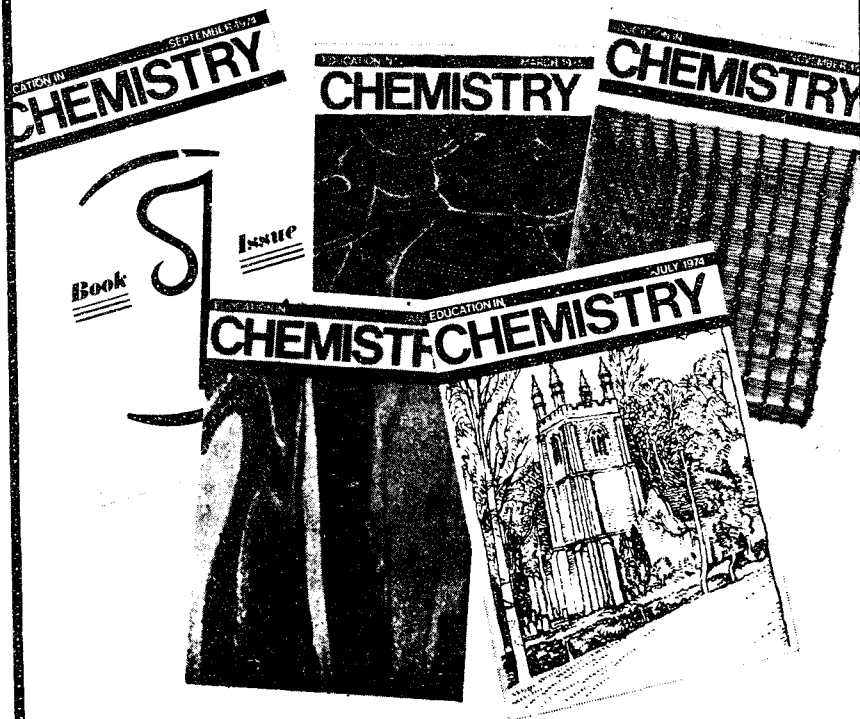


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SOME ASPECTS OF THE ELECTROCHEMISTRY OF SOLUTIONS

GRAHAM HILLS



CHEMISTRY CASSETTE

CHEMISTRY CASSETTES

General Editor:

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The University of Aston in Birmingham

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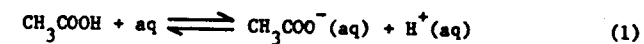
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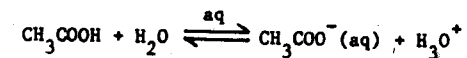
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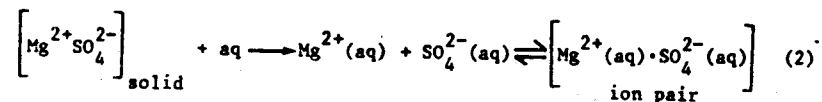
1



There is evidence that the hydrogen ion interacts with water in a specific way to form a complex H_3O^+ or even H_9O_4^+ . The use of symbol (aq) may therefore be inadequate in this context and equation (1) could be rewritten as



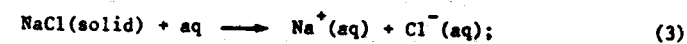
i.e. as a chemical reaction.



n.b. In spite of the ionic character of MgSO_4 , it does not completely dissociate into ions when dissolved in aqueous solutions. This is because of the strong electrostatic attraction between the two divalent ions. In solvents of much lower dielectric constant, even monovalent ions may form ion-pairs.

2

For the process

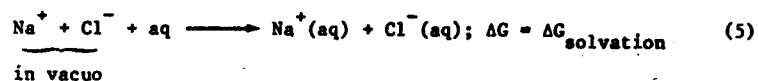
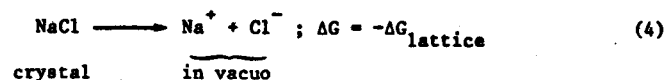


$\Delta G_{\text{solution}} \longrightarrow 0$ as the solution approaches saturation.

$\Delta G_{\text{solution}} = \Delta G_{\text{solution}}^\ominus$ for a solution of unit activity

(see below)

3



$$\Delta G_{\text{solution}} = \Delta G_{\text{solvation}} - \Delta G_{\text{lattice}} \quad (6)$$

4

The Madelung equation for the lattice energy per mole of a crystalline compound of two monovalent ions:

$$\Delta G_{\text{lattice}} = -\frac{N e^2 A}{d_{\pm}} \left(1 - \frac{1}{n}\right); \quad (7)$$

where N is the Avogadro number, e the electronic charge, A the geometric (Madelung) constant, d_{\pm} the inter-ionic separation and n is a repulsion constant derived from measurements of crystal compressibility and approximately equal to 10. You may care to check that the calculated value for sodium chloride [$A = 1.75$; $d_{\pm} = 2.8 \times 10^{-8}$ cm and $e = 4.8 \times 10^{-10}$ e.s.u.] is close to that observed, namely, -765 kJ/mol. [To be up-to-date one should use the S.I. system of units, namely $d_{\pm} = 2.8 \times 10^{-10}$ m and $e = 1.6 \times 10^{-19}$ coulomb. Because of the complications in defining electrical and magnetic units this will require a more complex formula, namely

$$\Delta G = -\frac{N e^2 A}{4\pi\epsilon_0 d_{\pm}} \left(1 - \frac{1}{n}\right),$$

where ϵ_0 is the so-called permittivity of free space (equal to $\frac{10^{-9}}{36\pi}$). Insertion of these values will give the same answer as before.]

5

The Born equation for the solvation energy of a single monovalent ion of radius r_i in a solvent of dielectric constant, ϵ , can be derived as follows:

$$\text{energy of the ion in a vacuum} = -\frac{e^2}{2r_i}$$

$$\text{energy of the ion in a dielectric} = -\frac{e^2}{2\epsilon r_i} \quad (8)$$

$$\text{free energy of transfer from vacuum to dielectric} = -\frac{e^2}{2\epsilon} \left(1 - \frac{1}{\epsilon}\right).$$

For one mole of both cations and anions (and in practice they are inseparable)

$$\Delta G_{\text{solvation}} = -\frac{N e^2 (r_+ + r_-)}{2r_+ r_-} \left(1 - \frac{1}{\epsilon}\right), \quad (9)$$

where r_+ and r_- are respectively the effective radii of the cationic and anionic species in solution.

Recalling that the dielectric constant of water at 25°C and 1 atm pressure is 78.5, then you may care to calculate $\Delta G_{\text{solvation}}$ for aqueous sodium chloride and compare it with the observed value of 715 kJ/mol. [$r_{\text{Na}^+} = 0.98 \times 10^{-10}$ m; $r_{\text{Cl}^-} = 1.81 \times 10^{-10}$ m.] It is far too high because the crystallographic radii are inappropriate for this calculation. We need instead to use the (unknown) radii of the cavities in the solvent in which the ions reside.

6

$$\Delta G_{\text{solution}} = \Delta H_{\text{solution}} - T\Delta S_{\text{solution}} \quad (10)$$

$$\Delta S_{\text{solution}} \approx -R \ln X \quad (11)$$

where X is the mole fraction of the solute species.

As $X \rightarrow 0$, $\Delta S_{\text{solution}} \rightarrow +\infty$.

The mole fraction of a species A is its fractional molecular content, i.v. $X_A = \frac{n_A}{n_A + n_B + \dots}$, where n = number of moles per unit volume or for any fixed amount of the system.

The concentration of a dilute aqueous solution at room temperature, c_A , in mol/dm³ is related to the mole fraction, X_A , by the density and molecular weight of water, i.e.

$$X_A \approx \frac{c_A}{c_A + 55.5}$$

and is thus much smaller than c_A .

7

Electric field at the surface of the ion of radius r and electronic charge e is $= \frac{e}{r^2}$ (12)

For an ion of radius 1 Å (10^{-8} cm = 0.1 nm = 10^{-10} m)

in vacuo

$$\frac{e}{r^2} = 1.44 \times 10^9 \text{ V/cm}$$

Even in solvents of high dielectric constant such as water ($\epsilon \approx 80$), the field is still 1.8×10^7 V/cm.

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7

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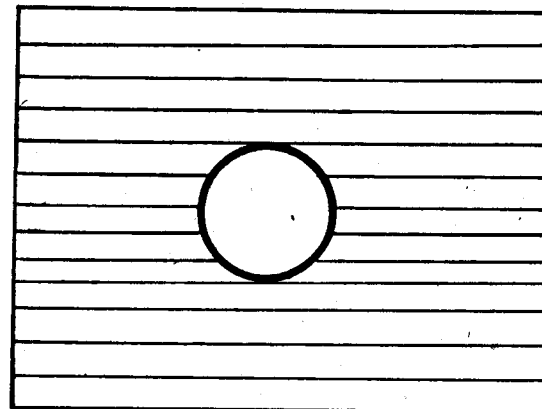


Figure 1a. The (Born) continuum model of an ion in a continuous dielectric

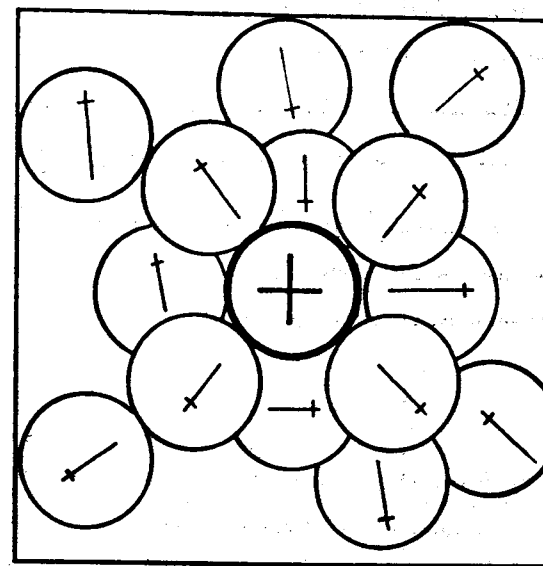


Figure 1b. The molecular model of an ion in a molecular dielectric.

- References
1. I. R. McDonald and K. Singer, *Chem. in Britain*, **9** (1973) 54.
 2. F. H. Stillinger and A. Rahman, *J. Chem. Phys.*, **60** (1974) 1545

8

$$\frac{\partial G}{\partial n_A} = \underbrace{\mu_A}_{\text{chemical potential}} = \underbrace{\mu_A^\ominus}_{\text{standard chemical potential}} + \underbrace{RT \ln a_A}_{\text{activity}} \quad (13)$$

independent of the units of concentration the separate values depend on the units of a_A .

As before n_A is the number of moles of A.

$$\mu_+ = \mu_+^\ominus + RT \ln a_+ \quad (14)$$

$$\mu_- = \mu_-^\ominus + RT \ln a_- \quad (15)$$

Because $\mu_+ + \mu_- = \mu$

$$a = a_+ a_- \quad (16)$$

$$\text{The mean ionic activity } a_{\pm} = \sqrt{a_+ a_-} = \sqrt{a} \quad (17)$$

for a simple (1:1) electrolyte

9

$$\text{activity coefficient} = \frac{\text{activity}}{\text{concentration}}$$

The activity coefficient is dimensionless; the activity and concentration can be expressed in any convenient units. If we use mol/dm^3 then we normally write this relationship

$$\frac{a}{c} = f,$$

where f is the molar activity coefficient or just the activity coefficient. In this type of study we often express concentrations as molalities, mol/kg of solvent, because then they are independent of temperature. In this case we redefine the activity coefficient as

(frame continued on next page)

9

CONTD

$$\frac{a}{m} = \gamma$$

where γ = molal activity coefficient.

n.b. for aqueous solutions where $1 \text{ dm}^3 \approx 1 \text{ kg}$, c and m are almost identical.

The mean ionic activity coefficient is the geometric mean of the two inseparable and indeterminate ionic activity coefficients.

$$f_{\pm} = \sqrt{f_+ f_-} = \sqrt{f}$$

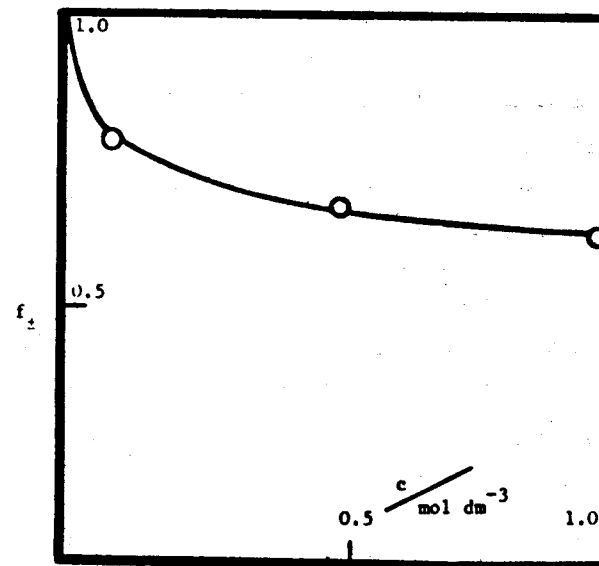


Figure 2. The mean ionic activity coefficient of KCl in aqueous solution at 25°C.

10 General methods of measuring activities and activity coefficients (taken from Electrolyte Solutions by Robinson & Stokes, Butterworths, London 1970).

1. Isopiestic method, where two solutions of different solutes in the same solvent are allowed to reach the same vapour pressure. The equilibrium molalities are determined analytically and found to be m_B and m_C .

If B is a standard substance the activity of which is known as a function of molality

$$\ln \gamma_C = \ln \gamma_B + \ln \frac{m_B}{m_C} + \int_0^{m_B} \left(\frac{m_B}{m_C} - 1 \right) d \ln \left(\gamma_B m_B \right)$$

2. Depression of the freezing point. The freezing point of the solution is measured as a function of concentration.

For dilute aqueous solutions, the cryoscopic constant can be evaluated and it follows that

$$\ln a_s = -4.207 \times 10^{-3} \theta + 2.1 \times 10^{-6} \theta^2,$$

where a_s is the activity of the solvent at the freezing point of the solution and θ is the depression of the freezing point. For dilute solutions $\ln a_s = -gN$, where N is the mole fraction of the solute and g is a constant, the so-called osmotic constant. It can be shown that

$$\ln \gamma = (g - 1) + \int_0^m (g - 1) d \ln m,$$

and thus γ can be found from g , a_s and θ .

(frame continued on next page)

10 3. Lowering of the vapour pressure. The solvent vapour pressure, P, is determined as a function of concentration.

CONTD

$\frac{P}{P^\circ} = \ln a_s$, where P° is the vapour pressure of the pure solvent at that temperature, and a_s is the activity of the solvent at the same temperature.

n.b. You will be seldom asked to remember or to derive these relationships. They are included here to show you that a and γ can be determined for any solution.

11

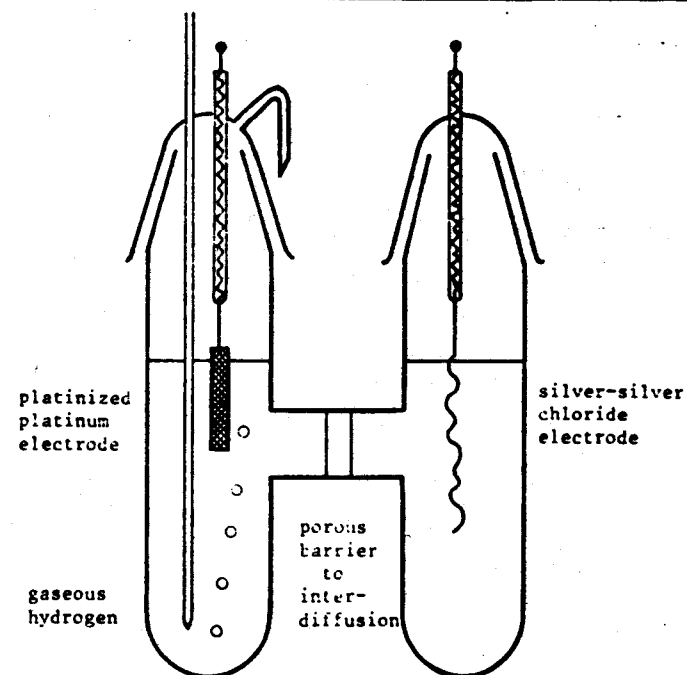
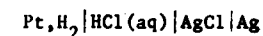
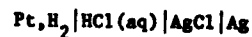


Figure 3. A simple galvanic cell for the study of activity coefficients, in this case:



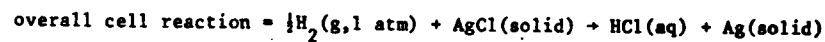
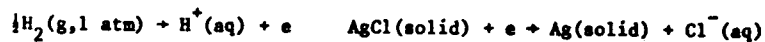
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11



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First half-cell reaction second half-cell reaction



For slight discharge of cell, the electric work done by the system

$$= -EF, \text{ where } F \text{ is the faraday constant.}$$

The corresponding chemical work done by the system

$$\begin{aligned} &= \nu_{\text{HCl}} \mu_{\text{HCl}} + \nu_{\text{Ag}} \mu_{\text{Ag}} - \frac{1}{2} \nu_{\text{H}_2} \mu_{\text{H}_2} - \nu_{\text{AgCl}} \mu_{\text{AgCl}} \\ &= K + RT \ln a_{\text{HCl}} \end{aligned}$$

K is a constant equal to the sum of all the constant quantities ν_{Ag} ,

$\frac{1}{2} \nu_{\text{H}_2}$, ν_{AgCl} and μ_{HCl}^\ominus .

Equating these two expressions for the work done by the system gives

$$-EF = K + RT \ln a_{\text{HCl}}$$

$$\text{or} \quad E = E^\ominus - \frac{RT}{F} \ln a_{\text{HCl}} \quad (18)$$

where E^\ominus is the standard e.m.f. of this particular cell

($= -\frac{K}{F}$), i.e. the value of E when $a_{\text{HCl}} = 1$.

a_{HCl} is found from measurements of E and a knowledge of E^\ominus . This is found by a simple extrapolation procedure: thus, by rearranging (18)

and recalling that $a = c^2 f_{\pm}^2 = c^2 f_{\pm}^2$

$$E = E^\ominus - \frac{2RT}{F} c - \frac{2RT}{F} \ln f_{\pm}$$

(frame continued on next page)

11

Writing $\ln f_{\pm} = 2.3 \log_{10} f_{\pm} = -2.3 A\sqrt{c}$ (and that is justified later)

CONTD

$$E + \frac{2RT}{F} \ln c = E^\ominus + \frac{2RT}{F} \cdot 2.3 A\sqrt{c} \quad (19)$$

The L.H.S. is therefore a linear function of \sqrt{c} , the slope gives the value of A and the intercept E^\ominus .

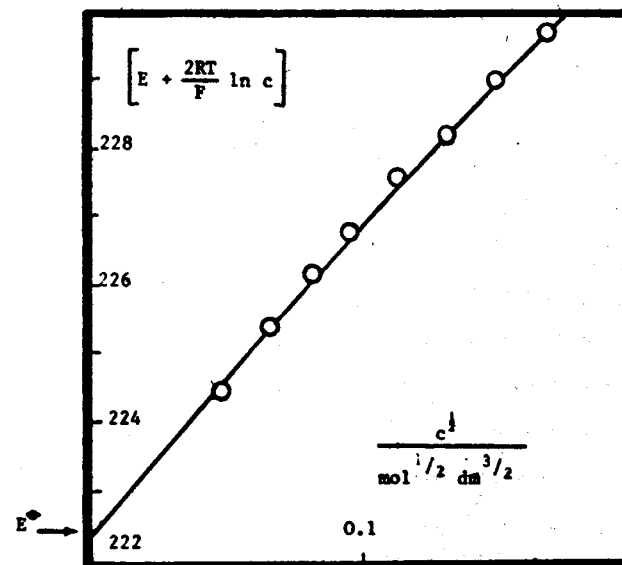


Figure 4. The extrapolation of equation (19) to find E^\ominus .

12 The Debye-Hückel theory of mean ionic activity coefficients

The derivation is based on two equations relating charge density, i.e. ionic concentration, to the electric potential $\psi(r)$ at a distance r from any given ion. The first equation, embodying the Maxwell-Boltzmann distribution law, relates the number density (number per unit volume) of any ionic species (at a distance r from a given ion) to the average, bulk value in terms of the electric potential at r due to the given ion, i.e.

$$n_{\pm,r} = n_{\pm,\infty} \exp \left[-\frac{z_{\pm} F \psi(r)}{RT} \right] \quad (20)$$

The subscript \pm indicates that we can write the equation for either positive or negative surrounding ions and for either a positive ($\psi = +ve$) or negative ($\psi = -ve$) central ion. We need only note that for oppositely charged ions the exponential term must be positive if equation (20) is to express the mutual attraction of these species.

The other equation is taken from classical electrostatics.

It is the Poisson equation which relates the divergence of the electric field at a point in the system to the charge density at that point. For a spherically symmetric system, this is written as

$$\frac{1}{r^2} \cdot \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} (r) \right) = -\frac{4\pi\rho(r)}{\epsilon}$$

where ϵ is the dielectric constant and ρ is the net charge density, also a function of r , the distance from the central ion.

These are two equations with two unknowns, namely $\psi(r)$ and $\rho(r)$. They can be solved and after a few pages of algebra (again see Robinson and Stokes) the final equation is obtained, i.e.

(frame continued on next page)

12

CONTD

$$\log_{10} f_{\pm} = -A\sqrt{c} \quad (22)$$

$$\text{where } A = \frac{F^3}{2.303eRTN} \left(\frac{2\pi}{1000eRT} \right)^{\frac{1}{2}}$$

For a multivalent electrolyte,

$$\log_{10} f_{\pm} = -|z_{+}||z_{-}|A\sqrt{I} \quad (23)$$

where

$$I = \frac{1}{2} \sum c_i z_i^2 \quad (24)$$

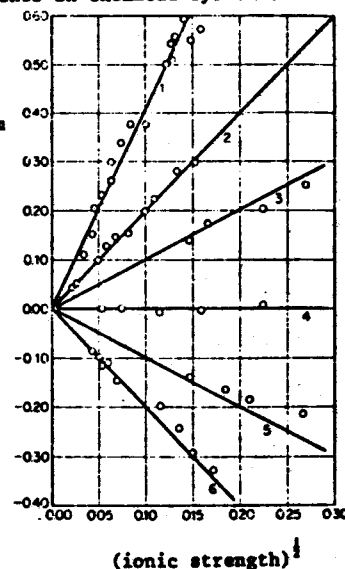
and where the concentration c is expressed in mol/dm³

A quick calculation will show that for a (1:1) electrolyte $I = c$ and you may care to prove to yourself that for other, multivalent ion systems this is not so.

13

Some examples of the importance of activities and activity coefficients in chemical systems.

Relative values of the logarithm of the rate constant for six reactions in aqueous solution



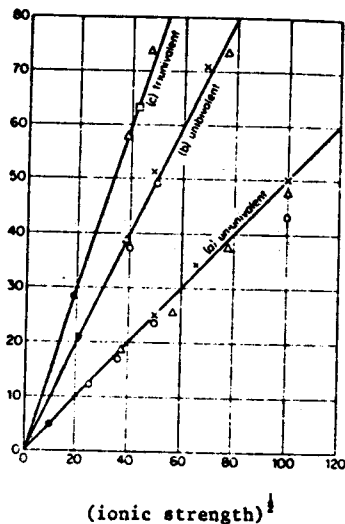
- (1) $2[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} + \text{Hg}^{2+} + 2\text{H}_2\text{O} \rightarrow 2[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+} + \text{HgBr}_2$
- (2) $\text{S}_2\text{O}_8^{2-} + 2\text{I}^- \rightarrow \text{I}_2 + 2\text{SO}_4^{2-}$
- (3) $[\text{NO}_2\text{NCOOC}_2\text{H}_5]^- + \text{OH}^- \rightarrow \text{N}_2\text{O} + \text{CO}_3^{2-} + \text{C}_2\text{H}_5\text{OH}$
- (4) Inversion of cane sugar
- (5) $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{Br}^- \rightarrow 2\text{H}_2\text{O} + \text{Br}_2$
- (6) $[\text{Co}(\text{NH}_3)_5\text{OH}]^{2+} + \text{OH}^- \rightarrow [\text{Co}(\text{NH}_3)_5\text{O}]^{2+} + \text{Br}^-$

Circles are experimental values; the lines are calculated from the Debye-Hückel theory. (frame continued on next page)

13

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Relative values of the logarithm of the activity coefficients for sparingly soluble salts in aqueous salt solution.



[After Brønsted and LaMer, J. Am. Chem. Soc., 46 555 (1924).]

14

$$z_i e \frac{dE}{dX} = 6\pi n r_i v_i \quad (25)$$

↑
potential
gradient

where z_i is the valence and r_i the radius of the ion, n the solvent viscosity, and v_i the ionic velocity.

$$\frac{v_i}{dE/dX} = \frac{z_i e}{6\pi n r_i} = u_i \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1} \quad (26)$$

mobility

Inserting the appropriate values for, say, the sodium ion in water, [$\eta = 0.01$ poise, $r_i \approx 0.1$ nm]

$$u_{\text{Na}^+}(\text{aq}) \approx 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ sec}^{-1}$$

[In case your answer is out by a power of 10, you should remember that the S.I. unit of viscosity is 10 times the poise].

(frame continued on next page)

14

CONTD

$$I = \sum_i 10^{-3} z_i u_i c_i F \frac{dE}{dX} \text{ amp cm}^{-2}, \quad (27)$$

current
density

where c_i = number density of charges, i.e. ionic concentration, in mol/dm³.

$$\frac{I}{dE/dX} = \sum_i 10^{-3} z_i u_i c_i F = \kappa \text{ ohm}^{-1} \text{ cm}^{-1} \quad (28)$$

conductivity

Typically, for a 0.1 M solution of KCl in H₂O at 25°C,

$$\kappa = 0.013 \text{ ohm}^{-1} \text{ cm}^{-1}$$

For a single (1:1) electrolyte, $z_+ = z_- = 1$, $c_+ = c_- = c$. Then

$$\begin{aligned} \frac{10^3 \kappa}{c} &= u_+ F + u_- F = \Lambda \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \quad (29) \\ &\text{molar conductivity} \\ &= (\lambda_+ + \lambda_-) \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \end{aligned}$$

For KCl in H₂O at 25°C,

$$\Lambda = \lambda_+ + \lambda_- = 149.85 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

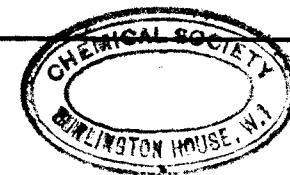
In its simplest form the Onsager equation can be written as

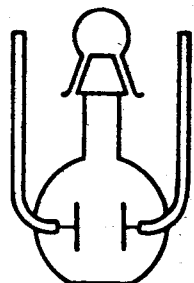
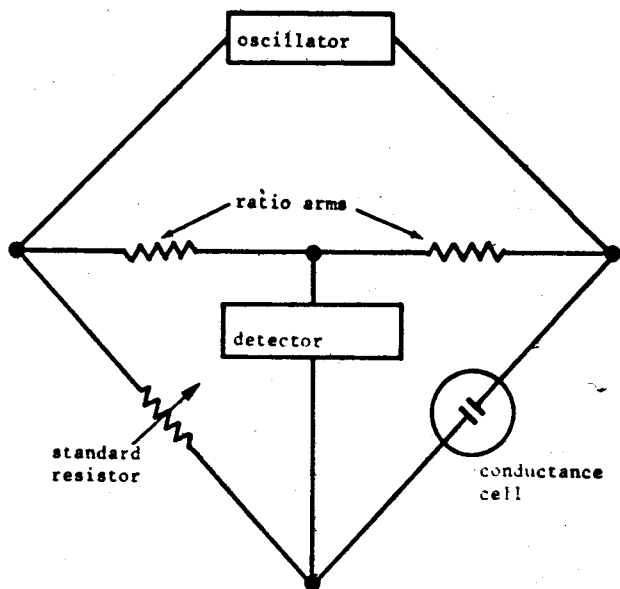
$$\Lambda = \Lambda^0 - k\sqrt{c},$$

where for a (1:1) electrolyte

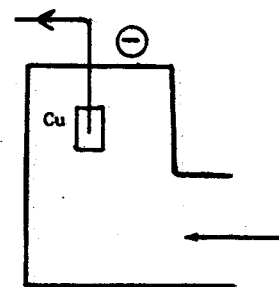
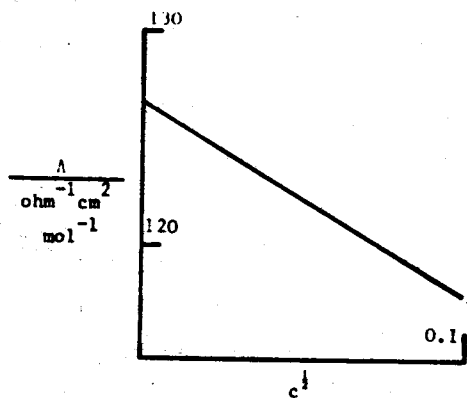
$$k = \left[\frac{(\Lambda^0)^2 F^2}{6N\epsilon RT} + \frac{F}{3\pi N\eta} \right] \left[\frac{8\pi F^4 N^2}{\epsilon RT} \right] \quad (30)$$

Here N is the Avogadro number, ϵ the dielectric constant and η the viscosity. For aqueous solutions of KCl, $k = 94.6$.



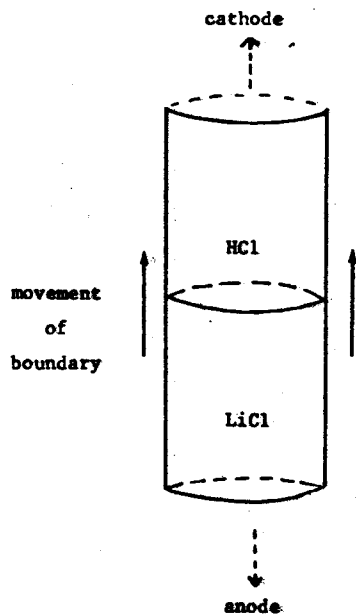


cell constant = $\frac{l}{A} \frac{1}{R}$



net loss of copper per faraday
 $= (1 - t_+)F$
 $= t_- F$

Moving boundary method



$t_+ = \frac{10^3 v A c F}{I}$

where v is the steady velocity of the boundary in m/sec, A is the cross-sectional area of the tube m^2 , c is the concentration in mol/dm^3 and I is the current in amps.

Limiting molar conductivities, λ° , of ions in aqueous solution at 25°C and 1 atm pressure.

Ion	λ°	Ion	λ°
H ⁺	349.8 ₁	OH ⁻	198.6
Li ⁺	38.6 ₈	F ⁻	55.4
Na ⁺	50.10	Cl ⁻	76.35
K ⁺	73.50	Br ⁻	78.14
Rb ⁺	77.8 ₁	I ⁻	76.8 ₄
Cs ⁺	77.2 ₆	NO ₃ ⁻	71.46
Ag ⁺	61.9 ₀	ClO ₃ ⁻	64.6
NH ₄ ⁺	74.5 ₅	BrO ₃ ⁻	55.7 ₄
NEt ₄ ⁺	32.6 ₆		
NMe ₄ ⁺	44.9 ₂		
NBu ₄ ⁺	19.4 ₇		
Mg ⁺⁺	53.0 ₅		
Ca ⁺⁺	59.50		
Sr ⁺⁺	59.4 ₅		
Ba ⁺⁺	63.6 ₃		
Cu ⁺⁺	56.6		
Zn ⁺⁺	52.8		

