Electrical Conductivity and Interionic Interactions

The Concept of Electrolyte Conductivity, *G*

Ions of charge ze_0, accelerated by the electric field strength, E, are subject to a frictional force, K_R. When this two forces become equal:

$$ze_0\boldsymbol{E} = 6\pi\eta r_I v_{max} \quad \text{and} \quad v_{max} = \frac{ze_0\boldsymbol{E}}{6\pi\eta r_I}$$

For an electrolyte containing anions and cations with total charge z^+e_0 and z^-e_0:

$$I = I^+ + I^- = \frac{dQ^+}{dt} + \frac{dQ^-}{dt} = Ae_0(n^+z^+v^+_{max} + n^-z^-v^-_{max})$$

The mobility u: $\quad u \equiv v_{max}/|E| = ze_0/6\pi\eta r \quad and \quad v_{max} = u/|E|$

Now replacing v_{max}, we get for current I: $\quad I = Ae_0(n^+z^+u^+ + n^-z^-u^-)\cdot|\boldsymbol{E}|$

The magnitude of the electric field, $|E| = \Delta V/l$: $\quad I = G\,\Delta V$

where G is termed conductance and is given by:

$$G = (A/l)e_0(n^+z^+u^+ + n^-z^-u^-)$$

Does Ionic Conduction Obey Ohm’s Law?

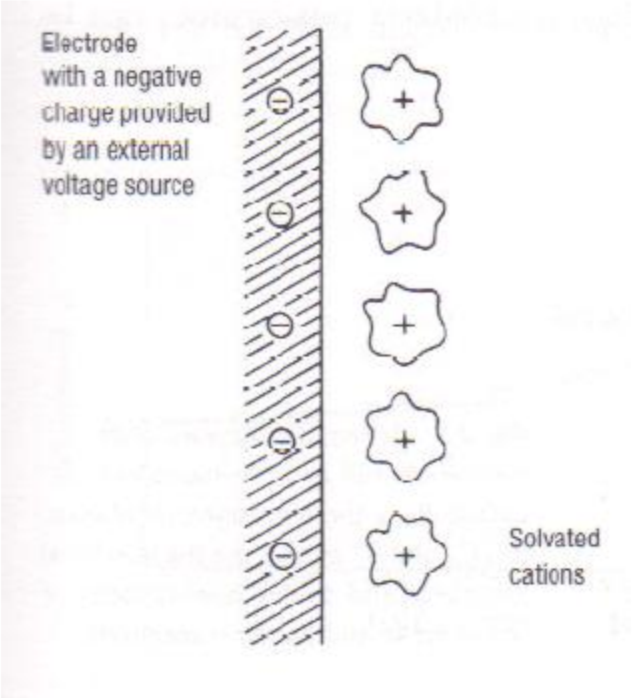
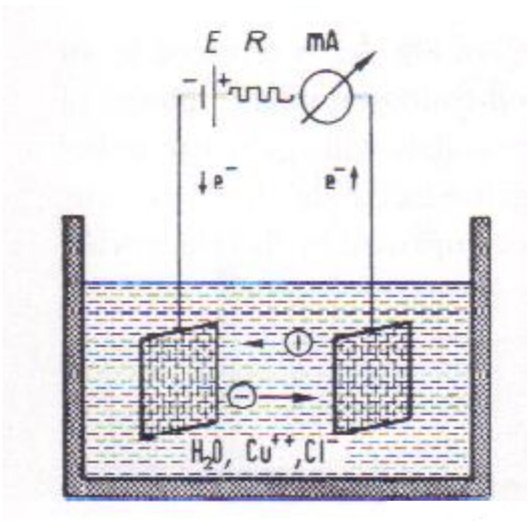


Fig. 2.1 Schematic representation of the electrolytic double layer at the metal/electrolyte interface.

Where Ohm’s Law is …. V = IR

Direct Current (DC) measurements

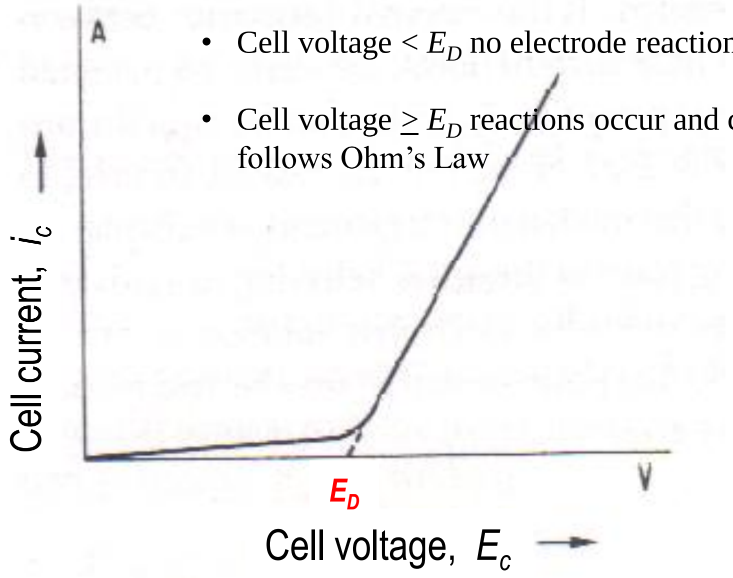
-once past E_D then ion conduction follows Ohm's Law



$2Cl^- \rightarrow Cl_2 + 2e^-$

$Cu^{2+} + 2e^- \rightarrow Cu^0$

Fig. 1.2 Electrochemical cell for the electrolysis of aqueous $CuCl_2$ solution - E: dc voltage; R: resistance; mA: galvanometer for current measurement.



- Cell voltage < E_D no electrode reactions
- Cell voltage ≥ E_D reactions occur and cell follows Ohm's Law

Fig. 1.3 Electrolysis current as a function of the cell voltage E. E_D is the decomposition voltage.

Electrode Reactions
$$\begin{cases} Cu^{++} + 2e^- \rightarrow Cu^0 \\ 2Cl^- \rightarrow Cl_2 + 2e^- \end{cases}$$

Cell Reaction $Cu^{++} + 2Cl^- \rightarrow Cu^0 + Cl_2$

Cell reaction voltage ≥ E_D

Alternating Current (AC) measurements

-at high AC frequencies each C_D is a short so *Re* can be measured

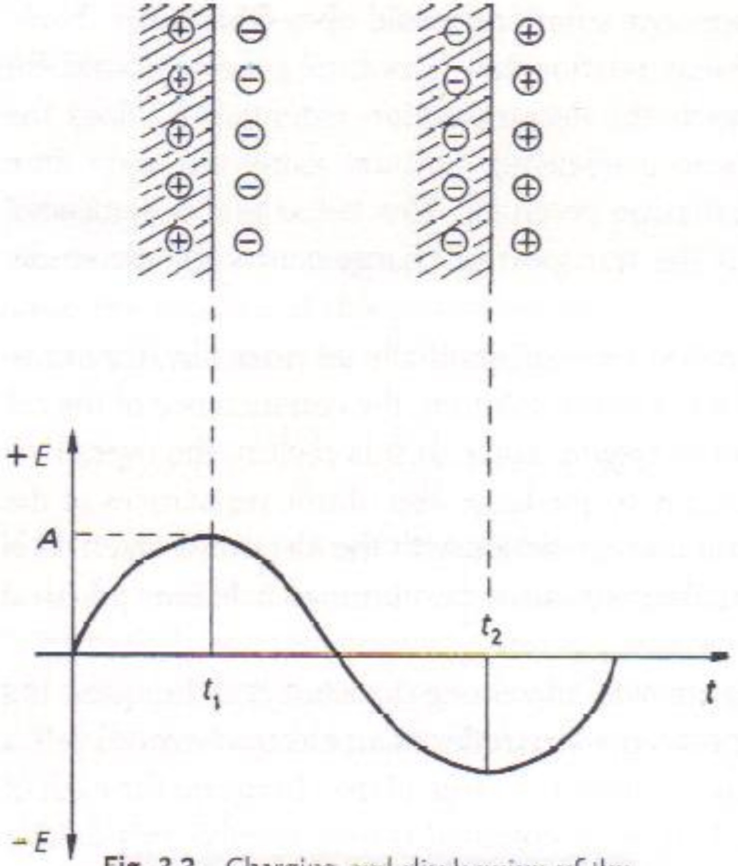


Fig. 2.2 Charging and discharging of the electrolytic double layer on imposition of an *ac* voltage $E_c = A\sin\omega t$; $\omega = 2\pi f$, f is the frequency of the *ac* signal. The potential drop across the interface, E, is shown as a function of time t.

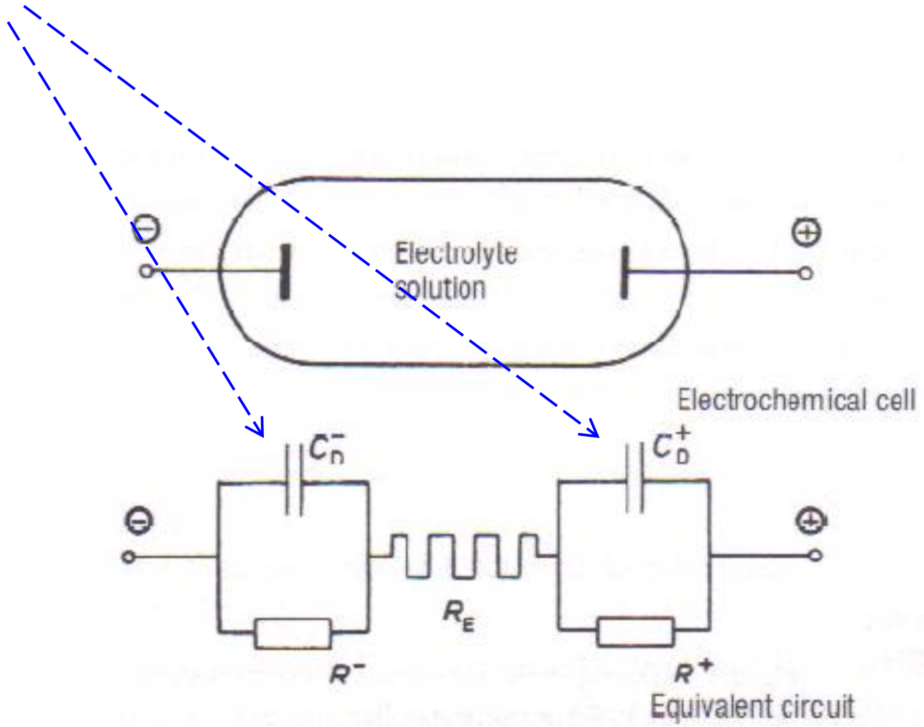
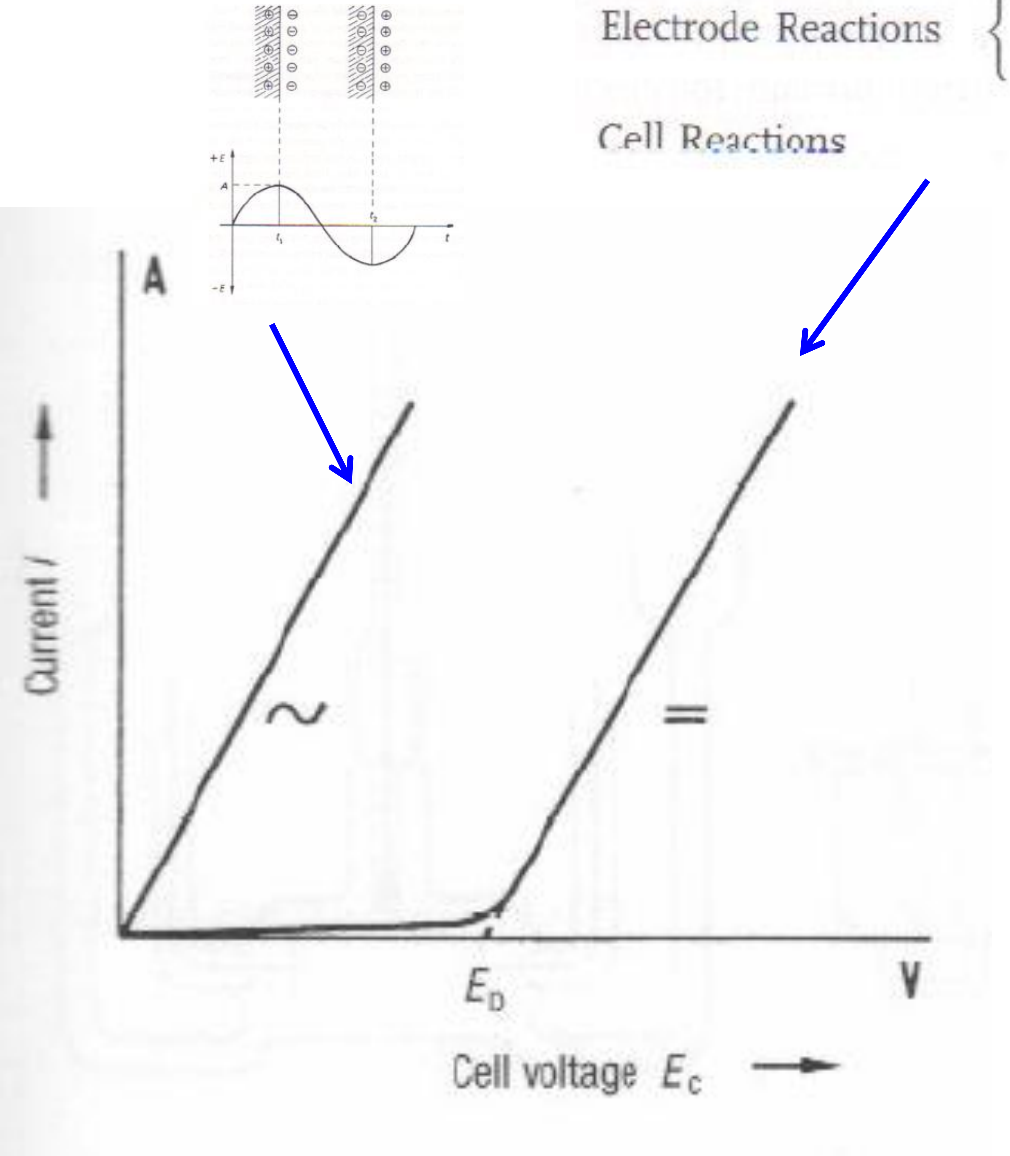


Fig. 2.3 Schematic diagram of an electrolysis cell and the equivalent *ac* circuit. R_E is the electrolytic resistance, R^-, C_D^- and R^+ and C_D^+ are the interfacial resistance and double layer capacity of the cathode and anode respectively.

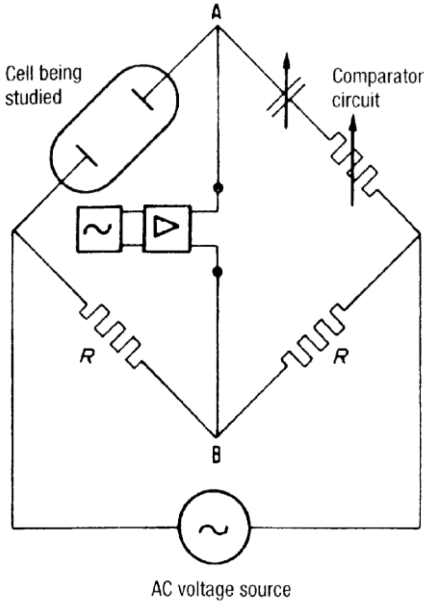
Summary AC versus DC methods

Electrode Reactions $\left\{ \begin{array}{l} Cu^{++} + 2e^- \rightarrow Cu^0 \\ 2Cl^- \rightarrow Cl_2 + 2e^- \end{array} \right.$

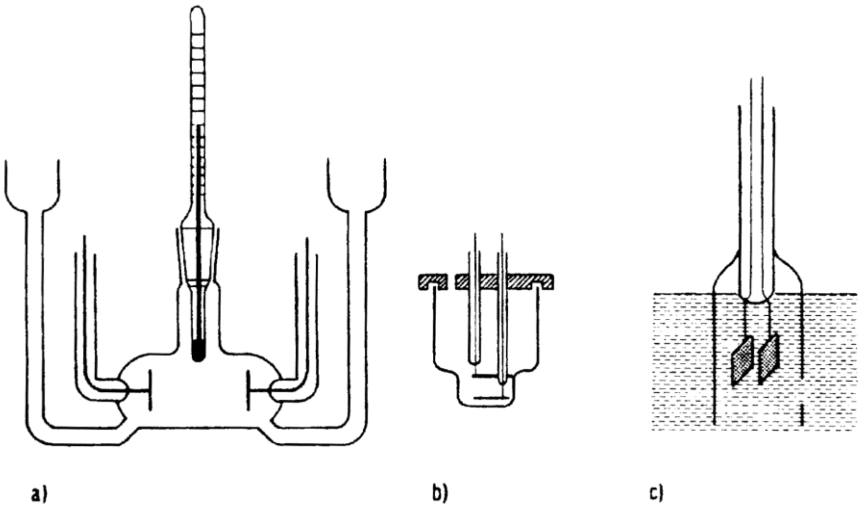
Cell Reactions $Cu^{++} + 2Cl^- \rightarrow Cu^0 + Cl_2$



Ionic Conductivity (k_I) Measurements (p18)



Wheatstone bridge circuit for the measurement of electrolyte resistance: null detection is by an amplifier and oscilloscope.

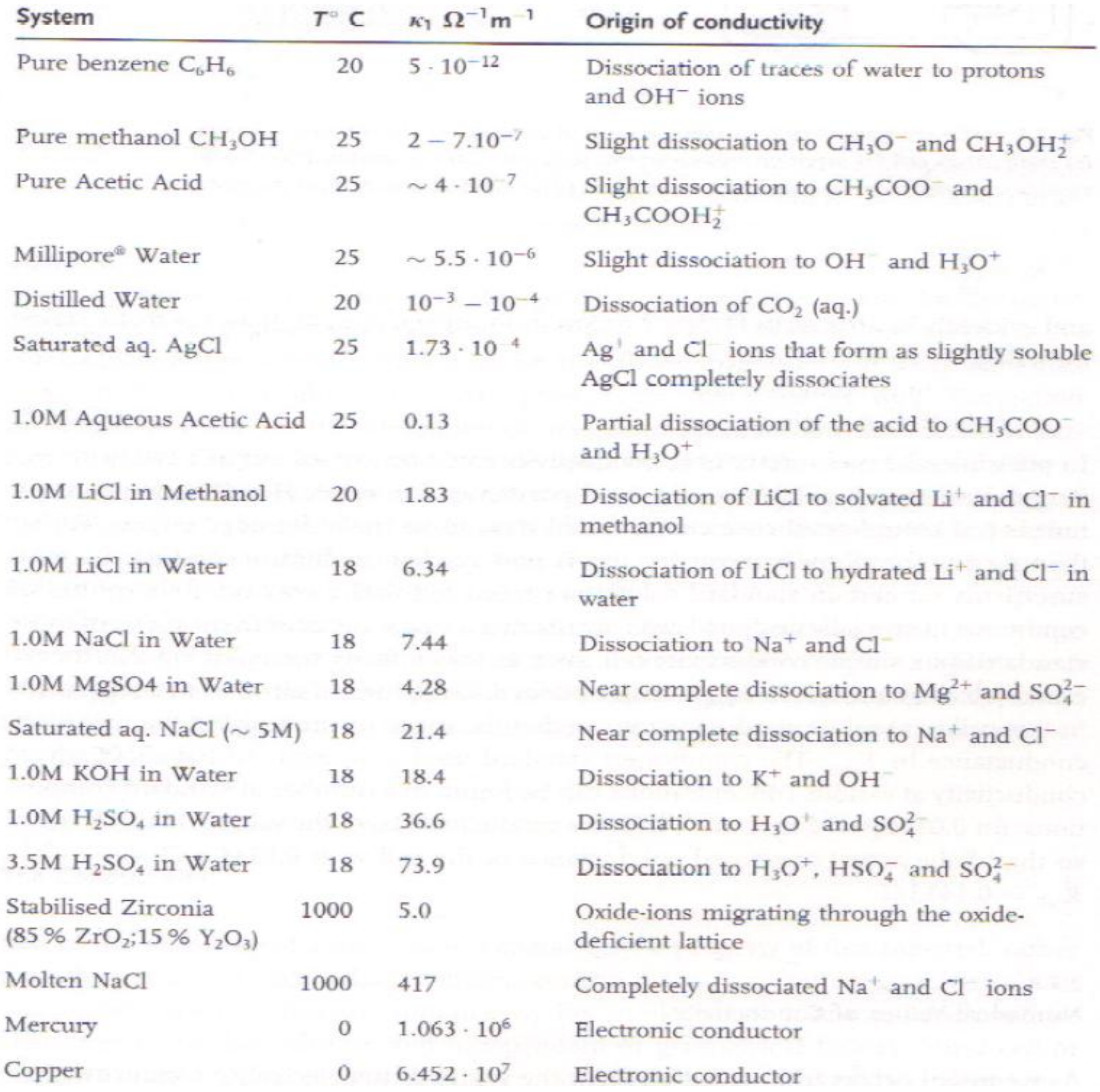


Different types of cell for the measurement of electrolyte solutions conductivity: (a) conductivity cell for precision measurements with built-in thermometer: (b) cell with variable inter-electrode separation, (c) immersion cell for rapid laboratory measurements.

Knowing that the conductivity (k_I) is connected to the conductance (

$$G = \frac{A}{l} \cdot \kappa_I$$

Table 2.1 Conductivities of different solvents and electrolytes, molten salts metals and solid electrolytes (From Landolt – Bornstein, Numerical Values and Fundtions, II 7, Springer-Verlag , 1960)

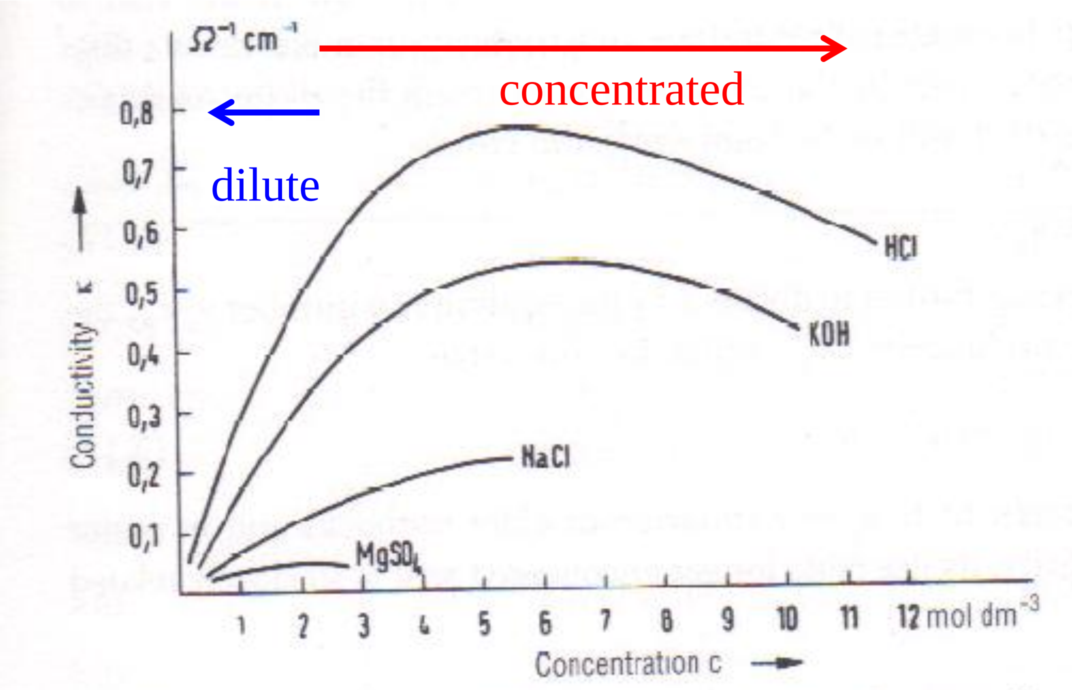


System	$T°$ C	κ_1 $\Omega^{-1}m^{-1}$	Origin of conductivity
Pure benzene C_6H_6	20	$5 \cdot 10^{-12}$	Dissociation of traces of water to protons and OH^- ions
Pure methanol CH_3OH	25	$2 - 7.10^{-7}$	Slight dissociation to CH_3O^- and $CH_3OH_2^+$
Pure Acetic Acid	25	$\sim 4 \cdot 10^{-7}$	Slight dissociation to CH_3COO^- and $CH_3COOH_2^+$
Millipore® Water	25	$\sim 5.5 \cdot 10^{-6}$	Slight dissociation to OH^- and H_3O^+
Distilled Water	20	$10^{-3} - 10^{-4}$	Dissociation of CO_2 (aq.)
Saturated aq. AgCl	25	$1.73 \cdot 10^{-4}$	Ag^+ and Cl^- ions that form as slightly soluble AgCl completely dissociates
1.0M Aqueous Acetic Acid	25	0.13	Partial dissociation of the acid to CH_3COO^- and H_3O^+
1.0M LiCl in Methanol	20	1.83	Dissociation of LiCl to solvated Li^+ and Cl^- in methanol
1.0M LiCl in Water	18	6.34	Dissociation of LiCl to hydrated Li^+ and Cl^- in water
1.0M NaCl in Water	18	7.44	Dissociation to Na^+ and Cl^-
1.0M MgSO4 in Water	18	4.28	Near complete dissociation to Mg^{2+} and SO_4^{2-}
Saturated aq. NaCl (~ 5M)	18	21.4	Near complete dissociation to Na^+ and Cl^-
1.0M KOH in Water	18	18.4	Dissociation to K^+ and OH^-
1.0M H_2SO_4 in Water	18	36.6	Dissociation to H_3O^+ and SO_4^{2-}
3.5M H_2SO_4 in Water	18	73.9	Dissociation to H_3O^+, HSO_4^- and SO_4^{2-}
Stabilised Zirconia ($85\%\ ZrO_2; 15\%\ Y_2O_3$)	1000	5.0	Oxide-ions migrating through the oxide-deficient lattice
Molten NaCl	1000	417	Completely dissociated Na^+ and Cl^- ions
Mercury	0	$1.063 \cdot 10^6$	Electronic conductor
Copper	0	$6.452 \cdot 10^7$	Electronic conductor

Effect of concentration on Ionic Conductivity

Strong electrolyte

- contain completely dissociated ions
- show linear dependence with concentration in dilute solutions



concentrated

dilute

Fig. 2.8 Conductivity of aqueous electrolyte solutions as a function of concentration at 18°C (from Landolt Bornstein).

- at high concentration (> 1 to 2 Molar) concentration, conductivity rises less rapidly with concentration due to inter ionic interactions

Molar Conductivity , Λ

To track effects of concentration on conductivity then the conductivity, κ_I (in units of 1/Ohm-cm) is normalized to concentration and a new term arises the molar conductivity, Λ (in units of 1/Ohm-mole-cm^2) .

Kohlrausch's Law

$$\Lambda = \Lambda_0 - k\sqrt{c/c^0}$$

Λo is molar conductivity at infinite dilution
c is concentration
c^o is standard concentration (1 Molar)

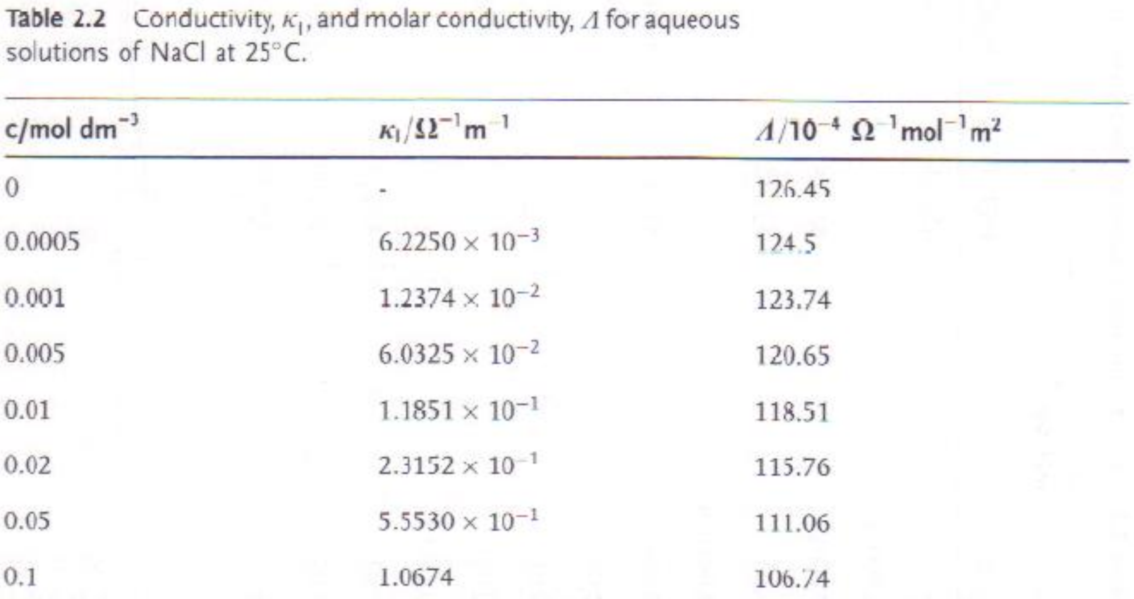


Table 2.2 Conductivity, κ_1, and molar conductivity, Λ for aqueous solutions of NaCl at 25°C.

c/mol dm^{-3}	κ_1/Ω^{-1}m^{-1}	$\Lambda/10^{-4}\ \Omega^{-1}$mol^{-1}m^2
0	-	126.45
0.0005	6.2250×10^{-3}	124.5
0.001	1.2374×10^{-2}	123.74
0.005	6.0325×10^{-2}	120.65
0.01	1.1851×10^{-1}	118.51
0.02	2.3152×10^{-1}	115.76
0.05	5.5530×10^{-1}	111.06
0.1	1.0674	106.74

Transport Number, t (p28)

Total ionic current, i, the sum of the positive ion current, i^+, and minus ion current, i^-.

The transport number of the positive ions is

$$t^+ = \frac{i^+}{i^+ + i^-}$$

The transport number of the negative ions is

$$t^- = \frac{i^-}{i^+ + i^-}$$

Hittorf Apparatus for measuring transport number

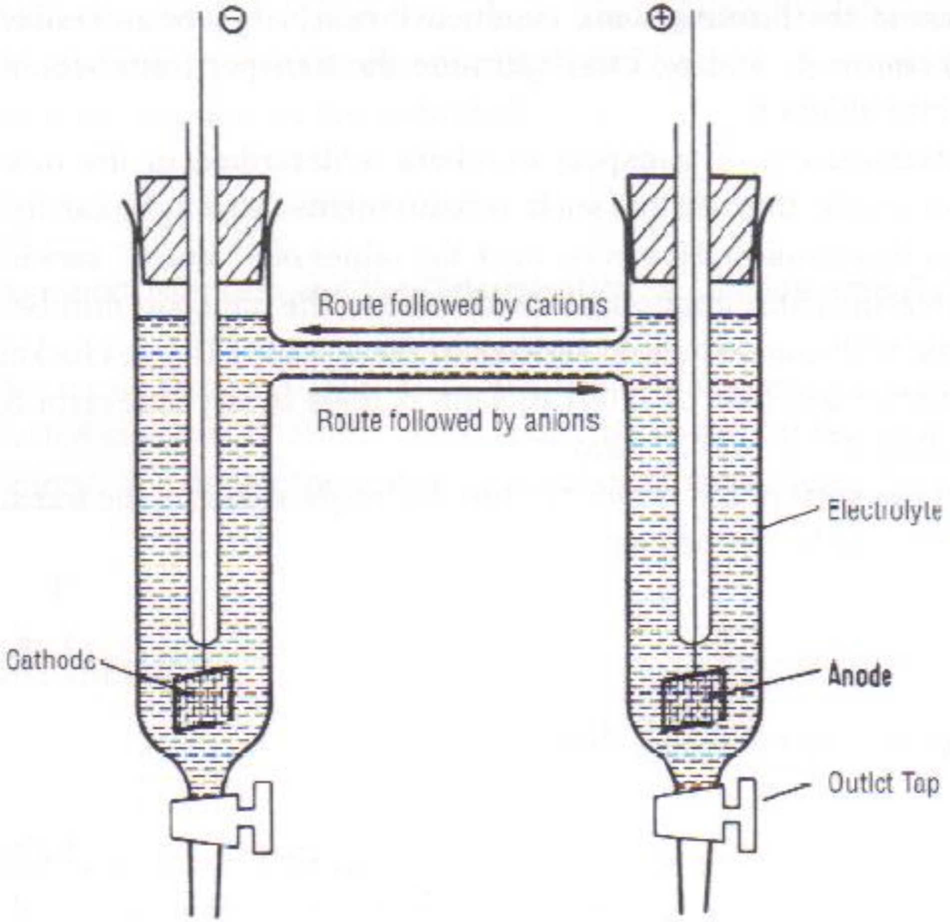
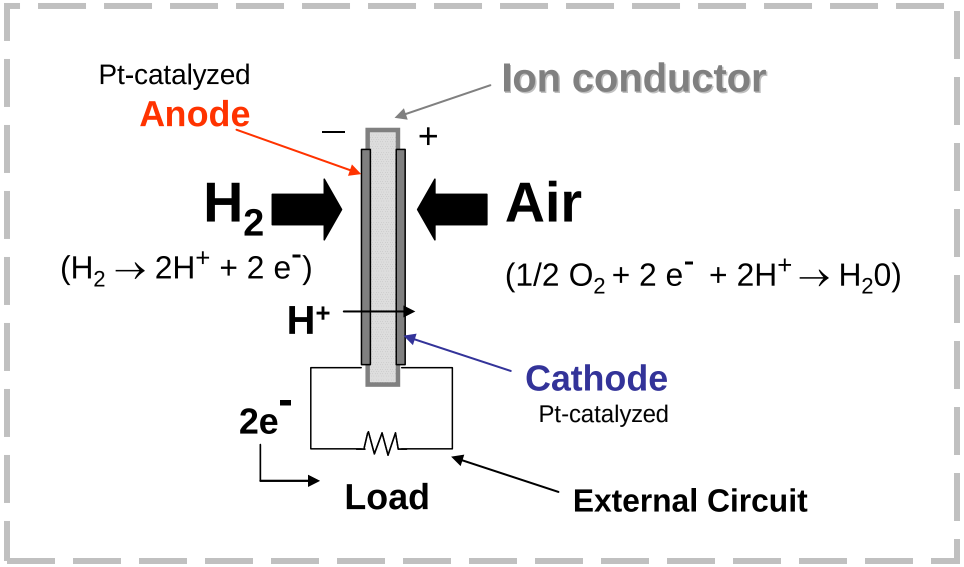


Fig. 2.11 Hittorf transport cell.

Table 2.6 Transport numbers t of anions and cations in selected aqueous electrolytes at 25°C, extrapolated to infinite dilution.

Electrolyte	t_0^+	t_0^- $(= 1 - t^+)$
KCl	0.4906	0.5094
NH_4Cl	0.4909	0.5091
HCl	0.821	0.179
KOH	0.274	0.726
NaCl	0.3962	0.6038
$NaOOCCH_3$	0.5507	0.4493
$KOOCCH_3$	0.6427	0.3573
$CuSO_4$	0.375	0.625

Why does ionic current flow? Ions flow in response to an electromotive force.
Example: Spontaneous current in H_2 / O_2 PEM Fuel Cell



PEM fuel cell

- ion conductor surrounded by two electrodes
- dissimilar feeds at the identical electrodes (hydrogen at anode, oxygen at cathode) spontaneously generate dissimilar electrode potentials whose difference is $E^0_C - E^0_A$
- the difference of these spontaneous potentials is $E^0_C - E^0_A$ is a spontaneous fuel cell voltage V^0_{FC}

Anode Reaction: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode Reaction: $\frac{1}{2}O_2 + 2e^- + 2H^+ \rightarrow H_2O$

Fuel Cell Reaction: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O + G^0$

$E^o_a = 0$ V

$E^o_c = 1.23$ V

$\Delta G^0 = -nFV^0_{FC} = -230$ kJ

$V^0_{FC} = E^0_c - E^0_a = 1.23$ V

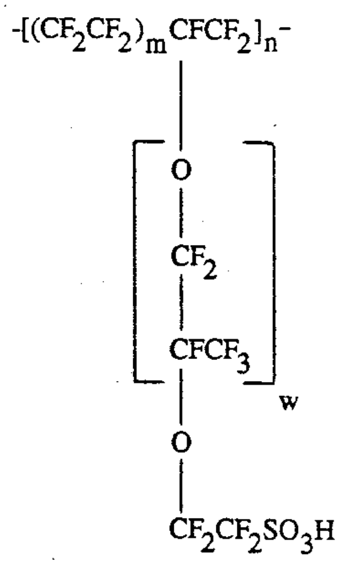
- A spontaneous current, i, is generated in an ion conductor in the presence of a spontaneous voltage, V^0_{FC} ,
- The magnitude of the current, i , depends on the resistance, R, of the ion conductor, as given by Ohm's Law, $i = V^0_{FC} / R$

Do transport numbers t^+, t^- have to be equal? No.
A real example of transport numbers (t^+, t^-) *NOT* being equal

Nafion is an ion conducting polymer with

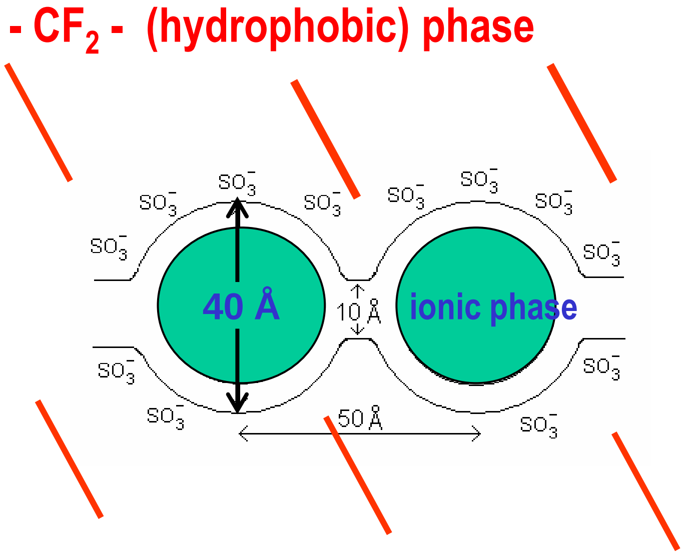
- fixed anions (SO_3^-) so **$t^- = 0$**
- mobile cations (H^+) so **$t^+ = 1$ (all ionic current carried by the proton)**

Nafion polymer



Nafion Polymer: Perfluorocarbon cation exchange polymer membrane, shown here in the H^+ form.

Nafion 117 polymer membrane



Nafion 117 membrane: A hydrated acid membrane conducts proton only

In the PEM fuel cell, electrical current is carried by:

- electrons in the wire to the cathode and
- protons in the Nafion electrolyte to the cathode.

End day 1 – intro (July 8)

Day 2 – Begin theory (July 10)

Theory of Electrolyte Conductivity

Debye-Huckel-Onsager Theory of Dilute Electrolytes (p38-46)

Introduction to the Model: Ionic Cloud, Relaxation and Electrophoretic Effects

Motion of ions in an electric field

- Ions in solution are ordered by attract ion ions of opposite charge and by repulsion of ion of like charge while thermal motion randomizes this order resulting in an ion being surrounded by an "***ionic cloud***" as shown in Figure 2.16
- Application of an electric field will accelerate charges of opposite sign in opposite directions

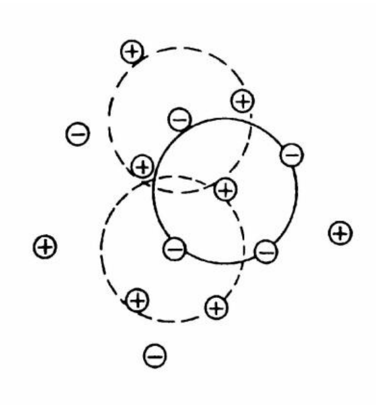


Fig 2.16 Schematic diagram of the ionic atmosphere in solution

Two effects decelerate the motion of a charge

- Each moving ion will experience a retarding force from the net opposite charge of its ionic cloud, which is migrating in the opposite direction, an effect termed the ***relaxation*** *or asymmetry effect*
- The ions form dipole bonds with solvent (because solvent dipoles stabilize ions) so solvent molecule (the solvation sheaths) are moving with the ions.
  Therefore an ion will experience an additional drag due to an increase of size associated with the ion due to its associated solvation sheath; this is termed the ***electrophoretic*** *effect*

How do we calculate the interaction between an ion and a charge cloud? The ion moves in a field created by a density of nearby ions. Equation 2.34 is the fundamental expression relating the field strength , ***E***, (in volts per meter) from the charge density, ρ (in C /cubic meter), of the ionic charge cloud at *r* from the ion

$$\mathrm{div}\, E = \rho / \varepsilon_0 \varepsilon_r \qquad \text{Eqn 2.34}$$

where ε_0 is the permittivity of the vacuum and ε_r is the permittivity of the ionic solution.

Calculating the interaction between ion and its charge cloud (cont.)

To solve equation 2.34, we start by considering that the div E = $\partial E/\partial x + \partial E/\partial y + \partial E/\partial z$ and $E = -\,grad\ \varphi$, then the fundamental equation , relating the charge density, ρ (in units of Coulomb m^{-3}), to the electric field strength, ***E*** (in units of V m^{-1}) of the charge cloud , can be re-written in spherical coordinates as equation 2.38, below.,

$$\frac{1}{r^2}\cdot\frac{d}{dr}\left(\frac{r^2 d\varphi}{dr}\right) = -\frac{\rho(r)}{\varepsilon_r\varepsilon_0}$$

since
E -the field strength is $\equiv \varphi / r$ where…
φ -is the potential
r - is distance from ion to ionic cloud
ρ -is charge density of the charge cloud at r from the ion

Equation 2.38 has two unknowns (φ, ρ), so another relationship is needed to solve it. This is done by considering the energy of ion $z_i e_o$ in the potential field φ and applying the Boltzman equation to find the number of ions, $n_i(r)$, of charge $z_i e_o$ at distance r from the central ion due to thermal effects, which leads to the equation 2.41 which is the Poisson-Boltzmann equation:

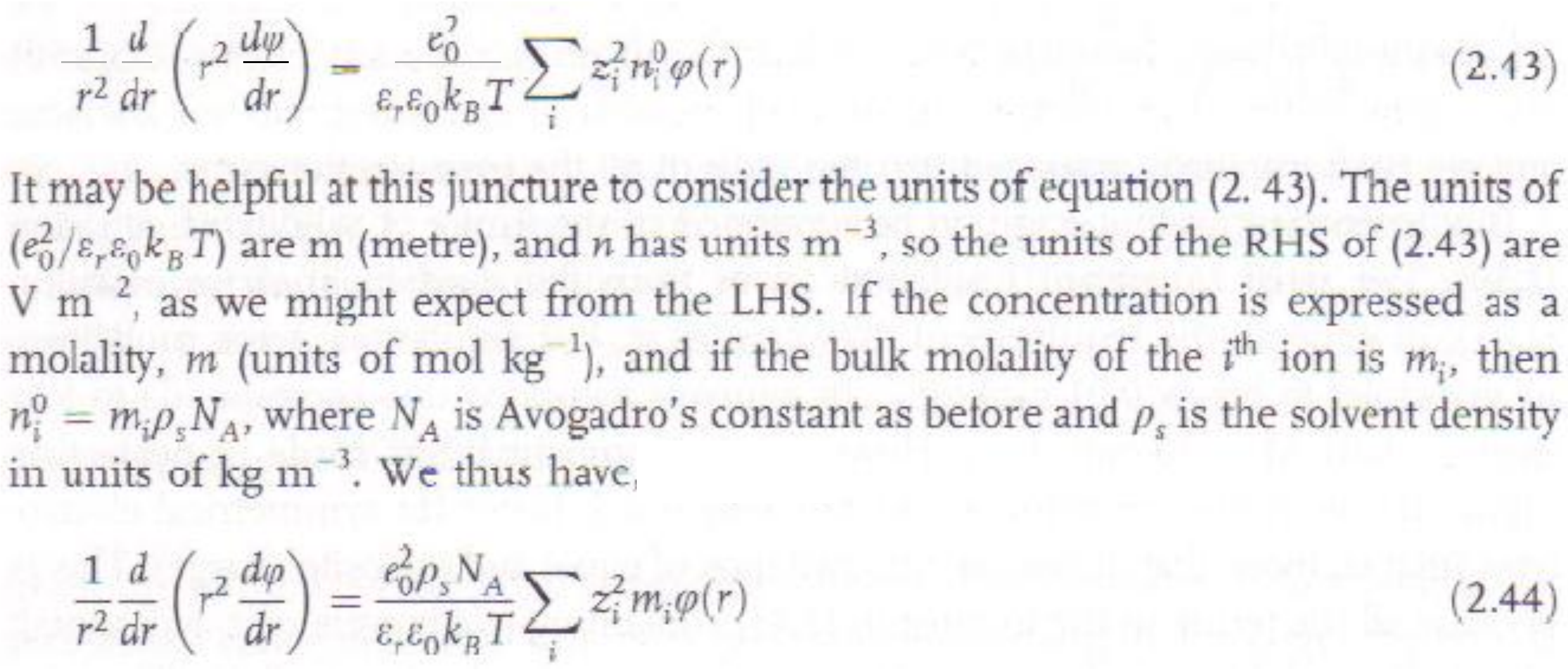
$$\frac{1}{r^2}\cdot\frac{d}{dr}\left(\frac{r^2 d\varphi}{dr}\right) = -\sum_i \left(z_i e_0 n_i^0 / \varepsilon_r \varepsilon^0\right)\ exp^{-(z_i e_0 \varphi[r] / k_B T)} \qquad \text{Eqn 2.41}$$

Equation 2.41 is a non linear differential equation that is difficult to solve and which double counts charges, which doubles the potential … *which is wrong !!*

The Poisson-Boltzmann equation is not useful in general but can be used to generate an expression that is valid for dilute ionic solutions. For dilute solutions, the exponential in Eqn. 2.41 can be expanded, using the expression that is true for small x, that is, for $x \ll 1$, $\boldsymbol{e^{-x} = \sim (1 - x)}$.

Calculating the interaction between ion and its charge cloud (cont.)

The expansion of the exponential in the Poisson Boltzmann equation (Eqn. 2.41) simplifies the second term in equation 2.41. This simplification leads to an expression (equation 2.43) which is an effective solution for the relationship between charge density, ρ , and Electric field strength, ***E***, for dilute solutions. This second expression is called the linearized Poisson-Boltman equation, shown in equation 2.43, below.



$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\varphi}{dr}\right) = \frac{e_0^2}{\varepsilon_r\varepsilon_0 k_B T}\sum_i z_i^2 n_i^0 \varphi(r) \qquad (2.13)$$

It may be helpful at this juncture to consider the units of equation (2. 43). The units of $(e_0^2/\varepsilon_r\varepsilon_0 k_B T)$ are m (metre), and n has units m^{-3}, so the units of the RHS of (2.43) are V m^{-2}, as we might expect from the LHS. If the concentration is expressed as a molality, m (units of mol kg^{-1}), and if the bulk molality of the i^{th} ion is m_i, then $n_i^0 = m_i \rho_s N_A$, where N_A is Avogadro's constant as before and ρ_s is the solvent density in units of kg m^{-3}. We thus have,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\varphi}{dr}\right) = \frac{e_0^2\rho_s N_A}{\varepsilon_r\varepsilon_0 k_B T}\sum_i z_i^2 m_i \varphi(r) \qquad (2.44)$$

Calculating the interaction between ion and its charge cloud (cont.)
the electric potential, φ_c

Introducing the ionic strength as $I = \frac{1}{2}\sum_i z_i^2\left(\frac{m_i}{m^0}\right)$ and noting that $\kappa^2 = [\, 2e^2_0 N_A \rho_s\, m^0 / \varepsilon_r\varepsilon_0 k_B T \,]\, I$

equation 2.44 can be written as equation 2.47 below.

$$\frac{1}{r^2}\cdot\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{r^2\,\mathrm{d}\varphi}{\mathrm{d}r}\right) = \kappa^2\varphi(r)$$

Eqn 2.47

This equation could be solved as equation 2.48, below, using the following boundary conditions:

- $\varphi(r) \to 0$ as $r \to \propto$
- if for ionic radius is a_0, and there is no charge inside $r < a_0$ that is, all charge is on the surface of the ion and then the solution must be like

$$\frac{1}{r^2}\cdot\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{r^2\,\mathrm{d}\varphi}{\mathrm{d}r}\right) = 0$$

Eqn 2.48

The complete solution for the electrical potential at r, $\varphi(r)$, is equation 2.50 below:

$$\varphi(r) = \frac{z_0 e_0}{4\pi\varepsilon_r\varepsilon_0 r}\left(\frac{\mathrm{e}^{\kappa a_0}}{1+\kappa a_0}\right)\mathrm{e}^{-\kappa r}$$

Eqn 2.50

Which can be divided into eqn 2.51, the potential due to the central ion, $\varphi_0(r) = z_0 e_0/4\pi\varepsilon_r\varepsilon_0 r$
and eqn 2.52, the potential due to the ionic cloud $\varphi_c(r) = z_0 e_0/4\pi\varepsilon_r\varepsilon_0 r\,\{(\mathrm{e}^{\kappa a_0} / 1 + \kappa a_0)\,\mathrm{e}^{-\kappa r} - 1\}$

Calculating the interaction between ion and its charge cloud (cont.)

the charge density $\rho(\ r\ )$

Linearizing equation 2.40

$$\rho(r) = -\sum_i \left(z_i e_0 n_i^0 / \varepsilon_r \varepsilon^0\right) \exp -\left(z_i e_0 \varphi[r] / k_B T\right)$$

Eqn 2.40

yields eqn 2.53, the solution for the charge density $\rho(\ r\ )$ is equation 2.53*:*

$$\rho(r) \approx -\sum_i \frac{z_i^2 e_0^2 n_i^0 \varphi(r)}{k_B T} \equiv -\sum_i z_i^2 e_0^2 n_i^0 \frac{z_0 e_0}{4\pi \varepsilon_r \varepsilon_0 r k_B T} \left(\frac{e^{-\kappa a_0}}{1 + \kappa a_0}\right) e^{-\kappa r}$$

Eqn 2.53

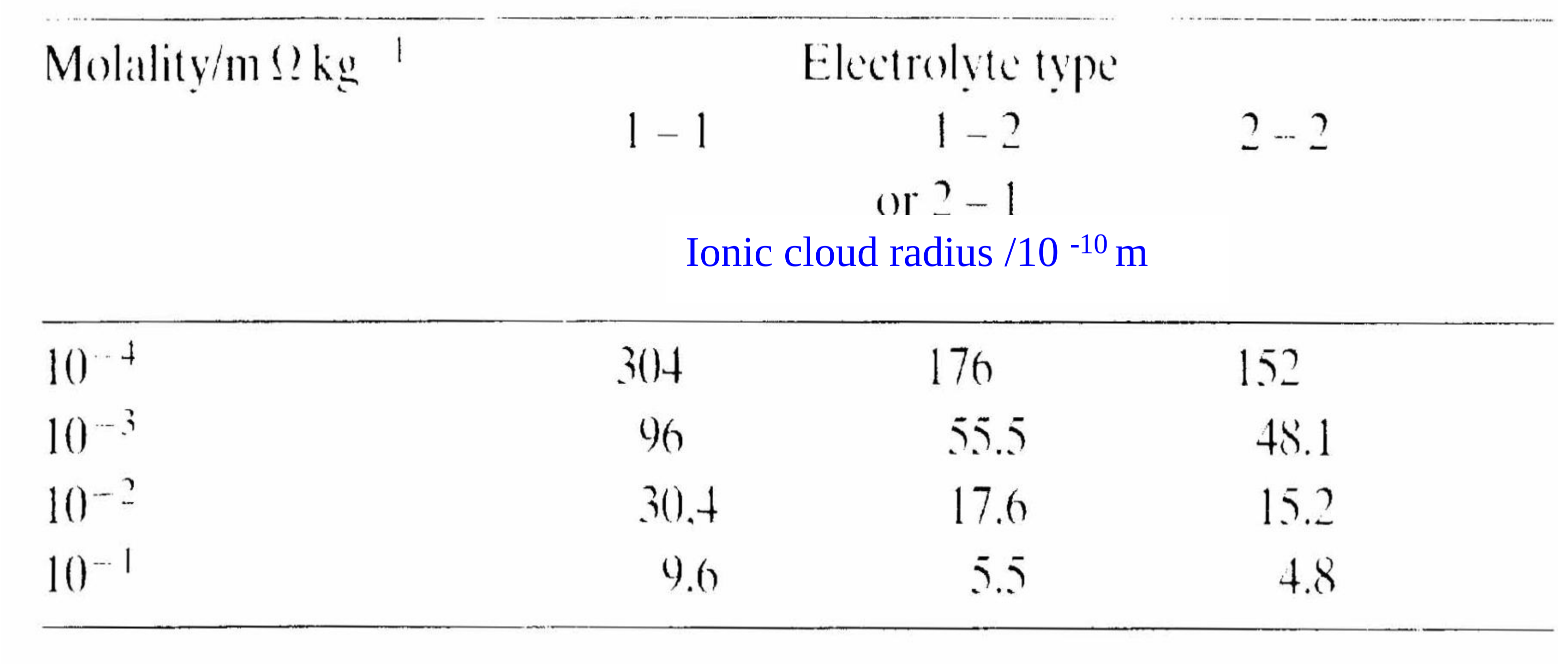
Equation 2.53 is an expression that tells the charge density of the ionic cloud that forms around an ion in solution. This gives the total charge $q(r)$ in a spherical shell over distance r from a central ion. Shell thickness, dr, is $4\ \pi r^2\ \rho(r)\ \mathrm{d}r \equiv$ const $r\ \mathrm{e}^{-\kappa r}$. Differentiation of this expression for $q(r)$ has a max when $r = r_c = 1/\ \kappa$ which is called the Debye length.

Debye screening length ($1/k$)

The value of ***k*** *(units inverse length)* is of considerable importance in electrolyte solution theory. Its inverse, $\boldsymbol{k^{-1}}$, is usually referred to as the Debye screening length (also called ionic cloud radius), since at distances greater than $\boldsymbol{k^{-1}}$ from the central ion, the electrostatic effect due to that ion becomes very small. It turns out that for ambient conditions:

$$\kappa^{-1}/\text{metre} = \frac{3.046 \times 10^{-10}}{(\mathbf{I})^{1/2}}$$

Table 2.5 Radius of ionic cloud in aqueous solution at 25°C for different electrolyte types & concentrations:



Molality/mol kg^{-1}	Electrolyte type		
	1 – 1	1 – 2 or 2 – 1	2 – 2
	Ionic cloud radius /10 $^{-10}$ m		
10^{-4}	304	176	152
10^{-3}	96	55.5	48.1
10^{-2}	30.4	17.6	15.2
10^{-1}	9.6	5.5	4.8

Debye-Onsager Equation for Conductivity p44

Not covered in detail (see pp. 44-45 of textbook for more).

The Debye-Onsager equation is a refinement of Debye-Huckel theory which attempts to take into account mainly the additional effects of :

i. Concentration of ions
ii. Viscosity of electrolyte solution
iii. Degree of dissociation, α. Of the ions in the electrolyte

However, like D-H theory, the D-O equation is only accurate for fairly dilute solutions (concentrations << 0.1M).

Next time …

i. **End chapter 2**
ii. **Begin reading chapter 3**

Some effects of interionic interactions

i. Activities p. 46
ii. Weak Electrolytes and Oswald dilution law p.61
iii. The Concept of pH and the Idea of Buffer Solutions (p64)

The Concept of Activity from the Electrochemical Viewpoint (p46)

The *central ion reactivity will be hindered by the ionic cloud*. There is an energy term ΔE representing the work to detach the central ion from its cloud. This term is higher at higher concentration, as the density of the ionic cloud rises.

To describe accurately the thermodynamic properties of more concentrated electrolytes, a correction for the concentration, called activity(*a)* is introduced, as follows:

$$a_i = \gamma_i \frac{m_i}{m^o}$$

where γ is the activity coefficient and $\gamma \equiv \gamma(\mathrm{I})$

recall $I = \frac{1}{2}\sum_i z_i^2 \left(\frac{m_i}{m^0}\right)$

m_i is molality
m^0 is standard molality (1 mol/kg electrolyte)

At infinite dilution, ionic strength (I) goes to 0; there are no interionic interactions, so $\gamma = 1$

$$\lim_{\mathbf{I}\to 0} \gamma_i = \lim_{\mathbf{I}\to 0} \left\{ \frac{a_i}{\frac{m_i}{m^0}} \right\} = 1$$

In summary:

- For no interionic interactions, so $\gamma = 1$, $a_i = m_i$ *since* $m^o = 1$
- For interionic interactions, $\gamma < 1$, $a_i < m_i$

Mean activity, $a_{\pm}$, and activity coefficient, $\gamma_{\pm}$

- Single ion is not capable of separate existence and a single ion activity, a_+ *or* a_- and activity coefficient γ_+ or γ_- are not accessible.

- So for the anions and cations in solution, a *mean* activity, $a_{\pm}$, and a mean activity coefficient, $\gamma_{\pm}$ are defined. For a 1—1 electrolyte:

$$a_{\pm} = (a_+ a_-)^{1/2} = \gamma_{\pm}\left(\frac{m}{m^0}\right) = \left(\gamma_+\gamma_-\left[\frac{m}{m^0}\right]^2\right)^{1/2}$$

Calculation of the *Concentration Dependence* of the Activity Coefficient (p48)

A central ion in an ionic cloud is more stable than a central ion alone, so energy must be liberated for the central ion to leave the ionic cloud.

- μ_i^{real} is the chemical potential for the ion in the cloud and
- μ_i^{ideal} is the chemical potential for the ion in the absence of the cloud and
- U is the potential energy when the ion associates with the cloud.

For the chemical potential of the ion, *i*, with its associated cloud, μ_i^{real} we have:

$$\mu_i \approx \mu_i^{0\dagger} + RT \ln\left(\frac{m_i}{m^0}\right)$$

- m_i is molality
- m^0 is standard molality (1 mol/kg electrolyte)
- $\mu^{o\dagger}$ is chemical potential of *i* at m^0 with no ion-ion interactions

For an real system where activity applies instead of a concentration:

$$\mu_i^{\text{real}} \equiv \mu_i^{0\dagger} + RT\ln a_i \tag{2.69}$$

$$\equiv \mu_i^{0\dagger} + RT\ln(m_i/m^0) + RT\ln\gamma_i \tag{2.70}$$

$$\equiv \mu_i^{\text{ideal}} + RT\ln\gamma_i \tag{2.71}$$

$$\equiv \mu_i^{\text{ideal}} + N_A U \tag{2.72}$$

From the expression for potential of the ionic cloud (eqn. 2.52), we find that the associated potential energy, *U*, for an ion, *i*, with a radius, a_0, is:

$$U = \frac{1}{2} z_i e_0 \varphi(a_0) = z_i e_0 \left(\frac{z_i e_0}{8\pi\varepsilon_r\varepsilon_0 a_0}\right)\left\{\left(\frac{e^{\kappa a_0}}{1+\kappa a_0}\right)e^{-\kappa a_0} - 1\right\} = \frac{-z_i^2 e_0^2 \kappa}{8\pi\varepsilon_r\varepsilon_0(1+\kappa a_0)} \tag{2.73}$$

Comparing 2.71 and 2.73 then we obtain:

$$-RT\ln\gamma_i = \frac{N_A z_i^2 e_0^2 \kappa}{8\pi\varepsilon_r\varepsilon_0(1+\kappa a_0)}$$

For very dilute solutions
where the radius of the ionic cloud $k^{-1} >> a_0$ (the ion diameter)
then $a_0 k << 1$ and knowing that $k^2 \equiv (2e_0^2 r_s L m^0/\varepsilon_r\varepsilon_0 k_B T)I$ (eqn 2.46) gives:

$$\ln\gamma_i = -A z_i^2 \sqrt{\mathbf{I}}$$

where *A* is a constant
depending only on the solvent

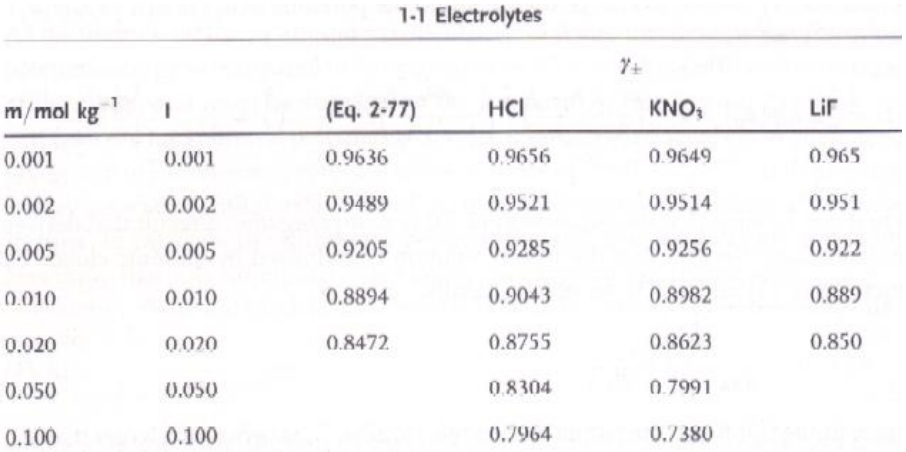
For water as the solvent, A = 1.172, which yields a relationship between mean activity coefficient, $\gamma_\pm$, and ionic strength, **I**, namely:

$$\ln\gamma_\pm = -1.172\,|z^+ z^-|\sqrt{\mathbf{I}}$$

Equation 2-77

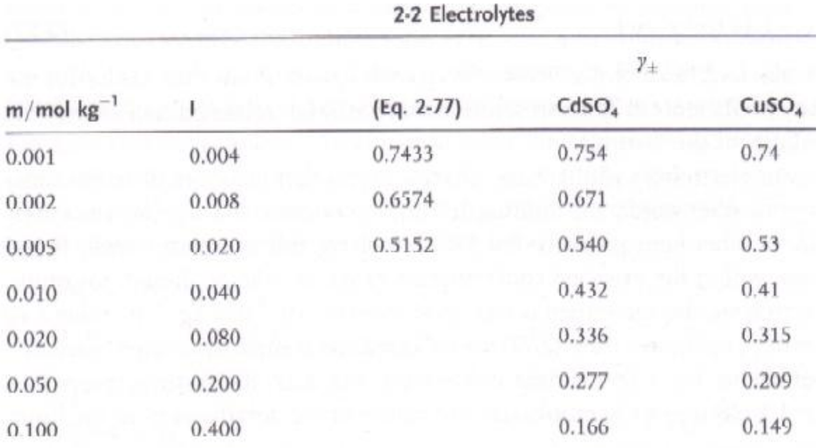
… the standard form of the so called Debye-Huckel limiting law (p49).

Table 2.10 Tabulated values of calculated and experimental results for mean activity coefficients for different electrolytes and concentrations at 25C



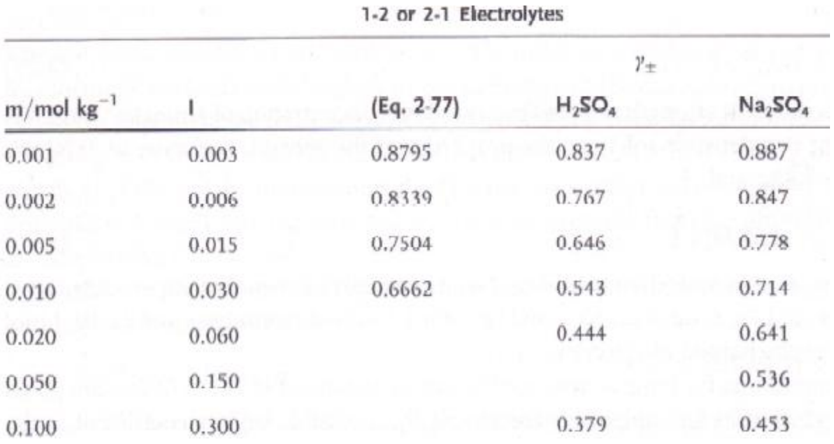
1-1 Electrolytes

		$\gamma_\pm$			
m/mol kg^{-1}	I	(Eq. 2-77)	HCl	KNO_3	LiF
0.001	0.001	0.9636	0.9656	0.9649	0.965
0.002	0.002	0.9489	0.9521	0.9514	0.951
0.005	0.005	0.9205	0.9285	0.9256	0.922
0.010	0.010	0.8894	0.9043	0.8982	0.889
0.020	0.020	0.8472	0.8755	0.8623	0.850
0.050	0.050		0.8304	0.7991	
0.100	0.100		0.7964	0.7380	



2-2 Electrolytes

		$\gamma_\pm$		
m/mol kg^{-1}	I	(Eq. 2-77)	$CdSO_4$	$CuSO_4$
0.001	0.004	0.7433	0.754	0.74
0.002	0.008	0.6574	0.671	
0.005	0.020	0.5152	0.540	0.53
0.010	0.040		0.432	0.41
0.020	0.080		0.336	0.315
0.050	0.200		0.277	0.209
0.100	0.400		0.166	0.149



1-2 or 2-1 Electrolytes

		$\gamma_\pm$		
m/mol kg^{-1}	I	(Eq. 2-77)	H_2SO_4	Na_2SO_4
0.001	0.003	0.8795	0.837	0.887
0.002	0.006	0.8339	0.767	0.847
0.005	0.015	0.7504	0.646	0.778
0.010	0.030	0.6662	0.543	0.714
0.020	0.060		0.444	0.641
0.050	0.150			0.536
0.100	0.300		0.379	0.453

Recall slide 21:

- No interionic interactions, so $\gamma = 1$, $a_i = m_i$ *since* $m^o = 1$
- Interionic interactions, $\gamma < 1$, $a_i < m_i$

Conclusion: at higher concentrations of salt, activity coefficient goes down, and there are therefore less ions available in solution

Graph of calculated and experimental results for mean activity coefficients for different electrolytes and concentrations at 25C

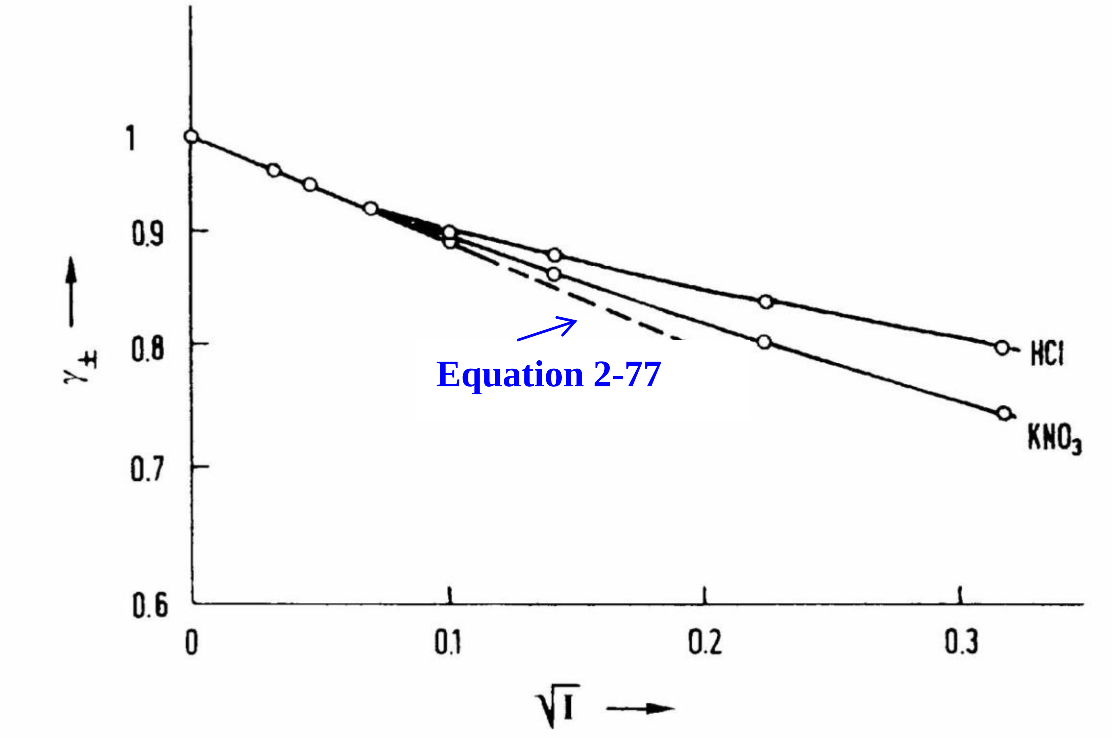


Fig 2.17 Theoretical variation of the activity coefficient $\gamma_{\pm}$ with √I from equation (2.78) and experimental results for 1-1 electrolytes at 25^0C

Activity Coefficients in Concentrated Electrolytes and Activity Coefficients of Neutral Molecules (p58)

Skip solvent-solvent and ion-solvent interactions p51-57

When the radius times the Debye length (the term a_0k) **cannot** be neglected we modify the Debye-Huckel limiting law (eqn. 2.77) good to 0.001 M

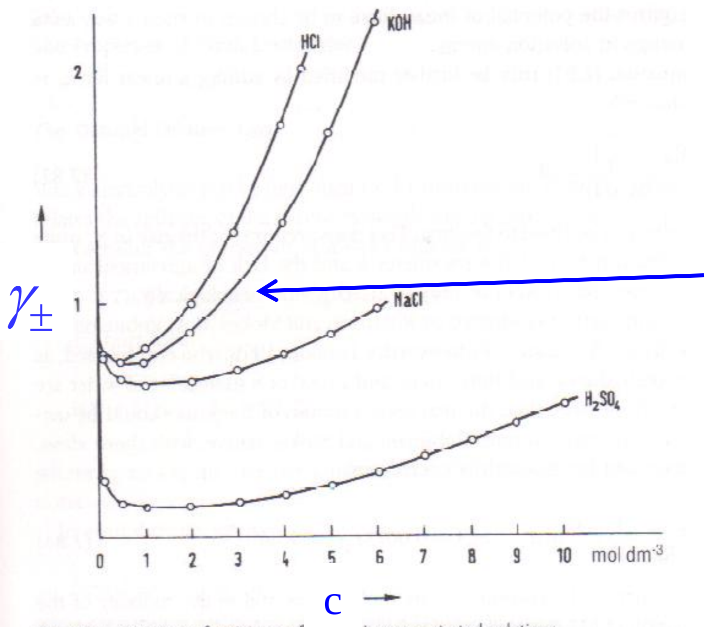
$$\ln \gamma_{\pm} = -1.172\,|z^{+}z^{-}|\sqrt{\mathbf{I}} \qquad 2.77$$

Leading to the expression (eqn. 2.81) for activity coefficient of concentrated electrolytes:

$$\ln \gamma_{\pm} = \frac{-L|z^{+}z^{-}|e_0^2\kappa}{8\pi\varepsilon_r\varepsilon_0(1 + a_0\kappa)} = \frac{-A|z^{+}z^{-}|\sqrt{\mathbf{I}}}{[1 + Ba_0\sqrt{\mathbf{I}}]} \qquad 2.81$$

which takes into account the size of the central ion but NOT the surrounding ions and is good to ~ 0.1M

Failure of 2.81 for more concentrated solutions of ions



Activity coefficient $\gamma_\pm$ can be > 1
at very high concentrations

Fig 2.20 Variation of activity coefficients in concentrated solutions

2 other theories for $\gamma_\pm$ good to ~ 1 to 2 M

1) Hitchcock empirical additive correction gives eqn. 2.82

$$\ln \gamma_\pm = -\frac{A|z_+z_-|\sqrt{\mathrm{I}}}{(1+Ba_0\sqrt{\mathrm{I}})} + b\mathrm{I} \qquad \text{eqn. 2.82}$$

2) Robinson-Stokes bulk solvent correction yields eqn. 2.83

$$\ln \gamma_\pm = \frac{A|z_+z_-|\sqrt{\mathrm{I}}}{(1+Ba_0\sqrt{\mathrm{I}})} - \frac{h}{\nu}\ln a_A - \ln[1+0.001M_A(\nu-h)m] \qquad \text{eqn. 2.83}$$

The Properties of Weak Electrolytes

Ostwald Dilution Law (p61)

Weak electrolytes can be described by the introduction of an equilibrium constant, *K*, that relates the splitting of the parent molecule into its constituent ions:

$$\text{R-COOH} + \text{H}_2\text{0} \underset{k_r}{\overset{k_d}{\Leftrightarrow}} \text{R-COO}^- + \text{H}_3\text{0}^+$$

Where k_d and k_r are the dissociation and recombination rate constants and C_i is concentration of species *i*. At equilibrium we have:

$$k_d C_{HA} C_{H20} - k_r C_A \text{-} C_{H30^+} = 0$$

Switching to molalities and incorporating the molality of water into k_d:

$$\frac{m_{A^-} m_{H_3O^+}}{m_{HA}} = \frac{k_d}{k_r} = K_m'$$

The acid dissociation constant, K_a , is defined as :

$$K_a = \frac{a_A \; a_{H_3O}}{a_{HA}} = \frac{(m_A \; / m^0)(m_{H_3O} \; / m^0)}{(m_{HA}/m^0)} \; \frac{\gamma_\pm^2}{\gamma_{HA}} \approx K_m \gamma_\pm^2$$

Eqn. 2.88

Weak Electrolytes (cont.)

From $K_a \cong K_m \gamma^2_{\pm}$ so K_a is approximately equal to K_m at low concentrations assuming $\gamma_{\mathrm{HA}} = 1$, so we have then the molality form of the acid dissociation constant which is written as a dimensionless quotient:

$$K_m = \frac{(m_{\mathrm{A}^-}/m^0)(m_{\mathrm{H_3O}^+}/m^0)}{(m_{\mathrm{HA}}/m^0)} \qquad \text{Eqn 2.89}$$

In which m_i is molality and m^0 is standard molality (1 mol/kg electrolyte)

and K_a is approximately equal to K_m and both are good to about 0.01M.

Degree of dissociation

Ostwald was the first to introduce the degree of dissociation, α , to clarify the connection between the equilibrium properties of weak electrolytes and the electrical conductivities of their solutions.

For

$$HA+ H_20 \underset{k_r}{\overset{k_d}{\Leftrightarrow}} A^- + H_30^+$$

and the dissociation equation 2.89

$$K_m = \frac{(m_{A^-}/m^{\ominus})(m_{H_3O^+}/m^{\ominus})}{(m_{HA}/m^{\ominus})}$$

and

$$m_{A^-} = m_{H_3O^+} = \alpha m \qquad m_{HA} = (1-\alpha)m$$

then by substituting these values of *m* into the dissociation equation we obtain K_m:

$$K_m = \frac{\alpha^2 (m/m^{\ominus})^2}{(1-\alpha)(m/m^{\ominus})} = \frac{\alpha^2 (m/m^{\ominus})}{(1-\alpha)}$$

Eqn. 2.91

If $\alpha << 1$ we get:

$$\alpha \sqrt{\frac{m}{m^{\ominus}}} \approx \sqrt{K_m}$$

$$\alpha = \Lambda / \Lambda_0$$

Eqn. 2.93

which follow from equations 2.11 and 2.12, since they tell that $\Lambda = \kappa / C$

Effect of Degree of Dissociation on Conductivity

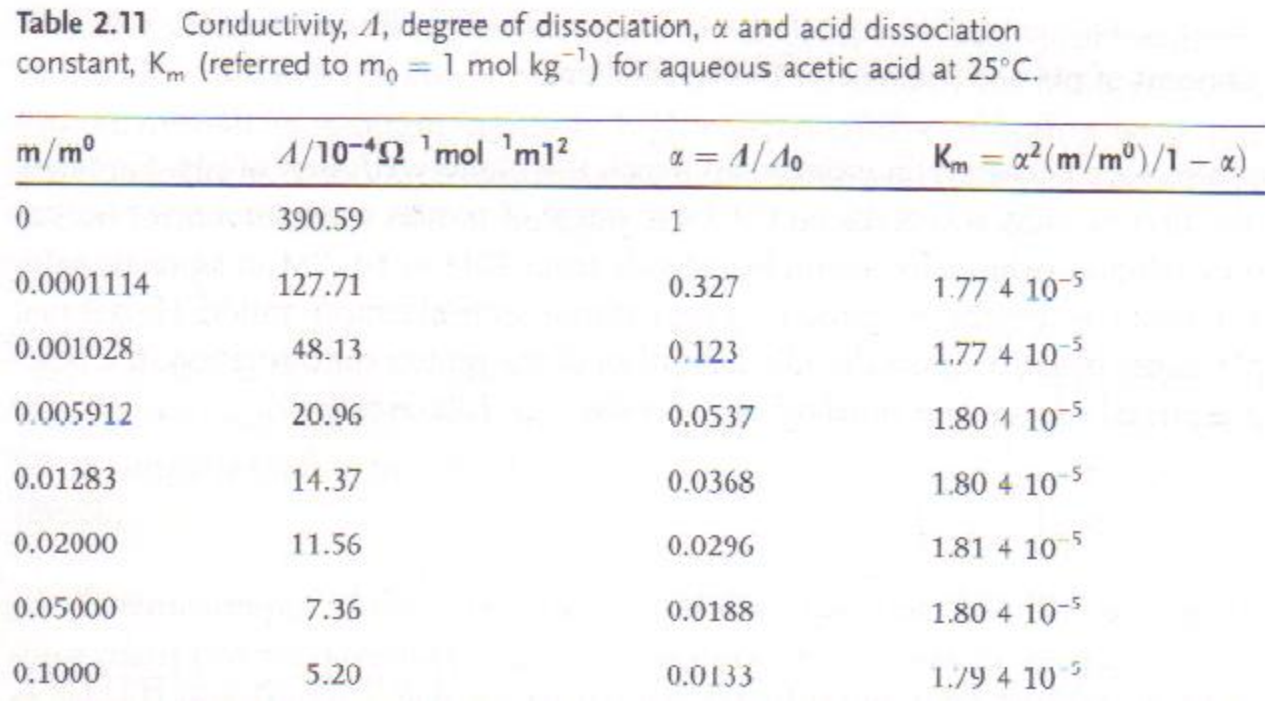


Table 2.11 Conductivity, Λ, degree of dissociation, α and acid dissociation constant, K_m (referred to $m_0 = 1$ mol kg^{-1}) for aqueous acetic acid at 25°C.

m/m^0	$\Lambda/10^{-4}\Omega\ ^{1}\text{mol}\ ^{1}\text{m}1^{2}$	$\alpha = \Lambda/\Lambda_0$	$K_m = \alpha^2(m/m^0)/1 - \alpha)$
0	390.59	1	
0.0001114	127.71	0.327	$1.77\ 4\ 10^{-5}$
0.001028	48.13	0.123	$1.77\ 4\ 10^{-5}$
0.005912	20.96	0.0537	$1.80\ 4\ 10^{-5}$
0.01283	14.37	0.0368	$1.80\ 4\ 10^{-5}$
0.02000	11.56	0.0296	$1.81\ 4\ 10^{-5}$
0.05000	7.36	0.0188	$1.80\ 4\ 10^{-5}$
0.1000	5.20	0.0133	$1.79\ 4\ 10^{-5}$

As solution is more concentrated in acetic acid,

- the dissociation constant does not change
- but the plus and minus ions associate,
- so there are less ions in solution
- and therefore the *conductivity decreases* !

The Concept of pH and the Idea of Buffer Solutions

(p64) … revisited in section 3.6.6 conventional pH scale

Sorensen defined pH as the negative of the base-10 logarithm of the proton concentration

$$\mathrm{pH}_c \equiv -\log_{10}\left(\frac{c_{\mathrm{H_3O^+}}}{c^0}\right)$$

Introducing the activity instead of the concentration gives a general definition of pH:

$$\mathrm{pH}_a \equiv -\log_{10} a_{\mathrm{H_3O^+}} \equiv -\log_{10}\gamma_{\mathrm{H_3O^+}}\left(\frac{\mathrm{H_3O^+}}{m^0}\right)$$ Eqn. 2.96

The water dissociation could be expressed as follows:

$$2\mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{OH^-}$$ Eqn. 2.97

For the product of water it is known:

$$a_{\mathrm{H_3O^+}} a_{\mathrm{OH^-}} = K_w^{\mathrm{H_2O}} \approx \left(\frac{m_{\mathrm{H_3O^+}}}{m^0}\right)\cdot\left(\frac{m_{\mathrm{OH^-}}}{m^0}\right)$$ Eqn. 2.98

where $K_w^{\mathrm{H_2O}}$ is ionic product of water 1.01 x 10^{-14} at $m^o = 1$ mol kg $^{-1}$ and 25C.
Transforming the product of water equation we get:

$$\mathrm{pH} = -\log_{10} K_w^{\mathrm{H_2O}} - \log_{10} a_{\mathrm{OH^-}} \equiv 13.9965 - \mathrm{pOH}$$ Eqn. 2.99

Buffers

Buffer solutions are electrolyte solutions whose pH is very stable to either dilution or the addition of small quantities of acid or base. Composition:
WEAK ACID + DISSOCIATED SALT WITH THE ACID ANION

$$HA + H_2O \overset{Ka}{\leftrightharpoons} A^- + H_3O^+$$

If the molality of HA and A^- are close to or greater than the molality of the acid or base being added, then the activity of H_3O^+ can be written as follows:

$$\begin{aligned} a_{H_3O^+} &= K_a\left(\frac{a_{HA}}{a_{A^-}}\right) \approx K_a\left(\frac{m_{HA}}{m_{A^-}}\right)\cdot\left(\frac{1}{\gamma_{A^-}}\right) \\ &\equiv K_a\left(\frac{m_{acid}}{m_{salt}}\right)\cdot\left(\frac{1}{\gamma_{A^-}}\right) \end{aligned}$$

Note:
assume $\gamma_{HA} = 1$

After applying a negative logarithm:

$$pH = pK_a + \cancelto{0}{\log_{10}\left(\frac{m_{salt}}{m_{acid}}\right)} - \log_{10}\gamma_{A^-}$$

since **γ_{A^-} is assumed constant and $m_{salt}/m_{acid} = 1$**
so pH is stable and is close to the value of pK_a
if added acid or base is less than m

End of Chapter 2

pp. 67 – 74 are applications that are specific examples of general discussion already covered

Section 2.8 Non-aqueous solutions
Section 2.9 Applications of Conductivity Measurements

Next time …

i. **Brief Quiz on Chapters 1 and 2**
ii. **Begin Chapter 3**