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ELECTROCHEMISTRY

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1. INTRODUCTION

Electrochemistry is a branch of chemistry, which deals the relationship between electrical energy and chemical changes taking place in redox reactions i.e., how chemical energy or how electrical energy can be used to bring about a redox reaction which is otherwise not spontaneous. It has many applications in electrolysis, energy producing cell etc. A flow of electricity through a substance may produce a chemical reaction, it involves study of electrolysis and conductance. While a chemical reaction causes flow of electricity through external circuit involves the measurement of electromotive force.

2. ELECTROLYSIS

Electrolysis is a process in which chemical reactions occur at the electrodes, dipping in the electrolytes, when voltage is applied across them. The electrode that is charged positively is called anode and the electrode that is charged negatively is called cathode.

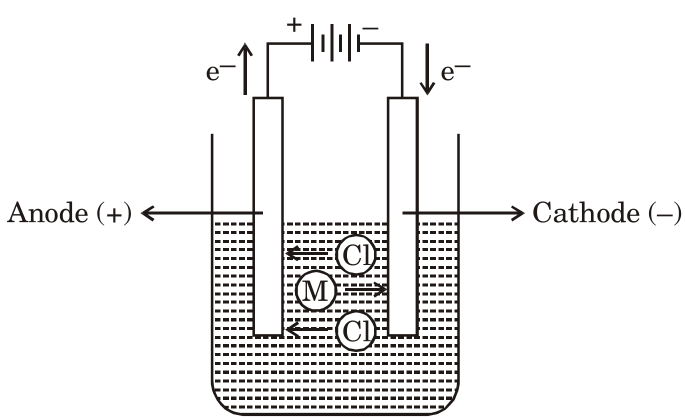
Let us two suitable metal electrodes, which are inserted in the electrolyte solution of MCl. The rods are now connected to a source of electromotive force (E.M.F.) As soon as the electrodes are connected to battery, the cations start moving towards cathode, take up electrons from the rod and get reduced to deposit as metal while anions (Cl^-) move towards anode and get oxidised to release Cl_2 gas. Thus, at anode, electrons are released at the rod and go into the battery and anode becomes positive electrode. The electrons from the battery enter cathode, making it negatively charged. Thus, flow of electrons takes place from anode the cathode outside the cell and inside the cell, electrons indirectly flow from cathode to anode.

The electrode at which oxidation takes place is called **anode** and the electrode at which reduction takes place is called **cathode.**

The reactions at the two electrodes are :

$$\text{At cathode : } M^+ + e^- \rightarrow M$$

$$\text{At anode : } Cl^- \rightarrow \tfrac{1}{2}Cl_2 + e^-$$



Thus, electrolysis is a process of chemical decomposition of the electrolyte by the passage of electric current. It is carried out in a cell called **electrolytic cell.**

3. ELECTROLYTIC CONDUCTANCE

3.1 Conductors

Any substance, which allows the electric current to pass through it, is called an electrical conductor. There are two types of conductors.

1. **Metallic conductors**

   Substances, which allow the passage of electricity through them without undergoing any chemical change.

   Example : Cu, Ag, Al etc.

2. **Electrolytic conductors**

   Substances that allow the passage of electricity through their molten state or aqueous solutions and undergo chemical decomposition.

Difference between metallic and electrolytic conduction

Metallic Conduction	Electrolytic Conduction
Passage of charge by electrons	Passage of charge by ions in molten and aqueous state.
Passage of charge brings about only physical changes. Does not involve transfer of matter.	Brings about physical and chemical changes. Involves transfer of matter in the form of ions
Resistance increases with temperature because of obstacles of vibrating kernels	Resistance decreases with temperature because viscosity decreases
Conducting power is high	Conducting power is low

3.2 Types of Electrolytes

There are three types of electrolytes : Strong, weak and non electrolytes.

1. **Strong electrolytes**

   A strong electrolyte is one which undergoes complete ionization when dissolved in water. The solution contains only the ions and not molecules.

   Examples : HCl, HNO_3, H_2SO_4, $NaOH$, $Ca(OH)_2$, $NaCl$, KCl, CH_3COONa etc.

$$HCl \rightarrow H^+ + Cl^-$$
$$NaCl \rightarrow Na^+ + Cl^-$$

2. Weak electrolytes

A weak electrolyte is one which undergoes partial ionization or dissociation. Here, in solution the ions and the dissociated molecules will be in equilibrium with each other. When such a solution is diluted, the degree of ionization increases. It becomes complete at infinite dilution.

Examples :

$HCOOH$, CH_3COOH, NH_4OH, CH_3NH_2, CH_3COONH_4, H_3PO_4 etc.

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

3. Non-electrolytes

A substance which doesn't allow the electric current to pass through is called a non electrolyte. These substances have no ions. Therefore they do not ionize in water (Covalent compounds).

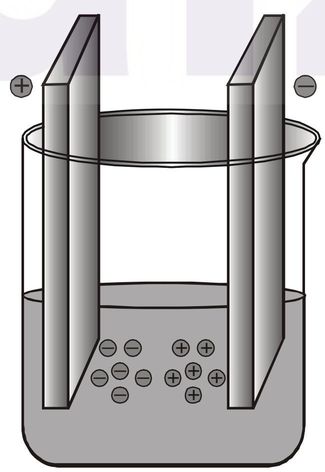
Examples :

C_6H_6, toluene, sugar, urea, CH_4, C_2H_6 etc.

3.3 Factors Influencing Electrolytic Conduction

1. The inter-ionic attraction

It is the intersection between the ions of the solute at low concentrations. It is now much at low concentrations the inter-ionic cone is very less, but at high concentrations it is appreciable.



The negative ion is pulled to the negative pole because it is surrounded by positive charges and vice versa.

2. The solvation of ions

This interaction is between the ions of the solute and the molecules of the solvent. Larger the interaction, greater is the solvation, lower will be the mobility of ions.

3. Viscosity of the medium

Interaction between the solvent molecules. The solvent-solvent interaction also lowers the mobility. More the viscosity less is the mobility.

4. Temperature

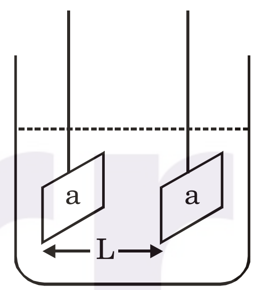
Ionic mobility increases with increase in temperature, thus the conductance increases.

Increase in temperature also decreases solute-solute, solute-solvent and solvent-solvent interaction.

4. Conductance, Specific Conductance, Equivalent Conductance and Molar Conductance

The reciprocal of resistance offered by an electrolyte to the flow of electricity through it is known as **conductance**. The unit of conductance is ohm^{-1} or mho.

$$\text{Conductance} = \frac{1}{\text{Resistance}}$$



Consider the portion of the electrolyte lying between the two parallel and equal electrodes as shown in the diagram; the area of each electrode being 'a' sq. cm and the distance between them is 'l' cm. Since the electrolytes like metallic conductors, also offer resistance to the flow of electricity, Ohm's law can be applied to the electrolytic conductor.

The Ohm's law relates the resistance 'R' offered by a medium with the applied voltage 'V' and the passing current 'I'.

$$V = IR$$

The resistance 'R' is related to the dimensions of the conductors as :

$$R \propto l$$

and

$$R \propto \frac{1}{a}$$

$\therefore$

$$R \propto \frac{l}{a};\ R = \rho \frac{l}{a}$$

where R = resistance, ρ = specific resistance

or

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

$\therefore$ Specific conductance = $\text{Conductance} \times \dfrac{l}{a}$

Just as $\dfrac{1}{R}$ is called conductance, $\dfrac{1}{\rho}$ is called specific conductance denoted by 'K'.

The solution under study is filled in a conductivity cell made of pyrex glass having two platinum electrodes fixed parallel to each other.

For a given cell, $\dfrac{l}{a}$ is known as cell constant. Thus :

Specific conductance = Conductance Cell constant

Note : The unit of specific conductance (K) is ohm^{-1} cm^{-1} or S cm^{-1}.

Molar Conductance ($\wedge$)

The molar conductance is defined as the conductance of all the ions produced by the ionisation of 1 gm mole of an electrolyte when present in V ml of solution. It is denoted by $\wedge_m$

Molar conductance $(\wedge_m) = K \times V$

where V is the volume in ml containing 1 gm mole of the electrolyte. If C is the concentration of the solution in g mole per litre, then :

$$\wedge = K \times \frac{1000}{c}$$

Its units are ohm^{-1} cm^2 mol^{-1} or S cm^2 mol^{-1}.

Equivalent Conductance ($\wedge_{eq.}$)

One of the factors on which the conductance of an electrolytic solution depends is the concentration of the solution. In order to obtain comparable results for different electrolytes, it is necessary take equivalent conductance.

Equivalent conductance is defined as the conductance of all the ions produced by one gram equivalent of an electrolyte in a given solution. It is denoted by $\wedge_{eq}$.

At concentration C (in gm-equivalent/L i.e., normality), equivalent conductance.

$$\wedge_{eq} = \frac{1000 \text{ specific conductance}}{c[\text{or Normality}]} \left(\text{ohm}^{-1}\text{cm}^{-1}\right)$$

$$= \frac{1000 \times K}{N}$$

4.1 Equivalent Conductance at infinite Dilution

Equivalent conductance increases with the increase in dilution but after a limit it becomes constant and does not further increase. The maximum value of equivalent conductance is known as equivalent conductance at ∞ dilution, denoted by $\wedge_\infty$. If this increase in equivalent conductance with dilution is only due to the increase in the degree of dissociation of the electrolyte, we can write,

$$\text{degree of dissociation } \alpha = \frac{\wedge_c}{\wedge_\infty}$$

4.2 Variation of Molar Conductivity With Concentration

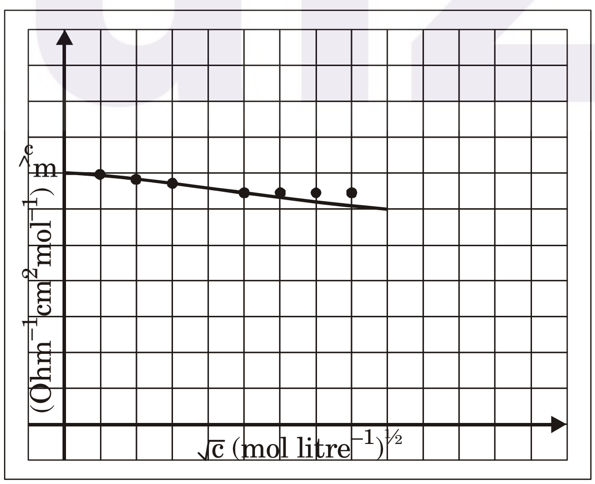
$\wedge_m$ of electrolytes increases with dilution.

The variation is different for strong and weak electrolytes.

Strong Electrolytes

It is given according to the equation $\wedge_m^c = \wedge_m^\infty - b\sqrt{c}$ (Debye Huckel onsager equation)

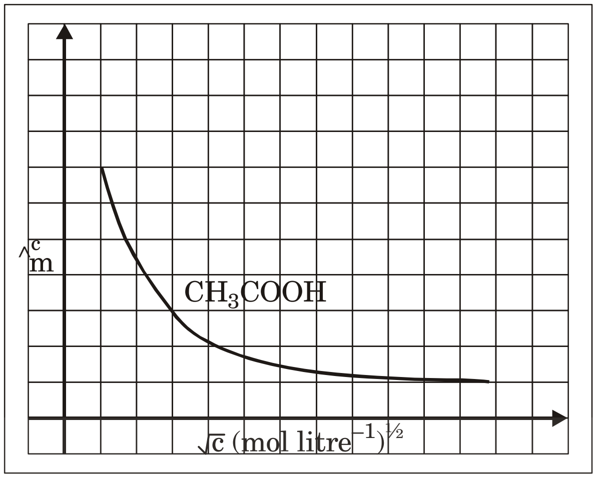
$\wedge_m^c$ and $\wedge_m^\infty$ are the molar conductance at a given concentration and at infinite dilution (respectively). b is a constant depending on the viscosity of the solvent. The graph shows that $\wedge_m$ decreases as the concentration increases.



This is because at higher concentration there is greater inter ionic attraction which retards the motion of the ions as conductance falls $\wedge_m^c$ and $\wedge_m^\infty$ is that conductance at infinite dilution where the ions are far apart and there is no inter-ionic attraction. This can be obtained by extrapolation of the graph to zero concentration.

Weak Electrolytes

A weak electrolyte dissociates to a much lesser extent so its conductance is lower than that of a strong electrolyte at the same concentration.



The very large increase at infinite dilution is because the ionization increases and so the number of ions in solution increases.

The value of $\wedge_m^c$ and $\wedge_m^\infty$ cannot be obtained by extrapolation as can be seen on the graph. It is obtained by applying Kohlrausch's law.

$\wedge_m$ values for strong electrolytes is larger than weak electrolytes for the same concentration.

Increase $\wedge_m$ for strong electrolyte is quite small as compared to that for weak electrolyte.

5. Relationship Between Molar and Equivalent Conductivities

According to the definition, $\wedge_m = \frac{k}{C_m}$ ...(i)

and $\wedge_{eq} = \frac{k}{C_{eq}}$ ...(ii)

For a solution containing a certain mass of solute per unit volume of the solution (let us say 'w' gram per litre), we can write

$$C_m = \frac{w}{\text{Molar mass of the electrolyte}} \quad \text{and} \quad C_{eq} = \frac{w}{\text{Equivalent mass of the electrolyte}}$$

From these relations, we can write $\frac{C_m}{C_{eq}} = \frac{\text{Equivalent mass of the electrolyte}}{\text{Molar mass of the electrolyte}}$

We know that molar mass of an electrolyte = z Equivalent mass of electrolyte where z is the number of equivalents of electrolytic charge per mole of the electrolyte. For example, n-factor of electrolyte).

$$\therefore \qquad \frac{C_m}{C_{eq}} = \frac{1}{z} \qquad \text{...(iii)}$$

Using equation (i) and (ii), we get $\frac{C_m}{C_{eq}} = \frac{\wedge_{eq}}{\wedge_m}$ ...(iv)

Then from equation (iii) and (iv), we get

$$\frac{C_m}{C_{eq}} = \frac{1}{z} \quad \text{or} \quad \wedge_m = z \times \wedge_{eq}$$

where z can have values equal to 1, 2, 3, ...

Example 1

When a certain conductivity cell was filled with 0.020 M KCl which has a specific conductivity of 0.2768 ohm^{-1} m^{-1}, it had a resistance of 82.40 Ω at 25 C. With 0.0025 M K_2SO_4, it has a resistance of 326.0 Ω. Calculate

(a) the cell constant

(b) conductivity of K_2SO_4 solution

(c) equivalent conductance and molar conductance of K_2SO_4 solution

Solution :

(a) Calculation has been done using 0.020 M KCl solution.

$$\text{specific conductance} = \frac{\text{cell constant}}{\text{resistance (R)}}$$

$\therefore$ cell constant = specific conductance resistance

= 0.2768 82.4

= 22.81 m^{-1}

(b) thus specific conductance of K_2SO_4 solution = 22.81/326

= 0.07 ohm^{-1} m^{-1}

(c) equivalent conductance $\wedge_c = \frac{1000 \times \text{specific conductance}}{\text{normality}}$

from (b) specific conductance = 0.07 ohm^{-1} m^{-1}

$= 0.0007 \ ohm^{-1} \ cm^{-1}$

normality $= 0.0025 \quad 2 = 0.005 \ N$

$\wedge_c = \dfrac{1000 \times 0.0007}{0.005}$

$= 140 \ ohm^{-1} \ cm^2 \ equiv.^{-1}$

molar conductance $\phi_c = \dfrac{1000 \times \text{specific conductance}}{\text{molarity}}$

$= \dfrac{1000 \times 0.0007}{0.0025}$

$= 280 \ ohm^{-1} \ cm^2 \ mol^{-1}$

Example 2

The resistance of a decinormal solution of a salt occupying a volume between two platinum electrodes 1.80 cm apart and 5.4 cm^2 in area was found to be 50 ohm. Calculate the equivalent conductance of the solution.

Solution :

We know equivalent conductance $\wedge_c = \dfrac{1000 \times \text{conductance} \times \text{cell constant}}{\text{normality}}$

given, conductance $= \dfrac{1}{\text{resistance}} = \dfrac{1}{50} ohm^{-1}$

cell constant $= \dfrac{l}{a} = \dfrac{\text{distance}}{\text{area}}$

$= \dfrac{1.80}{5.40} = \dfrac{1}{3} cm^{-1}$

normality $= 0.1 \ N$

$\therefore \quad \wedge_c = \dfrac{1000 \times \frac{1}{50} \times \frac{1}{3}}{0.1}$

$= 66.66 \ ohm^{-1} \ cm^2 \ equiv.^{-1}$

6. KOHLRAUSCH'S LAW

At infinite dilution an ionic specie (cation or anion) contributes a fixed value, at a given temperature, towards equivalent conductance of the electrolyte irrespective of the other ionic species in combination with it. There contributions are known as equivalent ionic conductance at ∞ dilution defined by λ_c^0 and λ_a^0 for cation and anion respectively.

Mathematically,

$$\wedge_m^{\infty} \text{ for } A_xB_y = x\lambda_{A^+}^{\infty} + y\lambda_{B^-}^{\infty}$$

where $+x\lambda_{B^-}^{\infty}$ and $y\lambda_{B^-}^{\infty}$ are the major conductance of A^+ and B^- at infinite dilution x and y are the ions provided by one formula unit of the electrolyte.

For example :

(1) $\wedge_m^{\infty}$ for NaCl $= \lambda_{Na^+}^{\infty} + \lambda_{Cl^-}^{\infty}$

(2) $\wedge_m^{\infty}$ for $BaCl_2 = \lambda_{Ba^{2+}}^{\infty} + 2\lambda_{Cl^-}^{\infty}$

(3) $\wedge_m^{\infty}$ for $Al_2(SO_4)_3 = 2\lambda_{Al^{3+}}^{\infty} + 3\lambda_{SO_4^{2-}}^{\infty}$

Applications of Kohlrausch's Law

Sometimes, the molar conductivity values for the ions are not available. In such cases, following procedure is adopted.

(i) Select a series of strong electrolytes such that the sum/difference of molar conductivities of their ions gives the molar conductivities of the ions of weak electrolyte.

(ii) Measure $\wedge_m^{\infty}$ values of these salts (strong electrolytes) at various concentrations (C_m) and plot $\wedge_m$ against $\sqrt{C_m}$ for each salt separately. Determine $\wedge_m^{\infty}$ for each salt (strong electrolyte) by extrapolation method.

(iii) Add and/or subtract the equations to get the $\wedge_m^{\infty}$ of the weak electrolyte. Let us determine the molar conductivity of a weak electrolyte, MA at infinite dilution. For this purpose, we take three salts MCl, NaA and NaCl and determine their $\wedge_m^{\infty}$ values by extrapolation method.

Calculation of molar conductivity at infinite dilution (A) for weak electrolytes (CH_3COOH)

$$\wedge^{\infty}_{(CH_3COOH)} = \lambda^{\infty}_{CH_3COO^-} + \lambda^{\infty}_{H^+}$$

The value of $\wedge^{\infty}$ for KCl, CH_3COOK and HCl can be obtained by extrapolation (they are strong electrolytes).

$$\wedge^{\infty}(KCl) = \lambda^{\infty}_{K+} + \lambda^{\infty}_{Cl^-}$$

$$\wedge^{\infty}(CH_3COOK) = \lambda^{\infty}_{CH_3COO^-} + \lambda^{\infty}_{K+}$$

$$\wedge^{\infty}(HCl) = \lambda^{\infty}_{H^+} + \lambda^{\infty}_{Cl^-}$$

$$\therefore \quad \wedge^{\infty}_{CH_3\,COOH} = \wedge^{\infty}_{CH_3COOK} + \wedge^{\infty}_{HCl} - \wedge^{\infty}_{KCl}$$

Example 3

The value of $\wedge^{\infty}_m$ for HCl, NaCl and CH_3CO_2Na are 426.1, 126.5 and 91 S cm^2 mol^{-1} respectively.

Calculate the value of $\wedge^{\infty}_m$ for acetic acid.

Solution :

Using Kohlrausch's law

$$\wedge^{\infty}_{HCl} = \lambda^{\infty}_{H^+} + \lambda^{\infty}_{Cl^-} \quad ...(i)$$

$$\wedge^{\infty}_{CH_3CO_2Na} = \lambda^{\infty}_{CH_3CO_2^-} + \lambda^{\infty}_{Na} \quad ...(ii)$$

and $\wedge^{\infty}_{NaCl} = \lambda^{\infty}_{Na^+} + \lambda^{\infty}_{Cl^-}$ ...(iii)

Adding equations (i) and (ii) and subtracting equation (iii), we get

$$\wedge^{\infty}_{HCl} + \wedge^{\infty}_{CH_3CO_2Na^-} - \wedge^{\infty}_{NaCl} = \lambda^{\infty}_{H^+} + \lambda^{\infty}_{Cl^-} + \lambda^{\infty}_{CH_3CO_2^-} + \lambda^{\infty}_{Na^-} - \lambda^{\infty}_{Na^+} - \lambda^{\infty}_{Cl^-}$$

$$= \lambda^{\infty}_{H^+} + \lambda^{\infty}_{CH_3CO_2^-} = \lambda^{\infty}_{CH_3CO_2H}$$

$$\therefore \quad \lambda^{\infty}_{CH_3CO_2H} = (426.1 + 9.1 - 126.5) = 390.6 \text{ S cm}^2 \text{ mol}^{-1}$$

Example 4

The equivalent conductance of silver nitrate solution at 250 C for an infinite dilution was found to be 133.3 ohm^{-1} cm^{2} equiv.$^{-1}$. The transport number of Ag^{+} ions in very dilute solution of $AgNO_3$ is 0.464. Calculate equivalent conductance of Ag^{+} and NO_3^- at infinite dilution.

Solution :

Given $\lambda_0(Ag^+)$ = transport number of Ag^+ $\wedge_0$

Given $\lambda_0(Ag^+) = n_{Ag^+} \quad \wedge_0 \ (AgNO_3)$

$= 61.9$ ohm^{-1} cm^{2} equiv^{-1}

By Kohlrausch's law

$$\wedge_0(AgNO_3) = \lambda_0(Ag^+) + \lambda_0(NO_3^-)$$

$$\therefore \quad \lambda_0(NO_3^-) = \wedge_0(AgNO_3) - \lambda_0(Ag^+)$$

$= 133.3 - 61.9$

$= 71.4$ ohm^{-1} cm^{2} equiv^{-1}

7. APPLICATIONS OF CONDUCTANCE MEASUREMENT

- Conductance is measured based on the **"Wheatstone Bridge"** principle.
- Conductivity cell is calibrated using saturated, 1N or 0.01 N KCl solution. Their specific conductances at a given temperature are constant values. If their conductances are known then,

$$\text{cell constant} = \frac{\text{specific conductance}}{\text{conductance}}$$

- Generally all measurement are made using conductivity water. If conductivity water is not available then

  True conductance = [exptl value – conductance of water]
- Conductance of conductivity water is taken as zero.

7.1 Degree of Ionisation and Ionisation Constant :

If $\wedge_c$ = equivalent conductance at concentration C gm equivalent L^{-1}

$\wedge_0$ = equivalent conductance at infinite dilution then $\quad x = \dfrac{\wedge_c}{\wedge_0}$

For weak acid, using Oswald's dilution law

$$HA \rightleftharpoons H^+ + A^-$$

K_a (ionisation constant of a weak acid) = $\dfrac{Cx^2}{(1-x)}$

Similarly K_b (ionisation constant of a weak base) can be calculated.

7.2 Solubility Product of a sparingly Soluble Salt :

If solute is sparingly soluble in a given solvent, its concentration is taken as its solubility in the saturated solution. Also $\text{Lt } C \to 0 \; \wedge_c = \wedge_0$

Thus $\quad \wedge_c = \wedge_0 = \dfrac{1000 \times \text{sp. conductance}}{C}$

$\wedge_0$ can be computed by use of Kohlrausch's law

Thus C (which is also the solubility of the sparingly soluble salt) and hence K_{sp} is known.

Solute	**K_{sp}**
AgCl	$K_{sp} = [Ag^+]\,[Cl^-] = S^2$
PbI_2	$K_{sp} = [Pb^{2+}]\,[I^-]^2 = 4S^3$
$Al(OH)_3$	$Ksp = [Al^{3+}]\,[OH^-]^3 = 27S^4$
A^xB^y	$K_{sp} = x^x y^y\ (S)^{x+y}$

S is the solubility in mol L^{-1}

Example 5

For a saturated solution of AgCl at 25 C, specific conductance is 3.41 10^{-6} ohm^{-1} cm^{-1} and that of water used for preparing the solution was 1.6 10^{-6} ohm^{-1} cm^{-1}. What is the solubility product of AgCl ? Given : $\wedge^{\infty}_{eqv}$ (AgCl) = 138.3 ohm^{-1} cm^{-1} equiv^{-1}.

Solution :

Specific conductance of AgCl = Specific conductance of solution – specific conductance of H_2O

$= (3.41 - 1.6) \quad 10^{-6} = 1.81 \quad 10^{-6}$ ohm^{-1} cm^{-1}.

For saturated solution of sparingly soluble salt,

$$\wedge_{eq} = \wedge^{\infty}_{eq}$$

and concentration of AgCl = solubility of AgCl.

$\therefore \quad \wedge_{eq}^{\infty} = \dfrac{1000 \times \text{specific conductance of AgCl}}{\text{Solubility of AgCl}}$ (since molarity = normality for AgCl)

$\therefore \quad 138.3 = \dfrac{1000 \times 1.81 \times 10^{-6}}{s}$

$\therefore \quad s = \dfrac{1000 \times 1.81 \times 10^{-6}}{138.3} = 1.31 \times 10^{-5}$ mol/lit

The solubility equilibrium of AgCl is shown as

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

$\therefore \quad K_{SP} = [Ag^{+}][Cl^{-}] = s \quad s = s^2$

$= (1.31 \quad 10^{-5})^2 = 1.72 \quad 10^{-10}\ M^2$

Example 6

At 25 C, the equivalent conductance of propanoic acid at infinite dilution is 386.6 ohm^{-1} cm^{2} equiv.$^{-1}$. If its ionisation constant is 1.4 10^{-5}, calculate equivalent conductance of 0.05 N propanoic acid solution at 25 C.

Solution :

$$K_a = \frac{Cx^2}{(1-x)} \approx Cx^2 \text{ (if } x << 1)$$

$$x = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.4 \times 10^{-5}}{0.05}}$$

$$= 0.0167$$

But $\quad x = \dfrac{\wedge_c}{\wedge_0}$

$\therefore \quad \wedge_c = x \quad \wedge_0$

$= 0.0167 \quad 386.6$

$= 6.47\ ohm^{-1}\ equiv.^{-1}$

Example 7

Kohlrausch found from conductivity measurement on very pure water that the degree of dissociation of water is 1.9 10^{-9}. Determine equivalent conductance of water.

$$\wedge_0(H^+) = 350,\ \wedge_0^{\circ}(OH^-) = 200$$

Solution :

$$x = \frac{\wedge_c}{\wedge_0}$$

$$\wedge_c = x\wedge_0$$

$$= x\left[\wedge_0(H^+) + \wedge_0(OH^-)\right]$$

$$= 1.9 \quad 10^{-9}\ [350 + 200]$$

$$= 1.045 \quad 10^{-6}\ ohm^{-1}\ cm^2\ equiv.^{-1}$$

Example 8

What is molar conductivity, the conductivity and the resistance (in a cell with constant 0.206 cm^{-1}) of an 0.040 M solution of acetic acid at 25 C ? Use K_a = 1.8 10^{-5}

Solution :

$$\left[\phi_m^{\circ}(CH_3COOH) = 390.5\ ohm^{-1}\ cm^2\ mol^{-1}\right]$$

$$\phi_m = \frac{1000 \quad conductivity}{molarity}$$

but $\frac{\phi_m}{\phi_m^{\circ}} = x$ (degree of ionisation)

$$\phi_m = \phi_m^{\circ} x$$

$\therefore$ $\phi_m = \phi_m^{\circ}\sqrt{\frac{K_a}{C}}$ (by Ostwald dilution Law)

$$= 390.5\sqrt{\frac{1.8 \times 10^{-5}}{0.04}}$$

$$= 8.28 \ \text{ohm}^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$$

$$\therefore \quad \text{conductivity} = \frac{\text{molarity} \times \phi_m}{1000}$$

$$= 3.31 \quad 10^{-4} \ \text{ohm}^{-1} \ \text{cm}^{-1}$$

$$\text{but conductivity (specific conductance)} = \text{cell constant} \quad \frac{1}{\text{resistance}}$$

$$\therefore \quad \text{resistance} = \frac{\text{cell constant}}{\text{conductivity}}$$

$$= \frac{0.206}{3.31 \times 10^{-4}} = 621.98 \ \text{ohm}$$

Example 9

The conductivity of the purest water is 5.5 10^{-8} ohm^{-1} cm^{-1}. What would be the resistance measured for a sample of this water in the conductivity cell (cell constant = 0.2063 cm^{-1}) ? What are the value of pK_w and pH of pure water ?

(λ (H^+) = 349.8 ohm^{-1} cm^2 mol^{-1}, λ (OH^{-1}) = 199.1 ohm^{-1} cm^2 mol^{-1})

Solution :

$$\text{Conductivity of pure water} = 5.5 \quad 10^{-8} \ \text{ohm}^{-1} \ \text{cm}^{-1}$$

$$\text{but conductivity} = \frac{\text{cell constant}}{\text{resistance}}$$

$$\therefore \quad \text{resistance} = \frac{\text{cell constant}}{\text{conductivity}}$$

$$= \frac{0.2063}{5.5 \times 10^{-8}} \ \text{ohm} = 3.751 \quad 10^6 \ \text{ohm}$$

water is weak electrolyte

$$\text{hence} \quad \wedge_0 (H_2O) = \lambda^0_{(H^+)} + \lambda^0_{(H^-)}$$

$$= 548.9 \ \text{ohm}^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$$

$$\wedge_c \text{ (calculated) at 55.5 M } H_2O = \frac{1000 \times \text{conductivity}}{\text{molarity}}$$

$$= \frac{1000 \times 5.5 \times 10^{-8}}{55.5}$$

$$= 9.91 \quad 10^{-7}$$

$$\therefore \quad x \text{ (degree of ionisation)} = \frac{\wedge_c}{\wedge_0}$$

$$= \frac{9.91 \times 10^{-7}}{548.9}$$

$$= 2 \quad 10^{-9}$$

$$\therefore \quad [H^+] = Cx = 55.5 \quad 2 \quad 10^{-9}$$

$$= 1 \quad 10^{-7}$$

$$\therefore \quad pH = -\log [H^+] = 7$$

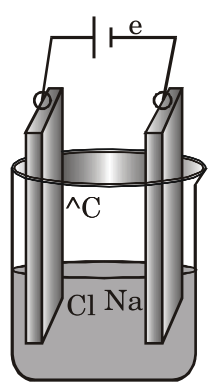
Also $[OH^-] = [H^+] = 1 \quad 10^{-7}$

$$\therefore \quad K_w = [H^+][OH^-] = 1 \quad 10^{-14}$$

$$\therefore \quad pK_w = -\log K_w = 14$$

8. QUANTITATIVE ASPECT OF ELECTROLYSIS

Decomposition of a compound into its constituents by passing electricity is called electrolysis. It consists of an electrolytic solution in a container. Two electrodes are dipped in it and they are connected to a battery. When the electricity is passed, the anion moves to the anode and gets oxidized. This releases electrons, these electrons pass through the outer circuit jump through the battery and these electrons are available at the cathode for reduction of cations.



At anode, $Cl^- \rightarrow Cl + 1e^-$ (oxidation)

At cathode, $Na^+ + e^- \rightarrow Na$ (reduction)

9. FARADAY'S LAWS

The quantitative relationship between the amount of electricity passed through a cell and the amount of substances discharged at the electrodes was systematised by Michael Faraday in the form of the following laws :

9.1 First law

The amount of substance discharged (deposited or dissolved) at the electrode is proportional to the quantity of the electricity passing through the electrolyte.

Mathematically :
$$\left.\begin{aligned} w &\propto q \\ w &\propto I.t \quad (q = I.t) \\ w &= z.I.t \end{aligned}\right\} \qquad ...(1)$$

where w is the weight of the substance discharged at an electrode in gram; q is the charge in coulomb, t is the time of flow of electricity in second, I is the current in ampere and z is a constant known as the Electrochemical Equivalent which is defined as the number of grams of the substance deposited or dissolved by one coulomb of electricity.

9.2 Second law

When the same quantity of electricity is passed through different solutions, the amounts of different substances deposited or dissolved at the electrodes in different electrolytic cells are proportional to their equivalent weights and in an electrolytic cell, chemically equivalent amounts of substances are discharged at both the electrodes.

Interpretation of Faraday's Second Law

Let us now interpret the second law of Faraday in a simple manner.

1 electron reduces and deposits 1 M^+ ion at an electrode (i.e., $M^+ + e^- \rightarrow M$)

$\therefore$ 1 mole of electrons shall reduce and deposit 1 mole of M^+ ions

If the ion has a valency of n,

n mole of electrons shall reduce 1 mole of M^{n+} ions.

$\therefore$ 1 mole of electrons shall reduce $\frac{1}{n}$ mole of M^{n+} ions.

For example : 1 mole of electrons reduces or deposits 1 mole of Ag^+ or $\frac{1}{2}$ mole of Cu^{2+} or $\frac{1}{3}$ mole or Al^{3+}.

Now, that (number of mole   valency) represents number of equivalents

$\therefore$ 1 mole of electrons shall reduce or deposit 1 equivalent of Ag^+ or Cu^{2+} or Al^{3+}. In general, 1 mole of electricity (electrons) liberates 1 equivalent of matter.

Again we know :

charge of 1 mole of electrons = charge of an electron   Av. const.

= $1.6021 \quad 10^{-19} \quad 6.022 \quad 10^{23}$ coulomb

= 96487 coulomb

= 96500 coulomb

= 26.8 ampere-hour per equivalent

= 1 faraday.

Thus the essential content of Faraday's second law is that 1 faraday, which corresponds to 1 mole of electrons, liberates 1 equivalent of matter.

In redox reactions, the amount of the reactant, corresponding to 1 mole of electrons is thus its equivalent mass.

Electrochemical Equivalent and Equivalent Weight

The weight in gram of a substance liberated by 1 coulomb of electricity is called electrochemical equivalent whereas the weight in gram liberated by 96500 (or 1 faraday or 1 mole electricity) is called Gram Equivalent Weight of the substance.

From Faraday's law, we can deduce the relationship between the electrochemical equivalent and equivalent weight.

$w \propto Q$ (Ist Law)

$w \propto E$ (IInd Law)

$\Rightarrow \quad w = \frac{Q\,E}{F} \qquad \left(\frac{1}{F} = \frac{1}{96500}\right)$

$\Rightarrow \quad \frac{w}{E} = \frac{Q}{F}$

No. of gram equivalents = No. of Faradays of electricity

$\Rightarrow$ 1 gm eq = any substance = 1 F of electricity

Now there are two approaches to solve a problem

First calculate the number of faradays of electricity by using :

$$\text{No. of faradays} = \frac{Q}{F} = \frac{I\,t}{96500}$$

(i) Now by using the definition :

1 gm eq. of any substance ≡ 1 F of electricity passed

Calculate the number of gm. eq. and by using the definition of gm. eq. (gmeq. = mass/E), determine the amount of substance deposited.

(ii) Using anodic and cathodic reactions as follows :

Let us consider a typical anode reaction

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

$\Rightarrow$ n (e's) ≡ 1 molecule of M

$\Rightarrow$ N_0 (n e's) ≡ N_0 molecule of M (N_0 : Avogadro number)

$\Rightarrow$ N_0 (n e's) ≡ 1 mole of M

$\Rightarrow$ n **F ≡ 1 mole of M** (charge of N_0 electrons ≡ 1 F = 96500 C)

So in this approach, first write anodic and cathodic reactions and derive the mole Vs faraday relation.

(iii) Using the combined relation obtained from Ist and IInd Laws :

w = Z I t

$$\Rightarrow \quad w = \frac{E\,I\,t}{96500}$$

Example 10

In the electrolysis of aq. $CuSO_4$, a current of 2.50 Amp is allowed to flow for exactly 3.0 hr. How many grams of Cu and lts. of O_2 are produced at 25 C and 1 atm. pressure ?

Solution :

The electrolysis of aqueous solution $CuSO_4$ solution takes place as follows :

$$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-}$$

Cathode : $Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$

Anode : $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $(4OH^- \rightarrow O_2 + 2H_2O + 4e^-)$

(sulphate ions and H^+ ions remain in the solution to given an acidic solution)

Now from cathode : $Cu^{2+} + 2e \rightarrow Cu_{(s)}$

$\Rightarrow$ 2F ≡ 1 mole of Cu

calculating number of faradays passed through the cell;

$$\text{No. of faradays} = \frac{I\,t}{96500} = \frac{2.5 \times 3 \times 3600}{96500} = 0.28\text{ F}$$

$\Rightarrow$ 2F ≡ 1 mole of Cu

⇒ 0.28 F ≡ 1/2 0.28 moles of Cu

≡ 1/2 0.28 63.5 gm

⇒ 8.9 gm of Cu have been deposited

Now from anode : $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

⇒ 4F ≡ 1 mole of O_2

⇒ 0.28 F ≡ 1/4 0.28

≡ 0.07 moles of O_2

Now using gas equation : PV = nRT

$$V_{(lt)} = \frac{nRT}{P} = \frac{0.07 \times 0.0821 \times 298}{1} = 1.71 \text{ lt}$$

Example 11

If 6.43 10^5 Coulombs of electricity are passed through an electrolytic cell containing $NaClO_3$. 245 gm of $NaClO_4$ are produced at the anode at the end of electrolysis. Determine the anode efficiency.

Solution :

$$\text{Anode efficiency} = \frac{\text{actual wt. of any substance liberated}}{\text{theoretical wt. as calculated by Faraday's Law}}$$

OR $$\text{Anode efficiency} = \frac{\text{actual No. of faradays used up}}{\text{total No. of Faradays used}}$$

Let us write anode reaction first :

$$ClO_3^- \rightarrow ClO_4^-$$

balancing by ion electron method :

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^-$$

⇒ 2F ≡ 1 moles of $NaClO_4$

⇒ 1 mole of $NaClO_4$ ≡ 2 F of electricity

⇒ $\frac{245}{122.5}$ moles of $NaClO_4$ ≡ 2 $\frac{245}{122.5}$ = 4 F of electricity

So for the production of 245 gm of $NaClO_4$, 4F of electricity i.e., 4 96500 C of charge is actually consumed. But we are given that a total of 6.43 10^5 C of electricity is passed through the cell, so some of the charge is wasted.

$\Rightarrow$ Anode efficiency $= \dfrac{4 \times 96500}{6.43 \times 10^5} \times 100$

$\Rightarrow$ Anode efficiency = 60.03%

Alternative Method :

First calculate the theoretical amount of $NaClO_4$ produced by passing 6.43 10^5 C.

$\Rightarrow$ 2F ≡ 1 moles of $NaClO_4$

$$\Rightarrow \quad \frac{6.43 \times 10^5}{96500} \text{ F} \equiv \frac{1}{2} \times \frac{6.43 \times 10^5}{96500} \text{ moles of } NaClO_4$$

$$\equiv \frac{1}{2} \times \frac{6.43 \times 10^5}{96500} \times 122.5$$

$$\equiv 408.12 \text{ gm of } NaClO_4$$

But in actual only 245 gm of $NaClO_4$ are produced (some of the current is lost as heat and against the resistance to flow of ions).

anode efficiency $= \dfrac{245}{408.12} \times 100 = 60.03\%$

Example 12

An acidic solution of Cu^{2+} salt containing 0.4 gm of Cu^{2+} is electrolysed until the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 mL and the current at 1.2 Amp. Calculate the volume of gases evolved at STP during the entire electrolysis.

Solution :

Assuming Cu^{2+} salt to be $CuSO_4$, the reactions occuring at the electrodes will be :

Anode : $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$

Cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

After complete deposition of copper, the reactions would be

Anode : $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$

Cathode : $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Now, amount of Cu deposited $= \dfrac{0.4 \text{ g}}{63.6 \text{ g mol}^{-1}}$

$= 0.00629$ mol

amount of oxygen liberated $= \frac{1}{2} \quad 0.00629$ mol

$= 0.003145$ mol

quantity of electricity passed in seven minutes after the deposition of the cutire copper

$= (1.2 \text{ A})\ (7 \quad 60 \text{ s}) = 504 \text{ C}$

Amount of electrons carrying this much of electricity $= \frac{504\,\text{C}}{96500 \text{ C mol}^{-1}} = 0.00522$ mol

From the electrode reactions, we can say that

amount of oxygen liberated $= \frac{1}{4} \quad 0.00522$ mol

$= 0.001305$ mol

amount of hydrogen liberated $= \frac{1}{2} \quad 0.00522$ mol

$= 0.00261$ mol

Total amount of gases liberated in the entire electrolysis

$= (0.003145 + 0.001305 + 0.00261)$ mol

$= 0.00706$ mol

volume of gases evolved at STP during entire electrolysis

$= (0.00706 \text{ mol})\ (22400 \text{ mL mol}^{-1})$

$= 158.2$ mL

Example 13

A current of 20.0 A is used to plate Ni from $NiSO_4$ solution. Both Ni and H_2 are liberated at cathode. The current efficiency with respect to liberation of Ni is 50%.

(a) What mass of Ni is plated on cathode per hour ?

(b) What is the thickness of plating ion on both the sides of the square cathode of edge length 4 cm ?

Given : Atomic mass of Ni = 58.79 amu and its density = 8.9 g cm^{-3}

Solution : Since the current efficiency with respect to liberation of Ni is 50%, 10 A out of 20 A current will be used for the liberation of Ni. Hence,

quantity of electricity available in 1 H to deposit Ni $= (10 \text{ A})\ (60 \quad 60 \text{ s}) = 36000 \text{ C}$

Amount of electrons used in plating out

$$Ni = \frac{36000\ C}{965000\ C\ mol^{-1}} = 0.373\ mol$$

$$\text{Amount of Ni plated out} = \frac{1}{2} \times 0.373\ mol$$

$$= 0.1865\ mol$$

$$\text{Mass of Ni plated out} = (0.1865\ mol)\ (58.79\ g\ mol^{-1})$$

$$= 10.964\ gm$$

$$\text{Mass of Ni plated out on either side of square cathode} = \frac{1}{2} \quad 10.964\ gm$$

$$= 5.482\ gm$$

$$\text{Volume of Ni plated out on either side of square cathode} = \frac{5.482}{8.9\ g\ cm^{-3}}$$

$$= 0.616\ cm^3$$

$$\text{Thickness of Ni plated out on either side of square cathode} = \frac{0.616\ cm^3}{(4\,cm)(4\,cm)}$$

$$= 0.0385\ cm$$

Example 14

Calculate the quantity of electricity required to reduce 12.3 gm of nitrobenzene to aniline if the current efficiency for the process is 50%. If the potential drop across the cell is 3.0 volts, how much energy is consumed ?

Solution :

Writing the ionic reaction for the reduction of nitro-benzene as follows :

$$C_6H_5NO_2 + 6H^+ + 6e^- \rightarrow C_6H_5NH_2 + 2H_2O$$

$\Rightarrow$ 6F of electricity ≡ 1 mole of nitro-benzene

Now moles of nitro-benzene = 12.3/123 = 0.1 moles

$\Rightarrow$ 0.1 mole ≡ 0.6 F

hence 0.6 F of electricity are used to reduce 12.3 gm of nitro-benzene if the current efficiency is 100%. But it is given that current efficiency is 50%, so

$$\text{No. of Faradays required} = \frac{0.6 \times 100}{50} = 1.2F$$

Now potential difference = 3 V

The energy (E) consumed is given by : E = charge potential difference

E = 115800 3 = 347400 J = 347.4 kJ

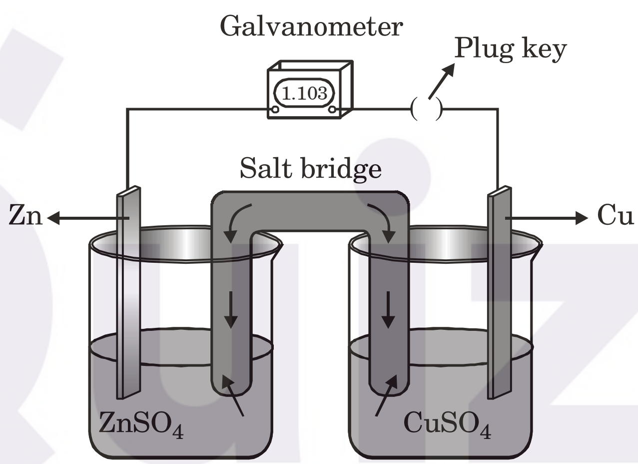
10. ELECTROCHEMICAL CELL

An electrochemical cell is a system consisting of electrodes that dip into an electrolyte and in which a chemical reaction either uses or generates an electric current.

A voltaic or galvanic cell is an electrochemical cell in which a spontaneous reaction generates an electric current.

Construction and Working

A zinc rod is dipped in $ZnSO_4$ solution and a Cu rod in $CuSO_4$ solution. The Zn rod is externally connected to the copper rod through a rheostate, a galvanometer and a plug key.



The two aqueous solutions are interlinked through a salt bridge which is an inverted 'u' tube which is filled with saturated semi solid paste of Agar Agar saturated in KCl or KNO_3 solution [Agar agar is a carbohydrate which forms a jelly like substance when dissolved in hot water]

Working

When the circuit is completed, a deflection is observed in the (G) towards the zinc electrode indicating that the e^- are flowing from the Zn electrode to Cu electrode.

At the Zn electrode, oxidation takes place.

$$Zn \rightarrow Zn^{+2} + 2e^- \text{ (oxidation)} \qquad ...(1)$$

The 'e' removed or lost or retained by the metal move through the material of the electrode and reach the Cu electrode at which they are accepted by Cu ions of the solution to form neutral copper atoms.

$$Cu^{+2} + 2e^- \rightarrow Cu \text{ (reduction)} \qquad ...(2)$$

In an electrochemical cell, each electrode constitutes one half of the cell and the reaction taking place at the electrode is called half-cell reaction. The overall cell reaction is obtained by adding the two half-cell reactions (1) and (2).

$$Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu \text{ (Overall reaction)}$$

From this it is found that when Zn is added to $CuSO_4$ solution, Zn displaces Cu from $CuSO_4$ with the liberation of heat. But in the electrochemical cell there is no direct contact between Zn and $CuSO_4$. Hence whatever the heat energy that would have been liberated appears in the form of electrical energy. Hence the electrochemical cell acts as a source of current although for a short interval.

The electrode at which oxidation takes place or the metal rod becomes negative charged is called negative electrode.

The electrode at which reduction takes place or the metal rod becomes positive charged is called positive electrode. Accordingly, in the above constructed electrochemical cell, zinc electrode acts as negative electrode while Cu electrode acts as positive.

The salt bridge

(a) acts as a link between the two aqueous solution.

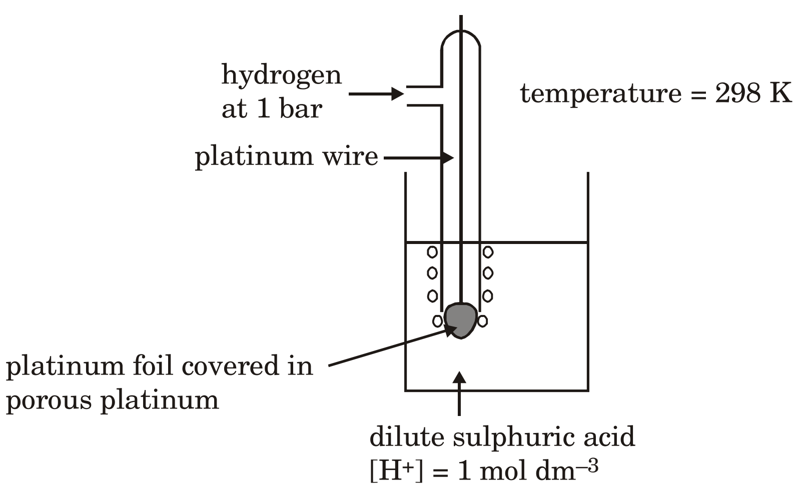
(b) overcomes liquid junction potential.

(c) Maintains the electrical neutrality of the aqueous solution of the electrodes by releasing or sending oppositely charged ions into the solution.

In general KCl salt bridge is used while KNO_3 salt bridge is used when silver electrode is involved as one of the electrodes.

11. THE STANDARD HYDROGEN ELECTRODE

The standard hydrogen electrode looks like this :



What is happening ?

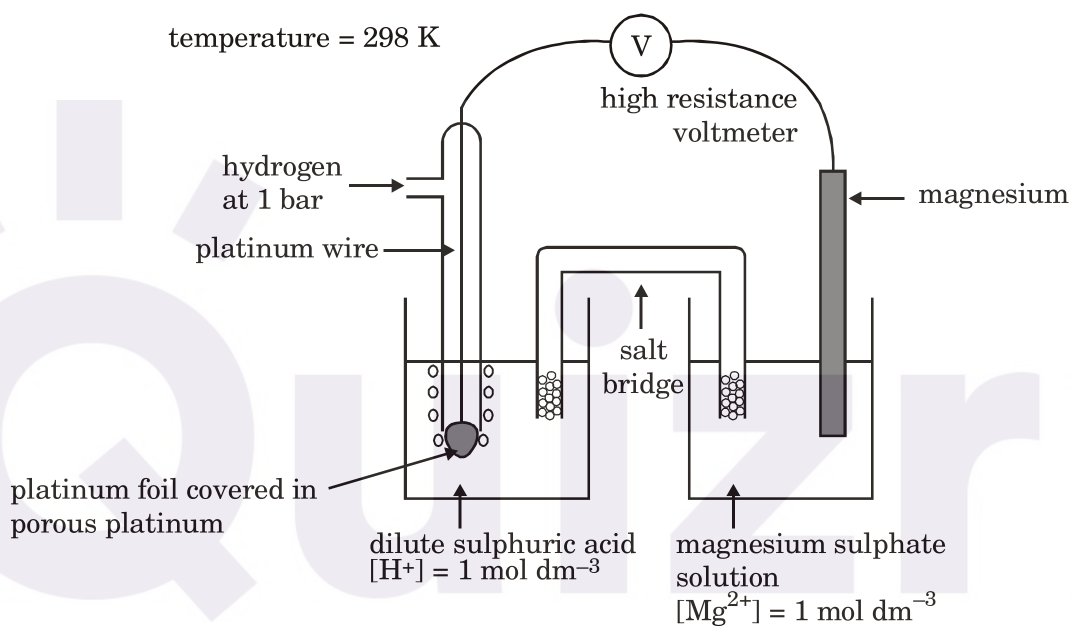
As the hydrogen gas flows over the porous platinum, an equilibrium is set up between hydrogen molecules and hydrogen ions in solution. The reaction is catalysed by the platinum.

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

This is the equilibrium that we are going to compare all the others with.

Using the standard hydrogen electrode

The standard hydrogen electrode is attached to the electrode system you are investigating–for example, a piece of magnesium in a solution containing magnesium ions.



Cells and half cells

The whole of this set-up is described as a cell. It is a simple system which generates a voltage. Each of the two beakers and their contents are described as half cells.

The salt bridge

The salt bridge is included to complete the electrical circuit but without introducing any more bits of metal into the system. It is just a glass tube filled with an electrolyte like potassium nitrate solution. The ends are "stoppered" by bits of control wool. This stops too much mixing of the contents of the salt bridge with the contents of the two beakers.

The electrolyte in the salt bridge is chosen so that it doesn't react with the contents of either beaker.

What happens ?

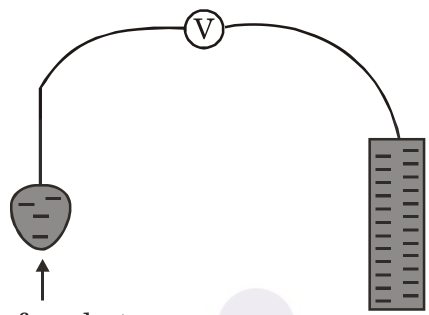
These two equilibria are set up on the two electrodes (the magnesium and the porous platinum) :

$$Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons Mg_{(s)}$$

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

Magnesium has a much greater tendency to form its ions than hydrogen does. The position of the magnesium equilibrium will be well to the left of that of the hydrogen equilibrium.

That means that there will be a much greater build-up of electrons on the piece of magnesium that on the platinum. Stripping all the rest of the diagram out, apart from the essential bits :



There is a major difference between the charge on the two electrodes - a potential difference which can be measured with a voltmeter. The voltage measured would be 2.37 volts and the voltmeter would show the magnesium as the negative electrode and the hydrogen electrode as being positive.

This sometimes confuses people! Obviously, the platinum in the hydrogen electrode isn't positive in real terms - there is a slight excess of electrons built up on it. But voltmeters doesn't deal in absolute terms - they simply measure a difference.

The magnesium has the greater amount of negativeness - the voltmeter records that as negative. The platinum of the hydrogen electrode isn't as negative - it is relatively more positive. The voltmeter records it as positive.

What if you replace the magnesium half cell by a copper one ?

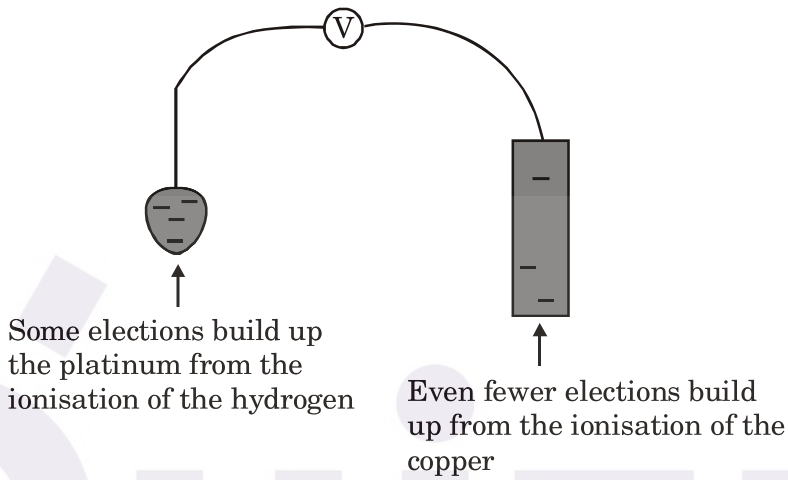
This means replacing the magnesium half cell by one with a piece of copper suspended in a solution containing Cu^{2+} ions with a concentration of 1 mol dm^{-3}. You would probably choose to use copper(II) sulphate solution.

Copper forms its ions less readily than hydrogen does. Of the two equilibria :

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$$

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

...the hydrogen one lies further to the left. That means that there will be less build up of electrons on the copper than there is on the platinum of the hydrogen electrode.



There is less difference between the electrical charges on the two electrodes, so the voltage measured will be less. This time it is only 0.34 volts.

The other major change is that this time the copper is the more positive (less negative) electrode. The voltmeter will show the hydrogen electrode as the negative one and the copper electrode as positive.

The emf of a cell measured under standard conditions is given the symbol E_{cell}.

12. CELL CONVENTIONS

A quick way of drawing a cell

Drawing a full diagram to represent a cell takes too long. Instead, the cell in which a magnesium electrode is coupled to a hydrogen electrode is represented like this :

Square brackets show the hydrogen flowing over the platinum.

Single vertical lines show a boundary between two phases - for example, between the magnesium ions and the solid metal.

$$Pt\ [H_{2(g)}]\ |\ 2H^{+}_{(aq)}\ \|\ Mg^{2+}_{(aq)}\ |\ Mg_{(s)}$$

Double vertical lines show the salt bridge. This is sometimes shown by a single (or double) broken vertical line (or lines).

You will often find variants on the way the hydrogen electrode is represented, such as :

$$Pt\ |\ H_{2(g)}\ |\ 2H^{+}_{(aq)}\ \| \qquad or \qquad Pt\ [H_{2(g)}]\ |\ H^{+}_{(aq)}\ \|$$

Square brackets replaced by a vertical line showing the boundary between the platinum and the hydrogen.

One hydrogen ion shown rather than the 2 from the equation.

Cell Notation of An Electrochemical Cell

(i) Anode is written on the left side and cathode is written on the right side.

(ii) Phase boundaries are indicated by vertical bar or slash.

(iii) Concentration of the electrolytes in the anode and cathode must be written in parenthesis.

(iv) In case of a gas, the partial pressure is to be mentioned in atm or mm Hg.

(v) A comma is used to separate two chemical species present in the same solution.

(vi) A double vertical line i.e. || denotes that a salt bridge is present.

(vii) EMF of the cell is written on the extreme right of the representation.

For example :

(i) $Zn(s)\ |ZnSO_4(c_1\ M)||\ CuSO_4(c_2\ M)|\ Cu(s)$; E_{cell}

(ii) $Pt\ |H_2(P_1\ atm)\ |\ HCl\ (c\ M)\ AgCl(s)|Ag$; E'_{cell}

(iii) $Pt\ |Fe^{2+}\ (c_1\ M),\ Fe^{3+}\ (c_2\ M)||\ Ag^{+}\ (c\ M)|\ Ag$; E''_{cell}

Note : In some cell representations (as in (ii) above), the salt bridge is not indicated which implies that the electrolyte is common to both anode and cathode compartments.

$$Pt\ [H_{2(g)}]\ |\ 2H^{+}_{(aq)}\ \|\ Mg^{2+}_{(aq)}\ |\ Mg_{(s)} \qquad E_{cell} = -\ 2.37\ V$$

Show that the magnesium (the right hand electrode) is the negative one.

In the copper case :

$$Pt\ [H_{2(g)}]\ |\ 2H^{+}_{(aq)}\ \|\ Cu^{2+}_{(aq)}\ |\ Cu_{(s)} \qquad E_{cell} = +\ 0.34\ V$$

Shows that the copper (the right-hand electrode) is the positive one.

Summarizing what standard electrode potentials tell

Remember that the standard electrode potential of a metal/metal ion combination is the emf measured when that metal/metal ion electrode is coupled to a hydrogen electrode under standard conditions.

What you are doing is comparing the position of the metal/metal ion equilibrium with the equilibrium involving hydrogen.

Here are a few typical standard electrode potentials :

Metal/metal ion combination	**E (volts)**
Mg^{2+} / Mg	– 2.37
Zn^{2+} / Zn	– 0.76
Cu^{2+} / Cu	+ 0.34
Ag^{+} / Ag	+ 0.80

Remember that each of these is comparing the position of the metal/metal ion equilibrium with the equilibrium involving hydrogen.

Here are the five equilibria (including the hydrogen one) :

$$Mg^{2+}_{(aq)} + 2e^{-} \rightleftharpoons Mg_{(s)}$$

$$Zn^{2+}_{(aq)} + 2e^{-} \rightleftharpoons Zn_{(s)}$$

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

$$Cu^{2+}_{(aq)} + 2e^{-} \rightleftharpoons Cu_{(s)}$$

$$Ag^{+}_{(aq)} + e^{-} \rightleftharpoons Ag_{(s)}$$

If you compare these with the E values, you can see that the ones whose positions of equilibrium lie furthest to the left have the most negative E values. That is because they form ions more readily - and leave more electrons behind on the metal, making it more negative.

Those which don't shed electrons as readily have positions of equilibrium further to the right. Their E values get progressively more positive.

Half Cell Potential (Single-Electrode Potential)

When a metal is dipped into a solution containing its own ions, a half cell or a single electrode is formed. In a half cell there are two opposing tendencies. Firstly, the metal, say M, may dissolve in the solution or rather may go into the solution in the form of ions ($M \rightleftharpoons M^{n+} + ne$; oxd.) and secondly, the ions M^{n+}, from the solution may deposit on the electrode ($M^{n+} + ne \rightleftharpoons M$; red.). When one of these two tendencies dominates over the other, there develops a half cell potential or electrode potential.

The tendency to lose electrons, i.e., to get oxidised is called **oxidation potential** and similarly the tendency to gain electrons, i.e., to get reduced is called **reduction potential.**

Since any half cell reaction can be written as a reversible process e.g., $Cu^{2+} + 2e \rightleftharpoons Cu$, the reduction potential and oxidation potential for a single electrode are equal in magnitude but opposite in sign. For the electrode $Cu/CuSO_4$ (1 M), the reduction potential, $E_{Cu^{2+}, Cu} = +0.34$ V and so its oxidation potential $E_{Cu, Cu^{2+}} = -0.34$ V at 25 C. The half cell potentials cannot be directly determined as there is no way of isolating a single half cell reaction. The electrode potential can be determined by coupling it with a standard hydrogen electrode (i.e., by forming a cell). As the electrode potential of a standard hydrogen electrode has been arbitrarily fixed as zero volt at 25 C, the emf of such a cell gives the single electrode potential or emf of half cell. A standard hydrogen electrode is represented as :

$$Pt, H_2 \text{ (1 atm)}, HCl \text{ ([}H^+\text{] = 1 M)}$$

Single Convention (IUPAC)

The reduction potential of a half cell is given a positive sign when the half cell reaction involves reduction, when coupled with a standard hydrogen electrode; and a negative sign when the half cell reaction involves oxidation, when connected with a standard hydrogen electrode.

Standard Half Cell Potential (Standard Electrode Potential) and Electrochemical Series

It will be discussed a little later that the half cell potential at a temperature depends upon the concentration of ions of the dissipated material. If for the half cell, $M \mid M^{n+}$ (aq), $[M^{n+}] = 1$ M at 25 potential is termed standard half cell potential or standard electrode potential.

Standard half cell potential, like half cell potential is also measured on standard hydrogen electrode scale.

Such a list of E values of various half cells arranged in the given orders is known as electrochemical series.

Some of the half cells or electrodes arranged in decreasing their E (reduction) values are as follows :

Standard Reduction Potentials at 298 K

Reduction half reaction	Standard reduction potential E (in volts)	Reduction half reduction	Standard reduction potential E (in volts)
$Li^+ + e^- \longrightarrow Li$	– 3.05	$Sn^{2+} + 2e^- \longrightarrow Sn$	– 0.14
$K^+ + e^- \longrightarrow K$	– 2.93	$Pb^{2+} + 2e^- \longrightarrow Pb$	– 0.13
$Ba^{2+} + 2e^- \longrightarrow Ba$	– 2.90	$2H^+ + 2e^- \longrightarrow H_2$	0.00
$Ca^{2+} + 2e^- \longrightarrow Ca$	– 2.87	$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	0.013
$Na^+ + e^- \longrightarrow Na$	– 2.71	$Cu^{2+} + e^- \longrightarrow Cu^+$	0.15
$Mg^{2+} + 2e^- \longrightarrow Mg$	– 2.37	$Cu^{2+} + 2e^- \longrightarrow Cu$	0.34
$Al^{3+} + 3e^- \longrightarrow Al$	– 1.66	$I_2 + 2e^- \longrightarrow 2I^-$	0.53
$Mn^{2+} + 2e^- \longrightarrow Mn$	– 1.18	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	0.77
$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2H^- (aq)$	– 0.83	$Ag^+ + e^- \longrightarrow Ag$	0.80
$Zn^{2+} + 2e^- \longrightarrow Zn$	– 0.76	$Br_2 + 2e^- \longrightarrow 2Br^-$	1.08
$Cr^{3+} + 3e^- \longrightarrow Cr$	– 0.74	$Cl_2 + 2e^- \longrightarrow 2Cl^-$	1.36
$Fe^{2+} + 2e^- \longrightarrow Fe$	– 0.44	$O_2 (g) + 4H^+ (aq) + 4e^- \longrightarrow 2H_2O$	1.23
$Cd^{2+} + 2e^- \longrightarrow Cd$	– 0.40	$Au^{3+} + 3e^- \longrightarrow Au$	1.50
$Co^{2+} + 2e^- \longrightarrow Co$	– 0.28	$Co^{3+} + e^- \longrightarrow Co^{2+}$	1.82
$Ni^{2+} + 2e^- \longrightarrow Ni$	– 0.25	$F_2 + 2e^- \longrightarrow 2F^-$	2.87

Note :

(i) The standard half cell potential E is an intensive property, like temperature or molar volume and so E shall be the same for half cell reaction whether it is represented as $2X^+ + 2e \rightleftharpoons X_2$, or X^+ e $\rightleftharpoons \frac{1}{2}X_2$. But unlike E, ΔG (standard free energy change) is an extensive property which depends upon the mass, that is to say, if a half reaction, $2X^+ + 2e \rightleftharpoons X_2$ is represented as $X^+ + e \rightleftharpoons \frac{1}{2}X_2$, ΔG of the latter would be half that of the former.

(ii) If the direction of a half cell (cell) reaction is reversed, its potential has the same magnitude but opposite sign, e.g., if for $Cu^{2+} + 2e \rightleftharpoons Cu$; E = + 0.34 V

then for $Cu \rightleftharpoons Cu^{2+} + 2e$; E = – 0.34 V

The same is also true for energy change.

(iii) Potentials are not thermodynamic functions and may not be added but the potential may be calculated from the free energy ΔG, using ΔG = – nFE . For example,

$Fe^{3+} + e \rightarrow Fe^{2+}$; E = + 0.77 V; ΔG = – 1(+ 0.77) F = – 0.77 F

$Fe^{2+} + 2e \rightarrow Fe$; E = – 0.44 V; ΔG = – 2(– 0.44) F = + 0.88 F

$Fe^{3+} + 3e \rightarrow Fe$ On adding : ΔG = + 0.11 F

$$\therefore \quad E \text{ for } (Fe^{3+} + 3e \rightarrow Fe) = \frac{\Delta G^\circ}{-nF} = \frac{0.11F}{-3F} = -0.04\,V$$

but not (0.77 – 0.44) = 0.33 V]

Characteristics of Electrochemical Series

(1) Reactive metals are placed on top (e.g. Li) and they have a great tendency to get oxidized. Non-reactive metals like Ag and Au.

(2) Any metal above hydrogen can displace it from dilute acids.

Example : $Zn + \text{dil. } 2HCl \longrightarrow ZnCl_2 + H_2$

$Cu + \text{dil. } HCl \longrightarrow$ no reaction

Any metal which is above another can displace that from its salt solutions.

Example : $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$

If two metals form a cell, the metal that is above undergoes oxidation and forms the anode while the one below forms the cathode.

Example : Zn-Anode ⟶ Cu-Cathode

(0.76 V) ⟶ (+ 0.34 V)

Calculation of Cell Potential

In an electrochemical cell, electrons flow from negative electrode to the positive electrode. This shows that there is a potential difference between the two electrodes.

The minimum potential which causes the flow of the electrons from the negative electrode to the positive electrode is called emf.

The emf of a cell is defined as the algebraic difference between the SRP of the positive electrode and the SRP of the negative electrode even though oxidation is taking place at the negative electrode.

$$\text{Cell Potential } (E_{cell}) = E_{Cathode} - E_{Anode}$$

Standard Reduction potential of cathode	Standard Reduction Potential of anode
$E_{Cathode}$	E_{Anode}
Or	
E Right	E Left

In general, for a given electrode, the magnitude of oxidation and reduction potentials remain same but they differ with respect to their signs.

Examples :

For a cell made of a zinc electrode in $ZnSO_4$ and copper electrode in $CuSO_4$.

$E_{cell} = E_{Cu+2/Cu} - E_{Zn+2/Zn}$

$= 0.35- (-0.76)$

$= 1.1$ V

Example 15

The electrode potentials A, B, C and D are –2.52 V, – 0.16 V, + 1.3 V and –3.01 V respectively. On the basis of this name the following :

D – 3.01 V
A – 2.52 V
B – 0.16 V
C + 1.3 V

$\}\longrightarrow$ **Electro chemical series**

Solution :

(a) Most electro positive $\longrightarrow$ D

(b) Most electro negative $\longrightarrow$ C

(c) Highest reducing power $\longrightarrow$ D

(d) Highest oxidising power $\longrightarrow$ C

(e) Lowest oxidising power $\longrightarrow$ D

(f) Displaced by all other system $\longrightarrow$ C

(g) Does not displace any other system $\longrightarrow$ C

(h) displaces H_2 $\longrightarrow$ D, A, B

(i) Always acts as negative electrode $\longrightarrow$ D

(j) Always acts as positive electrode $\longrightarrow$ C

(k) System which is not displaced by any other $\longrightarrow$ D

(i) A and B

A is negative and B is positive

(ii) B and C

B is negative and C is positive

(iii) C and D

C is positive and D is negative

(iv) D and A

D is negative and A is positive

Example 16

The dry cell (flash light battery) used to power flashlights, clocks, radios etc follows following reaction.

$$Zn(s) + 2\,MnO_2(s) + 8\,NH_4^+ \rightarrow Zn^{2+} + 2\,Mn^{3+} + 8\,NH_3 + 4\,H_2O$$

(a) Write anode and cathode reactions.

(b) Calculate the E^0 of the dry cell if the electrode potential of cathode (E^0) varies between + 0.49 V and + 0.74 V and of anode (E^0) is – 0.76 V.

Solution :

Note : A given electrode potential is to be taken as Reduction Potential.

Anode : $Zn - 2e \rightarrow Zn^{2+}$

Cathode : $2MnO_2(s) + 8NH_4^+ + 2e^- \rightarrow 2Mn^{3+} + 8NH_3 + 4H_2O$

E^0 of cathode varies between + 0.49 to + 0.74 V

E^0 of cell (for E^0_c = 0.49 V)

$E^0 = E^0_c - E^0_a$

$E^0 = 0.49 - (-0.76) = 1.25$ V

E^0 of cell (for $E^0_c = 0.74$ V)

$E^0 = E^0_c - E^0_a = 0.74 - (-0.76) = 1.50$ V

E^0 of the cell varies between 1.25 V to 1.50 V

Example 17

For each of the following cells :

(a) Write the equation for cell process.

(b) Find E^0 for each cell.

(c) Explain the significance of any negative answers in part (b).

1. $Fe/Fe(NO_3)_2$ (1.0 M) || Zn^{2+} (1.0 M)/Zn

2. $Pt/Cl_2(g)/KCl$ || $Hg_2Cl_2(s)/Hg$

3. Cd/Cd^{2+} (1.0 M) || $AgNO_3/Ag$

E^0(Fe) = 0.41 V; E^0(Cd) = 0.40 V; E^0(Zn) = 0.76 V

E^0(Cl^-/Cl_2) = – 1.36 V; E^0(Ag) = – 0.80 V; E^0 (Hg/Hg_2Cl_2) = – 0.27 V

Solution :

Note : The values of electrode potential given are their oxidation potentials. For reduction potential, change their i.e., E (Fe^{2+}/Fe) = – 0.41 V and so on...

1. $Fe + Zn^{2+} \rightarrow Fe^{2+} + Zn$

$E^0 = E_c^0 - E^0_a$

E = = – 0.76 – (–0.41) = – 0.35 V

negative EMF values means that the cell will not work in the manner shown i.e., Fe as anode and Zn as cathode. So reversing (interchanging) the anode and cathode i.e., making Zn as anode and Fe as cathode, can make the cell work.

2. Anode : $2Cl^- - 2e \rightarrow Cl_2$

Cathode : $Hg_2Cl_2 + 2e^- \rightarrow 2\ Hg + 2Cl^-$

$Hg_2Cl_2 \rightarrow Cl_2 + 2\ Hg$

$E^0 = E_c^0 - E^0_a$

$E^0 = 0.27 - (1.36) = -1.09$ V

negative EMF values means that the cell will not work in the manner shown i.e. Cl_2/Cl^- as anode and Hg_2Cl_2 as cathode. So reversing (interchanging) the anode and cathode i.e., making Hg_2Cl_2 (i.e., Hg/Hg_2Cl_2) as anode and Cl_2/Cl^- as cathode (i.e., Cl^-/Cl_2), can make the cell work.

3. $Cd + 2\,Ag^{+} \rightarrow Cd^{2+} + 2\,Ag$

$E^{0} = E^{0}_{c} - E^{0}_{a} = 0.8 - (-0.4) = 1.20$ V

EMF value is positive, hence cell will function with Cd as anode.

13. Cell Potential and Nernst Equation

Nernst equation is used to relate either half-cell potential or EMF of a cell with the concentration of the involved species. Let us first consider a redox change occurring in a electrochemical cell,

$$xA + yB \rightleftharpoons zC + aD$$

where A, B, C and D are the species whose concentrations vary i.e. they are either gases or solution phases. For species A, the free energy per mole of A can be given thermodynamically as

$$G_A = G_{\ A} + RT\ In\ [A]$$

For x moles A, $xG_A = xG_{\ A} + xRT\ ln[A] = xG\ A + RT\ ln[A]^x$

Similarly, for all other species,

$yG_B = yG_{\ B} + RT\ ln\ [B]^y$

$zG_C = zG_{\ C} + RT\ ln\ [C]^z$

and $aG_D = aG_{\ D} + RT\ ln\ [D]^a$

Now, the free energy change for the overall cell reaction can be deduced as

$$\Delta G = (zG_C + aG_D) - (xG_A + yG_B)$$

$$= zG_{\ C} + RT\ ln\ [C]^z + aG_{\ D} + RT\ ln\ [D]^a - xG^{\circ}_{\ A} - RT\ ln\ [A]^x - yG_{\ B} - RT\ ln\ [B]^y$$

$$= (zG_{\ C} + aG_{\ D}) - (xG_{\ A} + yG_{\ B}) + RT\ ln\ \frac{[C]^z [D]^a}{[A]^x\ [B]^y}$$

$$\Delta G = \Delta G^{\circ} + RT\ ln\ \frac{[C]^z\ [D]^a}{[A]^x [B]^y} \qquad \text{...(i)}$$

where ΔG is the free energy change when all the reactants and products are present at one molar concentration.

Any spontaneous reaction occuring in a cell, occurs with a decrease in free energy. This decrease in free energy brings in an equivalent amount of electric work obtainable from a given system over and above any PdV energy that can be delivered to the surrounding. This can be calculated by the total charge driven through cell and the potential difference. Thus

$$-\Delta G = \text{Total charge} \quad \text{EMF of the cell}$$

$$-\Delta G = nF \quad E_{cell}$$

[Negative sign indicates decrease of free energy and it implies that as E_{cell} becomes more and more positive, ΔG will become more and more negative, making the reaction spontaneous]

Similarly, $-\Delta G = nFE_{cell}$

Therefore, equation (i) can be written as

$$-nFE_{cell} = -nFE_{cell} + RT \ln \frac{[C]^z [D]^a}{[A]^x [B]^y}$$

Dividing both the sides by – nF gives,

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln \frac{[C]^z [D]^a}{[A]^x [B]^y}$$

Putting T = 298 K, R = 8.314 J/mol K, F = 96500 C, we get

$$\mathbf{E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log \frac{[C]^z [D]^a}{[A]^x [B]^y}} \qquad \text{...(ii)}$$

The equation (ii) is called Nernst equation, which is applicable to half-cell reactions as well as to complete cell reactions.

Daniel cell represented as $Zn(s) \mid Zn^{2+} (C_1\ M) \mid\mid Cu^{2+} (C_2\ M) \mid Cu(s)$ assumes that Zn is the anode and Cu is the cathode. Such an assumption would be true only if the cell potential (E_{cell}) is positive.

The cell potential is given in the following three ways of which we would choose the third one in all our problems.

$E_{cell} = E_{RP(Cathode)} + E_{OP(Anode)}$

or $E_{cell} = E_{OP(Anode)} - E_{OP(Cathode)}$

or $E_{cell} = E_{RP(Cathode)} - E_{RP(Anode)}$

$E_{RP(Cathode)}$ is the reduction potential of the cathode while $E_{RP(Anode)}$ is reduction potential of the anode. $E_{OP(Cathode)}$ is the oxidation potential of the cathode while $E_{OP(Anode)}$ is the oxidation potential of the anode.

Now, let us find the EMF of Daniel cell using Nernst equation. Since we need to represent the reduction potential of cathode and anode, we first need to write the relevant reduction reactions.

For cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$

$$E_{Cu^{2+}|Cu} = E^{\circ}_{Cu^{2+}|Cu} - \frac{RT}{nF} \log Q_c \left(\text{or } Q_{pc}\right)$$

$E^{\circ}_{Cu^{2+}|Cu}$ is the standard reduction potential of the given half reaction, R is the universal gas constant, T is the absolute temperature at which cell works, F is the Faraday constant and n is the number of mole of electrons as seen in the reaction. The expression in the log term should be that of K_c or K_{pc}. This means that if reaction involves no gases, then the expression in the log term should be that of K_c while if a gas is involved then the expression in the log term should be that of K_{pc}. In these expressions, the concentration should always be in moles per liter while the partial pressure should be in atmosphere units.

$$\therefore \quad E_{Cu^{2+}|Cu} = E^{\circ}_{Cu^{2+}|Cu} - \frac{0.059}{2}\log\frac{1}{[Cu^{2+}]}$$

For anode : $Zn^{2+} + 2e^- \longrightarrow Zn$

$$E_{Zn^{2+}|Zn} = E^{\circ}_{Zn^{2+}|Zn} - \frac{0.059}{2}\log\frac{1}{[Zn^{2+}]}$$

As $\quad E_{cell} = E_{Cu^{2+}|Cu} - E_{Zn^{2+}|Zn}$

$$\therefore \quad E_{cell} = E^{\circ}_{Cu^{2+}|Cu} - \frac{0.059}{2}\log\frac{1}{[Cu^{2+}]} - E^{\circ}_{Zn^{2+}|Zn} + \frac{0.059}{2}\log\frac{1}{[Zn^{2+}]}$$

$$E_{cell} = E^{\circ}_{Cu^{2+}|Cu} - E^{\circ}_{Zn^{2+}|Zn} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Zn^{2+}]}$$

$$\therefore \quad E_{cell} = E^{\circ}_{cell} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Note : Since E_{cell} has been defined as $E_{RP(Cathode)} - E_{RP(Anode)}$, the Nernst expression holds good even if the number of mole of electrons of the two half reactions are different.

For example, consider the cell,

$Pt \mid H_2 \mid HCl \mid\mid Cu^{2+} \mid Cu$

For cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$

$$E_{Cu^{2+}|Cu} = E^{\circ}_{Cu^{2+}|Cu} - \frac{0.059}{2}\log\frac{1}{[Cu^{2+}]}$$

For cathode : $H^+ + e^- \longrightarrow \frac{1}{2}H_2$

$$E_{H^+|H_2} = E^\circ_{H^+|H_2} - \frac{0.059}{1}\log\frac{[P_{H_2}]^{1/2}}{[H^+]}$$

$$\therefore \quad E_{cell} = E^\circ_{Cu^{2+}|Cu} - E^\circ_{H^+|H_2} - \frac{0.059}{2}\log\frac{1}{[Cu^{2+}]} + \frac{0.059}{2}\log\frac{[P_{H_2}]^{1/2}}{[H^+]}$$

It is also possible to balance the electrons in both the half cell reactions and then subtract $E_{RP(Anode)}$ from $E_{RP(Cathode)}$. That is,

For anode : $2H^+ + 2e^- \longrightarrow H_2$

$$E_{H^+|H_2} = E^\circ_{H^+|H_2} - \frac{0.059}{2}\log\frac{P_{H_2}}{[H^+]^2}$$

$$E_{cell} = E^\circ_{Cu^{2+}|Cu} - E^\circ_{H^+|H_2} - \frac{0.059}{2}\log\frac{[H^+]^{1/2}}{[Cu^{2+}]P_{H_2}}$$

14. EMF-MEASUREMENTS : APPLICATIONS

Emf measurements have wide applications such as in the determination of pH, K_{sp}, ΔH, ΔS etc.

14.1 Determination of Thermodynamic Data :

- ΔG can be determined

$$\Delta G = -nF\,E_{cell}$$

Using Gibbs-Helmholtz equation :

$$\Delta G = \Delta H + T\left(\frac{d(\Delta G)}{dT}\right)_p$$

$$-nFE_{cell} = \Delta H - nFT\left(\frac{d(E_{cell})}{dT}\right)_p$$

- Temp. coefficient of the emf of the cell can be determined

$$\left(\frac{d(E_{cell})}{dT}\right)_p = \frac{\Delta H + nFE_{cell}}{nFT}$$

$$\left(\frac{d(E_{cell})}{dT}\right)_p = \frac{\Delta H}{nFT} + \frac{E_{cell}}{T}$$

- Enthalply change can be determined

$$\Delta H = -nF\,E_{cell} + nFT\left(\frac{dE_{cell}}{dT}\right)$$

$$= -nF\left[E_{cell} - T\left(\frac{d\,E_{cell}}{dT}\right)_p\right]$$

- Entropy change can be determined

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

$$\Delta S = -\left(\frac{d\,(\Delta G)}{dT}\right)_p$$

$$\Delta S = -\left(\frac{d}{dT}(-nF\,E_{cell})\right)_p$$

$$\Delta S = nF\left(\frac{d\,E_{cell}}{dT}\right)_p$$

(a) $\Delta H = nF\left[T\left(\frac{dE}{dT}\right) - E\right]$ where $\frac{dE}{dT}$ is called temperature coefficient representing the change of EMF with the change of temperature, n is the number of mole of electrons involved, F is one Faraday, E is EMF of the cell at temperature T and T is the absolute temperature. Depending upon the value of $\left(\frac{dE}{dT}\right)$, ΔH can be negative or positive i.e., reaction can be exhothermic or endothermic.

(b) $\Delta S = nF\left(\frac{dE}{dT}\right)$. When $\left(\frac{dE}{dT}\right)$ is negative, the change in entropy would also be negative and when $\left(\frac{dE}{dT}\right)$ is positive change in entropy would be favoured, i.e., ΔS would be positive.

Determination of Equilibrium Constant :

Let us assume that the redox change occuring in Daniel cell attains equilibrium. At equilibrium, the reduction potential values of the two electrodes become equal and EMF of cell becomes zero.

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

The equilibrium constant for this reaction is given as

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

Apply Nernst equation to complete cell reaction

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\therefore \quad E^{\circ}_{cell} = \frac{RT}{nF}\ln K_{eq} \qquad (\text{as } E_{cell} = 0)$$

$$\therefore \quad nF\,E\,cell = RT\ln K_{eq}$$

$$-\Delta G = RT\ln K_{eq}$$

$$\boxed{\Delta G = -2.303\,RT\log K_{eq}}$$

Note : This relation is valid for many equilibrium constants like K_w, K_p, K_c, K_{sp}, K_f, K_d etc.

Ionisation Constants of Weak Acid

For such cases we determine $[H^+]$ using a suitable reference half cell.

$$Pt\,(H_2)\,|\,H^+, HA(C_1)\,||\,Cu^{2+}(C_2)\,|\,Cu$$

Its E_{cell} is measured. Thus $[H^+]$ in HA can be determined

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2}\log\frac{[H^+]^2}{[Cu^{2+}]}$$

If $[H^+]$ is known, then by **Ostwald's dilution** law

$$\left[H^+\right] = \sqrt{K_a\ C_1}$$

Determine pH of a Solution :

$$Pt(H_2)\ |\ H^+\ (pH = x)\ ||\ Cl^-\ (1\ M)\ |\ Hg_2Cl_2, Hg$$

calomel

L.H.S. half cell	$H_2(g) \rightarrow 2H^+ + 2e^-$	$E_{ox} = 0.00\ V$
R.H.S. half cell	$Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-$	$E_{red} = 0.2676$
Net	$H_2(g) + Hg_2Cl_2(s) \rightarrow 2H^+(aq) + 2Hg(l) + 2Cl^-(aq)$	$E_{cell} = 0.2676\ V$

$$K = [Cl^-]^2\ [H^+]^2$$
$$= [H^+]^2 \qquad \text{(since } [Cl^-] = 1\ M)$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2}\log[H^+]^2 = E^{\circ}_{cell} + 0.0591\ pH$$

$$pH = \frac{E_{cell} - E_{cell}}{0.0591}$$

Example 18

Given the overall formation constant of the $[Fe(CN)_6]^{4-}$ ion as 10^{35} and the standard potentials for the half reactions,

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \ ; \qquad E = 0.77\ V$$

$$[Fe(CN)_6]^{3-} + e- \rightleftharpoons [Fe(CN)_6]^{4-} \ ; \qquad E = 0.36\ V$$

Calculate the overall formation constant of the $[Fe(CN)_6]^{3-}$ ion

Solution :

Let K_f be the formation constant of $[Fe(CN)_6]^{3-}$ ion.

$Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}; K_f = 10^{35};$ $\qquad \Delta G_1^0 = -2.303\ RT\ \log\ K_f = -199704.69\ J$

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}\ ;\ E = 0.77\ V;$ $\qquad \Delta G_2^0 = -96500 \quad 0.77 = -74305\ J$

$[Fe(CN)_6]^{4-} \rightleftharpoons [Fe(CN)_6]^{3-} + e^-;\ E^{\circ} = -0.36\ V\ ;$ $\qquad \Delta G_3^0 = +96500 \quad 0.36 = 34740\ J$

$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-};$ $\qquad \Delta G_4^0 = \Delta G_1^0 + \Delta G_2^0 + \Delta G_3^0$

$$\Delta G_4^0 = -239269.69\ J$$

$$\Delta G_4^0 = -2.303\ RT\ \log\ K_f'$$

$$\therefore \quad K_f' = 8.59 \quad 10^{41}$$

Example 19

For the reaction $4Al(s) + 3O_2(g) + 6H_2O + 4OH^- \rightarrow 4[Al(OH)_4^-]$; E_{cell} = 2.73 V.

If $\Delta G_f^\circ (OH^-) = -157$ kJ mol^{-1} and $\Delta G_f^\circ (H_2O) = -237.2$ kJ mol^{-1}, determine $\Delta G_f^\circ (Al(OH)_4^-)$.

Solution :

The ΔG and E_{cell} are related by

$\Delta G = -nFE_{cell} = -12 \quad 96500 \quad 2.73 = -3.16 \quad 10^3$ kJ

$\Delta G = 4\,\Delta G_f^\circ (Al(OH)_4^-) - 6\ \Delta G_f^\circ\ (H_2O) - 4\ \Delta G_f^\circ\ (OH^-)$

(since ΔG_f° of Al(s) and $O_2(g)$ are zero)

$$\Delta G_f^\circ \left(Al(OH)_4^-\right) = \frac{-3.16 \times 10^3 + (6 \times -237.2) + (4 \times -157)}{4}$$

$= 1.30 \quad 10^3$ kJ mol^{-1}

Example 20

For the silver zinc button (miniature) cell net reaction is

$$Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2Ag(s)$$

$$\Delta G_f^\circ (Ag_2O) = -11.21 \text{ kJ mol}^{-1}$$

$$\Delta G_f^\circ (ZnO) = -318.3 \text{ kJ mol}^{-1}$$

Determine E_{cell} of this button cell.

Solution :

$\Delta G = \Delta G_f^\circ (ZnO) - \Delta G_f^\circ (Ag_2O)$

$= -318.3 - (-11.21)$

$= -307.09$ kJ mol^{-1} $= -307.09 \quad 10^3$ J mol^{-1}

Also $\Delta G = -nFE_{cell}$

$n = 2$

$$\therefore \quad E_{cell} = -\frac{\Delta G^\circ}{nF} = \frac{307.09 \times 10^3}{2 \times 96500} = 1.591 \text{ V}$$

Again note ΔG_f° (element) = Zero

Example 21

Find the equilibrium constant for the reaction, $In^{2+} + Cu^{2+} \longrightarrow In^{3+} + Cu^{+}$, at 298 K.

Given : $E^{\circ}_{Cu^{2+}/Cu^{+}} = 0.15$ V; $E^{\circ}_{In^{3+}/In^{+}} = -0.42$ V & $E^{\circ}_{In^{2+}/In^{+}} = -0.40$ V.

Solution :

$In^{+3} + 2e^{-} \longrightarrow In^{+1}$ ...(1)

$In^{+2} + e^{-} \longrightarrow In^{+1}$ ...(2)

$In^{+2} \longrightarrow In^{+3} + e^{-}$ ..(3) [can be obtained by subtracting equation (2) from equation (1)]

$-FE = -2F(-0.42) + F(-0.40)$; $E = -0.84 + 0.4 = -0.44$ V

$In^{+2} + Cu^{+2} \longrightarrow In^{+3} + Cu^{+}$; $E = 0.15 + 0.44 = 0.59$ V

$-nFE = -RT\ In\ K$; $\dfrac{0.59}{0.059} = \log K$; $K = 10^{10}$.

Example 22

A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6} M hydrogen ions. The emf of the cell is 0.118 V at 25 C. Calculate the concentration of hydrogen ions at the positive electrode.

Solution :

The given cell is

Pt / H_2 (1 bar) | H^+ (10^{-6} M) || H^+ (?) | H_2 (1 bar) / Pt

The cell reactions are

Cathode $(H^+)_R + e^- \longrightarrow \frac{1}{2}H_2$

Anode $\frac{1}{2}H_2 \longrightarrow (H^+)_L + e^-$

$(H^+)_R \rightarrow (H^+)_L$

The cell potential is given as

$$E_{cell} = -\frac{RT}{F} \ln \frac{[H^+]_L}{[H^+]_R}$$

which gives $0.118\ V = -(0.05915\ V) \log \dfrac{10^{-6}}{[H^+]_R / M}$

or $\log\left(\left[H^+\right]_R / M\right) = \log(10^{-6}) + 2 = -6 + 2 = -4$

i.e. $[H^+]_R = 10^{-4}$ M

Example 23

If excess of Zn is added to 1.0 M solution of $CuSO_4$, find the concentration of Cu^{2+} ions at equilibrium. The standard reduction potential of Zn and Cu at 25 are – 0.76 V and + 0.34 V.

Solution :

We know that at equilibrium, E_{cell} = 0.0 V and the reaction coefficient Q = K_{eq}. So first let us calculate the value of $K_{eq.}$ as follows :

$$E^0 = E_c^0 - E_a^0$$

$$E^0 = 0.34 - (-0.76) = 1.10 \text{ V}$$

Now using $E^0 = \frac{0.059}{n} \log K_{eq.}$

$$\Rightarrow \quad \log K_{eq} = \frac{E^0 \times n}{0.059} = \frac{1.10 \times 2}{0.059} = 37.288$$

$\Rightarrow$ Keq. = 1.94 10^{37}

Now writing the reaction at equilibrium :

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

Let x be the concentration of Cu^{2+} at equilibrium

	Zn	Cu^{2+}	Zn^{2+}	Cu	
initial concentration	∞	1.0	0	0	
final concentration	x	x	1 – x	1 – x	(Zn is in excess, so [Zn] = ∞]

$$K_{eq.} = \frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]} = \frac{1 - x}{x}$$

$$\Rightarrow \quad \frac{1 - x}{x} = 1.94 \times 10^{37}$$

$$\Rightarrow \quad x = \frac{1}{1 + 1.94 \times 10^{37}} = \frac{1}{1.94 \times 10^{37}}$$

$\Rightarrow$ x = 5.15 10^{-38} M   Note that $a_{Zn} = a_{Cu} = 1$

Example 24

The K_{SP} of CuI is 1.1 10^{-12} M^2. Determine EMF of the cell, represented as

Cu | CuI | I^- (1 M) || Cu^+ (1 M) | Cu

Solution :

The anode of the given cell is of metal-insoluble metal salt-anion type half-cell while cathode is of the type metal-metal ion. The half-cell reactions at anode are

$$Cu(s) \longrightarrow Cu^+ \; e^- \quad ; \quad \Delta G_1 = -FE_{cu|Cu+}$$

$$Cu^+ + I^- \rightleftharpoons CuI(s) \quad ; \quad \Delta G_2 = 0$$

Net anode reaction : $Cu(s) + I^- \rightleftharpoons CuI(s) + e^- \quad ; \quad \Delta G_3 = -FE_{Cu|CuI|I-}$

According to Hess's law, we know

$$\Delta G_1 + \Delta G_2 = \Delta G_3$$

$$\therefore \quad \Delta G_1 = \Delta G_3 \qquad (\text{as } \Delta G_2 = 0)$$

$$\therefore \quad -FE_{Cu|Cu+} = E_{Cu|Cu|I-}$$

Since, the E value of Cu $\longrightarrow Cu^+ + e^-$ and E value of Cu + I^- $\longrightarrow$ CuI + e^- are same, the representation of anode can be changed from metal-metal insoluble salt – anion half-cell to metal–metal ion half-cell, provided the concentration of Cu^+ in both the half-cells is same.

So, the complete cell can now be represented as

$$Cu|Cu^+\left(\frac{K_{SP}}{[I^-]}\right)||Cu^+(1\,M)|Cu$$

Reactions occurring at the two electrodes are

At anode : $Cu \longrightarrow Cu_A^+ + e^-$

At cathode : $Cu_C^+ + e^- \longrightarrow Cu$

Net cell reaction : $Cu_C^+ \longrightarrow Cu_A^+$

Applying Nernst equation gives

$$E_{cell} = E^\circ_{Cu_C^+|Cu} - E^\circ_{Cu_A^+|Cu} - \frac{RT}{F} \ln \frac{[Cu_A^+]}{[Cu_C^+]}$$

$$E_{cell} = E^\circ_{cell} + \frac{RT}{F} \ln \frac{[Cu_C^+]}{[Cu_A^+]}$$

$$E_{cell} = \frac{RT}{F} \text{In} \frac{[Cu_C^+]}{[Cu_A^+]} \qquad (\text{as } E_{cell} = 0)$$

$$E_{cell} = \frac{RT}{F} \text{In} \frac{[Cu_C^+] \times [I^-]}{K_{SP}} = 0.059 \log \frac{1 \times 1}{1.1 \times 10^{-12}}$$

$E_{cell} = 0.705$ V

15. CONCENTRATION CELLS

The cells whose E_{cell} is zero are called concentration cells. This means that the two compartments (cathode and anode) of the electrochemical cell involves same chemical species but the concentrations of the chemical species in the two compartments are different. The concentration cells are of basically two types.

(a) Electrode concentration cells and (b) Electrolyte concentration cells

1. Electrode Concentration Cells

In such cells, two similar electrodes at different concentrations/pressures are dipped in the same solution with similar concentration. Let us have an electrochemical cell represented as

Pt | H_2 (P_1 atm) | H^+ (c M) || H^+ (c M) | H_2 (P_2 atm) | Pt

For the given cell, the reactions occurring are

At cathode : $2H_C^+ + 2e^- \longrightarrow H_2(P_2)$

At anode : $H_2(P_1) \longrightarrow 2H_A^+ + 2e^-$

Net cell reaction : $H_2(P_1) \longrightarrow H_2(P_2)$

Since the H^+ concentration at the anode and cathode are same, so the net reaction is independent of the concentration of the electrolyte. Applying Nernst equation to the net cell reaction gives

$$E_{cell}(25°C) = E^\circ_{H_C^+|H_2(P_2)} - E^\circ_{H_A^+|H_2(P_1)} - \frac{0.059}{2} \log\left(\frac{P_2}{P_1}\right)$$

$$E_{cell}(25°C) = E^\circ_{cell} - \frac{0.059}{2} \log\left(\frac{P_2}{P_1}\right)$$

or $$E_{cell}(25°C) = -\frac{0.059}{2}\log\left(\frac{P_2}{P_1}\right) \qquad \text{(since, } E_{cell} = 0)$$

$$E_{cell}(25°C) = \frac{0.059}{2}\log\left(\frac{P_1}{P_2}\right)$$

The EMF of the given cell would be positive when $P_1 > P_2$ and the cell reaction would be spontaneous.

Another example of the electrode concentration cell is that of an amalgam with two different concentrations of the same metal dipped in same electrolyte solution.

The cell is represented as

Hg–Pb (c_1 M) | $PbSO_4$ (c M) | Hg–Pb (c_2 M)

The reactions for the given cell are

At cathode : $Pb^{2+}(c) + 2e^- \longrightarrow Pb(c_2)$

At anode : $Pb(c_1) \longrightarrow Pb^{2+}(c) + 2e^-$

Net cell reaction : $Pb(c_1) \longrightarrow Pb(c_2)$

Since, the concentration of Pb^{2+} for the two half cells is same as the electrolyte solution for the two compartments is same, so the net reaction is independent of the electrolyte concentration. Applying Nernst equation to the net cell reaction gives

$$E_{cell}(25\ C) = E^\circ_{Pb^{2+}(c)|Pb(c_2)} - E^\circ_{Pb^{2+}(c)|Pb(c_1)} - \frac{0.059}{2}\log\frac{c_2}{c_1}$$

$$E_{cell}(25\ C) = E_{cell} - \frac{0.059}{2}\log\frac{c_2}{c_1}$$

$$E_{cell}(25\ C) = -\frac{0.059}{2}\log\frac{c_2}{c_1} \qquad \text{(since } E_{cell} = 0)$$

$$E_{cell}(25\ C) = -\frac{0.059}{2}\log\frac{c_1}{c_2}$$

The net cell reaction would be spontaneous, when the EMF of the cell is positive, which is possible only when $c_1 > c_2$.

Example 25

Calculate the EMF of the electrode concentration cell

Hg–Zn (c_1 M) | Zn^{2+} (c M) | Hg–Zn(c_2 M)

at 25 C, if the concentration of the zinc amalgam are 2 g per 100 g of mercury and 1 g per 100 g of mercury in anode and cathode half cell respectively.

Solution :

The reactions at the two half cells are

At cathode : $Zn^{2+}(c) + 2e^- \longrightarrow Zn(c_2)$

At anode : $Zn(c_1) \longrightarrow Zn^{2+}(c) + 2e^-$

Net cell reaction : $Zn(c_1) \longrightarrow Zn(c_2)$

Applying Nernst equation to the net cell reaction gives

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\log\frac{c_2}{c_1} = \frac{0.059}{2}\log\frac{c_1}{c_2} \qquad \left(\text{since } E^\circ_{cell} = 0\right)$$

$$E_{cell} = \frac{0.059}{2}\log\left(\frac{2/65.4}{1/65.4}\right) = 8.9 \times 10^{-3}\ \text{V}$$

2. Electrolyte Concentration Cells

In such cells, two electrodes of the same metal are dipped in solutions of metal ions of different concentrations. Let us have an electrochemical cell represented as

Pt | H_2(P atm) | HA(c_1 M) || HB (c_2 M) | H_2 (P atm) | Pt

In such cells, HA and HB would represent strong acids, if their K_a's are not given while they would be weak acids, if their K_a's are mentioned.

For the given cell, the reactions occurring are

At cathode : $2H_c^+(c_2) + 2e^- \longrightarrow H_2(P)$

At anode : $H_2(P) \longrightarrow 2H_A^+(c_1) + 2e^-$

Net cell reaction : $2H_c^+ \longrightarrow 2H_A^+ \ (n = 2)$

or $H_c^+ \longrightarrow H_A^+ \ (n = 1)$

The net cell reaction is independent of the pressure terms as the pressure of H_2 in the two half cells is same.

Applying Nernst equation to the net cell reaction gives

$$E_{cell}(25\ C) = E^{\circ}_{H^+_C|H_2} - E^{\circ}_{H^+_A|H_2} - \frac{0.059}{1}\log\frac{[H^+_A]}{[H^+_C]} = E_{cell} - 0.059\log\frac{c_1}{c_2}$$

$$E_{cell}(25\ C) = 0.059\log\frac{c_2}{c_1}\quad (\text{since } E_{cell} = 0)$$

The net cell reaction would be feasible spontaneously only when the EMF of the cell is positive, which is possible only when concentration of H+ in cathode compartment (c_2) is greater than the concentration of H^+ in anode compartment (c_1).

Example 26

Calculate the EMF of the following galvanic cell

$Zn\ |\ Zn^{2+}$ (0.01 M) || Zn^{2+} (0.1 M) | Zn at 298 K.

Solution :

The reactions at the two half cells are

At cathode : $Zn^{2+}_C + 2e^- \longrightarrow Zn$

At anode : $Zn \longrightarrow Zn^{2+}_A + 2e^-$

Net cell reaction : $Zn^{2+}_C \longrightarrow Zn^{2+}_A$

Applying Nernst equation to the net cell reaction gives

$$E_{cell} = E_{cell} - \frac{0.059}{2}\log\frac{[Zn^{2+}_A]}{[Zn^{2+}_C]}$$

$$E_{cell} = \frac{0.059}{2}\log\frac{[Zn^{2+}_C]}{[Zn^{2+}_A]}\qquad (\text{since } E_{cell} = 0)$$

$$E_{cell} = \frac{0.059}{2}\log\frac{0.1}{0.01} = 0.0295\ V$$

Let us consider another electrochemical cell as

Ag | Ag_2CrO_4 (saturated soln.) ‖ AgC (saturated soln.) | Ag and the solubility products of Ag_2CrO_4 and AgCl are (K_{SP}) and $(K_{SP})_2$ respectively. The saturated solution of Ag_2CrO_4 and AgCl, each will give some $[Ag^+]$ and the $[Ag^+]$ in the two compartments will not be the same. So, the given cell would be an electrolyte concentration cell. For the given cell, the reactions occurring are

At cathode : $Ag_C^+ + e^- \longrightarrow Ag$

At anode : $Ag \longrightarrow Zn_A^+ + e^-$

Net cell reaction : $Ag_C^+ \longrightarrow Ag_A^+$

Applying Nernst equation to the net cell reaction gives

$$E_{cell}(25\ C) = E^\circ_{Ag_C^+|Ag} - E^\circ_{Ag_A^+|Ag} - 0.059 \log \frac{[Ag_A^+]}{[Ag_C^+]}$$

$$E_{cell}(25\ C) = E^\circ_{cell} - 0.059 \log \frac{[Ag_A^+]}{[Ag_C^+]}$$

$$E_{cell}(25\ C) = 0.059 \log \frac{[Ag_C^+]}{[Ag_A^+]} \qquad (\text{since } E_{cell} = 0)$$

The $[Ag^+]$ in anode and cathode half-cells is written in terms of K_{SP} as

$$\underset{}{Ag_2CrO_4(s)} \rightleftharpoons \underset{2x}{2Ag^+} + \underset{x}{CrO_4^-}$$

Let 'x' moles per litre be the solubility of Ag_2CrO_4.

$\therefore \quad (K_{sp})_1 = [Ag^+]^2\ [CrO_4^{2-}] = (2x)^2 x = 4x^3$

$$\therefore \quad x = \sqrt[3]{\frac{(K_{sp})_1}{4}}$$

$$[Ag_A^+] = 2x = 2 \times \sqrt[3]{\frac{(K_{sp})_1}{4}}$$

Similarly, let the solubility of AgCl be 'y' moles/litre.

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

$$(K_{sp})_2 = [Ag^+][Cl^-] = y^2$$

$$\therefore \quad y = \left[Ag^+_C\right] = \sqrt{(K_{sp})_2}$$

Substituting the values of $\left[Ag^+_A\right]$ and $\left[Ag^+_C\right]$ in the expression of E_{cell} gives

$$E_{cell} = 0.059 \log \frac{\sqrt{(K_{sp})_2}}{2 \times \sqrt[3]{\frac{(K_{sp})_1}{4}}}$$

For the net cell reaction to be spontaneous, $\sqrt{(K_{sp})_2}$ has to be greater than $2 \times \sqrt[3]{\frac{(K_{sp})_1}{4}}$ so that the EMF of the cell would be positive.

Example 27

Calculate the potential of the cell,

Mn(s) | $MnCl_2$ (0.001 M) | HCl (0.01 M) | O_2 (0.25 atm) | Pt.

Given that E = – 1.185 V for Mn^{2+} | Mn couple and 1.229 V for the O_2 | H_2O, H^+ couple.

Solution :

We can replace the cathode of the given cell by the half cell, $O_2|H_2O$, H^+ because we have already learnt in metal-insoluble salt-anion electrode that the potential of the two half cells is same.

Thus, the cell representation becomes Mn(s) | $MnCl_2$ (0.001 M) || H^+ (0.01 M), H_2O | O_2 (0.25 atm) | Pt

At cathode : $Mn \longrightarrow Mn^{2+} + 2e^-$

At anode : $2H^+ + ½O_2 + 2e^- \longrightarrow H_2O$

Net cell reaction : $Mn + 2H^+ + ½O_2 \longrightarrow Mn^{2+} + H_2O$

$$\therefore \quad E_{cell} = E^\circ_{O_2|H_2O,H^+} - E^\circ_{Mn^{2+}|Mn} - \frac{0.059}{2}\log\frac{\left[Mn^{2+}\right]}{\left[H^+\right]^2 \left(P_{O_2}\right)^{½}}$$

$$\therefore \quad E_{cell} = 1.229 - (-1.185) - \frac{0.059}{2}\log\frac{10^{-3}}{\left(10^{-2}\right)^2 \times \sqrt{0.25}}$$

$$E_{cell} = 2.37 \text{ V}$$

Example 28

By how much is the oxidising power of the $MnO_4^- | < Mn^{2-}$ couple decreased if the H^+ concentration is decreased from 1 M to 10^{-4} M at 25 C. Assume that the concentration of other species do not change.

Solution :

In acidic medium, MnO_4^- acts as oxidizing agent and reduces to Mn^{2+} as per the reaction

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$E_{MnO_4^-|Mn^{2+}} = E^\circ_{MnO_4^-|Mn^{2+}} - \frac{0.059}{5}\log\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

$$= E^\circ_{MnO_4^-|Mn^{2+}} - \frac{0.059}{5}\log\frac{[Mn^{2+}]}{[MnO_4^-](1)^8}$$

$$E'_{MnO_4^-|Mn^{2+}} = E^\circ_{MnO_4^-|Mn^{2+}} - \frac{0.059}{5}\log\frac{[Mn^{2+}]}{[MnO_4^-][10^{-4}]^8}$$

$$\therefore \left(E_{MnO_4^-|Mn^{2+}} - E'_{MnO_4^-|Mn^{2+}}\right) = \frac{0.059}{5}\left[\log\frac{[MnO_4^-](1)^8}{[Mn^{2+}]} \times \frac{[Mn^{2+}]}{[MnO_4^-](10^{-4})^8}\right] = 0.3776\text{ V}$$

Thus, the oxidizing of $MnO_4^- | Mn^{2+}$ couple decreases by 0.3776 V from its standard value.

Example 29

EMF of the following cell is 0.67 at 298 K.

Pt | H_2 (1 atm) | H^+ (pH = X) || KCl (1 N) | Hg_2Cl_2(s) | Hg

Calculate pH of the anode compartment. Given : $E^\circ_{Cl^-|Hg_2Cl_2|Hg} = 0.28$ V

Solution :

The reactions occurring in the electrochemical cell are

At anode : $H_2 \longrightarrow 2H^+ + 2e^-$

At Cathode : $Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$

Net cell reaction : $H_2 + Hg_2Cl_2 \longrightarrow 2H^+ + 2Hg + 2Cl^-$

$$\therefore \quad E_{cell} = E^\circ_{Cl^-|Hg_2Cl_2|Hg} - E^\circ_{H^+|H_2} - \frac{0.059}{2}\log\frac{\left[Cl^-\right]^2\left[H^+\right]^2}{P_{H_2}}$$

(Hg and Hg_2Cl_2 do not appear as they are pure liquid and pure solid respectively)

$$0.67 = 0.28 - \frac{0.059}{2}\log\frac{\left[H^+\right]^2 \times (1)^2}{1} = 0.28 - 0.059\log\left[H^+\right]$$

$0.67 = 0.28 + 0.059$ pH

$\therefore$ pH = 6.61

Example 30

The EMF of the cell, Hg | Mercurous nitrate (0.01 M) || Mercurous nitrate (0.1 M) | Hg was found to be 0.0295 V at 25 C. Calculate the molecular formula of mercurous nitrate.

Solution :

Let the formula of mercurous nitrate be $Hg_n(NO_3)_n$.

For the given cell, the reactions occurring at two electrodes are

At anode : $nHg \longrightarrow \left(Hg_n^{n+}\right)_A + ne^-$

At cathode : $\left(Hg_n^{n+}\right)_C + ne^- \longrightarrow nHg$

Net cell reaction : $\left(Hg_n^{n+}\right)_C \longrightarrow \left(Hg_n^{n+}\right)_A$

So, this is an electrolyte concentration cell for which $E_{cell} = 0$. The E_{cell} will be given as

$$\therefore \quad E_{cell} = -\frac{0.059}{n}\log\frac{\left[\left(Hg_n^{n+}\right)_A\right]}{\left[\left(Hg_n^{n+}\right)_C\right]}$$

$$\therefore \quad 0.0295 = \frac{0.059}{n}\log\frac{\left[\left(Hg_n^{n+}\right)_C\right]}{\left[\left(Hg_n^{n+}\right)_A\right]} = \frac{0.059}{n}\log\frac{0.1}{0.01}$$

$\therefore$ n = 2

Thus the formula of mercurous nitrate is $Hg_2(NO_3)_2$.

Example 31

It is desired to construct the following voltaic cell to have E_{cell} = 0.0860 V. What $[Cl^-]$ must be present in the cathode half cell to achieve this result ?

Ag(s) | Ag^+ (satd. AgI (aq)) || Ag^+ (satd. AgCl, x M Cl^-) | Ag^+(s)

K_{sp} [AgCl = 1.8 10^{-10}, AgI = 8.5 10^{-17}]

$$E^\circ_{Ag^+/Ag} = 0.80\ V$$

Solution :

Anode $\quad Ag(s) \rightarrow \underset{\text{anode}}{Ag^+}\ (aq) + e^- \qquad E^\circ_{Ag^+/Ag^+} = -\ 0.80\ V$

Cathode $\quad \underset{\text{cathode}}{Ag^+(aq)} + e^- \rightarrow Ag(s) \qquad E^\circ_{Ag^+/Ag} = -\ 0.80\ V$

$$\underset{\text{cathode}}{Ag^+\ (aq)} \rightarrow \underset{\text{anode}}{Ag^+\ (aq)} \qquad E_{cell} = 0.00\ V$$

Ag^+ (anode) is from AgI (satd, aq)

$$\therefore \quad AgI(s) \rightleftharpoons Ag^+(aq) + I^-\ (aq)$$

$$K_{sp} = [Ag^+]\ [I^-] = [Ag^+]^2$$

$$\therefore \quad [Ag^+]_{AgI} = [Ag^+]_{L.H.S.} = \sqrt{K_{sp}}$$

$$= \sqrt{8.5 \times 10^{-17}}$$

$$= 0.9220 \quad 10^{-8}\ M$$

Ag^+ (cathode) is from AgCl in presence of $[Cl^-]$ = x M

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-\ (aq)$$

$$\therefore \quad K_{sp} = [Ag^+]\ [Cl^-]$$

$$[Ag^+]_{R.H.S.} = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{x}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log K$$

$$= 0 - \frac{0.0591}{1} \log \frac{[Ag^+]_{L.H.S.}}{[Ag^+]_{R.H.S.}}$$

$$0.0860 = -0.0591 \log \frac{0.9220x \times 10^{-8}}{1.8 \times 10^{-10}}$$

$$-\frac{0.0860}{0.0591} = \log 51.22\ x$$

$$-1.4562 = \log 51.22 + \log x$$

$$= 1.7095 + \log x$$

$$\therefore \quad \log x = -3.1647$$

$$x = 7 \quad 10^{-4}\ M$$

$$[Cl^-] = 7 \quad 10^{-4}\ M$$

Example 32

Calculate the emf of the following cells at 298 K.

(i) $Fe \mid Fe^{2+} \mid\mid Sn^{2+} \mid Sn$
0.3 M　　0.1 M

(ii) $Pt\ (H_2) \mid HCl \mid Pt\ (H_2)$
2 atm　　10 atm

$E^\circ_{Fe^{2+}/Fe} = -0.44\ V$, $E^\circ_{Sn^{2+}/Sn} = -0.14\ V$

$E^\circ_{S.H.E.} = 0.00\ V$

Solution :

(i) $Fe \rightarrow Fe^{2+} + 2e^-$　　$E^\circ_{ox} = E^\circ_{Fe/Fe^{2+}} = +0.44\ V$

$Sn^{2+} + 2e^- \rightarrow Sn$　　$E^\circ_{red} = E^\circ_{Sn^{2+}/Sn} = -0.14\ V$

$Sn^{2+}\ Fe \rightarrow Sn + Fe^{2+}$　　$E^\circ_{cell} = 0.30\ V$

$$K = \frac{[Fe^{2+}]}{[Sn^{2+}]} = \frac{0.3}{0.1} = 3$$

$$\therefore \quad E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log K$$

$$= 0.30 - \frac{0.0591}{2} \log 3$$

$$= 0.30 - \frac{0.0591}{2} \times 0.4771$$

$$= 0.30 - 0.0141 = 0.2859 \text{ V}$$

(ii) Pt (H_2) | HCl | Pt (H_2)

2 atm 10 atm

This is concentration cell in which hydrogen electrodes at different pressures are dipped in HCl

at L.H.S. half cell H_2 (2 atm) $\rightarrow$ $2H^+ + 2e^-$ $E^\circ_{ox} = 0.00$ V

at R.H.S. half cell $2H^+ + 2e^- \rightarrow H_2$ (10 atm) $E^\circ_{red} = 0.00$ V

Net H_2 (2 atm) $\rightarrow$ H_2 (10 atm)

$$K = \frac{P_{H_2}(\text{R.H.S.})}{P_{H_2}(\text{L.H.S.})} = \frac{10}{2} = 5$$

$$\therefore \quad E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log K$$

$$= 0.00 - \frac{0.0591}{2} \log 5$$

$$= 0.0207 \text{ V.}$$

Example 33

The emf of the cell is 0.788 V

Ag | AgI, 0.05 M KI || 0.05 M $AgNO_3$ | Ag

Calculate the solubility product of AgI.

$$\mathbf{E^\circ_{Ag^+/Ag} = E^\circ_{redn} = 0.80\ V}$$

Solution :

KI is strong electrolyte, hence

$$[I^-]_{\text{L.H.S.}} = 0.05 \text{ M}$$

AgI(s) is sparingly soluble. If we manage to calculate Ag^+ (Ag) in L.H.S. half cell, K_{sp} can be calculated.

at Anode half cell Ag(s) $\rightarrow$ Ag^+ (x M) + e^- $E^\circ_{ox} = -0.80$ V

anode

at Cathode half cell	$Ag^+(0.05) + e^- \rightarrow Ag(s)$	$E^\circ_{red} = 0.80$ V
	cathode	
Net	$Ag^+\ (0.05) \rightarrow Ag^+\ (x\ M)$	$E_{cell} = 0.00$ V

$$K = \frac{[Ag^+]_{anode}}{[Ag^+]_{cathode}} = \frac{x}{0.05}$$

$$\therefore \quad E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log K$$

$$0.788 = 0 - \frac{0.0591}{1} \log\left(\frac{x}{0.05}\right)$$

$$\log\left(\frac{x}{0.05}\right) = -\ 13.3333 = \overline{14}.6667$$

$$\frac{x}{0.05} = 4.6416 \quad 10^{-14}$$

$$x = 2.321 \quad 10^{-15}$$

$$\therefore \quad [Ag^+]_{L.H.S.} = 2.321 \quad 10^{-15}\ M$$

$$[I^-]_{L.H.S.} = 0.05\ M$$

$$\therefore \quad K_{sp} = [Ag^+]\ [I^-]$$

$$= 2.321 \quad 10^{-15} \quad 0.05$$

$$= 1.16 \quad 10^{-16}$$

Example 34

When silver chloride is dissolved in a large excess of ammonia, practically all silver ion can be assumed to exist in form of a single ionic species $[Ag_x\ (NH_3)_y]^{x+}$**. Compute the values of** x **and** y **using the following two cells**

(A) Ag | 0.4 10^{-3} M AgCl, 1M NH_3 || 40 10^{-3} M AgCl, 1 M NH_3 | Ag

E_{cell} = 0.1185 V at 298 K

(B) Ag | 3 10^{-3} M AgCl, 1 M NH_3 || 3.0 10^{-3} M AgCl, 0.1 M NH_3 | Ag

Ecell = 0.1263 V at 298 K

Solution :

All the Ag^+(aq) from AgCl in each of the half cells is complexed to form $[Ag_x(NH_3)_y]^{x+}$

hence $[AgCl] = [Ag^+] = [Ag_x(NH_3)_y]^{x+}$

for the given cell

Electrode	**Reaction**	**E**
Anode	$\underset{\text{Anode}}{x\,Ag + y\,NH_3} \rightarrow \underset{\text{Anode}}{Agx(NH_3)_y^{x+}} + xe^-$	$E^\circ_{ox} = EV$
Cathode	$\underset{\text{cathode}}{Agx(NH_3)_y^{x+}} + xe^- \rightarrow xAg + \underset{\text{cathode}}{yNH_3}$	$E^\circ_{red} = -\,E\ V$
Net	$\underset{\text{cathode}}{Agx(NH_3)_y^{x+}} + \underset{\text{Anode}}{yNH_3} \rightarrow \underset{\text{Anode}}{[Agx(NH_3)_y]^{x+}} + \underset{\text{cathode}}{yNH_3}$	$E^\circ_{cell} = 0.00\ V$

$$\therefore \qquad K = \frac{\left[Agx(NH_3)_y^{x+}\right]_{anode}\,[NH_3]^y_{cathode}}{\left[Agx(NH_3)_y^{x+}\right]_{cathode}\,[NH_3]^y_{anode}}$$

in cell (A)

$$K = \frac{(0.4\times10^{-3})\,(1)^y}{\left(40\times10^{-3}\right)(1)^y} = \frac{1}{100}$$

$$E_{cell} = 0.1185\ V$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log K$$

$$0.185 = 0 - \frac{0.0591}{x}\log\left(\frac{1}{100}\right)$$

$$= \frac{0.0591\times 2}{x}$$

this give $x = 1$

In cell (B) using eq. (1),

$$K = \frac{\left(3\times10^{-3}\right)(0.1)^y}{\left(3\times10^{-3}\right)(1)^y} = \left(\frac{1}{10}\right)^y$$

$$E_{cell} = 0.1263\ V,\ x = 1$$

$\therefore \quad 0.1263 = 0 + \frac{0.0591}{1}\log(10)^y$

$= + y \quad 0.0591$

$y = 2$

Hence complex is $[Ag(NH_3)_2]^+$

Example 35

Calculate E of the following half cell reaction at 298 K

$$Ag(NH_3)_2^+ + e^- \rightarrow Ag + 2NH_3$$

Given $\quad Ag^+ + e^- \rightarrow Ag, \; E^\circ_{Ag^+/Ag} = 0.80 \text{ V}$

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3, \; K = 6 \quad 10^{-8}$$

Solution :

The cell uses Ag/Ag^+ electrodes as reference half cell.

Half cell	Reaction	E
L.H.S. half cell	$Ag(s) \rightarrow Ag^+ + e^-$	$E^\circ_{Ag/Ag^+} = 0.80$ V
R.H.S. half cell	$Ag(NH_3)_2^+ + e^- \rightarrow Ag(s) + 2NH_3$	$E = x$ V
Net	$Ag(NH_3)_2^+ \rightarrow Ag^+ + 2NH_3$	$E_{cell} = (x - 0.80)$

$$K = \frac{[Ag^+][NH_3]^2}{\left[Ag(NH_3)_2^+\right]} = 6 \times 10^{-8} \quad \text{(given)}$$

at equilibrium $\quad E_{cell} = 0.00 \text{ V}; \; K = K_{eq}$

$\therefore \quad E^\circ_{cell} = \frac{0.0591}{n} \log K_{eq}$

$$(x - 0.80) = \frac{0.0591}{1} \log 6 \times 10^{-8}$$

$= -0.4268$ V

$x = 0.80 - 0.4268$

$= 0.3732$ V

Hence E of the hall cell reaction

$$Ag(NH_3)_2^+ + e^- \rightarrow Ag + 2NH_3 \text{ is } 0.3732 \text{ V}$$

Example 36

Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K, if the EMF of the cell, Ag | Ag^+ (Satd. Ag_2CrO_4 solution) || Ag^+ (0.1 M) | Ag is 0.164 V at 298 K.

Solution :

For the given cell, the reactions occurring at the anode and cathode are

At anode : $Ag \longrightarrow Ag_A^+ + e^-$

At cathode : $Ag_C^+ + e^- \longrightarrow Ag$

Net cell reaction : $Ag_C^+ \longrightarrow Ag_A^+$

Thus, it is an electrolyte concentration cell with $E_{cell} = 0$

$$\therefore \quad E_{cell} = \frac{-0.059}{1}\log\frac{[Ag_A^+]}{[Ag_C^+]} = \frac{0.059}{1}\log\frac{[Ag_C^+]}{[Ag_A^+]}$$

The anode compartment have saturated solution of Ag_2CrO_4, supplying Ag^+ ion concentration. Let the solubility of Ag_2CrO_4 be x moles/litre.

$$Ag_2CrO_4(s) \rightleftharpoons \underset{2x}{2Ag^+} + \underset{x}{CrO_4^{2-}}$$

$$K_{SP} = [Ag_A^+]^2[CrO_4^{2-}] = (2x)^2 x = 4x^3$$

$$\therefore \quad [Ag_A^+] = 2x = 2 \times \sqrt[3]{\frac{K_{SP}}{4}}$$

$$\therefore \quad E_{cell} = 0.164 = \frac{0.059}{1}\log\frac{0.1}{2 \times \sqrt[3]{\frac{K_{SP}}{4}}}$$

$\therefore \quad K_{SP} = 2.29 \quad 10^{-12}\ M^3$

Example 37

An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed until all the Cu is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 ml and the current at 1.2 ampere. Calculate the volume of gases evolved at NTP during entire electrolysis.

Solution :

The problem does not mention about the acidic salt of Cu^{2+} i.e. what kind of acidic salt is this.

Does the acidic salt have chloride, sulphate or nitrate as anion against the cation Cu^{2+} and the answer will solely depend on the assumption we make in the beginning about the acidic salt. First, let us assume that the salt is cupric chloride ($CuCl_2$).

In the I part of electrolysis, the reactions occurring at the two electrodes are

At cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$

At anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$

[The reaction occurring at anode is the oxidation of Cl^- in preference to OH^- since the standard oxidation potential of $Cl^- > OH^-$]

Moles of Cu^{2+} reduced at cathode $= \dfrac{0.4}{63.5}$

Mole of electrons required at cathode $= \dfrac{2 \times 0.4}{63.5}$ = Mole of electrons released at anode

$\therefore$ Mole of Cl_2 liberated at anode $= \dfrac{2 \times 0.4 \times 1}{63.5 \times 2} = \dfrac{0.4}{63.5}$

Volume of Cl_2 liberated at STP at anode $= \dfrac{0.4}{63.5} \times 22400 = 141$ ml

In second part of electrolysis, when current is passed for 7 more minutes, the H^+ will be reduced at cathode since Cu^{2+} ions are discharged completely and OH^- ions are oxidized at anode since Cl^- is also completely oxidized. The reactions occurring are

At cathode : $2H^+ + 2e^- \longrightarrow H_2$

At anode : $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

Moles of electrons passed $= \dfrac{1.2 \times 7 \times 60}{96500}$

Volume of H_2 at STP released at cathode $= \dfrac{1.2 \times 7 \times 60}{96500 \times 2} \times 22400 = 58.49$ ml

Volume of H_2 at STP released at anode $= \dfrac{1.2 \times 7 \times 60}{96500 \times 4} \times 22400 = 29.245$ ml

$\therefore$ Total volume of gases ($Cl_2 + O_2 + H_2$) liberated at STP during antire electrolysis

$= 141 + 59.49 + 29.245 = 229.735$ ml

Second, let us assume that the salt is that of $CuSO_4$.

In part I of electrolysis, the ions discharged at cathode and anode are Cu^{2+} and OH^- respectively.

At cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$

At anode : $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

$\therefore$ Mole of O_2 liberated at anode = $\frac{2 \times 0.4}{63.5 \times 4} = \frac{0.4}{63.5 \times 2}$

$\therefore$ Volume of O_2 at STP liberated at anode = $\frac{0.4}{63.5 \times 2} \times 22400 = 70.55$ ml

In part II of electrolysis, the H^+ and OH^- ions are discharged at cathode and anode respectively.

At cathode : $2H^+ + 2e^- \longrightarrow H_2$

At anode : $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

Volume of H_2 at STP released at cathode = $\frac{1.2 \times 7 \times 60}{96500 \times 2} \times 22400 = 58.49$ ml

Volume of O_2 at STP released at anode = 29.245 ml

$\therefore$ Total volume of gases ($H_2 + O_2$) released at STP during entire electrolysis

= 70.55 + 58.49 + 29.245 = 158.285 ml

16. Selection of an oxidising or reducing agent

Choosing an oxidising agent

It is easier to explain this with a specific example. What could you use to oxidise iron (II) ions to iron (III) ions ? The E value for this reaction is :

$$Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)} \quad E = +0.77 \text{ V}$$

To change iron (II) ions into iron (III) ions, you need to persuade this equilibrium to move to the left. That means that when you couple it to a second equilibrium, this iron E value must be the more negative (less positive one).

You could use anything which has a more positive E value.

Dilute nitric acid :

$$NO_{3(aq)} + 4H^+_{(aq)} + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O_{(l)} \quad E = +0.96 \text{ v}$$

Acidified potassium dichromate(VI) :

$$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e^- \rightleftharpoons 2Cr^{3+}_{(aq)} + 7H_2O_{(l)} \quad E = +1.33 \text{ v}$$

Chlorine :

$$Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-_{(aq)} \quad E = +1.36 \text{ v}$$

Acidified potassium managanate (VII) :

$$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^- \rightleftharpoons Mn^{2+}_{(aq)} + 4H_2O_{(l)} \quad E = +1.51 \text{ v}$$

Choosing a reducing agent

Remember :

- Reduction is gain of electrons.
- A reducing agent reduces something by giving electrons to it. That means that the reducing agent loses electrons.

You have to be a little bit more careful this time, because the substance losing electrons is found on the right-hand side of one of theses redox equilibria. Again, a specific example makes it clearer.

For example, what could you use to reduce chromium (III) ions to chromium (II) ions ? The E value is :

$$Cr^{3+}_{(aq)} + e^- \rightleftharpoons Cr^{2+}_{(aq)} \quad E = 0.41 \text{ v}$$

You need this equilibrium to move to the right. That means that when you couple it with a second equilibrium, this chromium E value must be the most positive (least negative).

In principle, you could choose anything with a more negative E value - for example, zinc :

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn(s) \quad E = -0.76 \text{ v}$$

You would have to remember to start from metallic zinc, and not zinc ions. You need this second equilibrium to be able to move to the left to provide the electrons. If you started with zinc ions, it would already be on the left - and would have no electrons to give away. Nothing could possibly happen if you mixed chromium (III) ions and zinc ions.

That is fairly obvious in this simple case. If you were dealing with a more complicated equilibrium, you would have to be careful to think it through properly.

17. CELLS

For an electrochemical cell to be used as a commercial cell. It must

1. Be compact, light and rugged.
2. Voltage should not drop during use.

Battery

A number of cells connected in series forms a battery. There are three types of cells :

1. Primary cells

In these the redox reactions occur only once and cannot be used again.

Example : dry cells, mercury cells.

2. Secondary cells

These can be recharged by passing current and can be used again and again.

Example : Lead storage battery, Ni-Cd storage cell.

3. Fuel cell

Energy produced by combustion of fuels like H_2, CO, CH_4 can be directly converted to electric energy.

Primary cells

Dry cells

It is the compact form of the Leclanche cell.

Anode - Cylindrical Zn container.

Cathode - Central Graphite rod.

The space in between is filled with NH_4Cl and $ZnCl_2$. The graphite rod is surrounded by MnO_2 and carbon.

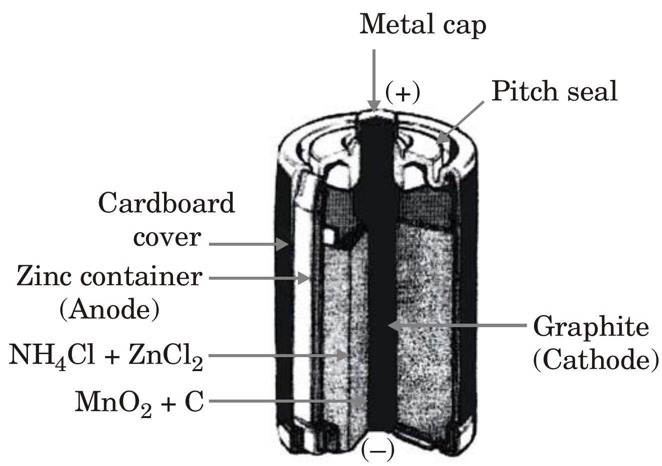
Reactions :

Anode : $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$

Cathode : $2\ MnO_{2(s)} + 2NH_4{}^+{}_{(aq)} + 2e^- \longrightarrow Mn_2O_{3(s)} + 2NH_3 + H_2O$

Voltage : 1.25 to 1.5 V

It does not have a long life because the acidic NH_4Cl corrodes the Zinc container.



Secondary Cell

Lead storage battery

Anode - Lead

Cathode - PbO_2

The electrodes are arranged alternately, separated by thin wooden or fibre glass sheet.

Electrolyte - dilute H_2SO_4.

Electron reaction (during discharging)

Anode : $Pb_{(s)} + SO_4^{2-} \longrightarrow Pb\,SO_4 + 2e^-$

Cathode : $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow Pb\,SO_4 + H_2O$

Over all : $Pb_{(s)} + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2Pb\,SO_4 + 2H_2O$

During charging, reverse reactions take place

$PbSO_4 + 2e^- \longrightarrow Pb_{(s)} + SO_4^{2-}$

$PbSO_4 + 2H_2O \longrightarrow PbO_2 + SO_4^{2-} + 4H^+ + 2e^-$

Over all $2PbSO_4 + 2H_2O \longrightarrow Pb_{(s)} + PbO_{2(s)} + 4H^+_{(aq)} + 2SO^{2-}_{4(aq)}$

Nickel Cadmium storage cell

Used mainly in calculators

Anode - Cadmium

Cathode - NiO_2

Reactions

Anode : $Cd_{(s)} + 2OH^-_{(aq)} \longrightarrow Cd(OH)_2 + 2e^-$

Cathode : $NiO_2 + 2H_2O + 2e^- \longrightarrow Ni\,(OH)_2 + 2OH^-$

can be recharged.

Mercury Cell

Used in small electric devices like hearing aids and watches.

Anode – Zinc container

Cathode – Carbon rod

Electrolyte – moist HgO mixed with KOH

Reactions :

Anode : $Zn_{(s)} + 2OH^- \longrightarrow ZnO_{(s)} + H_2O_{(l)} + 2e$

Cathode : $HgO(s) + H_2O_{(l)} + 2e \longrightarrow Hg_{(l)} + 2OH^-$

Overall reaction : $Zn_{(s)} + HgO_{(s)} \longrightarrow ZnO_{(s)} + Hg_{(l)}$

The cell shows a constant potential of 1.35 V throughout as it does not involve any ion whose concentration changes.

Fuel cell

These are devices which convert the energy produced during the combustion of fuels like H_2, CO and CH_4 directly into electrical energy. The most successful fuel cell is the H_2-O_2 fuel cell. It was used in the Apollo space programme and the water produced used as drinking water for the astronauts.

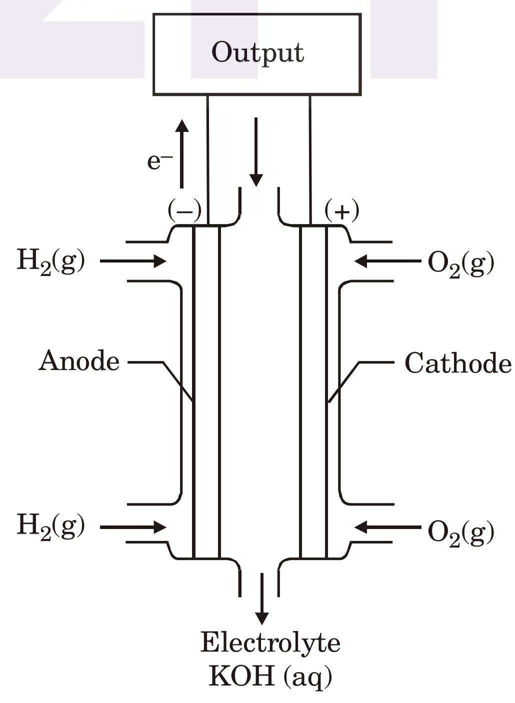
Working

H_2 and O_2 are bubbled through a porous carbon rod into concentrated NaOH. Catalysts are present in the electrodes.

Anode : $2[H_{2(g)} + 2OH^-_{(aq)} \longrightarrow 2H_2O + 2e]$

Cathode : $O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}$

Overall : $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(aq)}$



Advantages

(1) More efficient than conventional cells because the energy of the fuel is converted directly into electric energy. Efficiency = 60-70%

(2) They are free from pollution.

Example 38

During the discharge of a lead storage battery, the density of H_2SO_4 falls from ρ_1 g/cc to ρ_2g/c.c.H_2SO_4 of density of ρ_1 g/c.c. is X% by weight and that of density of ρ_2 g/c.c. is Y% by weight. The battery holds Vlitre of acid before discharging. Calculate the total charge released at anode of the battery. The reactions occurring during discharging are

At anode : $\mathbf{Pb + SO_4^{2-} \longrightarrow PbSO + 2e^-}$

At cathode : $\mathbf{PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O}$

Solution :

Mass of acid solution before discharge of lead storage batter (LSB) = (V 10^3 ρ_1) g

= (1000 $V\rho_1$) g

Mass of H_2SO_4 before discharge of LSB $= \left(1000 \times V\rho_1 \times \frac{X}{100}\right)$ g

$= (10 \quad V\rho_1 X)$g

Net reaction during discharging : $Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PBSO_4 + 2H_2O$

From the reaction, it is evident that the moles of electron exchanged (lost at anode and gain at cathode) is equal to the moles of H_2SO_4 consumed or moles of H_2O produced. Let the moles of H_2SO_4 produced be x, then

Mass of H_2O produced during discharge of LSB = (18x)g

Mass of H_2SO_4 consumed during discharge of LSB = (98x)g

∴ Mass of H_2SO_4 after discharge of LSB = [(10 $V\rho_1$X) – 98x]g

Mass of acid solution after discharge of LSB = [(1000 $V\rho_1$) – 98x + 18x] = [(1000 $V\rho_1$) – 80x]g

∴ % of H_2SO_4 after discharge of LSB = $\frac{\text{Mass of } H_2SO_4 \text{ after discharge}}{\text{Mass of acid solution after discharge}} \times 100$

$$Y = \frac{[(1000 \times V\rho_1 X) - 98x]}{[(1000 \times V\rho_1) - 80x]} \times 100$$

x can be calculated as all other quantities are known.

∴ Total charge released at cathode, Q = nF = xF

Example 39

During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 g/m to 1.139 g/m. Sulphuric acid of density 1.294 g/m was 39% H_2SO_4 by wt. while acid of density 1.139g/m contains 20% acid by wt. The battery holds 3.5 lts of acid and the value remained practically same through the discharging. Calculate the number of amp/hr for which the battery must have been used. The charging and discharging reactions are :

$$\mathbf{PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O} \text{ (discharging)}$$

$$\mathbf{PbSO_{4(s)} + 2e^- \rightarrow Pb(s) + SO_4^{2-}} \text{ (charging)}$$

Solution :

Note that density of sulphuric acid has decreased, i.e., discharging of battery takes place. First writing both the reaction for discharging.

Anode : $Pb(s) + SO_4^{2-} \rightarrow PbSO_4(s) + 2e^-$

Cathode : $PbO_2 + SO_4^{2-} + 4H^+ \; 2e^- \rightarrow PbSO_4 + 2H_2O$

Overall reaction : $Pb(s) + 2H_2SO_4 + PbO_2 \rightarrow PbSO_4(s) + 2H_2O$

$\Rightarrow$ for the consumption of 2 molecules of H_2SO_4, 2e are transferred

$\Rightarrow$ for the consumption of 2 moles of H_2SO_4, 2 moles of e's are transferred

$\Rightarrow$ 2 mole of $H_2SO_4 \equiv$ 2F of electricity

Now let us calculate the decrease in moles of H_2SO_4 from the data given.

volume of solution = 3.5 l = 3500 m

Let the mass of H_2SO_4 before discharging = m_i

and the mass of H_2SO_4 after discharging = m_f

$$\Rightarrow \quad m_i = \frac{39 \times 3500 \times 1.294}{100} = 1766.31 \text{ gm}$$

$$\Rightarrow \quad m_f = m_i = \frac{20 \times 3500 \times 1.139}{100} = 7973 \text{ gm}$$

$$\Rightarrow \quad \Delta m \text{ (the decrease in mass)} = 1767.31 - 797.3 = 970.01 \text{ gm}$$

$$\Rightarrow \quad \text{moles of } H_2SO_4 \text{ consumed} = \frac{\Delta m}{98} = \frac{970.01}{98} = 9.898$$

From the equation, we get 1 mol of $H_2SO_4 \equiv$ 1 F of charge

$\Rightarrow$ 9.898 moles $\equiv$ 1 9.898 F of charge

$\equiv$ 9.898 96500

$\equiv$ 955162.9 C of charge

Now

$$Q = It$$

$$\Rightarrow \quad I = \frac{Q}{t}$$

$$\Rightarrow \quad I = \frac{955162.9}{1 \times 60 \times 60} = 265.32 \text{ amp/hr}$$

Example 40

In the cell,

Tl | Tl^+ (0.1 M) || Sn^{+2} (0.01 M) | Sn

a current of 40 mA is flowing from tin to thallium electrode. An external battery of 1.2 V emf is connected to the cell so that its polarity is opposite to the natural polarity of the cell. If 0.38 g of thallium is deposited in one hour at 25 C, determine efficiency of thallium electrode. (Atomic mass of Tl = 204)

Solution :

For reversible cells, if an external voltage of opposing polarity is attached to the cell, a current flowing from thallium to tin electrode is given as :

$$I = \frac{E - E_b}{R} \qquad \text{...(i)}$$

where E = Applied voltage = 1.2 V, E_b = Back emf (i.e. reversible emf of cell) and R = Cell resistance.

Calculation of R :

For cell : Tl | Tl^+ (0.1 M) || Sn^{+2} (0.01 M) | Sn

$$E_b = E_{cell} = E^\circ_{cell} - \frac{0.0591}{1}\log\frac{[Tl^+]}{[Sn^{+2}]^{1/2}} = (0.340 - 0.140) - 0.059 \log\frac{0.1}{(0.01)^{1/2}}$$

$$\Rightarrow \quad E_b = 0.2 \text{ V}$$

$$I = \frac{E_{cell}}{R} \Rightarrow R = \frac{E_{cell}}{I} = \frac{0.2}{40 \times 10^{-3}}$$

$$R = 5\ \Omega$$

Using the value in equation (i)

$$I = \frac{1.2 - 0.2}{5} = 0.2 \text{ A}$$

Charge passed for 1 hour = 0.2   3600 C = 720 Coulomb

$$\text{Equivalent of thallium deposited} = \frac{720}{96500}$$

$$\text{Weight of thallium deposited} = \frac{720}{96500} \times 204 = 1.52 \text{ g}$$

$$\text{Efficiency of thallium electrode} = \frac{0.38}{1.52} \times 100 = 25\%$$