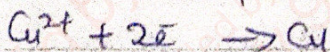
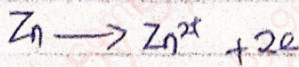
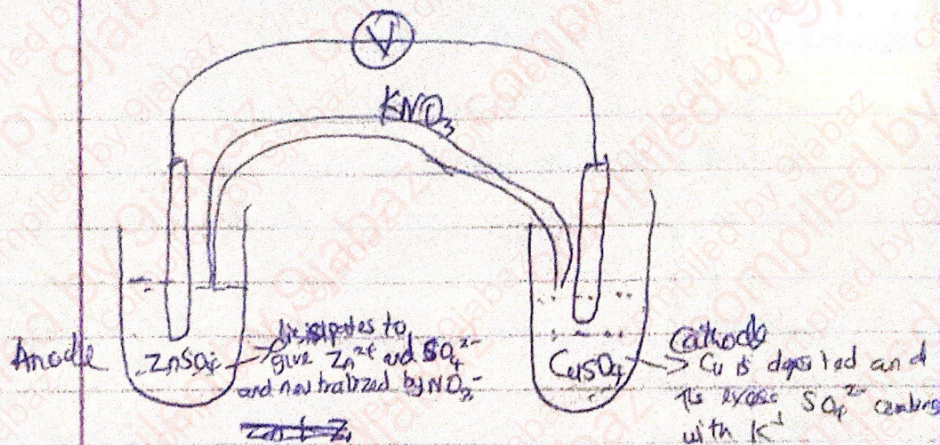


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The position of electrode in its electrochemical series

Electrical Conductance

Electrical Conductance

The Conductance of a system can be defined as a measure of its ability to carry an electric current. The values of conductance are important for evaluating solubilities of sparingly soluble salts, 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;

$$G = \frac{a}{\rho L} \quad ; \quad \text{where } G \text{ is known as the conductance}$$

ρ 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

$$\text{where } K = \frac{1}{\rho} \quad \therefore R = \frac{L}{K a} \Rightarrow K R = \frac{L}{a}$$

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

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

$$k = \frac{1}{Ra}$$

Variation of molar conductivity with Concentration

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

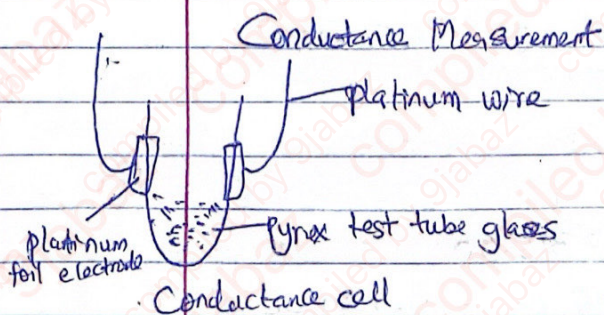
Generally, a strong electrolyte exhibits complete dissociation in solution, and the molar conductivity for strong electrolyte increases with increase in dilution.

This is explained by inter-ionic attraction theory of conductance which uses three modes of interaction of ions to explain the phenomenon.

(1) Ion-pair formation / Ion association

The cell constant $\frac{l}{a}$ 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 mol dm^{-3} KCl standard solution.

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



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 terminals 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 $1.286 \text{ ohm}^{-1} \text{ m}^{-1}$. Calculate the conductivity of the AgNO_3 solution. Calculate the molar conductivity of the AgNO_3 solution.

$$\frac{L}{a} = K R_{\text{KCl}} = 307.62 \times 1.286 = 395.60 \text{ m}^{-1}$$

$$K_{\text{AgNO}_3} \times R_{\text{AgNO}_3} = \frac{L}{a}$$

$$K_{\text{AgNO}_3} \times 189.54 = 395.60$$

$$K_{\text{AgNO}_3} = \frac{395.60}{189.54} = 2.0875 \text{ m}^{-1}$$

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

(1)

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

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

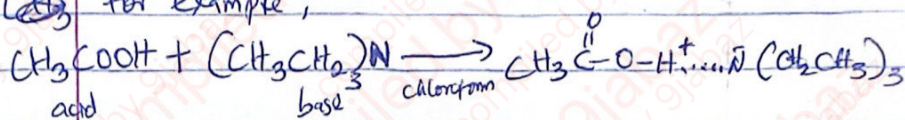
The resistance of a cell containing 0.1

$$(1) \quad \Lambda = \frac{K}{C} = \frac{2.087}{0.05 \times 10^3} = 4.17 \times 10^{-2} \Omega^{-1} \text{mol m}^2$$

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.

~~CH₃~~ 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 Asymmetric 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~~ agitation can help to restore the

Symmetry 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 asymmetric effect. The effect is minimal in dilute solutions because the ions are free.

③ Electrophoretic 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 inter-ionic effects are eliminated. The retarding forces described above are equated with force of electric field, giving rise to an equation which connects the molar conductivity with the electrolyte concentration C . When considering the variation of their conductivity with concentration, strong and weak electrolytes show distinct characteristics. For strong electrolyte, Kohlrausch establishes an empirical relationship

Λ

between Λ (molar conductivity) 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

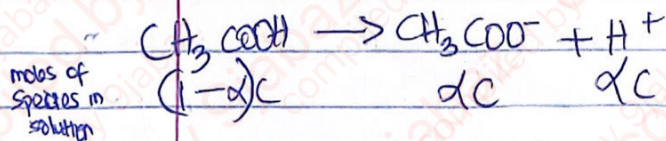
The above equation holds up to concentration in the region of 5 mol dm^{-3} .

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.



$$K = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{\alpha^2 c^2}{(1-\alpha)c} = \frac{\alpha^2 c}{1-\alpha}$$

But if $\alpha \ll 1$

$$K = \alpha^2 C$$

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

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

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

For Kohlsh 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

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

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

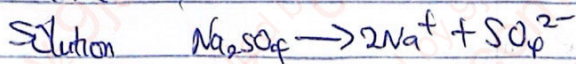
$$K = \Lambda C = \Lambda_+ C_+ + \Lambda_- C_-$$

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

This argument holds for complete dissociation only.

Example 1

The conductivity of a saturated solution of Na_2SO_4 at 25°C is $3.850 \times 10^{-4} \Omega^{-1}\text{m}^{-1}$ and the conductivity of the water used is $0.626 \times 10^{-4} \Omega^{-1}\text{m}^{-1}$. The limiting molar conductivity at zero concentration for Na^+ and $\frac{1}{2}\text{SO}_4^{2-}$ is 12.142×10^{-3} and $8.20 \times 10^{-2} \text{m}^2 \Omega^{-1}\text{mol}^{-1}$ respectively. Calculate the concentration of Na_2SO_4 at this temperature.



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

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

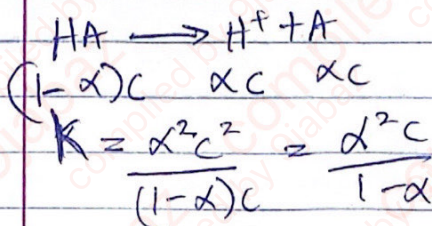
$$= 3.224 \times 10^{-4} \Omega^{-1}\text{m}^{-1}$$

$$\begin{aligned}\Lambda_0 &= \Lambda_0^+ + \Lambda_0^- \\ &= 2(12.142 \times 10^{-3}) + 2(8.20 \times 10^{-3}) \\ &= 40.684 \times 10^{-3} \text{ m}^2 \text{ S}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$C = \frac{k}{\Lambda} = \frac{3.224 \times 10^{-4}}{40.684 \times 10^{-3}} = 7.924 \times 10^{-3} \text{ mol m}^{-3}$$

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 $0.46 \times 10^{-2} \text{ m}^2 \text{ S}^{-1} \text{ mol}^{-1}$ respectively.



Assuming $\alpha \ll 1$

$$K \approx \alpha^2 C$$

$$\alpha^2 = \frac{K}{C} = \frac{1.42 \times 10^{-4}}{0.01 \times 10^3}$$

$$\alpha = \sqrt{\frac{1.42 \times 10^{-4}}{0.01 \times 10^3}} = 3.768 \times 10^{-3}$$

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

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

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

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

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

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

$$= 0.015 \Omega^{-1} \text{m}^{-1}$$

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

18/11/25

* ^{fermentation} Kohlrausch's Law of Independent Migration of Ions

Kohlrausch establish that an increase in molar conductivity results in a decrease in concentration when the molar conductivity of electrolytes were measured as a function of concentration at a constant temperature. The results were interpreted in terms of the independent contribution to conductance of each ion that makes the electrolyte. In other words, the constituent ions of the electrolyte contributes to the molar conductivity of electrolyte at infinite dilution.

$\Lambda_0 (\text{cm}^2 \Omega^{-1} \text{mol}^{-1})$	$\Lambda_0 (\text{m}^2 \Omega^{-1} \text{mol}^{-1})$	Difference
KCl = 149.9	NaCl = 126.5	23.4
KI = 150.3	NaI = 126.9	23.4
KNO ₃ = 147.5	NaNO ₃ = 124.1	23.4
KOH = 270.1	NaOH = 246.7	23.4

The difference is constant for all the pairs and represents the difference between the molar conductivity and infinite dilution of Na^+ and K^+ ions for each pair since the anions are common to both. This shows that the ions move independently in solution. The difference in the Λ_0 of K^+ and Na^+ ions is due to the degree of hydration of each ion. Since the ionic radius of K^+ is greater than the ionic radius of Na^+ ($r_{\text{K}^+} > r_{\text{Na}^+}$), the smaller Na^+ ions are more hydrated than the bigger K^+ ions. Thus the bigger hydrated Na^+ ions move slowly in solution compared to the hydrated K^+ ions.

The Λ_0 of weak electrolyte can be calculated from Kohlrausch law of independent migration of ion because their Λ_0 cannot be determined precisely from the equation $\Lambda_c = \Lambda_0 - b\sqrt{c}$.

The molar conductivity of ethanoic acid can be determined

$$\text{Ans} = 2.12 \times 10^{-2} \text{ m}^2 \text{ S}^{-1} \text{ mol}^{-1}$$

from the molar conductivities of strong electrolyte such as sodium ethanoate, sodium chloride, and hydrochloric acid. The molar conductivity at 180°C at a certain concentration of NH_4OH is $1.31 \times 10^{-2} \text{ m}^2 \text{ S}^{-1} \text{ mol}^{-1}$. Compute the molar conductivity at infinite diffusion (Λ_0) and the degree of dissociation of NH_4OH , if the molar conductivity at 180°C for Ba(OH)_2 , BaCl and NH_4Cl are 2.88×10^{-2} , 1.20×10^{-2} , and $1.29 \times 10^{-2} \text{ m}^2 \text{ S}^{-1} \text{ mol}^{-1}$ respectively.

$$2\Lambda_0(\text{NH}_4\text{OH}) = \Lambda_0(\text{Ba(OH)}_2) + 2\Lambda_0(\text{NH}_4\text{Cl}) - \Lambda_0(\text{BaCl}_2)$$

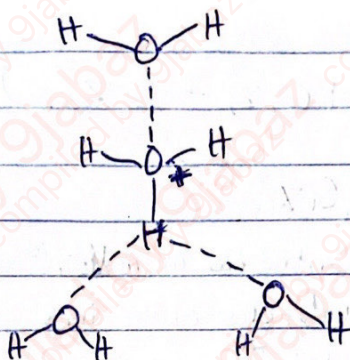
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Proton Jump Mechanism

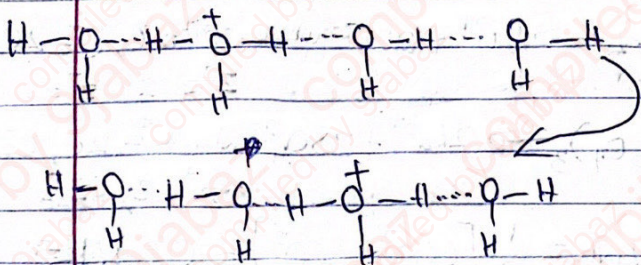
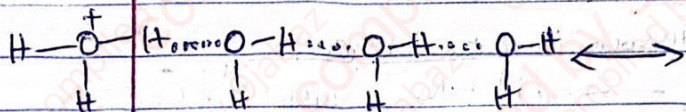
The molar conductivities at infinite dilution of some electrolytes were measured as $\Lambda_0 \text{ HCl} = 4.10 \times 10^{-2}$, $\Lambda_0 \text{ NaCl} = 1.26 \times 10^{-2}$, $\Lambda_0 \text{ NaOH} = 2.46 \times 10^{-2} \text{ m}^2 \text{ S}^{-1} \text{ mol}^{-1}$.

Comparing the obtained values indicates that H^+ and OH^- have higher mobilities than those of Na^+ and Cl^- ions. The mechanism responsible for these high mobilities of H^+ and OH^- is called proton jump mechanism.

The proton ions for trihydrate of H_3O^+ with a moiety structure



The high mobility of the structure is hinged on the positive that is on the H_3O^+ and it can be transferred to a nearby water molecule by converting a covalent bond to a hydrogen bond and vice versa.



Tonic

Tonic strength of an electrolyte has to do with the measure of an electrical environment in solution. It can be defined as,

$$I = \frac{1}{2} \sum (C_i Z_i^2 + C_2 Z_2^2 + C_3 Z_3^2)$$

$$\text{or } I = \frac{1}{2} \sum C_i Z_i^2$$

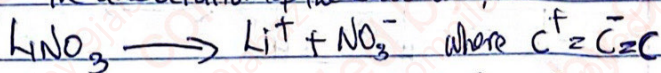
where C_i are concentrations in mol dm^{-3} and

Z_i are the valencies of the ions

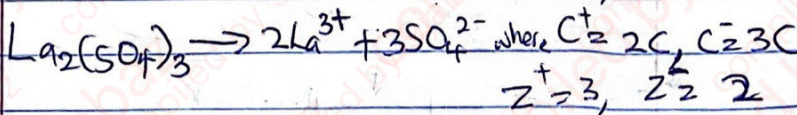
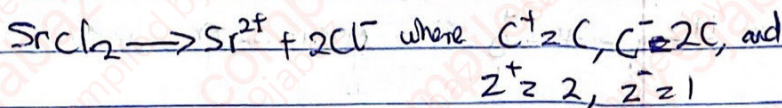
In the case of a 1:1 ions of an electrolyte, the molarity is equal to the ionic strength. For example, the ionic strength of the electrolyte, ~~for example~~,

LiNO_3 , SrCl_2 , $\text{La}_2(\text{SO}_4)_3$ are determined as follows:

The dissociation of the salt are;



$$\text{and } Z^+ = Z^- = 1$$



$$I_{\text{LiNO}_3} = \frac{1}{2} [C(1)^2 + C(1)^2] = C \text{ mol dm}^{-3}$$

$$I_{\text{SrCl}_2} = \frac{1}{2} [C(2)^2 + 2C(1)^2] = 3C \text{ mol dm}^{-3}$$

$$I_{\text{La}_2(\text{SO}_4)_3} = \frac{1}{2} [2C(3)^2 + 3C(2)^2] = 15C \text{ mol dm}^{-3}$$

Thus, the concentration and valences are the determining factors for calculating ionic strength in solution.

Example:

Calculate the ionic strength of the solution obtained by mixing

① 20 cm^3 of 0.10 mol dm^{-3} KCl with 30 cm^3 of 0.01 mol dm^{-3}

BaCl_2

② 15 cm^3 of 0.02 mol dm^{-3} NaOH with 20 cm^3 of 0.01 mol dm^{-3}

H_2SO_4

solution.

$$\text{No. of mol of KCl} = 20 \times 10^{-3} \times 0.1 \text{ mol dm}^{-3} = 2 \times 10^{-3} \text{ moles}$$

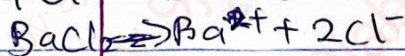
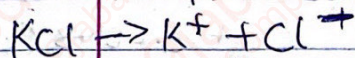
$$\text{No. of mole of BaCl}_2 = 30 \times 10^{-3} \times 0.01 = 0.3 \times 10^{-3} \text{ mole}$$

$$\text{Volume of solution} = 20 + 30 = 50\text{ cm}^3$$

$$\text{New molarity of KCl} = \frac{2 \times 10^{-3}}{50 \times 10^{-3}} = 0.04 \text{ mol dm}^{-3}$$

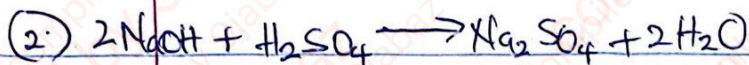
$$\text{New molarity of BaCl}_2 = \frac{0.3 \times 10^{-3}}{50 \times 10^{-3}} = 0.006 \text{ mol dm}^{-3}$$

But the ions in the solution are K^+ , Cl^- , Ba^{2+}



$$I = \frac{1}{2} \left[0.04(1)^2 + 0.04(1)^2 + 0.06(2)^2 + 0.06(1)^2 \right]$$

$$I = 0.058 \text{ mol dm}^{-3}$$



$$\text{no. of mole of NaOH} = 15 \times 10^{-3} \times 0.02 = 3 \times 10^{-4} \text{ mole}$$

$$\text{no. of moles of H}_2\text{SO}_4 = 20 \times 10^{-3} \times 0.01 = 2 \times 10^{-4} \text{ mole}$$

From the equation of reaction, 2 moles of NaOH $\equiv$ 1 mole of H_2SO_4

$$\text{Thus } 3 \times 10^{-4} \text{ mole of NaOH} \equiv 1.5 \times 10^{-4} \text{ mole of H}_2\text{SO}_4$$

So H_2SO_4 will be in excess $(2 \times 10^{-4} - 1.5 \times 10^{-4})$

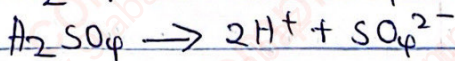
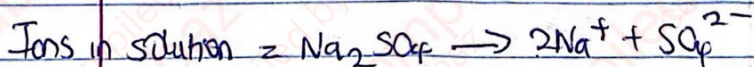
$$= 0.5 \times 10^{-4} \text{ mol from the rxn above.}$$

$$\text{no. of mole of Na}_2\text{SO}_4 = \frac{1}{2}(3 \times 10^{-4}) = 1.5 \times 10^{-4} \text{ mole}$$

$$\text{Volume of solution} = 15 + 20 = 35 \text{ cm}^3$$

$$\text{Molarity of Na}_2\text{SO}_4 = \frac{n}{V} = \frac{1.5 \times 10^{-4}}{35 \times 10^{-3}} = 0.00429 \text{ mol dm}^{-3}$$

$$\text{Molarity of H}_2\text{SO}_4 = \frac{0.5 \times 10^{-4}}{35 \times 10^{-3}} = 0.00143 \text{ mol dm}^{-3}$$



$$I = \frac{1}{2} \left[2(0.00429)(1)^2 + 0.00429(2)^2 + 2(0.00143)(1)^2 + 0.00143(2)^2 \right]$$

$$I = 0.01716 \text{ mol dm}^{-3}$$

Debye - Huckel Theory

According to ~~Debye~~^{Peter Debye} ~~Huckel~~, and ~~Erck~~^{Erck} Huckel, there are electrostatic forces between charged ions in solution which causes ions to form pairs and that there is ionic atmosphere of opposite charge formed around the central ion. The properties of the central ion are influenced by the interaction of the central ion and its atmosphere.

The nature of the ionic atmosphere is determined mainly by the velocities of the ions in solution and the concentration of the solution. The Debye - Huckel equation is given as;

$$\log \gamma_{\pm} = \frac{-A/z_+ z_- / \sqrt{I}}{1 + B a \sqrt{I}} \quad \text{--- (1)}$$

But $K = B \sqrt{I}$ is the fundamental quantity of the interionic theory of attraction.

For very dilute solution; $B a \sqrt{I} \ll 1$, i.e. the denominator is very little compared to unity (1). Thus, for such conditions the Debye - Huckel limiting law becomes

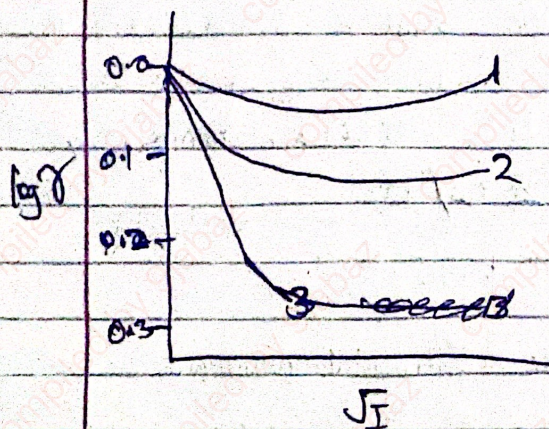
$$\log \gamma_{\pm} = -A/z_+ z_- / \sqrt{I} \quad \text{--- (2)}$$

In aqueous solution, there are brief interactions between ions and solvents, and between ions that are not covered by Debye - Huckel's sphere. ² This forces can be modified

by adding a linear term in concentration to the equation to give an empirical fit as

$$\log \gamma_{\pm} = \frac{-A/z_+z_-/\sqrt{I}}{1 + B\sqrt{I}} + CI \quad (3)$$

C is a constant that can be adjusted to give a smoother experimental curve



Curve 3 obeys the limiting law as presented by eqn (2) at low concentrations. The experimental Curve 2 obeys eqn (1) and Curve 1 obeys eqn (3)

Application of the Debye-Huckel Equation

The various forms of the equations resulting from the Debye-Huckel theory find practical application in the determination of activity coefficients and make possible

the determination of thermodynamic data

- ① Determination of thermodynamic equilibrium constant
- ② Effect of ionic strength on ion reaction rate in solution

Application of Conductivity Measurement

- ① Determination of solubilities of 'Sparingly Soluble salts': At infinite dilution, a very little amount of sparingly soluble salt is in solution to form ions such that

$$\Lambda_s = \Lambda_0 \quad \text{and} \quad \Lambda_0 = \frac{k}{C}$$

Thus, the solubilities, $C = \frac{k}{\Lambda_0}$ or $C = \frac{K}{\Lambda_0^+ + \Lambda_0^-}$

For a 1:1 electrolyte,

solubility product $K_{sp} = C^2$

For a 2:1 or 1:2 electrolyte

$$K_{sp} = 4C^3$$

Example

The electrolytic conductivity of $0.001 \text{ mol dm}^{-3}$ of Na_2SO_4 is $2.6 \times 10^{-2} \Omega^{-1} \text{ m}^{-1}$. If the solution is saturated with CaSO_4 , the conductivity rises to $7.0 \times 10^{-2} \Omega^{-1} \text{ m}^{-1}$.

Calculate the solubility product for CaSO_4 given the ionic molar conductivity.

$\Lambda_{\text{Na}^+} = 5.00 \times 10^{-3} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1}$ and $\Lambda_{\frac{1}{2}\text{Ca}^{2+}} = 5.95 \times 10^{-3} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1}$ at this concentration.

Solution

$$k_{\text{CaSO}_4} = (7.0 \times 10^{-2}) - (2.6 \times 10^{-2}) = 4.4 \times 10^{-2} \Omega^{-1} \text{ m}^{-1}$$

$$\Lambda_{\text{Na}_2\text{SO}_4} = \frac{k}{c} = \frac{2.6 \times 10^{-2}}{0.001 \times 10^3} = 2.6 \times 10^{-2} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1}$$

$$\Lambda_{\text{Na}_2\text{SO}_4} = \Lambda_{2\text{Na}^+} + \Lambda_{\text{SO}_4^{2-}}$$

$$2.6 \times 10^{-2} = 2(5.0 \times 10^{-3}) + \Lambda_{\text{SO}_4^{2-}}$$

$$\Lambda_{\text{SO}_4^{2-}} = (2.6 \times 10^{-2}) - (1.0 \times 10^{-2}) \\ = 1.6 \times 10^{-2} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1}$$

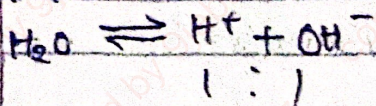
$$\Lambda_{\text{CaSO}_4} = \Lambda_{\text{Ca}^{2+}} + \Lambda_{\text{SO}_4^{2-}} \\ = 2(5.95 \times 10^{-3}) + (1.6 \times 10^{-2})$$

$$= 2.79 \times 10^{-2} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1}$$

$$C_{\text{CaSO}_4} = \frac{k_{\text{CaSO}_4}}{\Lambda_{\text{CaSO}_4}} \Rightarrow \Lambda_{\text{CaSO}_4} = \frac{k_{\text{CaSO}_4}}{C_{\text{CaSO}_4}}$$

$$C_{\text{CaSO}_4} = \frac{4.4 \times 10^{-2}}{2.79 \times 10^{-2}} = 1.58 \text{ mol dm}^{-3} \\ = 1.58 \times 10^{-3} \text{ mol dm}^{-3}$$

② Determination



$$K_w = C^2$$

$$= [1.01 \times 10^{-5}] [1.01 \times 10^{-5}]$$

$$K_w = 1.02 \times 10^{-10}$$

③ Determination of Dissociation Constant Weak Electrolyte for weak electrolytes,

$$K = \frac{\alpha^2 C}{1 - \alpha} ; \text{ but } \alpha = \frac{\Lambda_c}{\Lambda_0}$$

$$\text{So } K = \frac{\Lambda_c^2 C}{\Lambda_0^2} = \frac{\Lambda_c^2 C}{\Lambda_0 (\Lambda_0 - C)}$$

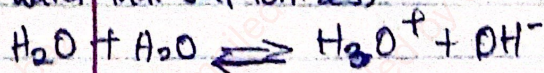
④* Conductometry Titration: This involves the replacement of fast moving H^+ by a slower moving metal ion. There are four common types are;

① Titration of a strong acid and a strong base
e.g. $\text{KOH} + \text{HCl} \rightarrow \text{HCl} + \text{H}_2\text{O}$

$$K_{sp} = [Ca^{2+}] [SO_4^{2-}] = [1.58 \times 10^{-3}]^2 \\ = 2.5 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6}$$

(2) Determination of the ionic product of self ionizing products.

For water that self ionizes,



$$K_w = [H_3O^+] [OH^-]$$

$$K_w = C^2. \quad \text{That is, } [H_3O^+] = [OH^-] = C$$

The conductivity K for pure water and molar conductivity at ∞ (Λ_0 for H^+ and Λ_0 for OH^-) at infinite dilution can be determined. The solubility $C = \frac{K}{\Lambda_0} = \frac{K}{\Lambda_0^+ + \Lambda_0^-}$

$$\text{solubility product } K_{sp} = K_w = C^2$$

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The conductivity of pure water at 25°C is $5.54 \times 10^{-8} \Omega^{-1} \text{ m}^{-1}$. If the molar conductivity of H^+ and OH^- ions at this temperature are 349.8 and 198.5 $\text{m}^2 \text{ mol}^{-1}$ respectively. Find the ionic product of water.

solution

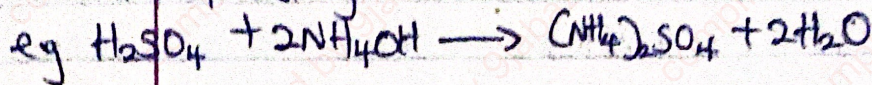
$$\Lambda_0(H_2O) = 349.8 + 198.5 = 548.3 \text{ m}^2 \text{ mol}^{-1}$$

$$\Lambda_0 = \frac{K}{C} \Rightarrow C = \frac{K}{\Lambda_0} = \frac{5.54 \times 10^{-8}}{548.3} = 1.01 \times 10^{-10} \text{ mol m}^{-3}$$

(i) Titration of a weak acid and a strong base



(ii) Titration of a strong acid and a weak base



(iv) Ionic Activities

Ionic Activities

The properties of electrolytes deviates from ideal behaviour due to ^{inter-ionic} ~~inter-ionic~~ ~~force~~ interactions. Except at infinite dilution, the properties of one ion are influenced by the presence of the atmosphere of opposite charged ions with which it interacts. This ion-ion influence leads to activity coefficient. Activity coefficient of a solution is a measure of the extent of interaction of ions in solution.

The behaviour of a solute can be given thermodynamically as;

$$M_1 = M_1^\circ + RT \ln C_1 \quad \text{--- ①}$$

* Ionic activity, Pg. 75

* Measurement of activity, Pg. 77-82

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Transport Properties

The transport number of an ion is defined as the fraction of the total current carried by an ion, through a solution. It can also be determined using molar conductivity.

$$t_+ = \frac{\Lambda_0^+}{\Lambda_0^+ + \Lambda_0^-}$$

$$t_i = \frac{\Lambda_i}{\Lambda_0}$$

For ions in solution;

- ① Current is transported in solution through the movement of ions
- ② The fraction of total current carried by each ion may not be the same.
- ③ The total current $t_+ + t_- = 1$, and the ions with higher part of the current migrate faster in solution
- ④ The current carried by the positive and negative

* Hittorf rule *

There are two methods used for measuring transport numbers.

① Hittorf Method of Measuring Transport Number

An electrolytic experiment is set up, and a direct current is passed which causes a change in concentration around each electrode. Under the influence of an applied current, there is migration of cation to the cathode compartment, and away from the anode compartment. While anions migrate to the anode compartment and away from the cathode compartment. The speed of anion moving away from the cathode is proportional to the fall of concentration of anions around the cathode. The same observation is made for the cations.

Thus, Hittorf's rule states that the loss of concentration around any electrode is proportional to the speed of the ion moving away from it.

$$\text{Thus, } \frac{\text{fall around anode}}{\text{loss around cathode}} = \frac{v^+}{V^-} = \frac{t^+}{1-t^+}$$

$$\text{And } t^+ = \frac{\text{loss around anode}}{\text{loss around anode and cathode}}$$

11.10

Ions are,

$$I_+ = \frac{n^+ v^+ z^+ e}{d}, \quad I_- = \frac{n^- v^- z^- e}{d}$$

where n is the number of ions

z = charge

v = speed of ion in solution

e = electronic charge

d = distance between the parallel plate through which current enters and leaves the solution

$$\begin{aligned} I &= I_+ + I_- \\ &= \frac{n^+ v^+ z^+ e + n^- v^- z^- e}{d} \end{aligned}$$

for a neutral salt $n^+ z^+ = n^- z^-$

$$\therefore I = \frac{n^+ z^+ e (v^+ + v^-)}{d}$$

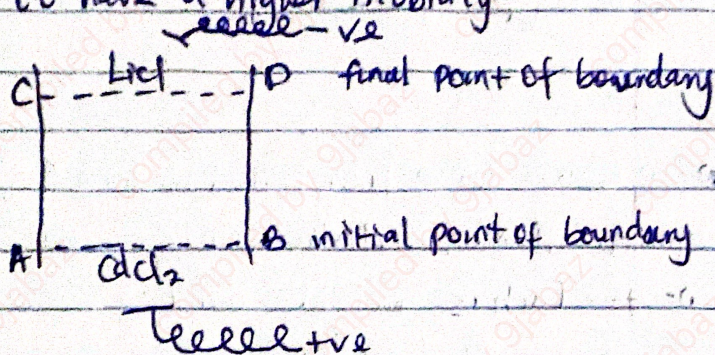
Current Carried by

$$\text{cation } t_+ = \frac{v^+ A^+ z^+ e}{A^+ z^+ e (v^+ + v^-)}$$

$$t_+ = \frac{I_+}{I}$$

$$\therefore t_+ = \frac{v^+}{v^+ + v^-} \quad (\text{cancel } A^+ z^+ e)$$

is added on top of the second electrolyte, CdCl_2 which is referred to as the indicator electrolyte while the H^+ is referred to as the leading ion. It is necessary for the H^+ to have a higher mobility.



When the current is turned on, the H^+ ion migrate to the cathode and evolves as H_2 gas while the Cd^{2+} migrates upwards taking the place of the H^+ and the boundary between the solution moves upwards.

The moving boundary method is based on the difference between the molar conductivity of the ions. For a given quantity of electricity passed through the cell, the volume swept is estimated and it is used to calculate the transport number t_{H^+} . If the boundary moves a distance x for the passage of electricity Q coulombs. The volume swept will be

$$V = \frac{t_{\text{H}^+} Q}{FC Z^+} \quad 31$$

where C = concentration
 z = charge

If the cross sectional area of the tube is " a ", then the volume

$$V = x a$$

$$x a = \frac{t_+ Q}{F C z^+} \Rightarrow t_+ = \frac{F C z^+ x a}{Q}$$

$$t_+ + t_- = 1$$

Example

In a moving boundary experiment to determine the cation transport number in 0.02 mol dm^{-3} LiCl solution, a current of $1.60 \times 10^{-3} \text{ A}$ cost the boundary to move a distance x of $7 \times 10^{-2} \text{ m}$ in 0.6705 hrs . If the cross section of the transport tube is $1.115 \times 10^{-5} \text{ m}^2$. Calculate the transport number for the cation and anion solution

~~Q/G~~

$$t_+ = \frac{F C z^+ x a}{Q}$$

$$t_+ = \frac{96500 \times 0.02 \times 10^3 \times 7 \times 10^{-2} \times 1.115 \times 10^{-5}}{1.6 \times 10^{-3} \times 0.6705 \times 60 \times 60}$$

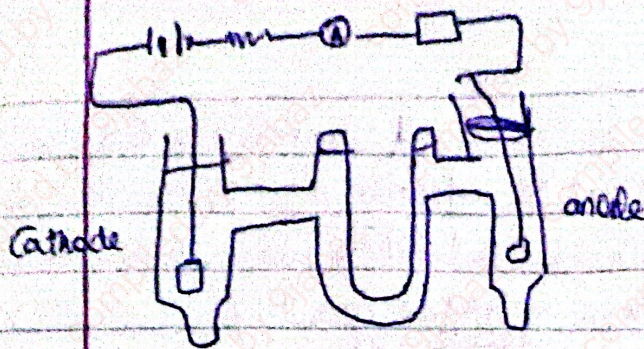
$$t_+ = 0.1029 \quad t_+ = 0.1029$$

$$t_+ + t_- = 1$$

$$t_- = 1 - t_+$$

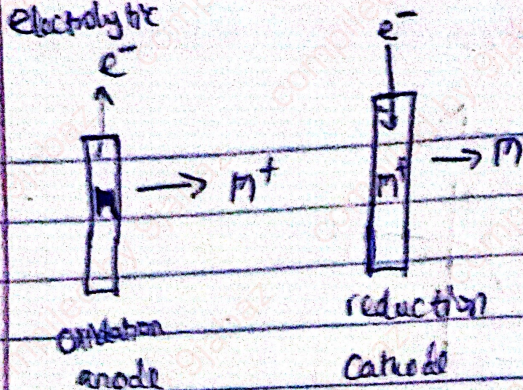
$$t_- = 1 - 0.39$$

$$t_- = 0.61$$



A known current for a known period of time to give $Q = It$. The solution around the electrode in each electrolyte compartment is run-off. Each is weighed and then analyzed to give the number of grams of electrolytes per given mass of electrolyte solution run-off. From this, the change in concentration around each electrode can be determined. Comparison with the theoretically expected change in concentration enables the transport number to be found.

- (2) Moving Boundary Method of Measuring Transport Number
 This is based on the observed rate of movement under the influence of an applied emf of a sharp boundary between solutions of two different electrolytes having a common ion. e.g. HCl and CdCl_2 .
 If the transport number of LiCl is required, the HCl



Heterogeneous electrolytic reaction.

The rate of a heterogeneous electrolytic reaction can be expressed as the number of equivalents of reaction that takes place per unit time

$$\frac{dN}{dt} = ?$$

Recall that $N = \frac{Q}{F}$

$$Q = It$$

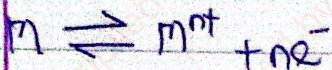
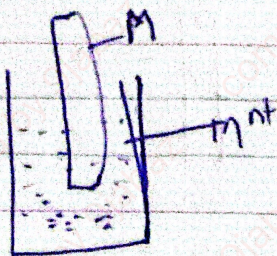
$$\Rightarrow N = \frac{It}{F}$$

$$\therefore \frac{dN}{dt} = \frac{I}{F}$$

This means that the rate of reaction can be expressed in terms of equivalents per seconds.

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Prof. Owayemi



By convention, electric potential is taken as reduction potential.

The amount of material deposited or dissolved depends on the quantity of electricity. To deposit one mole of electron we require 96500 C of electricity.

The charge of the electron is;

$$\begin{aligned} 6.022 \times 10^{23} \text{ electron} &\equiv 96500 \text{ C} \\ 1 e^- &= \frac{96500 \text{ C}}{6.022 \times 10^{23}} \\ &= 1.602 \times 10^{-19} \text{ C} \end{aligned}$$

The number of equivalent of material deposited/dissolved;

$$N = \frac{Q}{F}$$

where $1 \text{ F} \approx 96500 \text{ C}$ (1F)

$$\text{Also } \Rightarrow I = f \frac{dn}{dt}$$

This means that the current flowing is directly proportional to the rate of the reaction such that the rate of electrolysis can be expressed in terms of electrons flowing.

This also implies that the rate of the reaction can be controlled by controlling the flow of current.

The current flow per unit area of the electrode is called the current density, i.e.

$$j = \frac{I}{A}$$

Substituting for this for the expression in the rate of reaction we can write that

$$\frac{dn}{dt} = j \frac{A}{f}$$

$$\text{Such that } j = \frac{f}{A} \frac{dn}{dt}$$

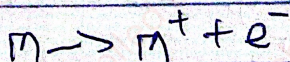
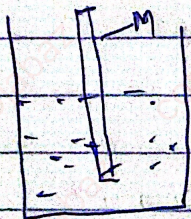
In one word, the current density is equal to the coulomb flux in the unit of ~~C/m²~~ Coulombs per area per time.

We can also relate the rate of electrode reaction to electron flux; $j = \frac{1}{f} \frac{dn}{A dt}$

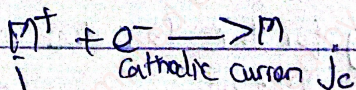
For a single electron transfer process, the chemical flux will be equals to the electron flux, i.e. the mole of substance transferred per unit area per time must be equal to the mole of electrons flowing per unit area per time

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$$K[C] = \frac{j}{F}$$



anodic current j_a



Cathodic current j_c

$$j_{net} = j_a - j_c$$

Anode $\rightarrow$ oxidation

$$K[C] = \frac{j}{F}$$

K = rate constant (s^{-1})

$[C]$ = mole per area deposited or dissolved

From the equality of the chemical and electron flux, we can write that

$$j = FK[C]$$

The implication of this is that current density is dependent on concentration of materials near the

electrode and independent on the size of the electrode

The current density is also dependent on the nature of half reaction, i.e it is a function of the nature of the electrode material

Later we are going to show that the electron density is a function of potential.

Therefore; from $j_{net} = j_a - j_c$
 $= F K_a [Red] - F K_c [Ox]$

In the presence of a zero external field, the net electron density is zero. In other words the system is in a state of equilibrium i.e no net flow of electron, $j_{net} = 0$ i.e electrons are continually transferred in both directions but no net transfer

$$\Rightarrow F K_a [Red] = F K_c [Ox]$$

However for a cell producing current, there is an imbalance of electron transfer, such that there is a net flow of electrons either into the electrode or into solution

For an ion to participate in charge transfer at an electrode, it must migrate towards electrons

$M^{+}_{(aq)} \rightarrow$ hydrated metal ion

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For any reaction to occur, the ion/electron must overcome the energy barrier before being transformed to the desired product.

For the anodic current, we can write that;

$$R_a = B_a e^{-\frac{\Delta G_a^{\ddagger}}{RT}}$$

For the Cathodic current;

$$R_c = B_c e^{-\frac{\Delta G_c^{\ddagger}}{RT}}$$

$$\therefore j_{net} = F B_a e^{-\frac{\Delta G_a^{\ddagger}}{RT}} [\text{red}] - F B_c e^{-\frac{\Delta G_c^{\ddagger}}{RT}} [\text{oxid}]$$

For the Cathodic current!

$$\Delta G_c^{\ddagger} = \Delta G_c^{\ddagger} + \alpha F \Delta \phi \quad \left(\begin{array}{l} \text{discharge is taking place} \\ M^{+} + e^{-} \rightarrow M \end{array} \right)$$

α = transfer coefficient

ϕ = electrode potential difference

For the anodic current

$$\Delta G_a^{\ddagger} = \Delta G_a^{\ddagger} - (1-\alpha) F \Delta \phi \quad \left(\begin{array}{l} \text{oxidation is taking place} \\ M \rightarrow M^{+} + e^{-} \end{array} \right)$$

Principles and application of electrochemistry by crowle

Net current density; $j_{net} = j_a - j_c$

$$\Rightarrow j_{net} = (F B_a [Red] e^{-\frac{\Delta G_a^\ddagger}{RT}}) e^{(1-\alpha) \frac{F \Delta \phi}{RT}} - (F B_c [Ox] e^{-\frac{\Delta G_c^\ddagger}{RT}}) e^{\frac{\alpha F \Delta \phi}{RT}}$$

$$\Rightarrow j_{net} = \left[\underbrace{(F B_a [Red] e^{-\frac{\Delta G_a^\ddagger}{RT}})}_{\text{anodic current density}} e^{(1-\alpha) \frac{F \Delta \phi}{RT}} \right] - \left[\underbrace{(F B_c [Ox] e^{-\frac{\Delta G_c^\ddagger}{RT}})}_{\text{cathodic current density}} e^{\frac{\alpha F \Delta \phi}{RT}} \right]$$

Since the net current density is zero at equilibrium, we can write that the anodic current density is cathodic current density

$$j_{a,e} = j_{c,e} = j_e$$

Such that the shift in electrode potential at equilibrium is known as the over potential, also known as over voltage

$$\eta = \Delta \phi - \Delta \phi_e$$

$$j_a = \left\{ F B_a [Red] e^{-\frac{\Delta G_a^\ddagger}{RT}} e^{(1-\alpha) \frac{F \Delta \phi_e}{RT}} \right\} e^{(1-\alpha) \frac{F \eta}{RT}}$$

$$= j_{a,e} e^{(1-\alpha) \frac{F \eta}{RT}}$$

Similarly

$$j_c = j_{c,e} e^{-\frac{\alpha F \eta}{RT}}$$

At equilibrium

$$j_c = j_a e^{-\alpha_2 F/RT}$$

$$j_{net} = j_a - j_c$$

$$= j_a \left(e^{-(1-\alpha)F\eta/RT} - e^{-\alpha F\eta/RT} \right)$$

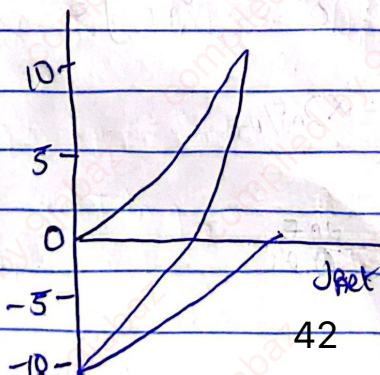
Butler-Volmer equation

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$$j_{net} = j_0 \left[\exp \left(\frac{(1-\alpha)F\eta}{RT} \right) - \exp \left(-\frac{\alpha F\eta}{RT} \right) \right]$$

over potential

A plot of the net current density against η is known as the polarization curve



The Butler-Volmer equation gives two limiting cases

(1) The limits of very small η volume, i.e. $\frac{F\eta}{RT} \ll 1$
 where $\eta \ll \frac{RT}{F}$

Using the approximation, $e^x \approx 1 + x$

such that the Butler-Volmer equation becomes

$$j = j_0 \left[1 + \frac{(1-\alpha)F\eta}{RT} - 1 + \frac{\alpha F\eta}{RT} \right]$$

$$j = j_0 \left[1 + \frac{F\eta}{RT} - \frac{\alpha F\eta}{RT} - 1 + \frac{\alpha F\eta}{RT} \right]$$

$$j \approx j_0 \frac{F\eta}{RT}$$

The value of the exchange current density ^{or net} determines the deviation of the electrode potential from the equilibrium value. The greater the deviation, the slower the electrode reaction. It follows therefore, ~~the potential deviation~~:

$$\left(\frac{\partial j}{\partial \eta} \right)_{\eta \rightarrow 0} = \frac{j_0 F}{RT}$$

The inverse of $\left(\frac{\partial j}{\partial \eta} \right)_{\eta \rightarrow 0}$ is polarization resistant, i.e. at equilibrium potential

$$R_p \approx \frac{RT}{j_0 F}$$

- ② When η is very large, in the limits of large overpotential, where $\eta \gg \frac{RT}{F}$

The second term in the Butler-Volmer equation is much larger than the first term.

We can write therefore,

$$j = j_0 \exp\left(\frac{(1-\alpha)F\eta}{RT}\right) \text{ when } \eta = +ve \text{ and large}$$

$$j = -j_0 \exp\left(-\frac{\alpha F\eta}{RT}\right) \text{ when } \eta = -ve \text{ and large}$$

The absolute value of j ,

$$|j| = j_0 \exp\left(-\frac{\alpha F\eta}{RT}\right)$$

Taking $\ln$ of both expression when η is -ve and large

$$\ln |j| = \ln j_0 - \frac{\alpha F\eta}{RT}$$

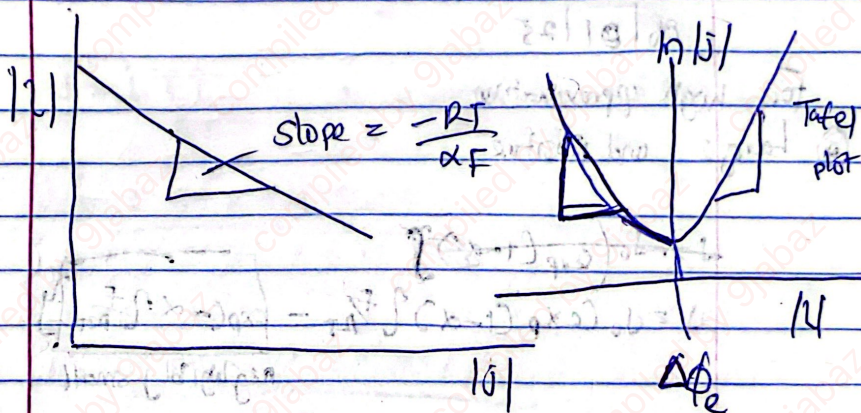
$$\text{or } \frac{\alpha F\eta}{RT} = \ln j_0 - \ln |j|$$

Such that

$$\eta = \frac{RT \ln j_0}{\alpha F} - \frac{RT}{\alpha F} \ln |j|$$

$$\therefore |i| = \frac{RT}{\alpha F} \ln j_0 - \frac{RT}{\alpha F} \ln |j| \quad \text{--- Tafel equation}$$

Such that the plot of $|i|$ and $|j|$



- a) i is +ve, when anode is smaller than that of the cathode
 i is -ve, if there's more current to the anode than the cathode

The Tafel equation is obtained from the Butler-Volmer equation in the limit where the overpotential is very large. The Tafel equation can be written in the form;

$$|i| = a + b \log |j|$$

∴ For an anodic process;

$$q = \frac{-2.303RT}{(1-\alpha)F} \log_{10} j_0$$

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for high approximation

① Large and positive

~~$$j = j_0 (\exp(1-\alpha) \eta_{RT})$$~~

$$j = j_0 (\exp(1-\alpha) \eta_{RT} - \exp(-\alpha \eta_{RT}))$$

negligibly small

$$j \approx j_0 (\exp(1-\alpha) \eta_{RT})$$

$$\ln j = \ln j_0 + (1-\alpha) \eta_{RT} \quad \text{for } \eta \text{ large and +ve}$$

For η large and -ve

$$j = -j_0 \exp(-\alpha \eta_{RT})$$

~~$$\ln j = \ln j_0$$~~

$$\ln |j| = \ln j_0 - \alpha \eta_{RT}$$

① If the exchange current density of a standard hydrogen electrode at 298K is 0.79 mA cm^{-2} . What is the current density of this electrode when the overpotential is $+5.0 \text{ mV}$

* The overpotential is deemed small when it is less than 10 mV and deemed high when it is greater than 10 mV

$$j = j_0 \frac{F\eta}{RT}$$

j_0 = exchange current density

$$j = \frac{0.79 \times 96500 \times 5}{8.314 \times 298}$$

$$j = 153.85$$

$$j = \frac{0.79 \times 10^{-3} \times 96500 \times 5 \times 10^{-3}}{8.314 \times 298}$$

② The transfer coefficient of a certain electrode in contact with M^{3+} and M^{4+} in aqueous solution is 0.25 is 0.39 . The current density is found to be 55.0 mA cm^{-2} when the overpotential is 125 mV . What is the overpotential required for a current density of 75 mA cm^{-2} • 47