

TOPIC 9:

ELECTRO CHEMISTRY

General Objective

By the end of this topic the learners should be able to outline the effect of electric current on substances and the ability of substances to generate electricity.

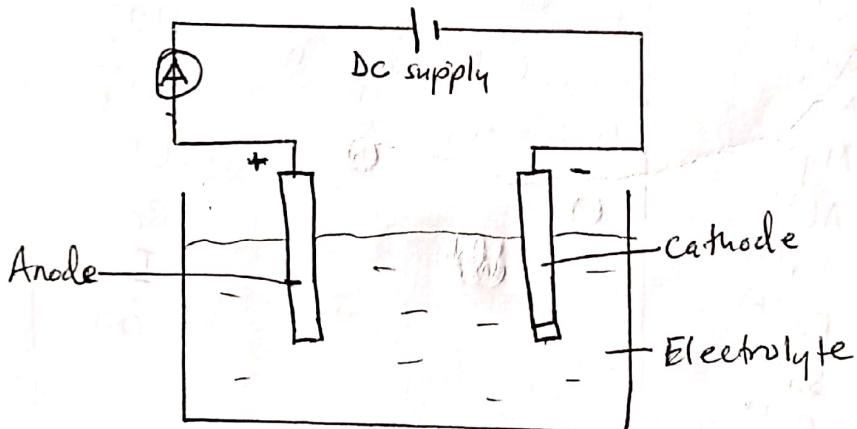
Electrochemistry is divided into 3 sub-topics.

That is to say:-

- Electrolysis
- Conductance (electro conductivity)
- Electrochemical cells

ELECTROLYSIS

Is defined as the decomposition of a compound, molten or in solution, by passage of an electric current.



Common terms

Anode: Is the electrode or terminal where oxidation occurs or where current flows in from outside.

Cathode: Is the electrode where reduction occurs, or where current flows out.

Electrolyte: A substance that conducts electricity in molten or in solution.

Weak and strong electrolytes:

Weak electrolyte is the electrolyte that ionises partially in aqueous solution, e.g. ethanoic acid, Ammonia Solution.

Strong electrolyte is one that ionises completely in aqueous solution. e.g. Sodium chloride.

During electrolysis ions migrate to oppositely charged electrodes and are discharged at the electrodes. The discharge of ions depends on a number of factors which include :-

1) Position of the ion in the Electrochemical series

When an ion is high up in the Electrochemical series, high energy is required to discharge it. Hence the ion lower in the E.C series will be discharged if other factors kept constant.

Electrochemical series

Cations

K^+
 Ca^{2+}
 Na^+
 Mg^{2+}
 Al^{3+}
 Zn^{2+}
 Fe^{2+}
 Sn^{2+}
 Pb^{2+}
 H_3O^+
 Cu^{2+}
 Ag^+
 Au^{3+}

Ease of discharge
Increases

Anions

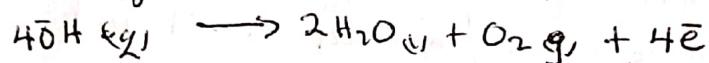
NO_3^-
 SO_4^{2-}
 Cl^-
 Br^-
 I^-
 OH^-

2) Concentration of the ions

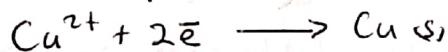
An ion present in low concentration is more difficult to discharge than an ion of the same charge but higher concentration.

3) Nature of electrode

Electrodes sometimes undergo electrolysis e.g. in the electrolysis of copper(II) sulphate using inert electrodes such as platinum or carbon. Oxygen is liberated at the anode



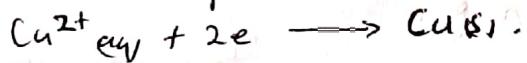
and copper ions are also preferentially discharged at the cathode to deposit copper metal



However when copper anode is used no oxygen is liberated instead the anode dissolves into the solution



and copper metal is deposited at the cathode



APPLICATION OF ELECTROLYSIS

1. Extraction of sodium metal by electrolysis of molten sodium chloride in the Down's process.
2. Manufacture of NaOH by the electrolysis of aqueous sodium chloride in a mercury cathode cell and a diaphragm cell.
3. Manufacture of sodium chlorate (I) and sodium chlorate (V) by the electrolysis of aqueous NaCl
4. Manufacture of chlorine by electrolysis of brine
5. Extraction of Mg and Ca by electrolysis of their fused chlorides.

6 - Extraction of Aluminium by Electrolysis of Bauxite

7 - Anodisation and dyeing of Aluminium

8 - Purification of Copper by electrolysis of $CuSO_4 \text{ eqy}$ using Impure Copper as Anode and pure copper at cathode.

9 - Electroplating e.g. tin plating, Chromium and gold plating.

Faraday's Laws of Electrolysis

1st - The mass of a substance liberated or deposited at an electrode is ^{directly} proportional to the quantity of electricity passed. $M \propto Q \Rightarrow M \propto It$ where t is time taken

$$Q = It \quad I = \text{direct current}$$

2nd - The quantity of electricity required to deposit or liberate one mole of a substance is ^{directly} proportional to the charge on the ion.

i.e. Cu^{2+} requires twice the quantity for Ag^+ .

Calculations

1) Calculate the mass of copper deposited when a current of 3.0 amperes was passed through a $CuSO_4 \text{ eqy}$ for 25 minutes.

Solution

$$Q = It \\ = 3 \times 25 \times 60 = 4.5 \times 10^3 \text{ coulombs.}$$

Copper is deposited by $Cu^{2+} \text{ eqy} + 2e \rightarrow Cu(s)$

1 mole of Cu^{2+} is deposited by $2F = 2 \times 96,500 = 193,000$ coulombs

$\Rightarrow 193,000$ coulombs deposited 1 mole of Cu^{2+}

+ 500 coulombs deposited $\left(\frac{1 \times 4500}{193,000} \right)$ moles

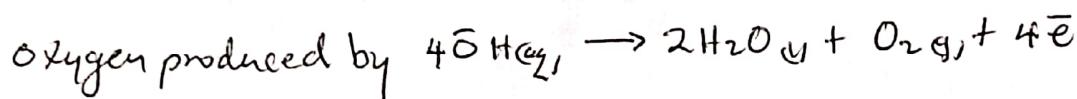
1 mole of Cu weighs 63.5 g

0.0233 moles of Cu weigh $63.5 \times 0.0233 = \underline{\underline{1.48}} \text{ g}$

2) An electric current was passed through an aqueous solution of Cobalt(II) solution. After 20 minutes, 600 cm³ of Oxygen were liberated. What is the mass of Cobalt deposited at the cathode.

Solution:

$$Q = I t \\ = I \times 20 \times 60$$



4 Faradays liberate 1 mole = 24000 cm³ of O₂ at r.t

\Rightarrow 24000 cm³ of O₂ are liberated by 4F

$$600 \text{ cm}^3 \text{ of O}_2 \text{ are liberated by } \left(\frac{4}{24000} \times 600\right) \text{ F} \\ = 0.1 \text{ F}$$

Cobalt is produced by $\text{Co}^{2+} + 2\bar{e} \rightarrow \text{Co(s)}$
at cathode

\Rightarrow 2F deposit 1 mole = 58.9 g of Co

$$0.1 \text{ F deposit } \left(\frac{58.9}{2} \times 0.1\right) \text{ g of Co} \\ = \underline{\underline{2.9 \text{ g}}}$$

3). In an experiment, 1.44 g of Silver were deposited in a cell of silver nitrate solution while 0.12 g of a metal X was deposited in another cell containing XCl₃ solution in series (same current). Calculate the atomic mass of X.

Silver is deposited by $\text{Ag}^+ + \bar{e} \rightarrow \text{Ag(s)}$

X is deposited by $\text{X}^{3+} + 3\bar{e} \rightarrow \text{X(s)}$

\Rightarrow Moles of X deposited = $\frac{1}{3}$ of Moles of Ag deposited ~~as per~~

$$\text{Moles of Ag deposited} = \frac{1.44}{108} = 0.0133 \text{ moles.}$$

$$\text{Moles of X deposited} = \frac{1}{3} \times 0.0133 = 0.0044 \text{ moles.}$$

0.0044 moles of X weigh 0.12 g

$$1 \text{ mole of X weighs } \frac{0.12}{0.0044} = \underline{\underline{27 \text{ g}}}$$

m
w
pm

5

Exercise

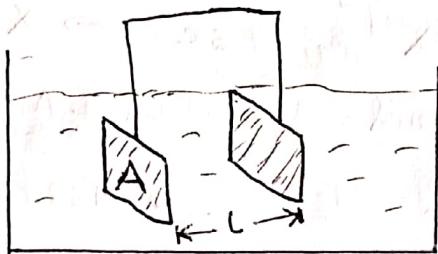
An electric current was passed through an electrolytic cell containing Silver nitrate solution. The same current was also passed through dilute sulphuric acid and 520 cm^3 of Hydrogen gas were produced at 18°C and 750 mmHg .

- Calculate the Mass of O_2 produced in the 2nd cell ($O=16$)
- Calculate the Mass of Silver that will be deposited ($\text{Ag}=108$)

ELECTROLYTIC conductivity (specific conductance)

Electrolytes or Solutions conduct electricity by movement of free ions. Electrolytes obey the same laws as metallic conductors with respect to electrical resistance and Conductance. i.e. At constant temperature, the resistance of an electrolyte is .

- Directly proportional to the distance, L , between the electrodes and
- Inversely proportional to the cross sectional area A , of the solution between the electrodes.



$$\Rightarrow R \propto L \quad \text{and} \quad R \propto \frac{1}{A}$$

$$\Rightarrow R = \frac{fL}{A} \quad \text{where } f = \text{Resistivity}$$

Conductance, G , is the reciprocal of resistance, $\frac{1}{R}$

$$G = \frac{1}{R} = \frac{A}{fL} = \frac{K A}{L} \quad \text{units } \text{Ohm}^{-1}, \text{S}^{-1} \text{ or } (\text{Siemens})$$

Conductivity is the reciprocal of resistivity

$$\text{Conductivity } K \text{ (Kappa)} = \frac{1}{R} = L \left(\frac{1}{A} \right) = \frac{L}{RA}$$

$$\Rightarrow K = \frac{L}{RA} \quad \text{N.P.I.} \left(\frac{L}{A} \right) \text{ is called cell constant}$$

Defn

Electrolytic Conductivity, K , is the conductance of a solution enclosed between electrodes which are of unit cross-sectional area and unit length apart.

Units of Electrolytic Conductivity K is $\Omega^{-1}\text{m}^{-1}$ or S m^{-1}

Calculations

- 1) A 0.01M solution of NaCl is placed in a conductance cell whose electrodes are 1cm^2 area and 0.5cm apart. The resistance of the solution is found to be $421.93\ \Omega$ and Conductivity of pure water is $8 \times 10^{-5}\ \Omega^{-1}\text{m}^{-1}$. calculate the conductivity of the salt.

Solution

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

$$K_{\text{solution}} = \frac{L}{RA} = \frac{0.5}{421.93 \times 1} = 1.185 \times 10^{-3}\ \Omega^{-1}\text{cm}^{-1} = 1.185 \times 10^{-1}\ \Omega^{-1}\text{m}^{-1}$$

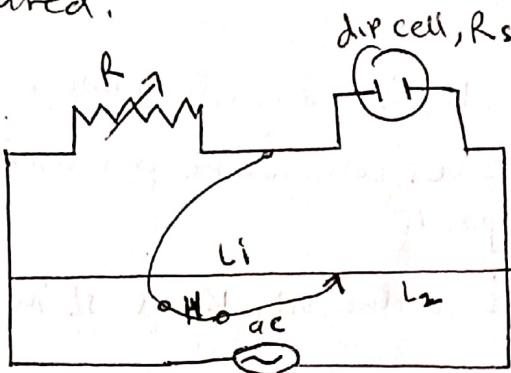
$$K_{\text{salt}} = 1.185 \times 10^{-1} - 8 \times 10^{-5} = \underline{\underline{1.1842 \times 10^{-1}\ \Omega^{-1}\text{m}^{-1}}}$$

Determination of conductivity

This can be determined indirectly using a meter bridge or Wheatstone Bridge.

A conductance cell or dip cell containing a solution of unknown resistance is connected in one gap and a known Resistor in another gap.

By using a centre zero galvanometer, the balance length L_1 and L_2 respectively are obtained. If the dip cell used has electrodes of a fixed area A , held at fixed separation L , from each other, the resistivity of the solution in a conductivity cell can be measured.



$$\frac{\text{Resistance}}{R} : \text{Resistance} = \frac{L_1}{L_2} : \frac{L_2}{R}$$

$$R : R_s = L_1 : L_2$$

$$R_s = \frac{L_2 R}{L_1}$$

$$\Rightarrow K = \frac{1}{R} \left(\frac{L}{A} \right)$$

Note:

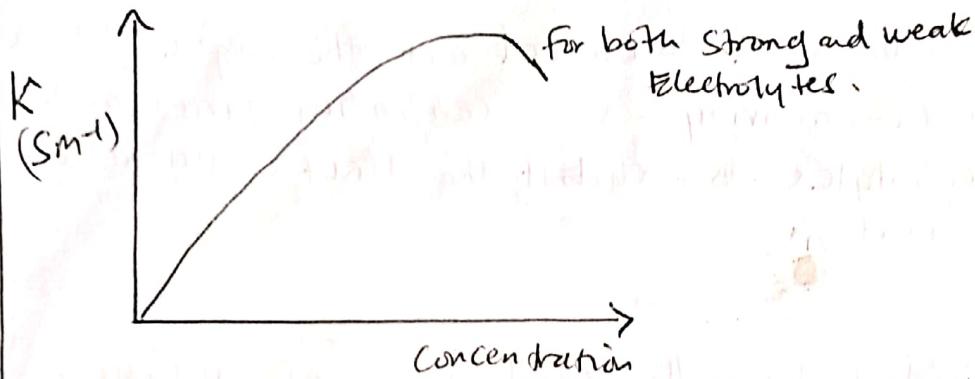
- ① An alternating Current is used, for a direct current would cause electrolysis of the solution.
- ② Since a galvanometer does not detect alternating current, we use Headphones, H, to find the point of balance when the sound of the headphones becomes minimum.

FACTORS AFFECTING CONDUCTIVITY

- ① Electrolytic conductivity depends on the concentration of the ions present and their speed for strong electrolytes. For weak electrolytes K depends on the degree of ionisation as dilution ($1/c$) increases.

In a solution containing a high concentration of ions a high degree of ionic interference is observed, which effectively decreases the mobility (ionic speed). As the solution is diluted, such interferences get smaller and so that further dilution results in no change in conductivity.

VAriation of K with concentration



Explanation

Strong electrolytes

Conductivity increases with increase in concentration at first because of the increase in the number of conducting ions per unit volume. At higher concentration, K decreases because of the increase in ionic interference resulting in decrease of ionic mobility. i.e. Ions of opposite charges come very close at high concentration and exert a dragging effect on one another.

Weak electrolytes

Conductivity increases with increase in concentration at first due to increase in number of conducting ions. At higher concentrations K decreases because of decrease in degree of ionisation leading to decrease in number of ions.

N.B. K is measured by means of the resistivity in actual practice, but it is not the most valuable data about the electrolyte, b'z it varies with dilution in a two fold way:-

① Dilution reduces the no. of ions in ^aunit volume of the electrolyte and this increases the resistance of the electrolyte.

② Weak electrolytes increase their ionisation on dilution, which decreases the resistance of the electrolyte.

MOLAR CONDUCTIVITY (Λ)

This is introduced to cancel out the simple dilution factor in conductivity as concentration varies and, for weak electrolytes to exhibit the effect of variation of Molar ionisation.

Defn.:

Molar conductivity is the conductance of a volume of a solution containing 1 mole of an electrolyte.

Λ is electrolytic conductivity divided by concentration of the electrolyte i.e

$$\Lambda = \frac{K}{C} \quad \text{or} \quad \Lambda = KV \quad \text{where } V \text{ is dilution.}$$

Units are $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ or $\text{S}^{-1} \text{m}^2 \text{mol}^{-1}$

FACTORS AFFECTING Molar Conductivity

① Concentration:

Λ for both strong and weak electrolytes decreases with increase in concentration.

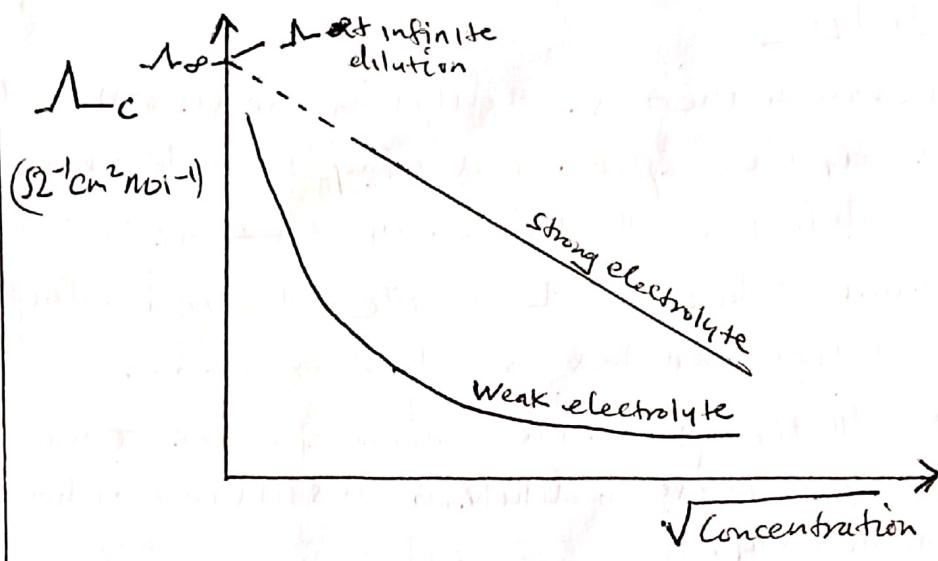
② The charge on the ion

The greater the ionic charge the more strongly attracted is the ion. The greater the mobility and hence the greater the Molar conductivity.

③ The radius of the ion / ionic size

The smaller the radius of the ion, the higher the charge density and hence the number of water molecules attracted is high. This lowers the mobility of the ion and hence its Molar conductivity. e.g. the Molar conductivities of Li^+ , Na^+ and K^+ are in the order 38.69, 50.1, and 733 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ respectively.

Variation of Λ with concentration



Explanation

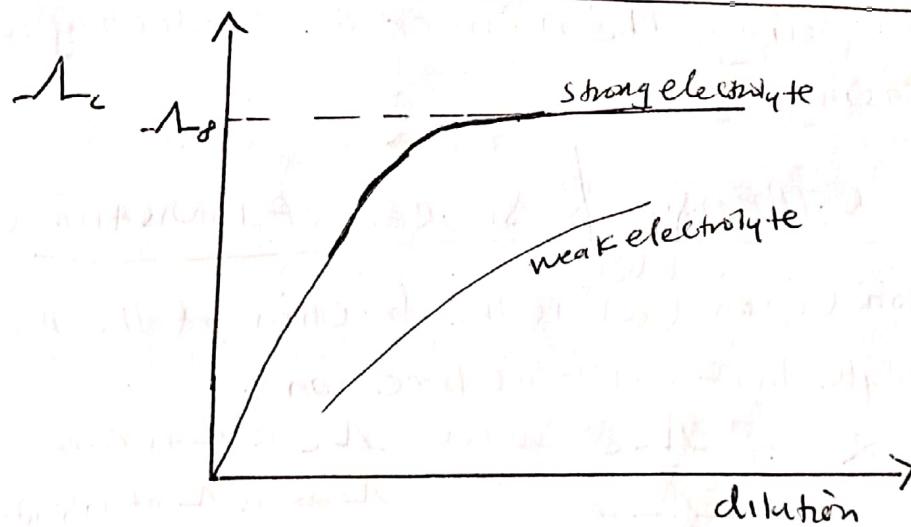
Strong Electrolyte

Molar Conductivity decreases with increase in Concentration. Because at low concentration, the ions of the electrolyte are wide apart with less ionic interferences. This gives the ions high mobility and thus high molar conductivity.

Weak electrolyte

Molar conductivity decreases with increase in concentration because at low concentration, more molecules ionise, the degree of ionisation is high. The number of ions per unit volume increase, consequently Λ also increases.

Variation of Λ with dilution



Explanation

Strong electrolyte

Λ increases with increase in dilution because as dilution ions become further apart reducing ionic interferences increasing mobility of the ionic.

The maximum value of Λ is called Molar conductivity at infinite dilution denoted as Λ_∞ or Λ_0 .

At Λ_∞ , All the ionic interferences are removed such that any increase in dilution results in no change in molar conductivity.

N.B: One of such interferences is the ion-ion interaction where by an ~~anion~~ ion is surrounded by an atmosphere of oppositely charged ions leading to formation of an ion atmosphere



Under the influence of an electric current, the atmosphere is attracted in opposite directions to the central ion leading to a dragging effect. This reduces the mobility of the central ion hence decrease in Λ .

Weak electrolyte

Molar conductivity increases with dilution. As dilution increases, the degree of ionisation of the electrolyte increases. Increasing the number of conducting ions hence increasing Λ .

ARRHENIUS THEORY & DEGREE OF IONISATION (α)

Degree of ionisation (α) is the fraction of the molecules of the electrolyte that exist as free ions.

$$\alpha = \frac{\Lambda_c}{\Lambda_\infty} \quad \text{where } \Lambda_c \text{ is } \Lambda \text{ at concentration } c \\ \Lambda_\infty \text{ is } \Lambda \text{ at infinite dilution}$$

NOTE: Since for all weak electrolytes ionisation becomes complete at Λ_∞ , the relation was thought to hold and as dilution increases α approximates to 1. and Λ would level off to a maximum value at Λ_∞

$\frac{\Lambda_c}{\Lambda_\infty}$ is also called the conductivity ratio.

Calculations

(i) The electrolytic conductivity of a 0.016M ethanoic acid solution at $20^\circ C$ is $1.96 \times 10^{-2} \text{ Sm}^{-1}$ and its Λ at infinite dilution is $3.5 \times 10^{-2} \text{ Smol}^{-1}\text{m}^2$, calculate (-)

(i) Molar conductivity of ethanoic acid at $20^\circ C$

(ii) the degree of ionisation of the Acid

(iii) the pH of the acid

Solution

$$(i) \Lambda = \frac{k}{c} \Rightarrow k = 1.96 \times 10^{-2} \text{ Sm}^{-1}$$

$$c = 0.016 \text{ M} = 0.016 \text{ mol dm}^{-3}$$

$$= 0.016 \times 10^3 \text{ mol m}^{-3}$$

$$= 16 \text{ mol m}^{-3}$$

$$\Rightarrow \Lambda = \frac{1.96 \times 10^{-2}}{16 \times 10^3} \text{ mol m}^{-3}$$

$$= 1.23 \times 10^{-3} \text{ Sm}^2 \text{ mol}^{-1}$$

$$(ii) \text{Using } \alpha = \frac{\Lambda_c}{\Lambda_\infty} = \frac{1.23 \times 10^{-3}}{3.5 \times 10^{-2}} = 0.035 = 3.5\%$$

Ethanoic acid is 3.5% ionised

$$(iii) [\text{H}_3\text{O}^+] = \alpha c = 0.035 \times 0.016$$

$$= 5.6 \times 10^{-4}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$= -\log (5.6 \times 10^{-4}) = \underline{\underline{3.25}}$$

KOHLRAUSCH'S LAW OF INDEPENDENT IONIC MIGRATION

At infinite dilution ions are furthest apart and conduct electricity independent of each other. Thus ~~The~~ the molar ionic conductivity of an electrolyte at infinite dilution is the sum of the molar conductivities of the individual constituent ions. This is Kohlrausch's law of independent ionic migration. i.e

$$\Lambda \infty AB = \Lambda \infty A^+ + \Lambda \infty B^-$$

CALCULATIONS

Given that:- The molar conductivities at infinite dilution for NaCl , NH_4Cl , NaOH , CH_3COONa and HCl are 113 , 134.1 , 225.1 , 101.2 and $397.8 \text{ S}^{-1}\text{cm}^2\text{mol}^{-1}$ respectively. Calculate:-

- $\Lambda \infty$ for CH_3COOH
- $\Lambda \infty$ for Ammonia solution.

Solution

- from Kohlrausch's Law,

$$\begin{aligned}\Lambda \infty \text{CH}_3\text{COOH} &= \Lambda \infty \text{CH}_3\text{COONa} + \Lambda \infty \text{HCl} - \Lambda \infty \text{NaCl} \\ &= 101.2 + 397.8 - 113 \\ &= \underline{\underline{386.05 \text{ S}^{-1}\text{cm}^2\text{mol}^{-1}}}\end{aligned}$$

$$\begin{aligned}\text{(ii)} \quad \Lambda \infty \text{NH}_4\text{OH} &= \Lambda \infty \text{NH}_4\text{Cl} + \Lambda \infty \text{NaOH} - \Lambda \infty \text{NaCl} \\ &= 134.1 + 225.1 - 113 \\ &= \underline{\underline{246.2 \text{ S}^{-1}\text{cm}^2\text{mol}^{-1}}}\end{aligned}$$

EXERCISE

1 (a) (i) State Kohlrausch's law of independent ion migration.

(ii) The Λ_∞ of KNO_3 , KCN and HNO_3 are 145 , 156 and $421 \text{ S}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Calculate the molar conductivity of HCN at infinite dilution.

(b) Explain how the molar conductivities of the following solution would vary with concentration.

(i) Sodium hydroxide (ii) Ammonia solution.

(2) The ionic conductivities of Na^+ and OH^- are 495×10^{-3} and $198 \times 10^{-2} \text{ S}^{-1} \text{ cm}^{-1}$. Calculate the molar conductivity of 0.1M NaOH solution.

(3) Calculate the molar conductivity of methanoic acid at infinite dilution. ($\Lambda_0 \text{ HCOONa} = 9.5 \times 10^{-2} \text{ Sm}^2 \text{ mol}^{-1}$, $\Lambda_0 \text{ NaCl} = 1.26 \times 10^{-1} \text{ Sm}^2 \text{ mol}^{-1}$, $\Lambda_0 \text{ HCl} = 4.26 \times 10^{-1} \text{ Sm}^2 \text{ mol}^{-1}$).

APPLICATIONS OF CONDUCTIVITY MEASUREMENTS AND KOHLRAUSCH'S LAW

① Indirect determination of Λ_0 for weak electrolytes. e.g. CH_3COOH . Since the Λ_0 for a weak electrolyte can't be measured directly owing to the very large dilution required to produce a constant limiting value.

② Determination of solubility of a sparingly soluble salt,

The $\frac{\text{electrolytic conductivity}}{\text{solubility}}$ of a salt $= \frac{K_{\text{solute}}}{K_{\text{solution}}} - \frac{K_{\text{solvent}}}{K_{\text{salt}}}$

and $\Lambda_c = \frac{K}{C}$ But for sparingly soluble salts the $\Lambda_c \approx \Lambda_0$.

$\Rightarrow \Lambda_0 = \frac{K}{C}$ But C is the solubility s , for salt.

$$\Rightarrow \Lambda_0 = \frac{K}{s} \quad \text{and thus} \quad s = \frac{K}{\Lambda_0}$$

Examples

(i) Calculate the solubility of a saturated solution of silver chloride at 25°C whose K is $4.36 \times 10^{-6} \text{ S}^2\text{m}^{-1}$ and for water is $2.5 \times 10^{-6} \text{ S}^2\text{m}^{-1}$. The molar conductivity of AgCl at 25°C is $1.46 \times 10^{-2} \text{ S}^2\text{m}^2\text{mol}^{-1}$. Give your answer in mol dm^{-3} .

$$S = \frac{K}{\Lambda_0}, \quad K_{\text{solute}} = K_{\text{solution}} - K_{\text{solvent}}$$

$$= 4.36 \times 10^{-6} - 2.5 \times 10^{-6}$$

$$= 1.86 \times 10^{-6} \text{ S}^2\text{m}^{-1}$$

$$\Lambda_0 = 1.46 \times 10^{-2} \text{ S}^2\text{m}^2\text{mol}^{-1}$$

$$\Rightarrow S = \frac{1.86 \times 10^{-6}}{1.46 \times 10^{-2}} \frac{\text{S}^2\text{m}^{-1}}{\text{S}^2\text{m}^2\text{mol}^{-1}}$$

$$= 1.27 \times 10^{-4} \text{ mol m}^{-3} \quad 1\text{m}^3 = 10^3 \text{ dm}^3 \Rightarrow 1\text{m}^{-3} = 10^{-3} \text{ dm}^{-3}$$

$$= 1.27 \times 10^{-7} \text{ mol dm}^{-3}$$

\therefore The solubility of AgCl = $1.27 \times 10^{-7} \text{ mol dm}^{-3}$ at 25°C

Exercise

1) At 25°C , the Λ_0 of AgNO_3 , KNO_3 and KCl are 133.4, 145.0 and $149.9 \text{ S}^2\text{cm}^2\text{mol}^{-1}$ respectively. At the same time the K of a saturated solution of AgCl is $3.14 \times 10^{-6} \text{ S}^2\text{cm}^2$. While that of pure water is $1.6 \times 10^{-6} \text{ S}^2\text{cm}^2$. Calculate the solubility of AgCl in mol dm^{-3} at that temperature.

2). The ionic conductivities of Rubidium and Sodium are 78.3 and $50.1 \text{ S}^2\text{cm}^2\text{mol}^{-1}$ respectively. Explain why the ~~size of~~ K of Rb^+ is higher than that of Na^+ .

3). The K of a saturated solution of thallium (I) chloride, TlCl is $2.4 \times 10^{-3} \text{ S}^2\text{cm}^2$ at 25°C . The Λ_0 of Tl(OH) , NaOH and NaCl are 273, 248 and $126 \text{ S}^2\text{cm}^2\text{mol}^{-1}$ respectively. K for water is $2.5 \times 10^{-6} \text{ S}^2\text{cm}^2$. Estimate:-

(i) Λ_0 of TlCl .

(ii) Solubility of TlCl in water at 25°C in mol/dm^3

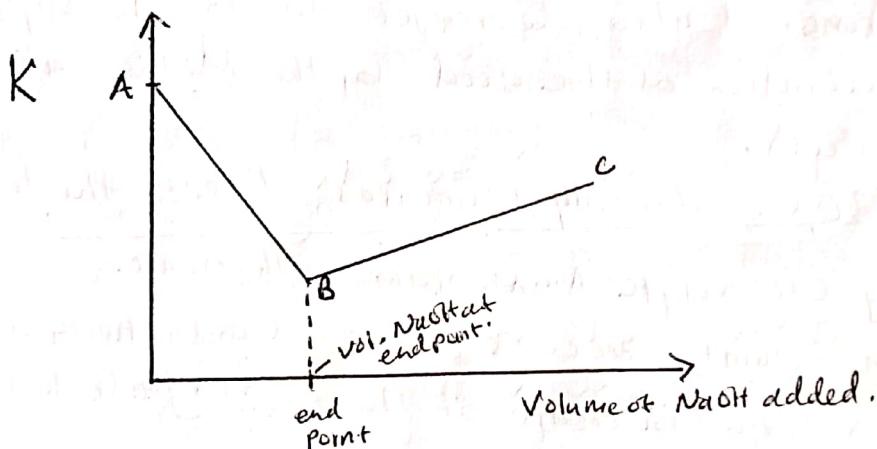
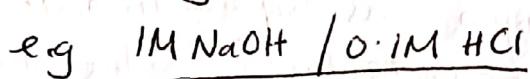
(iii) State any law assumed in your calculation.

4) The K of a saturated aqueous AgBr at 20°C is $5.42 \times 10^{-6} \text{ Sm}^{-1}$. The Λ of the Ag^+ and Br^- ions at infinite dilution at 20°C are 0.56×10^{-3} and $0.7 \times 10^{-2} \text{ Sm}^2 \text{ mol}^{-1}$ respectively. What is the solubility of the salt in mol L^{-1} at 20°C ? K of water is $2.5 \times 10^{-14} \text{ Sm}^{-1}$!

③ Conductometric titrations

Conductivity measurements can be applied in the determination of the end-point of an acid-base titration.

(a) Strong Acid against Strong Base - ~~eg~~



Initially the conductivity is high because HCl acid is completely ionised with many highly conducting hydrogen ions.

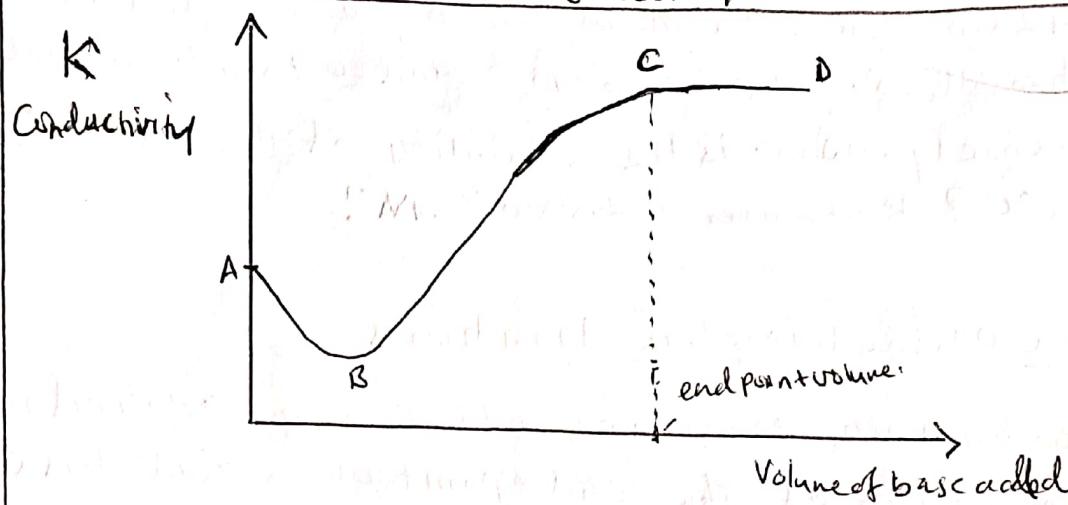
Conductivity then decreases with addition of the base, along AB, because the hydrogen ions are being neutralised by the hydroxide ions to form neutral water molecules. The fast moving H^+ ions are being replaced by slow moving Na^+ ions.

At the end point, there is minimum conductivity due to the conductivity of Na^+ ions and Cl^- ions.

Beyond the end point along BC, conductivity increases due to excess highly conducting hydroxide ions and many sodium ions.

(b) Weak acid Against Weak Alkali

e.g. 0.01M Methanoic acid / 0.1M Ammonia solution.



At A the Conductivity is low because the acid is a weak electrolyte. Along AB, Conductivity decreases due to Neutralisation of the hydrogen ions by ammonia. The fast moving hydrogen ions are being replaced by the slow moving ammonium ions. It also decreases due to the suppression of the dissociation of the acid by the Methanoate ions (Buffering effect).

Along BC, Conductivity increases due to the formation of a strong electrolyte, Ammonium methanoate.

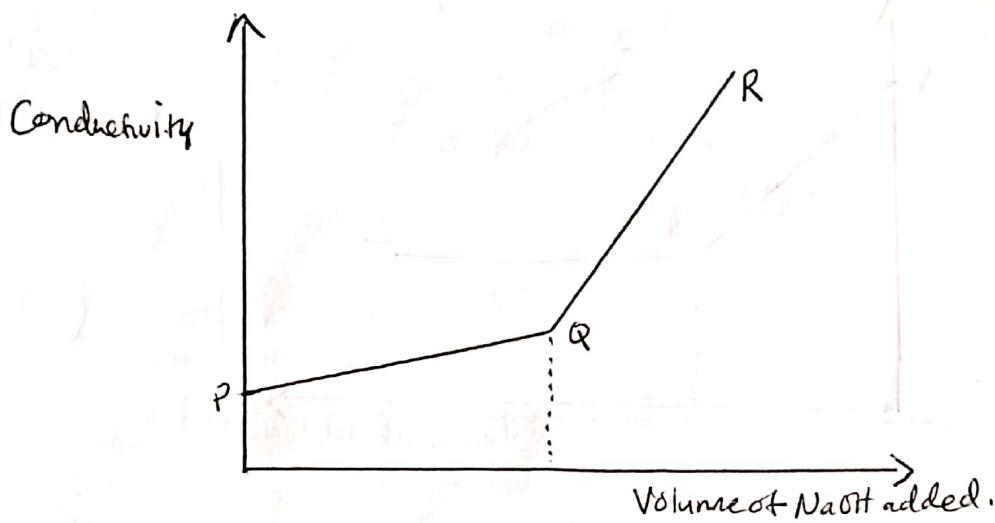
The end-point occurs at C. Conductivity at the endpoint is high because of the strong electrolyte formed compared to both reactants which are weak ~~electrolytes~~ electrolytes.

Along CD, Conductivity is constant because of the suppression of the dissociation of ammonia by the Ammonium ions (Buffering effect).

N.B.) The titrant is made about 10 times more concentrated than the titrand to ^{minimise} ~~cancel~~ the effect of dilution on the conductivity which would otherwise mask the underlying conductivity changes.

(C) Weak Acid Against Strong Alkali

e.g. (0.1M CH_3COOH / 1M. NaOH)



Initially, conductivity is low because the acid is a weak electrolyte.

Conductivity increases ^{gradually} along PQ as the number of ions increase, that is, the ions from the salt.

Any contribution to the overall conductivity over region PQ by that of the hydrogen ions is largely suppressed by the buffering action of the acetate ions.

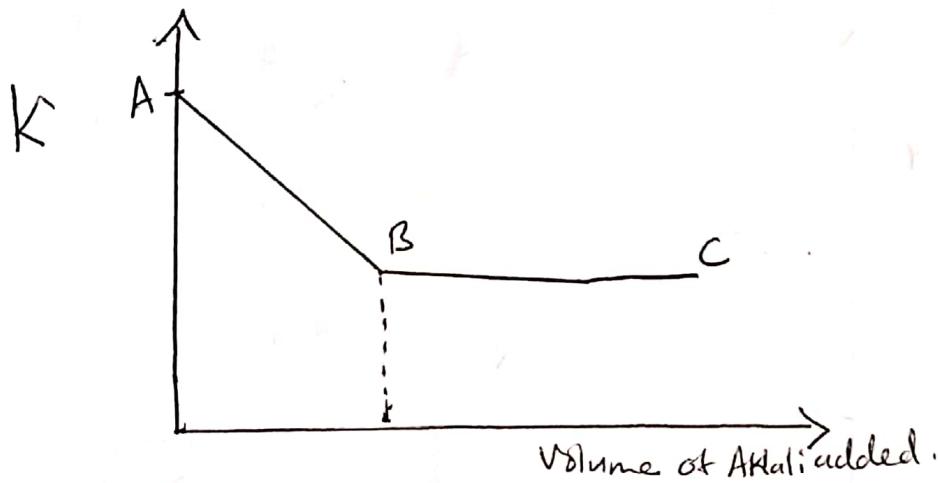
At point Q (endpoint), the conductivity is due to complete neutralisation of the acid to form a strong electrolyte, sodium ethanoate, that gives highly conducting ethanoate and sodium ions.

Beyond Q, conductivity increases along QR due to excess ~~OH⁻ ions~~ hydroxide ions added and are better electrolytes.

Note The rise is steeper along QR because the hydroxide ions are better conductors than the ethanoate ions, CH_3COO^- .

(d) Strong Acid against A Weak Base

e.g. 0.01M HCl / 0.1M NH₃ eqn



Initially the conductivity is high because the acid is a strong electrolyte i.e. fully ionised in solution to give many hydrogen ions that are highly conducting.

Along AB, there is a rapid decrease in conductivity due to the replacement of the fast moving hydrogen ion by the Ammonium ions.

Conductivity at the endpoint, B, is due to the presence of ions of Ammonium chloride.

Beyond B, Along BC, conductivity is almost constant because the ionisation of Ammonia is suppressed by the Ammonium ions already present in the solution.

Other Applications

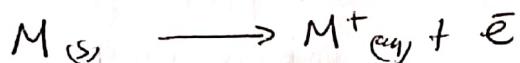
- ④ Determination of the dissociation constant of a weak electrolyte.
- A plot of $\log C$ against $\log \sigma$ has slope = $-K_e$
- ⑤ Study of complexes e.g. study of Fe^{3+} complex using EDTA. endpoint is when conductivity is minimum.

ELECTROCHEMICAL CELLS

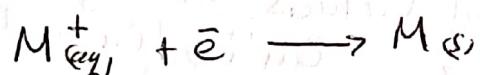
Electrochemical cells are devices that produce an emf as a result of chemical reaction taking place at the electrodes. These cells convert chemical energy into electrical energy. They consist of two half cells in which oxidation and reduction take place simultaneously (Redox reactions).

Usually these half cells are ~~made~~ electrodes made by placing a metal in a solution containing its ions.

When a metal high up in the electrochemical series is dipped in a solution containing its ions. It will tend to be attracted into the solution forming ~~tur~~ aqueous ions (oxidised). leaving electrons on the metal strip and making it negative with respect to the solution.



Metals low in the electrochemical series tend to be reduced, ~~by~~ and deposited on the metal strip taking electrons from the metal making it positive with respect to the solution.



In both cases, there develops a charge difference between the solution and the metal rod. This charge difference developed is referred to as an Electrode potential of the system and it is a measure of the metal to provide electrons i.e. to be oxidised or to act as a reducing agent.

FACTORS that Determine The Magnitude of Electrode Potential

- 1) Atomization energy. The higher the ~~higher~~ atomisation energy the lower the electrode potential.
- 2) Ionisation energy. The higher the ionisation energy the lower the electrode potential.

- ③ Hydration energy. The higher the hydration energy the higher the electrode potential.
- ④ Concentration of the ions at the metal surface. The higher the concentration of ions the less the formation of ions from the metal and hence the less the electrode potential.

⑤, Temperature. The temperature Affects electrode potential in accordance with le chatelier's principle. If the $M_{(s)} \rightleftharpoons M^{n+}_{(aq)} + n\bar{e}$ is endothermic, electrode potential will increase with temperature, if the above equilibrium is exothermic the electrode potential will decrease with temperature.

- ⑥ Nature of the Metal.

NOTE: The electrode reaction can be written as

$$M_{(s)} \xrightarrow[\text{energy.}]{\text{Atomisation}} M_{(g)} \xrightarrow{\text{I.E}} M^{n+}_{(g)} \xrightarrow{\text{H.E}} M^{n+}_{(aq)}$$

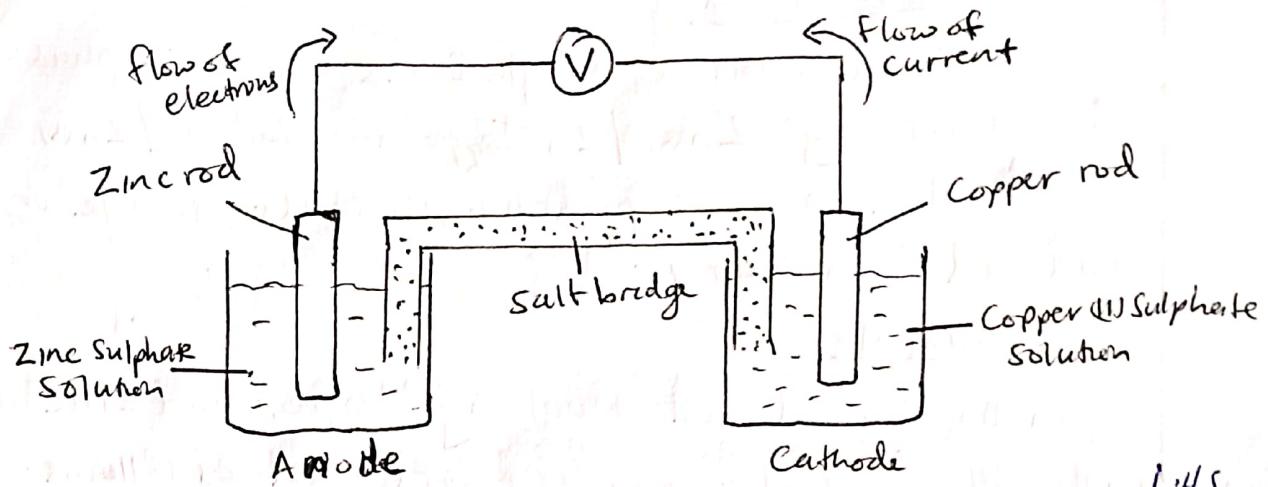
Electrode potential values are given as Reduction Potential Values e.g. $Cu^{2+}_{(aq)} | Cu_{(s)} | E = +0.34V$ OR
 $Cu^{2+}_{(aq)} + 2e \longrightarrow Cu_{(s)} | E = +0.34V$

The Daniel Cell

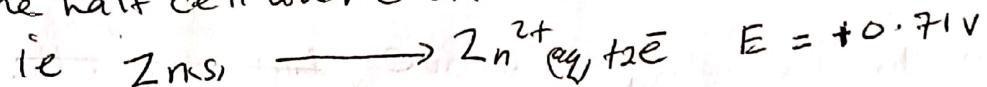
The Daniel cell is an example of an Electrochemical cell / voltaic / galvanic cell.

The Daniel cell is made up of two half cells, one has a Zinc rod in a Zinc Sulphate solution and the other has a copper rod in Copper Sulphate solution. The two solutions are connected by a salt bridge or separated by a porous partition. The salt bridge prevents excessive mixing of the two solutions and also completes the circuit.

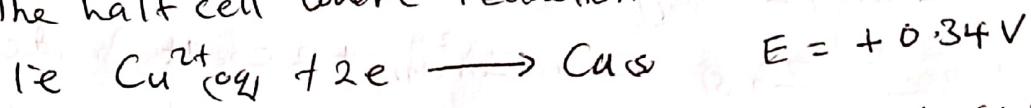
ILLUSTRATION



The half cell where oxidation occurs is the Anode (R.H.S)



The half cell where Reduction occurs is the Cathode (L.H.S)



By convention the Anode is always on the Left hand side
and the Cathode on the Right hand side

THE CELL DIAGRAM

An electrochemical cell may be represented by a cell diagram which summarises the reactions at the anode and cathode.

CELL CONVENTION

By convention, the electrode which is higher in the electrochemical series is written on the left hand side and the one lower on the right hand side

N.B) Reactions involving elements not clearly outlined in the E.C.S. may be treated using their Electrode Potentials.

- The electrode with a more negative (less positive) electrode potential is written on the left hand side (anode), whereas the electrode with a less negative (more positive) electrode potential is written on the right hand side (cathode)

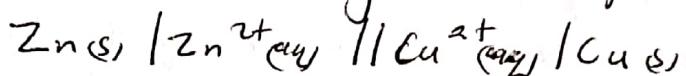
CELL NOTATION

In cell notation, Single lines represent phase boundaries e.g $\text{Zn(s)} / \text{Zn}^{2+}_{(\text{aq})}$ or $\text{Zn}^{2+}_{(\text{aq})} / \text{Zn(s)}$

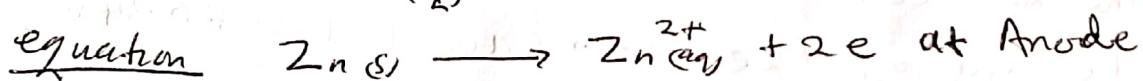
Double lines represent the salt bridge or the half cell boundary.

Example

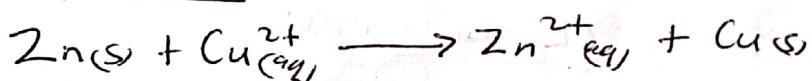
In the Daniel cell involving copper and zinc half cells, the cell diagram is represented as follows.



From the cell diagram above, ~~Zinc forms the~~ $\text{Zn(s)} / \text{Zn}^{2+}_{(\text{aq})}$ forms the Anode



equation overall



Since emf is due to flow of electrons from left to right, through the cell.

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{right}} - E^\ominus_{\text{left}}$$

And therefore, The standard electrode potential of cell E^\ominus_{cell} can be calculated.

Where; E^\ominus_{right} is the standard electrode potential of the half cell on the right and E^\ominus_{left} is for the left.

For the Daniel cell the emf or electrode potential is given by;

$$E^\ominus_{\text{cell}} = \cancel{0.34} + 0.34 - -0.71$$

$$= \underline{\underline{+1.10V}}$$

Standard Electrode Potentials

This is the reduction electrode Potential of an electrode which is the emf of the cell reaction with respect to the standard hydrogen electrode under standard conditions.

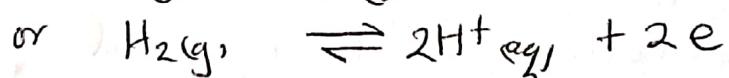
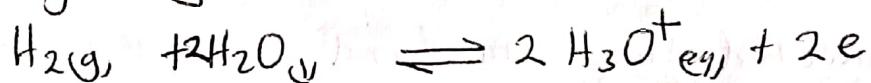
i.e., If a metal is immersed in a solution of H^+ ions of concentration 1M at 25°C , Then the potential acquired under standard conditions is the S.E.P, E^\ominus of the metal.

$$\text{e.g. } E^\ominus_{\text{Cu}} = +0.34 \text{ V}, \quad E^\ominus_{\text{Zn}} = -0.76 \text{ V.}$$

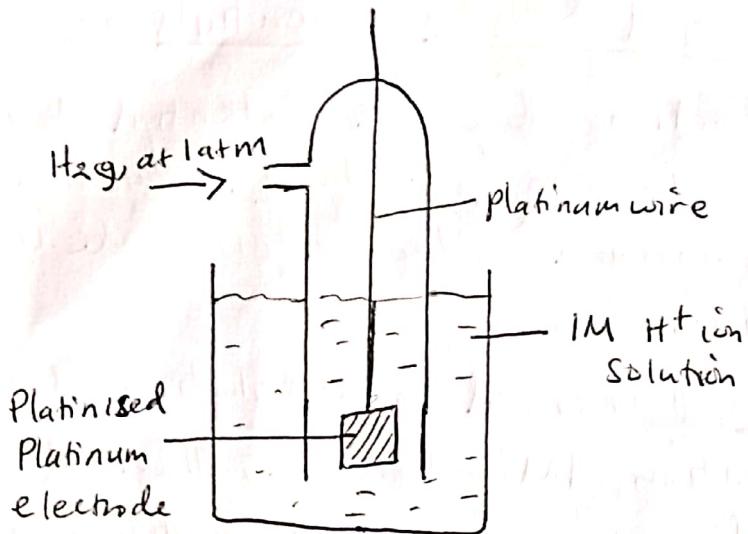
Standard electrode potentials are relative electrode potentials and not absolute because they are measured relative to a reference electrode called the Standard Hydrogen Electrode, S.H.E.

The Standard Hydrogen Electrode

It consists of a platinumized platinum electrode immersed in a solution of 1 mol dm^{-3} Hydrogen ions. Hydrogen gas at pressure of 1 atm is bubbled over the platinum electrode. On the surface of the platinum, An equilibrium is established between hydrogen gas and the hydrogen ions, $\text{H}^{+}(\text{aq})$.



A Potential develops on the surface of the Pt. It is assigned A value of zero Volts. 0.00 V

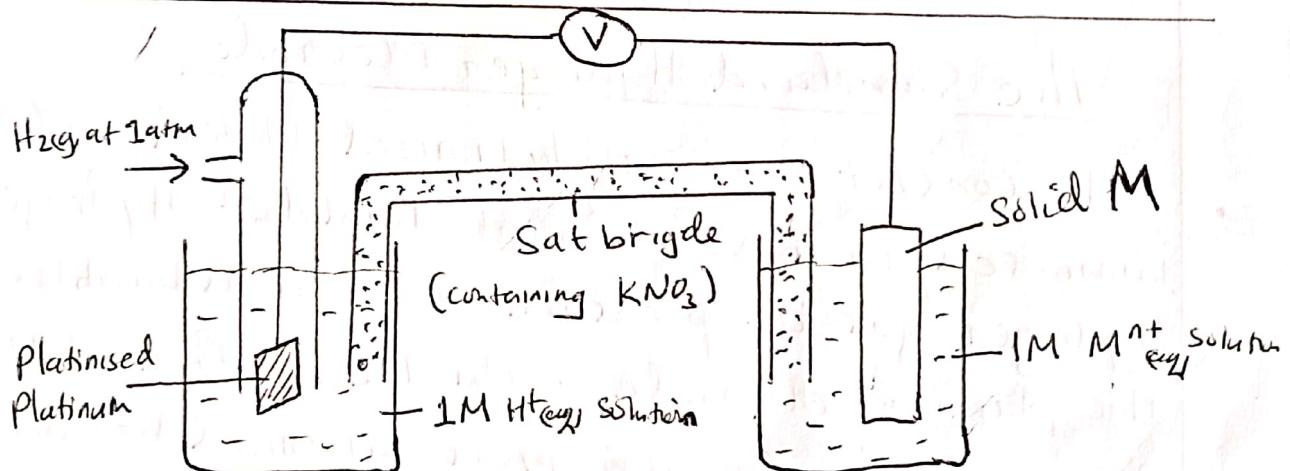


NB: Platinised platinum
is platinum plate covered
with a thin film of
Platinum black.

The Platinised Pt is useful as:

- (i) to allow H_2 to be absorbed on its surface
 - (ii) provides surface area so as to establish an equilibrium between H_2 and H^+ as rapidly as possible.
- * The SHE is by convention always on the left.

Determination of the S.E.P. of a metal



The metal is placed in a 1M solution of M^{+} ions and connected to a standard hydrogen electrode. The two electrodes are then joined by a salt bridge.

The voltmeter connected via the external circuit will show the emf of the cell.

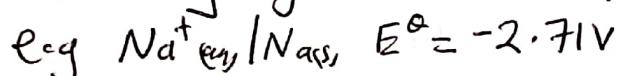
The Standard electrode potential of the metal will be equal to the emf of the cell measured by the Voltmeter. This is because the S.E.P of the S.H.E is taken as 0.00V.

N.B: By Convention each half-cell reaction is written as a reduction process.

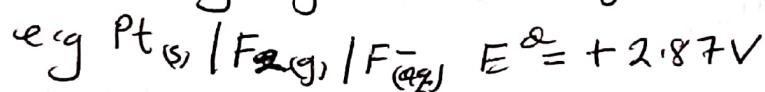


Therefore S.E.P.s are reduction potentials.

- Reducing agents have highly negative S.E.P.s

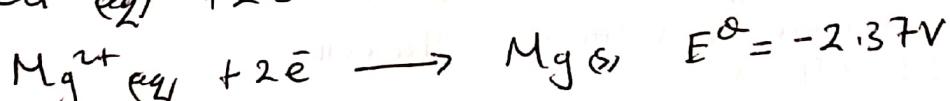
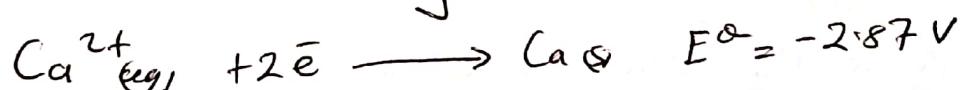


- Oxidising Agents have highly Positive S.E.P.s.



Questions

① Given the following half cell reactions



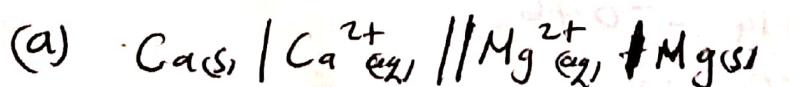
(a) Write the cell convention or diagram for the cell that can be formed

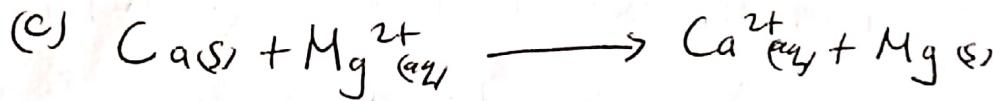
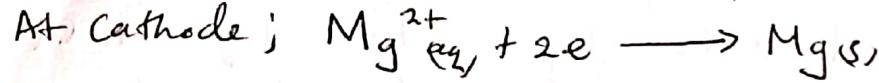
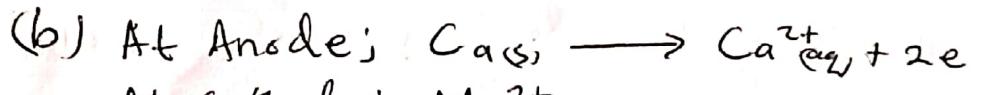
(b) Write the equation of reactions at each electrode

(c) Write the overall equation of the reaction.

(d) Calculate the emf of cell.

Solution





$$(d) E_{\text{cell}}^{\varnothing} = E_{\text{right}}^{\varnothing} - E_{\text{left}}^{\varnothing}$$

$$= -2.37 - -2.87 =$$

$$\underline{\underline{= +0.5V}}$$

②. The standard electrode potentials for some electrodes are given below:-

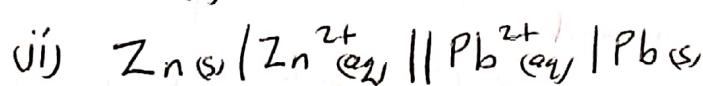
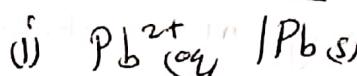
	E^{\varnothing}/V
$\text{Pb}^{2+}_{\text{aq}}/\text{Pb}_{(s)}$	-0.14
$\text{Zn}^{2+}_{\text{aq}}/\text{Zn}_{(s)}$	-0.76
$\text{Mg}^{2+}_{\text{aq}}/\text{Mg}_{(s)}$	-2.34

i) Which of the species listed is the strongest oxidising Agent. (IMK)

ii) Write the cell notation for the cell formed between $\text{Pb}^{2+}_{\text{aq}}/\text{Pb}_{(s)}$ and $\text{Zn}^{2+}_{\text{aq}}/\text{Zn}_{(s)}$ electrodes.

iii) Write the overall equation.

iv) Calculate the voltage for the cell.
Solution



iv) The voltage of the cell

$$E_{\text{cell}}^{\varnothing} = E_{\text{right}}^{\varnothing} - E_{\text{left}}^{\varnothing}$$

$$= -0.14 - -0.76$$

$$\underline{\underline{= +0.62V}}$$

APPLICATIONS OF E^\ominus values

- ① To predict feasibility of a reaction.

The spontaneity of a reaction is determined by the magnitude of the Gibbs free energy, G ,

$$\Delta G = -nE^\ominus F$$

where, n = no. of moles of electrons taking part in process.

F = Faraday's constant

E^\ominus = EMF of the cell.

If $\Delta G = 0$, the reaction is reversible.

$\Delta G > 0$, the reaction is not spontaneous.

$\Delta G < 0$, the reaction is feasible (energetically favoured)

Hence, for feasible reactions the E^\ominus is positive and

ΔG is negative.

- ② To determine the equilibrium constant, K for a reversible reaction,

$$\Delta G = -RT \ln K$$

$$-nE^\ominus F = -RT \ln K$$

$$\ln K = \frac{-nE^\ominus F}{-RT} \Rightarrow \ln K = \frac{nE^\ominus F}{RT}$$

$$\text{or } \log K = \frac{nE^\ominus F}{2.303 RT}$$

Where R is 8.314, T is temperature,

F is Faraday's constant 96500,

NB: K can be K_c , K_{sp} depending on the reaction.

③ To determine solubility of sparingly

soluble salt.

$$E = E^\circ + 0.059 \log [Ag^+] \quad \text{Generally } E = E^\circ + \frac{0.059}{z} \log [ion]$$

Example: Calculate the solubility of silver chloride given that the standard electrode potential E° for $Ag^{+}_{(aq)} / Ag_{(s)}$ is +0.8 V. When silver electrode is immersed in a saturated solution of silver chloride the electrode potential is +0.5 V.

Solution

$$E = E^\circ + 0.059 \log [Ag^+],$$

$$E^\circ = +0.8 \text{ V}$$

$$0.5 = 0.8 + 0.059 \log [Ag^+]$$

$$\Rightarrow \log [Ag^+] = \frac{0.5 - 0.8}{0.059} = -5.08$$

$$\Rightarrow [Ag^+] = 8.32 \times 10^{-6} \text{ mol dm}^{-3}$$

Since $[Ag^+] = [AgCl]$ solubility of $AgCl = 8.32 \times 10^{-6} \text{ mol dm}^{-3}$

Question

Given the S.E.P of Pb and Sn at 25°C as below:-
 $Pb^{2+}_{(aq)} / Pb_{(s)}$ $E^\circ = -0.13 \text{ V}$, $Sn^{2+}_{(aq)} | Sn_{(s)}$ $E^\circ = -0.14 \text{ V}$.

(a) Write the cell notation for the system and calculate the emf of cell.

(b) Calculate,

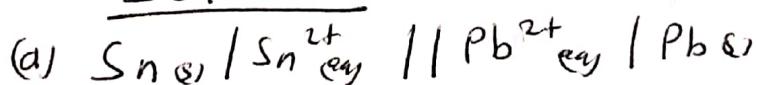
(i) The Gibbs free energy

(ii) The equilibrium constant K, for the system

(iii) Is the reaction feasible? Give reason

(iv) Is the reaction feasible?

Solution



$$(b) (i) \Delta G \neq 1/RT$$

$$\Delta G = -n F^{\circ} E$$

$$= -2 \times 0.01 \times 96500 \quad n=2, F=96500, E^{\circ}=?$$

$$= \underline{\underline{-1930 J}}$$

$$E_{\text{cell}}^{\circ} = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ}$$

$$= -0.13 - -0.14$$

$$= +0.01 V$$

$$(ii) \ln K_c = \frac{n E^{\circ} F}{R T}$$

$$\ln K_c = \frac{2 \times 0.01 \times 96500}{8.314 \times 25}$$

$$\ln K_c = 0.778$$

$$K_c = 2.18$$

(c) The reaction is feasible, because the E° is positive (or the Gibbs free energy is negative)

Types of Electrodes

(a) Gas electrode e.g

- The hydrogen electrode, $\text{Pt}_{(s)} | \text{H}_2(g) | \text{H}^+_{(\text{aq})}$

- The Fluorine electrode, $\text{Pt}_{(s)} | \text{F}_2(g) | \text{F}^-_{(\text{aq})}$

(b) Metal-Metal ion electrode e.g

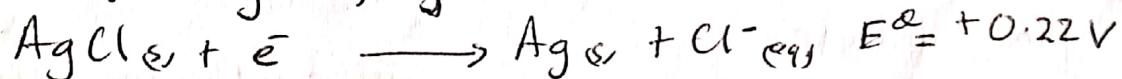
- $\text{Zn}^{2+}_{(\text{aq})} | \text{Zn}_{(s)}$, - $\text{Ag}^+_{(\text{aq})} | \text{Ag}_{(s)}$

(c) Metal-Insoluble Salt electrode e.g

$\text{Ag}_{(s)}, \text{AgCl}_{(\text{s})}, \text{Cl}^-_{(\text{aq})}$ Made by coating a suitable metal with an insoluble salt of that metal.

$\text{Pb}_{(s)}, \text{PbCl}_{2(\text{s})}, \text{Cl}^-_{(\text{aq})}$

In reduction; - $\text{AgCl}_{(\text{s})}, \text{Ag}_{(s)}, \text{Cl}^-_{(\text{aq})} \quad E^{\circ} = +0.22 \text{ V}$

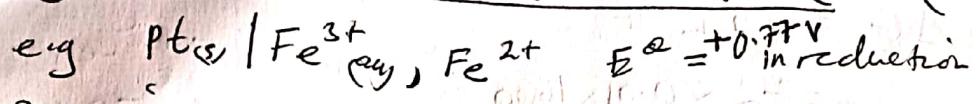


$\text{PbCl}_{2(\text{s})}, \text{Pb}_{(s)}, \text{Cl}^-_{(\text{aq})}$ NB: a comma(,) is used between

$\text{Hg}_2 \text{Cl}_2(\text{s}), \text{Hg}_{(l)}, \text{Cl}^-_{(\text{aq})}$

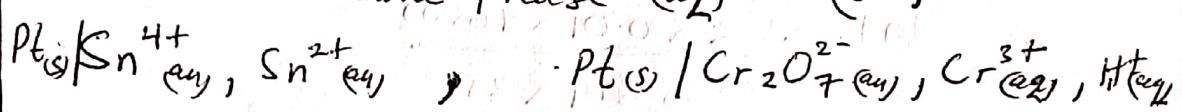
$\text{AgCl}_{(\text{s})}, \text{Ag}_{(s)}$. B'se same Phase (solid). Ox, Red

(4) Metal ion - Metal ion electrode OR (ion-ion)



~~Other ways~~. Pt_(s) is a catalyst. Nature of Pt is Pt in a Fe²⁺_(aq) and Fe³⁺_(aq) solution and Pt_(s) has to be on the electrode and in the cell diagram.

A comma (,) is used because the oxidized and reduced forms are of same phase (aq). (OX, Red)



~~# ways~~.

QUESTIONS

1) Given:- E^\ominus of $\text{Ag}^+_{(\text{aq})} / \text{Ag}_{(\text{s})} = +1.07\text{V}$,

E^\ominus of $\text{Cu}^{2+}_{(\text{aq})} / \text{Cu}_{(\text{s})} = +0.34\text{V}$

And the Cell diagram $\text{Ag}_{(\text{s})} | \text{Ag}^+_{(\text{aq})} || \text{Cu}^{2+}_{(\text{aq})} | \text{Cu}_{(\text{s})}$

(a) Calculate the emf of the cell.

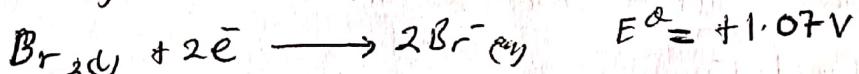
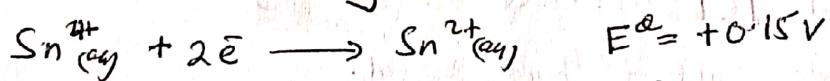
(b) Is the cell reaction spontaneous?

(c) Write the equations of reaction

(i) At cathode and Anode.

(ii) overall reaction.

2) Given the following values



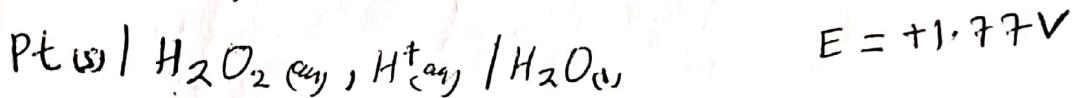
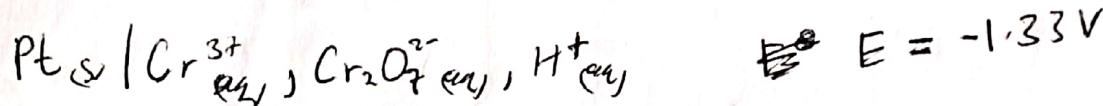
(a) Write the cell notation and calculate the emf of the cell

(b) Calculate,

(i) Gibb's free energy, (ii) equilibrium constant K ,

(iii) Is the reaction feasible? Give reason

③ The electrode potentials of the following are given



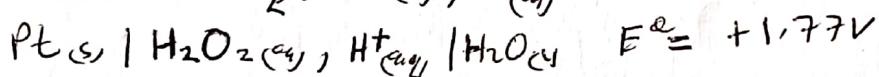
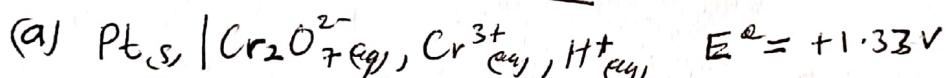
(a) Write the cell notation of cell that would be formed.

(b) Write the equations at Anode and Cathode and the overall equation.

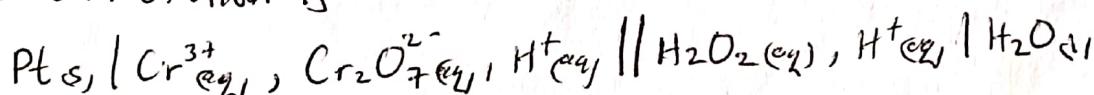
④ Give two differences between Electrolytic cell and galvanic cell.

⑤ Do questions on Chapter 13, No. 5, 6 and 7 on page 278, in EN. Ramsden, A-Level Chemistry 4th edition

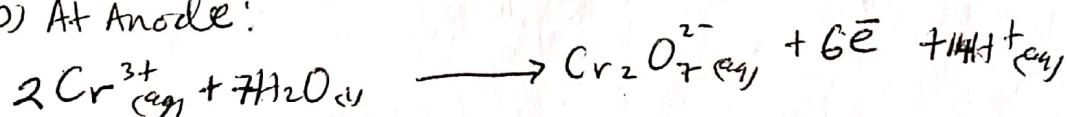
Solution of No. 3



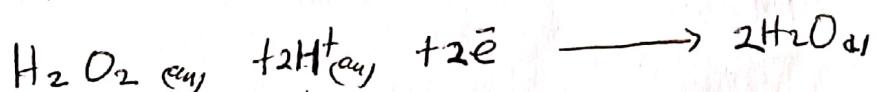
The cell notation is



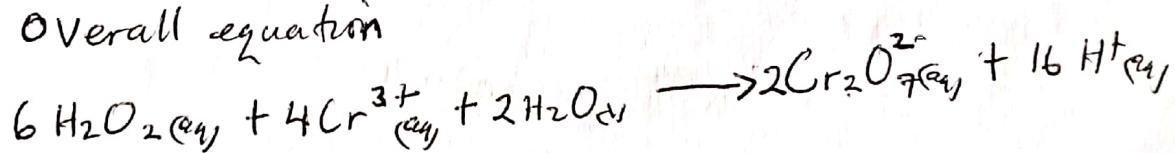
(b) At Anode:



At Cathode:



Overall equation



NB: Do the rest.