

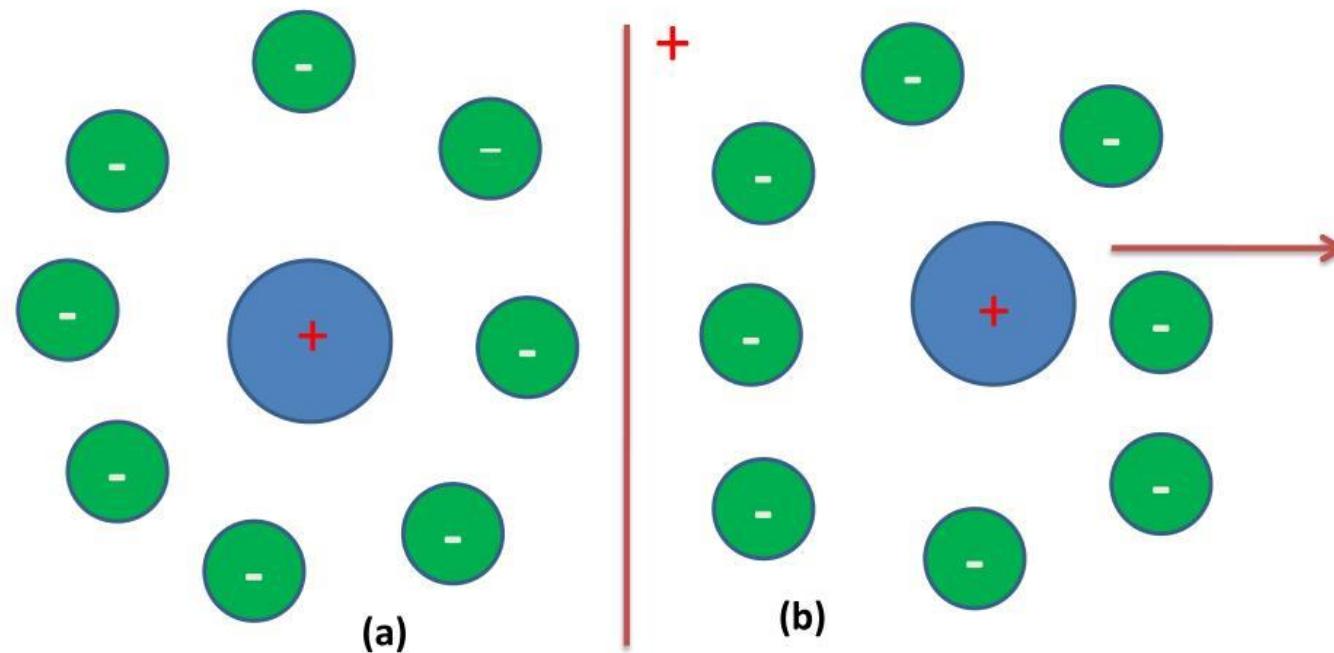
# DEBYE-HUCKEL THEORY

Debye-Hückel theory is the modern theory of strong electrolytes which explains their behaviour in solutions. According to this theory, strong electrolytes are completely ionized at all dilutions. Still equivalent conductance is less in concentrated solutions. This is due to fall in mobilities of ions as a result of inter-ionic attractions. The decrease in mobilities is accounted for by the following reasons.

- i) Asymmetric effect
- ii) Electrophoretic effect

# 1. ASYMMETRIC EFFECT

## RELAXATION EFFECTS OR ASYMMETRY EFFECTS



Symmetrical ionic atmosphere  
around a positive ion

Ionic atmosphere becoming  
asymmetrical when central ion moves

- In a solution, each ion is surrounded by ions of opposite charge, forming an **ionic atmosphere**.
- Without an electric field, this atmosphere is **symmetrical**, and the forces on the central ion are balanced.
- When an **electric field** is applied:
  - The positive ion moves toward the cathode.
  - The surrounding negative ions (ionic atmosphere) lag behind toward the anode.
- This **disturbs the symmetry**, creating more negative ions on one side.
- The positive ion now feels a **backward pull**, which **slows it down**.
- This slowing down due to the shifted ionic atmosphere is the **asymmetric effect**.

## 2.ELECTROPHORETIC EFFECT

- As the positive ion moves, it leaves its old ionic atmosphere behind and tries to form a **new, balanced atmosphere** around it.
- **Formation of the new atmosphere takes time**, slower than the decay of the old one.
- This **time lag** is called **relaxation time**.
- The slowing down of the ion due to this delayed reorganization is called the **relaxation effect**.

- Each ion in a solution is surrounded by water molecules (hydrated).
- When a **positive ion moves to the cathode**, the **negative ions and their water molecules** move in the **opposite direction** (toward the anode).
- Similarly, **negative ions** moving to the anode face **positive ions and water molecules** moving toward the cathode.
- As a result, each ion **swims against the moving solvent**, which **slows it down**.
- This slowing down is called the **electrophoretic effect**.

- 1.What is an **ionic atmosphere**?
- 2.Explain in simple terms what happens to the ionic atmosphere when an **electric field is applied**.
- 3.How does the **asymmetric effect** slow down the motion of an ion?
- 4.Define **relaxation effect** and explain its connection with **relaxation time**.
- 5.Why does the formation of a new ionic atmosphere take time?
- 6.How are the **asymmetric effect** and **relaxation effect** related?

# 1.What is an **ionic atmosphere**?

- An **ionic atmosphere** is a region around a charged ion in solution where the distribution of other ions is not random but influenced by electrostatic forces.
- When an ion (say a negatively charged chloride ion,  $\text{Cl}^-$ ) is in solution, it doesn't exist completely on its own.
- Oppositely charged ions (positive ones like  $\text{Na}^+$ ) are attracted towards it, while like-charged ions (other  $\text{Cl}^-$ ) are repelled.
- As a result, a “cloud” or *atmosphere* of more oppositely charged ions tends to surround any given ion.
- This **ionic atmosphere** helps reduce the effective charge felt by the ion, lowering its electrostatic potential.

**2. Explain in simple terms what happens to the ionic atmosphere when an electric field is applied.**

- In normal solution (no electric field): each ion is surrounded by its ionic atmosphere — oppositely charged ions cluster around it, making the system more stable.
- When an electric field is applied: The central ion and its ionic atmosphere don't move together perfectly. The central ion moves faster in the direction of the field (towards the oppositely charged electrode). The surrounding ionic atmosphere lags behind because the other ions are slower to rearrange.

### **3. How does the asymmetric effect slow down the motion of an ion?**

#### **Lagging atmosphere**

- The central ion moves quickly under the field.
- Its ionic atmosphere (made of opposite charges) moves more slowly, so it lags behind.

#### **Asymmetry created**

- This lag means that the central ion is no longer sitting in the middle of its opposite-charge “cloud.”
- Instead, more of the opposite charges are *behind* it than in front.

#### **Pulling backward**

- Because opposite charges attract, this shifted ionic atmosphere now **pulls the central ion backwards**.
- That backward pull resists the ion’s forward motion in the electric field.

#### **4. Define relaxation effect and explain its connection with relaxation time.**

- **Relaxation effect** is the **slowing of an ion** due to the **time it takes to rebuild a new symmetric ionic atmosphere** around it after it moves.
- **Relaxation time** is the **time required** for the ionic atmosphere to rearrange around the moving ion.

## **5. How are the asymmetric effect and relaxation effect related?**

- Both effects **slow down ion motion** in a solution.
- **Asymmetric effect** happens because the ionic atmosphere is **shifted backward** by the applied field.
- **Relaxation effect** happens because it **takes time to rebuild the atmosphere** around the moving ion.
- Together, they **reduce the ion's velocity** in an electric field.

Write a note on Galvanic cell

OR

Write a note on Daniel cell

# GALVANIC CELL

## What is a galvanic cell?

- **Answer:**  
A galvanic (voltaic) cell is an electrochemical cell that converts chemical energy into electrical energy through a **spontaneous redox reaction**.  
Example: Daniell cell (Zn–Cu cell).

Mention any two differences between anode and cathode in a galvanic cell.

| Property | Anode     | Cathode   |
|----------|-----------|-----------|
| Reaction | Oxidation | Reduction |
| Polarity | Negative  | Positive  |

What is the direction of electron and ion flow in a Daniell cell?

- **Answer:**
- **Electrons:** From Zn anode → Cu cathode through external wire.
- **Ions:**
  - **Anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ )** move → anode compartment
  - **Cations ( $\text{K}^+$ ,  $\text{NH}_4^+$ )** move → cathode compartment through the salt bridge.

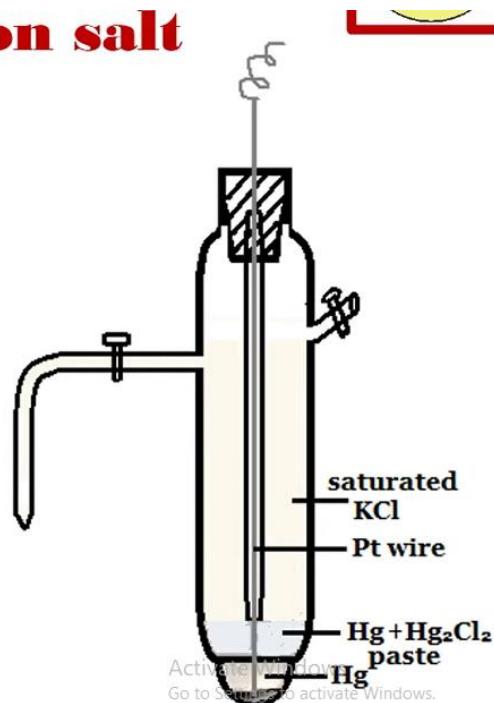
## What is the function of a salt bridge?

- **Answer:**
- It **completes the electrical circuit** by allowing ion flow between the two half-cells.
- It **maintains electrical neutrality** by permitting anions to move to the anode compartment and cations to the cathode compartment.
- It **prevents direct mixing** of the two solutions.

# Calomel electrode- Secondary reference electrode

## Metal-metal sparingly soluble ion salt Construction

- At the bottom : Hg liquid
- Above Hg : Hg-Hg<sub>2</sub>Cl<sub>2</sub> paste
- Rest of the glass tube : saturated KCl solution and side arm
- Electrical contact : Pt wire sealed in glass tube



- It's a secondary reference electrode used to determine the standard electrode potentials of various electrodes

### **Standard electrode potential**

**Saturated KCl** – **0.2422 V**

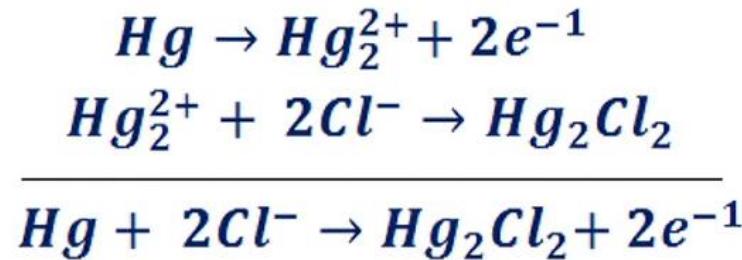
**I M KCl** – **0.280 V**

**0.1 M KCl** – **0.334 V**

## Half cell reactions

### When it acts as anode:

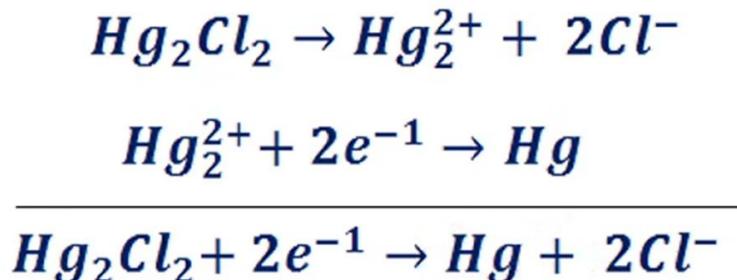
Hg gets oxidised to form  $\text{Hg}_2^{2+}$  ions and releases electrons.  $\text{Hg}_2^{2+}$  combines with  $\text{Cl}^-$  to form mercurous chloride ( $\text{Hg}_2\text{Cl}_2$ ).



## Half cell reactions

### When it acts as cathode:

Mercurous chloride ( $\text{Hg}_2\text{Cl}_2$ ) dissociates to form  $\text{Hg}_2^{2+}$  and  $\text{Cl}^-$  ion.  $\text{Hg}_2^{2+}$  ions gains electrons and gets reduced to Hg.



# Measurement of single electrode potential using Saturated calomel electrode (SCE)



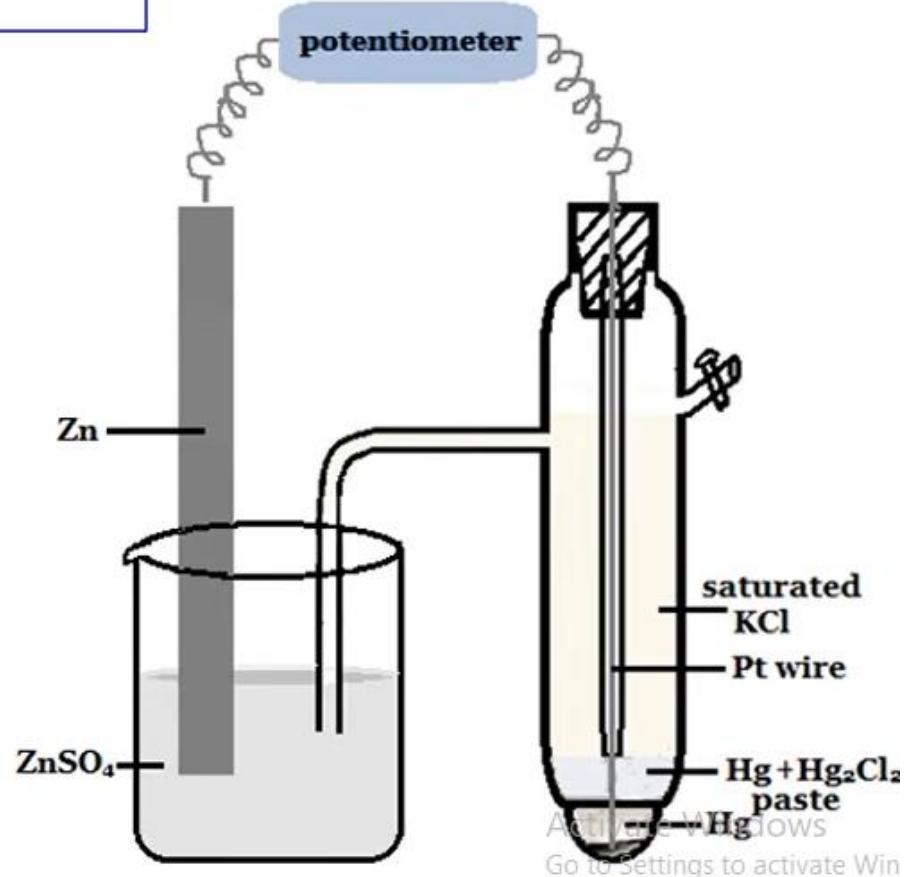
$$E_{Hg_2^{2+} \mid Hg}^o = 0.2422 \text{ V}$$

Zn - SCE

$$E_{cell}^o = E_c^o - E_a^o$$

$$1.0022 = 0.2422 - E_{Zn^{2+} \mid Zn}^o$$

$$E_{Zn^{2+} \mid Zn}^o = -0.76 \text{ V}$$



## Advantages

- The standard electrode potential is '**0.2422 V**'. Hence, in the determination of **single electrode potential** of an unknown electrode using SCE as the reference electrode.
- It is **cheap, compact** and **easy to transport**.
- Its electrode potential is **constant** and **easily reproducible**.
- Easy to **construct** and **maintain** the cell.



## Limitations/Drawbacks

- Solubility of KCl changes with temperature

## POTENTIOMETRIC TITRATION : PRINCIPLE



*Potentiometric titration* is a titration used to measure the amount of an analyte present in the given solution by measuring the change in the potential by a suitable indicator electrode, as a function of volume of titrant.

*Reference or Counter electrode : It has the constant potential/EMF*



*Ag/AgCl electrode, Calomel electrode*

*Indicator or Working electrode - It responds to the change in the concentration of the analyte solution.*

*Electrolyte - contains the analyte solution*

*Combination electrode - Both reference and indicator electrodes*

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# INDICATOR OR WORKING ELECTRODE :



*Inert electrodes - Redox reaction*

*When dipped in the analyte solution, it indicates the potential of the bulk solution*

*Metallic electrode - Pt, Au, Ag etc.*

*Other conductive electrodes - Graphite, glassy carbon etc.*

*Nernst equation -  $E = E^o - \frac{RT}{nF} \ln \frac{a_{red}}{a_{oxid}}$*

$$E = E^o - \frac{RT}{nF} \ln \frac{[\text{reduced species}]}{[\text{oxidised species}]}$$

# Redox reaction :Procedure

FAS (or)  $\text{FeSO}_4$  Vs  $\text{K}_2\text{Cr}_2\text{O}_7$

*Reference Electrode:* Calomel electrode

*Indicator Electrode:* Pt electrode

*Analyte solution* :  $\text{FeSO}_4$  (or) Ferrous ammonium sulphate +  $\text{H}_2\text{SO}_4$

*Titrant* :  $\text{K}_2\text{Cr}_2\text{O}_7$



# Redox reaction- Procedure

$$E = \left[ E^o - \frac{RT}{nF} \ln \frac{a_{red}}{a_{oxid}} \right] - E_{ref}^o$$

$$E = \left[ E^o - \frac{RT}{nF} \ln \frac{[Fe^{2+}]}{[Fe^{3+}]} \right] - 0.2422$$

$$E_{SCE}^o = 0.2422V$$

$$E_{Fe^{3+}|Fe^{2+}}^o = 0.77V$$

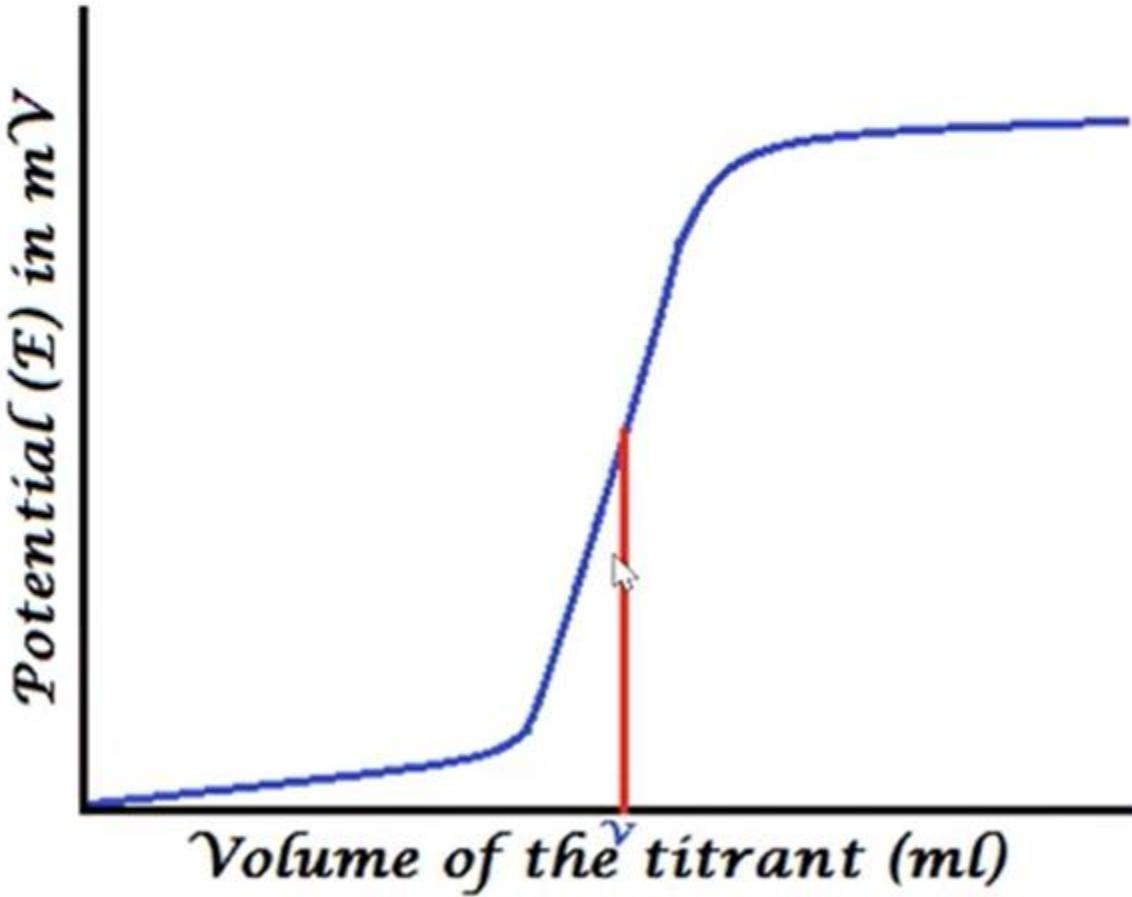


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# POTENTIOMETRIC TITRATION : Redox reaction

| V  | E   | $\Delta E$ | $\Delta V$ | $\Delta E/\Delta V$ | $\Delta(\Delta E/\Delta V)$ | $\Delta(\Delta E/\Delta V)/\Delta V = \Delta^2 E/\Delta V^2$ |
|----|-----|------------|------------|---------------------|-----------------------------|--|
| 0  | 374 | 6          | 1          | 6                   | 0                           | 0  |
| 1  | 380 | 6          | 1          | 6                   | -1                          | -1   |
| 2  | 386 | 5          | 1          | 5                   | 1                           | 1  |
| 3  | 391 | 6          | 1          | 6                   | 0                           | 0  |
| 4  | 397 | 6          | 1          | 6                   | 1                           | 1  |
| 5  | 403 | 7          | 1          | 7                   | 0                           | 0  |
| 6  | 410 | 7          | 1          | 7                   | -1                          | -1   |
| 7  | 417 | 6          | 1          | 6                   | 250                         | 250  |
| 8  | 423 | 256        | 1          | 256                 | -255                        | -255   |
| 9  | 679 | 1          | 1          | 1                   | -1                          | -1   |
| 10 | 680 | 0          | 1          | 0                   | 0                           | 0  |
| 11 | 680 | 0          | 1          | 0                   | 0                           | 0  |

# POTENTIOMETRIC TITRATION : EQUIVALENCE POINT: *Redox titration curve*

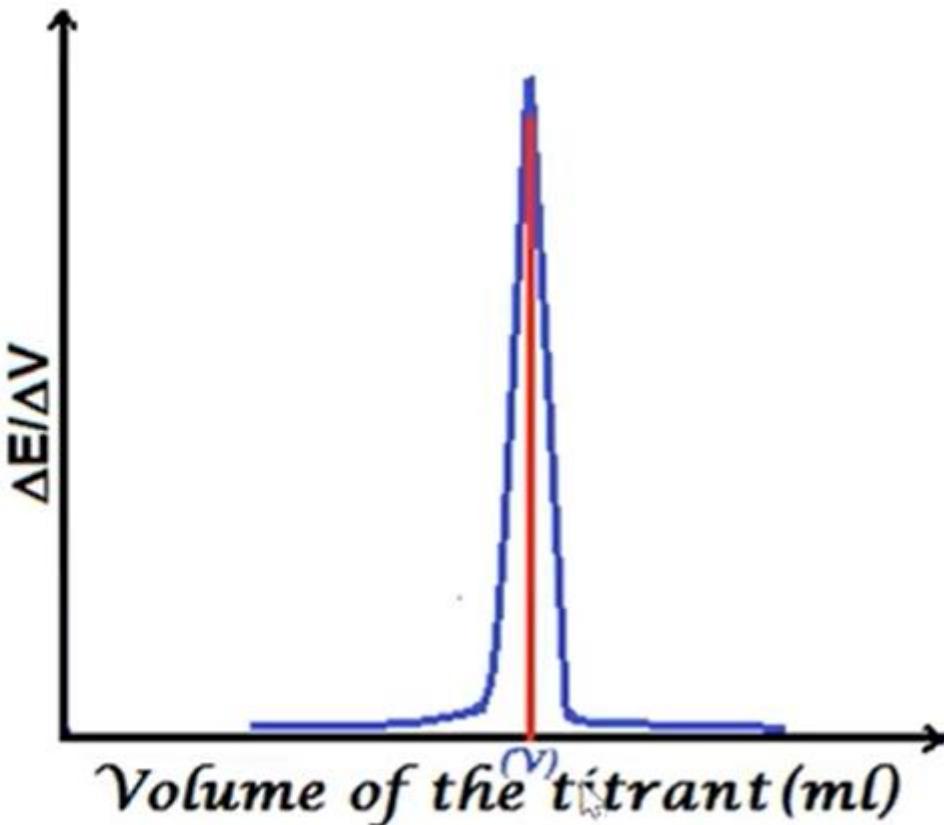


| V  | E   |
|----|-----|
| 0  | 374 |
| 1  | 380 |
| 2  | 386 |
| 3  | 391 |
| 4  | 397 |
| 5  | 403 |
| 6  | 410 |
| 7  | 417 |
| 8  | 423 |
| 9  | 679 |
| 10 | 680 |
| 11 | 680 |

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# POTENTIOMETRIC TITRATION : EQUIVALENCE POINT

*First derivative titration curve*



| V  | $\Delta E/\Delta V$                     |
|----|---|
| 0  | 6                                       |
| 1  | 6                                       |
| 2  | 5                                       |
| 3  | 6                                       |
| 4  | 6                                       |
| 5  | 7                                       |
| 6  | 7                                       |
| 7  | 6                                       |
| 8  | 256                                     |
| 9  | 1                                       |
| 10 | 0                                       |
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# Fuel cells

## Types

1. Alkaline fuel cells
2. Methanol fuel cells
3. Phosphoric acid fuel cells
4. Solid oxide fuel cells
5. Proton exchange membrane fuel cells
6. Microbial fuel cells

# Fuel cells

- Invented by William Grove in 1888
- In commercial use in the year 1932 by Francis Thomas

## Advantages

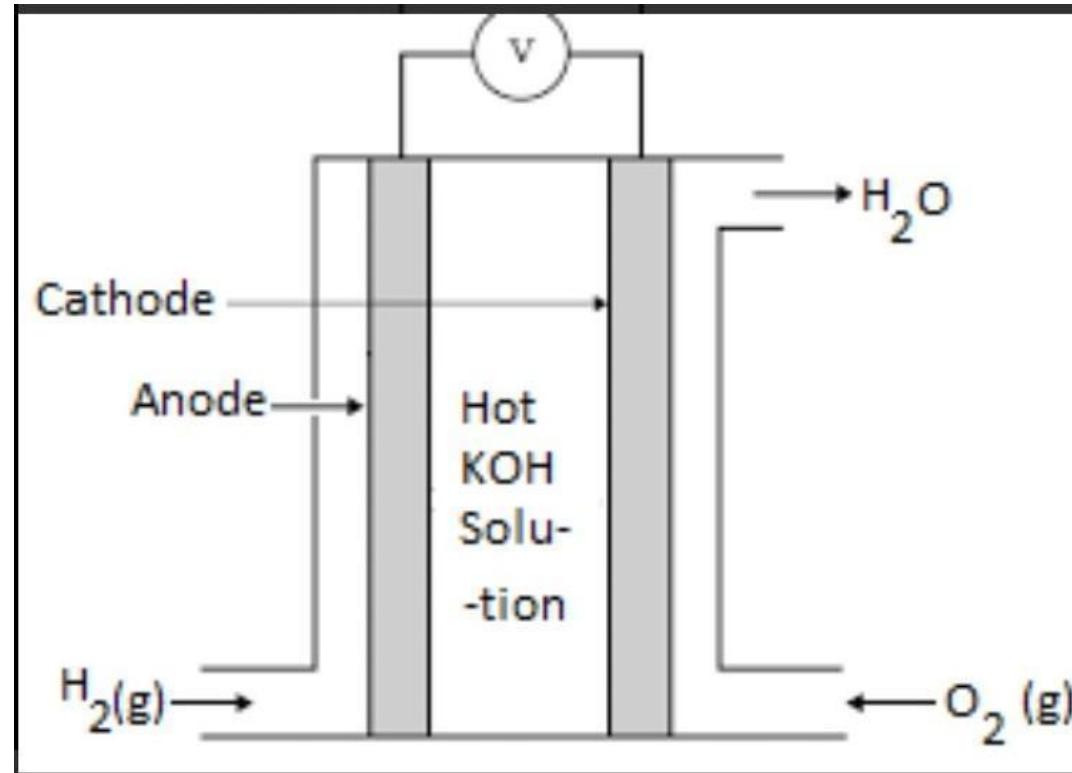
- It uses only  $H_2$
- The byproduct is  $H_2O$
- The refueling time is only 3-4 mins
- High energy efficiency (60-70%)

# Fuel cells

## Applications

- They are used in Portable electronics
- They are used in Ev's(cars), space ships, buses
- They are used as back up power for buildings

# Alkaline Fuel cells or H<sub>2</sub>-O<sub>2</sub> fuel cells



An H<sub>2</sub>-O<sub>2</sub> fuel cell is an electrochemical device that converts the chemical energy from the reaction of hydrogen and oxygen into electricity and water

## Working of Fuel Cell

The reaction between hydrogen and oxygen can be used to generate electricity via a fuel cell. Such a cell was used in the Apollo space programme and it served two different purposes – It was used as a fuel source as well as a source of drinking water (the water vapour produced from the cell, when condensed, was fit for human consumption).

The working of this fuel cell involved the passing of hydrogen and oxygen into a concentrated solution of sodium hydroxide via carbon electrodes. The cell reaction can be written as follows:

