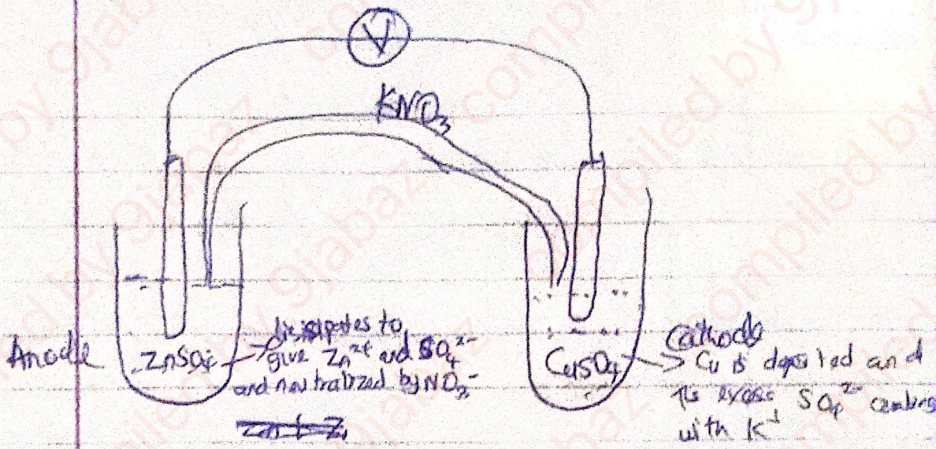


~~Zn + Zn~~

$Zn \longrightarrow Zn^{2+} + 2e$

$Cu^{2+} + 2e \longrightarrow Cu$

The position of electrode in the electrochemical series

Electrical Conductance

Electrical Conductance

deals with the movement of ions

The Conductance of a system can be defined as a major of its ability to carry an electric current. The values of conductance are important for evaluating solubilities of sparingly soluble salt, ionic product of solvents, dissociation constants of weak acids and bases.

Like a metallic conductor, the resistance of an electrolyte is proportional to the distance between the electrodes dipped into it, and inversely proportional to the area of the electrode

$$R \propto \frac{l}{a} \quad \text{or} \quad R = \frac{\rho l}{a}$$

Where ρ = resistivity/specific resistance

l = distance between the electrodes

a = Area of electrode

The equation can be written as;

$G = \frac{a}{l\rho}$; where G is known as the conductance and it is the inverse of R

Instead of referring to the resistance and resistivity of the electrolyte, Conductance G, and conductivity K are used

where $K = \frac{1}{\rho}$ $\therefore R = \frac{l}{Ka} \Rightarrow KR = \frac{l}{a}$

Ionic mobility

The unit of conductance G is Ohm^{-1} or Ω^{-1}

The unit of conductivity k is $Ohm^{-1}m^{-1}$ or $\Omega^{-1}m^{-1}$

$$K = \frac{1}{R} \times \frac{l}{a}$$

Variation of molar conductivity with Concentration

Molar conductivity increases with dilution, because the ions will spread out, and there will be increase in mobility.

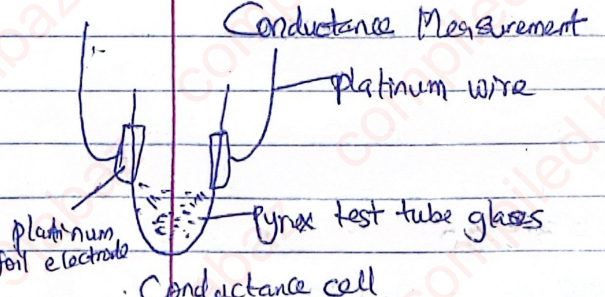
Generally a strong electrolyte exhibits complete dissociation in solution, and the molar conductivity for strong electrolyte increases with increase in dilution. This is explained by inter-ionic attraction theory of conductance which uses three modes of interaction of ions to explain the phenomenon

(i) Ion-pair formation / Ion association

Ex. ion-ion interaction

The cell constant l/a is the dimensions of a cell and its constant for a specific cell. The calibration of a cell is done by determining the dimensions $\frac{l}{a}$ by filling the cell with $0.01 mdm^{-3}$ KCl standard solution.

The conductance of the solution is measured. The product of K and R gives the cell constant at a particular temperature, hence, the conductivity of any other solution can be calculated once the resistance is measured



Conductance cell

A simple conductance cell is made up by fusing a flat platinum foil impregnated with platinum black to test tube to which a platinum wire is attached to serve as leads.

These can then be connected to the terminance of a conductance bridge. Conductance is the reciprocal of resistance of an electrolyte and this can be measured by the use of wheatstone bridge and ratio transformer-arm

bridge

Example

The resistance of a Cell Containing 0.10 mol dm^{-3} KCl Solution and 0.05 mol dm^{-3} $AgNO_3$ Solution are 307.62 and 189.54 ohms respectively. The conductivity of 0.01 mol dm^{-3} of KCl is 1.286 Ohm^{-1}m^{-1}, Calculate the Conductivity of the $AgNO_3$ Solution. Calculate the molar conductivity of the $AgNO_3$ Solution.

$$\frac{l}{a} = K_{KCl} R_{KCl} = 307.62 \times 1.286 = 395.60 m^{-1}$$

$$K_{AgNO_3} * R_{AgNO_3} = \frac{l}{a}$$

$$K_{AgNO_3} \times 189.54 = 395.60$$

$$K_{AgNO_3} = \frac{395.60}{189.54} = 2.087 \Omega^{-1} m^{-1}$$

The practical utilization of the conductivity of an electrolyte is restricted. The values of conductivity for different electrolyte cannot be compared the conductance ~~of~~ will have different number of ions. Thus, molar Conductivity is used instead.

(ii)

Molar conductivity, Λ is defined as the conductivity divided by the molar concentration of C of the electrolyte.

$$\Lambda = \frac{k}{C} = \frac{\Omega^{-1}m^{-1}}{mol\,m^{-3}} = \Omega^{-1}mol^{-1}m^{2}$$

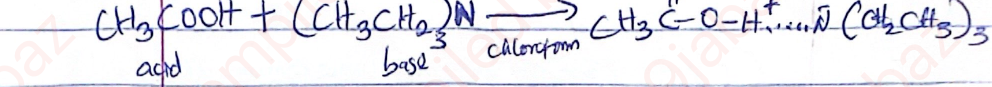
~~The resistance of a cell containing 0.1~~

(ii) $\Lambda = \frac{k}{C} = \frac{2.087}{0.05 \times 10^{3}} = 4.17 \times 10^{-2}\,\Omega^{-1}mol\,m^{2}$

Ion

(1) Ion Pair formation / Ion Association: This tends to reduce the mobility of ions under the influence of electric field because opposite charge ions tends to aggregate by electrostatic interaction. Under some situations multiple ions can aggregate without forming covalent bonds especially if the ions are small with high charges in solvents of low dielectric constants unlike water with high dielectric constant.

for example;



The above ion pairs occurs in relatively concentrated solution or molten salt state in which conductivity is reduced but when the concentration reduces due to dilution, conductivity increases

(2) Assymetric Effect: This effect occurs when an ion is surrounded by excess opposite charge ions, when an electric field is applied, the ion drags the excess ions surrounding it as it moves forward. Thus, it causes the ionic atmosphere around the moving central ion not to be symmetrical. However, the application of thermal agitation can help to restore the

symmentry of the ionic atmosphere, after a short interval called the relaxation time. This temporary delay that hinders the motion of the central ion is called the assymetric effect. The effect is minimal in dilute solutions because the ions are free.

(3) Electrophoric Effect: The phenomenon occurs because the applied potential has the tendency to move the ionic atmosphere, as a result the solvent molecules move with the ions due to force of attraction between the solvent molecule and the ions. This tends to hinder the motion of the central ion because the ionic atmosphere and the attached solvent molecules move in opposite directions. This effect reduces the mobility of the central ions as well as the conductivity.

In dilute solutions, all interionic effect are eleminated. The retarding forces described above are equated with force of electric field, giving rise to an equation which connects the molar conductivity (Λ) with the electrolyte concentration C. When considering the variation of their conductancy with concentration, strong and weak electrolyte show distinct characteristics. For strong electrolyte, Kohlraush establishes an emperical relationship

molar conductivity

between Λ and $\sqrt{c}$ as follows

$$\Lambda_c = \Lambda_0 - bc$$

where Λ_c = molar conductivity at a given concentration

Λ_0 = molar conductivity at infinite dilution

The above equation holds up to concentration in the region of $5 mol dm^{-3}$.

Weak electrolyte do not exhibit such relationship. Their dissociation tends to increase with increasing dilution and the degree of dissociation is given as follows;

~~The dissociation constant K~~

$$\alpha = \frac{\Lambda_c}{\Lambda_0}$$

The dissociation constant K can be obtained from the degree of dissociation. The magnitude of K indicates the strength of the weak electrolyte

$$CH_3COOH \longrightarrow CH_3COO^- + H^+$$

moles of species in solution: $(1-\alpha)c$ $\quad \alpha c$ $\quad \alpha c$

$$K = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{\alpha^2 c^2}{(1-\alpha)c} = \frac{\alpha^2 c}{1-\alpha}$$

But if $\alpha \ll\ll 1$

$K = \alpha^2 C$

But $\alpha = \frac{\Lambda_c}{\Lambda_0}$, Then; $K = \frac{\left(\frac{\Lambda_c}{\Lambda_0}\right)^2 C}{1 - \frac{\Lambda_c}{\Lambda_0}}$

$= \left(\frac{\Lambda_c}{\Lambda_0}\right)^2 C \div \frac{\Lambda_0 - \Lambda_c}{\Lambda_0} \Rightarrow \frac{\Lambda_c^2 C}{\Lambda_0^2} \times \frac{\Lambda_0}{\Lambda_0 - \Lambda_c}$

$\Rightarrow \frac{\Lambda_c^2 C}{\Lambda_0(\Lambda_0 - \Lambda_c)}$

For Kochsh law independent migration of ions Λ_0 can be calculated, while Λ_c can be measured. C is the concentration of the electrolyte, K = dissociated constant and can be calculated

At low concentration, ~~the other~~ order to obtain the conductivity of the electrolyte alone

$K_{solute} = K_{solution} - K_{solvent}$

For example;

The ions in solution consists of cations and anions of the electrolyte and these moves in opposite directions

as the current is passed. Thus the total current ~~carried~~ is made up of contributions from the cations and that of the anions

$$K = K_+ + K_-$$

And individual ionic molar conductivities can be defined as

$$K = \Lambda C = \Lambda_+ C_+ + \Lambda_- C_-$$

Therefore $K = K_+ + K_- = \Lambda_+ C_+ + \Lambda_- C_-$

This argument holds for complete dissociation only.

Example

The conductivity of a saturated solution of Na_2SO_4 at 25°C is $3.850 \times 10^{-4} \Omega^{-1} m^{-1}$ and the conductivity of the water used is $0.626 \times 10^{-4} \Omega^{-1} m^{-1}$. The limiting molar conductivity at zero concentration for Na^+ and $\frac{1}{2}SO_4^{2-}$ is 12.142×10^{-3} and $8.20 \times 10^{-3} m^2 \Omega^{-1} m$ respectively. Calculate the concentration of Na_2SO_4 at this temperature.

Solution $Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$

$K_{solute} = K_{solution} - K_{solvent}$ ~~$= 3.850 \times 10^{-4}$~~

$= 3.850 \times 10^{-4} - 0.62 \times 10^{-4}$

$= 3.224 \times 10^{-4} \Omega^{-1} m^{-1}$

$\Lambda_0 = \Lambda_0^+ + \Lambda_0^-$

$= 2(12.142\times10^{-3}) + 2(8.20\times10^{-3})$

$= 40.684\ m^2\Omega^{-1}mol^{-1}$

$C = \frac{K}{\Lambda} = \frac{3.224\times10^{-4}}{40.684\times10^{-2}} = 7.924\times10^{-3}\ mol\ m^{-3}$

Example 2

Calculate the conductivity and resistivity of $0.01 mol/dm^{-3}$ of an acid HA. If the classical dissociation constant of the acid HA is 1.42×10^{-4} at 55°C, and the limiting molar conductivity at zero concentration of the hydrogen ion H^+ and A^- ions are 3.50×10^{-2} and $0.46\times10^{-2}\ m^2\Omega^{-1}mol^{-1}$ respectively.

$HA \longrightarrow H^+ + A$

$(1-\alpha)C \quad \alpha C \quad \alpha C$

$K = \frac{\alpha^2C^2}{(1-\alpha)C} = \frac{\alpha^2C}{1-\alpha}$

Assuming $\alpha << 1$

$\therefore K = \alpha^2C$

$\alpha^2 = \frac{K}{C} = \frac{1.42\times10^{-4}}{0.01\times10^3}$

$\alpha = \sqrt{\frac{1.42\times10^{-4}}{0.01\times10^3}} = 3.768\times10^{-3}$

But $\alpha = \frac{\Lambda_c}{\Lambda_0}$

$\Lambda_c = \alpha \times \Lambda_0 = 3.768 \times 10^{-3} \times (3.50 + 0.48) \times 10^{-2}$

$\Rightarrow \Lambda_c = 1.50 \times 10^{-4}$

$= 0.15 \times 10^{-3}$

$\Lambda_c = \frac{K}{C}$

$K = \Lambda_c \times C \Rightarrow 0.15 \times 10^{-3} (0.01 \times 10^3)$

$= 0.0015 \Omega^{-1} m^{-1}$

$\rho = \frac{1}{K} = \frac{1}{0.015} = 66.6 \Omega m$