CHAPTER 9: ELECTROCHEMISTRY

9.2 Nernst Equation

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At the end of this topic, students should be able to:

- Write and apply the Nernst equation to determine

  a) the cell potential, E_{cell} at non-standard state conditions

  b) the ion concentration / partial pressure of a gas

  c) pH solution

  d) the equilibrium constant, K

- Discuss the effect of concentration and temperature on Ecell

Nernst Equation

$$E_{cell} = E^{o}_{cell} - \frac{R\,T}{n\,\mathcal{F}} \ln Q$$

E_{cell} : Cell potential at specified concentration (of ions) and temperature.

E^{o}_{cell} : Standard Cell Potential.

n : No. of moles of electrons involved in the Redox reaction.

T : Temperature of cell (in Kelvin).

R : Universal gas constant (8.314 J mol^{-1} K^{-1}).

F : Faraday constant (96500 C mol^{-1}).

Q : Mass action expression:

aA(s) + bB(aq) → cC(aq) + dD(g)

$$Q = \frac{[C]^{c}\, P_{D}^{\,d}}{[B]^{b}}$$

Nernst Equation

$$E_{cell} = E^{o}_{cell} - \frac{R\,T}{n\,\mathcal{F}} \ln Q$$

Since R and $\mathcal{F}$ are constants, at 25°C,

$$\frac{R\,T}{\mathcal{F}} = \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})\ (298 \text{ K})}{(9.65 \text{ X } 10^{4} \text{ C mol}^{-1})} = 0.0257$$

Therefore, Nernst equation can be symplified to...

At 25°C

$$E_{cell} = E^{o}_{cell} - \frac{0.0257}{n} \ln Q$$

At 25°C

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{n} \log Q$$

Points to remember

Solids and pure liquids do not appear in the reaction quotient, ***Q***…. But **included partial pressures.**

Cell potential is governed by

- **ion concentrations** or **partial pressure**
- **temperature**

Write the Nernst equation by referring to the **balanced overall cell equation** & **standard cell potential**.

Example 7:

$$Cr_{(s)}/\ Cr^{3+}{}_{(aq)}\ //Br_{2(l)}/Br^{-}{}_{(aq)}/Pt_{(s)}$$

Cell eqn:

**** e transferred , ________**

Nernst eqn:

Example 8:

$$Cu_{(s)}/Cu^{2+}{}_{(aq)}//Cl_{2(g)}/Cl^{-}{}_{(aq)}/\ Pt_{(s)}$$

Cell eqn:

**** e transferred , ________**

Nernst eqn:

Nernst Equation… calculate E_{cell}

Example 8:

Calculate the e.m.f. of the following cell:

$Zn(s)$ / $Zn^{2+}(1.8\ M, aq)$ // $Cu^{2+}(0.2\ M, aq)$ / $Cu(s)$

Solution:

Anode [O]:

Cathode [R]:

Nernst Equation… determine pH

Example 9:

Calculate pH of a galvanic cell built from the hydrogen electrode and zinc plate in 1.0 M zinc nitrate.

$[Zn^{2+}]$ = 1.0 M P_{H_2} = 1 atm E_{cell} = +0.58 V

Solution:

The cell reaction:

Nernst Equation… at equilibrium

- At equilibrium there is no net transfer of electrons,
- $E_{\mathbf{cell}} = 0$
- Q becomes $K_{\mathbf{c}}$ (equilibrium constant)

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{n} \log Q$$

$$0 = E^{0}_{cell} - \frac{0.0592}{n} \log K_{c}$$

Nernst Equation... determine *K*

Example 10:

Calculate the K_c for the following reaction:

$$Sn^{2+}(aq) + 2Ag^{+}(aq) \rightleftharpoons Sn^{4+}(aq) + 2Ag(s)$$

Solution

Anode :

Cathode :

Nernst Equation.. Predict spontaneity

Example 11:

Will the following reaction occur spontaneously at 25°C if $[Fe^{2+}]$ = 0.60 M and $[Cd^{2+}]$ = 0.010 M?

$Fe^{2+}(aq) + Cd(s) \longrightarrow Fe(s) + Cd^{2+}(aq)$

Solution:

Anode:

Cathode:

Points to Ponder

Question:

$3Ni^{2+}(aq) + 2Cr(s) \rightarrow 3Ni(s) + 2Cr^{3+}(aq)$ $E_{cell} = +0.42$ V

What would you do so as to increase the value of E_{cell}?

Solution:

Nernst Equation.. Predict spontaneity

E^o_{cell} or E_{cell} can be used to predict the spontaneity of a reaction between two species.

E^o_{cell} / E_{cell}	*Spontaneity of Reaction*
+ve	Spontaneous
0	The system is at equilibrium
-ve	Non-spontaneous

Points to Remember

1) The value of E°_{cell} does **not** indicate the reaction rate.

2) A reaction may occur spontaneously if the conditions (e.g.: conc. or temp.) have changed even though its E°_{cell} is negative.

3) When $E_{cell} = 0$, there is **no** difference in electrical potential between two electrodes and thus **no electron flow.**

4) If the reaction is at **non-**standard state conditions, use Nernst equation to determine the value of E_{cell} and then predict the spontaneity of the reaction.

Check Point

1) Calculate $E_{\mathbf{cell}}$ for the following reaction :

$$Co^{2+}_{(aq)} + Fe_{(s)} \longrightarrow Co_{(s)} + Fe^{2+}_{(aq)}$$

Given: $[Co^{2+}] = 0.15$ M & $[Fe^{2+}] = 0.68$ M

<+0.14 V>

2) Calculate the equilibrium constant for the reaction between Mg and aqueous solution of $ZnSO_4$ at 25°C and standard conditions.

<2.47×10^{54}>

Check Point

3) Electrode Al was placed in $Al(NO_3)_3$ 1.0 M and electrode Pb in $Pb(NO_3)_2$ 1.0 M.

Given $E^0_{Al^{3+}/Al} = -1.66$ V

$E^0_{Pb^{2+}/Pb} = -0.13$ V

a) Write the equations for the reactions at the cathode and anode.

b) Draw the cell diagram for the reaction

c) Calculate $E°_{cell}$

d) Calculate E_{cell} if $[Al(NO_3)_3]$ is diluted to 0.005 M

Check Point

4) A galvanic cell is made up of Zn electrode immersed in $ZnSO_4$ solution and standard hydrogen electrode.

a) Given $[Zn^{2+}]$ = 1.0 M , P_{H_2} = 1 atm and E_{cell} = +0.45 V at 25°C, calculate $[H^+]$.

b) If E_{cell} = +0.542 V & $[Zn^{2+}]$ = 0.10 M, calculate pH of the solution.

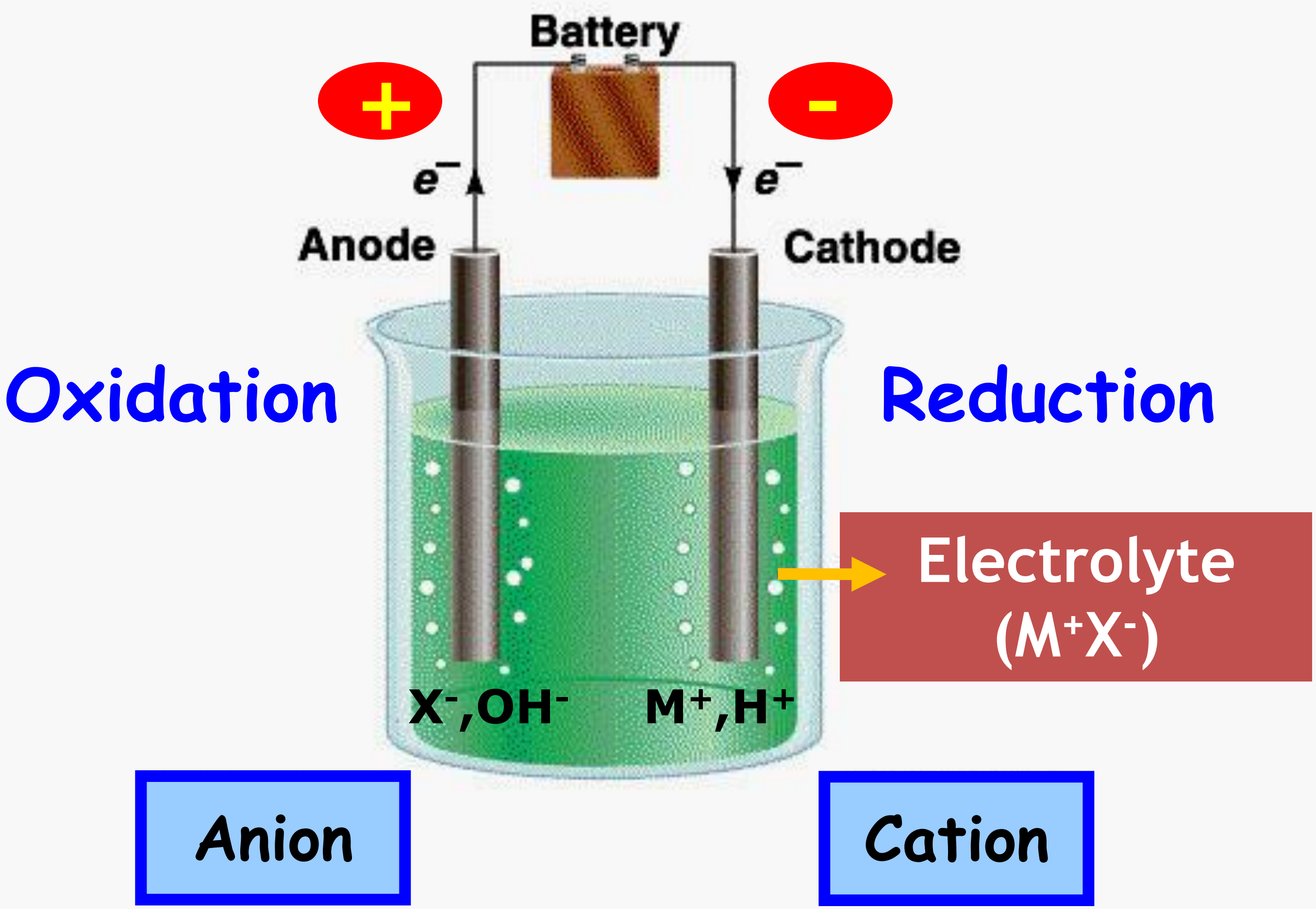
ELECTROLYSIS

Electrolysis is a chemical process that uses electricity for a non-spontaneous redox reaction to occur. Such reactions take place in **electrolytic cells.**

Electrolytic Cell

- ✓ It is made up of 2 electrodes immersed in an electrolyte.
- ✓ A direct current is passed through the electrolyte from an external source.
- ✓ Molten salt and aqueous ionic solution are commonly used as electrolytes.

Electrolytic Cell



Anode

- ☑ Positive electrode
- ☑ The electrode which is connected to the <u>positive terminal</u> of the battery
- ☑ Oxidation takes place

Electrons flow from anode to cathode

Cathode

- ☑ Negative electrode
- ☑ The electrode which is connected to the <u>negative terminal</u> of the battery
- ☑ Reduction takes place

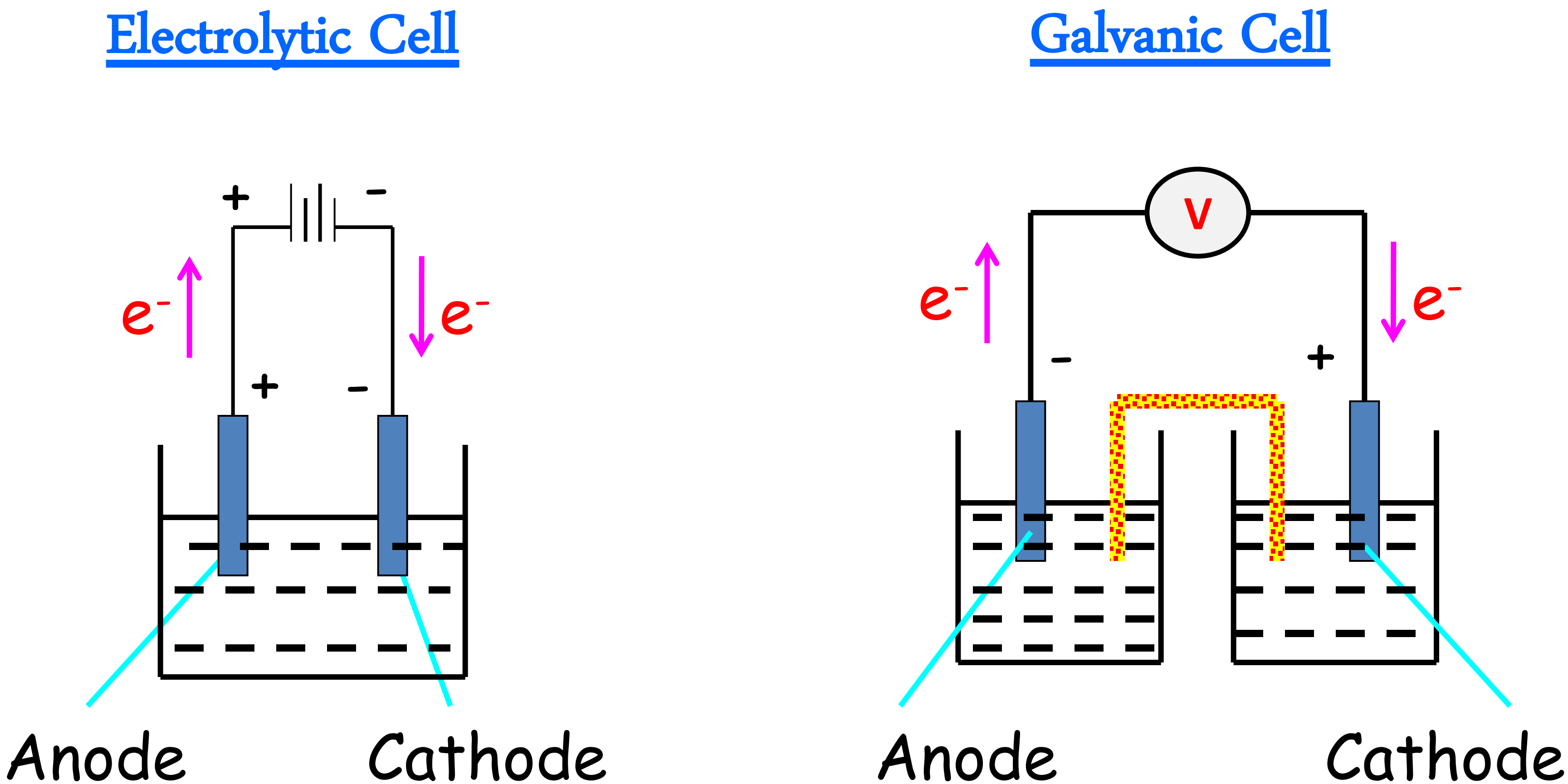
Electrode

- as circuit connectors
- as sites for the precipitation of insoluble products
- example: Platinum , Graphite (inert electrode)

Electrolyte

- a liquid that conducts electricity due to the presence of positive and negative ions
- type of electrolyte:
  - molten state or
  - in aqueous solution
- so that the ions can move freely

Comparison between a galvanic cell and an electrolytic cell



Electrolytic Cell

- Cathode = negative
- Anode = positive
- Non-spontaneous redox reaction requires energy to drive it

Galvanic Cell

- Cathode = positive
- Anode = negative
- Spontaneous redox reaction releases energy

Similarities:

- Oxidation occurs at anode, reduction occurs at cathode
- Anions move towards anode, cations move towards cathode.
- Electrons flow from anode to cathode in an external circuit.

Objectives:

At the end of the lesson,the students should be able to:

c) Decribe the influence of the factors on the selective discharge of a species at the electrode
   - Standard reduction/electrode potential of the species
   - Concentration of the species
   - Nature of electrode

d) Explain the electrolysis of the following electrolytes using inert electrode
   - molten salt
   - concentration and dilute aqueous NaCl
   - aqueous Na_2SO_4

e) Predict the product of electrolysis using examples

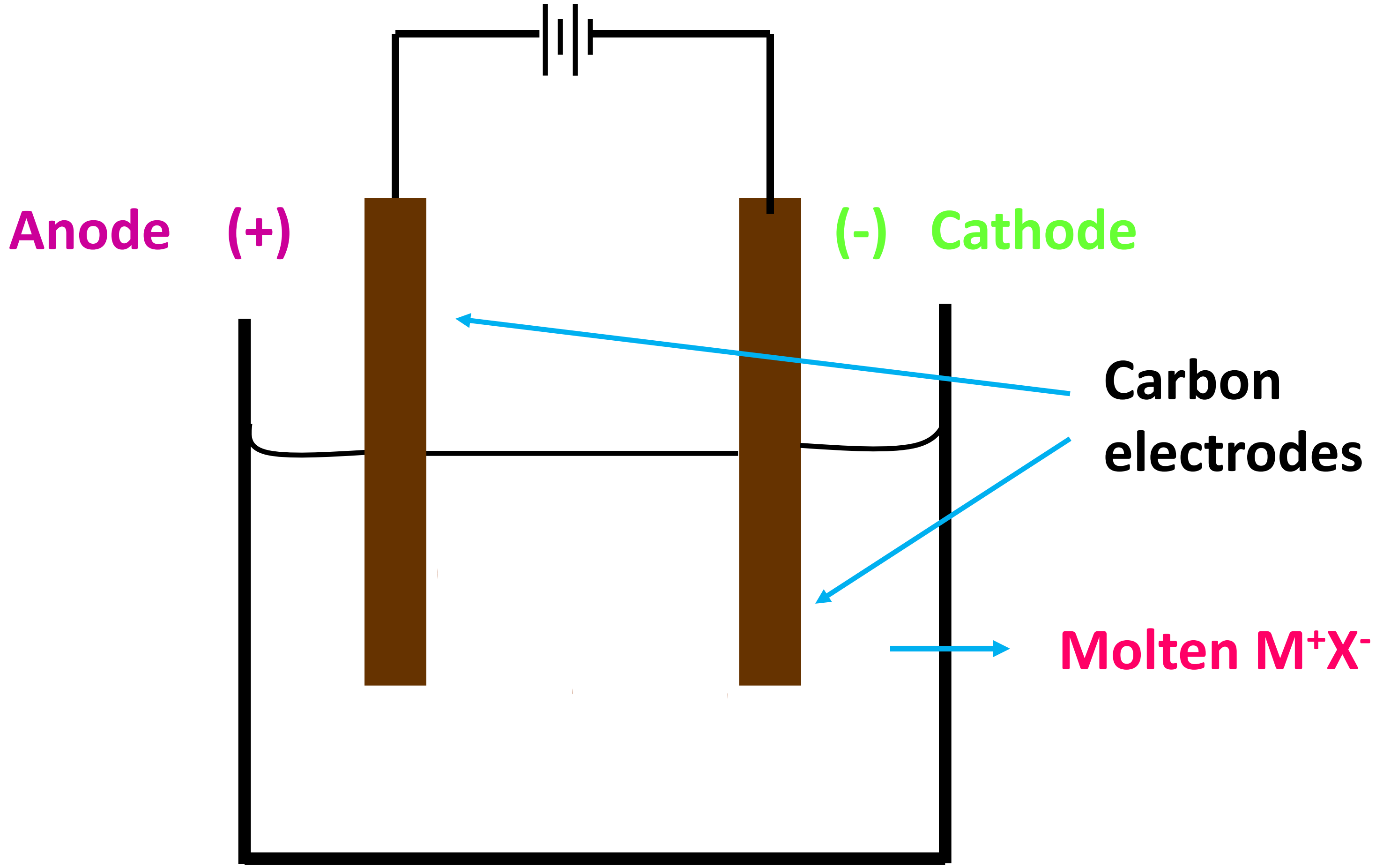
Predicting The Products of Electrolysis

Factors influencing the products :

1. **Standard reduction/electrode potential of the species**
2. **Concentrations of the species**
3. **Nature of electrodes used (inert)**

1. Electrolysis of molten salt

- Requires high temperature
- Example: Electrolysis of molten NaCl

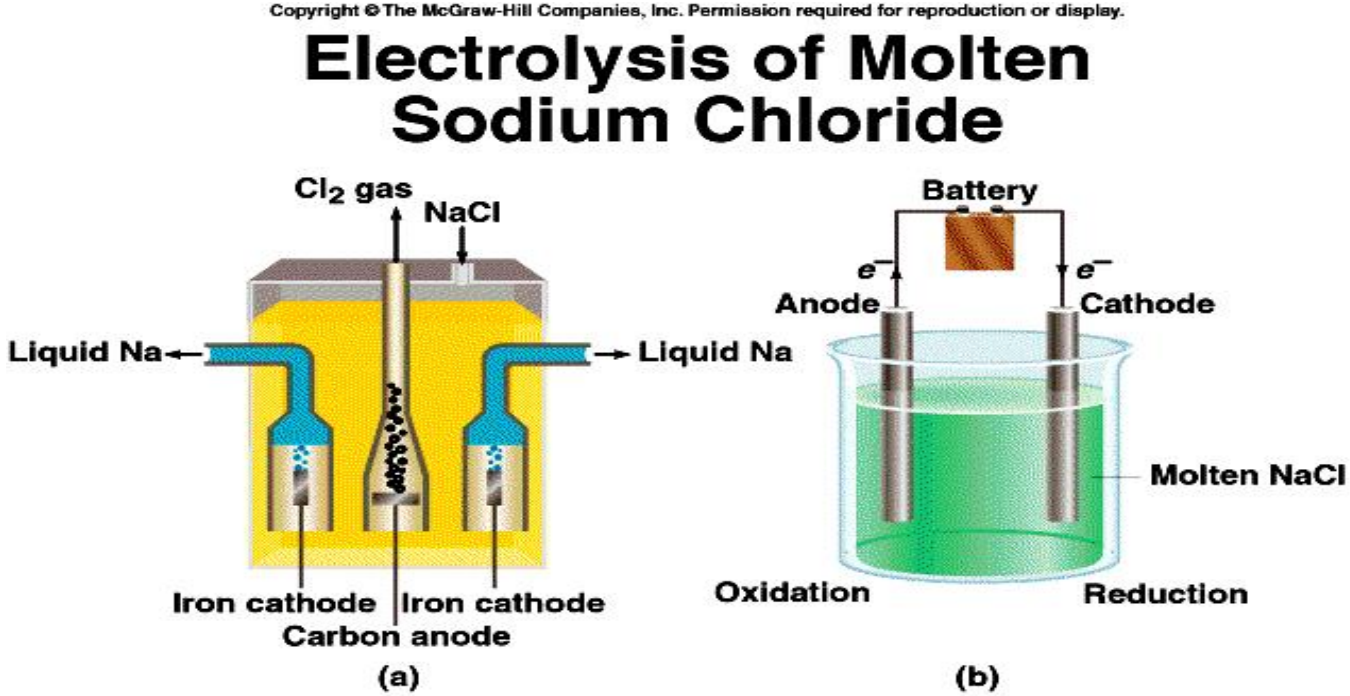


Example: Electrolysis of Molten NaCl

$$NaCl_{(S)} \longrightarrow Na^+_{(l)} + Cl^-_{(l)}$$

Cathode (-)	**Anode (+)**
Ions present: Na^+	**Ions present: Cl^-**
$Na^+_{(l)} + e \rightarrow Na_{(s)}$	$2Cl^-_{(l)} \rightarrow Cl_{2(g)} + 2e$
- **Reduction process**	- **Oxidation process**
- **The sodium metal forms**	- **Chlorine gas evolved**

- Electrolysis of molten NaCl is industrially important. The industrial cell is called *'Downs Cell'*



2. Electrolysis of Aqueous Salt

- Aqueous salt solutions contains anion, cation and water.
- Water is an electro-active substance that may be oxidised or reduced in the process depending on the condition of electrolysis.
- Electrolysis of aqueous salt is more complex.

Reduction :

Oxidation :

Example: Electrolysis of Aqueous NaCl

NaCl aqueous solution contains Na^+ cation, Cl^- anion and water molecules

On electrolysis,

- ✓ the cathode attracts Na^+ ion and H_2O molecules
- ✓ the anode attracts Cl^- ion and H_2O molecules

The electrolysis of aqueous NaCl depends on the <u>concentration of electrolyte.</u>

3. Electrolysis of Concentrated NaCl solution

Cathode:

$Na^+ (aq) + e^- \rightarrow Na (s)$ $E^0 = -2.71 V$

$2H_2O (l) + 2e^- \rightarrow H_2 (g) + 2OH^- (aq)$ $E^0 = -0.83 V$

- ✓ E^0 for water molecules is <u>more positive.</u>
- ✓ H_2O easier to be reduce.

Anode:

$Cl_2 (g) + 2e^- \rightarrow 2Cl^- (aq)$ $E^0 = +1.36 V$

$O_2 (g) + 4H^+ (aq) + 4e^- \rightarrow 2H_2O (l)$ $E^0 = +1.23 V$

- ✓ In concentrated solution, chloride ions will be oxidised because of its high concentration.

Reactions involved:

Cathode:

Anode:

Cell reaction:

4. Electrolysis of diluted NaCl solution

Cathode:

$Na^{+} (aq) + e^{-} \rightarrow Na (s)$ $E^0 = -2.71 V$

$2H_2O (l) + 2e^{-} \rightarrow H_2 (g) + 2OH^{-} (aq)$ $E^0 = -0.83 V$

- ✓ E^0 for water molecules is more positive.
- ✓ H_2O easier to reduce.

Anode:

$Cl_2 (g) + 2e^{-} \rightarrow 2Cl^{-} (aq)$ $E^0 = +1.36 V$

$O_2 (g) + 4H^{+} (aq) + 4e^{-} \rightarrow 2H_2O (l)$ $E^0 = +1.23 V$

✓ In dilute solution, water will be selected for oxidation because E^o water is less positive (lower E^o).

Reactions involved:

Cathode:

Anode:

Cell reaction:

Exercise:

Predict the electrolysis reaction when Na_2SO_4 solution is electrolysed using platinum electrodes.

Solution:

- Na_2SO_4 aqueous solution contains Na^+ ion, SO_4^{2-} ion and water molecules
- On electrolysis,
  - ✓ **Cathode:** attracts Na^+ ion and H_2O molecules
  - ✓ **Anode:** attracts SO_4^{2-} ion and H_2O molecules

Cathode:

$Na^+ (aq) + e^- \rightarrow Na (s)$ $E^0 = -2.71\ V$

$2H_2O (l) + 2e^- \rightarrow H_2 (g) + 2OH^- (aq)$ $E^0 = -0.83\ V$

✓ E^0 for water molecules is more positive
✓ H_2O easier to reduce

Anode :

$S_2O_8^{2-} (aq) + 2e^- \rightarrow 2SO_4^{2-} (aq)$ $E^0 = +2.01\ V$

$O_2 (g) + 4H^+ (aq) + 4e^- \rightarrow 2H_2O (l)$ $E^0 = +1.23\ V$

✓ E^0 for water molecules is less positive
✓ H_2O easier to oxidise

Reactions involved:

Cathode:

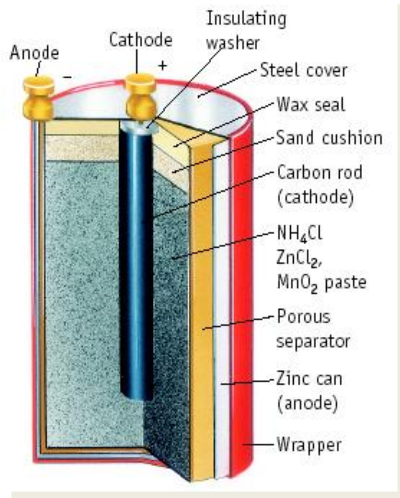
Anode:

Cell Reaction :

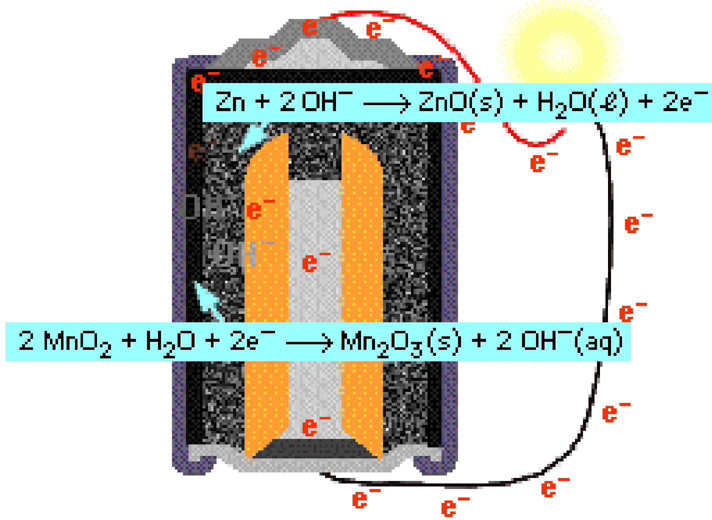
- Cathode =
- Anode =

Product of electrolysis

Dry Cell Battery

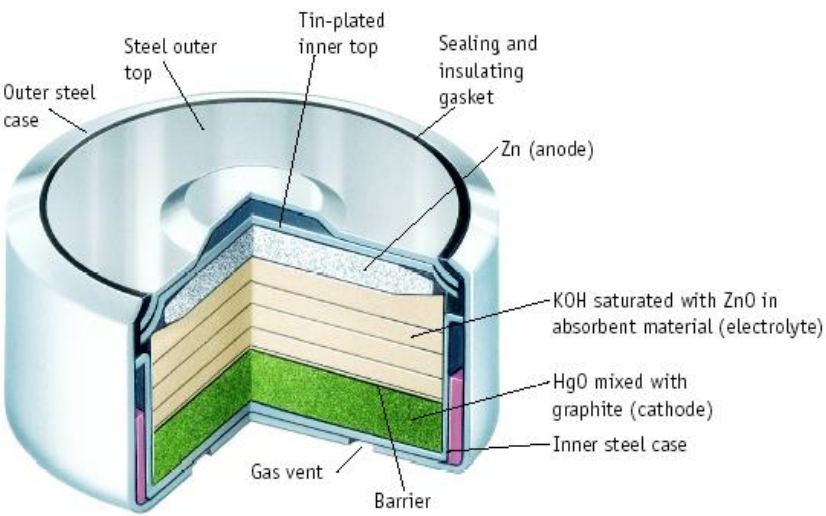


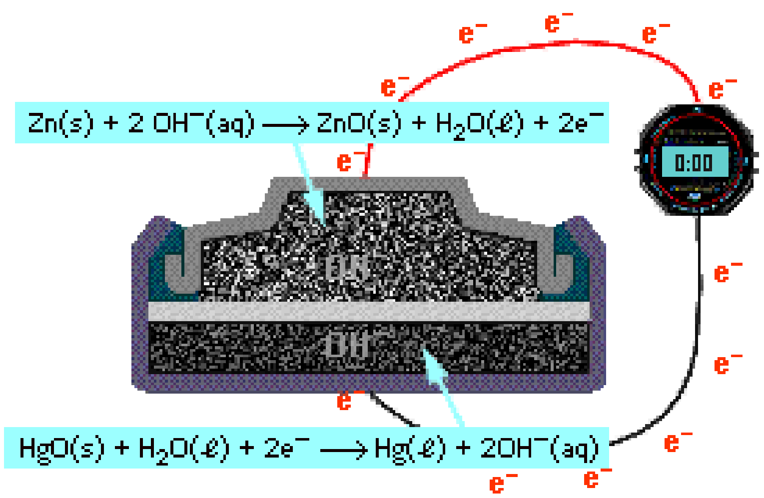
Alkaline Battery



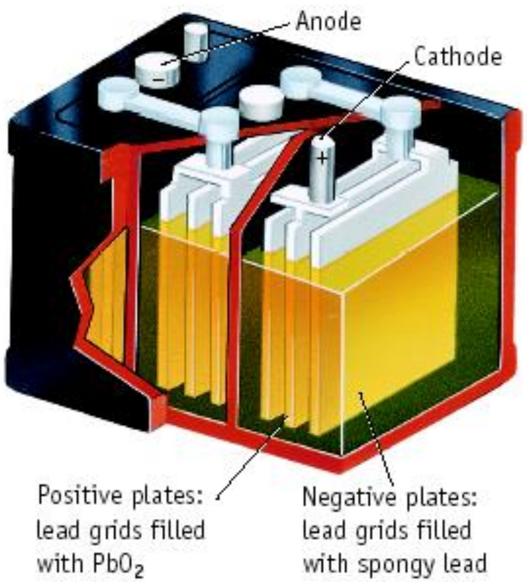
Nearly same reactions as in common dry cell, but under basic conditions.

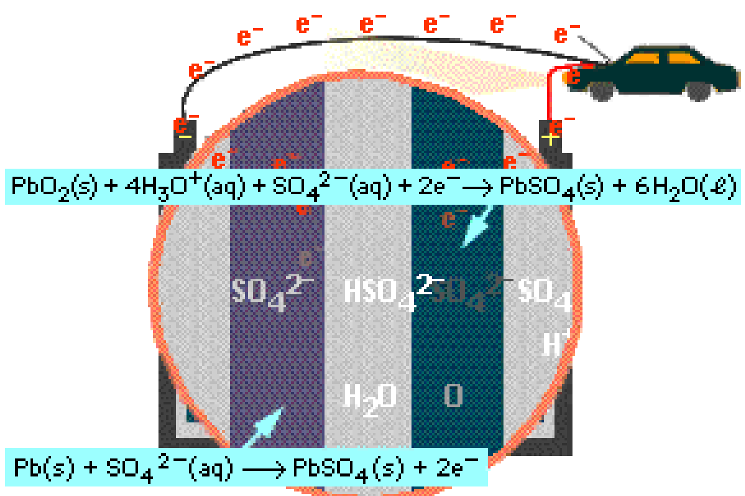
Mercury Battery





Lead Storage Battery





Ni-Cad Battery