

# General Chemistry

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## **Chapter 5: Oxidation & Reduction Reaction**

# **Oxidation and Reduction Reaction (Redox)**

## **Review yourself for Contents (Self-Study)**

- Oxidation reaction
- Reduction reaction
- Oxidizing agent (oxidant)
- Reducing agent (reductant)
- Oxidation number (or Oxidation state)

# Balancing redox reactions by ion-electron method

Follow the following steps:

1. Identify which one is **reduced** or **oxidized**.
2. Split a redox reaction into **two half reactions**.
3. **Balance each half reaction** with respect to **atom** and **electrical charge**.
  - a. Balance the **oxidized or reduced atom first**.
  - b. Balance the **change in O.N.** by **adding electrons on required site**.
  - c. Balance the **charge by adding  $\text{OH}^-$  ions (in alkaline medium) and  $\text{H}^+$  (in acidic medium)** on required site.
  - d. **Balance H or O atoms** by **adding  $\text{H}_2\text{O}$**  on required site.
4. **Combine balanced half reactions** to form the overall net redox reaction.

**Q.  $\text{H}_2\text{O}_2 + \text{I}^- = \text{I}_2 + \text{H}_2\text{O}$  (Acidic medium)**

Oxidation Half Reaction	Reduction Half Reaction
$\text{I}^- = \text{I}_2$	$\text{H}_2\text{O}_2 = \text{H}_2\text{O}$
$2 \text{I}^- = \text{I}_2$	$\text{H}_2\text{O}_2 = 2 \text{H}_2\text{O}$
Change in ON of $\text{I}^- = 2 \times \{0 - (-1)\}$ $= 2 \times (1) = 2$	Change in ON of O $= 2 \times \{(-2) - (-1)\}$ $= 2 \times (-1) = -2$
$2 \text{I}^- = \text{I}_2 + 2 \text{e}^-$	$\text{H}_2\text{O}_2 + 2 \text{e}^- = 2 \text{H}_2\text{O}$
	$\text{H}_2\text{O}_2 + 2 \text{e}^- + 2\text{H}^+ = 2 \text{H}_2\text{O}$
$2 \text{I}^- = \text{I}_2 + \cancel{2\text{e}^-}$	$\text{H}_2\text{O}_2 + \cancel{2\text{e}^-} + 2\text{H}^+ = 2 \text{H}_2\text{O}$
$2\text{H}^+ + 2 \text{I}^- + \text{H}_2\text{O}_2 = \text{I}_2 + 2 \text{H}_2\text{O}$	



Oxidation Half Reaction	Reduction Half Reaction
$\text{C}_6\text{H}_5\text{CHO} = \text{C}_6\text{H}_5\text{COOH}$	$\text{Cr}_2\text{O}_7^{2-} = \text{Cr}^{3+}$
	$[\text{Cr}_2\text{O}_7]^{2-} = 2 \text{Cr}^{3+}$
Change in ON of 7 C = $\{(-2) - (-4)\} = 2$	Change in ON of Cr = $2 \times \{(+3) - (+6)\} = 2 \times (-3) = -6$
$\text{C}_6\text{H}_5\text{CHO} = \text{C}_6\text{H}_5\text{COOH} + 2 \text{e}^-$	$\text{Cr}_2\text{O}_7^{2-} + 6 \text{e}^- = 2 \text{Cr}^{3+}$
$\text{C}_6\text{H}_5\text{CHO} = \text{C}_6\text{H}_5\text{COOH} + 2 \text{e}^- + 2\text{H}^+$	$14 \text{H}^+ + \text{Cr}_2\text{O}_7^{2-} + 6 \text{e}^- = 2 \text{Cr}^{3+}$
$\text{C}_6\text{H}_5\text{CHO} + \text{H}_2\text{O} = \text{C}_6\text{H}_5\text{COOH} + 2 \text{e}^- + 2\text{H}^+$	$14 \text{H}^+ + \text{Cr}_2\text{O}_7^{2-} + 6 \text{e}^- = 2\text{Cr}^{3+} + 7 \text{H}_2\text{O}$
$[\text{C}_6\text{H}_5\text{CHO} + \text{H}_2\text{O} = \text{C}_6\text{H}_5\text{COOH} + \cancel{2\text{e}^-} + 2\text{H}^+] \times 3$	$[14 \text{H}^+ + \text{Cr}_2\text{O}_7^{2-} + \cancel{6\text{e}^-} = 2\text{Cr}^{3+} + 7 \text{H}_2\text{O}] \times 1$
$3 \text{C}_6\text{H}_5\text{CHO} + \text{Cr}_2\text{O}_7^{2-} + 8 \text{H}^+ = 3 \text{C}_6\text{H}_5\text{COOH} + 2\text{Cr}^{3+} + 4 \text{H}_2\text{O}$	

**Q.  $\text{ClO}^- + \text{CrO}_2^- = \text{CrO}_4^{2-} + \text{Cl}^-$  (Basic medium)**

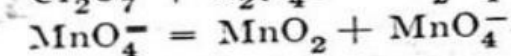
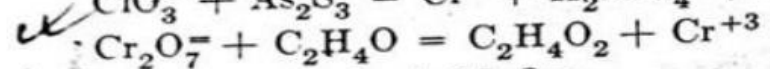
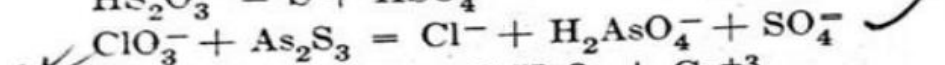
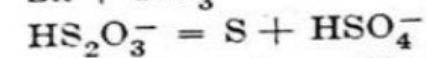
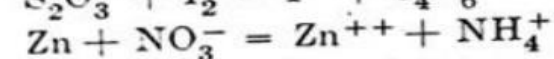
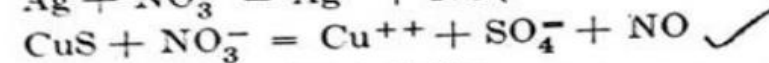
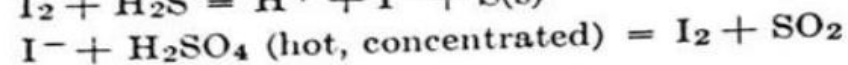
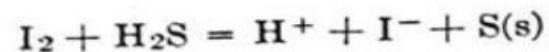
Oxidation Half Reaction	Reduction Half Reaction
$\text{CrO}_2^- = \text{CrO}_4^{2-}$	$\text{ClO}^- = \text{Cl}^-$
Change in ON of Cr = $(+6) - (+3) = 3$	Change in ON of Cl = $(-1) - (+1) = -2$
$\text{CrO}_2^- = \text{CrO}_4^{2-} + 3\text{e}^-$	$\text{ClO}^- + 2\text{e}^- = \text{Cl}^-$
$\text{CrO}_2^- + 4\text{OH}^- = \text{CrO}_4^{2-} + 3\text{e}^-$	$\text{ClO}^- + 2\text{e}^- = \text{Cl}^- + 2\text{OH}^-$
$\text{CrO}_2^- + 4\text{OH}^- = \text{CrO}_4^{2-} + 3\text{e}^- + 2\text{H}_2\text{O}$	$\text{ClO}^- + 2\text{e}^- + \text{H}_2\text{O} = \text{Cl}^- + 2\text{OH}^-$
$[\text{CrO}_2^- + 4\text{OH}^- = \text{CrO}_4^{2-} + 3\text{e}^- + 2\text{H}_2\text{O}] \times 2$	$[\text{ClO}^- + 2\text{e}^- + \text{H}_2\text{O} = \text{Cl}^- + 2\text{OH}^-] \times 3$
$2\text{CrO}_2^- + 2\text{OH}^- + 3\text{ClO}^- = 2\text{CrO}_4^{2-} + \text{H}_2\text{O} + 3\text{Cl}^-$	

**Q.  $P_4 + OH^- = PH_3 + H_2PO_2^-$  (Basic medium and Disproportionation reaction )**

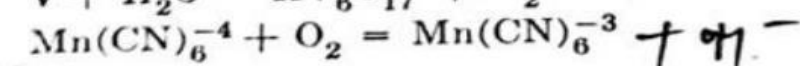
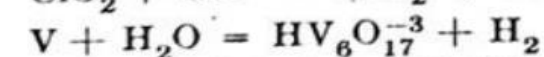
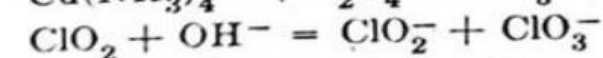
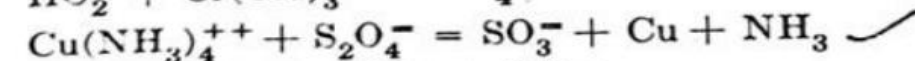
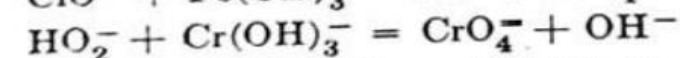
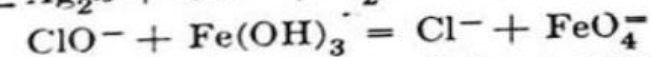
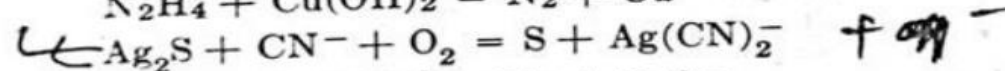
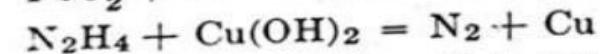
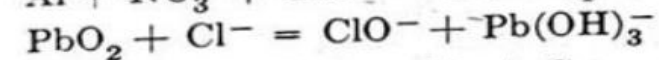
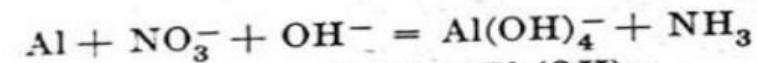
Oxidation Half Reaction	Reduction Half Reaction
$P_4 = H_2PO_2^-$	$P_4 = PH_3$
$P_4 = 4 H_2PO_2^-$	$P_4 = 4 PH_3$
Change in ON of P = $4 \times \{(+1) - 0\} = 4$	Change in ON of P = $4 \{(-3) - 0\} = -12$
$P_4 = 4 H_2PO_2^- + 4 e^-$	$P_4 + 12 e^- = 4 PH_3$
$P_4 + 8 OH^- = 4 H_2PO_2^- + 4 e^-$	$P_4 + 12 e^- = 4 PH_3 + 12 OH^-$
	$P_4 + 12 e^- + 12 H_2O = 4 PH_3 + 12 OH^-$
$[P_4 + 8 OH^- = 4 H_2PO_2^- + 4 e^-] \times 3$	$[P_4 + 12 e^- + 12 H_2O = 4 PH_3 + 12 OH^-] \times 1$
$4P_4 + 12 OH^- + 12 H_2O = 4 H_2PO_2^- + 4 PH_3$	

## Exercise Problems

7.1 Complete and balance the following reactions which occur in acidic aqueous solution.



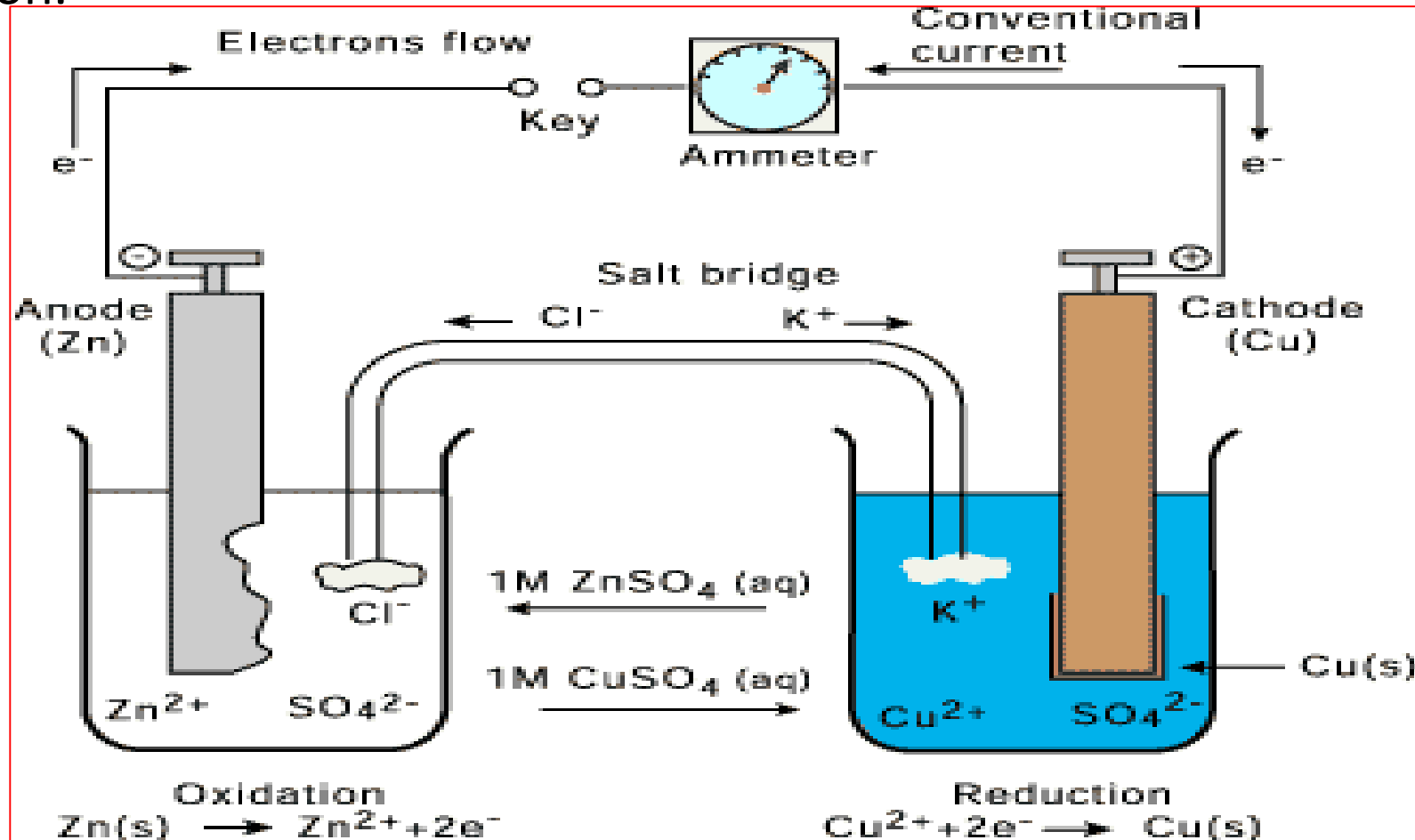
7.2 Complete and balance the following reactions which occur in basic aqueous solution.





# Galvanic Cell (also known as a Voltaic cell)

- A device which converts **chemical energy** into **electrical energy** as a result of **spontaneous redox reaction**. i.e. **electrical current is generated by a spontaneous redox reaction**.



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- Two beakers are connected through a salt bridge and electrodes are connected by copper wire with an ammeter.
- When a cell is set up, a redox reaction occurs.

- **At anode/ left pole/ negative pole (Zinc rod):**



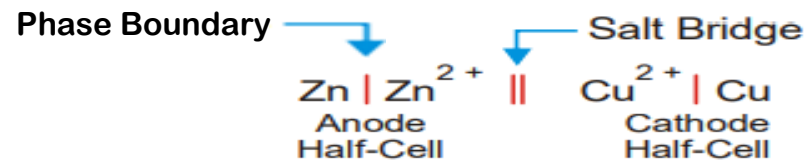
- **At cathode/ right pole/ positive pole (copper rod):**



- Net redox reaction:



- **Representation of a Cell**



# Salt Bridge

- U shaped tube containing **KCl or KNO<sub>3</sub> or NH<sub>4</sub>NO<sub>3</sub>** solution in agar-agar gel.
- Establishes **electrical contact between two half cells** .
- **Does not participate chemically** in cell reaction.
- **Prevents any net charge accumulation in either half cell.**
  - The excess positive charge (Zn<sup>2+</sup>) in anode is reduced by NO<sub>3</sub><sup>-</sup> ions moving out from salt bridge to anode **or** Zn<sup>2+</sup> ions moving into salt bridge.
  - The excess negative ions (SO<sub>4</sub><sup>2-</sup>) in cathode is reduced by K<sup>+</sup> diffusing out from salt bridge to cathode solution **or** SO<sub>4</sub><sup>2-</sup> ions moving into salt bridge.

# Common types of electrodes used in Galvanic Cells

- **Active metal electrodes**

- They are active metals and they are **dissolved or formed** during cell reaction. e.g., Zn and Cu electrodes in,  $\text{Zn} / \text{Zn}^{2+} // \text{Cu}^{2+} / \text{Cu}$  ;  
 $\text{Zn} + \text{Cu}^{2+} = \text{Zn}^{2+} + \text{Cu}$

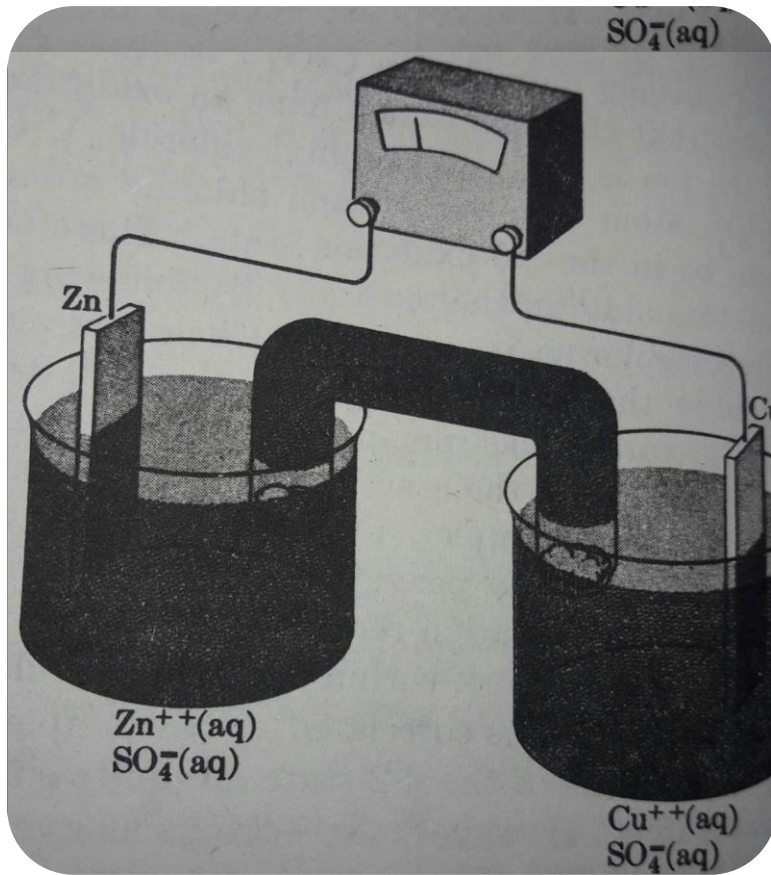
- **Inert or sensing electrodes**

- They **remain unchanged** by net cell reaction. e.g., platinum and graphite (C) electrode  $\text{Cu} / \text{Cu}^{2+} // \text{Fe}^{3+} / \text{Fe}^{2+}$  , (Pt);  
 $\text{Cu} + 2 \text{Fe}^{3+} = \text{Cu}^{2+} + 2 \text{Fe}^{2+}$

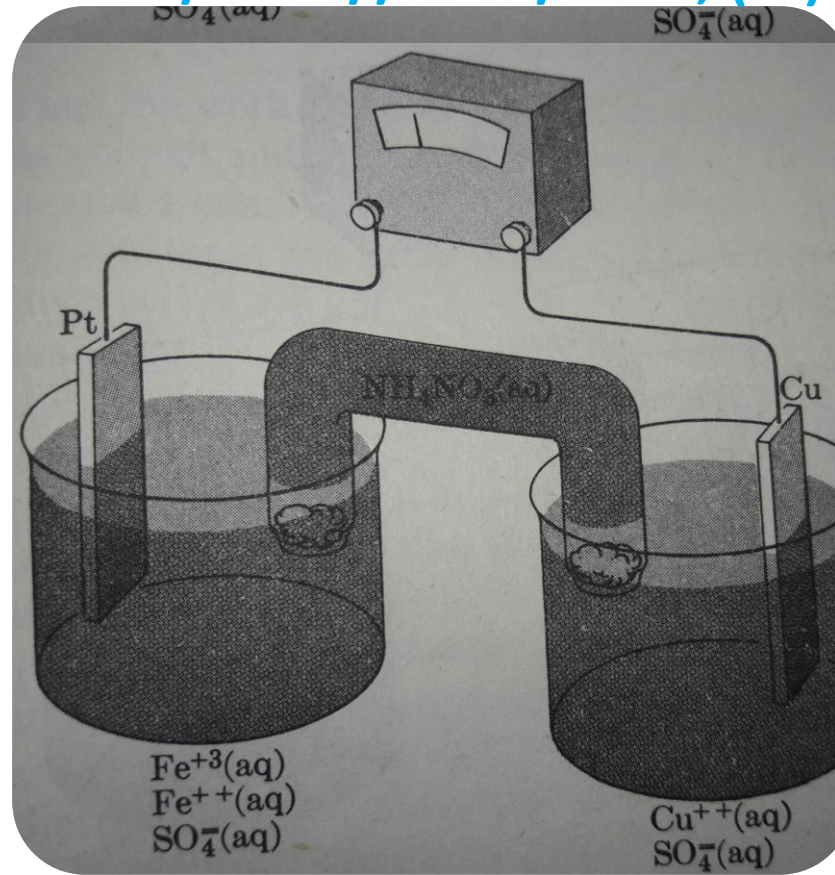
- **Gas electrodes**

- They also **remain unchanged by cell reaction** similar to inert electrode. e.g., **standard hydrogen electrode**,  
(Pt),  $\text{H}_2 / 2\text{H}^+ // \text{Cu}^{2+} / \text{Cu}$  ;  $\text{H}_2(\text{g}) + \text{Cu}^{2+} = 2\text{H}^+(\text{aq}) + \text{Cu}(\text{s})$

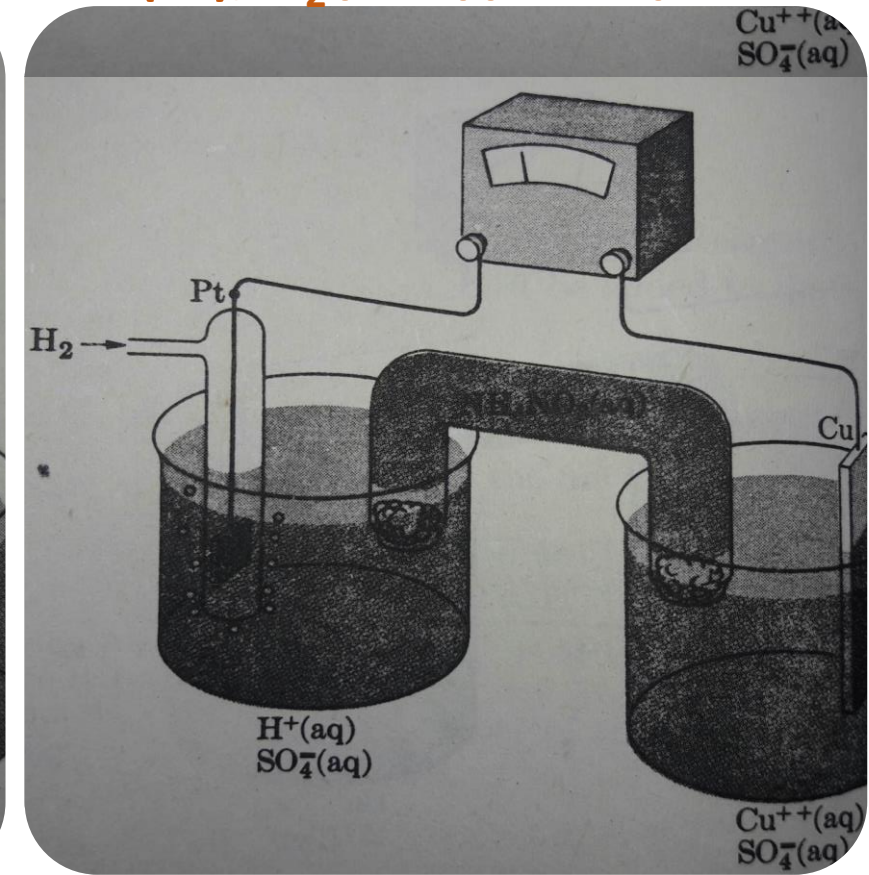
**Zn / Zn<sup>2+</sup> // Cu<sup>2+</sup> / Cu**



**Cu / Cu<sup>2+</sup> // Fe<sup>3+</sup> / Fe<sup>2+</sup>, (Pt)**



**(Pt), H<sub>2</sub> / H<sup>+</sup> // Cu<sup>2+</sup> / Cu**



- a. A Galvanic cell (Half cell on left using a **zinc strip** and on right copper rod as **active metal electrode**)
- b. A Galvanic cell (Half cell on left using a **platinum strip as inert sensing electrode**)
- c. A Galvanic cell (Half cell on left using a **hydrogen gas electrode**)

contd...

- A **Galvanic cell made up of the zinc and copper half-cells**, in which the **two electrodes are** connected **to the terminals of a voltmeter**, then at constant temperature, **voltage of the galvanic cell (cell potential) is the function of :**
  - a). The ratio of the concentration of the **zinc and cupric ions**
    - If the temperature is  $25^{\circ}\text{C}$  and the concentrations are equal, the voltmeter reads the cell potential of **1.0 Volts**
    - If  **$\text{Zn}^{++}$  ion concentration is increased**, or the **concentration of  $\text{Cu}^{++}$  ion decreased**, the **voltage decreases and vice-versa**
  - **i.e. the voltage increases as the concentration of reactant increased or decreases cell voltage as concentration of product increased.**
  - If we make Galvanic cell of the **zinc and silver half-cells**, replacing copper half cell, at same conditions as above, cell potential is **1.56 Volts**. Therefore,
- b). The voltage of Galvanic cell is **the characteristic both of the chemical substances involved in the cell reaction and of their concentrations.**

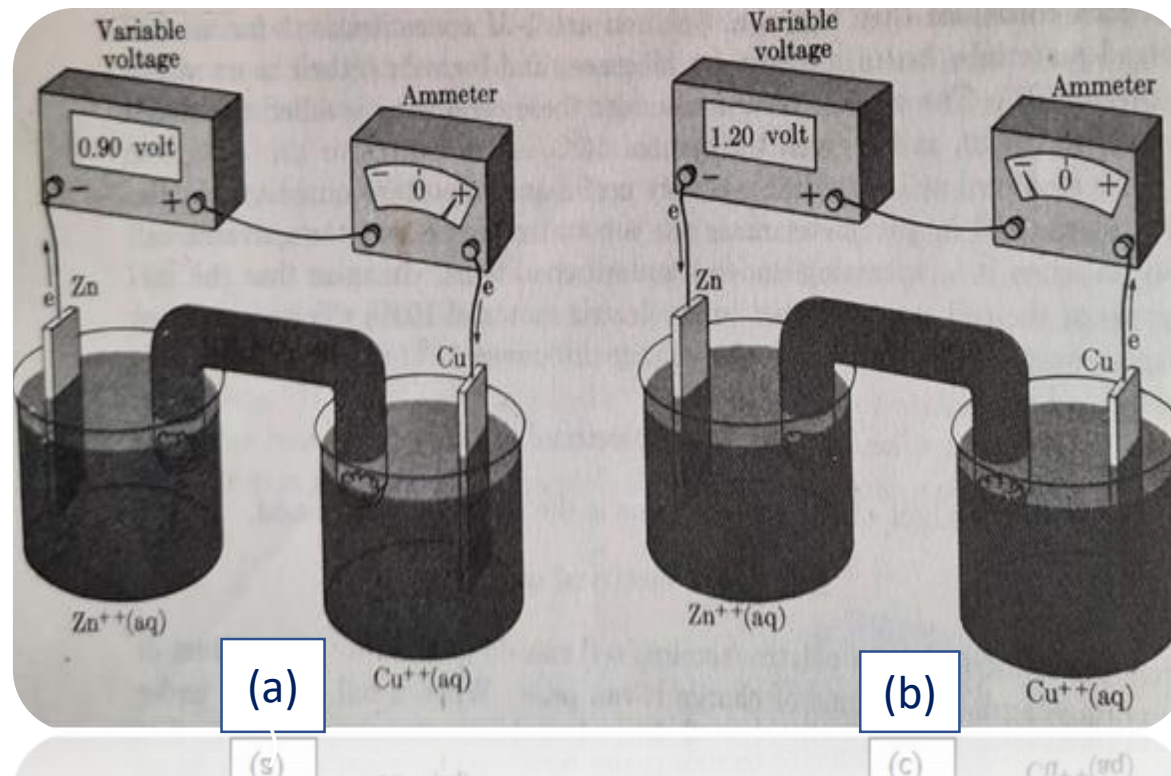


# Cell potential (or emf) and standard cell potential ( $\Delta E^\circ$ )

- **Cell potential** is the difference between the **electrode potentials** of the **electrodes** present in two half cells of an **electrochemical cell**. or **net reduction to proceed from left to right**.
- It is **driving force** that sends **electrons from anode to cathode through the circuit**.
- **Standard Cell Potential** or emf of a cell ( $\Delta E^\circ$ ) is cell potential of a galvanic measured at standard conditions of
  - **1-M concentrations for all dissolved materials**
  - **1-atm pressure for all gases and,**
  - **for solids, their most stable form at 25°C**
- For example,  **$\text{Zn} + \text{Cu}^{2+} = \text{Zn}^{2+} + \text{Cu}$  ;  $\Delta E^\circ = 1.1\text{volts}$**
- **$\text{Zn} + 2\text{Ag}^+ = \text{Zn}^{2+} + 2\text{Ag}$  ;  $\Delta E^\circ = 1.56\text{ volts}$**
- **$\text{Cu} + 2\text{Ag}^+ = \text{Cu}^{2+} + 2\text{Ag}$  ;  $\Delta E^\circ = 0.46\text{ volts}$**

# “Standard Cell Potential ( $\Delta E^\circ$ ) is the driving force of the cell reaction”

- **Standard Cell Potential ( $\Delta E^\circ$ )** is the quantitative measure of the tendency of reactants to form products in their standard states. It represents the **driving force of the chemical reaction**.
- Illustration: A zinc-copper standard cell ( $\Delta E^\circ = 1.1 \text{ v}$ ) is connected to the **external variable voltage** that **opposes the cell voltage** and an **ammeter** that indicates the direction of the flow of electrons.





# contd...

There are three distinct cases:

## 1. External variable voltage < 1.1 v

- The ammeter shows the electron flow from Zn to Cu electrode through external circuit. Then, the spontaneous cell reaction takes place as:
  - $\text{Zn} + \text{Cu}^{2+} = \text{Zn}^{2+} + \text{Cu}$

## 2. External variable voltage = 1.1 v

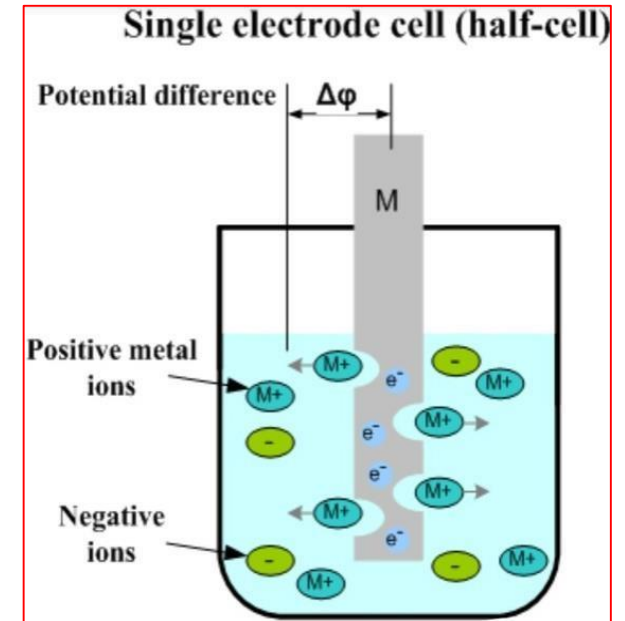
- No current flows through the ammeter and no net cell reaction occurs.
- The chemical driving force of cell reaction is opposed by equal amount of external variable voltage.

## 3. External variable voltage > 1.1 v

- The ammeter shows the electron flow from Cu to Zn electrode.
- Then, the spontaneous cell reaction is reversed and electrolysis occurs.
  - $\text{Cu} + \text{Zn}^{2+} = \text{Cu}^{2+} + \text{Zn}$

# Electrode Potential (E)

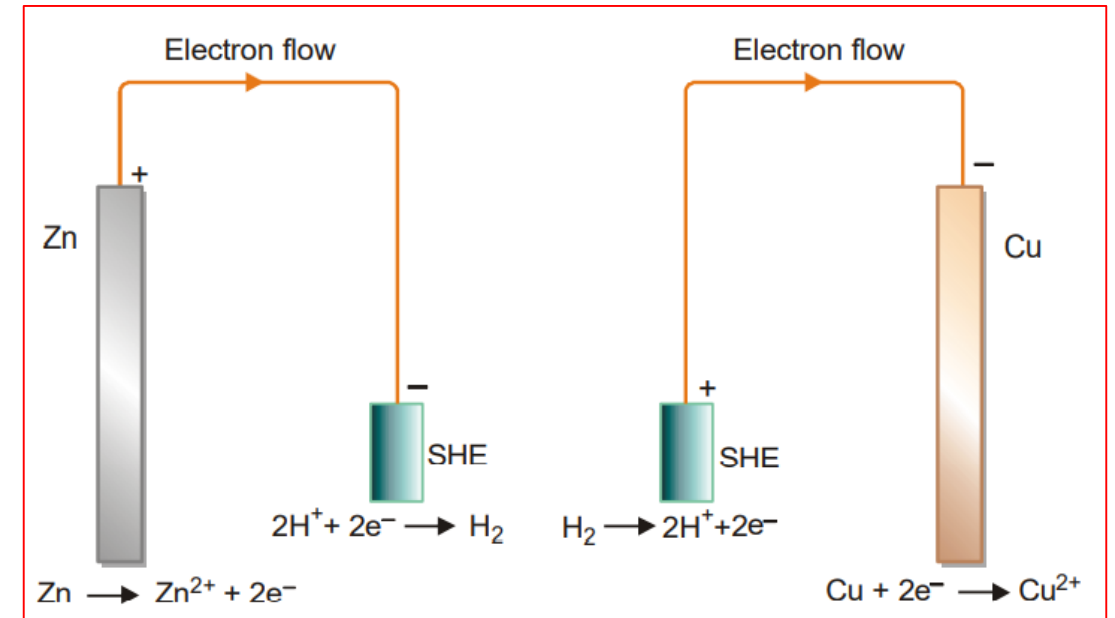
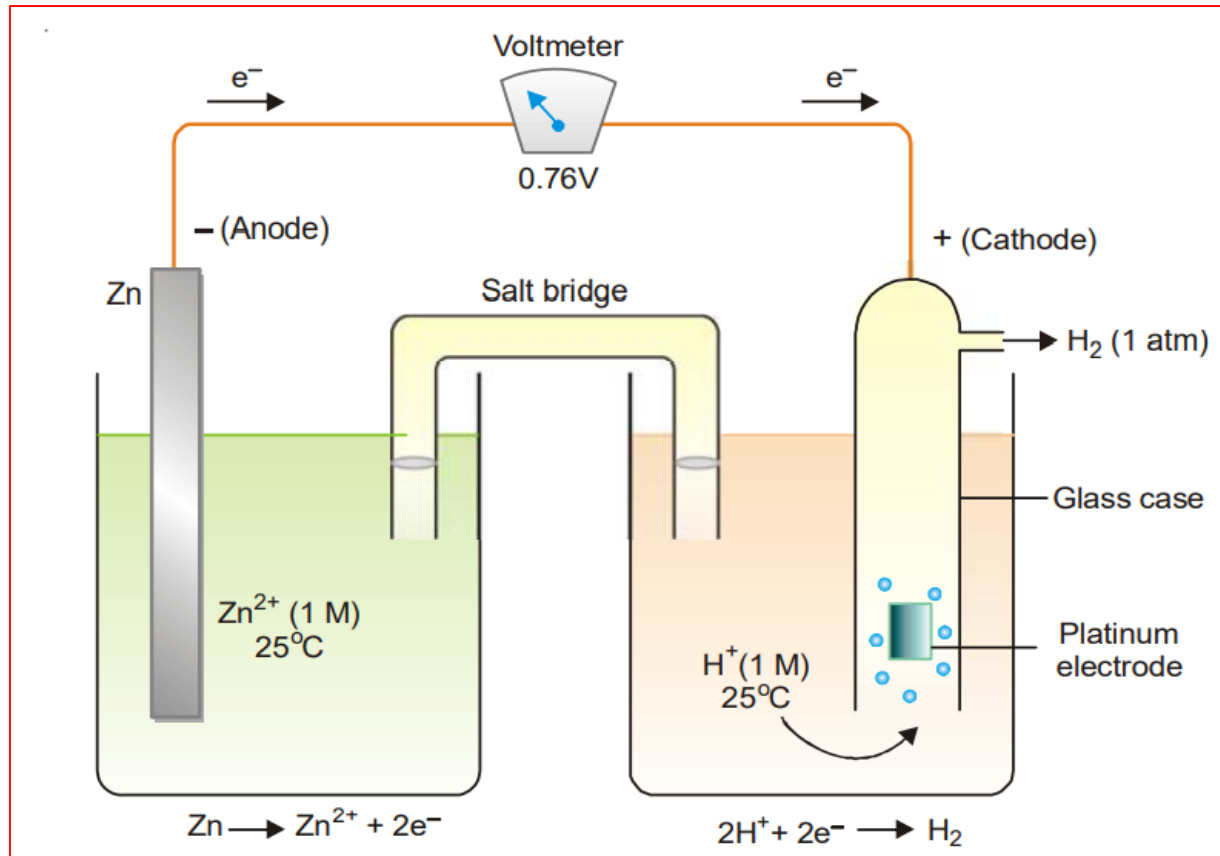
- The potential difference developed at the **interface between metal and electrolyte solution containing its own ions** at equilibrium.
- **Electrode potential** also refers to the **ability** of an **electrode** in a **cell** to get **reduced or oxidized**
- **Standard electrode potential ( $E^\circ$ ):**
  - 1 M, 25°C (298 K), 1 atm
- $E^\circ$  = Standard reduction potential  
or Standard oxidation potential
- Both have equal numerical value but opposite sign.
- But, IUPAC has recommended the use of **standard reduction potential** as **standard electrode potential ( $E^\circ$ )**. Examples,
  - $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$  ;  $E^\circ = + 0.34 \text{ v}$       and       $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$  ;  $E^\circ = - 0.76 \text{ v}$



# Single electrode potentials and its measurement

- Determination of emf of a half-cell
- The potential of a single electrode in a half cell.
- It is measured by **coupling with standard hydrogen electrode (SHE) as reference electrode. SHE has zero volt electrode potential** .
- Generally, **reference electrode. is always used as anode** and **other single electrode is cathode**. Then, the cell potential produced by cell is the single electrode potential of that electrode.
- **Example, (Pt),  $\text{H}_2 / \text{H}^+ // \text{Zn}^{2+} / \text{Zn}$**  during measurement. It gives  $-0.76 \text{ v}$  cell potential. So standard electrode potential for Zinc electrode is  **$-0.76 \text{ v}$** .  
 **$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn} ; E^\circ = -0.76 \text{ v}$**
- **Example, (Pt)  $\text{H}_2 / \text{H}^+ // \text{Cu}^{2+} / \text{Cu}$**  during measurement. It gives  $+0.34 \text{ v}$  cell potential. So standard electrode potential for Copper electrode is  **$+0.34 \text{ v}$** .  
 **$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu} ; E^\circ = +0.34 \text{ v}$**

# The zinc electrode (Zn, Zn ) coupled with hydrogen electrode.



SHE can act both as cathode and anode when joined with another half-cell

# Determination of Standard Cell Potential or emf of a cell ( $\Delta E^\circ$ )

- $\Delta E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ 
  - $\Delta E^\circ = \text{positive}$ , the reaction is spontaneous/feasible.
  - $\Delta E^\circ = \text{negative}$ , the reaction is non-spontaneous/not feasible.

**Q.  $\text{Zn}^{2+} + 2\text{e}^- = \text{Zn}$  ;  $E^\circ = - 0.76 \text{ v}$  and  $\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$  ;  $E^\circ = + 0.34 \text{ v}$**

- Calculate the  $\Delta E^\circ$  of a cell.
- Write net cell reaction and cell representation .
- **$E^\circ = \text{High} = \text{Reduction} = \text{Cathode}$  and  $E^\circ = \text{Low} = \text{Oxidation} = \text{Anode}$** 
  - **Anode:**  $\text{Zn} = \text{Zn}^{2+} + 2\text{e}^-$   $E^\circ = + 0.76 \text{ v}$
  - **Cathode:**  $\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$   $E^\circ = + 0.34 \text{ v}$

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- **Net cell reaction:  $\text{Zn} + \text{Cu}^{2+} = \text{Zn}^{2+} + \text{Cu}$   $\Delta E^\circ = 1.1\text{volt}$**
- $\Delta E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.34 - (- 0.76) = 1.1 \text{ volt}$
- **$\text{Zn} / \text{Zn}^{2+} // \text{Cu}^{2+} / \text{Cu}$**

contd..



- Answer the following questions
  - Write net cell reaction.
  - Write cell representation.
  - Calculate the  $\Delta E^\circ$  of a cell.

# Nernst equation

- **Nernst equation** is an **equation** that relates the reduction potential of a reaction (half-cell or full cell reaction) to the standard electrode potential, temperature, and activities (often approximated by concentrations) of the chemical species undergoing reduction and oxidation.

- Consider a reaction,  $a A + b B = c C + d D$ ;

$$\Delta E = \Delta E^\circ - \frac{0.059}{n} \log \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)_{eq^n}$$

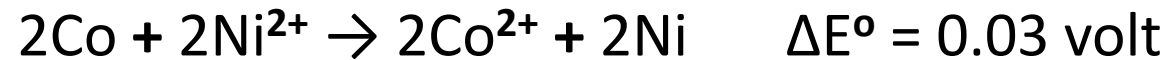
- Where,  $\Delta E$  = **cell potential**,  $\Delta E^\circ$  = **standard cell potential** and  $n$  = **number of electrons transferred** in the reaction.
- Upon substituting the values of **R**, **F** and **T** at 25°C, the quantity **[2.303 RT]/F** is equal to **0.0591**.

Q. For a redox reaction,  $Co + Ni^{++} = Co^{++} + Ni$  ;  $\Delta E^\circ = 0.03 \text{ v}$ ,  $[Ni^{++}] = 1 \text{ M}$  ;  $[Co^{++}] = 0.1 \text{ M}$ ,  
Then,  $\Delta E = ?$  **0.06 volt**

Q. For the above reaction, if  $[Ni^{++}] = 0.01 \text{ M}$  ;  $[Co^{++}] = 1 \text{ M}$ .  
Then,  $\Delta E = ?$  **-0.03 volt**

# Applications of Nernst equation

**1. Cell potential of a reaction remains unaffected by multiplying that reaction by any positive number.**



$$\Delta E = \Delta E^\circ - \frac{0.059}{4} \log \left( \frac{[\text{Co}^{2+}]^2}{[\text{Ni}^{2+}]^2} \right)$$

$$\Delta E = \Delta E^\circ - \frac{0.059}{2} \log \left( \frac{[\text{Co}^{2+}]}{[\text{Ni}^{2+}]} \right)$$

- Here, **the form of Nernst equation is consistent** with the idea that the voltage associated with a reaction is unaffected by multiplying that reaction by a positive number.



contd..

## 2. To predict the spontaneity of reaction

- $\Delta E = +ve$ , reaction is spontaneous in forward direction
- $\Delta E = -ve$ , reaction is spontaneous in backward direction
- The change of electrolyte concentration can change the **direction of spontaneity of a reaction**.
  - a) If the **reactant concentration is increased or the product** concentration is decreased, the **cell voltage becomes more positive**. The reaction is spontaneous to forward.
- For,  $\text{Co} + \text{Ni}^{++} = \text{Co}^{++} + \text{Ni}$  ;  $\Delta E^\circ = 0.03 \text{ v}$ . If  $[\text{Ni}^{++}] = 1\text{M}$  ;  $[\text{Co}^{++}] = 0.1 \text{ M}$ , Then,

$$\Delta E = \Delta E^\circ - \frac{0.059}{2} \log \left( \frac{0.1}{1} \right) = 0.03 - \frac{0.059}{2} \log 0.1 = 0.03 + 0.03 = 0.06 \text{ v}$$

contd..

b) If the **reactant concentration is decreased** or **the product concentration is increased**, the **cell voltage becomes negative**. The reaction is **spontaneous to backward**.

- For,  $\text{Co} + \text{Ni}^{++} = \text{Co}^{++} + \text{Ni}$  ;  $\Delta E^\circ = 0.03 \text{ v}$ . If  $[\text{Ni}^{++}] = 0.01\text{M}$  ;  $[\text{Co}^{++}] = 1.0 \text{ M}$ ,  
Then,

$$\Delta E = \Delta E^\circ - \frac{0.059}{2} \log \left( \frac{1}{0.01} \right) = 0.03 - \frac{0.059}{2} \log 10^2 = 0.03 - 0.06 = -0.03 \text{ v}$$

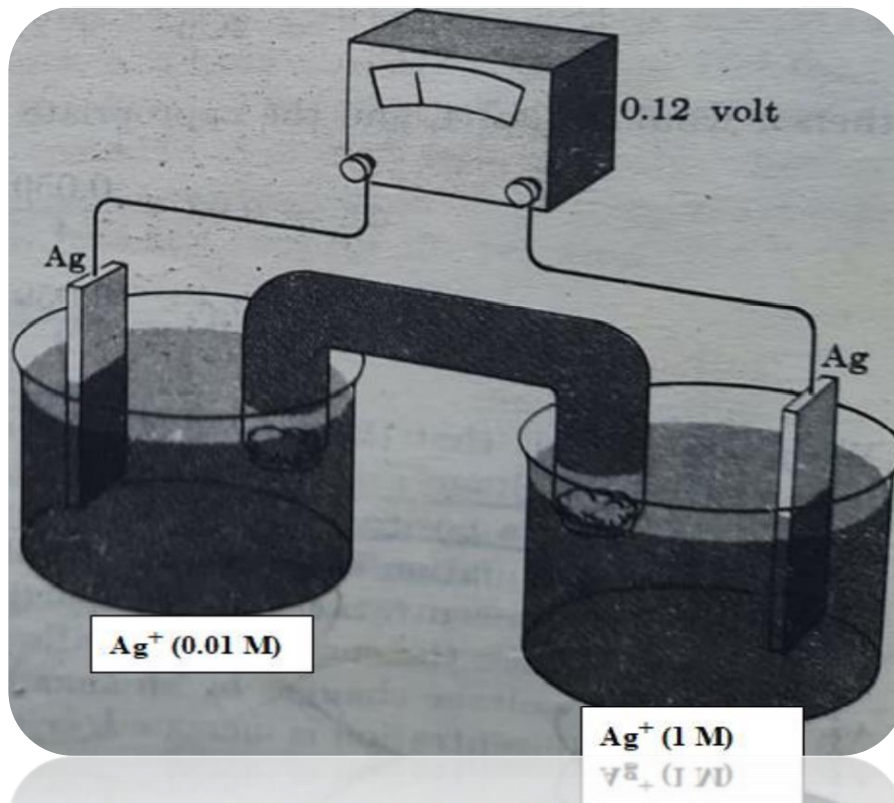
### 3. Calculation of equilibrium constant (K): Relation between equilibrium constant, K and standard cell potential, $\Delta E^\circ$

- Consider a reaction,  $a A + b B = c C + d D$
- At equilibrium,  $\Delta E = 0$ , Then
- Required equation for the relation between equilibrium constant (K) and standard cell potential ( $\Delta E^\circ$  ).
  - If  $\Delta E^\circ = +ve$  or  $\Delta E^\circ > 0$ , then,  $K > 1$  and **forward reaction is spontaneous**.
  - If  $\Delta E^\circ = -ve$  or  $\Delta E^\circ < 0$ , then,  $K < 1$  and **backward reaction is spontaneous**.

$$\Delta E = \Delta E^\circ - \frac{0.059}{n} \log \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)_{eq^n}$$
$$0 = \Delta E^\circ - \frac{0.059}{n} \log K$$
$$\log K = \frac{n \Delta E^\circ}{0.059}$$
$$\therefore K = 10^{\frac{n \Delta E^\circ}{0.059}}$$

## 4. Concentration cell

- The galvanic cell obtained by using same type of electrodes dipped in same type of electrolytic solution having different concentration. e.g., silver ion concentration cell.
- **More dilute solution = anode** ; **More concentrated solution = cathode**



- **At anode:**  $\text{Ag(s)} \rightarrow \text{Ag}^+ (0.01\text{M}) + \text{e}^-$
- **At cathode:**  $\text{Ag}^+ (1\text{M}) + \text{e}^- \rightarrow \text{Ag(s)}$
- Net cell reaction:  
$$\text{Ag}^+ (1\text{M}) \rightarrow \text{Ag}^+ (0.01\text{M})$$

contd..

- The **cell reaction is spontaneous** until both anode and cathode have equal concentrations.
- **The standard cell voltage ( $\Delta E^\circ$ ) is zero** for concentration cell.
- But, the cell voltage is given by **Nernst equation**,

$$\Delta E = \Delta E^\circ - \frac{0.059}{n} \log \left( \frac{[\text{Ag}^+]_{\text{dilute}}}{[\text{Ag}^+]_{\text{concentrated}}} \right)$$

$$\Delta E = 0 - \frac{0.059}{1} \log \left( \frac{0.01}{1} \right)$$

$$\therefore \Delta E = 0.12 \text{ volt}$$

# Electrolysis

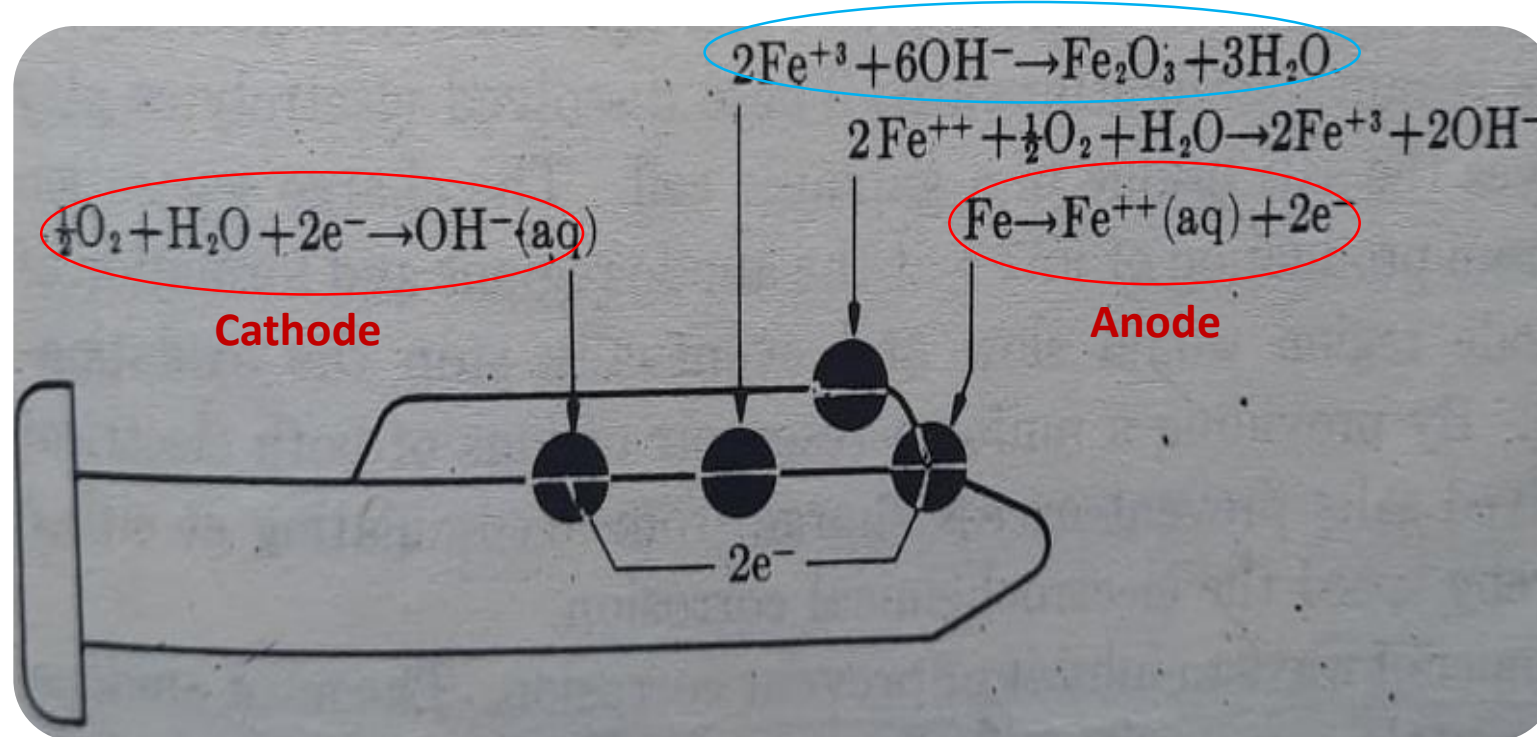
- **1 faraday** = Total charge of one mole of electrons =  $(1.6 \times 10^{-19}) (6.023 \times 10^{23}) = 96,487 \text{ coulomb} \equiv \mathbf{96,500 \text{ coulomb}}$
- **Charge (coulomb) = current (ampere)  $\times$  time (second)**
- **1 amp = 1 coul/sec**
- 1 mole of  $e^-$  (1 F charge) can reduce 1 mole  $\text{Na}^+$ ,  $\frac{1}{2}$  mole  $\text{Ca}^{2+}$  and  $\frac{1}{3}$  mole  $\text{Al}^{3+}$ .



- $\text{CuSO}_4$  solution is electrolyzed for 7 minutes with 0.6 ampere current.  
Charge =  $0.6 \times (7 \times 60) = \mathbf{252 \text{ coul}} = (252 \div 96500) \text{ F} = 2.61 \times 10^{-3} \text{ F}$
- $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$
- So,  $\mathbf{1.3 \times 10^{-3}}$  mole of copper metal is deposited in the electrolysis.

# Corrosion / Rusting of iron

- The **spontaneous destruction** of metals due to its interaction with environment forming a **brown scale**, called **rust**.
- Among many theories, **electrochemical theory** of rusting is the most convincing one.
- The iron spike with its wet surface when exposed to atmospheric oxygen undergoes corrosion as follows.



contd..

- Some site of its surface acts as **anode** where **oxidation** of Fe to  $\text{Fe}^{2+}$  occurs.



- Iron being good conductor, electrons move towards the next site, **cathode** where **reduction** of dissolved oxygen takes place.



- In solution,  $\text{Fe}^{2+}$  undergo direct oxidation with dissolved oxygen.



- Finally,  $\text{Fe}^{3+}$  and  $\text{OH}^-$  combine to give insoluble solid hydrated iron oxide (rust),  **$\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$**  and it gets deposited on the iron surface.



- **Note:** • Cathode and anode part are very close to each other and • Water containing  $\text{O}_2$  (electrolyte) helps in the flow of electrons. • These accelerate the rate of corrosion.



## Prevention of corrosion:

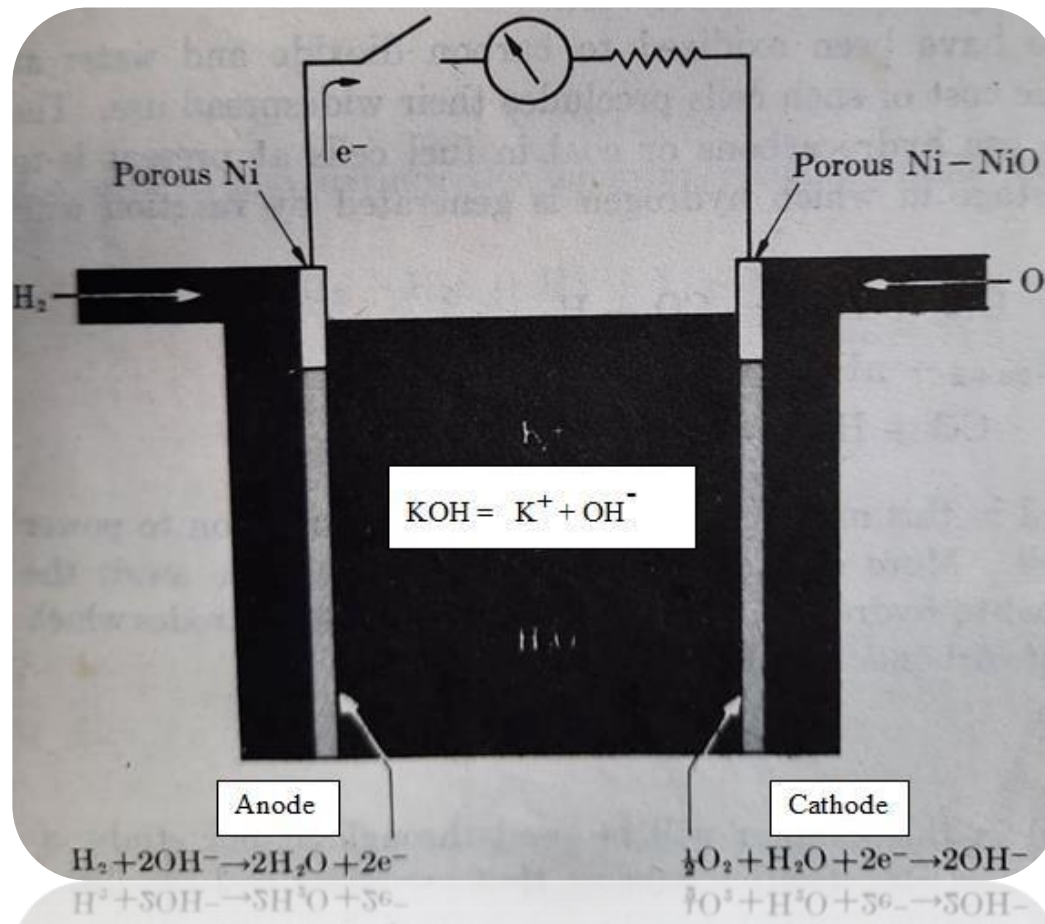
- By **coating the metal surface** with **paints**, enamel etc.
- By **coating with noble metals** like Au, Ag, Cu.
- By **using sacrificial** anode (by coating with metal like Zn (galvanization), Sn, Ni ,Cr etc.)

## Types of Cell:

- **Primary cell:** can't be recharged.  
e.g.; **Lechlanche dry cell; Mercury cell** etc.
- **Secondary cell:** can be recharged.  
Eg; **Lead acid cell (lead storage cell); Nickel-cadmium cell; Alkali metal-sulfur cell** etc.

# Fuel cells

- Primary cells in which reactants are continuously supplied to its electrode from outside as fuel and the energy obtained from the **combustion of fuel** is directly converted into **electrical energy**.



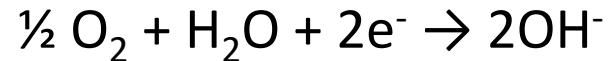
Hydrogen and Oxygen fuel cell

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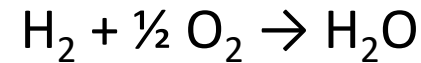
- At **anode**: Oxidation of  $\text{H}_2$  to water.



- At **cathode**: Reduction of  $\text{O}_2$  to  $\text{OH}^-$ .



- **Net cell reaction:**



- The cell works at high pressure (40 atm).
- For low current demand, it can function at 1 atm and high concentration of KOH. It is used in spacecraft.

## Advantage:

- They are pollution free and more efficient.

## Disadvantage:

- **Difficulty in finding the suitable fuel-electrode-electrolyte combination.**
- **Difficulties in handling the gaseous fuels.**

- **Q.** An electrode chemical cell is constructed of one half-cell in which a platinum wire dips into a solution containing 1-M  $\text{Fe}^{3+}$  and 1-M  $\text{Fe}^{2+}$ ; the other half-cell consists of thallium metal immersed in 1-M  $\text{Tl}^{+}$  solution. Given the following standard electrode potentials,  $\text{Tl}^{+} + e^{-} = \text{Tl}$ ,  $\epsilon^{\circ} = -0.34$ ,  $\text{Fe}^{3+} + e^{-} = \text{Fe}^{2+}$ ,  $\epsilon^{\circ} = 0.77$ , supply the desired information. (a) Which electrode is **negative terminal**? (b) Which electrode is **cathode**? (c) What is **cell voltage**? (d) Write the **reactions that proceed from left to right as the cell operates spontaneously**. (e) What is the **equilibrium constant of the reaction**? (f) How will the **voltage of the cell changed by decreasing the concentration of  $\text{Tl}^{+}$**  ?

- Thallium electrode acts as a negative terminal
- Platinum electrode dipped in  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ion solution will be cathode
- Cell voltage = 1.11 V
- $\text{Fe}^{3+} + e^{-} = \text{Fe}^{2+}$  (Cathode half cell reaction)  $\epsilon^{\circ} = 0.77$   $\text{Tl} = \text{Tl}^{+} + e^{-}$ , (Anode half cell reaction) Thus,  $\text{Fe}^{3+} + \text{Tl} = \text{Fe}^{2+} + \text{Tl}^{+}$  (spontaneous cell reaction)
- $K = 6.5 \times 10^{18}$
- From Nernst equation we can say that, decreasing the concentration of  $\text{Tl}^{+}$ , the voltage of the cell increases

- **Q.** A Galvanic cell consists of a strip of cobalt metal, Co, dipped into 1-M  $\text{Co}^{2+}$  solution, and another half cell in which a piece of platinum dips into 1-M solution of  $\text{Cl}^-$ . Chlorine gas at 1-atm pressure is bubbled into the solution. Observed cell voltage is 1.63 volts, and as the cell operates cobalt electrode is negative. Given only the standard potential for the chlorine-chloride ion half-cell is  $\frac{1}{2} \text{Cl}_2 + e^- = \text{Cl}^-$ ,  $\epsilon^0 = 1.36$  volts, supply the desired information. (a) What is the **spontaneous cell reaction**? (b) What is **the standard potential of the cobalt electrode**? (c) Would the **cell voltage increases or decreases if the pressure of chlorine gas increased**? (d) **What would the cell voltage be if the concentration  $\text{Co}^{2+}$  were reduced to 0.01 M?**

- Spontaneous cell reaction is :  $\text{Co} + \text{Cl}_2 = \text{Co}^{2+} + 2\text{Cl}^-$
- $\epsilon^0_{\text{Co}} = -0.27 \text{ V}$
- if the pressure of chlorine gas increased cell voltage increases.
- If the concentration  $\text{Co}^{2+}$  were reduced to 0.01 M, using Nernst equation,  $\Delta\epsilon = 1.686 \text{ V}$ . Thus, the cell voltage is increased from its value of standard condition, which was 1.63 V