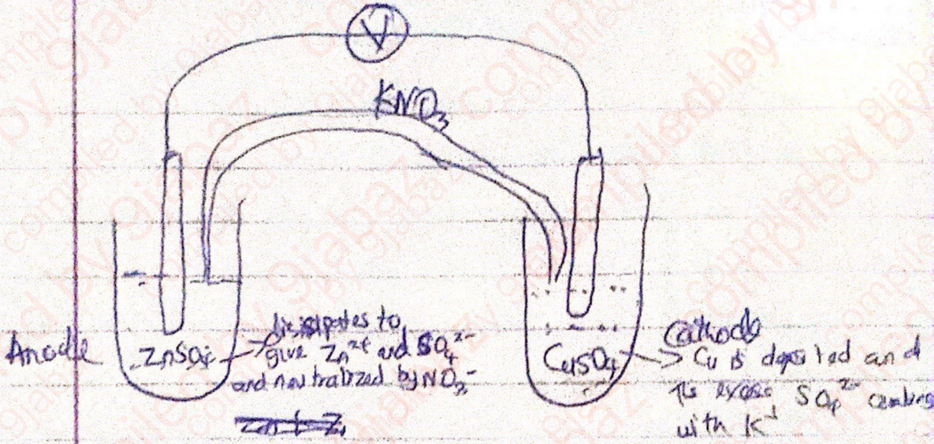


$ZnSO_4$ → dissociates to give Zn^{2+} and SO_4^{2-} and neutralized by NO_3^-

$CuSO_4$ → Cu is deposited and the excess SO_4^{2-} combines with K^+

~~Zn + Zn~~

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

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

The position of electrode in the electrochemical series

Electrical Conductance

deals with movement of ions

Electrical Conductance

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 basises.

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 electron

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 refering to the resistance and resistivity of the electrolytes conductance G, and conductivity κ are used

where $\kappa = \frac{1}{\rho}$ $\therefore R = \frac{l}{\kappa a} \Rightarrow \kappa R = \frac{l}{a}$

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

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

$$K = \frac{l}{Ra} =$$

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

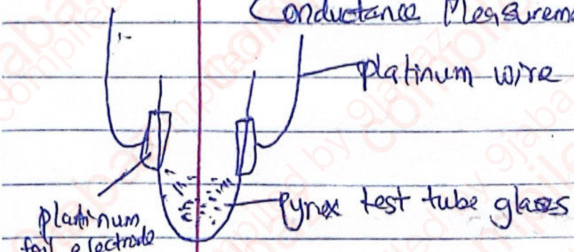
(1) Ion-pair formation / Ion association

One ion is surrounded

The cell constant l/a is the dimensions of a cell and it's 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 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 Measurement



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 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 moldm^{-3} KCl solution and 0.05 moldm^{-3} $AgNO_3$ solution are 307.62 and 189.54 ohms respectively. The conductivity of 0.01 moldm^{-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.

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

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

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

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

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

(i)

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

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

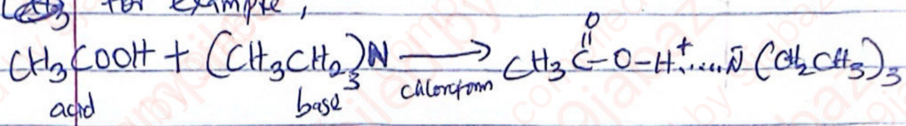
~~The resistance of a cell containing 0.~~

(ii) $\Lambda = \frac{K}{C} = \frac{2.087}{0.05\times10^{3}} = 4.17\times10^{-2}\,\Omega^{-1} mol\, m^{2}$

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 carges in solvents of low dielectric constants unlike water with high dielectric constant.

~~CH_3~~ For example;



$$\underset{acid}{CH_3COOH} + \underset{base}{(CH_3CH_2)_3N} \xrightarrow[chloroform]{} CH_3\overset{O}{\overset{\|}{C}}-O-H^{+}\cdots\bar{N}(CH_2CH_3)_3$$

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 symmentrical. However, the application of thermal ~~applicatio~~ 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 inter ionic 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 Λ

between Λ and $\sqrt{C}$ as follows

$$\Lambda_c = \Lambda_0 - bC$$

where Λ_c = molar conductivity at agiving 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 $\quad (1-\alpha)C \qquad \alpha C \qquad \alpha C$

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

But if $\alpha <<<< 1$

$$K = \alpha^2 C$$

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

$$\kappa = \kappa_+ + \kappa_-$$

And individual ionic molar conductivities can be defined as

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

Therefore $\kappa = \kappa_+ + \kappa_- = \Lambda_+ C_+ + \Lambda_- C_-$

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 $8.20 \times 10^{-3} m^2 \Omega^{-1}$ mo respectively. Calculate the concentration of Na_2SO_4 at this temperature.

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

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

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

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

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

$$= 2(12.142 \times 10^{-3}) + 2(8.20 \times 10^{-3})$$

$$= 40.684 \times 10^{-3}\ m^2 \Omega^{-1} mol^{-1}$$

$$C = \frac{K}{\Lambda} = \frac{3.224 \times 10^{-4}}{40.684 \times 10^{-2}} = 7.924 \times 10^{-3}\ mol\ m^{-3}$$

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 $0.48 \times 10^{-2}\ m^2 \Omega^{-1} mol^{-1}$ respectively.

$$HA \longrightarrow H^+ + A$$

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

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

Assuming $\alpha <<< 1$

$$\therefore K = \alpha^2 c$$

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

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

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

$\Lambda_c = \alpha \times \Lambda_0 = 3.768\times10^{-3} \times (3.50 + 0.48)\times10^{-2}$

$\Rightarrow \Lambda_c = 1.50\times10^{-4}$

$= 0.15\times10^{-3}$

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

$K = \Lambda_c \times C \Rightarrow 0.15\times10^{-3}(0.01\times10^{3})$

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

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

18/11/25

test/exam

* 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 ion of the electrolyte contributes to the molar conductivity of electrolyte at infinite dilution.

$\Lambda_0 (cm^2 \Omega^{-1} mol^{-1})$	$\Lambda_0 (m^2 \Omega^{-1} mol^{-1})$	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. These shows that the ions move independent 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^+ ($r_{K^+} > r_{Na^+}$), the smaller Na^+ ions are more hydrated than the bigger K^+ ions. Thus the bigger hydrated Na^+ ions moves 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

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

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 $1.31 \times 10^{-2}\ m^2\ \Omega^{-1}\ mol^{-1}$ 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 $1.29 \times 10^{-2}\ m^2\ \Omega^{-1}\ mol^{-1}$ respectively

$$2\Lambda_0(NH_4OH) = Ba(OH)_2 + 2\Lambda_0(NH_4Cl) - \Lambda_0(BaCl_2)$$

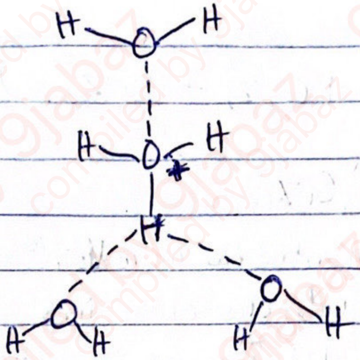
20/11/25

Proton Jump Mechanism

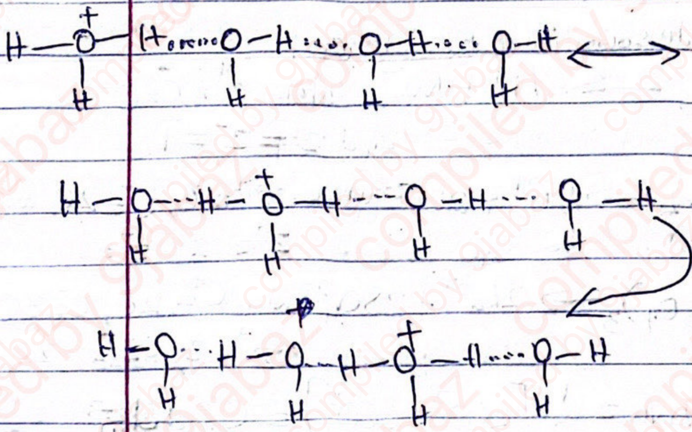
The molar conductivities at infinite dilution of some electrolytes were measured as $\Lambda_0\ HCl = 4.10 \times 10^{-2}$, $\Lambda_0\ NaCl = 1.26 \times 10^{-2}$, $\Lambda_0\ NaOH = 2.46 \times 10^{-2}\ m^2\ \Omega^{-1}\ mol^{-1}$

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 heaped 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 an hydrogen bond and viseversa



Ionic

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

$$I = \frac{1}{2}\sum(C_1 Z_1^2 + C_2 Z_2^2 + C_3 Z_3^2)$$

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~~;
$LiNO_3$, $SrCl_2$, $La_2(SO_4)_3$ are determined as follows;

The dissociation of the salt are;

$LiNO_3 \longrightarrow Li^+ + NO_3^-$ where $C^+ = C^- = C$
and $Z^+ = Z^- = 1$

$SrCl_2 \longrightarrow Sr^{2+} + 2Cl^-$ where $C^+ = C$, $C^- = 2C$, and
$Z^+ = 2$, $Z^- = 1$

$La_2(SO_4)_3 \longrightarrow 2La^{3+} + 3SO_4^{2-}$ where $C^+ = 2C$, $C^- = 3C$
$Z^+ = 3$, $Z^- = 2$

$$I_{LiNO_3} = \frac{1}{2}[C(1)^2 + C(1)^2] = C \text{ mol dm}^{-3}$$

$$I_{SrCl_2} = \frac{1}{2}[C(2)^2 + 2C(1)^2] = 3C \text{ mol dm}^{-3}$$

$$I_{La_2(SO_4)_3} = \frac{1}{2}[2C(3)^2 + 3C(2)^2 = 15C \text{ mol dm}^{-3}$$

Dec 11

Thus, the concentration and valencies 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

No of mol of KCl $= 20\times10^{-3}_{dm^3}\times 0.1\,mol\,dm^{-3} = 2\times10^{-3}$ moles

No. of mole of $BaCl_2 = 30\times10^{-3}\times 0.01 = 0.3\times10^{-3}$ mole

Volume of solution $= 20 + 30 = 50\,cm^3$

New molarity of KCl $= \frac{2\times10^{-3}}{50\times10^{-3}} = 0.04\,mol\,dm^{-3}$

New molarity of $BaCl_2 = \frac{0.3\times10^{-3}}{50\times10^{-3}} = 0.006\,mol\,dm^{-3}$

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

$KCl \rightarrow K^+ + Cl^-$

$BaCl_2 \rightarrow Ba^{2+} + 2Cl^-$

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

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

② $2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$

no. of mole of NaOH $= 15\times10^{-3} \times 0.02 = 3\times10^{-4}$ mole

no. of moles of $H_2SO_4 = 20\times10^{-3} \times 0.01 = 2\times10^{-4}$ mole

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

Thus 3×10^{-4} mole of NaOH $\equiv 1.5\times10^{-4}$ mole of H_2SO_4

So H_2SO_4 will be in excess $(2\times10^{-4} - 1.5\times10^{-4})$

$= 0.5\times10^{-4}$ mol from the rxn above.

no. of mole of $Na_2SO_4 = \frac{1}{2}(3\times10^{-4}) = 1.5\times10^{-4}$ mole

Volume of solution $= 15 + 20 = 35\,cm^3$

Molarity of $Na_2SO_4 = \frac{n}{V} = \frac{1.5\times10^{-4}}{35\times10^{-3}} = 0.00429\ mol\ dm^{-3}$

Molarity of $H_2SO_4 = \frac{0.5\times10^{-4}}{35\times10^{-3}} = 0.00143\ mol\ dm^{-3}$

Ions in solution $= Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$

$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$

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

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

Debye – Huckel Theory

According to Peter Debye ~~Debye – huckel~~, and Erick 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 valencies of the ions in solution and the concentration of the solution. The Debye – Huckel equation is given as;

$$\log \gamma_{I} = \frac{-A|z_{+}z_{-}|\sqrt{I}}{1 + Ba\sqrt{I}} \text{ ——— ①}$$

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

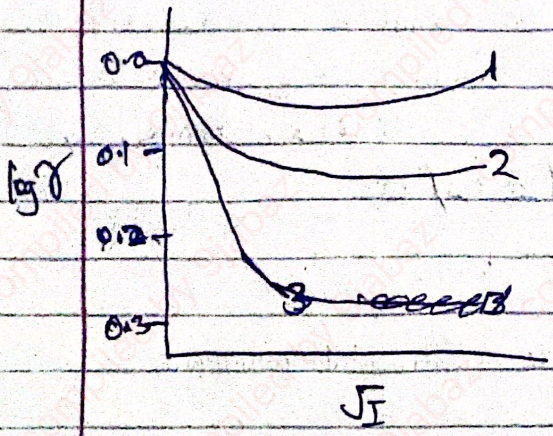
For very dilute solution; $Ba\sqrt{I} \lll 1$, i.e the denominator is very little compared to unity (1). Thus, for such conditions the Debye – Huckel limiting law becomes

$$\log \gamma_{I} = -A|z_{+}z_{-}|\sqrt{I} \text{ ——— ②}$$

In aqueous solution, there are brief interactions between ions and solvents, and between ions that are not covered by Debye – Huckel's sphere. This forces can be modified by adding a linear term in concentration to the equation to give an empirical fit as

$$\log \gamma_\pm = \frac{-A|z_+z_-|\sqrt{I}}{1+Ba\sqrt{I}} + CI \longleftarrow ③$$

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

C - solubility for sparingly soluble salt

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 mol dm^{-3} of Na_2SO_4 is $2.6\times10^{-2}\,\Omega^{-1}m^{-1}$. If the solution is saturated with $CaSO_4$, the conductivity rises to $7.0\times10^{-2}\,\Omega^{-1}m^{-1}$. Calculate the solubility product for $CaSO_4$ given the ionic molar conductivity.

$\Lambda_{Na^+} = 5.00\times10^{-3}$ and $\Lambda_{1/2\,Ca^{2+}} = 5.95\times10^{-3}\,m^2\,\Omega^{-1}\,mol$ at this concentration.

Solution

$$\kappa_{CaSO_4} = (7.0\times10^{-2}) - (2.6\times10^{-2}) = 4.4\times10^{-2}\,\Omega^{-1}m^{-1}$$

$$\lambda_{Na_2SO_4} = \frac{K}{C} = \frac{2.6\times10^{-2}}{0.001\times10^{3}} = 2.6\times10^{-2}\,m^2\,\Omega^{-1}\,mol$$

$$\Lambda_{Na_2SO_4} = \lambda_{2Na^+} + \Lambda_{SO_4^{2-}}$$

$$2.6\times10^{-2} = 2(5.0\times10^{-3}) + \Lambda_{SO_4^{2-}}$$

$$\lambda_{SO_4^{2-}} = (2.6\times10^{-2}) - (1.0\times10^{-2})$$

$$= 1.6\times10^{-2}\,m^2\,\Omega^{-1}\,mol^{-1}$$

$$\lambda_{CaSO_4} = \Lambda_{Ca^{2+}} + \Lambda_{SO_4^{2-}}$$

$$= 2(5.95\times10^{-3}) + (1.6\times10^{-2})$$

$$= 2.79\times10^{-2}\,m^2\,\Omega^{-1}\,mol^{-1}$$

$$C_{CaSO_4} = \frac{\kappa_{CaSO_4}}{\Lambda_{CaSO_4}} \Rightarrow \Lambda_{CaSO_4} = \frac{\kappa_{CaSO_4}}{C_{CaSO_4}}$$

$$C_{CaSO_4} = \frac{4.4\times10^{-2}}{2.79\times10^{-2}} = 1.58\,mol\,dm^{-3}$$

$$= 1.58\times10^{-3}\,mol\,dm^{-3}$$

② Determination

$H_2O \rightleftharpoons H^+ + OH^-$

1 : 1

$k_w = C^2$

$= [1.01 \times 10^{-13}][1.01 \times 10^{-13}]$

$k_w = 1.02 \times 10^{-26}$

③ Determination of Dissociation Constant Weak Electrolyte:

For weak electrolytes,

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

$$\text{So } K = \frac{\frac{\Lambda_c^2 C}{\Lambda_0^2}}{1 - \frac{\Lambda_c}{\Lambda_0}} = \frac{\Lambda_c^2 C}{\Lambda_0(\Lambda_0 - C)}$$

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

① Titration of a strong acid and a strong base

e.g $KOH + HCl \longrightarrow HCl + H_2O$

$K_{sp} = [Ca^{2+}][SO_4^{2-}] = [1.58\times10^{-3}]^2$

$= 2.5\times10^{-6}\,mol^2dm^{-6}$

② Determination of the ionic product of self ionizing products.

For water that self ionizes,

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

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

$K_w = C^2$. That is, $[H_3O^+] = [OH] = C$

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

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

27/11/25

The conductivity of pure water at 25°c is $5.54\times10^{-8}\Omega^{-1}m^{-1}$! If the molar conductivity of H^+ and OH^- ions at this temperature are 349.8 and 198.5 $m^2\Omega^{-1}mol$ respectively. Find the ionic product of water.

solution

$\Lambda_o(H_2O) = 349.8 + 198.5 = 548.3\,m^2\Omega^{-1}mol^{-1}$

$\Lambda_o = \frac{K}{C} \Rightarrow C = \frac{K}{\Lambda_o} = \frac{5.54\times10^{-8}}{548.3} = 1.01\times10^{-10}\,mol\,m^{-3}$

$\longrightarrow 1.01\times10^{-13}\,mol\,dm^{-3}$

(ii) Titration of a weak acid and a strong base
eg $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

(iii) Titration of a strong acid and a weak base
eg $H_2SO_4 + 2NH_4OH \longrightarrow (NH_4)_2SO_4 + 2H_2O$

(iv) ~~Ionic Activities~~

Ionic Activities

The properties of electrolytes deviates from ideal behaviour due to ~~interionic~~ inter-ionic ~~forces~~ 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;

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

75-82

* 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 ions 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 *

know it

There are a two methods used for measuring transport numbe

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 an ion moving away from the cathode is proportional to the fall of concentration of anions aroun 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.

Thus,

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

and

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

'' rej

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 current enters and leaves the solution

~~$I = I_+$~~ $$I = I_+ + I_-$$

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

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

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

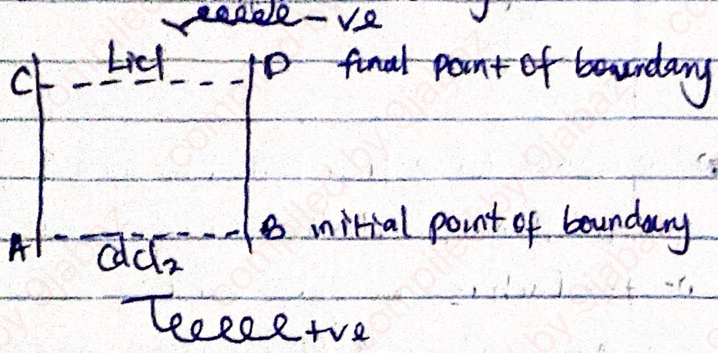
Current carried by

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

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

$$\therefore t_+ = \frac{v^+}{v^+ + v^-}$$ (~~[illegible]~~ ~~[illegible]~~ =

is added on top of the second electrolyte, $CdCl_2$ which is referred to as the indicator electrolyte while the H^+ is refered 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 cathod 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

$$V = \frac{t_+ Q}{FCZ^+}$$

where C = concentration
z = charge

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

$$V = xa$$

$$xa = \frac{t_+ Q}{FCz^+} \Rightarrow t_+ = \frac{FCz^+ xa}{Q}$$

$$t_+ + t_- = 1$$

Example

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

solution

$$t_+ = \frac{FCz^+ xa}{Q}$$

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

$t_+ =$ [illegible]39

$t_+ + t_- = 1$

$t_- = 1 - t_+$

$t_- = 1 - 0.39$

$t_- = 0.61$

Calculate the mean activity coefficient of Na^+ and SO_4^{2-} ~~of the~~ ions in $0.005 moldm^{-3}$ $NaSO_4$ solution @ $25^\circ C$, $A = 0.509$

$$\log \gamma_I = -A|Z_+ Z_-|\sqrt{I}$$

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

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

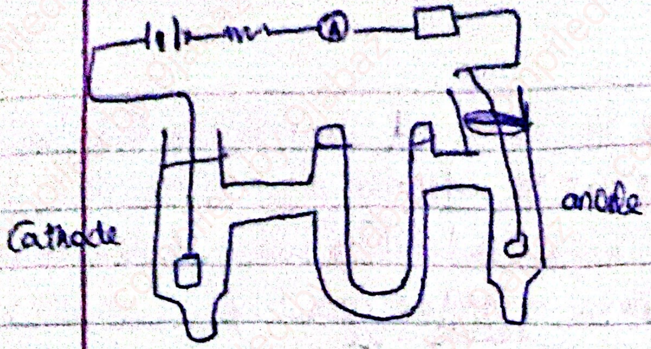
$$\therefore I = \frac{1}{2}\left[2 \times 0.005 \times (1)^2 + 1 \times 0.005 \times (2)^2\right]$$

$$I = 0.015 moldm^{-3}$$

$$\log \gamma_I = -0.509(1 \times 2) \times \sqrt{0.015}$$

$$\log \gamma_I = -0.[illegible]2468$$

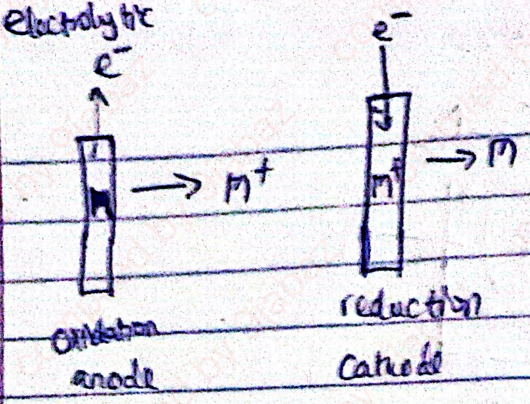
$$\gamma_I = \underline{0.750}$$



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 weighted 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. Comparision with the theoretically expected change in concentration enables the transport number to be found.

② Moving Boundary Method of Measuring Transport Numb

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 HCl is required, the HCl



Heterogeneous electrolytic reaction.

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

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

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

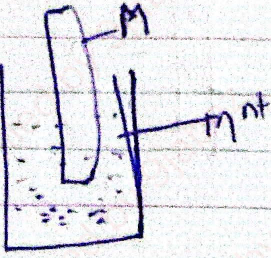
$Q = It$

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

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

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

9/12/25 Rof. Owoyomi



$$M \rightleftharpoons M^{n+} + ne^-$$

By convection, electric potential is taken as reduction potential

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

The Charge of the electron is;

$$6.022 \times 10^{23} \text{ electron} \equiv 96500\,C$$

$$1\,e^- = \frac{96500C}{6.022 \times 10^{23}}$$

$$\simeq 1.602 \times 10^{-19} C$$

The number of equivalent of material deposite/dissolved;

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

where 1 N = 96500 C (1F)

Also => $I = F\frac{dn}{dt}$

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

$$\frac{dn}{dt} = \frac{jA}{F}$$

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

In one word, the current density is equals to the coulomb flux in the unit of [illegible] coulomb per area per time

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

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

$\nearrow$ chemical flux

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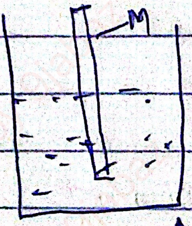
Anode — oxidation

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



$M \rightarrow M^+ + e^-$

anodic current J_a

$M^+ + e^- \longrightarrow M$

cathodic curren J_c

$J_{net} = J_a - J_c$

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

K = rate constan (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 structure of the electrode material
Later we are going to show that the electron density is a function of potential.

Therefore; from $j_{net} = j_a - j_c$

$$= fk_a[Red] - fK_c[Ox]$$

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

$$\Rightarrow fK_a[Red] = fK_c[Ox]$$

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

$M^+_{(aq)}$ → 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;

$$K_a = B_a e^{-\frac{\Delta G_a^{\neq}}{RT}}$$

For the cathodic current;

$$K_c = B_c e^{-\frac{\Delta G_c^{\neq}}{RT}}$$

$$\therefore j_{net} = FB_a e^{-\frac{\Delta G_a^{\neq}}{RT}}[Red] - FB_c e^{-\frac{\Delta G_c^{\neq}}{RT}}[oxid]$$

For the cathodic current!

$$\Delta G^{\neq} = \Delta G_c^{\neq} + \alpha F \Delta \phi$$ (discharge is taking place $M^+ + ne^- \rightarrow M$)

α = transfer coefficient

φ = electrode potential difference

For the anodic current

$$\Delta G^{\neq} = \Delta G_a^{\neq} - (1-\alpha) F \Delta \phi$$ (dissolution is taking place $M \rightarrow M^+ + e^-$)

principles and application of electrochemistry by crowe

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

~~$\Rightarrow J_{net} = \left(FB_a[Red] e^{-\frac{\Delta G_a^\ddagger}{RT}}\right) B^{1-\alpha}$~~

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

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

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

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

$$= j_{a_e} e^{(1-\alpha)\eta F/RT}$$

Similarly

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

Atkins chapter 16 5th edition Dynamic electrochemistry

At equilibrium

$$j_c = j_{c_1} e^{-\alpha \eta F/RT}$$

$$J_{net} = J_a - j_c$$

$$= j_e \left(e^{1-\alpha \frac{nF}{RT}} - e^{-\alpha n F/RT} \right]$$

Butler - Volmer equation

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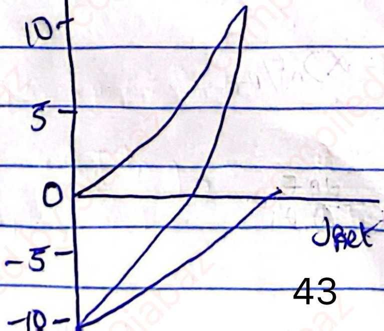
$$J_{net} = j_0 \left[\left(\exp \frac{(1-\alpha) F \eta}{RT} \right) - \left(\exp - \frac{\alpha F \eta}{RT} \right) \right]$$

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 limit of very small η volume, i.e $\frac{F\eta}{RT} << 1$
where $\eta << \frac{RT}{F}$

Using the approximation, $e^x = 1 + x$

Such that the Butler Volmer equation becomes

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

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

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

The value of the $\overset{\text{or net}}{\text{exchange}}$ current density determines the deviation of the electrode potential from the equilibrium value. The greater the deviation, the slower the electrode reaction. It follows therefore, ~~the partial de~~rav:

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

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

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

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

The second term in the butler volmer equation is much larger than the first term.

We can write therefore;

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

$$j = -j_0 \exp \left(\frac{-\alpha F \eta}{R} \right)$$ when η = -ve 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

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

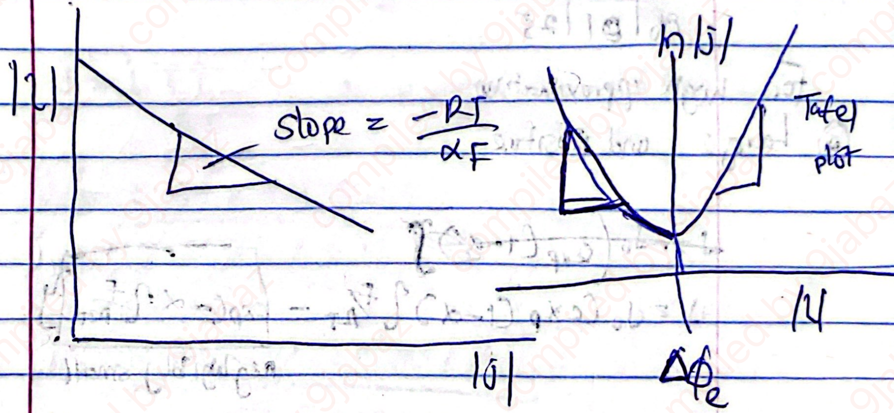
or $$\frac{\alpha F \eta}{RT} = \ln j_0 - \ln |j|$$

Such that

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

$$\therefore |\eta| = \frac{RT}{\alpha F}\ln J_0 - \frac{RT}{\alpha F}\ln|j|$$ — Tafel equation

Such that the ~~p~~plot of $|\eta|$ and $|j|$



- η is +ve, when anode is smaller than that of the cathod
- η 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;

$$|\eta| = a + b\log_{10}|j|$$

∴ for an anodic process;

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

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For high approximation

ⓐ Large and positive

~~$J = J_0 \{ exp (1-$~~ [illegible]

$$J = J_0 (exp (1-\alpha) \eta F/RT - \underbrace{\boxed{exp(-\alpha \eta \frac{F}{RT}}}_{\text{negligibly small}} \})$$

$$J \simeq J_0 (exp (1-\alpha) \eta \frac{F}{RT})$$

$\ln j = \ln j_0 + (1-\alpha) \eta F/RT$ for η large and +ve

For η large and -ve

$$J = -j_0 \exp(-\alpha \eta F/RT)$$

~~$\ln J = \ln J_0$~~

$$\ln|-j| = \ln J_0 - \alpha \eta \frac{F}{RT}$$

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 mV

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

$$j = j_0 \frac{F\eta}{RT}$$ J_0 = exchange current density

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

$$\cancel{\hat{j} = 153.85}$$

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

② The transfer coefficient of a certain electrode in contact with M^{3+} and M^{4+} in aqueous solution is are 25°C is 0.39. The current density is found to be ~~55.0~~ 55.0 mA cm^{-2} when the overpotential is 125mV. What is the overpotential required for a current density of 75 mA cm^{-2}.

~~$J = J_0 (\exp$~~

$J = J_0 \exp (1-\alpha) \frac{F\eta}{RT}$ because η is large and +ve the anodic current predominates

~~$J_0 = \frac{J}{Q}$~~ Given that $\frac{F}{RT} = \frac{96500\,C}{8.314 \times 298\,K}$

$= 38.95\,V^{-1}$

$\Rightarrow \ln J = \ln J_0 + (1-\alpha)F\eta$ where $f = 38.95\,V^{-1}$

$\Rightarrow \ln J_1 = \ln J_0 + (1-\alpha)F\eta_1$

$\ln J_2 = \ln J_0 + (1-\alpha)F\eta_2$

$\ln J_2 - \ln J_1 = (1-\alpha)F\eta_2 - (1-\alpha)F\eta_1)$

$\ln J_2 - \ln J_1 = (1-\alpha)F(\eta_2 - \eta_1)$

$\frac{\ln J_2 - \ln J_1}{(1-\alpha)F} = \eta_2 - \eta_1$

$\Rightarrow \frac{\ln\left(\frac{J_2}{J_1}\right)}{(1-\alpha)F} + \eta_1 = \eta_2 \Rightarrow \frac{\ln\left(\frac{75}{55}\right)}{(1-0.39)38.95} + 125$

$\eta_2 = 138\,mV$

Causes of Overpotential

A slow electron transfer process has a high activation energy, for such process to proceed at a reasonable rate and to produce an efficient quantity of product, a significant increase of the applied potential over the equilibrium value is necessary. This excess potential is known as activation potential (η_A)

$$\eta_A = \phi_{slow} - \phi_{equilibrium}$$

This description emphasizes that the slow rate determining step in an electron transfer process is due to the high activation ~~barrier~~ energy barrier.

There are two other over potential/voltage that occurs simultaneously with the activation potential

(1) resistance over voltage: When an electric current is passed through a solution of an electrolyte, since such solution is not at infinite conductivity. A resistance to the flow of current is posed by such solution resulting in an ohmic drop in potential between the working electrode.

This ohmic drop may be offset by insulating the solution of the reference electrode from the working solution by enclosing the reference electrode in a fine glass

Capillary. Another form of ohmic overvoltage is caused by the formation on the surface of the electrode of an adhering layer of reaction product, which may be a poor conductor of electricity.

~~Corrosion~~

Surface oxide films shows such behaviour and their resistance leads to overvoltages of several hundred voltage.

② Concentration overvoltage: This arises due to concentration changes induced in the vicinity of electrode by electrochemical reaction occuring at the electrode. Although, the effect is usually very small, howbeit, very important especially in electro analytical techniques

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The overvoltage of an individual electrode maybe expressed as a some of contributions from activation concentration and resistance thin overvoltages

$$\eta = \eta_A + \eta_c + \eta_R$$

The resistant overvoltage unlike the activation and concentration overvoltages appears and dissapears instantaneously when the vaporising circuit is removed or broken. Activation overvoltage increases rapidly and exponentially after a polarising current is caused to flow and of course decreases in a complementary way when the flow of current is stopped. This exponential growth and decay are in accordance with the concept of activation overpotential as a function of the activation energy of an electrode process.

The magnetude of the activation over potential is after by the physical and chemical nature of the electrode material

Concentration Overpotential

Concentration overpotential grows and decays slowly on application or interuption of the current flow at a rate that is characteristics of the diffusion coefficient of the species involved

It is the only type of overpotential that is affected by stirring and not by the nature of the surface of the electrode material

The Thermodynamics of Electrochemical Process / Cell Reaction

The measurement of the electromotive force of a reversibly operating cell as well as it's temperature dependent enables the determination of the Gibbs free energy, enthalpy change as well as the entropy change.

Recall at any given temperature $\Delta G = -nFE$

Also recall that for any spontanoues process;

$$\Delta G = \Delta H - T\Delta S$$

Also,

$$\left(\frac{\partial G}{\partial T}\right)_p = -\partial S$$

$$\Delta H = \Delta G + T\Delta S$$

$$\Delta H = \Delta G - T\left(\frac{\partial G}{\partial T}\right)_p$$

$$\Rightarrow \Delta H = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_p$$

The $\frac{\partial E}{\partial T}$ is the temperature coefficient of the cell emf at constant pressure.

$\frac{\partial S}{\partial T}$

This temperature coefficient can be determined carefully by measuring the emf of the cell over a wide range of temperature. So that the tangiet to E—T plot at any given temperature may be drawn and the slope measured

$$dE = Tds - Pdv$$

$$ds = \frac{dE}{T} + \frac{Pdv}{T}$$

$$\left(\frac{\partial S}{\partial E}\right)_v = \frac{1}{T}$$

$$\partial S = -\left(\frac{\partial G}{\partial T}\right)_P$$

$$\partial S = -\left(\frac{-nf\,\partial E}{\partial T}\right)_P$$

$$\partial s = nF\left(\frac{\partial E}{\partial T}\right)_P$$

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$\Delta G = \Delta G^\circ + RT\ln Q$ where Q = reaction quotient

Recall that

$\Delta G = -nFE$

$\Delta G^\circ = -nFE^\circ$

$\therefore nFE = -nFE^\circ + RT\ln Q$

$E = E^\circ - \frac{RT}{nF}\ln Q$

$E = E^\circ - \frac{2.303RT}{nF}\log_{10} Q$ ---- Nerst equation

At equilibrium Q becomes K

This ~~equilibrium~~ equation is known as the Nerst equation for determining the emf of the electrochemical process in a non standard state

$Cu^{2+}_{(aq)} + Zn_{(s)} \longrightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$

$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$

$Cu^{2+}_{(aq)} + Zn_{(s)} \rightleftharpoons Cu_{(s)} + Zn^{2+}_{(aq)}$

$Q_c = K_c = \frac{[Zn^{2+}]}{[Cu^{2+}]}$

$$H^{+}_{(aq)} + e^{-} \rightleftharpoons \frac{1}{2}H_{2(g)}$$

$$E = E^{0} - \frac{2.303RT}{F}\log_{10}\frac{[H_2]^{1/2}}{[H^+]}$$

Since H_2 is a gas, we can't measure the molar concentration

$$\therefore E = E^{0} - \frac{2.303RT}{F}\left(\log_{10} P_{H_2}^{1/2} - \log_{10}[H^+]\right)$$

$$\Rightarrow E = E^{0} + \frac{2.303RT}{F}\left(\log_{10}[H^+] - P_{H_2}^{1/2}\right)$$

when $P_{H_2} = 1\text{ atm}$

$$\Rightarrow E = E^{0} + \frac{2.303RT}{F}\left(\log_{10}[H^+]\right) \qquad \{pH = -\log_{10}[H^+]\}$$

$$\Rightarrow E = E^{0} - \frac{2.303RT}{F}pH$$

Importance of Nerst Equation

(i)

(ii) Can be used to determine solubility product which is the equilibrium constant ~~for a solution~~ that exist between sparingly soluble salt and its dissolved ion.

$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

$K_{eq} = [Ag^+][Cl^-] \Rightarrow$ solubility product

Show that

$$\ln K_{AgCl} = \left(E - E^0_{Ag}\right)\frac{F}{RT} + \ln a_{Cl^-}$$

where $a_{Cl^-} \Rightarrow$ activity of chloride ion

and

$$E = \left(E^0_{Cl_2} - E^0_{Ag}\right) - \frac{RT}{F}\ln K_{AgCl}$$

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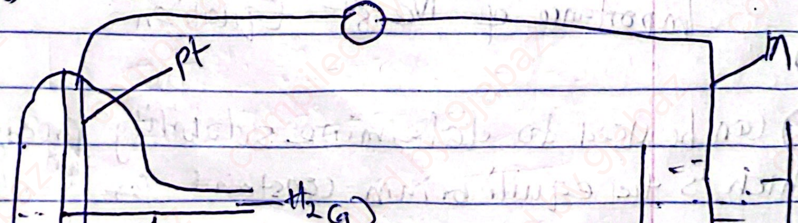
Types of Electrodes

Hydrogen- hydrogen ion system



$H^+_{(aq)} + e^- \rightleftharpoons \frac{1}{2}H_{2(g)}$ $M^{n+} + ne \rightleftharpoons M$

ⓐ 25°, 1 atm and 1M of H^+, $E^\circ_{reduction} = 0.00V$

E° ~~reduction = 0.00V~~ $M^{n+} + ne \rightleftharpoons M$

in Zn and H

Since Zn is higher than H in the electrochemical series, Zn will undergo oxidization and H is undergo reduction

in H and Ag

H is higher, H = oxidation, Ag = reduction

The direction of deflection depend on whether oxidation of Zn & H_2, the deflection will be anticlockwise

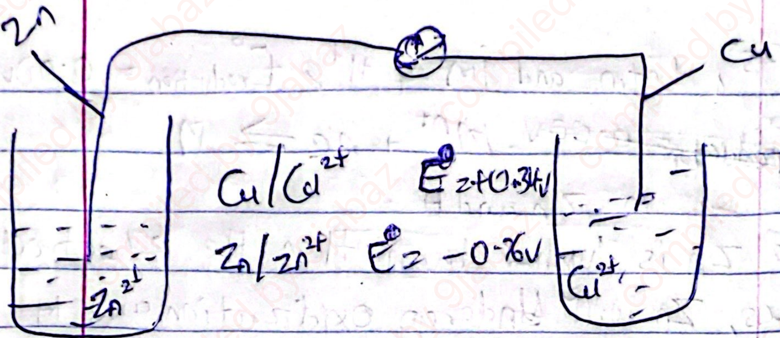
If it is Ag & H_2, deflection is clockwise

$M^{n+} + ne^- \rightleftharpoons M \qquad E^\circ_{red} = xV$

$M \longrightarrow M^{n+} + ne^- \qquad E^\circ_{oxi} = -xV$

$Cu/Cu^{2+} \qquad E^\circ = +0.$[illegible]

$Zn/Zn^{2+} \qquad E^\circ = -0.75V$



Cu/Cu^{2+} $E^{\theta} = +0.34V$

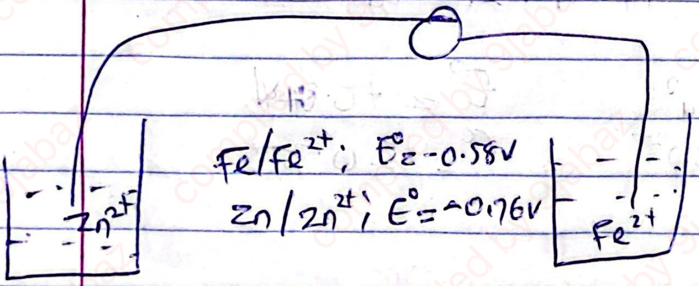
Zn/Zn^{2+} $E^{\theta} = -0.76V$

$$\left.\begin{array}{ll} Cu^{2+} + 2e^- \longrightarrow Cu_{(s)} & +0.34V \\ Zn \longrightarrow Zn^{2+} + 2e^- & -(-0.76V) \end{array}\right\}$$

$$Cu^{2+}_{(aq)} + Zn_{(s)} \longrightarrow Cu_{(s)} + Zn^{2+}_{(aq)} \quad +1.10V$$

Since the overall E° is +ve, it means the reaction is spontaneous, using

$\Delta G = -nFE^{\circ}$; $\Delta G < 0$



Fe/Fe^{2+} ; $E^{\circ} = -0.58V$

Zn/Zn^{2+} ; $E^{\circ} = -0.76V$

The E° that is more positive, it is undergo oxidation

$Fe^{2+} + 2e^- \rightarrow Fe \quad -0.58V$

$Zn \rightarrow Zn^{2+} + 2e^- \quad -(-0.78V)$

$Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe \quad +0.18V$

The electrode potential is an intensive property, we don't multiply by no. of electrons, e.g.,

$Cu/Cu^{2+} \quad +0.34V$

$Ag/Ag^+ \quad +0.80$

$2Ag^+ + 2e^- \rightarrow 2Ag \quad 0.80V$ } → still remains

$Cu \rightarrow Cu^{2+} + 2e \quad -0.34$

$\frac{\partial S}{\partial T}$

This temperature coefficient can be determined carefully by measuring the emf of the cell over a wide range of temperature. So that the tangent to E—T plot at any given temperature may be drawn and the slope measured

$$dE = Tds - Pdv$$

$$ds = \frac{dE}{T} + \frac{Pdv}{T}$$

$$\left(\frac{\partial S}{\partial E}\right)_v = \frac{1}{T}$$

$$\partial S = -\left(\frac{\partial G}{\partial T}\right)_P$$

$$\partial S = -\left(\frac{-nF\,\partial E}{\partial T}\right)_P$$

$$\partial S = nF\left(\frac{\partial E}{\partial T}\right)_P$$

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$\Delta G = \Delta G^\circ + RT\ln Q$ where Q = reaction quotient

Recall that

$\Delta G = -nFE$

$\Delta G^\circ = -nFE^\circ$

$\therefore nFE = -nFE^\circ + RT\ln Q$

$$E = E^\circ - \frac{RT}{nF}\ln Q$$

$$E = E^\circ - \frac{2.303RT}{nF}\log_{10} Q$$ ---- Nerst equation

At equilibrium Q becomes K

This ~~equilibrium~~ equation is known as the Nerst equation for determining the emf of the electrochemical process in a non standard state

$$Cu^{2+}_{(aq)} + Zn_{(s)} \longrightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$Cu^{2+}_{(aq)} + Zn_{(s)} \rightleftharpoons Cu_{(s)} + Zn^{2+}_{(aq)}$$

$$Q_c = K_c = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$H^+_{(aq)} + e^- \rightleftharpoons \tfrac{1}{2}H_{2(g)}$$

$$E = E^0 - \frac{2.303RT}{F}\log_{10}\frac{[H_2]^{1/2}}{[H^+]}$$ Since H_2 is a gas, we can't measure the molar concentration

$$\therefore E = E^0 - \frac{2.303RT}{F}\left(\log_{10} P_{H_2}^{1/2} - \log_{10}[H^+]\right)$$

$$\Rightarrow E = E^0 + \frac{2.303RT}{F}\left(\log_{10}[H^+] - P_{H_2}^{1/2}\right)$$

When $P_{H_2} = 1$ atm

$$\Rightarrow E = E^0 + \frac{2.303RT}{F}\left(\log_{10}[H^+]\right)$$ $\{pH = -\log_{10}[H^+]\}$

$$\Rightarrow E = E^0 \cancel{+} \frac{2.303RT}{F}pH$$

Importance of Nerst Equation

(i)

(ii) Can be used to determine solubility product which is the equilibrium constant ~~for a solution~~ that exist between sparingly soluble salt and its dissolved ion.

$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

$K_{eq} = [Ag^+][Cl^-]$ ⇒ solubility product

Show that

$$\ln K_{AgCl} = \left(E - E^0_{Ag}\right)\frac{F}{RT} + \ln a_{Cl^-}$$

where a_{Cl^-} is activity of chloride ion

and

$$E = \left(E^0_{Cl_2} - E^0_{Ag}\right) - \frac{RT}{F}\ln K_{AgCl}$$

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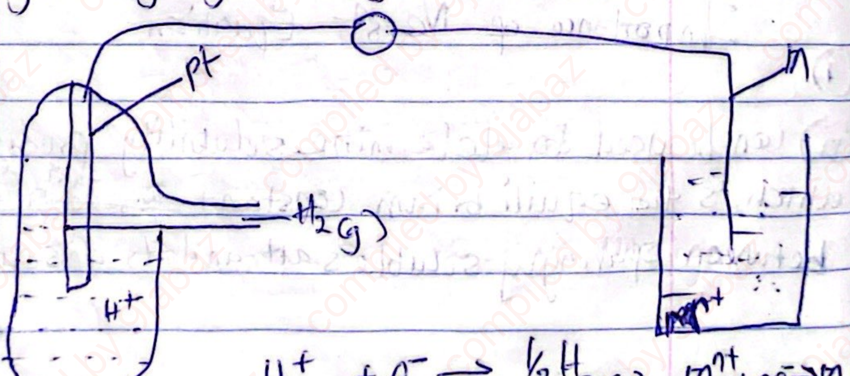
Types of Electrodes

Hydrogen - hydrogen ion system



$H^+_{(aq)} + e^- \rightleftharpoons \frac{1}{2}H_{2(g)}$ $M^{n+} + ne \rightleftharpoons M$

ⓐ 25°, 1 atm and 1M of H^+, $E^\circ_{reduction} = 0.00V$

~~$E^\circ_{reduction} = 0.00V$~~ $M^{n+} + ne \rightleftharpoons M$

~~Since~~ in Zn and H

Since Zn is hygher than H in the electrochemical series, Zn will undergo oxidization and H is undergo reduction

in H and Ag

A is higher, H = oxidation, Ag = reduction

The direction of deflection depend on whether oxidation of Zn & H_2, the deflection will be anticlockwise

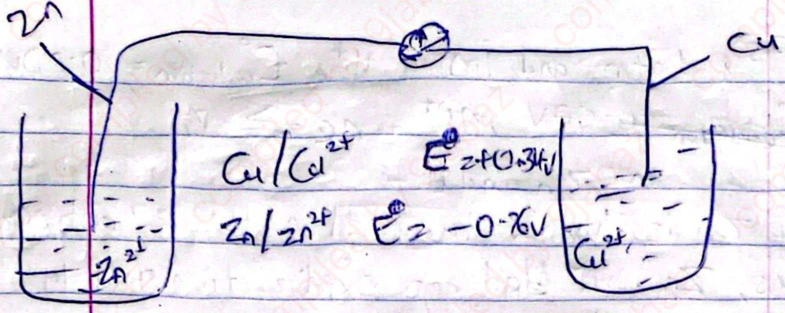
If it is Ag & H_2, deflection is clockwise

$M^{n+} + ne^- \rightleftharpoons M$ $\quad E^\circ_{red} = xV$

$M \longrightarrow M^{n+} + ne^-$ $\quad E^\circ_{oxi} = -xV$

Cu/Cu^{2+} $\quad E^\circ = +0.$[illegible]

Zn/Zn^{2+} $\quad E^\circ = -0.75V$



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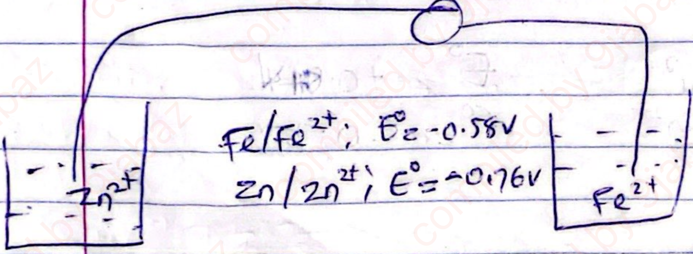

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$Cu \rightarrow Cu^{2+} + 2e \quad -0.34$

19 (1)

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Properties of Ideal Reference Electrode

① An ideal reference electrode must be reversible and obeys the Nerst equation with some of its species in solution.

(ii) Another important thing is that the potential must be stable with time

(iii) The potential should return to its initial value after small current are passed through the electrode

(iv) For a reference electrode of the second kind, the solid phase must not be appreciably soluble in the electrolyte

(v.) A ideal reference electrode should ~~not~~ exhibit hysteresis

Reversible electrode can be divided into three groups:

(1) Electrodes of the first kind, which includes cationic electrodes

$$M^{z+}_{(aq)} + ze^- \rightleftharpoons M_{(s)}$$

$$E = E^0 + \frac{2.303RT}{zF} \log_{10} a_{M^{z+}}$$

It also includes amalgum, gas electrode and hydrogen electrode

For this electrodes equilibrium is established between atoms and moleculos of the substance of corresponding cation in the solution

activity = conc, when activity coefficient = 1

② Electrodes of the second kind; These electrodes consist of three phases; ① The metal is covered by a layer of sparingly soluble salt usually with the character of a solid electrolyte and immersed ~~with~~ in a solution containing the anions of the salt.

② The solution ~~between~~ contains the soluble salt of this anion because of these two interfaces, equilibrium is established between the metal atoms and anions in solution

③ The ~~solution~~ equilibrium between the metal atom and the cation in the

③ Sparingly soluble salt

Examples includes (from the 2nd kind); AgCl electron

$$AgCl_{(s)} + e^- \rightleftharpoons Ag + Cl^-$$

(calculate the solubility product)

Other examples of 2nd kind is the calomel electrode

$$KCl / Hg_2Cl_{2(s)} / Hg$$

$$E_{Hg_2Cl_2/Hg} = E^\circ_{Hg_2Cl_2/Hg} - \frac{RT}{F} \ln a_{Cl^-}$$

Another examples are mercurous sulphate electrode and mercuric oxide electrode.

③ Oxidation – Reduction electrode (Redox electrode)

This consist of an inert metal, such as, pt, Au, Ag immersed in a solution containing two forms of a single substance in different oxidation state. The inert metal merely acts as a medium for the transfer of electrons between the two forms.

$$Ox + ne^- \rightleftharpoons Red$$

eg $Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}$

$Cr^{6+}_{(aq)} + 3e^- \rightleftharpoons Cr^{3+}_{(aq)}$

The nerst equation for this reaction;

$$E = E^\circ + \frac{RT}{nF}\ln\frac{a_{ox}}{a_{red}}$$

We can also express the nerst ~~electrode~~ equation of the redox electrode with the degree of oxidation as;

$$E = E^\circ + \frac{RT}{nF}\ln\frac{\alpha}{1-\alpha}$$ where α = degree of oxidation

Organic Redox Electrode

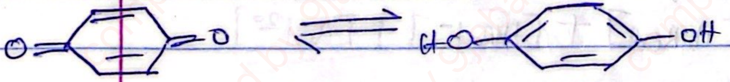
quinone ⇌ hydroquinone

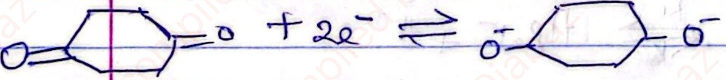
$$Ox + 2e^- \rightleftharpoons red^{2-}$$

This is a 2 electron process, quinone is oxidized to form while hydroquinone in the reduced form

The ~~hydroquinone~~ quinhydrone electrose is a solid state associate of quinone and hydroquinone decomposes in solution of its component. It is a more complex of the organic redox electrode whose potential is affect

If the quinone molecule is denoted as OX and the hydroquinone molecule is denoted as H_2Red





This reaction is accompanied by reaction between the quinone ion and the solvent

The hydroquinone is a weak dibasic acid with a corresponding dissociation constant

$$H_2Red \overset{K_1}{\rightleftharpoons} HRed^- + H^+ \qquad K_1 = \frac{[HRed^-][H^+]}{[H_2Red]}$$

$$HRed^- \overset{K_2}{\rightleftharpoons} Red^{2-} + H^+ \qquad K_2 = \frac{[Red^{2-}][H^+]}{[HRed^-]}$$

The Nerst equation for this electrode is

$$E_{ox/Red^{2-}} = E^{\circ}_{ox/Red^{2-}} + \frac{RT}{2F}\ln\frac{a_{ox}}{a_{red^{2-}}}$$

$$= E^{\circ}_{ox/Red^{2-}} + \frac{RT}{2F}\ln\frac{[Ox]}{[Red^{2-}]}$$

how do we determine this?

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Applying mass concept, the overall concentration of the reduced form is;

$$C_{Red} = [H_2Red] + [HRed^-] + [Red^{2-}]$$

$$H_2Red \overset{K_1}{\rightleftharpoons} HRed^- + H^+$$

$$HRed^- \overset{K_2}{\rightleftharpoons} Red^{2-} + H^+$$

$$C_{Red} = \frac{[H^+]^2[Red^{2-}]}{K_1K_2} + \frac{[H^+][Red^-]}{K_2} + [Red^{2-}]$$

Such that;

$$[Red^{2-}] = C_{Red}K_1K_2 / \left([H^+]^2 + K_1[H^+] + K_1K_2\right)$$

$\Rightarrow$ ~~$E_{qh} = E^0$~~ (solve)

$$\Rightarrow E_{qh} = E^0 + \frac{RT}{2F}\ln\left\{\frac{[Ox]}{C_{Red}}\right\} - \frac{RT}{2F}\ln K_1K_2 + \frac{RT}{2F}\ln\left\{[H^+]^2 + K_1[H^+] + K_1K_2\right\}$$

but $[Ox] = C_{Red}$

$\rightarrow = 0$

$$E_{qh} = E^0_{qh} + \frac{RT}{2F}\ln\left\{[H^+]^2 + K_1[H^+] + K_1K_2\right\}$$

where

$$E^0_{qh} = \boxed{E^0 - \frac{RT}{2F}\ln K_1K_2}$$

$\downarrow$

formal electrode potential

The fourth term is simplified in different pH ranges as follows;

In a very acidic medium $[H^+]^2 >> (K_1[H^+] + K_1K_2)$

$$E_{qh} = E^0_{qh} + \frac{RT}{F}\ln[H^+]$$

$$= E^0_{qh} - \frac{2.303RT}{F}pH$$

If $K[H^+] >> \{[H^+]^2 + K_1K_2$

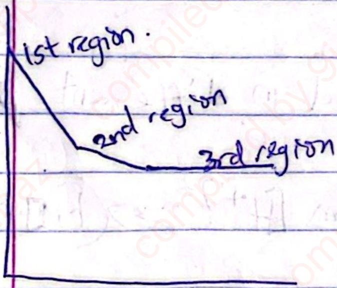
$$E_{qh} = E^0_{qh} + \frac{RT}{2F}\ln K_1 - \frac{2.303RT}{2F}pH$$

For basic medium where;

$K_1K_2 >> \{[H^+]^2 + K_1[H^+]\}$

$$\Rightarrow E_{qh} = E^0_{qh} + \frac{RT}{2F}\ln K_1K_2$$

Ploting the graph of E_{qh} as a function of pH



Buttervolmar's -key points

① When the overpotential is zero, there is no net current density. However, current flow are equal and opposite for both the cathodic and anodic electrode

② If the transfer coefficient is zero, it also implies that the cathodic current density is equal to the exchange current density and is independent of the overpotential. If ~~d~~transfer coefficient α is 1, it implies that the anodic current density is equal to the exchange current density and also indepedent on the overpot

③ For $0 < \alpha < 1$, as the Overpotential becomes increasingly positive, the anodic current density dominates the cathodic current density. Such as the dominate process will be

$$Red \longrightarrow Ox + e^- \ (\text{for } \underset{\text{overpotential}}{\text{highly positive}})$$

④ As the overpotential becomes increasely negative, the cathodic current density dominates the anodic current density. Such that the dominate process will be

$$Ox + e \longrightarrow Red \ (\text{for high}$$

electrolysis is a non-spontaneous

To induce the flow of current through an electrolytic cell and consequently bringing about a non spontaneous cell reaction. The applied potential difference must exceed the zero current potential by at least the cell potential which is the sum of the overpotentials of the two electrodes and the ohmic drop (IR) where R is resistance to the flow of current by the electrolyte.

The relative rate of gas evolution or metal deposition during electrolysis can be estimated from the Bultervolmer equation

① If the transfer coefficient is assumed to be equal, the ratio of the cathodic current

$$\frac{\text{rate of metal deposition}}{\text{rate of gas evolution}} = \frac{J'}{J} = \frac{J_0'}{J_0} \exp(\eta - \eta')\frac{\alpha F}{RT}$$

where J = current density for gas, J' = current density for metal deposition

J_0 = exchange current density

η = overpotential for gas evolution

η' - overpotential for metal deposition

The equation above shows that metal deposition is favoured by a large exchange current density for that process and a relatively high evolution gas evolution overpotential, where $\eta - \eta'$ is +ve and large
Recall that overpotential is negative for a cathodic process which implies that $-\eta' > 0$

The exchange current density depends strongly on the nature of the electrode surface and changes in the course of the electrode decomposition of one metal on another.

The exchange current density also depends on the crystal phase exposed.