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ELECTROCHEMICAL DATA

Part I

by

Walter J. Hamer

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Electrochemical Data

I. Introduction

Defined Values. Defined values which will be used throughout this critical evaluation and tabulation of electrochemical data follow below. These defined values are based, for the most part, on those recommended in 1963 by the committee on fundamental constants of the National Academy of Sciences-National Research Council [Chem. & Eng. News, Nov. 11, 1963, page 39].

Meter, m = 1,650,763.73 wave lengths in vacuo of the unperturbed transition $2p_{10}$-$5d_5$ in ^{86}Kr

Centimeter, cm = one hundredth of the meter

Kilogram, kg = mass of the international kilogram at Sèvres, France.

Gram, g = mass standard, one thousandth of the mass of the international kilogram at Sèvres, France.

Second, s = 1/31,556,925.9747 of the tropical year at 12^hET,0 January 1900

Unified atomic mass unit, u = 1/12 the mass of an atom of the ^{12}C nuclide

Mole, mol = amount of substance, in grams, containing the same number of atoms, or undissociated molecules, or undissociated radicals as 12 grams of pure ^{12}C.

Degree Kelvin, °K = defined in the thermodynamic scale by assigning 273.16°K to the triple point of water (freezing point of water, 273.15°K = 0°C)

Standard acceleration of free fall, $g_n = 9.80665 \text{ m s}^{-2} = 980.665 \text{ cm s}^{-2}$

Normal atmospheric pressure, atm = 101,325 newtons m^{-2} = 1,013,250 dyn cm^{-2} = 760 mm Hg

Thermochemical calorie (defined), cal_{th} = 4.1840 joules

Liter, ℓ = 1000.028 cm^3; in 1965 the liter has been redefined as exactly 1 dm^3 but the literature data is based on the older definition.

Inch, in = 0.0254 m = 2.54 cm

Pound (avdp), ℓb = 0.45359237 kg = 453.59237 g

Note: the inch and pound are not used in this evaluation of electrochemical data but the conversion factors to the meter (or centimeter) and kilogram (or gram), respectively, are given here for completeness.

Physical Constants. Physical constants which will be used throughout this critical evaluation and tabulation of electrochemical data follow below. Values for these constants are those recommended in 1963 by the committee on fundamental constants of the National Academy of Sciences-National Research Council [Chem. & Eng. News, Nov. 11, 1963, page 39]. The values given in parenthesis in each case represent established limits of error based on three standard deviation applied to the last digits in the listed value of the physical constant. The symbol used for each constant is the italic form of that given.

Avogadro constant, N_A = 6.02252(28)x 10^{23} mol^{-1}

Speed of light in vacuum, c = 2.997925(3) x 10^{8} m s^{-1} = 2.997925(3) x 10^{10} cm s^{-1}

Elementary charge (sometimes called the electronic or protonic charge), e = 4.80298(20) e.s.u. = 1.60210(7) coulomb

Faraday constant, F = 96487.0(1.6) coulomb $(\text{g-equivalent})^{-1}$ = 2.89261(5) x 10^{4} e.s.u. $(\text{g-equiv})^{-1}$ = 23060.9(0.4) cal_{th}volt equiv^{-1}

Normal volume perfect gas, V_o = 2.24136(30) x 10^{-2} m^{3} mol^{-1} = 2.24136(30) x 10^{4} cm^{3} mol^{-1}

Gas constant, R = 8.3143(12) J $°K^{-1}$ mol^{-1} = 1.98717(29) cal_{th} $°K^{-1}$ mol^{-1} = 82.0558(118) cm^{3} atm $°K^{-1}$ mol^{-1}

Boltzmann constant, k = 1.38054(18) x 10^{-23}J $°K^{-1}$

Planck constant, h = 6.6256(5) x 10^{-34} J s

Planck constant, $\hbar$ = h/2π = 1.05450(7) x 10^{-34} J s

Conversion Factors. The following conversion factors for the electrical units were used in the evaluations (Nat. Bur. Standards Circular 459, 1947):

1 international volt (US) = 1.000330 absolute volts
1 international ohm (US) = 1.000495 absolute ohms
1 international ampere (US) = 0.999835 absolute ampere
1 international coulomb (US) = 0.999835 absolute coulomb
1 international joule (US) = 1.000165 absolute joules

These conversion factors were used for all data determined in the United States prior to 1949. After 1949 these conversion factors do not apply since all electrical measurements after January 1, 1948 have been based on absolute units (the transition was assumed to be one year from Jan. 1, 1948 to Jan. 1, 1949).

The conversion factors used for all data determined outside the United States were:

1 international volt = 1.00034 absolute volts
1 international ohm = 1.00049 absolute ohms
1 international ampere = 0.99985 absolute ampere
1 international coulomb = 0.99985 absolute coulomb
1 international joule = 1.00019 absolute joules

Miscellaneous Values. The following values were used in the evaluations:

$$\pi = 3.14159265$$

$$\ell n\ 10 = 2.302585\ \ell og\ 10$$

Standard Conventions. The following conventions are used throughout the critical evaluations:

Reference electrode. The reference electrode to which all electrode potentials are referred is the standard hydrogen electrode (SHE) to which a zero potential is conventionally assigned at all temperatures when the pressure (fugacity) of the hydrogen gas is one atmosphere and the hydrogen ion (hydronium ion) is at unit activity.

Sign of electrode potentials. The Stockholm convention [J. A. Christiansen and M. Pourbaix, Compt. rend. conf. union intern. chim. pure et appl., 17th Conf. Stockholm, p. 83 (1953)] in regard to the sign of electrode potentials is followed. The symbol $\mathcal{V}^\circ$ recommended by Pitzer and Brewer [Lewis and Randall's Thermodynamics, 2nd ed., Chap. 24, McGraw-Hill Book Company, Inc., 1961] is used for the standard electrode potential with E° reserved for the standard oxidation potential. $\mathcal{V}^\circ$ and E° are of opposite sign. According to the Stockholm convention the sign of the potential is positive if the electrode in question is the plus (+) terminal of a cell whose other electrode is the standard hydrogen electrode.

Standard States. The standard states used follow the conventions of Pitzer and Brewer, loc. cit. They are defined as follows:

The standard state of an element at all temperatures is that form which is the most stable or more common at the temperature under consideration. For a gas the standard state is the hypothetical ideal gas at unit fugacity, in which state the enthalpy and heat capacity are those of the real gas at the same temperature and at zero pressure.

The standard state for a pure solid or liquid is taken as the pure substance in the condensed phase under a pressure of one atmosphere.

The standard state for a solute in aqueous solution is taken as the hypothetical ideal solution of unit molality, in which state the partial molal enthalpy and heat capacity of the solute are the same as those in the infinitely dilute solution.

The thermodynamic properties of individual ions in aqueous solution are based on the convention that ΔH_f°, ΔG_f°, S°, and C_p° for H^+ (aqueous standard state, m = 1) are zero. H, G, S, and C_p denote, respectively, enthalpy, Gibbs energy, entropy, and heat capacity.

Atomic Weight Scale. In 1961 the unified atomic weight scale based on $^{12}C = 12$ was adopted [Chem. & Eng. News, p. 43, Nov. 20 (1961)]. Previously the chemists had used a scale based on a mass of 16 for naturally occurring oxygen atoms; the physicists had used 16 for the nuclide ^{16}O. The change to $^{12}C = 12$ introduced an overall change in mole quantities of 0.0043% for the chemist and 0.0318% for the physicist. When these changes were effected some slight adjustments were made in the atomic weights (1961) and these factors do not apply to all elements. These latter adjustments have also been incorporated in the present evaluations of electrochemical data.

Factors. The factors that are being considered in the critical evaluation of electrochemical data may be summarized as follows:

(1) The change in the temperature scale, i.e.,from 273.16°K to 273.15°K for the ice point.

(2) The change from "international" to "absolute" electrical units.

(3) The change in the Faraday constant

(4) The change in the scale of atomic weights.

II. Standard of Electromotive Force

The physical standard of electromotive force (emf) is the cadmium sulfate (or Weston) cell of the saturated type where saturated refers to the state of the electrolyte. It consists of an anode (negative terminal) of a 2-phase cadmium amalgam (10%) and a mercury-mercurous sulfate cathode (positive terminal) in a saturated solution of cadmium sulfate with crystals of $CdSO_4.8/3H_2O$ over the surface of both electrodes. This cell may be represented by:

$$(-)\mathrm{Cd,Hg(2p)}\,|\,\mathrm{CdSO_4\cdot 8/3H_2O(c)}\,|\,\mathrm{CdSO_4(sat\ aq)}\,|\,\mathrm{CdSO_4\cdot 8/3H_2O(c)}\,|\,\mathrm{Hg_2SO_4(s)}\,|\,\mathrm{Hg(\ell)}(+)$$

where 2p = 2 phase, c = crystal, sat aq = saturated aqueous solution, s = solid, and ℓ = liquid. The overall reaction of the cell is:

$$\mathrm{xCd,yHg(2p)} + \mathrm{Hg_2SO_4(s)} + \frac{8/3}{m-8/3}\ (\mathrm{CdSO_4\cdot mH_2O})(\mathrm{sat\ aq}) = \frac{m}{m-8/3}\ (\mathrm{CdSO_4\cdot 8/3H_2O})(\mathrm{c})$$

$$+\ 2\mathrm{Hg}(\ell) + (\mathrm{x}-1)\mathrm{Cd,yHg(2p)}$$

where x moles of Cd are associated with y moles of Hg in the amalgam and m is the number of moles of water associated with 1 mole of $CdSO_4$ in the saturated solution [W. J. Hamer, Natl. Bur. Standards Monograph 84,(1965)].

This cell is used to maintain the unit of electromotive force in the United States and in countries abroad. All emf data, therefore, directly or indirectly relate back to this cell as maintained.

In table 1 values of the emf of the cell are given for a series of temperatures from 0°C to 43.6°C. The thermodynamic data are given in joules, the unit of energy in the Systѐme International d'Unites (SI) adopted in a resolution of the 11th General Conference on Weights and Measures, October 1960, Paris, France [W. J. Hamer, J. Wash. Acad. Sciences 54, 297 (1964)]. In table 2 the thermodynamic data are given in terms of the thermochemical calorie.

Thermodynamic quantities. The Gibbs energy change, ΔG, the enthalpy change, ΔH, the entropy change, ΔS, and the change in heat capacity, ΔC_p, for a cell or electrode reaction, are obtained from the emf or electrode potential by the respective equations:

$$\Delta G = -nFE$$

$$\Delta H = -nFE + nFT(dE/dT)$$

$$\Delta S = nF(dE/dT)$$

$$\Delta C_p = [d(\Delta H)/dT] = nFT(d^2E/dT^2)$$

III. The Nernst Factor

The electromotive force of a galvanic (or voltaic) cell and the electrode potential of an electrode are given as functions of the activities of the reacting and produced substances in the cell or electrode reaction by:

$$E = E^\circ - (1/n)(RT/F)\ell n\ Q = E^\circ - (1/n)(2.302585RT/F)\ell og\ Q$$

where Q is the product of the activities (or fugacities) of the produced substances divided by the product of the activities of the reacting substances, each activity raised to that power whose exponent is the coefficient of the substance in the chemical equation and n is the number of faradays involved in the reaction as written. For the equilibrium state Q becomes the equilibrium constant, K, and since E for the reaction at equilibrium is zero,

$$E^\circ = (1/n)(RT/F)\ell n\ K = (1/n)(2.302585RT/F)\ell og\ K$$

The factor $(RT/F)\ell n\ 10$ or $(2.302585RT/F)\ell og\ X$ is referred to here as the Nernst factor. Values of this factor for temperatures from 0°C to 100°C are given in table 3; values above 100°C for use mainly in emf studies of molten (or fused) electrolytes are given in table 4.

IV. Chemical Potentials, Activities, and Activity Coefficients

For closed isolated systems to which no matter is added or withdrawn thermodynamics give:

$$dU = TdS - pdV$$

where U is energy, T the absolute temperature, S the entropy, p the pressure, and V the volume. For an open system to which matter may be added or withdrawn (for example, addition of a salt to water or removal of water from a salt solution by evaporation) Gibbs' gave (Gibbs used different symbols):

$$dU = TdS - pdV + \mu_A dn_A + \mu_B dn_B + \text{--------} \mu_Z dn_Z$$

where here n represents the number of moles of component A, B, etc., represented by subscripts and the μ's represent the Gibbs' "chemical potentials" of the various components. Since from thermodynamic considerations,

$$G = U - TS + pV = \text{Gibbs energy}$$

$$H = U + pV = \text{Heat content}$$

$$F(\text{or } A) = U - TS = \text{Helmholtz energy}$$

the Gibbs' "chemical potentials" for component A, for example, may be defined in a multiplicity of ways as follows:

$$\mu_A = (dU/dn_A)_{S,V,n'} = (dH/dn_A)_{S,p,n'} = (dF/dn_A)_{T,V,n'} = (dG/dn_A)_{T,p,n'}$$

where n' represents the constancy of all components except component A. Thus, Gibbs' "chemical potential" can be expressed in various ways depending on what conditions are held constant during an experiment. The last equality is the one generally used in defining the "chemical potential" in that experiments may easily be designed wherein the temperature and pressure are maintained constant. It is inconvenient to conduct experiments at constant volume and temperature, under which conditions the third equality applies; and it is indeed difficult to conceive of ways to conduct experiments either at constant entropy and volume (first equality) or at constant entropy and pressure (second equality).

Since the energy, entropy, heat content, Helmholtz energy, and Gibbs energy are defined only by differential equations, we can determine only differences of these quantities between two states of a system containing the same quantity of matter. It is therefore customary to tabulate the differences from some standard state, which is equivalent to an arbitrary assumption that the various functions are each zero in the standard states. For general purposes it is customary to assume that the energy, or the heat content, of each element at some standard temperature, usually 25°C, and some standard pressure, usually one atmosphere, and in its most stable form under these conditions is zero. This same standard state may be adopted for the entropy, Helmholtz energy, and Gibbs energy, although the entropy is sometimes taken as zero at absolute zero in accordance with the third law of thermodynamics. A knowledge of the individual heat capacities and volumes permits the calculation of these quantities under other conditions.

The same considerations apply to the chemical potential, i.e., only differences from an arbitrarily selected standard state can be determined. Throughout this evaluation the chemical potential shall be defined in terms of the partial molal Gibbs energy (fourth equality in equation above). The difference in chemical potential between two states (compositions) of an ideal solution is given by:

$$\mu_i - \mu_i' = RT\ell n \frac{p_i}{p_i'} = RT\ell n \frac{x_i}{x_i'}$$

where i = component i and p and x denote, respectively, the vapor pressure and mole fraction. If one of the compositions is the pure component with $x_i' = 1$, $p_i' = p_i^\circ$, and $\mu_i' = \mu_i^\circ$, then $\mu_i = \mu_i^\circ + RT\ell n \frac{p_i}{p_i^\circ} = \mu_i^\circ + RT\ell n\, x_i$

where the relative vapor pressure of component i is equal to the mole fraction of component i. For real or non-ideal solutions this equation becomes

$$\mu_i = \mu_i^\circ + RT\ln \frac{f_i}{f_i^\circ} = \mu_i^\circ + RT\ln a_i$$

where a_i is the activity of component i and defined as the relative fugacity.

For solutions of electrolytes the standard state is chosen so that the ratio of the activity to the concentration is equal to unity at infinite dilution where the laws of ideal solutions are obeyed. G. N. Lewis [Proc. Am. Acad., 13, 359 (1907)] called this ratio the activity coefficient, thus $a = x\gamma_x$.

It is more usual, however, to express the composition of a solution either in terms of concentration (molarity), c, i.e., moles of solute per liter, or as molalities, m, in moles of solute per 1000 grams of solvent. In each of these cases, the numerical values of the activity coefficient differ from those expressed on the basis of mole fraction; γ_c and γ_m are used here to denote the activity coefficient on the molarity and molality scales, respectively. The relation between γ_x, γ_c, and γ_m are given by:

$$\gamma_x = \gamma_c\ (d - 0.001\ Mc + 0.001\ M_s c\nu)/d_\circ$$

$$\gamma_x = \gamma_m\ (1 + 0.001\ \nu m\ M_s)$$

$$c\gamma_c = d_\circ\ m\ \gamma_m$$

where d = density of solution, $d_\circ$ = density of solvent, M_s = molecular weight of solvent, M = molecular weight of solute, and ν = the number of ions into which one molecule of the solute dissociates.

As electroneutrality must prevail in electrolytic solutions, the activity of an electrolyte that ionizes into ν_+ cations and ν_- anions is given by:

$$a_{salt} = a_2 = a_+^{\nu+} \times a_-^{\nu-} = a_\pm^{\nu}$$

where $\nu = \nu_+ + \nu_-$. Therefore, for an electrolytic solution, its mean activity, $a_\pm$, would be given by:

$$\mu = \mu^\circ + \nu \, RT \ell n \, a_\pm$$

Thus $a_\pm = \gamma_\pm m_\pm$ and $a_2 = (\gamma_\pm m_\pm)^\nu$ where $m_\pm$ and $\gamma_\pm$ denote, respectively, the mean molality and mean activity coefficient. The mean activity coefficient is given by:

$$\gamma_\pm = (\gamma_+^{\nu_+} \gamma_-^{\nu_-})^{1/\nu}$$

and the mean ionic concentration (in molality, for example) by:

$$m_\pm = (\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu} \quad m = Xm$$

The properties of electrolytic solutions are, in general, directly related to the ionic strength of the solution, defined by:

$$I = 1/2 \sum_i z_i^2 m_i = Ym$$

where z is the ionic valence.

Values of Xm and Ym as well as $\gamma_\pm$ and a_2 are given in table 5 for various valence types of electrolytes.

V. Theoretical Expressions for Activity Coefficients

Activity coefficients give a measure of the deviations of real solutions from ideality and include the magnitude of all effects that lead to these deviations. In dilute solutions the main effect is that of interionic attraction, i.e., the attraction between electrical (ionic) charges of unlike sign, and for which Debye and Hückel [Physik. Z., 24, 185 (1923)], assuming that ions were point charges derived a solution which leads to the following expression (generally known as the Debye-Hückel limiting law) for the mean activity coefficient of an electrolyte (γ shall be used hereafter for $\gamma_{\pm}$):

$$\ell og\ \gamma_c = -z_+ z_- A_c \sqrt{I_c}$$

where the subscript c refers to concentrations on the volume basis and

$$A_c = \left(\frac{2\pi N}{1000}\right)^{1/2} \frac{e^3}{2.302585\ k^{3/2}} \left(\frac{1}{T^{3/2} \epsilon^{3/2}}\right) = \frac{1.824829238 \times 10^6}{(T\ \epsilon)^{3/2}},$$

where ϵ denotes the dielectric constant of the solvent and the other symbols having the meanings and numerical values given under Physical constants above. Values of ϵ for water at various temperatures are given in table 6. A_m on the molality (or weight) basis is given by $A_m = A_c(d_\circ)^{1/2}$ where $d_\circ$ is the density of the solvent.

When the size, a_i, of the ions are taken into account, the Debye-Hückel equation becomes:

$$\ell og\ \gamma_c = \frac{-z_+ z_- A_c \sqrt{I_c}}{1 + B_c a_i \sqrt{I_c}}$$

where

$$B_c = \left(\frac{8\pi N}{1000}\right)^{1/2} \frac{e}{k^{1/2}} \left(\frac{1}{T^{1/2} \epsilon^{1/2}}\right) = \frac{50.29158649 \times 10^8}{(T\ \epsilon)^{1/2}}$$

where the symbols have the significances given above. B_m on the molality (or weight) basis is given by $B_m = B_c\ (d_\circ)^{1/2}$.

Values of A_c, A_m, B_c, and B_m for aqueous solutions at a series of temperatures from 0°C to 100°C are given in table 7.

Güntelberg [Z. phys. Chem., 123, 199 (1926)] suggested the simpler form

$$\ell og\ \gamma_c = \frac{-z_+\ z_-\ A_c\ \sqrt{I}_c}{1 + \sqrt{I}_c}$$

which is equivalent to assigning a value of approximately 3A° to the ion size at all temperatures. A modified Güntelberg equation would be

$$\ell og\ \gamma_c = \frac{-z_+\ z_-\ A_c\ \sqrt{I}_c}{1 + 3B_c\ \sqrt{I}_c}$$

where the denominator would now be temperature dependent since B_c is a function of temperature. These two expressions for the activity coefficient give a fair representation of a number of electrolytes up to I = 0.1. However, a better representation is obtained if a term linear in the ionic strength is added to the right side of the equations. Thus, Guggenheim [Phil. Mag. 19, 588 (1935)] proposed the equation

$$\ell og\ \gamma_c = \frac{-z_+\ z_-\ A_c\ \sqrt{I}_c}{1 + \sqrt{I}_c} + b\ I_c$$

where b is an adjustable parameter.

Davies [J. Chem. Soc., (1938) 2093] altered the Guggenheim equation by putting $b = 0.2A\ z_+\ z_-$, thus:

$$\ell og\ \gamma_c = \frac{-z_+\ z_-\ A_c\ \sqrt{I}_c}{1 + \sqrt{I}_c} + 0.2A\ z_+\ z_-\ I_c$$

where the denominator of the first term on the right is again independent of temperature.

Scatchard ["The Structure of Electrolytic Solutions", Ed. W. J. Hamer, p. 9, John Wiley & Sons, Inc., New York, 1959] suggested that a better average fit is obtained if $(1 + 1.5\ \sqrt{I})$ were used in the denominator of the first term on the right, thus:

$$\ell og\ \gamma_c = \frac{-z_+\ z_-\ A_c\ \sqrt{I}_c}{1 + 1.5\ \sqrt{I}_c}$$

and if the denominator is made temperature dependent

$$\ell og\ \gamma_c = \frac{-z_+ z_- A_c \sqrt{I_c}}{1 + 4.5\ B_c \sqrt{I_c}}$$

Scatchard actually used a linear term in I with an adjustable coefficient on the right side of these equations, but it is omitted here.

Bjerrum [K. danske vidensk. Selsk., 1, No. 9 (1926)] has shown that ion pairs (associated ions with chargers of unlike sign] occur if the diameter of the ion is less than

$$a_B = \frac{z_+ z_- e^2}{2\ \epsilon\ kT}$$

Values of a_B for aqueous solutions from 0°C to 100°C are given in table 8. As the dielectric constant becomes lower a_B becomes larger. Values of a_B for uni-univalent electrolytes at 25°C as a function of dielectric constant are given in table 9. The Bjerrum expression for the activity coefficient is:

$$\ell og\ \gamma_c = \frac{-z_+ z_- A_c \sqrt{I_c}}{1 + B_c a_B \sqrt{I_c}}$$

Values of the activity coefficients of uni-univalent electrolytes in aqueous solutions at 25°C according to the above seven expressions are given in table 10.

The expressions may also be used to obtain values of γ_m using values of A_m, B_m, and I_m

VI. Activity coefficients of potassium chloride in dilute aqueous solutions at 25°C (preliminary)

The activity coefficients of potassium chloride in dilute aqueous solutions (0.1m or 0.1c or lower) at 25°C are given in table 11. These values are based on the emf measurements of Shedlovsky and MacInnes [J. Am. Chem. Soc., 59, 503 (1937)] and of Hornibrook, Janz, and Gordon [J. Am. Chem. Soc., 64, 513 (1942)] of galvanic cells with transference. These values are suitable as standards in isopiestic (or isotonic) measurements; accordingly, they are given to the fourth decimal. They should be considered as preliminary pending further checks.

VII. Activity coefficients of sodium chloride in dilute aqueous solutions at 25°C (preliminary)

The activity coefficients of sodium chloride in dilute aqueous solutions (0.1m or 0.1c or lower) at 25°C are given in table 12. These values are based on the emf measurements of Brown and MacInnes [J. Am. Chem. Soc., 57, 1356 (1935)] and of Janz and Gordon [J. Am. Chem. Soc., 65, 218 (1943)] of galvanic cells with transference. These values are suitable as standards in isopiestic (or isotonic) measurements; accordingly, they are given to the fourth decimal. They should be considered as preliminary pending further checks.

VIII. Standards for Electrolytic Conductivity

All conductivity measurements are referred to the standards of Jones and Bradshaw [J. Am. Chem. Soc., 55, 1780 (1933)]. Their specific conductances of standard solutions of potassium chloride, reported in international electrical units, are given in table 13, corrected to absolute electrical units. A "demal" solution, in terms of which Jones and Bradshaw expressed their concentration, is defined as a solution containing a gram mole of salt dissolved in a cubic centimeter of solution at zero degrees Celsius. The data given in table 13 are used in the calibration of conductivity cells.

IX. Theoretical Expressions for Equivalent Conductances

The Onsager [Physik. Z., 27, 388 (1926); 28, 277 (1927)] limiting equation for the equivalent conductance of an electrolytic solution as a function of concentration is:

$$\Lambda = \Lambda^\circ - \frac{z_+ \, z_- \; e^2 \Lambda^\circ q}{3 \, \epsilon \, kT(1 + \sqrt{q})} \left(\frac{8\pi N e^2}{1000D \; kT}\right)^{1/2} \sqrt{I} - \frac{F^2}{6\pi \eta N} (z_+ + z_-) \left(\frac{8\pi N e^2}{1000 \; \epsilon \; kT}\right)^{1/2} \sqrt{I}$$

where

$$q = \frac{z_+ \, z_- \; (\lambda_+^\circ + \lambda_-^\circ)}{(z_+ + z_-)(z_+ \, \lambda_+^\circ + z_- \, \lambda_-^\circ)}$$

or for a uni-univalent electrolyte:

$$\Lambda = \Lambda^\circ - [B_1 \, \Lambda^\circ + B_2] \sqrt{I}$$

where

$$B_1 = \frac{e^2 \; \Lambda_\circ}{6 \; \epsilon \; kT(1 + \sqrt{1/2})} \left(\frac{8\pi N e^2}{1000 \; \epsilon \; kT}\right)^{1/2}$$

and

$$B_2 = \frac{F^2}{3\pi \eta N} \left(\frac{8\pi N e^2}{1000 \; \epsilon \; kT}\right)^{1/2}$$

Values of B_1 and B_2 for aqueous solutions, on the weight and volume basis, from 0°C to 100°C are given in table 14 for uni-univalent electrolytes.

Considerations of more extensive expressions for equivalent conductances as a function of concentration will be given in a subsequent report.

Table 1. - Electromotive forces in volts and thermodynamic data in joules for the reaction in the Weston saturated standard cell made with 10 percent cadmium amalgam

Temperature t °C	Emf E volts	Gibbs energy change ΔG J mol^{-1}	Enthalpy change ΔH J mol^{-1}	Entropy change ΔS J mole^{-1}°K^{-1}	Heat capacity change ΔC_p J mole^{-1}°K^{-1}
0	1.0189860(0)[a]	-196,637.8(8)[b]	-196,139.7(5)[b]	+1.824(4)[b]	-174.89(95)[b]
2.994[c]	1.0189999(9)	-196,640.5(5)	-196,640.5(5)	0 (0)	-159.87(91)
3	1.0189999(9)	-196,640.5(5)	-196,941.5(5)	-0.003(3)	-159.84(9)
5	1.0189940(0)	-196,639.3(3)	-196,951.7(8)	-1.123(3)	-150.56(61)
10	1.0189316(7)	-196,627.3(3)	-197,651.8(21)	-3.618(9)	-130.15(9)
15	1.0188096(6)	-196,603.8(8)	-198,260.3(8)	-5.749(50)	-113.94(7)
20	1.0186360(1)	-196,570.3(3)	-198,798.6(93)	-7.601(3)	-102.17(20)
25	1.0184172(2)	-196,528.0(0)	-199,289.7(905)	-9.263(5)	-95.11(3)
30	1.0181568(9)	-196,477.8(8)	-199,757.9(89)	-10.820(3)	-93.02(4)
35	1.0178564(5)	-196,419.8(8)	-200,228.5(96)	-12.360(4)	-96.15(8)
40	1.0175155(6)	-196,354.0(1)	-200,728.5(99)	-13.969(73)	-104.79(82)
43.6[d]	1.0172433(4)	-196,301.5(5)	-201,122.6(38)	-15.220(4)	-114.55(81)

a - figure in parenthesis is last figure in emf calculated by the equation

$$E(\text{in volts}) = 1.0189860 + (9.453 \times 10^{-6})t - (16.595 \times 10^{-7})t^2 + (18.606 \times 10^{-9})t^3 - (15.005 \times 10^{-11})t^4$$

b - figure in parenthesis is last figure in thermodynamic quantity calculated from emf given by equation in a above.

c - cell has zero emf-temperature coefficient at this temperature; value calculated from equation given in a above.

d - transition temperature of cadmium sulfate from $CdSO_4 \cdot 8/3H_2O$ to $CdSO_4 \cdot H_2O$

Table 2. - Electromotive forces in volts and thermodynamic data in thermochemical calories for the reaction in the Weston saturated standard cell made with 10 percent cadmium amalgam*

Temperature	Emf	Gibbs energy change	Enthalpy change	Entropy change	Heat capacity change
t	E	ΔG	ΔH	ΔS	ΔC_p
°C	volts	$\mathrm{cal_{th}mol^{-1}}$	$\mathrm{cal_{th}mol^{-1}}$	$\mathrm{cal_{th}mol^{-1}{}^\circ K^{-1}}$	$\mathrm{cal_{th}mol^{-1}{}^\circ K^{-1}}$
0	1.0189860(0)	-46,997.5(5)	-46,878.5(4)	+0.436(6)	-41.80(1)
2.994	1.0189999(9)	-46,998.1(1)	-46,998.1(1)	0 (0)	-38.21(2)
3	1.0189999(9)	-46,998.1(1)	-46,998.3(3)	-0.001(1)	-38.20(1)
5	1.0189940(0)	-46,997.8(8)	-47,072.5(5)	-0.268(9)	-35.98(600)
10	1.0189316(7)	-46,995.0(0)	-47,239.9(9)	-0.865(5)	-31.11(2)
15	1.0188096(6)	-46,989.3(3)	-47,385.2(3)	-1.374(4)	-27.23(4)
20	1.0186360(1)	-46,981.3(3)	-47,513.9(40)	-1.817(7)	-24.42(3)
25	1.0184172(2)	-46,971.2(2)	-47,631.3(5)	-2.214(4)	-22.73(4)
30	1.0181568(9)	-46,959.2(2)	-47,743.2(4)	-2.586(7)	-22.23(4)
35	1.0178564(5)	-46,945.4(4)	-47,855.7(60)	-2.954(5)	-22.98(9)
40	1.0175155(6)	-46,929.6(7)	-47,975.1(5)	-3.339(40)	-25.04(5)
43.6	1.0172433(4)	-46,917.1(1)	-48,069.3(7)	-3.638(9)	-27.38(9)

*See footnotes of table 1.

Table 3. - Values of (RT/F) ln 10 from 0°C to 100°C

$R = 8.3143$ joule $°K^{-1} mole^{-1}$

$T°K = t°C + 273.150$

$F = 96487.0$ coulombs per gram-equivalent

$\ln 10 = 2.302585$

t°C	T°K	(RT/F) ln 10 volt	t°C	T°K	(RT/F) ln 10 volt
0	273.15	0.054197	50	323.15	0.064118
5	278.15	.055189	55	328.15	.065110
10	283.15	.056181	60	333.15	.066102
15	288.15	.057173	65	338.15	.067094
18	291.15	.057768	70	343.15	.068086
20	293.15	.058165	75	348.15	.069078
25	298.15	.059157	80	353.15	.070070
30	303.15	.060149	85	358.15	.071062
35	308.15	.061141	90	363.15	.072054
38	311.15	.061737	95	368.15	.073046
40	313.15	.062133	100	373.15	.074038
45	318.15	.063125			

Table 4. - Values of (RT/F) ln 10 for temperatures above 100°C
(Especially for emf studies of molten electrolytes)

$R = 8.3143$ joule $°K^{-1}$mole^{-1}

$T°K = t°C + 273.150$

$F = 96487.0$ coulombs per gram-equivalent

$\ln 10 = 2.302585$

t°C	T°K	(RT/F) ln 10 volt	t°C	T°K	(RT/F) ln 10 volt
150	423.15	0.083959	1200	1473.15	0.29229
200	473.15	.093880	1300	1573.15	.31214
250	523.15	.10380	1400	1673.15	.33198
300	573.15	.11372	1500	1773.15	.35182
350	623.15	.12364	1600	1873.15	.37166
400	673.15	.13356	1700	1973.15	.39150
450	723.15	.14348	1800	2073.15	.41134
500	773.15	.15340	1900	2173.15	.43118
550	823.15	.16333	2000	2273.15	.45103
600	873.15	.17325	2100	2373.15	.47087
650	923.15	.18317	2200	2473.15	.49071
700	973.15	.19309	2300	2573.15	.51055
750	1023.15	.20301	2400	2673.15	.53039
800	1073.15	.21293	2500	2773.15	.55023
850	1123.15	.22285	2600	2873.15	.57007
900	1173.15	.23277	2700	2973.15	.58992
950	1223.15	.24269	2800	3073.15	.60976
1000	1273.15	.25261	2900	3173.15	.62960
1100	1373.15	.27245	3000	3273.15	.64944

Table 5. - Values of mean molality, mean activity coefficient, solute activity, and ionic strength for various valence types of electrolytes

Type	Example	$m_\pm =$ Xm	$\gamma_\pm$	$a_2 =$ $a_\pm^\nu$	$I =$ $1/2 \sum_i z_i^2 m$
1-1	KCl	m	$(\gamma_+\gamma_-)^{1/2}$	$m^2\gamma_\pm^2$	m
1-2	Na_2SO_4	$4^{1/3}$ m	$(\gamma_+^2\gamma_-)^{1/3}$	$4m^3\gamma_\pm^3$	3m
1-3	$K_3Fe(CN)_6$	$27^{1/4}$ m	$(\gamma_+^3\gamma_-)^{1/4}$	$27m^4\gamma_\pm^4$	6m
1-4	$K_4Fe(CN)_6$	$256^{1/5}$ m	$(\gamma_+^4\gamma_-)^{1/5}$	$256m^5\gamma_\pm^5$	10m
2-1	$BaCl_2$	$4^{1/3}$ m	$(\gamma_+\gamma_-^2)^{1/3}$	$4m^3\gamma_\pm^3$	3m
2-2	$MgSO_4$	m	$(\gamma_+\gamma_-)^{1/2}$	$m^2\gamma_\pm^2$	4m
2-3	$Sn_3[Fe(CN)_6]_2$	$108^{1/5}$ m	$(\gamma_+^3\gamma_-^2)^{1/5}$	$108m^5\gamma_\pm^5$	15m
2-4	$Mg_2Fe(CN)_6$	$4^{1/3}$ m	$(\gamma_+^2\gamma_-)^{1/3}$	$4m^3\gamma_\pm^3$	12m
3-1	$AlCl_3$	$27^{1/4}$ m	$(\gamma_+\gamma_-^3)^{1/4}$	$27m^4\gamma_\pm^4$	6m
3-2	$Al_2(SO_4)_3$	$108^{1/5}$ m	$(\gamma_+^2\gamma_-^3)^{1/5}$	$108m^5\gamma_\pm^5$	15m
3-3	$LaFe(CN)_6$	m	$(\gamma_+\gamma_-)^{1/2}$	$m^2\gamma_\pm^2$	9m
3-4	$Al_4[Fe(CN)_6]_3$	$6912^{1/7}$ m	$(\gamma_+^4\gamma_-^3)^{1/7}$	$6912m^7\gamma_\pm^7$	42m
4-1	$Th(NO_3)_4$	$256^{1/5}$ m	$(\gamma_+\gamma_-^4)^{1/5}$	$256m^5\gamma_\pm^5$	10m
4-2	$Th(SO_4)_2$	$4^{1/3}$ m	$(\gamma_+\gamma_-^2)^{1/3}$	$4m^3\gamma_\pm^3$	12m
4-3	$Th_3(PO_4)_4$	$6912^{1/7}$ m	$(\gamma_+^3\gamma_-^4)^{1/7}$	$6912m^7\gamma_\pm^7$	42m
4-4	$SnFe(CN)_6$	m	$(\gamma_+\gamma_-)^{1/2}$	$m^2\gamma_\pm^2$	16m

Table 6. - Physical Properties of Water

Temperature	Density[1]	Specific volume[1]	Vapor pressure[2]	Viscosity[3]	Dielectric constant[4]
t	d	v	p	η	ε
°C	g/ml	ml/g	mm Hg*	centipose	
0**	0.99987	1.00013	4.580	1.787	87.74
5	.99999	1.00001	6.538	1.517	85.76
10	.99973	1.00027	9.203	1.306	83.83
15	.99913	1.00087	12.782	1.138	81.95
18	.99862	1.00138	15.471	1.053	80.84
20	.99823	1.00177	17.529	1.002	80.10
25	.99707	1.00293	23.753	0.8903	78.30
30	.99567	1.00434	31.824	.7974	76.55
35	.99406	1.00598	42.180	.7194	74.83
38	.99299	1.00706	49.702	.6783	73.82
40	.99224	1.00782	55.338	.6531	73.15
45	.99025	1.00985	71.90	.5963	71.51
50	.98807	1.01207	92.56	.5471	69.91
55	.98573	1.01448	118.11	.5044	68.34
60	.98324	1.01705	149.47	.4669	66.81
65	.98059	1.01979	187.65	.4338	65.32
70	.97781	1.02270	233.81	.4044	63.86
75	.97489	1.02576	289.22	.3782	62.43
80	.97183	1.02899	355.31	.3547	61.03
85	.96865	1.03237	433.64	.3340	59.66
90	.96534	1.03590	525.92	.3149	58.32
95	.96192	1.03959	634.04	.2976	57.01
100***	.95838	1.04343	760.00	.2822	55.72

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* - 760 mm Hg = 1 atmosphere = 1,013,250 dyn cm^{-2} = 101,325 newtons m^{-2}; on the Système International d'Unites, adopted in a resolution, 11th General Conference on Weights and Measures, Paris, October 1960, the international unit of pressure is the newton per square meter.

** - The freezing point is zero degrees Celsius, exactly; the triple point of water is 0.001°C or 273.16°K.

*** - The boiling point

Table 7. - Values of the Debye-Hückel Constants for Activity Coefficients for Aqueous Solutions from 0°C to 100°C

	A		B	
t°C	Weight basis	Volume basis	Weight basis	Volume basis
	$\text{kg}^{1/2}\text{mole}^{-1/2}$	$\ell^{1/2}\text{mole}^{-1/2}$	$\text{kg}^{1/2}\ \text{cm}^{8}\ \text{mole}^{-1/2}$	$\ell^{1/2}\ \text{cm}^{8}\ \text{mole}^{-1/2}$
0	0.4918	0.4918	0.3248	0.3249
5	.4953	.4953	.3256	.3256
10	.4989	.4990	.3264	.3264
15	.5027	.5029	.3271	.3273
18	.5050	.5054	.3276	.3278
20	.5067	.5072	.3279	.3282
25	.5108	.5116	.3287	.3292
30	.5151	.5162	.3294	.3301
35	.5196	.5212	.3302	.3312
38	.5224	.5242	.3307	.3318
40	.5243	.5263	.3310	.3323
45	.5292	.5318	.3318	.3334
50	.5342	.5374	.3326	.3346
55	.5395	.5434	.3334	.3358
60	.5449	.5495	.3343	.3371
65	.5505	.5559	.3351	.3384
70	.5563	.5625	.3359	.3397
75	.5623	.5695	.3368	.3411
80	.5685	.5767	.3377	.3426
85	.5750	.5843	.3386	.3440
90	.5817	.5921	.3395	.3456
95	.5886	.6001	.3405	.3471
100	.5959	.6087	.3414	.3488

Table 8. - Bjerrum's Minimum Ion Parameter* for Uni-univalent Electrolytes in Aqueous Solutions from 0°C to 100°C

Temperature	Ion parameter	Temperature	Ion parameter
t	a_i	t	a_i
°C	cm^{-8}	°C	cm^{-8}
0	3.49	50	3.70
5	3.50	55	3.73
10	3.52	60	3.75
15	3.54	65	3.78
18	3.55	70	3.81
20	3.56	75	3.84
25	3.58	80	3.88
30	3.60	85	3.91
35	3.62	90	3.94
38	3.64	95	3.98
40	3.65	100	4.02
45	3.67		

* - Sometimes called the ion size.

Table 9. - Bjerrum's Minimum Ion Parameter* as a Function of Dielectric Constant for Uni-univalent Electrolytes at 25°C

Dielectric Constant ϵ	Ion parameter a_i	Dielectric Constant ϵ	Ion parameter a_i
	cm^{-8}		cm^{-8}
1	280	50	5.60
2	140	55	5.10
5	56	60	4.67
10	28	65	4.31
15	18.7	70	4.00
20	14.0	75	3.74
25	11.2	80	3.50
30	9.34	85	3.30
35	8.01	90	3.11
40	7.01	95	2.95
45	6.23	100	2.80

* - Sometimes called the ion size.

Table 10. - Activity coefficients of uni-univalent electrolytes in aqueous solutions at 25°C according to several theoretical equations.

c	1	2	3	4	5	6	7
0.0001	0.9883	0.9884	0.9884	0.9884	0.9885	0.9885	0.9884
.0002	.9835	.9837	.9837	.9838	.9838	.9838	.9838
.0003	.9798	.9801	.9801	.9802	.9803	.9803	.9802
.0004	.9767	.9772	.9772	.9773	.9774	.9774	.9773
.0005	.9740	.9746	.9746	.9747	.9748	.9748	.9747
.0006	.9716	.9722	.9722	.9724	.9725	.9725	.9724
.0007	.9693	.9701	.9701	.9703	.9705	.9705	.9703
.0008	.9672	.9681	.9681	.9682	.9685	.9685	.9683
.0009	.9653	.9663	.9663	.9665	.9667	.9667	.9665
.001	.9634	.9645	.9645	.9648	.9651	.9650	.9648
.002	.9487	.9508	.9508	.9513	.9518	.9518	.9513
.003	.9375	.9407	.9406	.9413	.9421	.9421	.9413
.004	.9282	.9323	.9323	.9332	.9342	.9341	.9331
.005	.9201	.9252	.9251	.9262	.9275	.9274	.9261
.006	.9128	.9188	.9187	.9201	.9215	.9214	.9199
.007	.9061	.9131	.9130	.9146	.9162	.9160	.9143
.008	.9000	.9078	.9077	.9095	.9113	.9112	.9092
.009	.8943	.9030	.9029	.9049	.9068	.9067	.9045
.01	.8889	.8984	.8983	.9006	.9026	.9025	.9001
.02	.8465	.8642	.8640	.8683	.8716	.8714	.8671
.03	.8154	.8404	.8401	.8463	.8505	.8501	.8443
.04	.7901	.8217	.8214	.8295	.8342	.8338	.8266
.05	.7684	.8063	.8059	.8159	.8210	.8205	.8120
.06	.7493	.7931	.7927	.8044	.8098	.8092	.7996
.07	.7322	.7816	.7810	.7946	.8000	.7994	.7888
.08	.7166	.7713	.7707	.7859	.7915	.7907	.7791
.09	.7023	.7620	.7614	.7783	.7837	.7830	.7704
.10	.6890	.7535	.7529	.7715	.7767	.7759	.7626

1	Limiting law of Debye and Hückel
2	Güntelberg
3	Modified Güntelberg
4	Davies
5	Scatchard
6	Modified Scatchard
7	Bjerrum

Table 11. - Activity coefficients of potassium chloride in aqueous solutions at 25°C (preliminary).

m	γ_m	c	γ_c
0.0001	0.9884	0.0001	0.9884
.0002	.9838	.0002	.9838
.0003	.9802	.0003	.9802
.0004	.9773	.0004	.9773
.0005	.9747	.0005	.9747
.0006	.9725	.0006	.9725
.0007	.9704	.0007	.9704
.0008	.9684	.0008	.9684
.0009	.9666	.0009	.9666
.001	.9649	.001	.9649
.002	.9515	.002	.9515
.003	.9417	.003	.9417
.004	.9336	.004	.9336
.005	.9266	.005	.9268
.006	.9205	.006	.9207
.007	.9151	.007	.9153
.008	.9101	.008	.9103
.009	.9055	.009	.9057
.01	.9012	.01	.9015
.02	.8691	.02	.8696
.03	.8471	.03	.8478
.04	.8301	.04	.8309
.05	.8161	.05	.8170
.06	.8042	.06	.8054
.07	.7938	.07	.7952
.08	.7846	.08	.7861
.09	.7765	.09	.7781
.10	.7690	.10	.7708

Table 12. - Activity coefficients of sodium chloride in aqueous solutions at 25°C (preliminary).

m	γ_m	c	γ_c
0.0001	0.9885	0.0001	0.9885
.0002	.9839	.0002	.9839
.0003	.9804	.0003	.9804
.0004	.9775	.0004	.9775
.0005	.9750	.0005	.9750
.0006	.9727	.0006	.9727
.0007	.9706	.0007	.9706
.0008	.9687	.0008	.9687
.0009	.9669	.0009	.9669
.001	.9652	.001	.9652
.002	.9521	.002	.9521
.003	.9424	.003	.9424
.004	.9345	.004	.9345
.005	.9277	.005	.9277
.006	.9218	.006	.9218
.007	.9165	.007	.9165
.008	.9116	.008	.9116
.009	.9071	.009	.9072
.01	.9030	.01	.9031
.02	.8720	.02	.8722
.03	.8510	.03	.8513
.04	.8349	.04	.8354
.05	.8217	.05	.8223
.06	.8106	.06	.8113
.07	.8011	.07	.8019
.08	.7926	.08	.7934
.09	.7851	.09	.7860
.10	.7783	.10	.7793

Table 13. - Specific conductances of standard solutions of potassium chloride

Demal*	Grams KCl per 1000 grams solution in vacuum*	Specific conductances		
		0°C $\text{ohm}^{-1}\ \text{cm}^{-1}$	18°C $\text{ohm}^{-1}\ \text{cm}^{-1}$	25°C $\text{ohm}^{-1}\ \text{cm}^{-1}$
1.0	71.1352	0.065144	0.097790	0.111287
0.1	7.41913	0.0071344	0.0111612	0.0128496
0.01	0.745263	0.00077326	0.00121992	0.00140807

*Based on the atomic weights of 1933.

Table 14.- Values of the Debye-Hückel-Onsager Constants for Equivalent Conductances for Aqueous Solutions from 0°C to 100°C

	B_1		B_2	
t°C	Weight basis	Volume basis	Weight basis	Volume basis
	$kg^{1/2} mole^{-1/2}$	$\ell^{1/2} mole^{-1/2}$	$ohm^{-1} kg^{1/2} mole^{-1/2}$	$ohm^{-1} \ell^{1/2} mole^{-1/2}$
0	0.2211	0.2211	29.81	29.82
5	.2227	.2227	35.21	35.21
10	.2243	.2244	40.99	41.00
15	.2260	.2261	47.15	47.17
18	.2271	.2272	51.03	51.06
20	.2278	.2280	53.67	53.72
25	.2297	.2300	60.55	60.64
30	.2316	.2321	67.76	67.91
35	.2336	.2343	75.28	75.51
38	.2349	.2357	79.96	80.24
40	.2357	.2366	83.12	83.45
45	.2379	.2391	91.26	91.71
50	.2402	.2416	99.71	100.3
55	.2426	.2443	108.4	109.2
60	.2450	.2471	117.4	118.4
65	.2475	.2499	126.7	127.9
70	.2501	.2529	136.3	137.8
75	.2528	.2560	146.1	147.9
80	.2556	.2593	156.2	158.4
85	.2585	.2627	166.3	169.0
90	.2615	.2662	176.8	180.0
95	.2646	.2698	187.6	191.3
100	.2679	.2737	198.4	202.7