

Since each i-ion has a charge z_ie the net charge density of i-ion in the vicinity of a j-ion, ρ_j, is given by

$$\rho_j=\sum_i n_iz_ie \exp\left(-z_ie\Psi_j^0/kT\right) \tag{A.3}$$

Debye and Hückel also used Poisson's equation to relate ρ_j and Ψ_j, namely,

$$\nabla^2\Psi_j^0=\frac{-4\pi}{\epsilon}\rho_j \tag{A.4}$$

where ϵ is the dielectric constant of the medium in which the ions exist. This relation states that at any point in a medium located by three space coordinates $(x, y, z; r, \theta, \phi)$ the divergence of the gradient of the potential is proportional to the charge density at this point. Eliminating ρ_j between eqs (A.3) and (A.4) gives

$$\nabla^2\Psi_j^0=\frac{-4\pi}{\epsilon}\sum_i n_iz_ie \exp\left(-z_ie\Psi_j^0/kT\right) \tag{A.5}$$

This relation implies a contradiction of the superposition principle of electrostatics, namely, that the potential due to an assembly of charges is simply the sum of the potentials due to each of the charges acting alone. The left side of eq (A.5) is a linear function of Ψ whereas the right side is not; it is exponential. Debye and Hückel resolved this dilemma by restricting the application to dilute solutions where the ionic potential energy is small compared with the thermal energy (see eq (A.7) below).

For unperturbed electrolytic solutions the "ionic atmosphere" is assumed to be spherical. Therefore, it is most convenient to express $\nabla^2\Psi_j^0$ in spherical coordinates, thus,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\Psi_j^0}{dr}\right)=-\frac{4\pi}{\epsilon}\sum n_iz_ie \exp\left(-z_ie\Psi_j^0/kT\right) \tag{A.6}$$

If we expand the exponential function as a series and drop quadratic and higher terms (quadratic terms may be retained for symmetrical electrolytes because $\sum ne^3$ vanishes), since the problem is restricted to dilute solutions, we have

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\Psi_j^0}{dr}\right)=\frac{4\pi}{\epsilon kT}\sum_i n_i z_i^2 e^2\Psi_j^0=\kappa^2\Psi_j^0 \tag{A.7}$$

where κ is defined by

$$\kappa=\left(\frac{4\pi e^2}{\epsilon kT}\sum_i n_i z_i^2\right)^{1/2} \tag{A.8}$$

κ has the dimensions of reciprocal length and increases with the square root of the concentration; $1/\kappa$ may be considered the average radius or thickness of the "ionic atmosphere." Equation (A.7) is consistent with the superposition principle since both sides are now linear functions of the potential. Since $n_i=c_iN/1000$ where N is Avogadro's number and c_i is the concentration in moles per liter, eq (A.8) may be written:

$$\kappa=\left(\frac{4\pi e^2N}{1000kT}\right)^{1/2}\sqrt{\sum_i z_i^2c_i} \tag{A.9}$$

Since the ionic strength, I, is defined as $1/2\sum_i z_i^2c_i$ eq (A.9) may also be written

$$\kappa=\left(\frac{8\pi e^2N}{1000kT}\right)^{1/2}\sqrt{I} \tag{A.10}$$

Equation (A.7) has the general solution:

$$\Psi_j^0(r)=A\,\frac{\exp\,(-\kappa r)}{r}+A'\,\frac{\exp\,(\kappa r)}{r} \tag{A.11}$$

where A and A' are integration constants. They may be evaluated upon the following considerations. First A' must equal zero since $\Psi_j^0\rightarrow 0$ as r increases. The evaluation of A rests on the principle of electroneutrality. The total charge in the space around a given charge e_j must be exactly equal to this charge but of opposite sign. The total charge is obtained by integrating the density over the entire space around j, thus

$$-z_je_j=\int_{a_j}^{\infty}4\pi r^2\rho_j dr \tag{A.12}$$

where $4\pi r^2dr$ is the total volume of the shells in the "ionic atmosphere" around the central ion. The integration is from the "distance of closest approach" of the ions given by the sum of the effective radii of the ions in "contact" to infinity. Since from eqs (A.4) and (A.7), $\kappa^2\Psi^0=-4\pi\rho/\epsilon$ eq (A.12) may be written

$$z_je_j=\int_{a_j}^{\infty}\kappa^2\Psi_j^0\epsilon r^2dr \tag{A.13}$$

Combining eqs (A.11) and (A.13) gives

$$z_je_j=\int_{a_j}^{\infty}\kappa^2\epsilon rA\,\exp\,(-\kappa r)dr \tag{A.14}$$

which upon integration in parts gives

$$\begin{aligned} z_je_j&=\left[-\epsilon A(\kappa r+1)\,\exp\,(-\kappa r)\right]_{a_j}^{\infty}\\ &=\epsilon A(\kappa a_j+1)\,\exp\,(-\kappa a_j) \end{aligned} \tag{A.15}$$

Accordingly,

$$A=\frac{z_je_j\,\exp\,(\kappa a_j)}{\epsilon(1+\kappa a_j)} \tag{A.16}$$

which upon substitution in eq (A.11) gives

$$\Psi_j^0(r)=\frac{z_je_j\,\exp\,[\kappa(a_j-r)]}{\epsilon r(1+\kappa a_j)} \tag{A.17}$$

At the distance of closest approach $r=a_j$, so that

$$\Psi_j^0(r)=\frac{z_je_j}{\epsilon a_j(1+\kappa a_j)}=\frac{z_je_j}{\epsilon a_j}-\frac{z_je_j\kappa}{\epsilon(1+\kappa a_j)} \tag{A.18}$$

where the first term on the right is the potential at the surface of the ion due to the charge on the ion itself and is independent of the concentration. The second term on the right is that portion of $\Psi_j^0(r)$ due to the "ionic atmosphere" and is dependent on the concentration through the value of κ.

In the foregoing we have considered electrolytic solutions in the absence of external fields. We shall now consider such solutions when subjected to potential gradients as encountered in electrolytic conductance. In the first place, ions are neither created nor destroyed during their motion under a dc field in an electrolytic solution (this is known as the equation of continuity analogous to the equation of continuity in hydrodynamics which states that matter is conserved in liquid flow). In the second place, we have two main effects as a consequence of the interactions between ions: the *relaxation-field effect* and the *electrophoretic effect.* When an electrolytic solution is subjected to a potential field the "ionic atmosphere" leads to these two effects.

When the "ionic atmosphere" is unperturbed, i.e., not exposed to an applied electrical field or shearing force tending to cause ions to move relative to the solvent it is assumed to have spherical symmetry. However, when the ion is caused to move under an applied electrical field the spherical symmetry of the "ionic atmosphere" is disturbed. If a particular kind of ion moves to the right, for example, each ion will constantly have to build up its ionic atmosphere to the right while the charge density to the left gradually decays. The rate at which the atmosphere to the right forms and the one on the left decays is expressed in terms of a quantity known as the *time of relaxation* of the "ionic atmosphere." The decay occurs exponentially and the return is asymptotic to the original random distribution. The time required for the "ionic atmosphere" to fall essentially to zero is given by $4q\theta$ where θ is the time of relaxation and q is defined by

$$q=\frac{z_+z_-}{z_++z_-}\left(\frac{\lambda_++\lambda_-}{z_+\lambda_++z_-\lambda_-}\right) \qquad \text{(A.19)}$$

with z_+, z_-, λ_+, and λ_- having the same significance as given previously.

The asymmetry of the ion atmosphere owing to the effect of the time of relaxation leads to an excess charge of opposite sign behind the moving ion. This excess charge of opposite sign causes a retardation of the moving ion. Onsager by using the Debye-Hückel approach, taking care of the Brownian movement of the ions, and dropping higher terms in the equation of continuity obtained:

$$X_1=-\operatorname{grad}\Psi^0_{1(r=0)}=\frac{e_1e_2}{3\epsilon kT}\,\frac{q}{1+\sqrt{q}}\,\kappa X \qquad \text{(A.20)}$$

for the relaxation effect for a dilute electrolyte solution dissociating into two kinds of ions. Here q is defined by eq (A.19), X is the electrical field intensity acting in the x direction and X_1 is the relaxation field acting in the same direction but in the opposite sense, as a result of the perturbation of the "ionic atmosphere." The resultant field is then:

$$X+X_1=X+\frac{e_1e_2}{3\epsilon kT}\,\frac{q}{1+\sqrt{q}}\,\kappa X \qquad \text{(A.21)}$$

The total electrical force acting on the ion is then

$$e_j(X+X_1)=e_jX\left(1+\frac{e_1e_2}{3\epsilon kT}\,\frac{q}{1+\sqrt{q}}\,\kappa\right) \qquad \text{(A.22)}$$

which leads to a movement of the ion with a velocity, v'_j, of:

$$v'_j=e_j(X+X_1)u^*_j=e_jX\left(1+\frac{e_1e_2}{3\epsilon kT}\,\frac{q}{1+\sqrt{q}}\,\kappa\right)u^*_j \qquad \text{(A.23)}$$

where u^*_j is the "absolute" mobility of the ion. Since the product e_1e_2 is negative, the relaxation field opposes the external field.

The other factor, the *electrophoretic effect*, arises from the tendency of the "ionic atmosphere" shell to move with its associated solvent molecules under an applied electrical field in a direction opposite to the motion of the ion. The forces, k_j, acting on the ions must be balanced by other forces acting on the solvent molecules, k_s, hence:

$$\sum n_jk_j=-n_sk_s \qquad \text{(A.24)}$$

where bulk concentrations are denoted by n_j and n_s. At a distance r from the central ion and within a volume element, dV, the localized concentration for the ion will differ from the bulk concentration and the directed ion force near a j-ion will be $\sum n_{ji}k_idV$ which differs from the gross volume average force $\sum\limits_i n_ik_idV$ because of the j-ion concentrations within its vicinity (see later). For the solvent molecules, the force remains unchanged and is given by n_sk_sdV for the volume element dV. The net force acting on the volume element near a j-ion is, therefore,

$$\left(\sum_i n_{ji}k_i+n_sk_s\right)dV=\sum_i\,(n_{ji}-n_i)k_idV \qquad \text{(A.25)}$$

A spherical shell of radius r and thickness dr is, therefore, subject to the resultant force, $d\mathscr{F}$, given by:

$$d\mathscr{F}=\sum_i\,(n_{ji}-n_i)k_i(4\pi r^2dr) \qquad \text{(A.26)}$$

Neglecting the asymmetry of the "ion atmosphere", Fuoss used the distribution function:

$$n_{ji}=n_i[1-e_i\Psi^0_j/kT+\tfrac{1}{2}\,(e_i\Psi^0_j/kT)^2] \qquad \text{(A.27)}$$

to express $(n_{ji}-n_i)$ as a function of r and the Debye-Hückel expression (eq (A.17)) for the potential $\Psi^0_j\,(r)$. Thus, the resultant force on the shell is given by:

$$\begin{aligned}d\mathscr{F}=4\pi r^2\sum_i\,[&-n_ie_ie_j(1+\kappa a_i)\\ &\exp(-\kappa r)/\epsilon kTr\,\exp(\kappa a_i)+n_ie_ie_j^2(1+\kappa a_i)^2\\ &\exp(-2\kappa r)/2(\epsilon kTr)^2\exp(2\kappa a_i)]\,Xz_jedr\end{aligned} \qquad \text{(A.28)}$$

where k_i is replaced by the electrical force, Xe_i. Debye and Hückel originally considered that this force imparted a velocity to the reference ion which they assumed followed Stokes law (eq (3.4)) for a rigid sphere having a radius $=b$ (hydrodynamic radius). Later Onsager considered that the force (eq (A.28)) imparted a velocity to the reference ion and its atmosphere which he assumed followed Stokes volume equation:

$$dv''_j=d\mathscr{F}/6\pi\eta r \qquad \text{(A.29)}$$

where η is the viscosity of the medium and the average radius $=r$, thus eliminating the hydrodynamic parameter b (see also Fuoss and Accascina [15], p. 164). The total velocity, $\Delta v''_j$, produced by all the ions in the atmosphere on the j-ion is then given by the integral of the combination of eqs (A.28) and (A.29) from the "distance of closest approach" of the ions, a, to infinity, or:

$$\Delta v_j'' = \left(\frac{2}{3}\eta\right)\int_a^\infty [-A_1 \exp(-\kappa r) + A_2 \exp(-2\kappa r)/r]\,dr \qquad (A.30)$$

Inserting values of A_1 and A_2 from (A.28) gives:

$$\Delta v_j'' = -2Xe_j \sum n_i e_i^2/3\eta\epsilon kT\kappa(1+\kappa a) + Xe_j(1+\kappa a)^2 Ei(2\kappa a) \sum n_i e_i^3/3\eta(\epsilon kT)^2 \exp(2\kappa a) \qquad (A.31)$$

where $Ei\ (2\kappa a)$ is the exponential integral $e^{-2\kappa r}dr$. For symmetrical electrolytes $e_1 = e_2$ and the second term of equation (A.31) vanishes. Thus,

$$\Delta v_j'' = -2Xe_je_i \sum n_i e_i^2/3\eta\epsilon kT(1+\kappa a) \qquad (A.32)$$

Multiplication of the numerator and denominator of (A.32) by κ and substitution in the denominator of the value for κ^2 given by (A.8) give for $\Delta v_j''$

$$\Delta v_j'' = -Xe_j\kappa/6\pi\eta(1+\kappa a) \qquad (A.33)$$

which is the original result presented by Onsager. If $a=0$ (ions are point charges)(A.33) becomes:

$$\Delta v_j'' = -Xe_j\kappa/6\pi\eta \qquad (A.34)$$

the limiting value derived by Onsager.

Combining (A.23) for the relaxation effect and (A.34) for the electrophoretic effect gives:

$$v_j = v_j' + \Delta v_j'' = e_jX\left(u_i^* + \frac{e_1e_2}{3\epsilon kT}\frac{q}{1+\sqrt{q}}u_i^* - \kappa/6\pi\eta\right) \qquad (A.35)$$

for the velocity of the ion. Since $e_jXu^* = v_{jo}$ this equation may be written, for an electrolyte containing two kinds of ions:

$$v_j = v_{jo} - \frac{e^2}{3\epsilon kT}\frac{|z_1z_2|q}{1+\sqrt{q}}\kappa v_{jo} - \frac{ez_j}{6\pi\eta}\kappa \qquad (A.36)$$

where the valence of the ions, z, is now introduced. Upon introduction of κ as defined by (A.9) and substitution of $z_1^2c_1 + z_2^2c_2$ for $\sum z_i^2c_i$ and W for $2z_1z_2q/(1+\sqrt{q})$ we have:

$$v_j = v_{jo} - \left(\frac{e^2W}{6\epsilon kT}v_{jo} + \frac{ez_j}{6\pi\eta}\right)\left(\frac{4\pi e^2N}{1000kT}\right)^{1/2}\sqrt{z_1^2c_1 + z_2^2c_2}. \qquad (A.37)$$

Onsager replaced c_1 and c_2 by equivalent concentrations (c is then the same for both types of ions), here denoted by c; hence:

$$v_j = v_{jo} - \left(\frac{e^2W}{6\epsilon kT}v_{jo} + \frac{ez_j}{6\pi\eta}\right)\left(\frac{4\pi e^2N}{1000kT}\right)^{1/2}\sqrt{(|z_1| + |z_2|)c}. \qquad (A.38)$$

For uni-univalent electrolytes $z_1 = z_2 = 1$ and $W = 2-\sqrt{2}$,

$$v_j = v_{jo} - \left(\frac{e^2(2-\sqrt{2})}{6\epsilon kT}v_{jo} + \frac{ez_j}{6\pi\eta}\right)\left(\frac{8\pi e^2N}{1000kT}\right)^{1/2}\sqrt{c}. \qquad (A.39)$$

Now for a potential gradient of 1 V/cm,

$$V = 1/299.7925 \text{ esu}$$

and letting $v_j/299.7925 = u_j$, the mobility, we have:

$$u_j = u_{jo} - \left(\frac{e^2(2-\sqrt{2})}{6\epsilon kT}u_{jo} + \frac{ez_j}{6(299.7925)\pi\eta}\right)\left(\frac{8\pi e^2N}{1000kT}\right)^{1/2}\sqrt{c}. \qquad (A.40)$$

Now, since $u_jF = \lambda_j$, where λ_j is the equivalent conductance of the j-ion, eq (A.40) may be written:

$$\lambda_j = \lambda_{jo} - \left(\frac{e^2(2-\sqrt{2})}{6\epsilon kT}\lambda_{jo} + \frac{ez_jF}{6(299.7925)\pi\eta}\right)\left(\frac{8\pi e^2N}{1000kT}\right)^{1/2}\sqrt{c}. \qquad (A.41)$$

Since $e = 299.7925\,F/N$ eq (A.41) may also be written:

$$\lambda_j = \lambda_{jo} - \left(\frac{e^2(2-\sqrt{2})}{6\epsilon kT}\lambda_{jo} + \frac{z_jF^2}{6N\pi\eta}\right)\left(\frac{8\pi e^2N}{1000kT}\right)^{1/2}\sqrt{c}. \qquad (A.42)$$

Now the equivalent conductance, Λ, of an electrolytic solution is the sum of the equivalent conductances of the constituent ions, thus:

$$\Lambda=\Lambda_0-\left(\frac{e^2(2-\sqrt{2})|z_1z_2|}{6\epsilon kT}\Lambda_0+\frac{(z_1+z_2)F^2}{6N\pi\eta}\right)\left(\frac{8\pi e^2N}{1000kT}\right)^{1/2}\sqrt{c}\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{equiv}^{-1} \qquad (A.43)$$

which may be written in the form:

$$\Lambda=\Lambda_0-(B_1\Lambda_0+B_2)\sqrt{c}\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{equiv}^{-1} \qquad (A.44)$$

where B_1 and B_2 denote, respectively,

$$B_1=\frac{e^2(2-\sqrt{2})}{6\epsilon kT}\left(\frac{8\pi e^2N}{1000kT}\right)^{1/2}|z_1z_2| \qquad (A.45)$$

and

$$B_2=\frac{(z_1+z_2)F^2}{6N\pi\eta}\left(\frac{8\pi e^2N}{1000kT}\right)^{1/2} \qquad (A.46)$$

(See also eqs (5.4) and (5.5)). Equation (A.44) is the limiting law of Onsager.

The Onsager equation, as stated above, gives the tangent to the conductance curve at zero concentration; it is based on point charges as the model for the ions. In 1932, Onsager and Fuoss recalculated the electrophoresis term, using charged rigid spheres to represent the ions. For symmetrical electrolytes the electrophoretic term $B_2c^{1/2}$ was replaced by $B_2c^{1/2}/(1+\kappa a)$. Later in a series of papers Fuoss and Onsager gave a more comprehensive treatment in which they retained the higher terms in the Boltzmann factor and the equation of continuity and gave a list of numerical values for certain transcendental functions related to the exponential integral functions. In their comprehensive treatment they considered ions as charged spheres rather than point charges, included the osmotic-pressure and viscosity effects, and used Oseen's equation for the volume force rather than Stokes' equation for directional force to obtain the ionic velocity in the field direction. A rather complicated expression for the electrophoretic term resulted; it was shown however, by Fuoss and Hsia that the function could be closely approximated up to about 0.1 M for 1–1 electrolytes in water by the 1932 result of Onsager and Fuoss. In 1969 Chen found that Fuoss and Onsager had omitted an interaction between the relaxation field and the electrophoretic flow, which leads to an additional term of the order of $c \log c$ with the result that the coefficient of the $c \log c$ term in eqs (5.6) and (5.11) of the main text becomes $E_1\Lambda_0-2E_2$ and the $L(a)$ function (see eqs (5.19) and (5.20)) acquires a different functional form from that published in 1965 The replacement of E_2 by $2E_2$ has little effect on the values of the limiting conductance obtained by extrapolation because E_2 is small compared to $E_1\Lambda_0$. The final equations resulting from the theory are eqs (5.21) and (5.22) in the main text.

A. Bibliography for Appendix A

[1] Fuoss, R. M., and Accascina, F., Electrolytic Conductance (Interscience Publishers, Inc., New York, 1959).

[2] Harned, H. S., and Owen, B. B., The Physical Chemistry of Electrolytic Solutions, 3rd ed., Ch. 4 (Reinhold Publishing Corp., New York, 1958).

[3] Robinson, R. A., and Stokes, R. H., Electrolyte Solutions, 2nd ed., Ch. 7 (Butterworth Scientific Publications, London, 1959).

[4] Fuoss, R. M., and Onsager, L., J. Phys. Chem. **66**, 1722 (1962); **67**, 621, 628 (1963); **68**, 1 (1964).

[5] Fuoss, R. M., Onsager, L., and Skinner, J. F., J. Phys. Chem. **69**, 2581 (1965).

[6] Fuoss, R. M., and Onsager, L., Proc. Nat. Acad. Sci., U.S. **41**, 274, 1010 (1955).

[7] Fuoss, R. M., and Onsager, L., J. Phys. Chem. **61**, 668 (1957).

[8] Fuoss, R. M., J. Am. Chem. Soc. **79**, 3301 (1957).

[9] Fuoss, R. M., and Onsager, L., Proc. Nat. Acad. Sci., U.S. **47**, 818 (1961).

[10] Onsager, L., and Fuoss, R. M., J. Phys. Chem. **36**, 2689 (1932).

[11] Onsager, L., Physik. Z. **27**, 388 (1926); **28**, 277 (1927).

[12] Debye, P., and Hückel, E., Physik. Z. **24**, 185, 305 (1923).

[13] Fuoss, R. M., and Hsia, K. L., Proc. Nat. Acad. Sci., U.S. **57**, 1550; **58**, 1818 (1967).

[14] Chen, M. S., Dissertation, Yale University, June 1969.

11. Appendix B. Densities of aqueous solutions of HF

$$d=A+Bx+Cx^2+Dx^3+Ex^4+Fx^5$$

x = weight percent

t	Range	A	$B\times10^3$	$C\times10^5$	$D\times10^7$	$E\times10^8$	$F\times10^{10}$	s [a] $\times10^4$
°C	*wt %*							
0	0–30	0.99987	3.92	*1.14	………	………	………	12.5
0	0–55	.99987	4.705	−4.451	5.675	………	………	29.2
0	0–100	.99987	4.6518	−3.5739	−1.8571	2.3603	−2.3029	73.1
15	0–36	.99913	3.53	*5.15	………	………	………	5.0
15	0–54	.99913	3.507	*6.143	………	………	………	5.0
18	0–30	.99862	3.97	−1.56	………	………	………	5.0
20	0–30	.99823	4.06	−1.85	………	………	………	3.9
25	0–36	.99707	4.39	−1.71	………	………	………	3.0
25	0–66	.99707	4.8587	−7.2689	*1.8184	−1.6497	………	9.8

[a] – standard deviation of fit to equation

* – $\times10^6$

0 °C – E. G. Hill and A. P. Sirkar [31]

15 °C – L. Domange [32]

18 °C – E. G. Hill and A. P. Sirkar [31]

20 °C – F. Winteler [33]

25 °C – K. Fredenhagen and M. Wellmann [34]

12. Appendix C. Use of the Systѐme International d'Unites

In 1964 the National Bureau of Standards adopted the International System of Units (abbreviated SI for Systѐme International). This International System of Units was defined and given official status in a resolution of the 11th General Conference on Weights and Measures which met in Paris in October 1960. The SI is based on the meter (m) as the unit of length; the kilogram (kg) for mass; the second (s) for time; the ampere (A) for electric current; the Kelvin (K) for temperature; and the candela (cd) for luminous intensity. Of these units, those for mass, length, time, and temperature are independent; that is, a definition of one does not depend on definitions of others. However, the ampere and the candela involve other units in their definition. For example, the ampere involves the units of length, mass, and time and is defined as the magnitude of electricity that, when flowing through each of two long parallel wires separated by one meter in free space, results in a force between two wires (owing to their magnetic fields) of 2×10^{-7} newton (N) (kg m s^{-2}) for each meter of length. The candela needs not concern us here.

As has been customary heretofore in dealing with the electrolytic conductance of solutions, the cgs (centimeter-gram-second) system of units was used in this paper. In converting to the SI system the following changes are required:

General—The unit of length is changed from the centimeter to the meter, the unit of mass from the gram to the kilogram, the unit of force from the dyne to the newton, and the unit of energy from the erg to the joule (J). Concentrations are then expressed in kilomoles or kiloequivalent per cubic meter. The ionic velocity (v) is given in m s^{-1} rather than cm s^{-1} and the "electrical mobility" of an ion see page 3) would be the velocity attained by an on under a unit of potential gradient of 1 V per meter rather than 1 V per centimeter. Accordingly, equivalent conductances would retain the values commonly used, but with the unit being $m^2\Omega^{-1}$ $kequiv^{-1}$. The elementary charge is also given in coulombs rather than in electrostatic units and ion sizes are expressed in fractions of the meter rather than in angstroms.

Theoretical constants in the expressions for equivalent conductances and activity coefficients—In converting to SI, the following changes are required:

(1) In equations 4.8, 4.9, 4.10, 5.1, 5.2, 5.15, 5.18, 7.14, A.9, A.10, A.37, A.38, A.39, A.40, A.41, A.42, A.43, A.45, and A.46 1000 (moles per liter) is replaced by 1 m^3.

(2) Since the unit of charge is not defined through Coulomb's law on SI, e is replaced by $e/(4\pi\epsilon_0)^{1/2}$ in all equations where e appears. The constant, ϵ_0 is known as the permittivity of free space and has the value $8.85417(3)\times10^{-12}C^2J^{-1}m^{-1}$.

(3) The constants in the various equations have the following values:

$$k = 1.38054(18)\times10^{-23}\text{J deg}^{-1}$$
$$N = 6.02252(28)\times10^{26}\text{ kmol}^{-1}$$
$$e = 1.60210(2)\times10^{-19}\text{C}$$
$$F = 9.64870(16)\times10^{17}\text{C kequiv}^{-1}$$

and the unit of viscosity is 10^{-1} N s m^{-2}. Here as in the text, the numbers in parentheses represent established limits of error.

13. Tables

TABLE 1. *Specific conductances of standard aqueous solutions of* KCl

Demal*	Grams KCl per 1000 g solution in vacuum	Specific conductances, $\Omega^{-1}cm^{-1}$, at		
		0 °C	18 °C	25 °C
1.0	71.1352	0.065144	0.097790	0.111287
0.1	7.41913	.0071344	.0111612	.0128496
.01	0.745263	.00077326	.00121992	.00140807

*Based on the international atomic weights of 1933.

TABLE 2. *Physical properties of water*

Temperature t	Density [a] d	Viscosity [b] η	Dielectric constant [c] ϵ
°C	g/ml	cP	
0	0.99987	1.787	[d] 87.74 (87.90)
5	.99999	1.517	85.76 (85.90)
10	.99973	1.306	83.83 (83.95)
15	.99913	1.138	81.95 (82.04)
18	.99862	1.053	80.84 (80.93)
20	.99823	1.002	80.10 (80.18)
25	.99707	0.8903	78.30 (78.36)
30	.99567	.7974	76.55 (76.58)
35	.99406	.7194	74.83 (74.85)
38	.99299	.6783	73.82 (73.83)
40	.99224	.6531	73.15 (73.15)
45	.99025	.5963	71.51 (71.50)
50	.98807	.5471	69.91 (69.88)
55	.98573	.5044	68.34 (68.30)
60	.98324	.4669	66.81 (66.76)
65	.98059	.4338	65.32 (65.25)
70	.97781	.4044	63.86 (63.78)
75	.97489	.3782	62.43 (62.34)
80	.97183	.3547	61.03 (60.93)
85	.96865	.3340	59.66 (59.55)
90	.96534	.3149	58.32 (58.20)
95	.96192	.2976	57.01 (56.88)
100	.95838	.2822	55.72 (55.58)

[a] M. Thiesen [6]; International Critical Tables [7].

[b] J. F. Swindells, J. R. Coe, and T. B. Godfrey [8], R. C. Hardy and R. L. Cottington [9]; and J. R. Coe and T. B. Godfrey [10].

[c] C. G. Malmberg and A. A. Maryott [11].

[d] Values in parentheses are those found by B. B. Owen, R. C. Miller, C. E. Milner, and H. L. Cogan [12]; values above 70 °C were calculated from their equation expressing the values obtained at lower temperatures as a function of temperature.

TABLE 3. *Values of the Debye-Hückel-Onsager constants* B_1 *and* B_2 *for equivalent conductances for 1–1 aqueous solutions from 0 to 100 °C*

t	B_1	B_2
°C	$l^{1/2}$ equiv$^{-1/2}$	Ω^{-1} cm^{2} $l^{1/2}$ equiv$^{-3/2}$
0	[a] 0.2211(1)	[a] 29.817(6)
5	.2227(1)	35.206(8)
10	.2244(1)	40.995(9)
15	.2261(1)	47.169(10)
18	.2272(1)	51.060(11)
20	.2280(1)	53.722(11)
25	.2300(1)	60.639(13)
30	.2321(1)	67.906(14)
35	.2343(1)	75.508(16)
38	.2357(1)	80.240(17)
40	.2366(1)	83.449(18)
45	.2391(1)	91.711(19)
50	.2416(1)	100.31 (2)
55	.2443(1)	109.20 (2)
60	.2471(1)	118.42 (3)
65	.2499(1)	127.94 (3)
70	.2529(1)	137.79 (3)
75	.2560(1)	147.94 (3)
80	.2593(1)	158.41 (3)
85	.2627(1)	169.95 (4)
90	.2662(1)	179.99 (4)
95	.2698(1)	191.32 (4)
100	.2737(1)	202.71 (4)

[a] The numbers in the parentheses gives the ± uncertainty in the last decimal arising from the uncertainties in the physical constants.

Table 4. *Values of the Fuoss-Onsager* E_1 *and* E_2 *constants for equivalent conductances for 1–1 aqueous solutions from 0 to 100 °C*

t	E_1	E_2 [a]
°C	l $equiv^{-1}$	$\Omega^{-1}cm^2$ l $equiv^{-2}$
0	[b] 0.4922(3)	[b] 9.72(1)
5	.4992(3)	11.56(1)
10	.5066(3)	13.56(1)
15	.5146(4)	15.72(1)
18	.5196(4)	17.10(1)
20	.5233(4)	18.06(1)
25	.5325(4)	20.56(1)
30	.5422(4)	23.23(1)
35	.5526(4)	26.08(1)
38	.5591(4)	27.88(1)
40	.5637(4)	29.11(1)
45	.5754(4)	32.32(1)
50	.5876(4)	35.73(2)
55	.6008(4)	39.33(2)
60	.6145(4)	43.13(2)
65	.6287(4)	47.14(3)
70	.6439(4)	51.37(3)
75	.6599(5)	55.83(3)
80	.6768(5)	60.55(3)
85	.6945(5)	65.42(4)
90	.7132(5)	70.63(4)
95	.7328(5)	76.10(4)
100	.7538(5)	81.77(5)

[a] Note that $2E_2$ is involved in the final conductance equations (eqs (5.21) and (5.22)).

[b] The numbers in the parentheses give the ± uncertainty in the last decimal arising from the uncertainties in the physical constants.

Table 5. *Differences in the values of* B_1 *and* B_2 *from those given in table 3 if the dielectric constants of water determined by Owen et al. are used instead of those of Malmberg and Maryott**

t	ΔB_1	ΔB_2
°C	$l^{1/2}$ $equiv^{-1/2}$	Ω^{-1} cm^2 $l^{1/2}$ $equiv^{-3/2}$
0	−0.0006	−0.027
5	−.0005	−.029
10	−.0005	−.029
15	−.0004	−.026
18	−.0004	−.028
20	−.0003	−.027
25	−.0003	−.024
30	−.0001	−.014
35	−.0001	−.010
38	0.0000	−.006
40	.0000	0.000
45	.0001	.006
50	.0002	.02
55	.0002	.04
60	.0003	.04
65	.0004	.07
70	.0005	.09
75	.0006	.11
80	.0006	.13
85	.0007	.16
90	.0008	.19
95	.0009	.22
100	.0010	.26

*Owen et al. value minus Malmberg-Maryott value.

TABLE 6. *Differences in the values of* E_1 *and* E_2 *from those given in table 4 if the dielectric constants of water determined by Owen et al. are used instead of those of Malmberg and Maryott**

t	ΔE_1	ΔE_2 [a]
°C	$l\ equiv^{-1}$	$\Omega^{-1}\ cm^2\ l^{1/2}\ equiv^{-3/2}$
0	−0.0027	−0.04
5	−.0025	−.04
10	−.0021	−.04
15	−.0017	−.03
18	−.0017	−.04
20	−.0015	−.04
25	−.0012	−.03
30	−.0007	−.02
35	−.0004	−.01
38	−.0002	−.01
40	0.0000	0.00
45	.0002	.01
50	.0008	.02
55	.0010	.04
60	.0013	.06
65	.0021	.10
70	.0024	.13
75	.0028	.17
80	.0033	.19
85	.0039	.24
90	.0045	.29
95	.0051	.34
100	.0057	.41

*Owen et al. value minus Malmberg-Maryott value.

[a] Note that the total difference is $2\Delta E_2$; see eqs (5.21) and (5.22).

TABLE 7. *Values of the Debye-Hückel constants* A_c *and* B_c *for activity coefficients of aqueous solutions from 0 to 100 °C*

(On a volume basis)

t	A_c	B_c
°C	$l^{1/2}\ mol^{-1/2}$	$l^{1/2}\ mol^{-1/2}$
0	0.4918	0.3249
5	.4953	.3256
10	.4990	.3264
15	.5029	.3273
18	.5054	.3278
20	.5072	.3282
25	.5116	.3292
30	.5162	.3301
35	.5212	.3312
38	.5242	.3318
40	.5263	.3323
45	.5318	.3334
50	.5374	.3346
55	.5434	.3358
60	.5495	.3371
65	.5559	.3384
70	.5625	.3397
75	.5695	.3411
80	.5767	.3426
85	.5843	.3440
90	.5921	.3456
95	.6001	.3471
100	.6087	.3488

Table 8. *Values of* Λ_0 *for* HF

t	Values	Experimenters
°*C*	$\Omega^{-1}cm^2equiv^{-1}$	
0	255	C. B. Wooster [35]
16	350.3	W. A. Roth [36]
18	361.7	W. A. Roth [36]
18	364	E. G. Hill and A. P. Sirkar [31]
20	374.2	W. A. Roth [36]
25	393.2	E. Deussen [37]
25	399	R. Wegscheider [38]
25	397.3	H. Pick [39]
25	400.2	C. W. Davies and L. J. Hudleston [40]
25	400.2	K. Fredenhagen and M. Wellmann [34]
25	404	W. A. Roth [36]
25	404	C. B. Wooster [35]

Table 9. *Values of the constants governing the dissociation of* HF [a]

t	K	k	s_x
°*C*	*mol* l^{-1}	*mol* l^{-1}	Ω^{-1} cm^2 $equiv^{-1}$
0	0.00109	0.413	0.7
16	.000782	.362	1.2
18	.000755	.355	1.1
20	.000731	.347	1.1
25	.000684	.381	0.6

[a] See eqs (7.3) and (7.4).

Table 10. *Equivalent conductances* (Ω^{-1} cm^2 $equiv^{-1}$) *of aqueous solutions of* HF *at 0, 16, 18, 20, and 25 °C*

c	0 °C	16 °C	18 °C	20 °C	25 °C
mol l^{-1}					
0.004	106.7	....	....	....	140.5
.005	97.7	....	....	....	128.1
.006	90.9	112.9	114.6	116.3	118.8
.007	85.5	105.7	107.3	108.9	111.4
.008	81.1	99.9	101.3	102.9	105.4
.009	77.3	95.0	96.4	97.8	100.4
.01	74.2	90.8	92.1	93.5	96.1
.02	56.2	67.7	68.8	69.8	72.2
.05	39.3	46.8	47.6	48.3	50.1
.07	34.7	41.3	41.9	42.6	44.3
.10	30.7	36.4	37.0	37.7	39.1
.20	24.8	29.6	30.1	30.7	31.7
.50	20.4	....	....	....	26.3
.70	19.5	....	....	....	25.1
1.0	18.8	....	....	....	24.3

TABLE 11. *Equivalent conductances* (Ω^{-1} *cm*^{2} *equiv*$^{-1}$) *of aqueous solutions of* HCl *from* −20 *to* 65 °C

c	−20 °C	−10 °C	0 °C	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	55 °C	65 °C
mol l^{-1}															
0.0001				296.4		360.8		424.5		487.0		547.9	577.7	606.6	662.9
.0005				295.2		359.2		422.6		484.7		545.2	575.1	603.5	660.0
.001				294.3		358.0		421.2		483.1		543.2	573.1	601.3	657.8
.005				291.0		353.5		415.7		476.7		535.5	564.4	592.6	647.3
.01				288.6		350.3		411.9		472.2		530.3	558.7	586.5	641.2
.05				280.3		339.9		398.9		456.7		512.4		565.6	616.9
.1				275.0		333.3		391.1		446.8		501.1		552.8	602.8
.5			228.7	254.8	283.0	308.1	336.4	360.7	386.8	411.9	436.9	461.1	482.4	508.0	552.3
1.0			211.7	235.2	261.6	283.9	312.2	332.2	359.0	379.4	402.9	424.8	445.3	468.1	509.3
1.5			196.2	216.9	241.5	261.5	287.5	305.8	331.1	349.4	371.6	391.5	410.8	431.7	469.9
2.0			182.0	199.9	222.7	240.7	262.9	281.4	303.3	321.6	342.4	360.6	378.2	398.0	433.6
2.5		131.7	168.5	184.3	205.1	221.4	239.8	258.9	277.0	295.8	315.2	332.0	347.6	366.7	399.9
3.0		120.8	154.6	169.5	188.5	203.4	219.3	237.6	253.3	271.5	289.3	304.8	319.0	336.9	368.0
3.5	85.5	111.3	139.6	155.6	172.2	186.5	201.6	218.3	232.9	248.6	263.9	279.4	292.1	308.6	337.2
4.0	79.3	102.7	129.2	143.4	158.1	171.5	185.6	200.0	214.2	228.4	242.2	256.6	268.2	283.6	310.1
4.5	73.7	94.9	119.5	132.0	145.4	157.4	170.6	183.1	196.6	209.5	222.5	235.2	246.7	260.2	284.7
5.0	68.5	87.8	110.3	121.3	133.5	144.4	156.6	167.4	180.2	191.9	204.1	215.4	226.5	238.4	261.0
5.5	63.6	81.1	101.7	111.4	122.5	132.3	143.6	152.9	165.0	175.6	187.1	197.1	207.7	218.3	239.1
6.0	58.9	74.9	93.7	102.2	112.3	121.2	131.5	139.7	151.0	160.6	171.3	180.2	190.3	199.7	218.9
6.5	54.4	69.1	86.2	93.8	103.0	111.0	120.4	127.7	138.2	146.8	156.9	164.8	174.3	182.7	200.4
7.0	50.2	63.7	79.3	86.0	94.4	101.7	110.2	116.9	126.4	134.3	143.3	150.8	159.7	167.2	183.5
7.5	46.3	58.6	73.0	78.9	86.5	93.3	100.9	107.0	115.7	122.9	131.6	138.1	146.2	153.1	168.1
8.0	42.7	54.0	67.1	72.4	79.4	85.6	92.4	98.2	106.1	112.6	120.6	126.7	134.0	140.4	154.1
8.5	39.4	49.8	61.7	66.5	72.9	78.7	84.7	90.3	97.3	103.2	110.7	116.4	123.0	128.8	141.5
9.0	36.4	45.9	56.8	61.2	67.1	72.5	77.8	83.1	89.4	94.8	101.7	107.1	112.9	118.3	130.1
9.5	33.6	42.3	52.3	56.4	61.8	66.8	71.5	76.6	82.3	87.3	93.6	98.7	103.9	108.8	119.7
10.0	31.2	39.1	48.2	52.0	57.0	61.6	65.8	70.7	75.9	80.5	86.3	91.1	95.7		
10.5	28.9	36.1	44.5	48.0	52.7	56.9	60.7	65.3	70.1	74.3	79.6	84.1	88.4		
11.0	26.8	33.4	41.1	44.4	48.8	52.6	56.1	60.2	64.9	68.7	73.6	77.7	81.7		
11.5	24.9	31.0	38.0	41.1	45.3	48.5	51.9	55.3	60.1	63.6	68.0	71.7	75.6		
12.0	23.1	28.7	35.3	38.0	42.0		48.0		55.6		62.8		70.0		
12.5	21.4	26.7	32.7		39.0		44.4		51.4		57.9		64.8		
13.0	20.0	24.9													

TABLE 12. *Interpolation equations, constants, and coefficients for* Λ *for* HCl[a], [b], [c]

$$\Lambda = A + Bc + Cc^2 + Dc^3 + Ec^4 + Fc^5 + Gc^6$$

t °C	A	B	C	D	$E \times 10^{-1}$	$F \times 10^{-2}$	$G \times 10^{-4}$	s	c
−20	188.486	−63.0162	16.8512	−2.88586	2.76616	−1.36131	2.68729	0.1	3.5−13.0
−10	225.132	−58.7706	12.3280	−1.88762	1.71785	−0.819972	1.58613	0.1	3.5−13.0

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \log c + Ac + Bc^{3/2} + Cc^2 + Dc^{5/2}$$

t °C	Λ_0	S	E	A	B	C	D	s	c
0	265.03	88.42	....	137.963	−177.413	92.7510	−18.2200	0.07	0.5–3.5
0	265.03	88.42	....	57.5126	−43.3796	12.0843	−1.10359	0.10	3.5–12.5
5	297.42	101.45	125.32	558.938	−1752.15	....	....	0.10	0 −0.01
5	297.42	101.45	....	103.189	414.041	−2474.81	3477.47	0.01	0.01–0.1
5	297.42	101.45	....	143.672	−169.686	78.5958	−13.3975	0.09	0.1–3.3
5	297.42	101.45	....	76.6573	−60.7656	17.6613	−1.69413	0.08	3.3–12.0
10	329.78	115.00	....	167.354	−194.674	89.2927	−15.1538	0.14	0.5–3.6
10	329.78	115.00	....	87.9928	−69.0294	19.9793	−1.91012	0.12	3.6–12.5
15	362.05	129.03	154.83	576.443	−1512.88	....	....	0.12	0 −0.01
15	362.05	129.03	....	30.2129	1403.63	−5817.09	7203.38	0.06	0.01–0.1
15	362.05	129.03	....	178.321	−204.494	92.4328	−15.3605	0.08	0.1–3.4
15	362.05	129.03	....	104.249	−83.4819	24.7903	−2.44755	0.06	3.4–11.5
20	394.16	143.59	....	175.522	−150.370	36.5182	....	0.01	0.5–3.2
20	394.16	143.59	....	107.020	−81.4337	23.2970	−2.21043	0.14	3.2–12.5
[c] 25	426.06	158.63	185.76	747.385	−2095.71	....	....	0.05	0 −0.01
[c] 25	426.06	158.63	....	173.105	43.5147	−345.464	....	0.14	0.01–0.1
[c] 25	426.06	158.63	....	221.501	−252.771	115.606	−19.5824	0.10	0.1–3.0
[c] 25	426.06	158.63	....	143.554	−116.628	35.2535	−3.56231	0.15	3.0–11.6
30	457.65	174.13	....	202.319	−166.121	39.2792	....	0.01	0.5–3.2
30	457.65	174.13	....	139.378	−105.934	30.5564	−2.94264	0.15	3.2–12.5
35	488.91	190.06	218.01	937.656	−2717.23	....	....	0.07	0 −0.01
35	488.91	190.06	....	62.4686	2225.76	−10030.0	13176.0	0.06	0.01–0.1
35	488.91	190.06	....	264.592	−295.287	133.716	−22.5186	0.10	0.1–3.3
35	488.91	190.06	....	157.608	−119.583	34.5545	−3.34375	0.14	3.3–11.5
40	519.75	206.42	....	284.745	−310.940	139.117	−23.3201	0.01	0.5–3.6
40	519.75	206.42	....	165.451	−122.051	34.7804	−3.33198	0.13	3.6–12.5
45	550.12	223.24	251.84	960.692	−2068.98	....	....	0.10	0 −0.01
45	550.12	223.24	....	143.352	1716.09	−8031.14	10523.2	0.10	0.01–0.1
45	550.12	223.24	....	311.829	−343.170	155.721	−26.4600	0.11	0.1–3.3
45	550.12	223.24	....	196.780	−148.978	43.3720	−4.25969	0.12	3.3–11.5

TABLE 12. *Interpolation equations, constants, and coefficients for* Λ *for* HCl[a], [b], [c]—Continued

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \log c + Ac + Bc^{3/2} + Cc^2 + Dc^{5/2}$$

t °C	Λ_0	*S*	*E*	*A*	*B*	*C*	*D*	*s*	*c*
50	579.94	240.42	269.31	3501.14	−90352.7	1060726	−4254317	0.15	0 −0.01
50	579.94	240.42	....	301.922	−296.692	117.737	−17.2082	0.08	0.5−3.7
50	579.94	240.42	....	188.591	−133.516	37.1664	−3.49219	0.09	3.7−12.5
55	609.17	258.02	287.27	1258.14	−3704.21	....	....	0.10	0 −0.01
55	609.17	258.02	....	255.518	877.709	−4758.72	6156.27	0.06	0.01−0.1
55	609.17	258.02	....	361.044	−390.808	176.840	−30.1100	0.10	0.1−3.3
55	609.17	258.02	....	229.922	−170.083	49.1104	−4.82221	0.01	3.3−9.5
65	665.55	294.26	324.15	5257.15	−117982	1107235	−3375389	0.09	0 −0.01
65	665.55	294.26	....	565.968	−1787.61	4760.06	−5501.35	0.13	0.01−0.1
65	665.55	294.26	....	413.887	−439.598	196.840	−33.1617	0.24	0.1−3.4
65	665.55	294.26	....	267.714	−193.878	55.3978	−5.41006	0.01	3.4−9.5

[a] The dimensions of the coefficients are such that their product with the appropriate power of *c* is Ω^{-1} cm^2 equiv^{-1}.

[b] The *c* log *c* term was not used for temperatures of 0, 10, 20, 30, and 40 °C because data were not available below 0.5 N.

[c] Equations also given in text.

TABLE 13. *Equivalent conductances* ($\Omega^{-1}cm^2$ *equiv*$^{-1}$) *of aqueous solutions of* HBr *at 25 °C*

c	Λ	*c*	Λ	*c*	Λ
mol l^{-1}		*mol l*$^{-1}$		*mol l*$^{-1}$	
0.0002	425.5	0.04	402.7	0.80	345.3
.0003	425.0	.05	400.4	.85	342.6
.0004	424.6	.06	398.4	.90	339.9
.0005	424.3	.07	396.5	.95	337.2
.0006	424.0	.08	394.9	1.0	334.5
.0007	423.7	.09	393.4	1.5	307.6
.0008	423.4	.10	391.9	2.0	281.7
.0009	423.2	.15	386.0	2.5	257.8
.001	422.9	.20	381.4	3.0	236.8
.002	421.1	.25	377.5	3.5	217.5
.003	419.7	.30	374.0	4.0	199.4
.004	418.5	.35	370.8	4.5	182.4
.005	417.6	.40	367.7	5.0	166.5
.006	416.7	.45	364.7	5.5	151.8
.007	415.8	.50	361.9	6.0	138.2
.008	415.1	.55	359.0	6.5	125.7
.009	414.4	.60	356.2	7.0	114.2
.01	413.7	.65	353.5	7.5	103.8
.02	408.9	.70	350.8	8.0	94.4
.03	405.4	.75	348.0	8.5	85.8

TABLE 14. *Equivalent conductances (Ω^{-1} cm^2 equiv^{-1}) of aqueous solutions of* HBr *from −20 to 50 °C*

c	−20 °C	−10 °C	0 °C	10 °C	20 °C	30 °C	40 °C	50 °C
mol l^{-1}								
0.50	....	....	240.9	295.9	347.0	398.9	453.6	496.8
.75	....	....	234.7	284.9	339.0	387.2	433.8	480.6
1.00	....	....	229.6	276.0	329.0	380.4	418.6	465.2
1.25	....	....	221.7	265.8	314.9	362.8	401.8	442.9
1.50	....	....	209.5	254.9	298.9	340.6	381.8	421.4
1.75	....	....	198.3	243.1	284.6	327.3	366.2	404.8
2.00	....	150.8	188.6	231.3	271.8	314.1	350.5	387.4
2.25	....	143.4	180.1	219.6	258.3	296.9	332.3	367.0
2.50	....	136.8	171.7	208.3	244.8	281.7	316.0	349.1
2.75	....	131.1	164.1	198.3	232.9	267.6	301.2	333.2
3.00	....	125.7	157.2	189.5	222.2	255.0	287.8	318.6
3.25	....	120.6	150.8	181.7	212.4	244.3	275.4	304.9
3.50	....	116.1	144.1	174.6	203.2	234.4	263.7	291.9
3.75	87.1	112.0	137.6	167.4	194.7	224.2	252.2	279.4
4.00	84.0	107.5	132.3	160.2	186.8	214.2	239.7	266.9
4.25	80.9	103.1	127.7	153.2	179.0	204.5	228.8	254.6
4.50	78.0	99.0	123.0	146.4	171.2	195.1	218.8	242.6
4.75	75.1	95.1	117.7	139.9	163.1	186.1	209.3	231.3
5.00	72.3	91.4	112.6	134.0	155.7	178.2	199.6	221.3
5.25	69.6	87.8	107.8	128.3	148.7	170.5	190.0	211.4
5.50	67.0	84.2	103.1	122.7	142.1	162.8	181.4	201.8
5.75	64.4	80.6	98.6	117.3	135.7	155.3	173.2	192.4
6.00	61.8	77.2	94.3	112.0	129.6	148.0	165.4	183.4
6.25	59.3	73.8	90.1	106.9	123.7	140.9	157.8	174.7
6.50	56.8	70.7	86.0	102.0	118.0	134.1	150.5	166.3
6.75	54.4	67.7	82.1	97.2	112.5	127.6	143.3	158.4
7.00	51.9	64.6	78.4	92.6	107.1	121.4	136.3	150.8

TABLE 15. *Interpolation equations, constants, coefficients, and standard deviations of fits for* Λ *for* HBr[a, b]

$$\Lambda = A + Bc + Cc^2 + Dc^3 + Ec^4 + Fc^5 + Gc^6$$

t °C	A	B	C	D	E	F	G	s	c
	$\sigma^{-1}cm^2$ $equiv^{-1}$								
−20	153.2186	−23.74458	1.984868	−0.09437269	…	…	…	0.0	3.85−7.12
−10	269.7145	−96.49953	23.22557	−2.354479	…	…	…	0.0	2.12−3.43
−10	−2182.739	2809.984	−1391.051	359.8999	−51.69493	3.913505	−0.1220707	0.1	3.43−7.08

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ac + Bc^{3/2} + Cc^2 + Dc^{5/2} \qquad (s = 0.0)$$

t °C	Λ_0	S	A	B	C	D	c
	$\sigma^{-1}cm^2equiv^{-1}$						
0	267.47	88.96	383.7746	−924.1801	909.7568	−318.2496	0.65−1.27
0	267.47	88.96	221.8995	−206.9480	21.53078	18.09947	1.27−2.09
0	267.47	88.96	303.0124	−422.2153	209.3597	−35.63960	2.09−3.42
0	267.47	88.96	1030.928	−1472.506	711.2473	−115.0276	3.42−4.78
0	267.47	88.96	53.84782	−33.86838	6.592146	−0.2034687	4.78−7.05
10	331.59	115.41	517.3115	−1217.696	1138.968	−378.8095	0.65−1.18
10	331.59	115.41	−14.86989	305.0183	−326.0611	94.43531	1.18−2.11
10	331.59	115.41	418.1359	−573.9359	276.5141	−45.09855	2.11−3.29
10	331.59	115.41	−39.21039	125.1741	−77.38015	14.15616	3.29−4.81
10	331.59	115.41	66.16035	−43.75662	10.46823	−76.65289	4.81−7.01
20	398.05	144.48	182.2736	−162.3090	103.8241	−48.40040	0.65−1.23
20	398.05	144.48	565.2512	−928.6667	560.8808	−118.3103	1.23−2.12
20	398.05	144.48	581.8613	−844.4378	433.9378	−76.25953	2.12−3.25
20	398.05	144.48	479.9294	−643.1428	305.0230	−49.29015	3.25−4.76
20	398.05	144.48	174.1218	−164.6092	57.37973	−6.869268	4.76−6.98
30	460.14	174.71	952.2020	−2645.858	2806.021	−1017.448	0.65−1.23
30	460.14	174.71	2796.582	−6065.851	4514.621	−1130.280	1.23−2.04
30	460.14	174.71	251.6347	−189.8346	19.28790	9.967165	2.04−3.32
30	460.14	174.71	114.8066	−62.75681	6.837291	1.154146	3.32−4.74
30	460.14	174.71	−1.499032	63.95883	−37.66776	6.133478	4.74−6.91
40	523.06	207.21	771.4765	−1706.708	1518.772	−480.7958	0.65−1.21
40	523.06	207.21	1596.403	−3278.587	2389.530	−593.4768	1.21−2.00
40	523.06	207.21	622.8765	−851.3158	423.1395	−72.47076	2.00−3.74
40	523.06	207.21	1231.781	−1628.505	743.0089	−114.2550	3.74−5.08
40	523.06	207.21	280.8612	−268.7814	96.02265	−11.81506	5.08−6.89
50	584.43	241.50	647.1861	−1412.163	1392.202	−504.9734	0.64−1.25
50	584.43	241.50	1870.611	−3887.601	2867.502	−719.6425	1.25−2.01
50	584.43	241.50	850.1113	−1230.670	646.5982	−116.9136	2.01−3.32
50	584.43	241.50	28.24088	109.7581	−84.59918	16.49943	3.32−4.70
50	584.43	241.50	75.99004	3.194942	−18.72547	4.101969	4.70−6.85

[a] The dimensions of the coefficients are such that their product with the c quantity is Ω^{-1} cm^2 equiv^{-1}.

[b] The c log c term was not used for these temperatures because data were not available below 0.5 N.

TABLE 16. *Equivalent conductances* (Ω^{-1} *cm*^{2} *equiv*$^{-1}$) *of aqueous solutions of* HI *at 25 °C*

c	Λ	c	Λ	c	Λ
mol l^{-1}		*mol* l^{-1}		*mol* l^{-1}	
0.00045	423.2	0.0085	413.7	0.35	377.4
.00050	423.0	.0090	413.4	.40	374.9
.00055	422.9	.0095	413.1	.45	372.3
.00060	422.7	.010	412.8	.50	369.8
.00065	422.6	.015	410.3	.55	367.3
.00070	422.4	.020	408.3	.60	364.8
.00075	422.3	.025	406.6	.65	362.2
.00080	422.2	.030	405.2	.70	359.7
.00085	422.0	.035	403.9	.75	357.1
.00090	421.9	.040	402.8	.80	354.5
.00095	421.8	.045	401.7	.85	351.9
.0010	421.7	.050	400.8	.90	349.2
.0015	420.7	.055	399.9	.95	346.6
.0020	419.8	.060	399.1	1.0	343.9
.0025	419.1	.065	398.3	1.5	316.4
.0030	418.5	.070	397.6	2.0	288.9
.0035	417.9	.075	396.9	2.5	262.5
.0040	417.3	.080	396.3	3.0	237.9
.0045	416.8	.085	395.6	3.5	215.4
.0050	416.4	.090	395.1	4.0	195.1
.0055	415.9	.095	394.5	4.5	176.8
.0060	415.5	.10	394.0	5.0	160.4
.0065	415.1	.15	389.5	5.5	145.5
.0070	414.8	.20	385.9	6.0	131.7
.0075	414.4	.25	382.9	6.5	118.6
.0080	414.1	.30	380.1	7.0	105.7

Table 17. *Equivalent conductances* (Ω^{-1} cm^2 $equiv^{-1}$) *of aqueous solutions of* HI *from* −20 *to* 50 °C

c	−20 °C	−10 °C	0 °C	10 °C	20 °C	30 °C	40 °C	50 °C
mol l^{-1}								
0.4	....	....	253.9	300.7	354.5	411.9	453.6	501.8
0.6	....	....	249.1	293.6	344.6	401.1	441.5	488.4
0.8	....	....	242.4	285.5	333.9	389.1	429.3	474.8
1.0	....	....	234.8	276.9	322.7	376.3	416.5	460.8
1.2	....	....	226.6	267.9	311.4	363.1	403.4	446.3
1.4	....	....	218.2	258.8	300.2	349.8	390.0	431.4
1.6	....	....	209.9	249.7	289.1	336.6	376.5	416.3
1.8	....	....	201.8	240.7	278.4	323.7	363.0	401.2
2.0	....	....	194.0	231.9	268.1	311.1	349.6	386.1
2.2	....	147.7	186.6	223.4	258.2	299.0	336.3	371.2
2.4	....	143.5	179.5	215.1	248.8	287.3	323.3	356.5
2.6	....	138.8	172.8	207.2	239.7	276.1	310.5	342.2
2.8	....	133.9	166.5	199.5	231.0	265.4	298.1	328.2
3.0	99.9	129.0	160.5	192.0	222.7	255.1	286.1	314.7
3.2	97.4	124.1	154.7	184.8	214.6	245.2	274.5	301.7
3.4	94.2	119.5	149.1	177.8	206.7	235.7	263.4	289.2
3.6	90.6	115.0	143.7	171.0	198.9	226.4	252.6	277.3
3.8	86.9	110.9	138.3	164.3	191.2	217.4	242.3	266.0
4.0	83.6	106.9	132.8	157.6	183.5	208.4	232.5	255.3
4.2	80.9	103.0	127.3	151.0	175.6	199.6	223.1	245.3
4.4	79.3	99.2	121.6	144.3	167.5	190.7	214.1	235.9

TABLE 18. *Interpolation formulas for Λ for HI* [a, d, e]

t °C	
−20	$\Lambda = -188.5 + 268.0c - 79.17c^2 + 7.294c^3$
−10	$\Lambda = 55.399 + 157.67c - 82.804c^2 + 16.276c^3 - 1.1560c^4$
0	$\Lambda = 266.31 - 88.70c^{1/2} + 280.455c - 370.407c^{3/2} + 176.385c^2 - 29.2746c^{5/2}$
10	$\Lambda = 330.58 - 115.18c^{1/2} + 248.768c - 298.965c^{3/2} + 132.508c^2 - 20.8142c^{5/2}$
20	$\Lambda = 394.66 - 143.70c^{1/2} + 302.982c - 379.036c^{3/2} + 177.129c^2 - 29.2963c^{5/2}$
[b] 25	$\Lambda = 426.45 - 158.72c^{1/2} + 185.96c \log c + 1085.7c - 11678c^{3/2} + 107071c^2 - 394591c^{5/2}$
[c] 25	$\Lambda = 426.45 - 158.72c^{1/2} + 248.885c - 256.566c^{3/2} + 96.2195c^2 - 12.3887c^{5/2}$
30	$\Lambda = 457.93 - 174.20c^{1/2} + 370.263c - 445.069c^{3/2} + 198.665c^2 - 31.2569c^{5/2}$
40	$\Lambda = 519.72 - 206.42c^{1/2} + 317.597c - 312.945c^{5/2} + 112.255c^2 - 13.6656c^{5/2}$
50	$\Lambda = 579.38 - 240.28c^{1/2} + 354.327c - 331.163c^{5/2} + 110.209c^2 - 11.7132c^{5/2}$

[a] The c log c term was not used for temperatures other than 25 °C because data were not available below 0.4N.

[b] 0.0000 − 0.01N.

[c] 0.01N − 7.0N.

[d] The dimensions of the coefficients are such that their product with the c quantity is Ω^{-1} cm^2 equiv^{-1}.

[e] Statistical Information.

t °C	s	n	Standard error
−20	0.07	5	0.03
−10	.14	7	.05
0	1.05	15	.3
10	.75	15	.2
20	1.63	15	.4
25	1.03	30	.2
30	1.14	12	.3
40	1.40	13	.4
50	2.38	13	.6

TABLE 19. *Limiting equivalent conductances* (Ω^{-1}*cm*^{2}*equiv*$^{-1}$) *of* HF, HCl, HBr *and* HI *in water at 25 °C*

	This paper	MacInnes [64]*	Harned and Owen [65]*	Robinson and Stokes [66]*
		25 °C		
HF	405.10	....	....	405.01
HCl	426.06	425.95	425.94	425.9_5
HBr	427.74	428.0_1	427.7_9	427.7_4
HI	426.45	426.4_6	426.4_9	426.4_4

*Values converted to absolute electrical units.

14. Glossary of Symbols

a, activity; also ion size, "ion-size" parameter, or "distance of closest approach" of ions.

b, Bjerrum ion parameter in conductance (see eq. (5.10)).

c, concentration in equivalents per 1000 cm^3.

d, density.

e, elementary charge.

i, electric current.

j_1, j_1', j_2, j_2', constants in the expression relating Λ for HF with the concentration of HF (see p. 10).

k, Boltzmann constant; also constant relating the equilibrium between HF_2^- and HF and F^- (see table 9).

k_i, general forces acting on ions.

k_s, general forces acting on solvent molecules.

l, length in cm; liter.

m, molar concentration.

m', ionic mobility coefficient.

m, meter.

n, localized average concentration of ions.

n_i, number of i ions per volume V.

n_{ji}, average concentration of i ions in the vicinity of j ions.

q, function in theory of conductance (see p. 5).

r, distance of separation of charges.

$\mathbf{r}_1$, unit vector.

s_x, standard deviations for equation fits.

t, transference or transport number; temperature.

u, ionic mobility.

u^0, limiting ionic mobility.

u_i^*, "absolute" mobility of an ion.

u_i', "electrical ionic mobility."

v, velocity.

y, ratio of the concentration of F^- to the stoichiometric concentration of HF.

γ_3, ratio of the concentration of HF_2^- to the stoichiometric concentration of HF.

z_i, ionic charge.

A, area in cm^2.

A', A'', integration constants (see equation (A.11)).

A_c, coefficient in the limiting law of Debye and Hückel for activity coefficients, on molar basis (see table 7).

A, B, C, D, E, F, G, constants in polynomials.

B_1, coefficient of the relaxation term in the theory of conductance (see table 3).

B_2, coefficient of the electrophoretic term in the theory of conductance (see table 3).

B_c, coefficient of ion-size term in the Debye-Hückel theory for activity coefficients, on molar scale (see table 7).

C, stoichiometric concentration.

E, constant in Fuoss-Onsager theory of conductance.

E_1, constant needed to calculate E (see table 4).

E_2, constant needed to calculate E (see table 4).

E_a, applied potential.

F, Faraday.

I, ionic strength.

$J(a)$, coefficient of c term in the Fuoss-Onsager theory of conductance.

J_c, cell constant.

K, dissociation constant.

K_A, association constant.

K_A°, association constant including effects of solute-solvent interactions and the free volume of the solute.

$L(a)$, coefficient of the c term in the Fuoss-Onsager-Skinner theory of conductance.

M, molarity.

N, Avogadro constant.

N_i, number of i ions.

$Q(b)$, the definite integral $\int_2^b \exp(x) x^{-4} dx$ where $x = e^2/r\epsilon kT$.

R, electrical resistance.

R_{sp}, specific electrical resistance or electrical resistivity.

S, constant equal to $B_1\Lambda_0 + B_2$.

T, Kelvin temperature.

U, potential energy.

V, volume.

W, function in the theory of conductance and related to q (see page 17).

X, vector electric field in the x-direction.

$\mathscr{F}$, force.

$\mathscr{F}_e$, electrical force.

α, degree of dissociation or ionization or complex formation.

$1-\alpha$, degree of association.

γ, activity coefficient.

ϵ, dielectric constant.

ϵ_0, permittivity of free space.

η, viscosity.

η_0, viscosity of solvent.

κ, the reciprocal of the average radius of an ionic atmosphere.

σ, electrical conductance.

σ_{sp}, specific electrical conductance or electrical conductivity.

$(\sigma_{sp})_s$, standard specific electrical conductivity.

σ_e, electrical conductance of an experimental solution.

λ, ionic equivalent conductance.

λ_0, limiting ionic equivalent conductance.

ν, number of ions in one molecule of electrolyte.

ρ_c, charge density.

ρ_i, coefficient of ionic friction.

τ, relation of the Bjerrum parameter and $1/\kappa$.

Λ, equivalent conductance.

Λ_0, limiting equivalent conductance.

Λ^m, molar conductance.

Λ_0^m, limiting molar conductance.

θ, function of volume (see p. 14).

Ψ^0, electric potential.

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