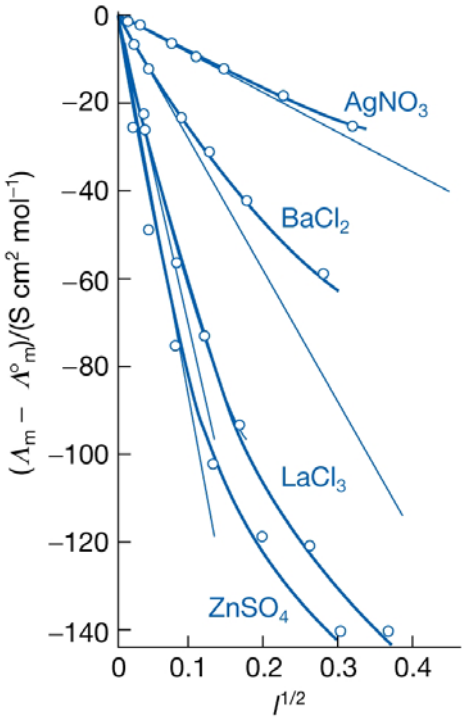
Note : This topic is assigned to student self directed learning.



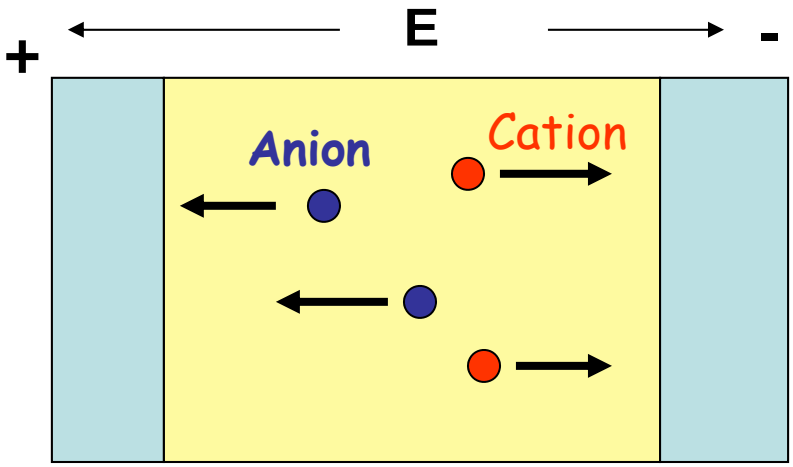
Lecture 16

Ionics :

Physical chemistry of electrolyte solutions.

Ionics: the physical chemistry of ionic solutions.

- Up until now we have looked at electron transfer reactions at the interface region between an ionic solution and a metal electrode.
- We now focus attention on the movement of ionic species through the ionic solution.
- This subject is called Ionics .



Ionic solution

- Recall from physics that an electric current i is simply a flow of charge. A material that can carry an electric current is called a conductor.
- Electrical conduction can arise from the movement of electrons or positive and negative ions.
- Hence we have two general classes of conductor.
  - Electronic conductor : mobile charge carriers are electrons, current is ascribed to electron movement. E.g. metals (Cu), semiconductors (Si).
  - Ionic conductor: mobile charge carriers are positive and negative ions (charged atoms or groups of atoms, e.g. Na^+, Cl^-). Example NaCl (aq).
- Conduction or electromigration is the transport of charged species under the influence of an electric field.

- We concentrate on ionic conduction in electrolyte solutions (solvent, usually water + solvated ions).
- Have two major classes of electrolytes:

Strong (true) electrolytes :

Have complete dissociation into solvated ions.

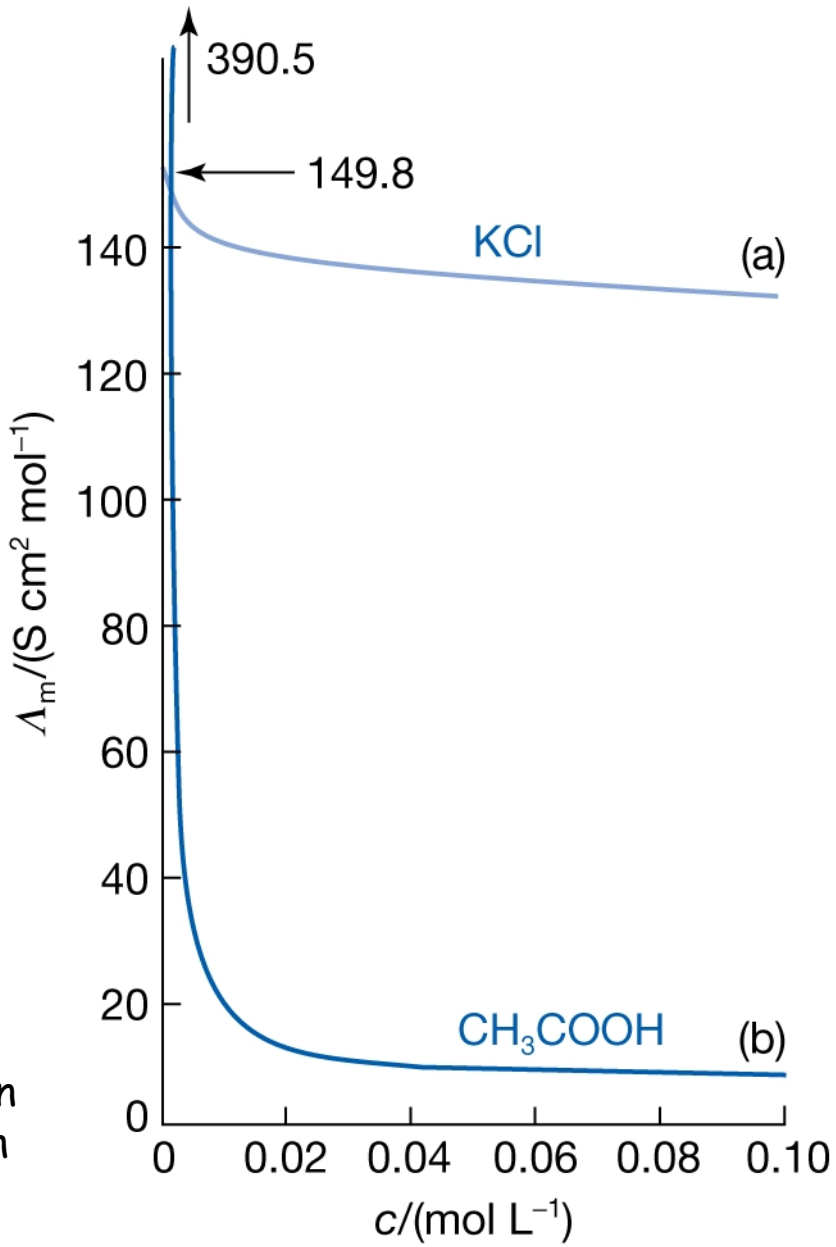
E.g. $KCl \rightarrow K^+(aq) + Cl^-(aq)$.

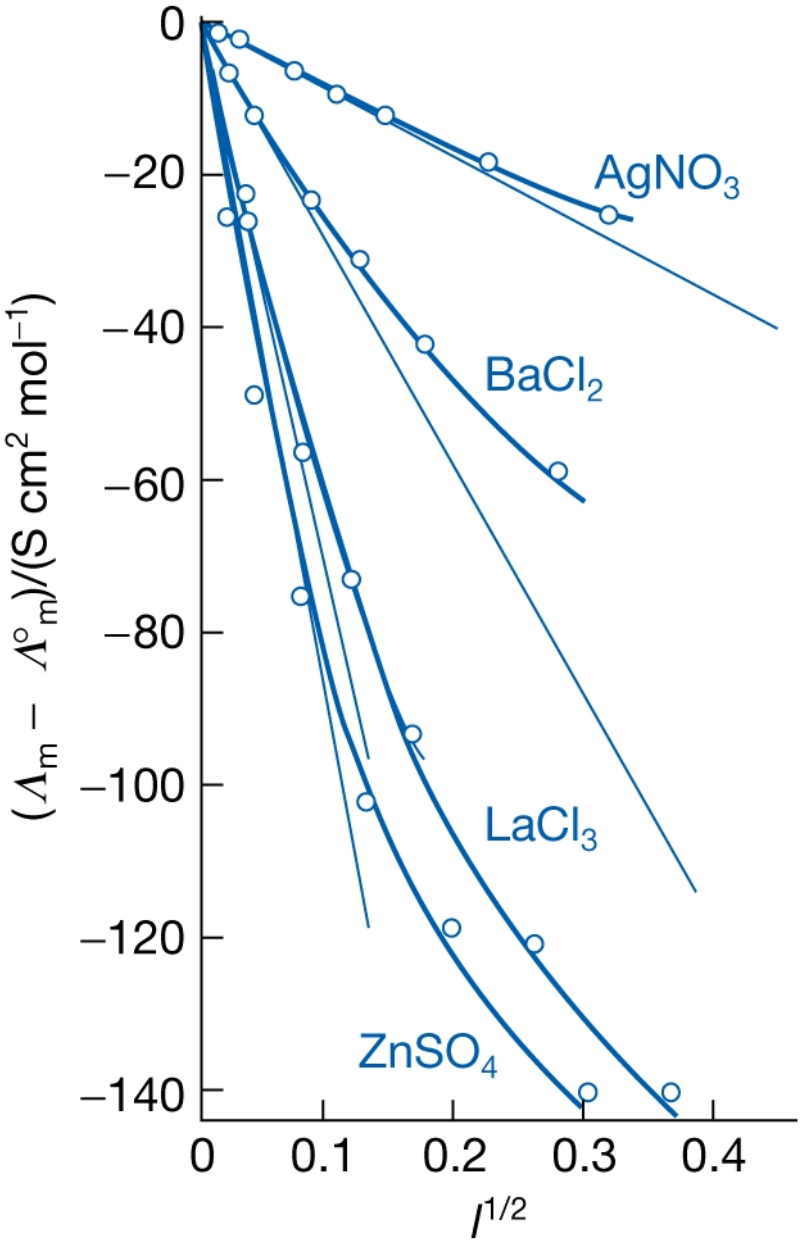
Weak (potential) electrolytes :

Have partial (incomplete) dissociation into ions.

E.g. $CH_3COOH \rightarrow CH_3COO^-(aq) + H_3O^+(aq)$.

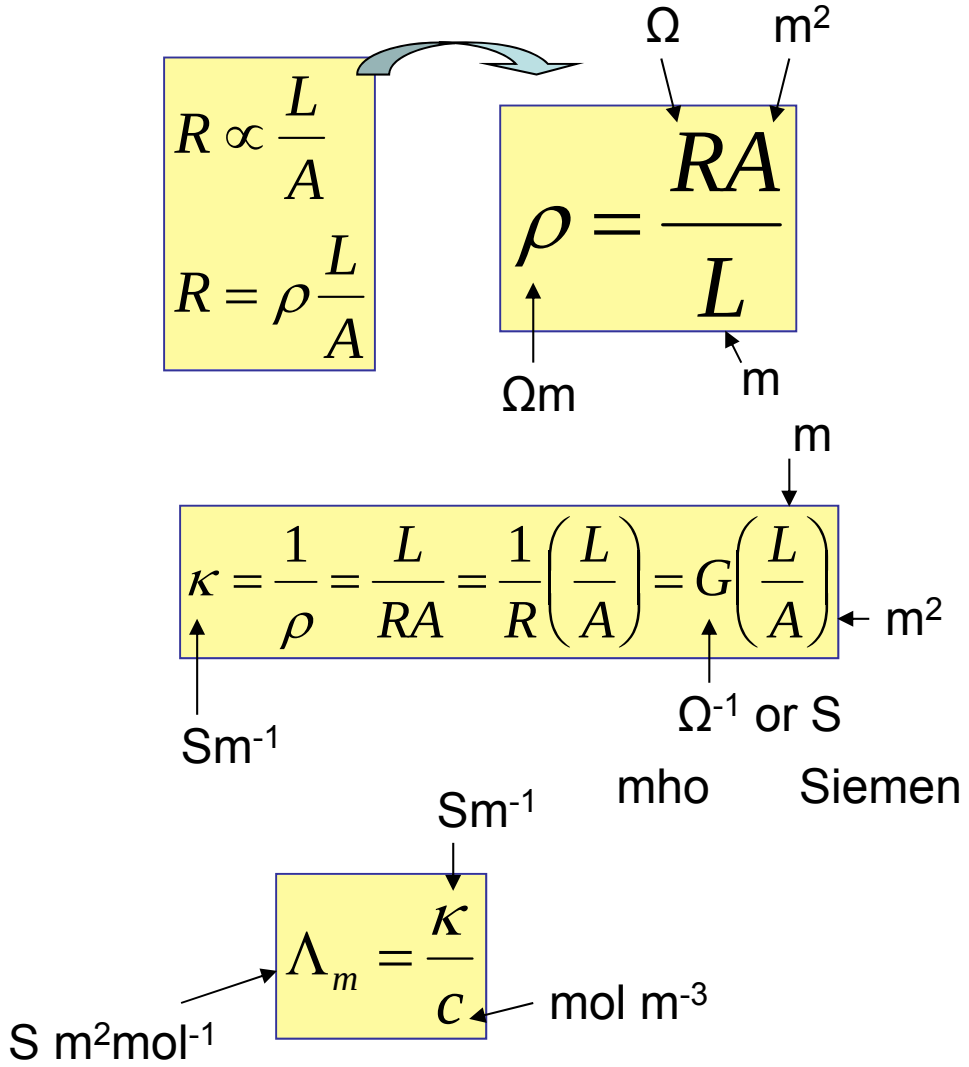
- The magnitude of the conductivity exhibited by the ionic solution depends on a number of factors.
  - number of solvated ions free to move in solution.
  - Mobility (related to speed) of ions in solution phase.
  - Charge on ion.
- Variation of conductivity with concentration c of ionic solution can be used to distinguish between true and potential electrolytes.




0
−20
−40
−60
−80
−100
−120
−140
0
0.1
0.2
0.3
0.4
$I^{1/2}$
$(\Lambda_m - \Lambda^\circ_m)/(S\ cm^2\ mol^{-1})$
$AgNO_3$
$BaCl_2$
$LaCl_3$
$ZnSO_4$

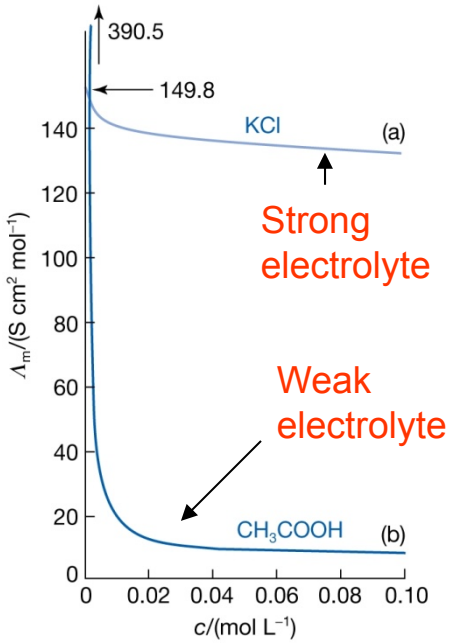
Conductivity.

- Ionic solutions are characterised by their conductivity κ.
- Recall from basic physics that the resistance R of a material sample depends on the geometry of the sample. R is directly proportional to the length L of the sample, and inversely proportional to the cross sectional area A of the sample.
- We can define a material property ρ called the resistivity of the material which does not depend on the geometry of the sample.
- The conductivity κ is the inverse of resistivity.
- We can also introduce the conductance G of the material which is the inverse resistance.
- It is usual to define the molar conductivity Λ_m as the conductivity of a solution of unit concentration.



Variation of molar conductivity with electrolyte concentration.

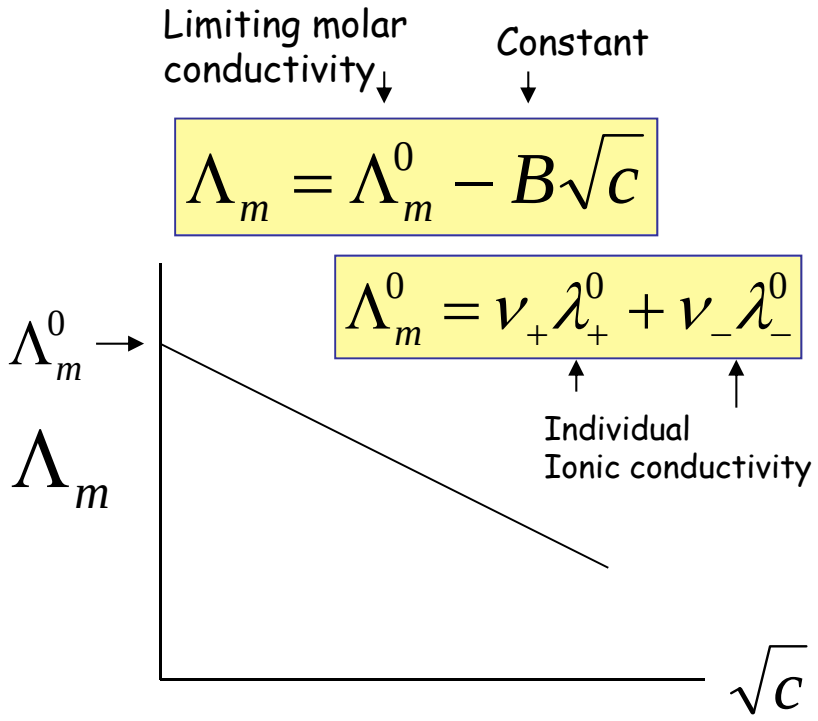
- The molar conductivity of an ionic solution is found to vary with the concentration of the solution.
- This is due to two major reasons:
  - The number of ions present in the solution is not necessarily proportional to the electrolyte concentration.
  - The solution conductivity is not exactly proportional to the number of ions present due to the fact that the charged ions experience electrostatic forces and interact with one another.



- The characteristic behaviour exhibited by a strong or true electrolyte such as KCl is that Λ_m depends only slightly on electrolyte concentration c and generally decreases slightly as the molar concentration is increased.
- In contrast, the molar conductivity of a potential electrolyte such as CH_3COOH decreases in a very marked manner with increasing electrolyte concentration.
- Strong electrolytes are virtually completely ionized in solution, and so the concentration of free ions is directly proportional to the concentration of strong electrolyte added. In contrast weak electrolytes are only partially ionized in solution and so the number of free ions depends on the concentration of weak electrolyte in a complicated manner.
- The conductivity depends on the number of free ions in solution and so for a weak electrolyte will depend on the degree of dissociation α . As the electrolyte concentration decreases the degree of dissociation will increase and so we expect that the conductivity of a weak electrolyte increases with decreasing electrolyte concentration.

Conductivity of strong electrolytes.

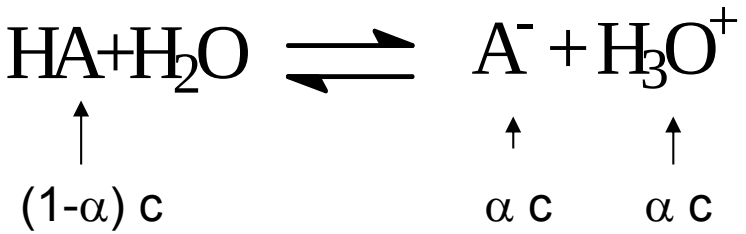
- Kohlaursch showed that at low concentrations, the molar conductivity of a strong electrolyte varied in a linear manner with the square root of the electrolyte concentration.
- This result could be explained using classical electrostatic theory involving the Coulombic interaction between the mobile charged ions and neighbouring ions in the solution. This was accomplished by Debye, Huckel and Onsager.
- A more complex relationship between molar conductivity and electrolyte concentration can be invoked to fit the experimental data over a wider range of electrolyte concentrations.
- Main point to note is that the variation of conductivity with concentration can be understood in terms of ion/ion interactions using classical physics.



The limiting molar conductivity corresponds to the situation where the solution is infinitely dilute : the ions are very far apart and do not interact with one another. Hence we can assume that positive and negative ions migrate independently of one another. The molar conductivity at infinite dilution is the sum of the individual ionic conductivities λ_j^0.

Conductivity of weak electrolytes.

- Molar conductivity of a weak electrolyte increases rapidly with decreasing electrolyte concentration.
- The more dilute the solution the greater the extent of dissociation and the greater the relative proportion of ions present and hence the greater the molar conductivity.
- Arrhenius calculated the degree of ionization or dissociation α from conductivity data by assuming that at infinite dilution all electrolytes are completely ionized, and hence as c → 0, α → 1.
- Hence we note that $\Lambda_m = \alpha \Lambda_m^0$.



$$K_A = \frac{\alpha^2 c}{1-\alpha}$$

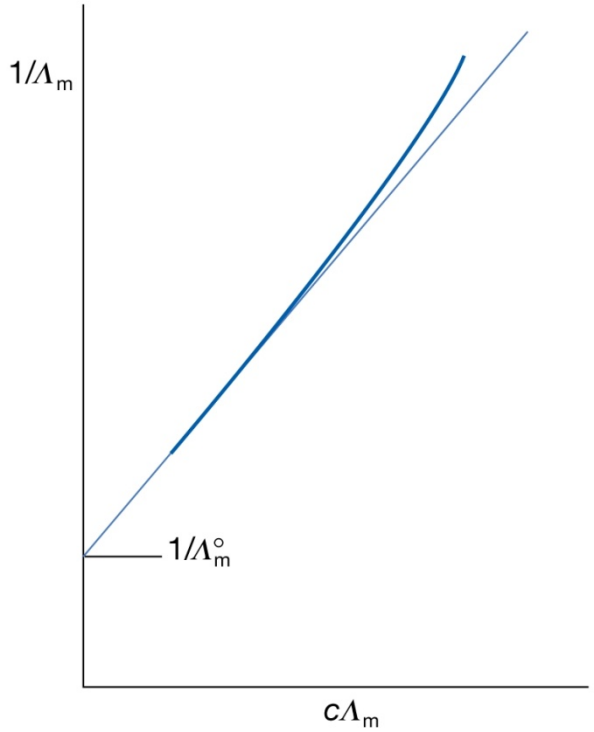
$$c\alpha^2 + K_A\alpha - K_A = 0$$

$$\alpha = \frac{K_A}{2c}\left\{\left(1+\frac{4c}{K_A}\right)^{1/2} - 1\right\}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0}$$

Hence we can relate α to the molar conductivity.

Ostwald dilution equation.



Ostwald Plot.

$$K_A = \frac{\alpha^2 c}{1-\alpha}$$

$$\frac{1}{\alpha} = 1 + \frac{\alpha\, c}{K_A}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0}$$

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \left\{ \frac{1}{K_A \left(\Lambda_m^0\right)^2} \right\} \Lambda_m c$$

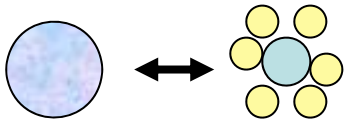
The Ostwald dilution law states that a plot of $1/\Lambda_m$ versus c Λ_m is linear with a positive slope And a positive intercept. The intercept can be Used to determine Λ_m^0. Once the latter is known the dissociation constant K_A can be determined from the slope.

The physical basis of ionic conductivity (I).

The basic physical idea is the analogy between an ion drifting in an electrolyte solution and a sphere moving in an incompressible medium of the same viscosity as that of the electrolyte.

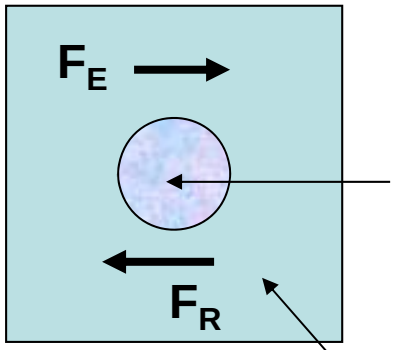
What forces are felt by the ion as it migrates through the electrolyte solution?
We need to consider two forces :

- an electrical force F_E (calculated using electrostatics)
- a frictional retarding force F_R(calculated using hydrodynamics).



Radius of sphere = radius of solvated ion (ion + water molecules)

The two forces act in opposite directions and very quickly they will be in balance and then the ion will exhibit a net drift speed v_D .
This quantity can be calculated by setting $F_E = F_R$.



Ion = sphere of radius a.

Electrolyte solution = incompressible medium of viscosity η.

The physical basis of ionic conductivity (II).

Electrical force. $F_E = qE = zeE$ ← Electric field strength

Ion charge $q = z\,e$ ← fundamental charge

Ion valence

Frictional retarding force. $F_R = 6\pi\eta a v_D$

Spherical ion, radius a

Solvent viscosity

At steady state $F_E = F_R$

$$zeE = 6\pi\eta a v_D$$

Drift speed $v_D = \dfrac{zeE}{6\pi\eta a}$

The drift speed governs the rate at which charge is transported through the solution.

A better parameter is the mobility of an ion u.

$v_D = uE$ (ms^{-1} ← Vm^{-1})

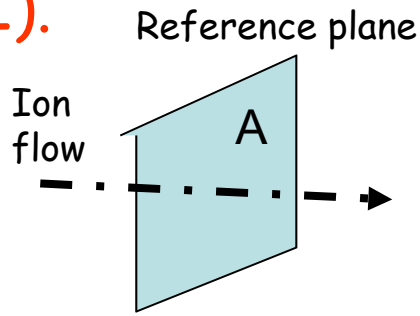
Units of mobility : $m^2V^{-1}s^{-1}$

Hence the ionic mobility depends on the size of the moving ion (via the solvated radius a), its charge, and on the physical properties of the solvent (via the viscosity term η).

$$u = \frac{ze}{6\pi\eta a}$$

$$u = \frac{v_D}{E}$$

The physical basis of ionic conductivity (III).



- We consider a solution of fully dissociated strong electrolyte at a molar concentration c (units: mol/m^3).
- Each formula unit gives rise to v_+ cations of charge z_+e and v_- anions of charge z_-e.
- The molar concentration of each type of ion is therefore given by vc (where v = v_+ or v_-).
- The number density (unit: m^{-3}) of each type of ion (# ions per unit volume) is $N_A$vc.
- The electric current due to the flow of ions (charge carriers) across any reference plane in the solution is given by:

current (i) = # charge carriers per unit volume ($N_A$vc) x cross sectional area (A) x carrier charge (ze) x average carrier speed (v_D)

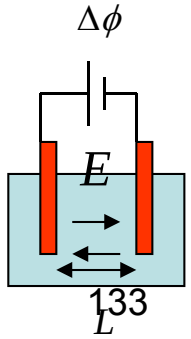
Hence $$i = \frac{dQ}{dt} = zeN_A A\upsilon c v_D = zFA\upsilon c v_D = f_Q A$$

f_Q = charge flux
Units: $Cm^{-2}s^{-1}$

We recall that the drift speed of the ion is $v_D = uE$

$$E = \frac{\Delta\phi}{L}$$

Hence the current i is given by $$i = zFA\upsilon cuE = \frac{zFA\upsilon cu\Delta\phi}{L}$$



We now note that ion transport in electrolyte solution is governed by Ohm's Law.

$$i = \frac{\Delta\phi}{R} = G\Delta\phi = \left\{\frac{\kappa A}{L}\right\}\Delta\phi$$

We now compare the two expressions derived for the current to obtain an Expression for the conductivity associated with an individual ion.

$$i = \frac{zFA\upsilon cu\Delta\phi}{L} = \left\{\frac{\kappa A}{L}\right\}\Delta\phi \quad \Rightarrow \quad \kappa = zF\upsilon cu$$

$\Lambda^0_m \cong 10\,\mathrm{mS\,m^2\,mol^{-1}}$

for $z = 1$ and $u_i \cong 5\times10^{-8}\,\mathrm{m^2V^{-1}s^{-1}}$

The molar conductivity λ_i of an individual ion labelled i is given by:

$$\kappa_i = z_i F \upsilon_i c u_i \quad \Rightarrow \quad c_i = \upsilon_i c \quad \Rightarrow \quad \lambda_i = \frac{\kappa_i}{\upsilon_i c} = \frac{\kappa_i}{c_i} = z_i F u_i$$

Hence the conductivity of an individual ion i depends on the ion valence z_i and on its ionic mobility u_i. Hence ions exhibit different conductivities since they have different mobilities (different drift speeds in a unit electric field). The molar conductivity of the solution at infinite dilution as c → 0 can easily be evaluated.

$$\Lambda^0_m = \lambda^0_+ + \lambda^0_- = F\left\{z_+u_+\upsilon_+ + z_-u_-\upsilon_-\right\}$$

Symmetrical (z,z) electrolyte with $z_+ = z_- = z$ and $v_+ = v_- = 1$ (e.g. $CuSO_4$) :

$$\Lambda^0_m = zF\left\{u_+ + u_-\right\}$$

Transport numbers.

- Since ions migrate at different speeds what fraction of the total current is carried by a particular ion?
- This question is answered by introducing the concept of a transport number t_i.
- The transport number $t_\pm$ is defined as the fraction of the total current i carried by an ion of a specified type (either a cation labeled + or an anion labeled -).

$$t_+ = \frac{i_+}{i} \qquad t_- = \frac{i_-}{i}$$

We note that

$$i = i_+ + i_- \qquad t_+ + t_- = 1$$

- We can introduce a limiting transport number t_i^0 corresponding to the case as c → 0.
- This can be related to the ionic mobilities.

$$t_\pm^0 = \frac{z_\pm \upsilon_\pm u_\pm}{z_+ \upsilon_+ u_+ + z_- \upsilon_- u_-}$$

For any electrolyte the principle of Electroneutrality must pertain.

$$z_+ \upsilon_+ = z_- \upsilon_-$$

Hence

$$t_\pm^0 = \frac{u_\pm}{u_+ + u_-}$$

Relaxation and electrophoretic effects.

- We assume that a given ion (such as a cation) is surrounded by neighbouring ions of opposite charge (anions). These surrounding counter-ions are said to form an ionic atmosphere which can be visualized as a charged cloud surrounding the central ion of interest.
- In the absence of an electric field the ionic atmosphere is spherically distributed around the central ion.
- When an electric field is present the central ion migrates through the solution and so the ionic atmosphere is no longer spherically symmetric.
- Because the ions forming the atmosphere do not adjust to the moving ion immediately, the atmosphere is incompletely formed in front of the moving ion, and incompletely decayed behind the moving ion.
- The net result is the displacement of the centre of charge of the atmosphere behind the moving ion. Because the charge on the ion and the atmosphere are opposite, the result is a retardation in the motion of the moving central ion.
- This reduction in the mobility of the ion is called the relaxation effect.
- We also note that the moving ion experiences an enhanced viscous drag force. This arises because the ionic atmosphere moves in a direction opposite to that of the ion thereby reducing the mobility and hence the conductivity of the latter. This is called the electrophoretic effect.

