Physical and Inorganic chemistry

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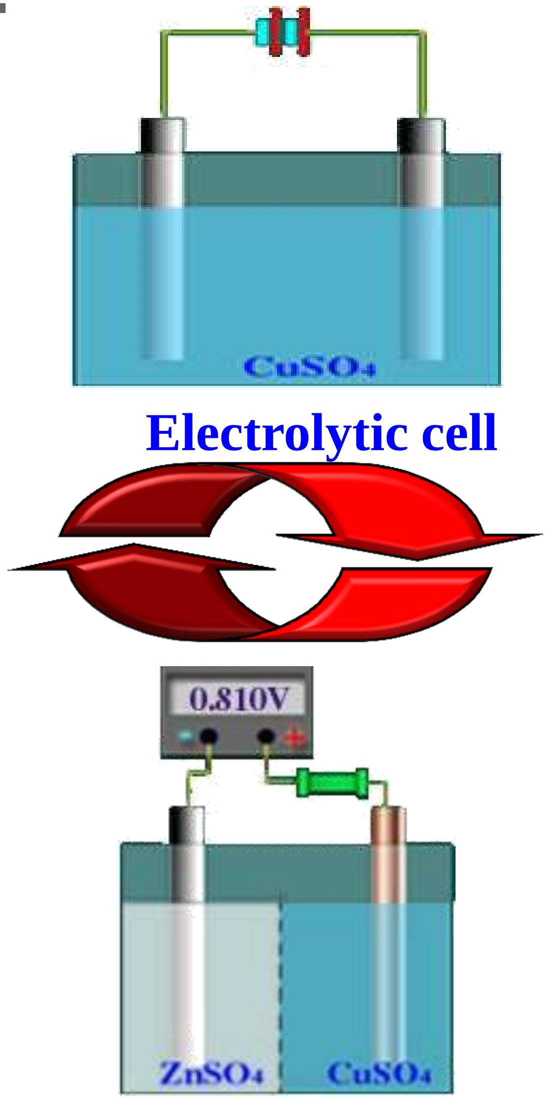
Code : 351Ch
For
3rd Students
(Zoology and Entomology group)

ELECTROCHEMISTRY 1
PART 1

Electrochemical Cells

1. Galvanic cells
2. Electrolytic cells



Electrolytic cell

Electric Energy **Chemical Energy**

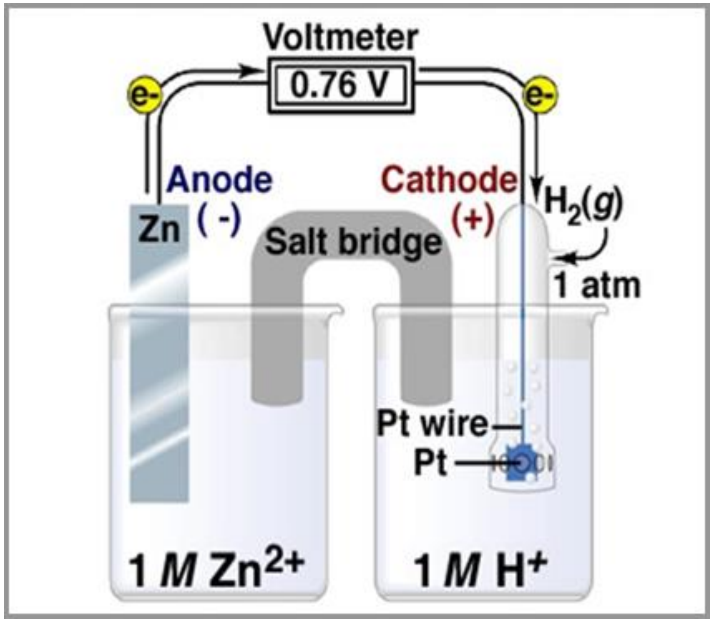
Galvanic cell

The ANODE…	**The CATHODE…**
Supplies electrons to external circuit (wire)	**Accepts electrons** from external circuit (wire)
Is **negative** pole of battery	Is **positive** pole of battery
Is site of **OXIDATION**	Is site of **REDUCTION**
Is written on **left- hand side** if convention is followed	Is written on **right-hand side** if convention is followed
Is half-cell with **lowest** electrode potential	Is half-cell with **highest** electrode potential

Origin of Electromotive Force or Cell Potential

Cell potential is the potential difference between anode and cathode and is called:

- **Cell potential or emf (electromotive force)**



Zn/Zn^{+2} (1 M)//H^+ (1 M)/H_2 (1atm), Pt

- Suppose that we have a Daniel cell of potential 1.1 V in the standard conditions.

- The standard potential of the two half-cell is:

$$Cu^{2+}\ (aq) + 2e^{-} \rightarrow Cu \quad E^{o} = 0.337\ V$$

$$Zn^{2+}\ (aq) + 2e^{-} \rightarrow Zn\ E^{o} = -0.7628\ V$$

- The experiment showed that zinc dissolves while copper deposited from solution
- The measured cell potential is called reduction potential:

- The reduction potential of the cell is the difference between the reduction potential of the cathode and the reduction potential of the anode

$$E_{cell} = E^{o}_{Right} - E^{o}_{Left}$$

$$E_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$

$$E^{o}_{cell} = 0.337 - (-0.7628) = 1.1 \text{ Volt}$$

- The question is wheatear the reduction potentials are affected by the concentration of the species?

- In the non-standard condition the cell potential is

$$E_{cell} = E_{rev,\,c} - E_{rev,\,a}$$

$$E_{rev.} = E^{o} + \frac{RT}{ZF}\ln\frac{a_{Ox}}{a_{Red.}} \qquad \text{(Nernest eqn.)}$$

- For a spontaneous reaction that leads to obtain electricity form a galvanic cell E = +ve

$$\begin{array}{l} Cu^{2+}\ (aq) + 2e^{-} \rightarrow Cu \quad E^{o} = 0.337\ V \\ Zn^{2+}\ (aq) + 2e^{-} \rightarrow Zn\ E^{o} = -0.7628\ V \\ \hline Cu^{2+}\ (aq)\ + Zn \rightarrow Cu + Zn^{2+}\ (aq)\ E_{cell} = 1.0998\ V \end{array}$$

- If E_{cell} has a negative value this means that the reaction is not spontaneous and it need a potential of 1.1 V from external source to force the chemical reaction to occur

$$Cu + Zn^{2+}\ (aq) \rightarrow Cu^{2+}\ (aq)\ + Zn\ E_{cell} = -1.0998\ V$$

Standard electrode potential

- When a piece of a metal is immersed in a solution of its ions, atoms will transfer to solution as positive ions leaving electrons on the metal under dissolution pressure.
- Ions in the solution tend to deposit on the metal surface under Osmotic pressure.

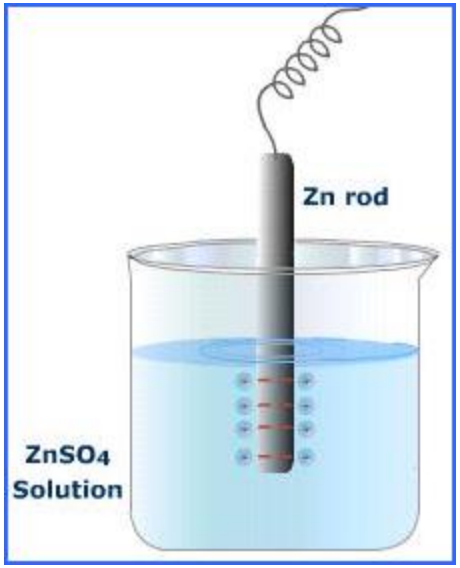
$$M \rightarrow M^{n+} + ne^{-} \quad \text{Ionization (oxidation) process}$$

$$M^{n+} + ne^{-} \rightarrow M \quad \text{Deposition (reduction) proces}$$

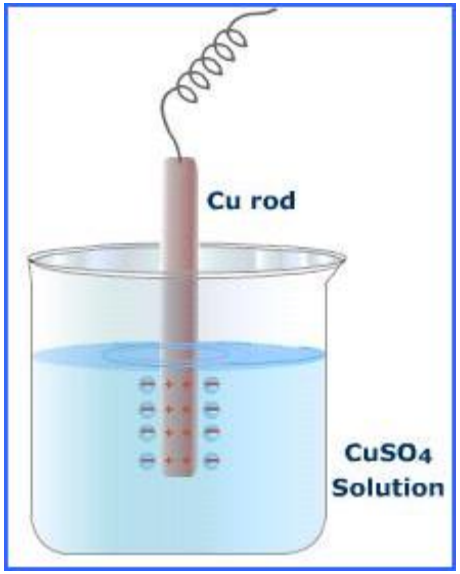
$$M^{n+} + ne^{-} = M \quad E^{o}\ \text{Reversible Potentia}$$

- At beginning the electric dissolution pressure is much higher than the osmotic pressure.
- With increasing time the dissolution pressure decreases and the osmotic pressure increases till they equal each other and then the electrode is said to be at equilibrium.
- Electric dissolution and osmotic pressures depend on the nature of the metal.

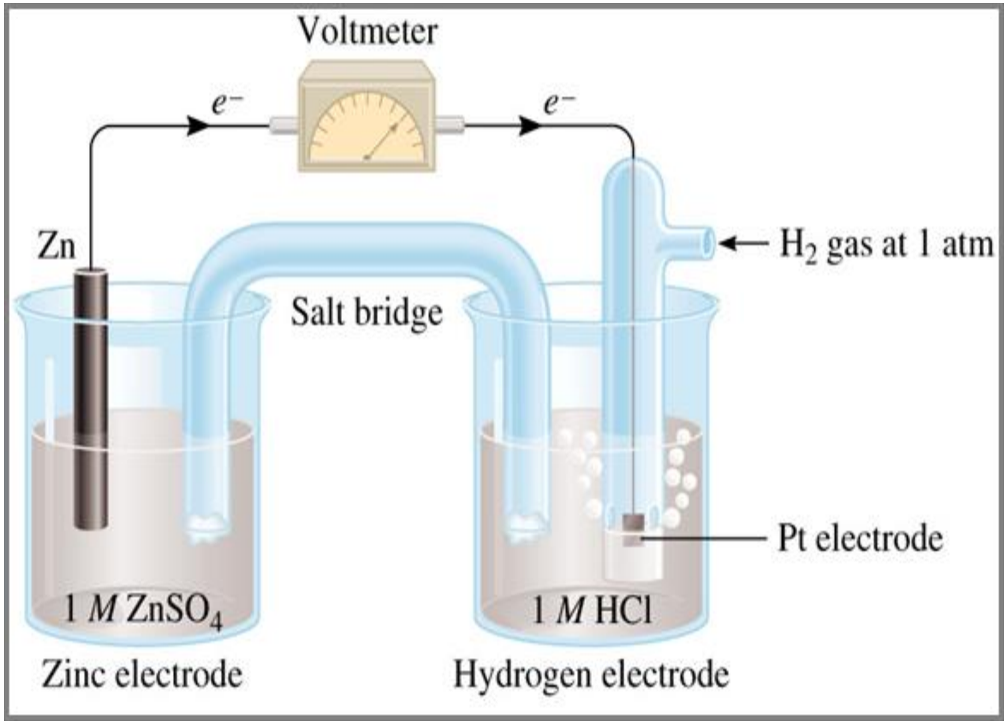
- For zinc electric dissolution pressure > Osmotic pressure, zinc is charged negatively while the solution is charged positively.



- For copper electric dissolution pressure < Osmotic pressure, copper is charged positively while solution is charged negatively.



Standard reduction Potentials



Standard conditions are:

- Concentration is 1 M
- Temperature is 25°C
- Pressure of a gas is 1 atm.

Reference electrode is hydrogen electrode

- $[H^+]$ (1 M)
- H_2 (1 atm)

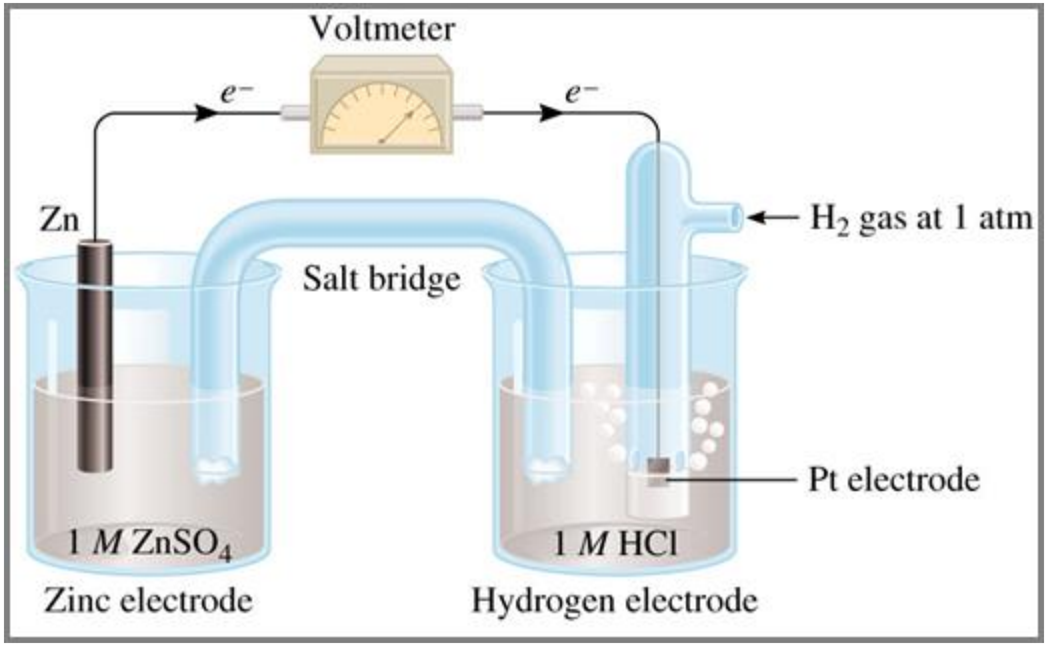
$Zn\ (s)\ |\ Zn^{2+}\ (1\ M)\ ||\ H^+\ (1\ M)\ |\ H_2\ (1\ atm)\ |\ Pt\ (s)$

Anode (oxidation): $Zn\ (s) \longrightarrow Zn^{2+}\ (1\ M) + 2e^-$

Cathode (reduction): $2e^- + 2H^+\ (1\ M) \longrightarrow H_2\ (1\ atm)$

$Zn\ (s) + 2H^+\ (1\ M) \longrightarrow Zn^{2+} + H_2\ (1\ atm)$

$E^0_{cell} = 0.76\ V$



Standard emf (E^0_{cell})

$$\boxed{E^0_{cell} = E^0_{cathode} - E^0_{anode}}$$

Zn (*s*) | Zn^{2+} (1 *M*) || H^+ (1 *M*) | H_2 (1 atm) | Pt (*s*)

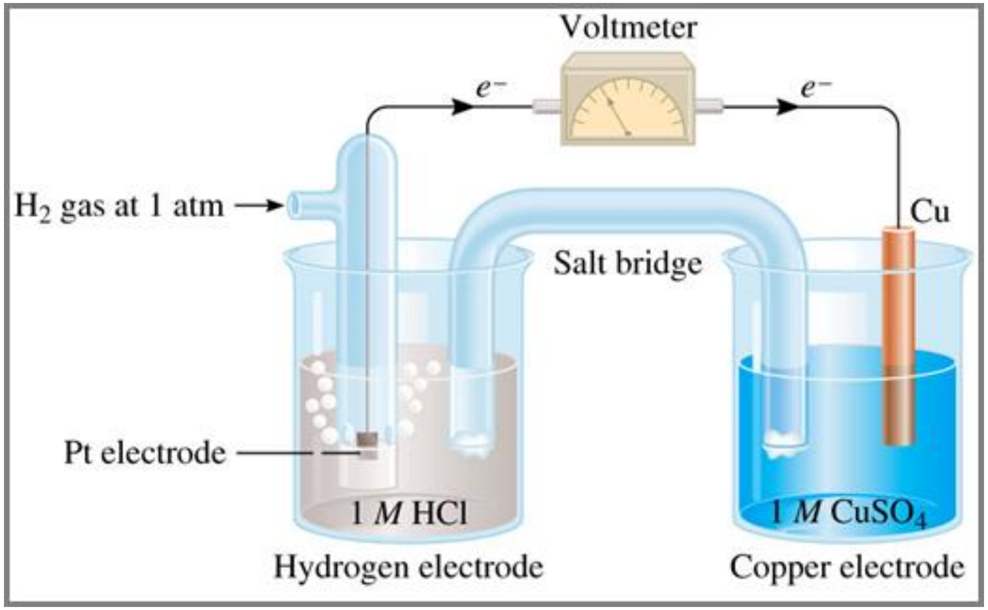
$$E^0_{cell} = E^0_{H^+/H_2} - E^0_{Zn^{2+}/Zn}$$

$$0.76\ V = 0 - E^0_{Zn^{2+}/Zn}$$

$$E^0_{Zn^{2+}/Zn} = -0.76\ V$$

$$Zn^{2+}\ (1\ M) + 2e^- \longrightarrow Zn \qquad E^0 = -0.76\ V$$

$E^0_{cell} = 0.34\ V$



$E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$E^0_{cell} = E^0_{Cu^{2+}/Cu} - E^0_{H^+/H_2}$

$0.34 = E^0_{Cu^{2+}/Cu} - 0$

$E^0_{Cu^{2+}/Cu} = 0.34\ V$

Pt (*s*) | H_2 (1 *atm*) | H^+ (1 *M*) || Cu^{2+} (1 *M*) | Cu (*s*)

Anode (oxidation): $H_2\ (1\ atm) \longrightarrow 2H^+\ (1\ M) + 2e^-$

Cathode (reduction): $2e^- + Cu^{2+}\ (1\ M) \longrightarrow Cu\ (s)$

$H_2\ (1\ atm) + Cu^{2+}\ (1\ M) \longrightarrow Cu\ (s) + 2H^+\ (1\ M)$

ELECTROCHEMISTRY 1
PART 2

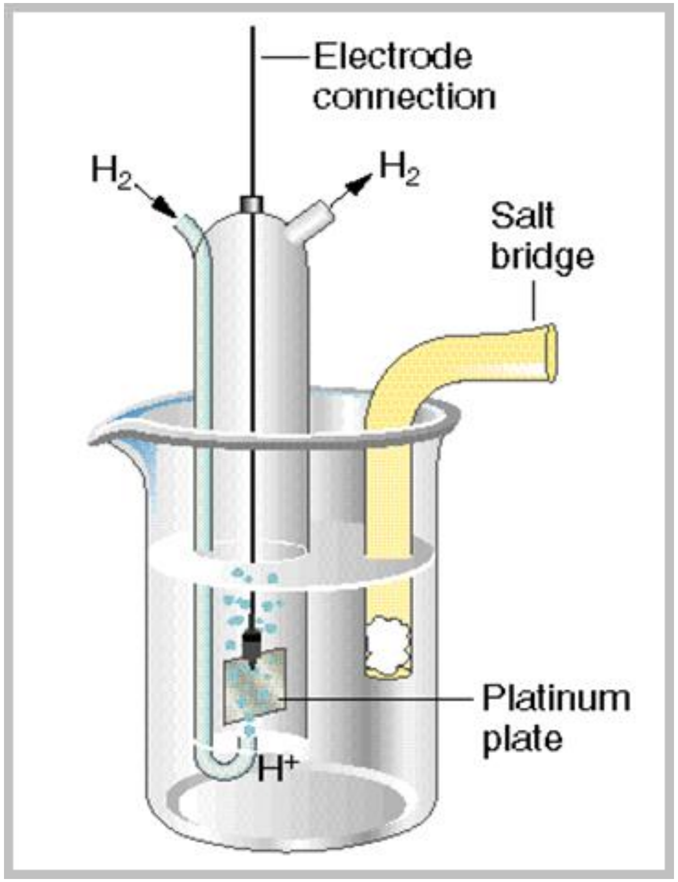
Reference electrode

- Has a constant and known potential
- Non-polarizable electrodes

Types

- Primary reference electrodes
- Secondary reference Electrodes

Standard Hydrogen Electrode



Primary reference electrode

Electrode reaction

$2H^+ + 2e^- = H_2$

Half-cell:

Pt, H_2 | H^+ (1.0 M) ||

E^o = zero

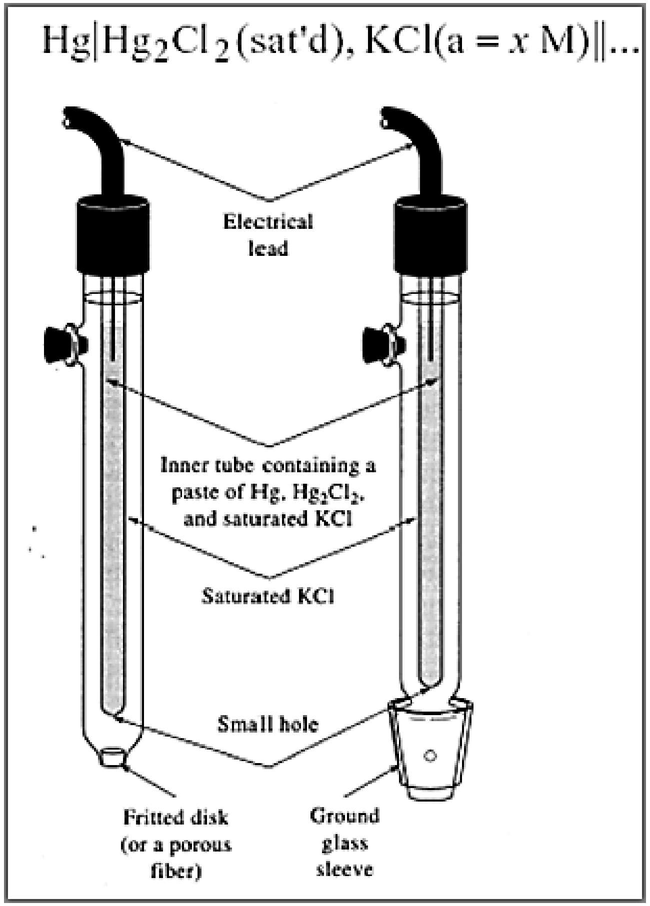
Disadvantages of the electrode

1. Difficult to be used regularly since we should keep the gas pressure constant at 1 atm during experiments.
2. It is needed to plate the platinum electrode periodically with black platinum

Seondary Reference Electrodes

Calomel electrode

KCl	*E volt*
Saturated	*0.241*
1M	*0.280*
0.1 M	*0.334*



$\mathrm{Hg}|\mathrm{Hg_2Cl_2(sat'd), KCl}(a = x\ \mathrm{M})\|\ldots$

The electrode potential shifts to more negative value with increasing chloride ion concentration

$$E_{25} = E^{o}_{Hg/Hg_2^{+}} + \frac{0.059}{2}\log[Hg_2^{+2}]$$

$$Hg_2Cl_2 \Leftrightarrow Hg_2^{+2} + 2Cl^{-}$$

$$K_{sp} = [Hg_2^{+2}]\,[Cl^{-}]^2 \Rightarrow [Hg_2^{+2}] = \frac{K_{sp}}{[Cl^{-}]^2}$$

$$E_{25} = \boxed{E^{o}_{Hg/Hg_2^{+}} + \frac{0.059}{2}\log K_{sp}} - \frac{0.059}{2}\log[Cl^{-}]^2$$

$$E_{25} = E^{o\prime}_{Hg/Hg_2^{+}} - 0.059\log[Cl^{-}]$$

Silver/Silver Chloride reference electrode

Electrode reaction

$Ag^+ + e = Ag^o$

Half-cell

Ag/AgCl, saturated KCl ||
or 1.0 N KCl ||
or 0.1 N KCl ||

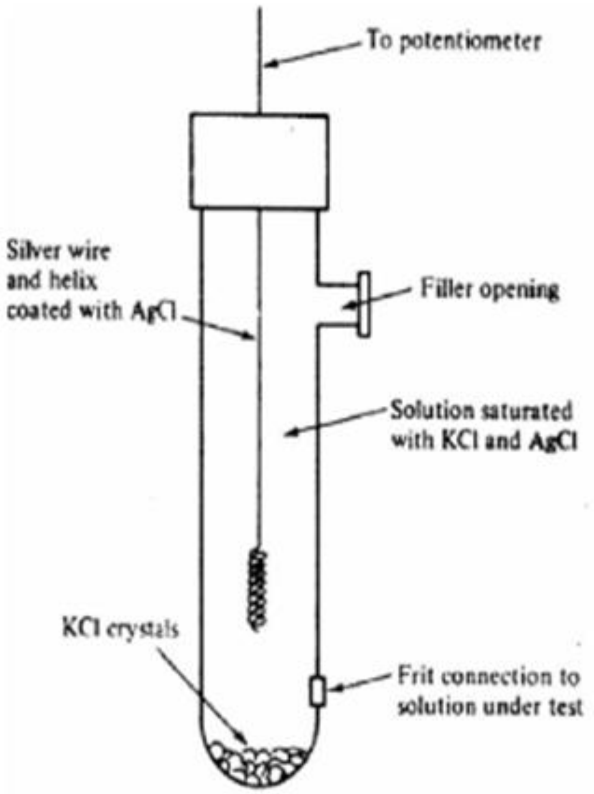
$$E_{Ag/Ag} = E^o - 0.0591 \log \frac{1}{[Ag^+]}$$

$$AgCl \Leftrightarrow Ag^+ + Cl^-$$

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

$$E_{25} = E^o + 0.0591 \log K_{sp} - 0.0591 \log[Cl^-]$$

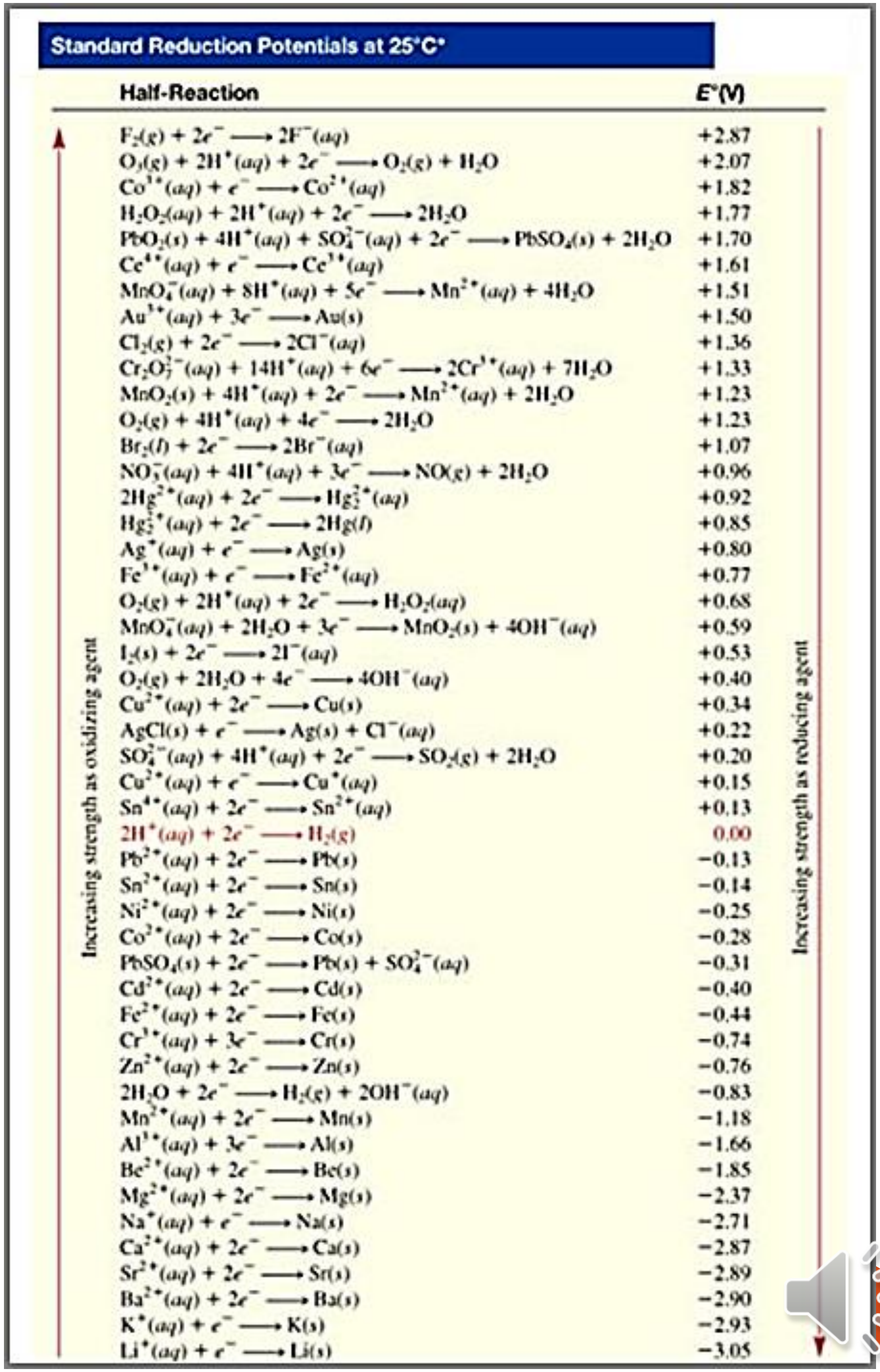
$$E_{25} = E^{o\backslash} - 0.0591 \log[Cl^-]$$



Saturated KCl Ag/AgCl electrode.

Electromotive series:

- Reduction reactions of the calf-cells are arranged according to their standard reduction potentials.
- The reactions on the **bottom** of the series has negative potentials.
- The reactions on the **top** of the series has positive potentials.
- For a cell consists of two half-cell reactions, the half-cell of more potential value will act as oxidant and will be reduced, i.e. will be cathode.
- The other half-cell reaction that of less potential value will act as reductant and will be oxidized, i.e. act as anode.



Standard Reduction Potentials at 25°C*

Half-Reaction	E°(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

What is the standard potential of a cell consists of Cd and Cr electrodes immersed in solutions of their ions of concentrations 1 M.

$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s) \quad E^0 = -0.40\text{ V}$ Cd is the stronger oxidizer

$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s) \quad E^0 = -0.74\text{ V}$ Cd will oxidize Cr

Anode (oxidation): $Cr(s) \longrightarrow Cr^{3+}(1\ M) + \boxed{3e^-} \quad \times 2$

Cathode (reduction): $\boxed{2e^-} + Cd^{2+}(1\ M) \longrightarrow Cd(s) \quad \times 3$

$$2Cr(s) + 3Cd^{2+}(1\ M) \longrightarrow 3Cd(s) + 2Cr^{3+}(1\ M)$$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = -0.40 - (-0.74)$$

$$E^0_{cell} = 0.34\text{ V}$$

ELECTROCHEMISTRY 1
PART 3

Ex: Can you construct a galvanic cell from the following reactions?

A) $Sn^{2+} + Cu \rightarrow Sn + Cu^{2+}$

B) $3Cu^{2+} + 2Al \rightarrow 3Cu + 2Al^{3+}$

$E^{o}Cu^{+2}/Cu = 0.337\ V$

$E^{o}\ Sn^{2+}/Sn = -0.136\ V$

$E^{o}Al^{3+}/Al = -1.662\ V$

Answer

A)

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

$Sn^{2+} + 2e^{-} \rightarrow Sn$

$$\frac{\phantom{Sn^{2+} + Cu \rightarrow Sn + Cu^{2+}}}{Sn^{2+} + Cu \rightarrow Sn + Cu^{2+}}$$

$E_{cell} = E^{o}_{cathode} - E^{o}_{anode}$

$E_{cell} = -0.136 - 0.337 = -0.463\ Volt$

This means that the reaction will not occur spontaneously in a galvanic cell and no current will be obtained. For this reaction to occur it is needed to apply a potential of 0.46 V from outside source in electrochemical cell.

B)

$$2Al \rightarrow 2Al^{3+} + 6e^-$$

$$3Cu^{2+} + 6e^- \rightarrow 3Cu$$

$$3Cu^{2+} + 2Al \rightarrow 3Cu + 2Al^{3+}$$

$$E_{cell} = E^o_{cathode} - E^o_{anode}$$

$$E_{cell} = E^o_{Cu} - E^o_{Al}$$

$$E_{cell} = 0.337 - (-1.662) = 1.999 \text{ Volt}$$

The reaction is spontaneous and the cell is galvanic cell

Liquid Junction Potential جهد الاتصال

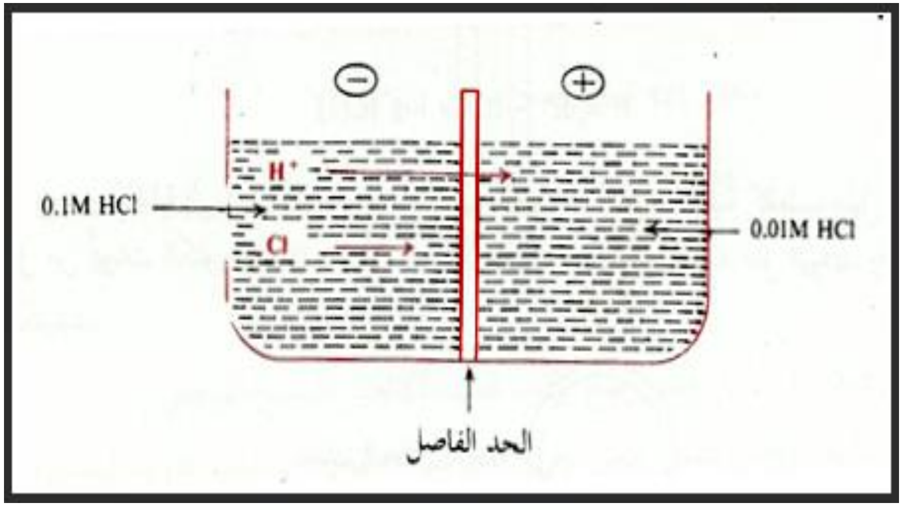
مؤجل

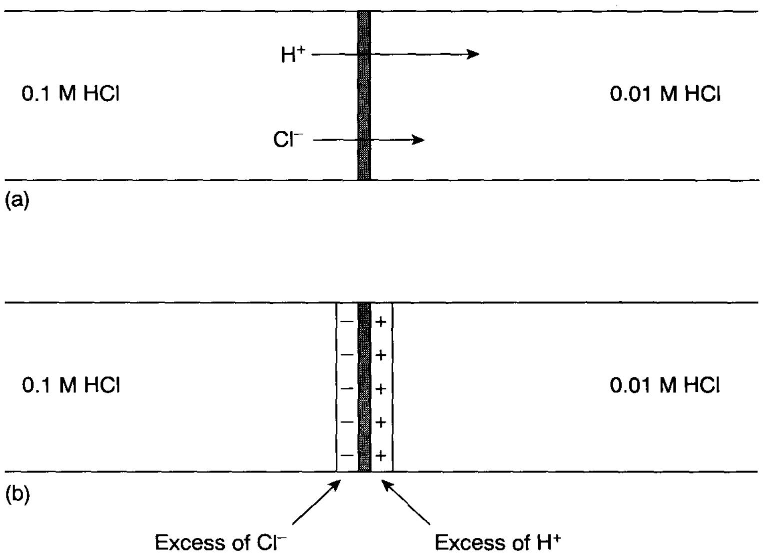
For correct calculations the cell potential is:

$$\boxed{E_{cell} = E_c - E_a + E_j}$$

- Where E_j is the liquid junction potential
- Junction potential may have positive or negative values.

- It's origin arises from the contact of the solutions of two different concentration or composition of the two electrodes, working electrode and reference electrode, in the porous membrane.
- Suppose that we have two solutions separated with a porous membrane, the solution of the reference electrode is of concentration of 0.01 M and the solution of the working electrode have a concentration of 0.1 M





- Hydrogen and chloride ions will move from the concentrated to the diluted solutions through the porous membrane

.

- Since the diffusion velocity of hydrogen ion is much greater than that of chloride ions then the diluted solution will charged positively while the concentrated solution will charged negatively and liquid junction potential will be formed and will have a value of -40 mV.

- Liquid junction potential could be minimized by using a salt bridge contains a salt of two ions have equal diffusion velocities as KCl

Evolution of hydrogen from molar acidic solutions

- Metals lie **after** hydrogen in the electromotive force series , I.e. have negative potential values, can replace hydrogen ions and evolve hydrogen gas.

$$\mathrm{Zn}\ (s)\ |\ \mathrm{Zn}^{2+}\ (1\ M)\ ||\ \mathrm{H}^{+}\ (1\ M)\ |\ \mathrm{H}_2\ (1\ \mathrm{atm})\ |\ \mathrm{Pt}\ (s)$$

$$E^0_{cell} = E^0_{H^+/H_2} - E^0_{Zn^{2+}/Zn}$$

$$0.76\ \mathrm{V} = 0\ -\ -0.76$$

$$\mathrm{Zn} + \mathrm{H}^+\ (1\ M) \longrightarrow \mathrm{Zn}^{+2} + \mathrm{H}_2 \qquad E^0{}_{cell} = 0.76\ \mathrm{V}$$

- The tendency to replace hydrogen ion decreases as the potential value increases, i.e. shifts to less negative value.

- Metals lie **before** hydrogen in the electromotive force series, has positive potential values, cannot replace hydrogen from standard acidic solutions.

Thermodynamic of Galvanic Cells

Change in the Gibbs free energy, ΔG, gives an indication weather the reaction is spontaneous, nonspontaneous or at equilibrium.

$\Delta G < 0$:Spontaneous reaction
$\Delta G > 0$:Non-spontaneous reaction
$\Delta G = 0$:equilibrium

$\Delta G = W_{max}$:
W_{max} Is the maximum work

Change in free energy, cell potential and rate constant are related via the following equations:

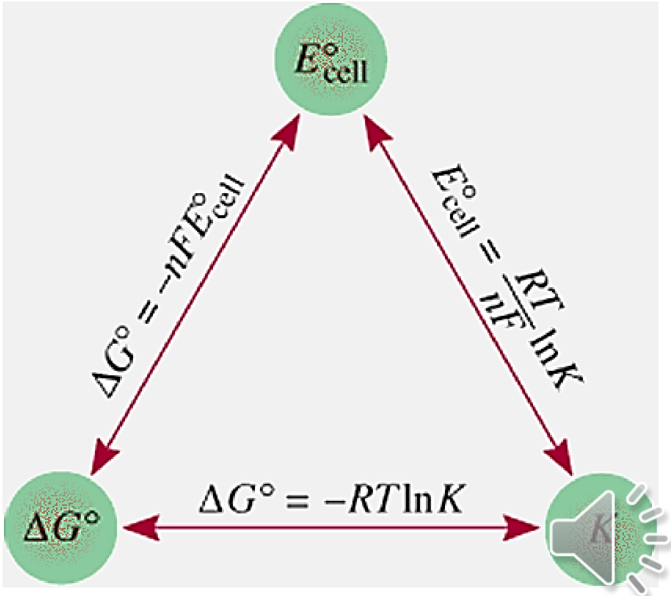
$\Delta G = -nFE_{cell}$ n = number of moles of electrons in reaction

$\Delta G^0 = -nFE^0_{cell}$ $F = 96{,}500 \dfrac{\text{J (Joul)}}{\text{V (Volt)} \cdot \text{mol}} = 96{,}500 \text{ C/mol}$

$$\Delta G^0 = -RT \ln K = -nFE^0_{cell}$$

$$E^0_{cell} = \frac{RT}{nF} \ln K = \frac{(8.314 \cancel{\text{J}}/\cancel{\text{K}}\text{•}\cancel{\text{mol}})(298 \cancel{\text{K}})}{n\,(96{,}500 \cancel{\text{J}}/\text{V•}\cancel{\text{mol}})} \ln K$$

$$E^0_{cell} = \frac{0.0257 \text{ V}}{n} \ln K$$



What is the rate constant of the following reaction at room temperature?

$$\mathrm{Fe^{2+}}\,(aq) + 2\mathrm{Ag}\,(s) \rightleftharpoons \mathrm{Fe}\,(s) + 2\mathrm{Ag^{+}}\,(aq)$$

$$E^0_{\mathrm{cell}} = \frac{0.0257\ \mathrm{V}}{n} \ln K$$

Oxidation: $2\mathrm{Ag} \longrightarrow 2\mathrm{Ag^{+}} + \boxed{2e^{-}}$

Reduction: $\boxed{2e^{-}} + \mathrm{Fe^{2+}} \longrightarrow \mathrm{Fe}$

$n = 2$

$$E^0 = E^0_{Fe^{2+}/Fe} - E^0_{Ag^{+}/Ag}$$

$$E^0 = -0.44 - (0.80)$$

$$E^0 = -1.24\ \mathrm{V}$$

$$k = e^{\left[\frac{E^o_{cell} x n}{0.0257V}\right]} = e^{\left[\frac{-1.24x2}{0.0257V}\right]}$$

$$k = 1.23x10^{-42}$$

Case	E	ΔG	K
Spontaneous	+ve	-Ve	large
Non-spontaneous	-ve	+ve	small
Equilibrium	0	0	1

For the following reaction

$$A + B \leftrightarrow C + D$$

مؤجل

$$\Delta G = \Delta G^0 + RT \ln Q$$

$$\boxed{Q = \frac{a_C . a_D}{a_A . a_B}}$$

بما أن

$$\Delta G = W$$

$$\Delta G = W_{ele}$$

$$W_{ele} = -nFE$$

حيث W_{ele} هو الشغل الكهربى

$$\Delta G = -zFE$$

$$\Delta G^0 = -zFE^0$$

حيث E^o هو الجهد القياسى للقطب

$$-zFE = -zFE^0 + RT \ln(Q)$$

$$E = E^0 - \frac{RT}{zF} \ln(Q)$$ *Nernst equation*

$$E = E^0 - \frac{8.314 \times 298T}{Z \times 96500} \ln(Q)$$ At 298 K

$$E = E^0 - \frac{0.02567}{z} \ln(Q)$$

At standard conditions i.e. when the activity of ions is unity.

$$\boxed{\begin{array}{l} Q = 1 \\ \ln Q = 0 \\ \therefore E = E^o \end{array}}$$

Effect of concentration on the electrode potential

At non standard conditions, when a≠1

M^{+2} +2e↔ M

$$Q = \frac{a_M}{a_{M^{+2}}} \neq 1$$

$$\ln Q \neq 0$$

$$\therefore E \neq E^o$$

$$E = E^0 - \frac{0.02567}{z} \ln (Q)$$

$$E = E^o - \frac{0.02567}{z} \ln \frac{1}{a_{M^{+2}}}$$

$$E = E^o - \frac{0.02567}{z} \ln \frac{1}{10} = E^o + \frac{0.02567}{z} x2.3$$

$$E = E^o - \frac{0.02567}{z} \ln \frac{1}{10^{-1}} = E^o - \frac{0.02567}{z} x2.3$$

- By increasing metal ion concentration, the equilibrium shifts to right side of the reaction and the potential will shift to less negative or more positive value, i.e. increases.

- By decreasing metal ion concentration, the equilibrium shifts to left side of the reaction and the potential will shift to more negative or less positive value, i.e. decreases.

Example:

Calculate the potential of the following half-cell:

Zn^{2+} (a=0.1) | Zn

From the electrochemical series:

Zn^{2+} (a=0.1) +2e → Zn **$E^0 = -0.7628$ V**

$$E = E^o - \frac{0.02567}{2} \ln \frac{1}{0.1}$$

$$E = -0.7628 - \frac{0.02567}{2} \ln \frac{1}{0.1}$$

$$E = -0.7923$$

Is the following reaction occurs spontaneously at room temperature?

$[Fe^{2+}] = 0.60\ M$ and $[Cd^{2+}] = 0.010\ M$?

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

Oxidation: $$Cd \longrightarrow Cd^{2+} + \boxed{2e^-}$$

Reduction: $$\boxed{2e^-} + Fe^{2+} \longrightarrow Fe$$

$n = 2$

$$E^0 = E^0_{Fe^{2+}/Fe} - E^0_{Cd^{2+}/Cd}$$

$$E^0 = -0.44 - (-0.40)$$

$$E^0 = -0.04\ V$$

$$E = E^0 - \frac{0.0257\ V}{n} \ln Q$$

$$E = -0.04 - \frac{0.0257}{2} \ln \frac{0.010}{0.60}$$

$$E = 0.013$$

$E > 0$ Spontaneous

Reaction of metals with water

- Some metals with negative potential values can replace hydrogen ions and evolve hydrogen gas from water while others with negative potential values cannot depending on the value of the cell potential.
- Ex:Zn/Zn^{+2} (IM)//H^{+} (10^{-7} M)/H$_2$ (1 atm),Pt

$$Zn^{+2} + 2e \Leftrightarrow Zn \qquad E^{o} = -0.76V$$

$$2H^{+}(10^{-7}M) + 2e \Leftrightarrow H_2 \qquad E^{o} = 0V$$

$$Zn + 2H^{+}(10^{-7}M) \Leftrightarrow Zn^{+2} + H_2 \qquad E = ?V$$

$$E_{H^{+}/H_2} = E^{o} - \frac{0.02567}{2}\ln\frac{1}{10^{-7}}$$

$$E_{H^{+}/H_2} = 0 - \frac{0.02567}{2}\ln\frac{1}{10^{-7}}$$

$$E_{H^{+}/H_2} = -0.2$$

$$E_{cell} = E_c - E_a = -0.2 - (-0.76) = 0.55V$$

$$\mathrm{Zncando}$$

- Ex: Sn/Sn^{+2} (IM)//H^{+} (10^{-7} M)/H_2 (1 atm), Pt

$$Sn + 2e \Leftrightarrow Sn^{+2} \qquad E^{o} = -0.14V$$

$$2H^{+}(10^{-7}M) + 2e \Leftrightarrow H_2 \qquad E^{o} = 0V$$

$$Sn + 2H^{+}(10^{-7}M) \Leftrightarrow Sn^{+2} + H_2 \qquad E = ?V$$

$$E_{H^{+}/H_2} = E^{o} - \frac{0.02567}{2} \ln \frac{1}{10^{-7}}$$

$$E_{H^{+}/H_2} = 0 - \frac{0.02567}{2} \ln \frac{1}{10^{-7}}$$

$$E_{H^{+}/H_2} = -0.21$$

$$E_{cell} = E_c - E_a = -0.21 - (-0.14) = -0.07V$$

Sn cannot do

ELECTROCHEMISTRY 1
PART 4

Reversible and irreversible cells

a) Reversible cells

- Ex: Zn/Zn^{+2} (IM)//Cu^{+2} /Cu
- In this cell when it act as a galvanic cell, Zn will dissolve in the Zn half-cell while copper will deposit in the copper half-cell.

$$\boxed{\begin{array}{l} Zn \Rightarrow Zn^{+2} + 2e \\ Cu^{+2} + 2e \Rightarrow Cu \\ \hline Zn + Cu^{+2} \Rightarrow Zn^{+2} + Cu \end{array}}$$

- If an equal amount of current is passes in the opposite direction of the produced current, copper will dissolve in the copper half-cell and zinc will deposit in the zinc half-cell

$$\boxed{\begin{array}{l} Zn^{+2} + 2e \Rightarrow Zn \\ Cu \Rightarrow Cu^{+2} + 2e \\ \hline Zn^{+2} + Cu \Rightarrow Zn + Cu^{+2} \end{array}}$$

b) Irreversible cells

- Zn/H_2SO_4 (aq)/Cu
- In this cell when it act as a galvanic cell, Zn will dissolve in the Zn half-cell while hydrogen gas will be evolved in the copper half-cell

$$\boxed{\begin{array}{l} Zn \Rightarrow Zn^{+2} + 2e \\ 2H^{+} + 2e \Rightarrow H_2 \\ \\ \hline Zn + 2H^{+} \Rightarrow Zn^{+2} + H_2 \end{array}}$$

- If an equal amount of current passes in the opposite direction of the produced current, copper will dissolve in the copper half-cell and zinc will deposit in the zinc half-cell

$$\boxed{\begin{array}{l} Zn^{+2} + 2e \Rightarrow Zn \\ Cu \Rightarrow 2Cu^{+2} + 2e \\ \\ \hline Zn^{+2} + Cu \Rightarrow Zn + Cu^{+2} \end{array}}$$

Changes in Enthalby and Entropy

$$\Delta H = \Delta G - T\left[\partial \frac{\Delta G}{\Delta T}\right]_P$$

$$\because \Delta G = -zFE$$

$$\therefore \Delta H = -zFE + zFT\left[\frac{\partial E}{\partial T}\right]_P$$

$$\left[\partial \frac{\Delta G}{\Delta T}\right]_P = 0 \qquad \text{at constant } T$$

From Gibbs – Helmholtz equation

$$\left[\partial\frac{\Delta G}{\Delta T}\right]_P = -\Delta S$$

$$;\Delta H = \Delta G + T\Delta S$$

$$\therefore \Delta S = zF\left[\frac{\partial E}{\partial T}\right]_P$$

Calculate the standard potential of the following cell at 80°C

$$\mathrm{Ag, AgCl \mid KCl \parallel KBr \mid Br_2, Pt}$$

الحل:

$$\mathrm{Br_2 + \enclose{circle}{2e^-} \rightarrow 2Br^-}$$

$$\mathrm{2Ag + 2Cl^- \rightarrow 2AgCl + \enclose{circle}{2e^-}}$$

$$\overline{\mathrm{Br_2 + 2Ag + 2Cl^- \rightarrow 2Br^- + 2AgCl}}$$

At 25°C, the standard potential of the cell is 0.8428 and we will calculate it at 80°C as follows:

Substance	ΔH^o_f kJ mol^{-1}	S^0 J K^{-1} mol^{-1}	C_p J K^{-1} mol^{-1}
Br^-	-121.55	82.4	-141.8
AgCl	-127.07	96.11	50.74
Br2	0	152.32	75.69
Ag	0	42.55	25.35
Cl^-	-167.16	56.5	-136.4

$$\Delta H^o = -162.92\,\mathrm{kJ}$$

$$\Delta S^o = 6.69\,\mathrm{J\,K^{-1}}$$

$$\Delta C_p^o = -35.611\,\mathrm{J\,K^{-1}}$$

$$\because T_1 = 298\,\mathrm{K}, \qquad T_2 = 353\,\mathrm{K}$$

$$\because \Delta \mathrm{H}_2 = \Delta H_1 + \Delta C_P (T_2 - T_1)$$

$$\because \Delta \mathrm{S}_2 = \Delta S_1 + \Delta C_P (T_2 - T_1)$$

$$\therefore \Delta H^0(353) = -164.878\ \mathrm{kJ}$$

$$, \Delta S^0(353) = 0.658\ \mathrm{J\,K^{-1}}$$

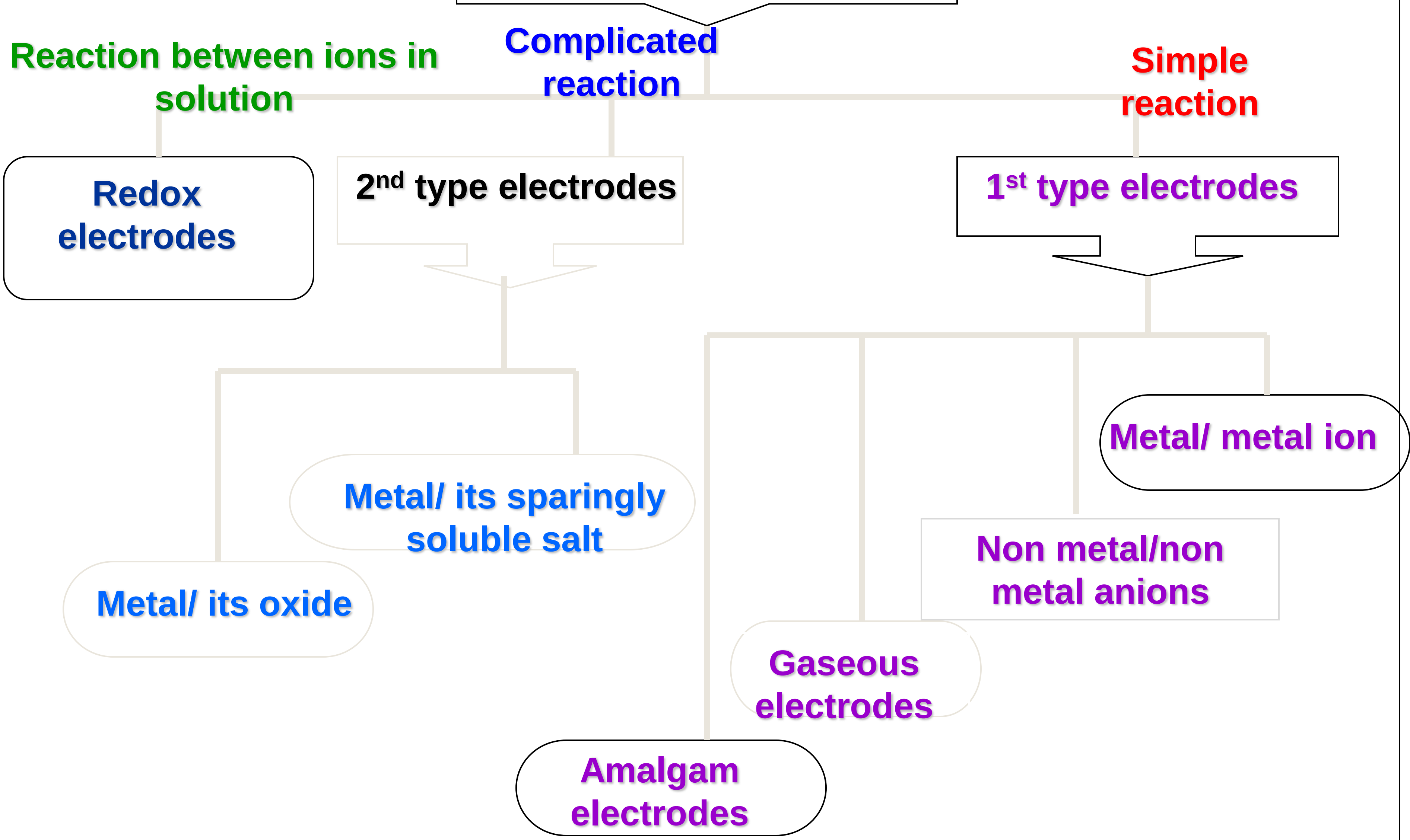
$$\because \Delta G^o = \Delta H^o - T\Delta S^0$$

$$\therefore \Delta G^o = -165.11\ \mathrm{kJ}$$

$$, \because E^o = -\frac{\Delta G^o}{2F}$$

$$\therefore E^o = 0.855 \qquad \mathrm{at}\,353$$

Electrodes



Reaction between ions in solution

Redox electrodes

Complicated reaction

2^nd^ type electrodes

Metal/ its sparingly soluble salt

Metal/ its oxide

Simple reaction

1^st^ type electrodes

Metal/ metal ion

Non metal/non metal anions

Gaseous electrodes

Amalgam electrodes

I- 1st typt electrodes

2- non metal/ its anion

Electrode notation

$$Me|Me^{-z}$$

$$Se|Se^{-2}$$

Electrode reaction

$$Me + ze^{-} \Leftrightarrow Me^{-z}$$

$$Se + 2e^{-} \Leftrightarrow Se^{-2}$$

Nernst equation

$$E = E^{\circ} - \frac{RT}{zF} \ln a_{Me^{-z}}$$

$$E = E^{\circ} - \frac{RT}{2F} \ln a_{Se^{-2}}$$

1- metal/ metal ion

Electrode notation

$$M^{+z}|M$$

$$Cu^{+2}|Cu$$

Electrode reaction

$$M^{+z} + ze^{-} \Leftrightarrow M$$

$$Cu^{+2} + 2e^{-} \Leftrightarrow Cu$$

Nernst equation

$$E = E^{\circ} - \frac{RT}{zF} \ln \frac{1}{a_{M^{+z}}}$$

$$E = E^{\circ} - \frac{RT}{2F} \ln \frac{1}{a_{Cu^{+2}}}$$

3-gaseous electrode

$Pt, X_2|X^{-z}$ ← **Electrode notation** → $X^{+z}|X_2, Pt$

$Pt, Cl_2|Cl^-$

Electrode reaction

$$X_2 + 2ze^- \Leftrightarrow 2X^{-z}$$

$$Cl_2 + 2e^- \Leftrightarrow 2Cl^-$$

Nernst equation

$$E = E^\circ - \frac{RT}{2zF} \ln \frac{(a_{X^{-z}})^2}{a_{X_2}}$$

$$E = E^\circ - \frac{RT}{2F} \ln \frac{(a_{Cl^-})^2}{a_{Cl_2}}$$

$H^+|H_2, Pt$

Electrode reaction

$$2X^{+z} + 2ze^- \Leftrightarrow X_2$$

$$2H^+ + 2e^- \Leftrightarrow H_2$$

Nernst equation

$$E = E^\circ - \frac{RT}{2zF} \ln \frac{a_{X_2}}{(a_{X^{+z}})^2}$$

$$E = E^\circ - \frac{RT}{2F} \ln \frac{a_{H_2}}{(a_{H^+})^2}$$

Amalgam electrode

Electrode notation

$$M^{+z}|M,Hg$$

$$Cd^{+2}|Cd,Hg$$

Electrode reaction

$$M^{+z}+ze^{-}\Leftrightarrow M(Hg)$$

$$Cd^{+2}+2e^{-}\Leftrightarrow Cd(Hg)$$

Nernst equation

$$E=E^{\circ}-\frac{RT}{zF}\ln\frac{a_{M(Hg)}}{a_{M^{+z}}}$$

$$E=E^{\circ}-\frac{RT}{2F}\ln\frac{a_{Cd(Hg)}}{a_{Cd^{+2}}}$$

II. 2nd type electrodes

Metal/ its oxide electrode

$$OH^{-}|Sb_2O_3,Sb$$

$$OH^{-}|HgO,Hg$$

Metal/ its sparingly soluble salt electrode

As calomel electrode, Ag/AgCl, Hg/Hg_2SO_4. The metal is immersed in a solution of the anions of its sparingly soluble salt.

Electrode notation $SO_4^{-2}|Hg_2SO_4,Hg$

Electrode reaction $Hg_2SO_4\ (s)+2e^{-}\Leftrightarrow 2Hg(l)+SO_4^{-2}(aq)$

Nernst equation

$$E=E^{\circ}-\frac{RT}{2F}\ln a_{SO_4^{-2}}$$

This electrode is sensitive to the sulphate ion concentration therefore it is used to the determination of sulphate ion concentration

Metal / metal oxide electrode

1. stibium / stibium oxide (Antimony/Antimony oxide) electrode

Electrode notation

$$OH^-|Sb_2O_3,Sb$$

Electrode reaction

$$Sb_2O_3(s)+3H_2O+6e^- \Leftrightarrow 2Sb+6OH^-(aq)$$

Nernst equation

$$E=E^\circ-\frac{RT}{6F}ln\left(a_{OH^-}\right)^6$$

This electrode is reversible to hydroxide ion concentration so its potential depends on pH and is called indicator electrode

2. Mercury / mercuric oxide electrode

Electrode notation

$$OH^-|HgO,Hg$$

Electrode reaction

$$HgO(s)+H_2O+2e^- \Leftrightarrow Hg+2OH^-(aq)$$

Nernst equation

$$E=E^\circ-\frac{RT}{2F}ln\left(a_{OH^-}\right)^2$$

Generally, this kind of electrodes is used as reference electrodes in acidic and alkaline solutions.

$$a_{OH^-} = \frac{K_W}{a_{H^+}}$$

$$\ln a_{OH^-} = \ln K_W - \ln a_{H^+}$$

$$\ln a_{OH^-} = \ln K_W - 2.303 \log a_{H^+}$$

$$\ln a_{OH^-} = \ln K_W + 2.303\left(-\log a_{H^+}\right)$$

$$\ln a_{OH^-} = \ln K_W + 2.303\, pH$$

From Nernst equation

$$E = E^\circ - \frac{RT}{F} \ln a_{OH^-}$$

$$E = E^\circ - \frac{RT}{F} \ln K_W - \frac{2.303\,RT}{F} pH$$

This electrode is sensitive to the change in solution pH.

III. Redox electrodes

Electrode notation

$$M^{+X}, M^{(X-Z)+} | Pt$$

$$Cu^{+2}, Cu^{+} | Pt$$

Electrode reaction

$$M^{+X} + ze \Leftrightarrow M^{(X-Z)+}$$

$$Cu^{+2} + e \Leftrightarrow Cu^{+}$$

Nernst equation

$$E = E^{\circ} - \frac{RT}{zF} ln \frac{a_{M^{(X-Z)+}}}{a_{M^{+X}}}$$

$$E = E^{\circ} - \frac{RT}{F} ln \frac{a_{Cu^{+}}}{a_{Cu^{+2}}}$$

Electrochemistry 1
Part 4

Reversible and irreversible cells

a) Reversible cells

Å Ex: Zn/Zn^{+2} (IM)//Cu^{+2} /Cu

Å In this cell when it act as a galvanic cell, Zn will dissolve in the Zn half-cell while copper will deposit in the copper half-cell.

$$Zn \text{Ý} Zn^{+2}+2e$$

$$Cu^{+2}+2e \text{Ý} Cu$$

$$Zn+Cu^{+2} \text{Ý} Zn^{+2}+Cu$$

Å If an equal amount of current is passes in the opposite direction of the produced current, copper will dissolve in the copper half-cell and zinc will deposit in the zinc half-cell

$$Zn^{+2}+2e \text{Ý} Zn$$

$$Cu \text{Ý} Cu^{+2}+2e$$

$$Zn^{+2}+Cu \text{Ý} Zn+Cu^{+2}$$

b) Irreversible cells

- Zn/H_2SO_4 (aq)/Cu
- In this cell when it act as a galvanic cell, Zn will dissolve in the Zn half-cell while hydrogen gas will be evolved in the copper half-cell

$$\begin{array}{l} Zn \rightarrow Zn^{+2} + 2e \\ 2H^{+} + 2e \rightarrow H_2 \\ \hline Zn + 2H^{+} \rightarrow Zn^{+2} + H_2 \end{array}$$

- If an equal amount of current passes in the opposite direction of the produced current, copper will dissolve in the copper half-cell and zinc will deposit in the zinc half-cell

$$\begin{array}{l} Zn^{+2} + 2e \rightarrow Zn \\ Cu \rightarrow 2Cu^{+2} + 2e \\ \hline Zn^{+2} + Cu \rightarrow Zn + Cu^{+2} \end{array}$$

Changes in Enthalby and Entropy

$$\Delta H = \Delta G - T\left(\frac{\Delta G}{\Delta T}\right)_P$$

$$7\ \Delta G = -zFE$$

$$\therefore\ \Delta H = -zFE + zFT\left(\frac{E}{T}\right)_P$$

$$\left(\frac{\Delta G}{\Delta T}\right)_P = 0 \qquad \text{at constant } T$$

From Gibbs – Helmholtz equation

$$\boxed{\begin{gathered}\left(\frac{\Delta G}{\Delta T}\right)_P = -\Delta S \\ ;\Delta H = \Delta G + T\Delta S \\ \therefore\ \Delta S = zF\left(\frac{E}{T}\right)_P\end{gathered}}$$

Calculate the standard potential of the following cell at 80^oC

Ag, AgCl¼KCl¼ ¼KBr¼Br$_2$,Pt

:Э j

$$Br_2 + 2e^- - 2Br^-$$

$$2Ag + 2Cl^- - 2AgCl + 2e^-$$

$$Br_2 + 2Ag + 2Cl^- - 2Br^- + 2AgCl$$

At 25^{o}C, the standard potential of the cell is 0.8428 and we will calculate it at 80^{o}C as follows:

Substance	ΔH^o_f kJ mol^{-1}	S^0 J K^{-1} mol^{-1}	C_p J K^{-1} mol^{-1}
Br^-	-121.55	82.4	-141.8
AgCl	-127.07	96.11	50.74
Br2	0	152.32	75.69
Ag	0	42.55	25.35
Cl^-	-167.16	56.5	-136.4

$$\Delta H^o = -162.92\ \mathrm{kJ}$$

$$\Delta S^o = 6.69\ \mathrm{J\ K^{-1}}$$

$$\Delta C_p^o = -35.611\ \mathrm{J\ K^{-1}}$$

$$7T_1 = 298\,\mathrm{K}, \qquad T_2 = 353\,\mathrm{K}$$

$$7D\mathrm{H}_2 = DH_1 + DC_P(T_2 - T_1)$$

$$7DS_2 = DS_1 + DC_P(T_2 - T_1)$$

$$\backslash \quad DH^0(353) = -164.878\,\mathrm{kJ}$$

$$, DS^0(353) = 0.658\,\mathrm{J\,K^{-1}}$$

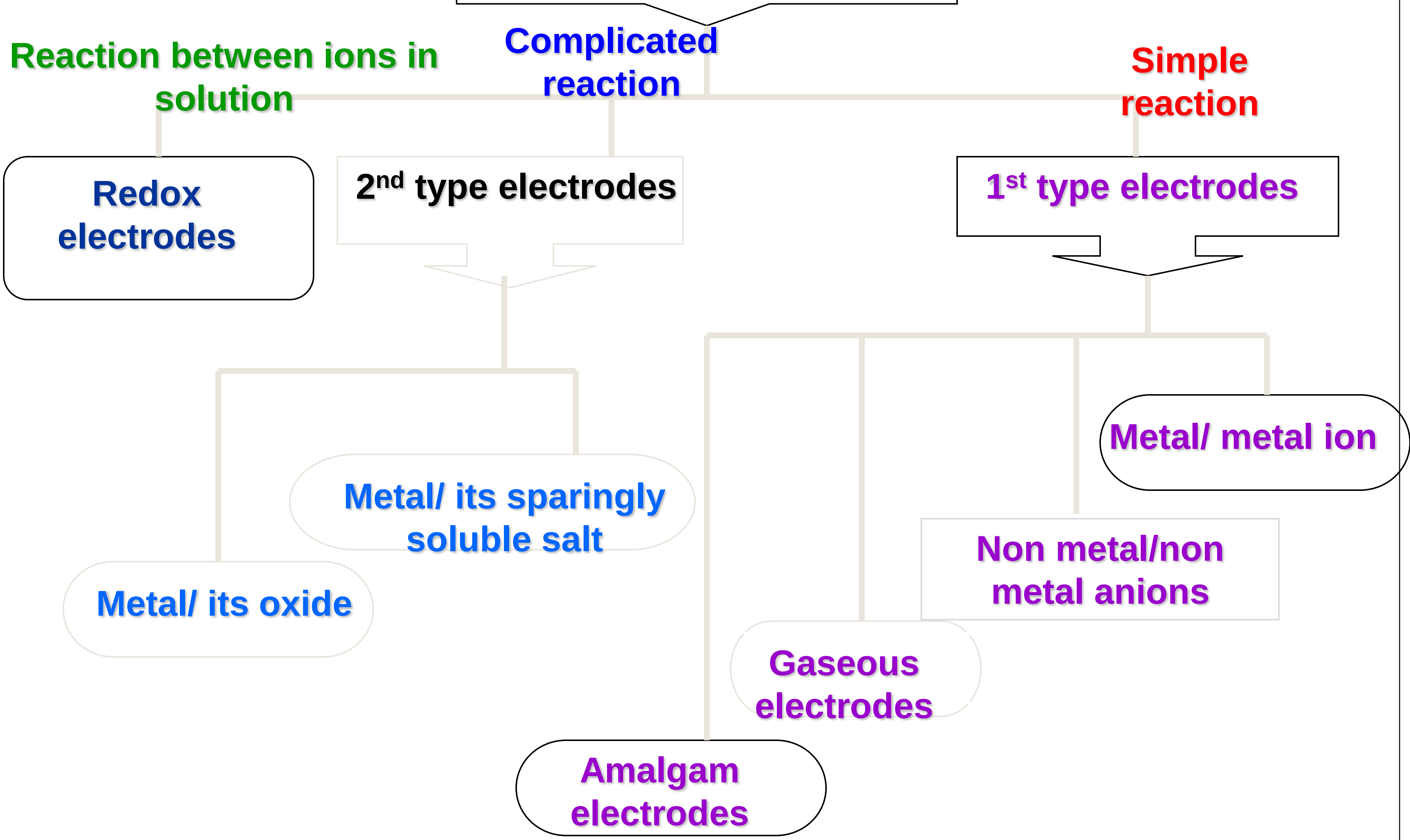
$$7DG^o = DH^o - TDS^0$$

$$\backslash \quad DG^o = -165.11\,\mathrm{kJ}$$

$$, 7E^o = -\frac{DG^o}{2F}$$

$$\backslash \quad E^o = 0.855 \qquad \mathrm{at}\,353$$

Electrodes



Reaction between ions in solution

Redox electrodes

Complicated reaction

2nd type electrodes

- Metal/ its sparingly soluble salt
- Metal/ its oxide

Simple reaction

1st type electrodes

- Metal/ metal ion
- Non metal/non metal anions
- Gaseous electrodes
- Amalgam electrodes

I- 1st typt electrodes

← Electrode notation →

1- metal/ metal ion

$$M^{+z}|M$$

$$Cu^{+2}|Cu$$

Electrode reaction

$$M^{+z} + ze^{-} \text{ Ú } M$$

$$Cu^{+2} + 2e^{-} \text{ Ú } Cu$$

Nernst equation

$$E = E^{\wedge} - \frac{RT}{zF} \ln \frac{1}{a_{M^{+z}}}$$

$$E = E^{\wedge} - \frac{RT}{2F} \ln \frac{1}{a_{Cu^{+2}}}$$

2- non metal/ its anion

$$Me|Me^{-z}$$

$$Se|Se^{-2}$$

Electrode reaction

$$Me + ze^{-} \text{ Ú } Me^{-z}$$

$$Se + 2e^{-} \text{ Ú } Se^{-2}$$

Nernst equation

$$E = E^{\wedge} - \frac{RT}{zF} \ln a_{Me^{-z}}$$

$$E = E^{\wedge} - \frac{RT}{2F} \ln a_{Se^{-2}}$$

3-gaseous electrode

$Pt, X_2|X^{-z}$ ← **Electrode notation** → $X^{+z}|X_2, Pt$

$Pt, Cl_2|Cl^-$

Electrode reaction

$$X_2 + 2ze^- \text{ Ú } 2X^{-z}$$

$$Cl_2 + 2e^- \text{ Ú } 2Cl^-$$

Nernst equation

$$E = E^{\text{A}} - \frac{RT}{2zF} \ln \frac{(a_{X^{-z}})^2}{a_{X_2}}$$

$$E = E^{\text{A}} - \frac{RT}{2F} \ln \frac{(a_{Cl^-})^2}{a_{Cl_2}}$$

$H^+|H_2, Pt$

Electrode reaction

$$2X^{+z} + 2ze^- \text{ Ú } X_2$$

$$2H^+ + 2e^- \text{ Ú } H_2$$

Nernst equation

$$E = E^{\text{A}} - \frac{RT}{2zF} \ln \frac{a_{X_2}}{(a_{X^{+z}})^2}$$

$$E = E^{\text{A}} - \frac{RT}{2F} \ln \frac{a_{H_2}}{(a_{H^+})^2}$$

Amalgam electrode

Electrode notation

$$M^{+z}|M,Hg$$

$$Cd^{+2}|Cd,Hg$$

Electrode reaction

$$M^{+z}+ze^{-} \rightleftharpoons M(Hg)$$

$$Cd^{+2}+2e^{-} \rightleftharpoons Cd(Hg)$$

Nernst equation

$$E=E^{\circ}-\frac{RT}{zF}\ln\frac{a_{M(Hg)}}{a_{M^{+z}}}$$

$$E=E^{\circ}-\frac{RT}{2F}\ln\frac{a_{Cd(Hg)}}{a_{Cd^{+2}}}$$

II. 2nd type electrodes

Metal/ its oxide electrode

$OH^-|Sb_2O_3,Sb$

$OH^-|HgO,Hg$

Metal/ its sparingly soluble salt electrode

As calomel electrode, Ag/AgCl, Hg/Hg_2SO_4. The metal is immersed in a solution of the anions of its sparingly soluble salt.

Electrode notation $SO_4^{2-}|Hg_2SO_4,Hg$

Electrode reaction $Hg_2SO_4(s)+2e^- \rightleftharpoons 2Hg(l)+SO_4^{2-}(aq)$

Nernst equation

$$E=E^{-}-\frac{RT}{2F}\ln a_{SO_4^{2-}}$$

This electrode is sensitive to the sulphate ion concentration therefore it is used to the determination of sulphate ion concentration

Metal / metal oxide electrode

1. stibium / stibium oxide (Antimony/Antimony oxide) electrode

Electrode notation

Electrode reaction

Nernst equation

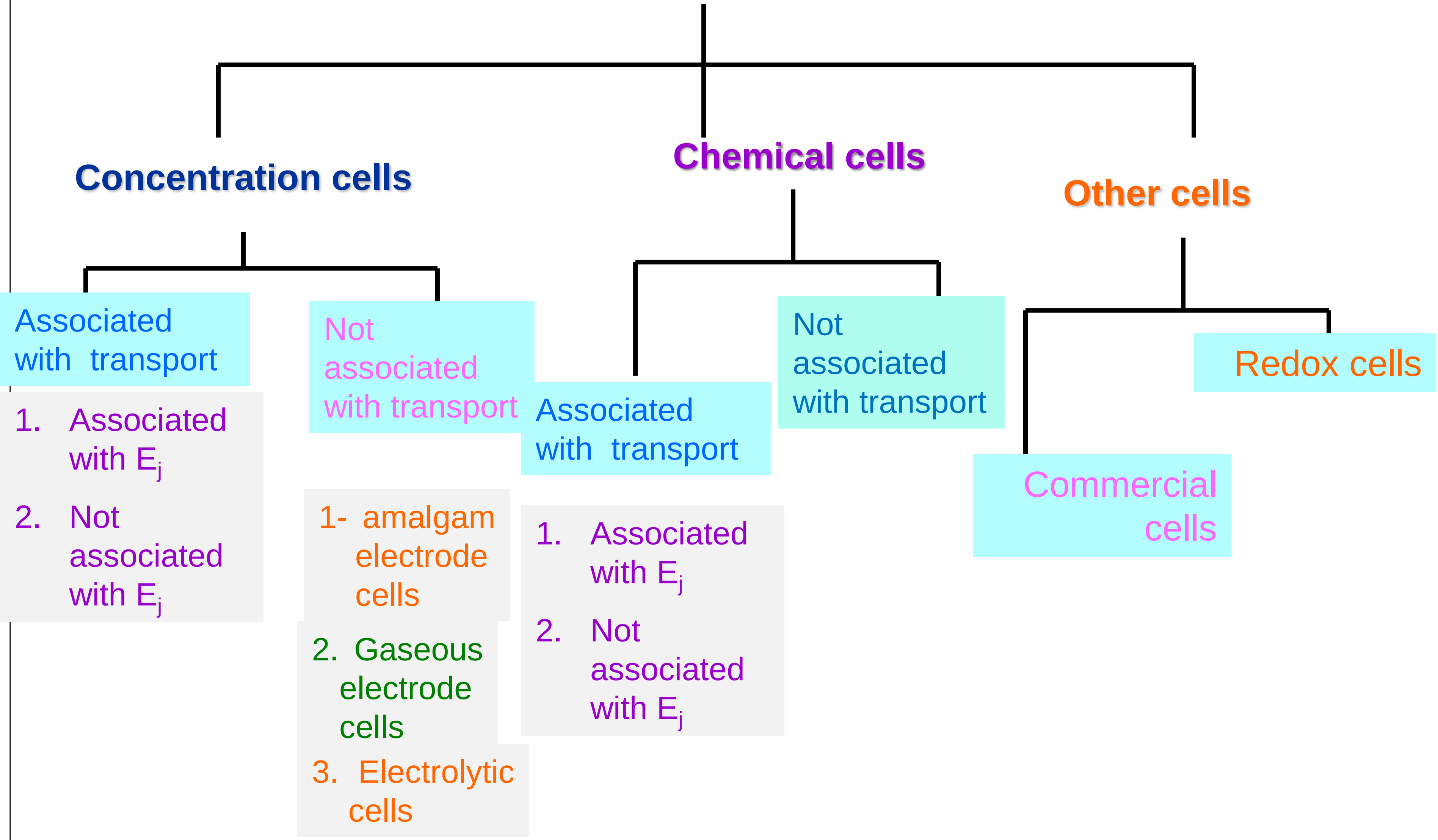
This electrode is reversible to [redacted] ion concentration so its potential depends on pH and is called indicator electrode

ELECTROCHEMISTRY 1
PART 5

Classification of Cells

- **Method of half-cells connection**
  - **Salt bridge (not associated with transport)**
  - **Porous membrane (associated with transport)**
- **Reason of the difference in the potential of the two half-cells**
  - **Different electrodes (different reactions)**
  - **Electrode concentration**
  - **Solution concentration**

Classification of Cells



Concentration cells

Associated with transport

1. Associated with E_j
2. Not associated with E_j

Not associated with transport

1- amalgam electrode cells

2. Gaseous electrode cells

3. Electrolytic cells

Chemical cells

Associated with transport

1. Associated with E_j
2. Not associated with E_j

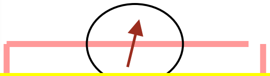
Not associated with transport

Other cells

Commercial cells

Redox cells

I. concentration cells: *a. not associated with transport*



$$E_{Cell}=E_c-E_a$$

$$E_{Cell}=[E_c^o-\frac{RT}{zF}\ln\frac{M_{(a2)}}{M^{+z}}]-[E_a^o-\frac{RT}{zF}\ln\frac{M_{(a1)}}{M^{+z}}]$$

$a_1 > a_2$

$$E_{Cell}=[-\frac{RT}{zF}\ln\frac{M_{(a2)}}{M^{+z}}]-[-\frac{RT}{zF}\ln\frac{M_{(a1)}}{M^{+z}}]$$

$$E_{Cell}=-\frac{RT}{zF}\ln\frac{M_{(a2)}}{M_{(a1)}}$$

What is the main demand to keep the cell working?

Answer: $a_1 \neq a_2$

I. concentration cells: *a. not associated with transport*

2. gaseous cells

it consists of two same electrodes of different gas pressures immersed in a solution containing a cation of the gas

$$Pt, H_{2(a_1)} | HCl | H_{2(a_2)}, Pt$$

$$2H^+ + 2e \rightarrow H_{2(a2)}$$

$$H_{2(a_1)} \rightarrow 2H^+ + 2e$$

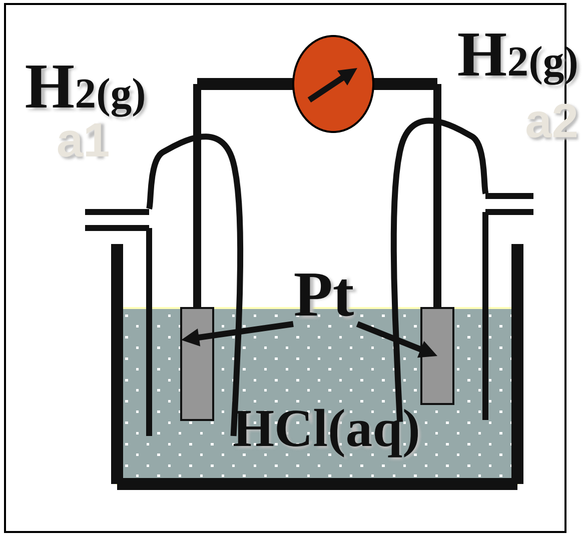
$$H_{2(a_1)} \rightarrow H_{2(a_2)}$$

$$Pt, X_{2(a_1)} | X^{\pm z} | X_{2(a_2)}, Pt$$

$$2X^{+z} + 2ze \rightarrow X_{2(a2)}$$

$$X_{2(a_1)} \rightarrow 2X^{+z} + 2ze$$

$$X_{2(a_1)} \rightarrow X_{2(a_2)}$$



$$E = -\frac{RT}{2F} \ln \frac{(a_2)}{(a_1)}$$

$$E = -\frac{RT}{zF} \ln \frac{(a_2)}{(a_1)}$$

$a_1 > a_2$

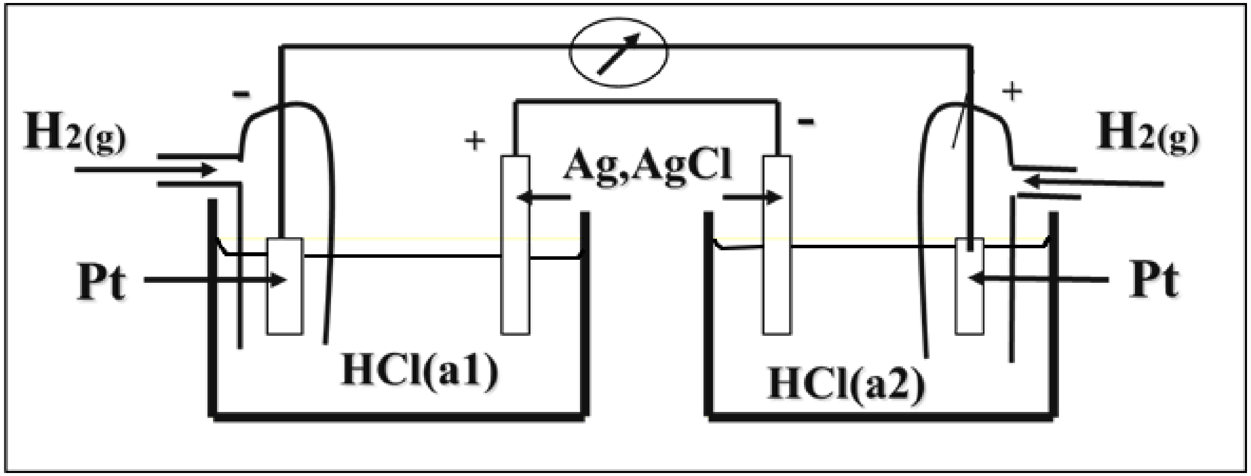
What is the main demand to keep the cell working?

Answer: $a_1 \neq a_2$

I. concentration cells: *a. not associated with transport*

3- Electrolytic concentration cells (not associated with transport)

- Each half-cell is a cell in itself consists of two different electrodes in the same solution that contains ions reversible to the two electrodes.
- Electrodes are arranged in opposite direction.
- Solutions concentration is different in the two half-cells
- There is no direct contact between the solutions in the two half cells either via porous membrane or salt bridge and the connection occurs via electrical wires



$a_1 < a_2$

Cell notation

$$Pt,H_2|HCl_{(a_1)}|AgCl,Ag$$ **1st half-cell**

$$Pt,H_2|HCl_{(a_2)}|AgCl,Ag$$ **2nd half-cell**

$$Pt,H_2|HCl_{(a_1)}|AgCl,Ag \quad - \quad Ag,AgCl|HCl_{(a_2)}|H_2,Pt$$

Cell reaction

$$\begin{array}{c} 2H^+(a_2)+2Cl^-(a_2)+2Ag \rightarrow 2AgCl+H_{2(g)} \\ H_{2(g)}+2AgCl \rightarrow 2H^+(a_1)+2Ag+2Cl^-(a_1) \\ \hline 2HCl_{(a_2)} \rightarrow 2HCl_{(a1)} \end{array}$$

Nernst equation

$$E=-\frac{RT}{2F}ln\left(\frac{a_1}{a_2}\right)^2 \longrightarrow E=-\frac{RT}{F}ln\frac{a_1}{a_2}$$

What is the main demand to keep the cell working?

Answer: $a_1 \neq a_2$

I. concentration cells: *b. associated with transport: 1. with E_j*

Two electrodes of the same material immersed in two half cells containing two solution of same solute but of different concentrations. The two half cells are contacted via porous membrane where some processes occurs in addition of redox processes..

Cell notation

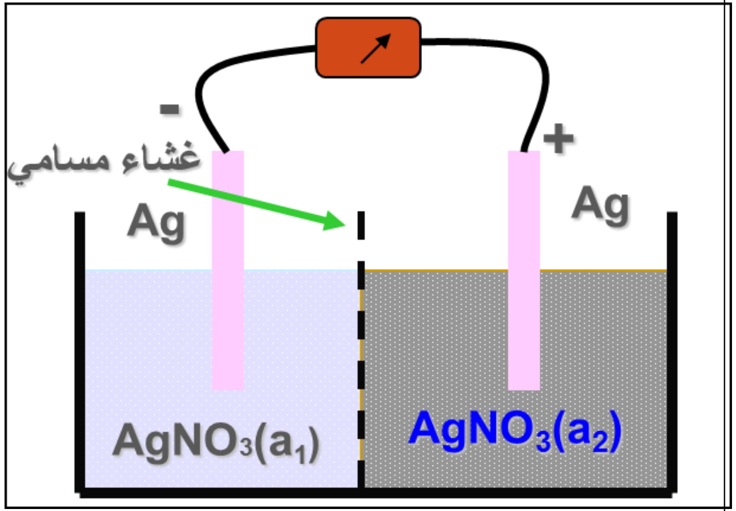
$$Ag|AgNO_3(a_1)\vdots AgNO_3(a_2)|Ag$$

Cell reaction

$$Ag^+(a_2)+e\rightarrow Ag$$

$$Ag\rightarrow Ag^+(a_1)+e$$

$$Ag^+(a_2)\rightarrow Ag^+(a_1)$$



$a_1 < a_2$

Nernst equation

$$E=-\frac{RT}{F}\ln\frac{a_1}{a_2}$$

Where is E°?

What is the main demand to keep the cell working?

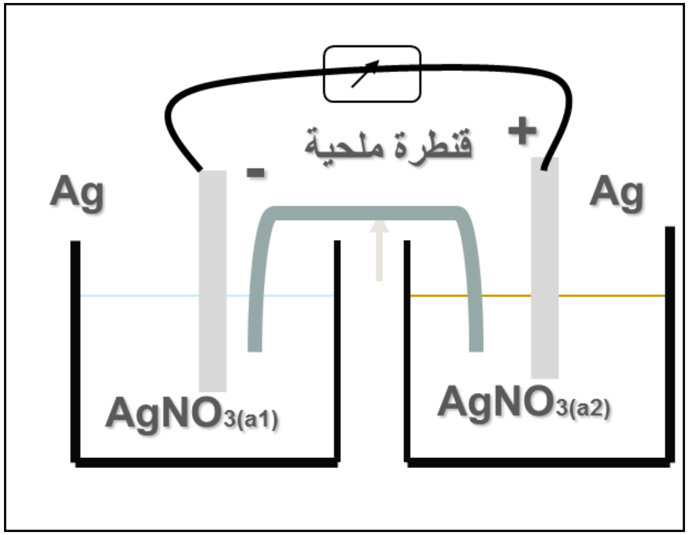
Answer: $a_1 \neq a_2$

I. concentration cells: *b. associated with transport: 2. without E_j*

Two electrodes of the same material immersed two half cells containing two solution of same solute but of different concentrations. The two half cells are contacted via salt bridge.

Cell notation

$$Ag|AgNO_3(a_1)||Ag\,NO_3(a_2)|Ag$$



Cell reaction

$$Ag^+(a_2)+e\rightarrow Ag$$

$$Ag\rightarrow Ag^+(a_1)+e$$

$$Ag^+(a_2)\rightarrow Ag^+(a_1)$$

Nernst equation

$$E=-\frac{RT}{F}ln\frac{a_1}{a_2}$$

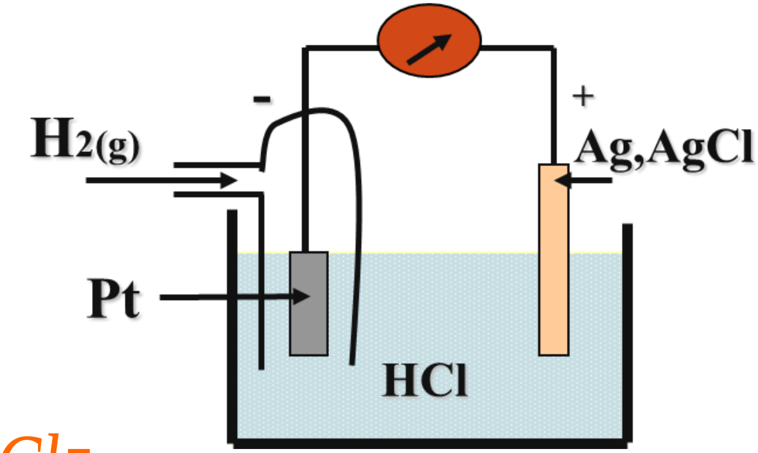
Where is E°?

What is the main demand to keep the cell working?

Answer: $a_1 \neq a_2$

II. Chemical cells: *a. not associated with transport*

- One electrolytic solutions contains cations and anions reversible to the two electrodes.
- Two Different electrodes.
- Different reactions occur at the two electrodes



Cell notation $Pt, H_2|HCl|AgCl, Ag$

Cell reaction

$$2AgCl + 2e \rightarrow 2Ag + 2Cl^-$$

$$H_2 \rightarrow 2H^+ + 2e$$

$$2AgCl + H_2 \rightarrow 2Ag + 2Cl^- + 2H^+$$

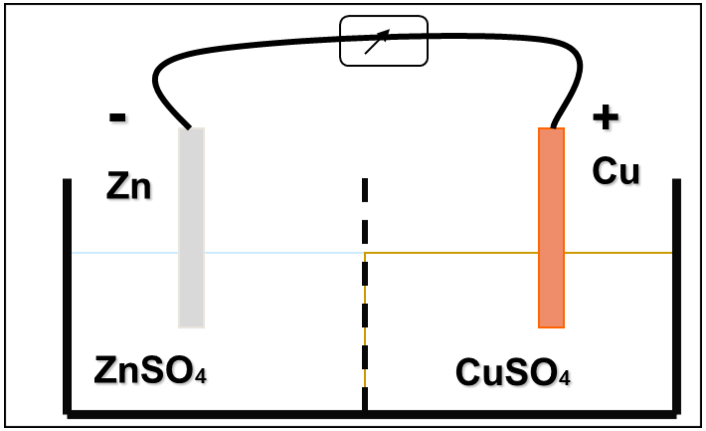
remember that $E^\circ \neq 0$

Nernst equation

$$E = E^\circ - \frac{RT}{2F} ln \frac{(a_{H^+})^2 (a_{Cl^-})^2}{a_{H_2}}$$

II. Chemical cells: *b. associated with transport: 1. with E_j*

- Different two electrodes and two different solution connected via porous membrane..
- Different reactions occur in the vicinity of the two electrodes



Cell notation

$$Zn|ZnSO_4 \vdots CuSO_4|Cu$$

Cell reaction

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

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

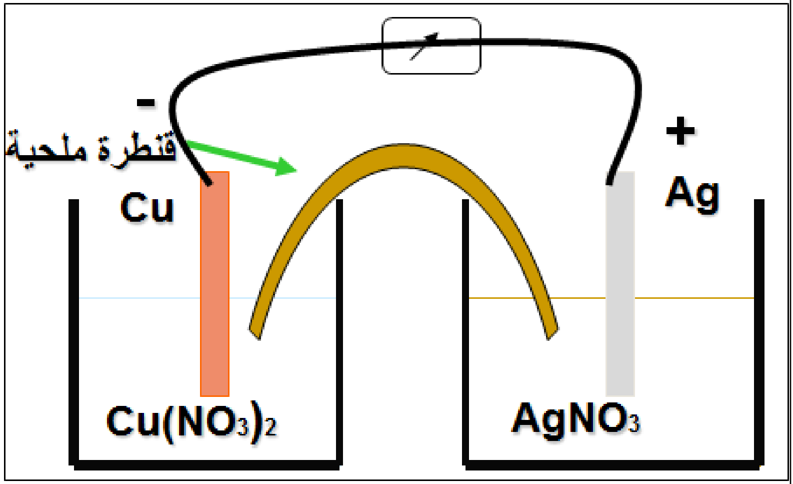
$$Cu^{+2} + Zn \rightarrow Zn^{+2} + Cu$$

Nernst equation

$$E = E^{\circ} - \frac{RT}{2F} \ln \frac{a_{Zn^{+2}}}{a_{Cu^{+2}}}$$

II. Chemical cells: *b. associated with transport: 2. without E_j*

- Different two electrodes and two different solution connected via salt bridge.
- Different reactions occur in the vicinity of the two electrodes



Cell notation $Cu|Cu(NO_3)_2\|AgNO_3|Ag$

Cell reaction

$$2Ag^+ + 2e \rightarrow 2Ag$$

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

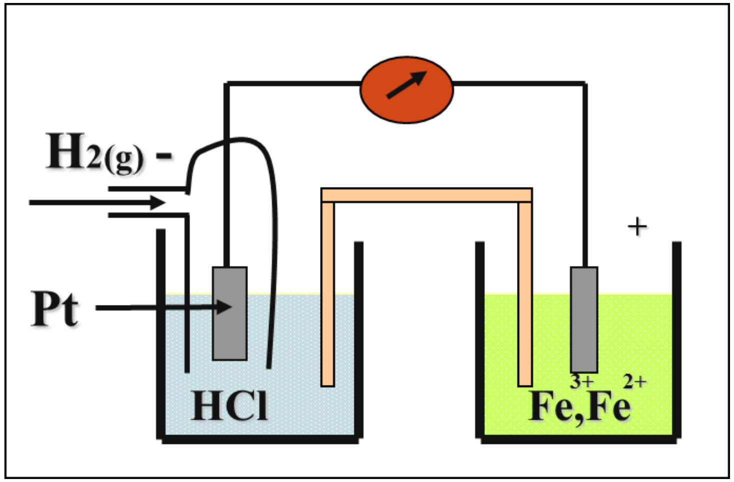
$$2Ag^+ + Cu \rightarrow 2Ag + Cu^{+2}$$

Nernst equation

$$E = E^\circ - \frac{RT}{2F} ln \frac{a_{Cu^{+2}}}{(a_{Ag^+})^2}$$

III. a) Redox cells

- Different two electrodes (redox and inert) and two different solution connected via salt bridge.
- Different reactions occur in the vicinity of the two electrodes



Cell notation

$$Pt,H_2|H^+\|Fe^{+3},Fe^{+2}|Pt$$

Cell reaction

$$2Fe^{+3}+2e\rightarrow 2Fe^{+2}$$
$$H_2\rightarrow 2H^++2e$$
$$2Fe^{+3}+H_2\rightarrow 2Fe^{+2}+2H^+$$

Nernst equation

$$E=E^\circ-\frac{RT}{2F}ln\frac{(a_{Fe^{+2}})^2(a_{H^+})^2}{(a_{Fe^{+3}})^2(a_{H_2})}$$

If we use NHE

$$E=E_c^\circ-\frac{RT}{F}ln\frac{(a_{Fe^{+2}})}{(a_{Fe^{+3}})}$$

III. b) Commercial Cells

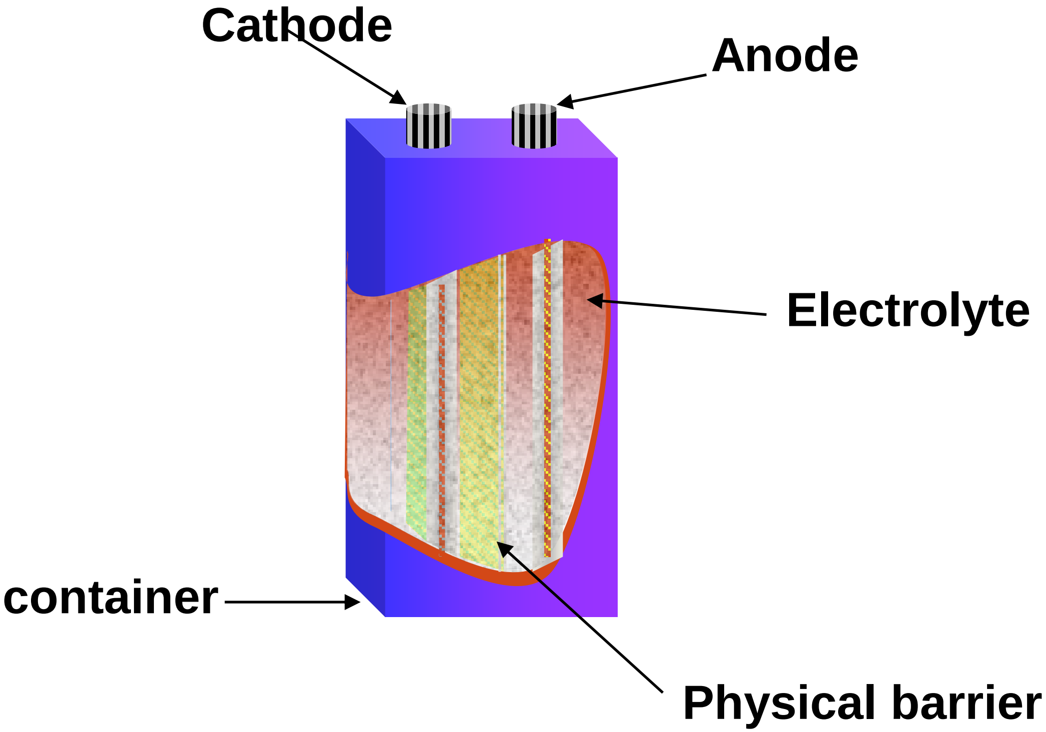
Primary cells

1. Non rechargeable batteries (disposable)
2. Conduct electricity till achieves equilibrium
3. Reactions could not be reversed during charging process
4. Example: Zn/Mg battery

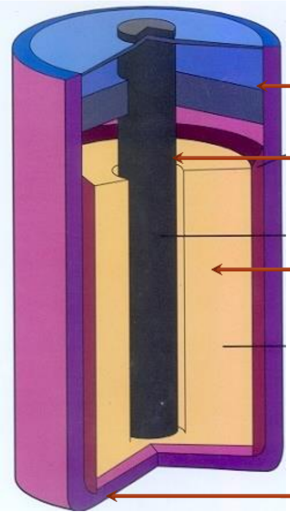
Secondary cells

1. Rechargeable batteries
2. Conduct electricity till discharge
3. Reactions could be reversed during charging process
4. Example: Pb/$PbSO_4$ battery

Primary constituents of the cell



Primary batteries : example: solid Zn/C



Zn anode

Carbon cathode

(carbon, electrolyte(NH_4Cl) and MnO_2)

insulator

Anode $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

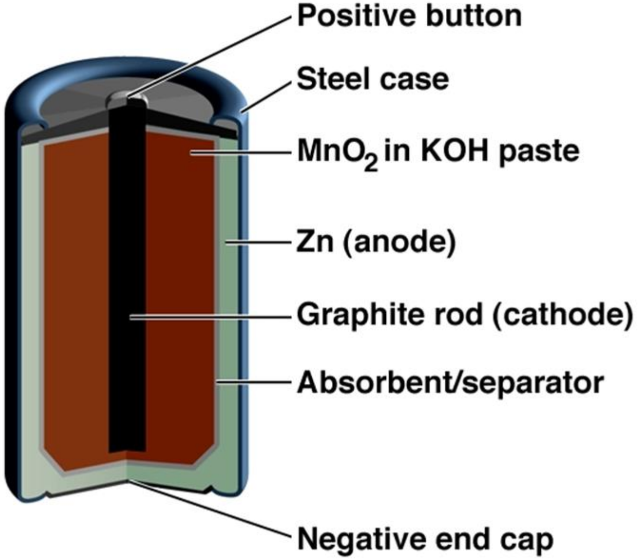
Cathode $2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$

$Zn(s) + 2MnO_2(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2OH^-(aq)$

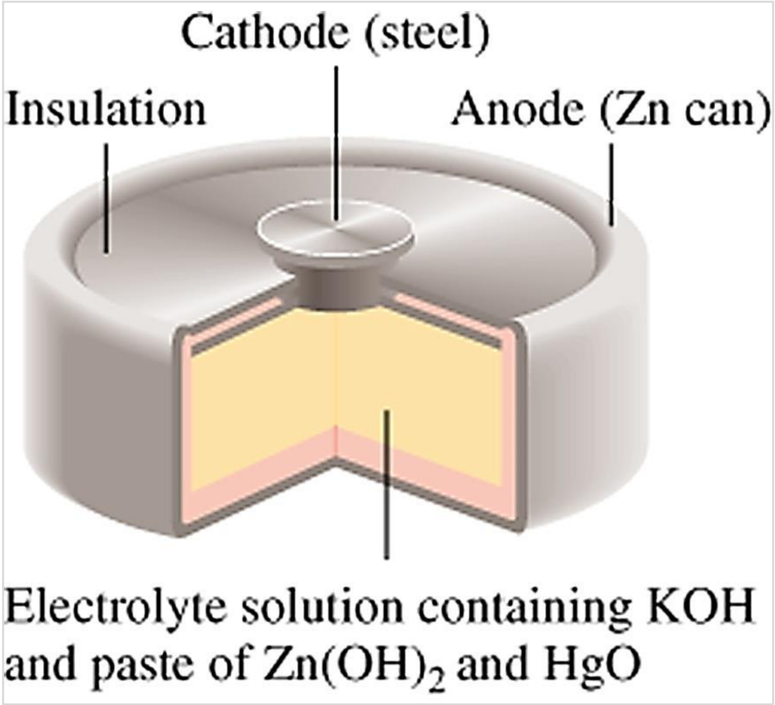
Electrolyte : NH_4Cl / $ZnCl_2$ / MnO_2 / C Powder

Solid alkaline batteries

- NH_4Cl is replaced with KOH or NaOH
- It has longer time than that of solid acidic batteries since Zn dissolves slowly in alkaline solutions
- The cathode is made of Graphite immersed in a paste composed of manganese dioxide, water and potassium hydroxide
- $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + \boxed{H_2O} + 2e^-$ (anode)
- $2MnO_2(s) + H_2O + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$ (cathode)
- EMF is 1.5 V
- It is non-rechargable



Mercury Battery



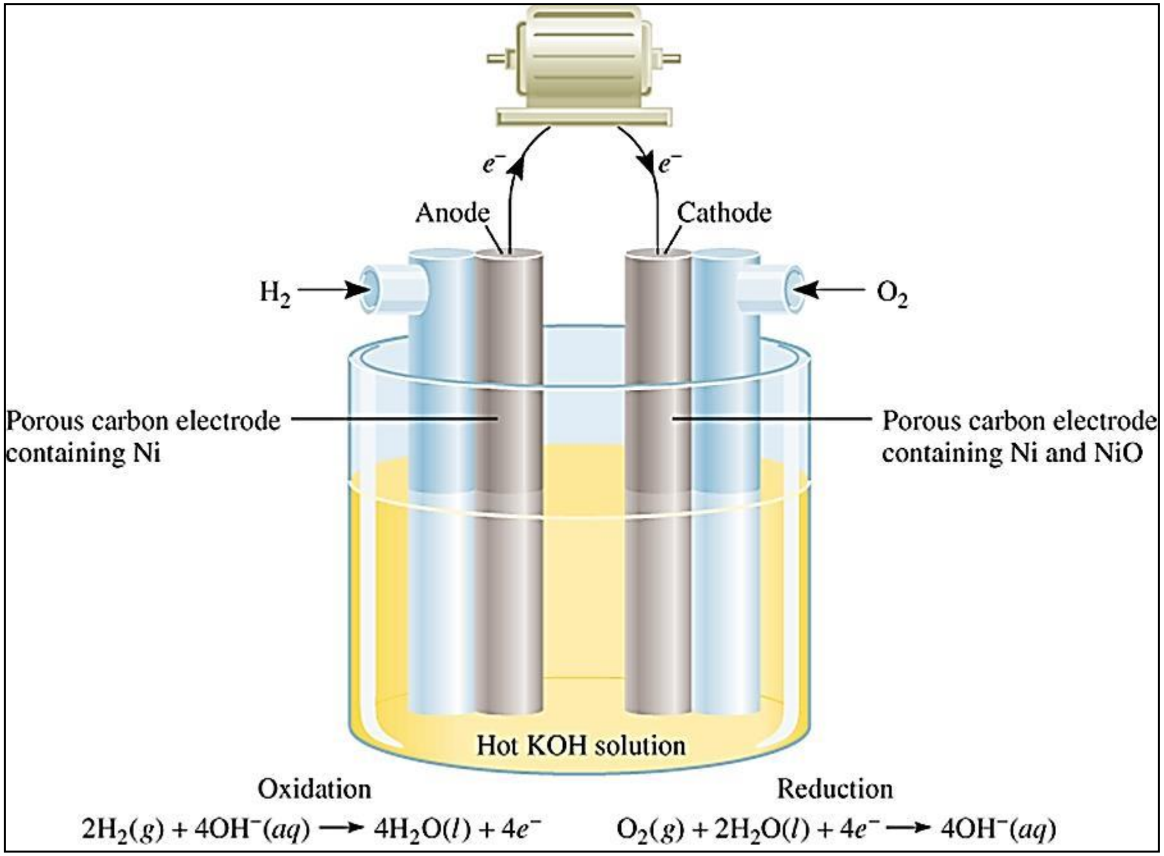
Anode: $Zn(Hg) + 2OH^- (aq) \longrightarrow ZnO (s) + H_2O (l) + 2e^-$

Cathode: $HgO (s) + H_2O (l) + 2e^- \longrightarrow Hg (l) + 2OH^- (aq)$

$Zn(Hg) + HgO (s) \longrightarrow ZnO (s) + Hg (l)$

fuel cell

A ***fuel cell*** is an electrochemical cell that requires a continuous supply of reactants to keep functioning



Anode: $2H_2\ (g) + 4OH^-\ (aq) \longrightarrow 4H_2O\ (l) + 4e^-$

Cathode: $O_2\ (g) + 2H_2O\ (l) + 4e^- \longrightarrow 4OH^-\ (aq)$

$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (l)$

Secondary batteries

Nickel / Cadmium Battery

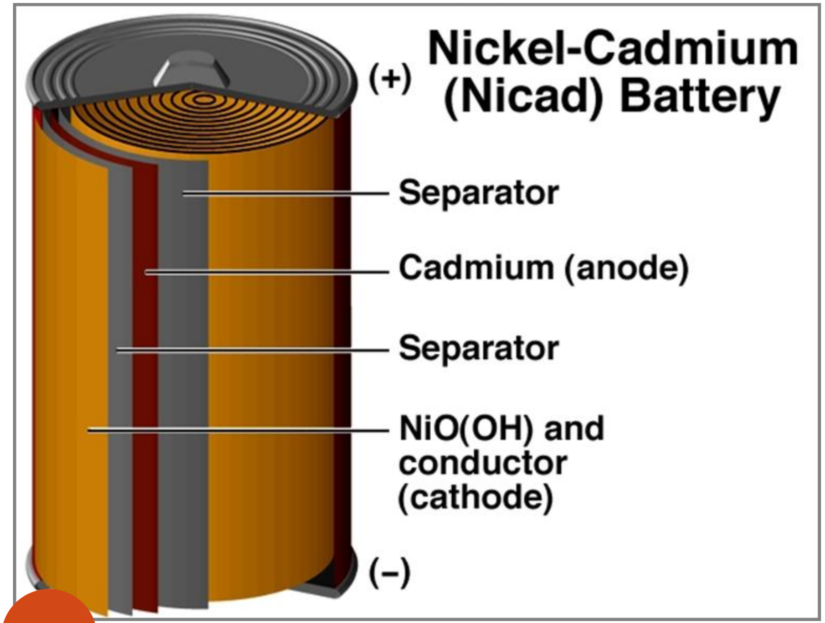
Electrolyte : KOH

Current collectors : Ni & Cd

Anode $Cd(s) + 2OH^{-}(aq) \rightarrow Cd(OH)_2(s) + 2e^{-}$

Cathode $2NiO(OH)(s) + 2H_2O(l) + 2e^{-} \rightarrow 2Ni(OH)_2(s) + 2OH^{-}$

$$2NiO(OH)(s) + Cd(s) + 2H_2O(l) \rightarrow 2Ni(OH)_2(s) + Cd(OH)_2(s)$$



Lead / Acid Battery

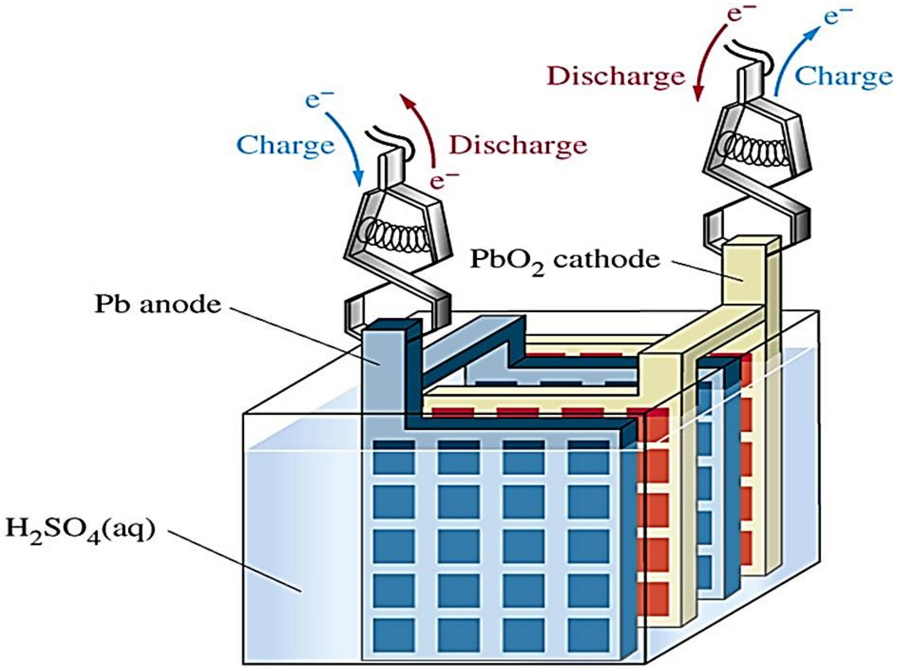
Electrolyte : H_2SO_4

Current collectors : Both Pb

Anode rxn $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

Cathode rxn $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow 2H_2O(l) + PbSO_4(s)$

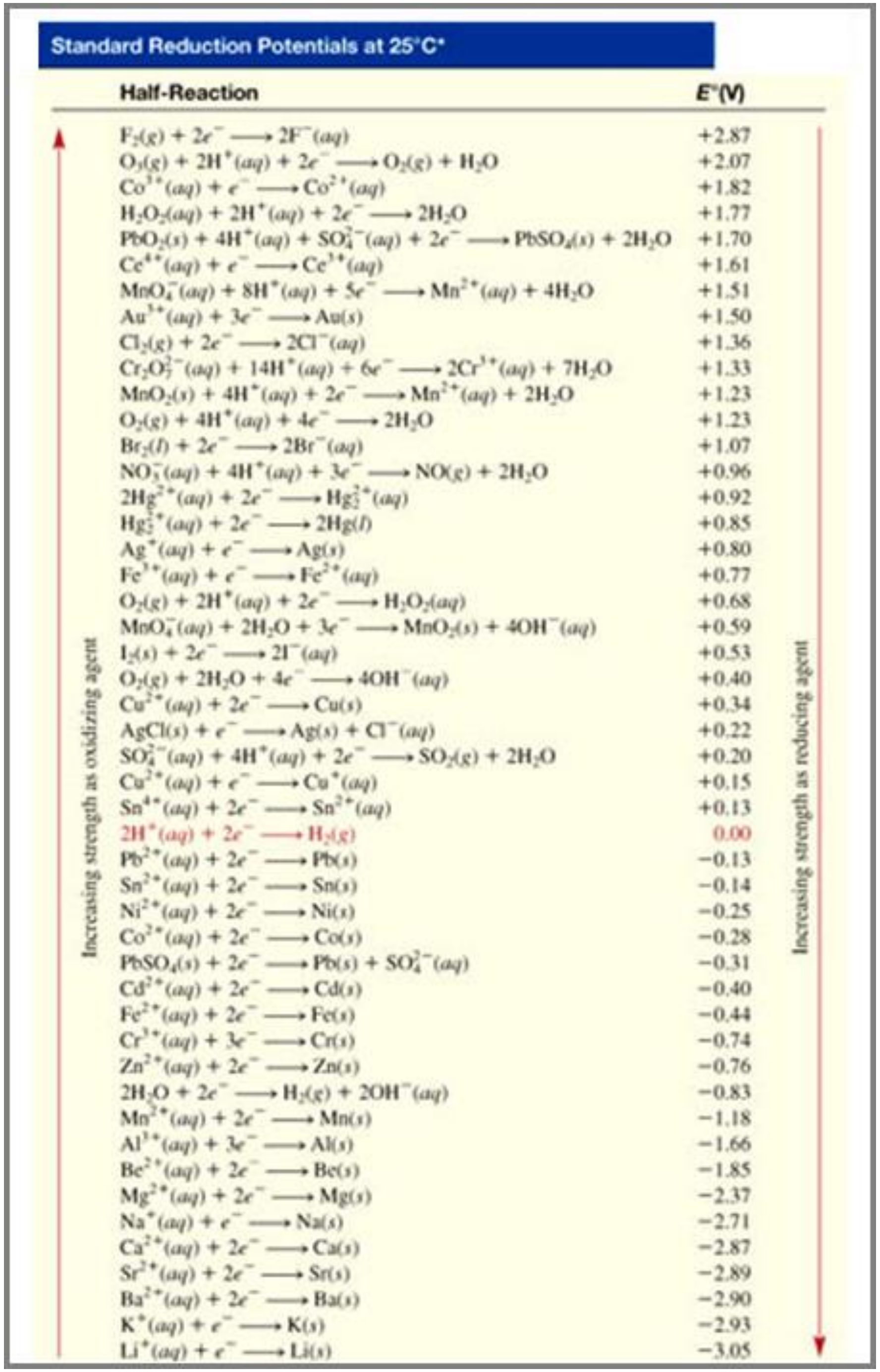
Cell rxn $PbO_2(s) + Pb(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$



Type of Battery	Advantages	Disadvantages
Lead acid	Rechargeable Long life 12 V	Heavy Contain acid Weather issues
Alkaline/Dry cell	Inexpensive No toxic metals used Lots of power (1.5 V down to 1.2 V)	Heavier
Lithium (solid state)	Lightweight Higher capacity (3.6-3.9 V) Rechargeable Longer lasting Less likely to leak/explode	Expensive
Fuel cells	No recharging No harmful pollutants	high initial cost Fuel not readily available
Nickel-Cadmium (Ni-Cd)	Fast/simple charge (rechargeable) High # charges 1.2 V continuously	Toxic metals Expensive
Mercury	More constant voltage (1.35 V) Longer life Lighter	More expensive

Why are some batteries rechargeable while others are not?

Attempting to recharge a non-rechargeable batteries does not regenerate the chemicals but usually forms hydrogen gas and case to burst explosively.



Standard Reduction Potentials at 25°C*

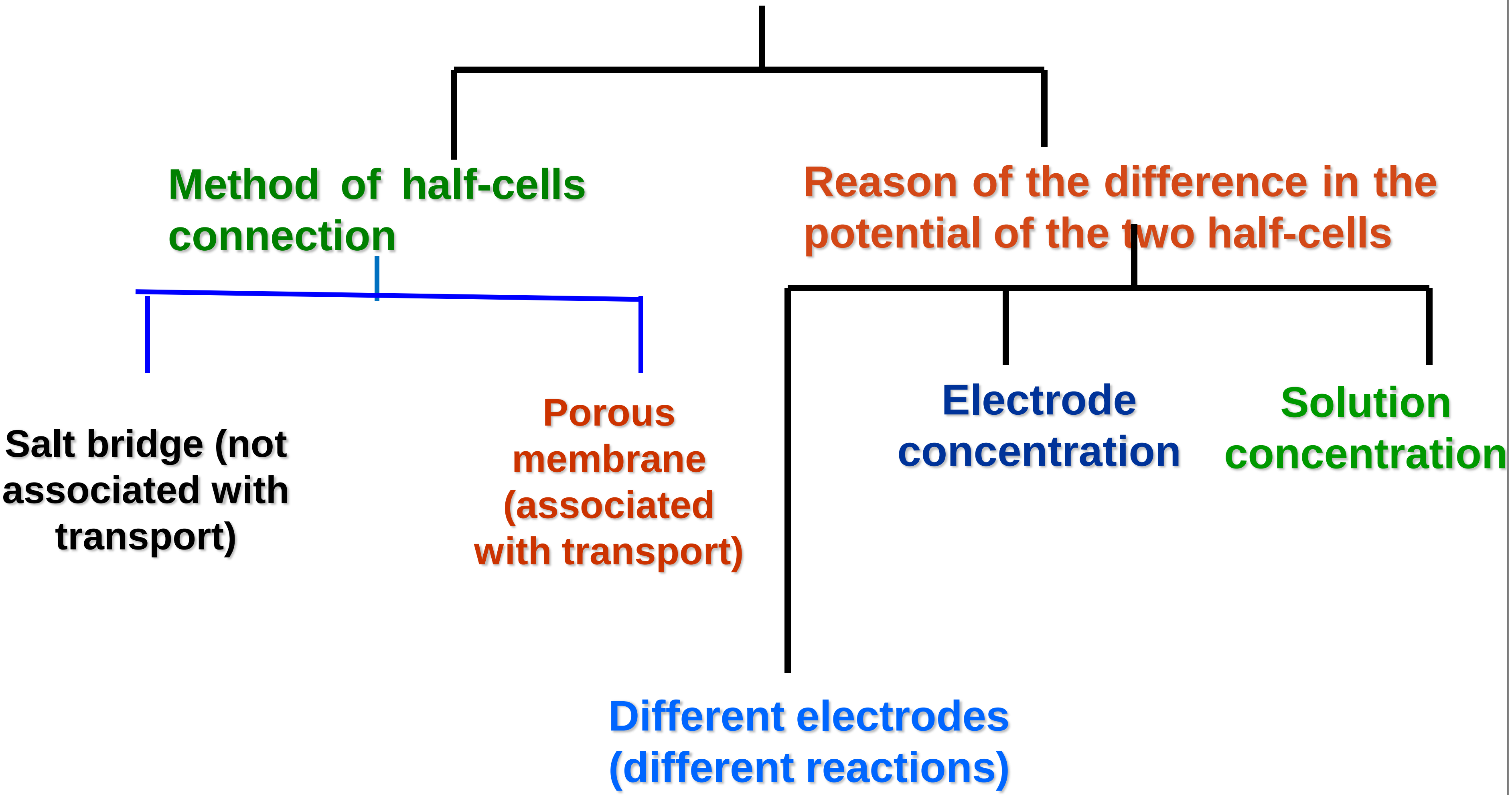
Half-Reaction	E°(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as oxidizing agent

Increasing strength as reducing agent

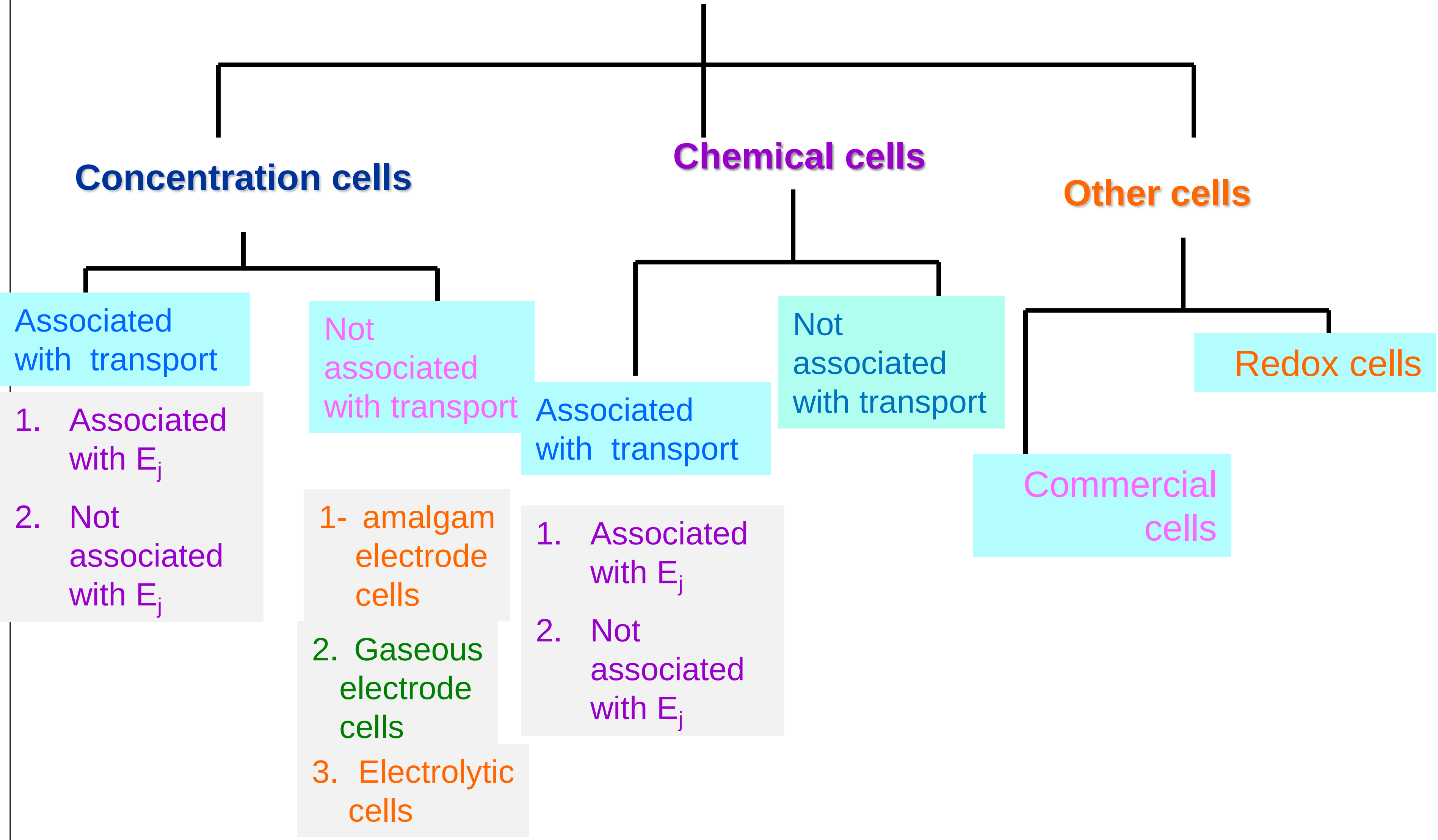
Electrochemistry 1
Part 5

Classification of Cells



- Method of half-cells connection
  - Salt bridge (not associated with transport)
  - Porous membrane (associated with transport)
- Reason of the difference in the potential of the two half-cells
  - Different electrodes (different reactions)
  - Electrode concentration
  - Solution concentration

Classification of Cells



Concentration cells

Associated with transport

1. Associated with E_j
2. Not associated with E_j

Not associated with transport

1- amalgam electrode cells
2. Gaseous electrode cells
3. Electrolytic cells

Chemical cells

Associated with transport

1. Associated with E_j
2. Not associated with E_j

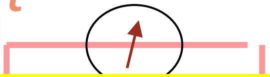
Not associated with transport

Other cells

Redox cells

Commercial cells

I. concentration cells: *a not associated with transport*



$a_1 > a_2$

What is the main demand to keep the cell working?

[redacted]

Answer: a_1Í a_2

ELECTROCHEMISTRY 1
PART 6

Measurement of the EMF of a cell

1. Direct method

- **The potential of an electrochemical cell is measured using voltammeter**
- **Disadvantages:**

a) It is not accurate.

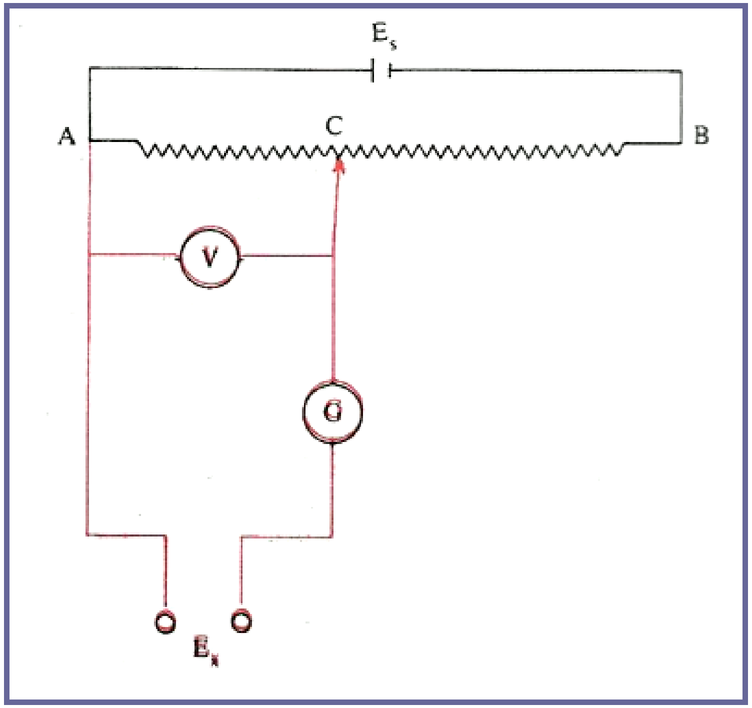
b) A high current is drawn from the cell which causes the occurrence of chemical reactions in the vicinity of the electrodes leading to changes in the composition of the solution and/or the electrode. The voltage value obtained by the voltammeter is smaller in value than that obtained in measurements without current passage.

Potentiometric Method

- To determine the potential of a cell E_x it will be inserted in the following circuit
- The potential of the cell E_x will be equal to the potential of E_{AC} when the current passing in the galvanometer equals to zero

$$E_{AC} = i.R_{AC}$$

- The potential E_{AC} is given by the voltammeter



- AB: variable resistance
- G: Galvanometer
- V: Voltammeter

Applications of EMF measurements

1. Determination of solubility product of sparingly soluble salt

$$PbSO_4 \Leftrightarrow Pb^{+2} + SO_4^{-2}$$

cell

$$PbSO_4 + 2e \rightarrow Pb + SO_4^{-2}$$

cathode

$$Pb \rightarrow Pb^{+2} + 2e$$

anode

$$Pb / PbSO_4 // Pb^{+2} / Pb$$

$$E^\circ_{cell} = E^\circ_c - E^\circ_a$$

$$E^\circ_{cell} = -0.36 - \left(-0.126\right) = -0.234V$$

$$\ln K = \frac{ZFE^\circ}{RT} = -\frac{2 \times 96500 \times 0.234}{8.314 \times 298} = -18.23$$

$$K_{sp} = 1.21 \times 10^{-8}$$

2. Solubility product of complex ions

$$[Cu(NH_3)_4]^{+2} \Leftrightarrow Cu^{+2} + 4NH_3$$

$$1-\alpha \qquad\qquad \alpha \qquad\qquad 4\alpha$$

$$K_{dis} = \frac{[Cu^{+2}][NH_3]^4}{[Cu(NH_3)_4]^{+2}}$$

$$K_{dis} = \frac{\alpha.(4\alpha)^4}{(1-\alpha)}$$

if C is the solution concentration

$$K_{dis} = \frac{\alpha C.(4\alpha C)^4}{(1-\alpha)C}$$

If we determine the concentration of Cu^{+2} the other values will be known

$$Cu/CuSO_4(0.1M)+NH_4OH(0.1M)//CuSO_4(0.1M)/Cu$$

The potential of the cell is given by the following equation

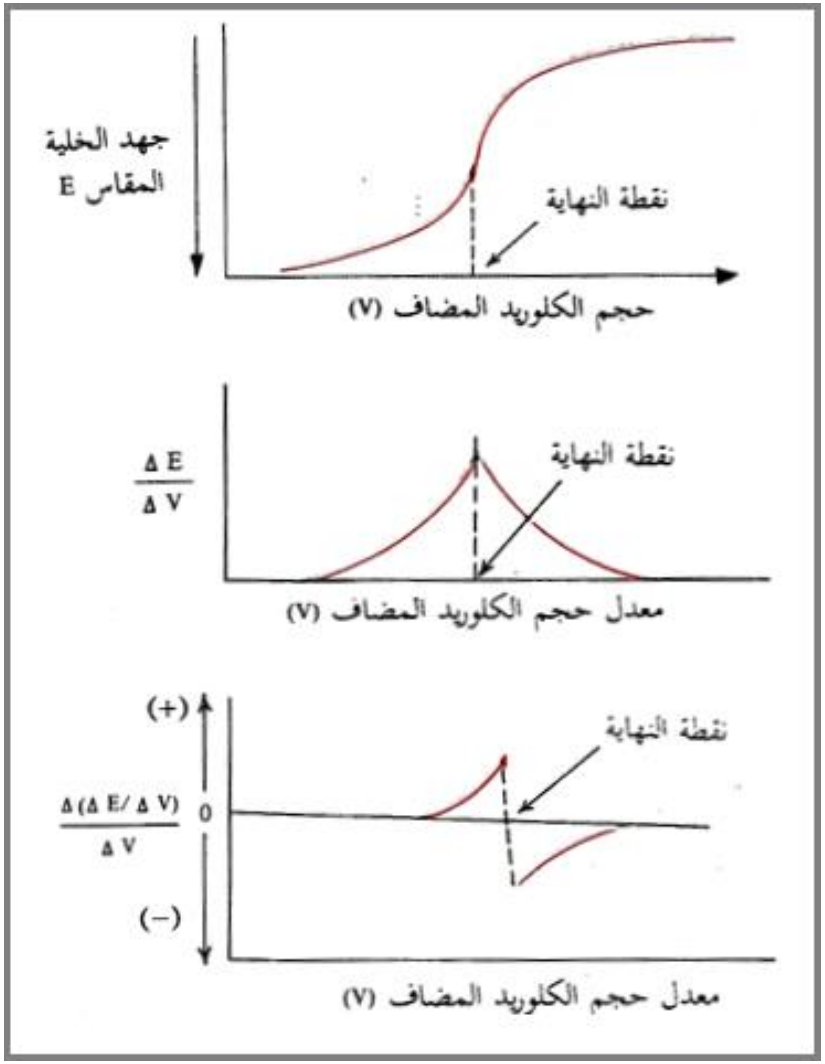
$$E=-\frac{2.303RT}{nF}\log\frac{[Cu^{+2}]}{0.1}$$

$$K_{dis}=\frac{\alpha C.(4\alpha C)^4}{(1-\alpha)C}$$

3.Potentiometric titration

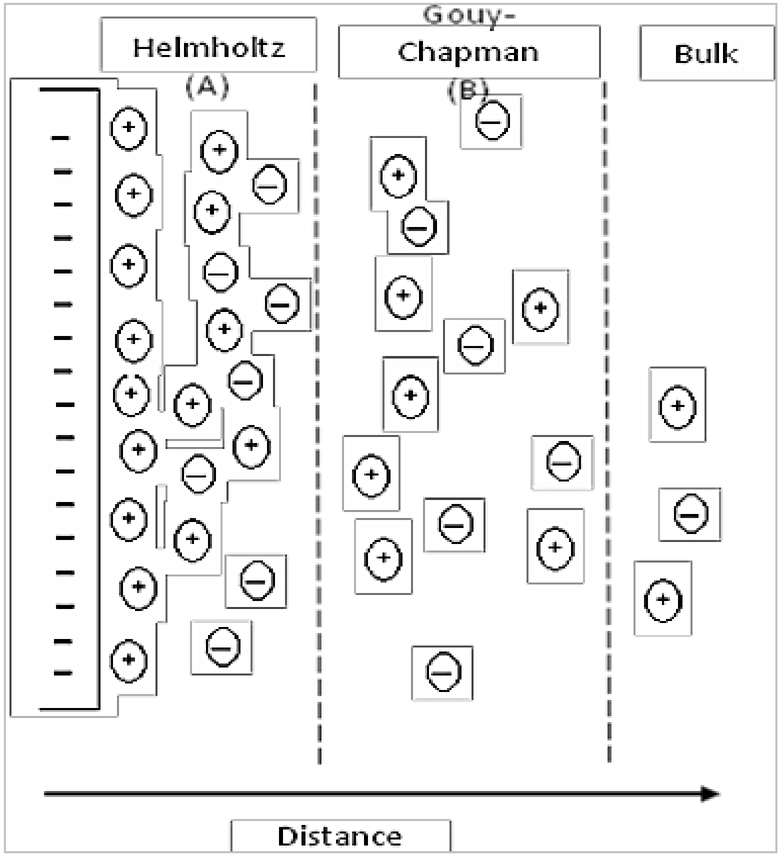
Potentiometric titration could be used to determine strong, weak and Polly-alkaline acids via titration with strong alkali using glass electrode which is sensitive to solution pH.

Determination of silver nitrate concentration is carried out using standard solution of NaCl and solid electrode which is sensitive to silver cation in solution. At end point sudden rise in cell potential is obtained

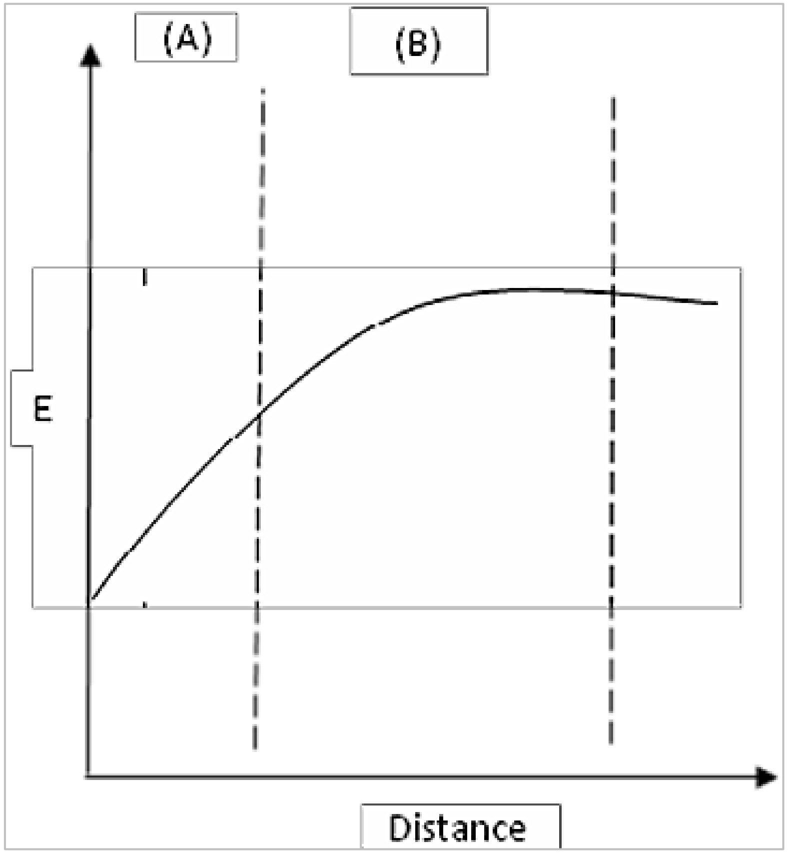


$$E_{cell} = (K + E^{o}_{Ag}) + 0.059 \log[Ag^{+}]$$

Ionic Double Layer and Potential Distribution

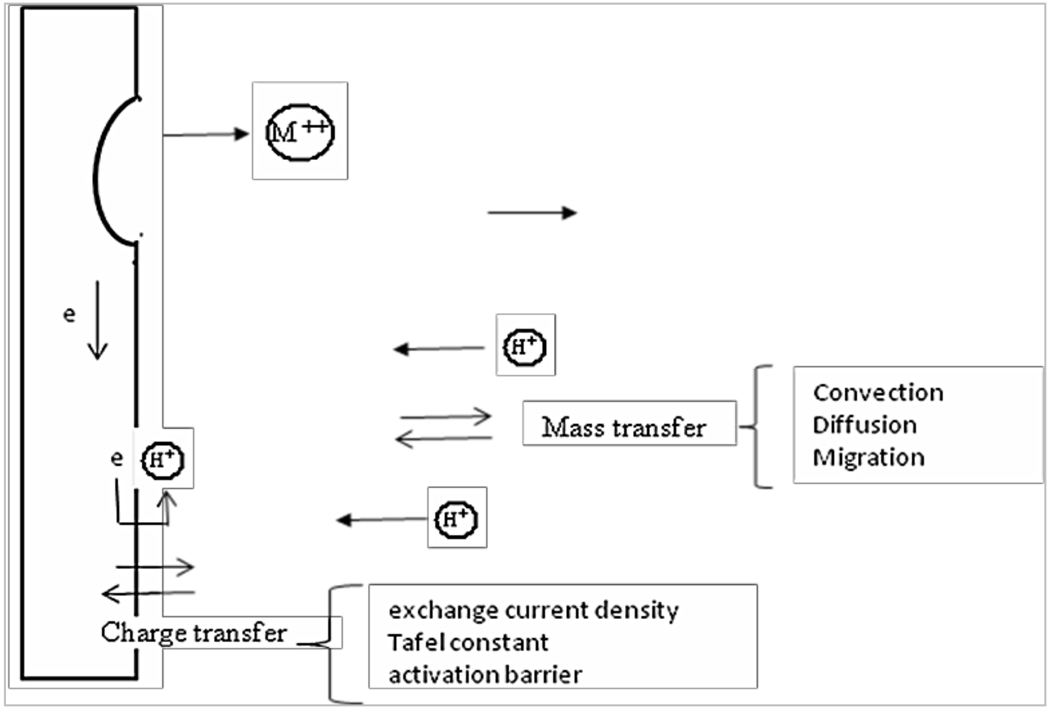


. *Double layer at electrode – solution interface*



Potential distribution across distance

Processes at an electrochemical interface are schematically represented below



Transport processes at electrochemical interface

Mass transport to metal surface involves forces such as convection, diffusion and migration, depending on presence or absence of electric field and flow conditions. Concentration polarization is controlled by diffusion gradients.

Polarization

- The deviation of voltage from the value at equilibrium upon the passage of current is called **polarization**.
- For an electrode, the deviation of electrode potential from its equilibrium state is called the **electrode polarization**.
- **overpotential**, denoted as *η* and expressed in volts.

$$\boxed{\begin{aligned}\eta_C &= E_C^o - E_C \\ \eta_a &= E_a - E_a^o\end{aligned}}$$

Various overpotentials

- **Concentration overpotential**
- **Activation overpotential** (electrochemical overpotential)
- **Ohmic overpotential**

Types of Polarization

Activation polarization

It is due to the decrease in the rate of the electrode reaction

Concentration polarization

It is due to the difference in the concentration of the electroactive species between baulk solution and electrode surface

Ohmic polarization

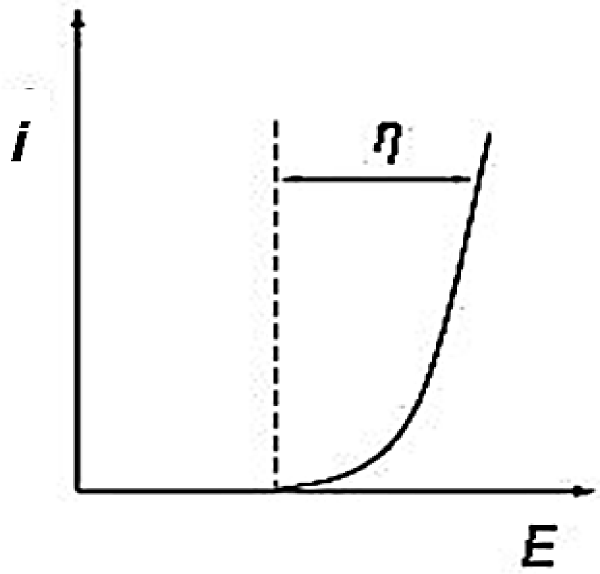
It arises from the inability to decrease the distance between the working and the reference electrodes to zero value

The contribution to polarization due to IR drops is referred to as Resistance polarization, so Total polarization:

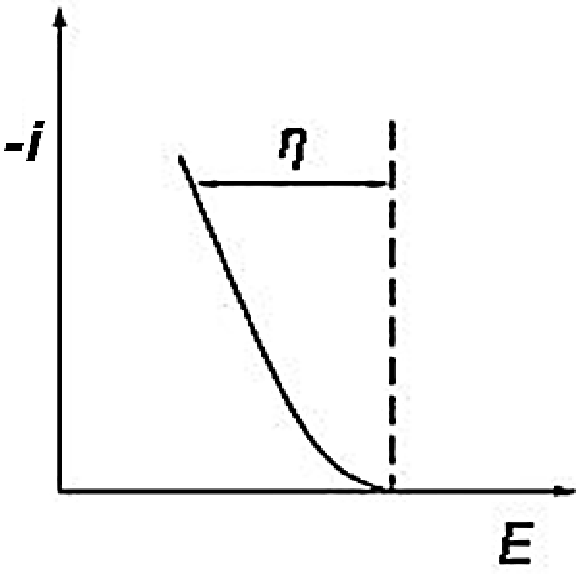
$$\eta_T = \eta_{Act} + \eta_{Conc} + \eta_{resist}$$

Anodic and cathodic polarization

- Anodic polarization is the shift of the electrode potential to more positive (or less negative) value and the electrode acts as anode
- Cathodic polarization is the shift of the electrode potential to more negative (or less positive) value and the electrode acts as cathode

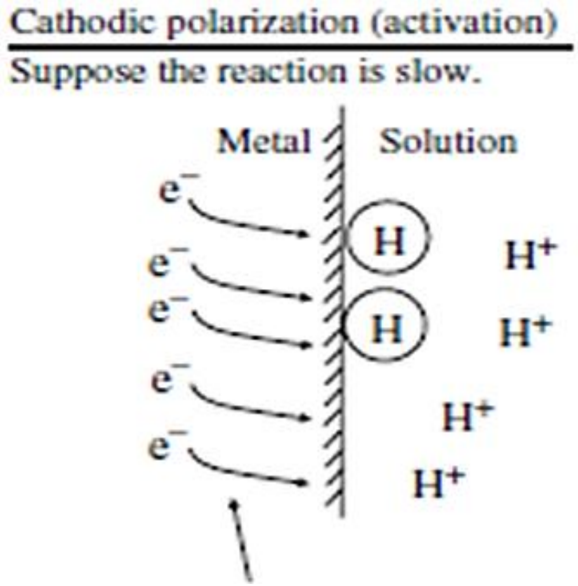


$$\boxed{\eta_a = E_a - E_a^o}$$



$$\boxed{\eta_C = E_C^o - E_C}$$

What happens in the cathodic polarization?



- Suppose the evolution of hydrogen gas at the electrode surface.
- Initially hydrogen atoms is formed at electrode surface as follows:

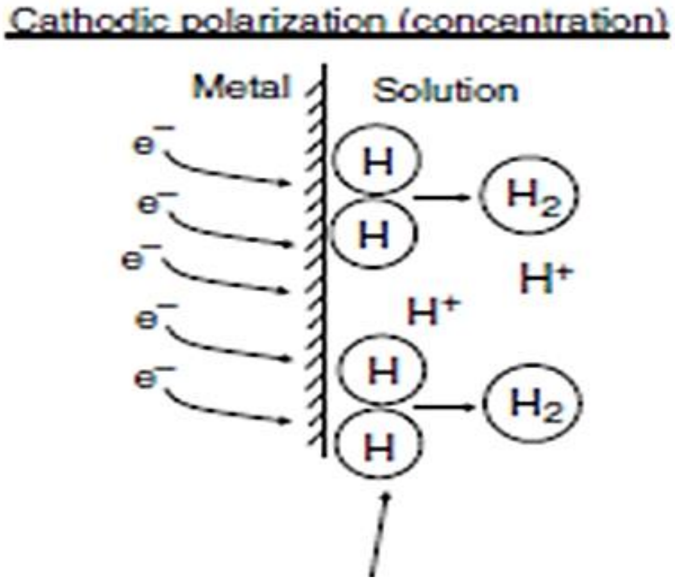
$$2H^+ + 2e \longrightarrow 2H_{ads}$$

- The adsorbed hydrogen gas will combine to form hydrogen gas::

$$2H_{ads} \longrightarrow H_2$$

- If the electrons will arrive to the electrode faster than its reaction with hydrogen ions to form adsorbed atoms then the concentration of electrons in the metallic side of the interface will be increased where the electrode will be charged negatively and the electrode potential will be shifted to negative value due to activation polarization.

- If hydrogen ions diffuse slowly to the electrode surface then the gain of electrons will be slowly leading to electrons to be accumulated at the electrode surface and then the electrode will be charged negatively and the electrode potential is shifted to negative value but due to concentration polarization



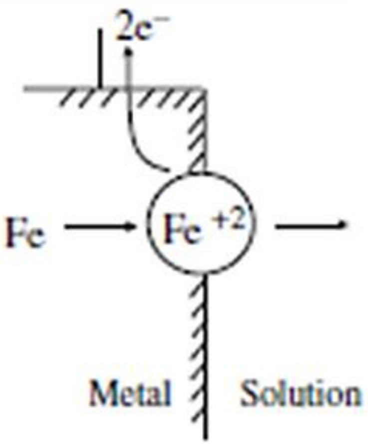
What happens in the anodic polarization?

- Suppose the reaction is slow

$$Fe \rightarrow Fe^{+2} + 2e$$

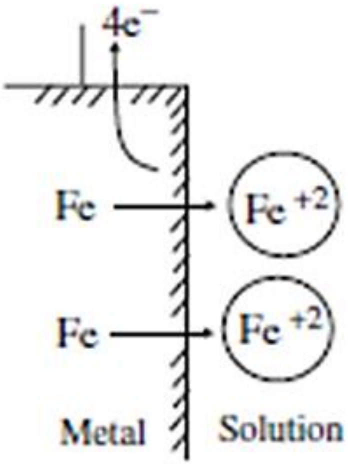
- Then the electrons exit from the surface faster than Fe atoms leave the matrix
- The concentration of electrons is decreased at the the metal side of the interface .
- The electrode potential is shifted to more positive value due to activation polarization.

Anodic polarization (activation)



- Suppose the products are slow to diffuse away from the interface.
- The surface will be charged positively and the electrode potential is shifted to more positive value due to concentration polarization.

Anodic polarization (concentration)



Concentration polarization

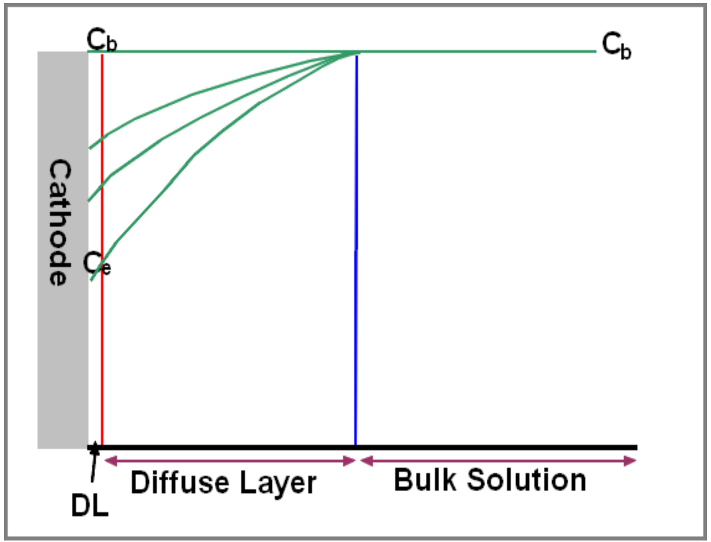
- **If the concentration of hydrogen gas in the bulk solution is C_b and at he electrode surface is C_e**
- **When the circuit is opened, the electrode potential is**

$$2H^+ + 2e^- \Leftrightarrow H_2$$

$$E = E^o + \frac{RT}{zF}\ln\frac{Ox}{Red}$$

$$E = E^o + \frac{RT}{zF}\ln H^+$$

$$E_{rev} = E^o + \frac{RT}{zF}\ln C_b \rightarrow (1)$$



- **Where E_{rev} is the reversible potential of the electrode**
- **When the circuit is closed and If the electrode reaction is fast and reversible and if the rate of diffusion of hydrogen ions (from bulk solution to the electrode surface) is slow, then the concentration of hydrogen ions at the elctrode surface will drop to Ce and the reaction is controlled with diffusion.**

In this case, The electrode potential is the irreversible potential E_{irr}

$$2H^+ + 2e^- \Rightarrow H_2$$

$$E_{irr} = E^o + \frac{RT}{zF}\ln C_e \rightarrow (2)$$

- To keep the rate of hydrogen gas evolution is constant and to keep the current is constant the potential is raised from E_{rev} to E_{irr} by amount is called overpotential (which is concentration overpotential)

$$\eta = E_{irr} - E_{rev}$$

$$\eta = (E^o + \frac{RT}{zF}\ln C_e) - (E^o + \frac{RT}{zF}\ln C_b)$$

$$\eta = \frac{RT}{zF}\ln C_e - \frac{RT}{zF}\ln C_b$$

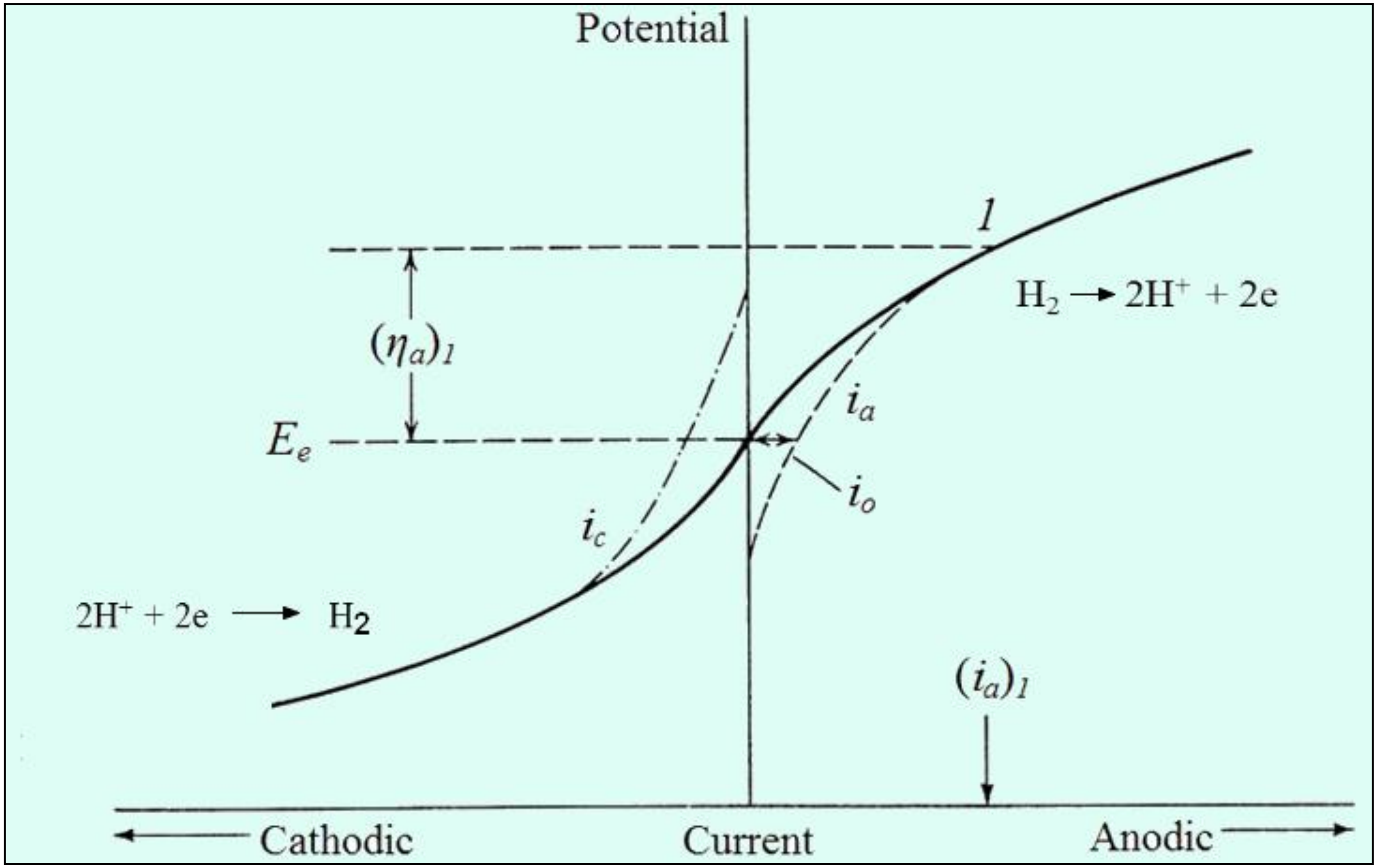
$$\eta = \frac{RT}{zF}\ln\frac{C_e}{C_b}$$

Activation polarization

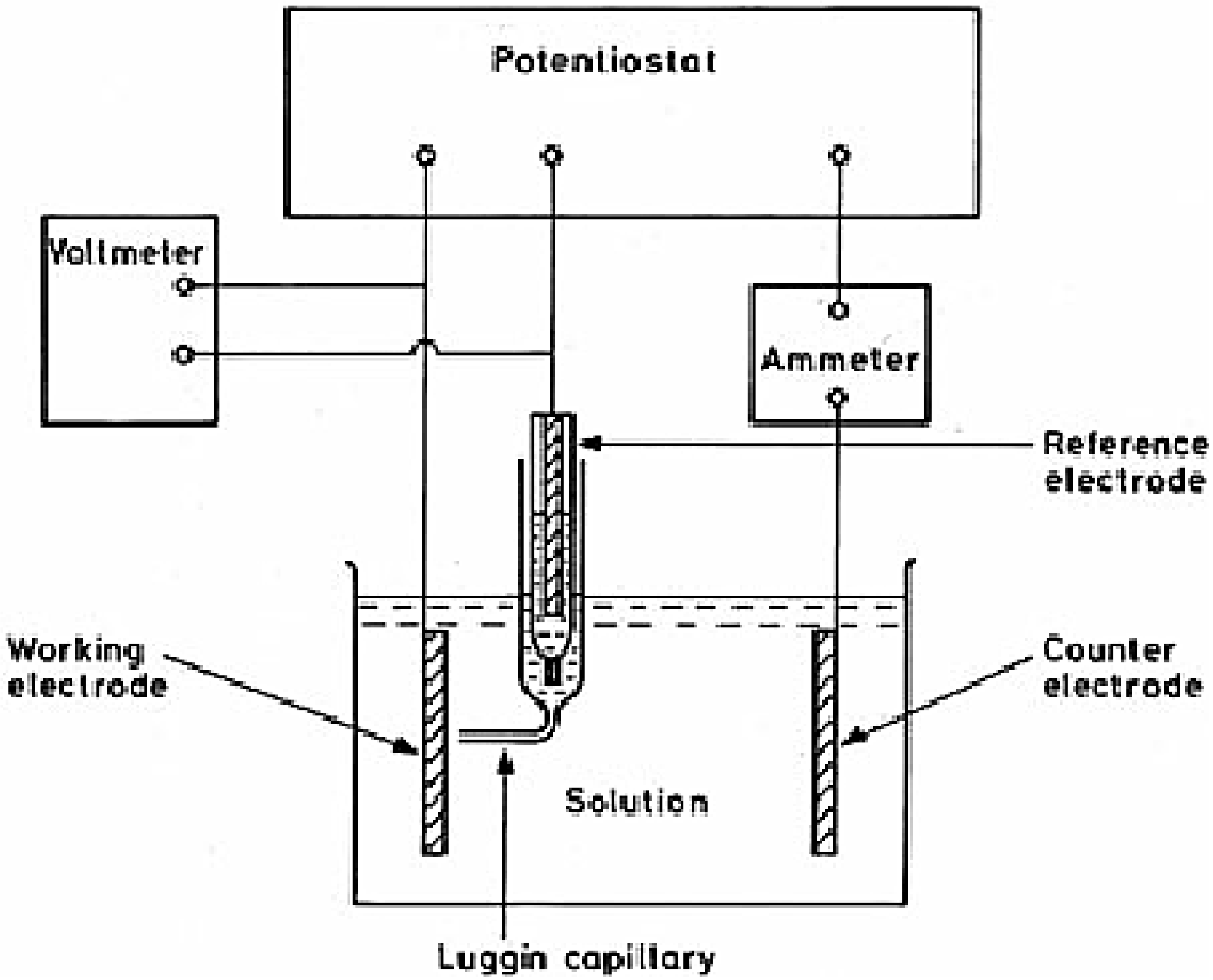
Butler-Volmer equation

$$i_{net} = i_o \left\{ e^{\left(\alpha \frac{nF}{RT}\eta\right)} - e^{\left(-[1-\alpha]\frac{nF}{RT}\eta\right)} \right\};$$

α: is charge transfer coefficient



Determination of polarization curves



Coordination Chemistry

Code : 351Ch

For

3^{rd} Students

(Zoology and Entomology group)

By

Dr. Heba Nassar Abeit

القائم بالتدريس:

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COORDINATION COMPOUNDS

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- **Introduction**
- **Ligands and their types**
- **Werner's coordination theory**
- **Effective atomic number concept**
- **Nomenclature of coordination compounds**
- **Isomerism of coordination compounds**
- **Importance and applications of Coordination Compounds**
- **References**

1. **INTRODUCTION**

You have already studied in your earlier classes that there are two types of compounds. The compounds that can easily dissociate into their constituent ions in aqueous medium are called simple salts and double salts such as NaCl, $MgCl_2$, $FeSO_4.(NH_4)_2SO_4.6H_2O$, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, etc. On the other hand, the compounds which do not dissociate into their constituent ions in any solvent are known as coordination or complex compounds such as $[Cu(NH_3)_4]^{2+}$. Transition metals have an ability to form a number of coordination compounds due to their small size, high charge and presence of empty d orbitals on the metal ion. A compound formed from the union of metal ion (an electron deficient species, central metal atom/ion; Lewis acid) and electron rich species (ligand; Lewis base) which can donate one electron pair is called coordination compound or complex compound. The coordination compounds can be represented by the general formula, $[MLn]^{\pm m}$, where M is a metal ion, L is electron rich species; n is the number of L attached to the metal atom/ion and m is the charge on complex ion.

Some metal complexes were prepared and used in the eighteenth century in the form of metal salts and vegetable extracts as paints.

In 1798, $CoCl_3.6NH_3$ was discovered. Werner gave a theory to understand the bonding in such compounds about a century later in 1893. We are studying chemistry of coordination compounds because they have many applications in analytical / environmental chemistry, metallurgy, biological systems, industries and medicine.

A salt is formed by the neutralization of an acid by a base. There are different types of salts. They are:-

a) Simple salt
b) Molecular (or) addition compounds

a) **Simple salt**

A simple salt is formed by the neutralization of an acid by a base. KOH + HCl → KCl + H2O

Normally, a simple salt ionizes in water and produces ions in solution. The solution of the simple salt exhibits the properties of its component ions.

b) **Molecular (or) addition compounds**

i) **Double salts**

These are molecular compounds which are formed by the evaporation of solution containing two (or) more salts in stoichiometric proportions. Hence the molecular compounds which dissociate in solution into its constituent ions are known as double salt. Double salts retain their properties only in solid state.

They are also called as lattice compounds.

Example

Mohr’s salt

$K_2SO_4 \,.\, Al_2(SO_4)_3 \,.\, 24H_2O \rightarrow 2K^+ + 2Al^{3+} + 4SO_4^{2-} + 24H_2O$

The double salts give the test of all their constituent ions in solution.

ii) **Coordination (or complex) compounds**

Coordination compound is ‘a compound formed from a Lewis acid and a Lewis base’. The molecular compounds, do not dissociate into its constituent ions in solution are called coordination compounds.

Example

$Fe(CN)_2 + 4KCN \rightarrow Fe(CN)_2 \,.\, 4KCN$ (or) $K_4[Fe(CN)_6]$

Ferrous cyanide

$Fe(CN)_2 \,.\, 4KCN \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$

Complex anion

In $K_4[Fe\ (CN)_6]$ the individual components lose their identity.

The metal of the complex ion is not free in solution unlike metal in double salt in solution.

Nature of coordination (or) complex compounds

i) An anionic complex compound contains a complex anion and simple cation.

$K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$

simple cation   complex anion

ii) A cationic complex contains complex cation and simple anion

$[Co(NH_3)_6]Cl_3 \rightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$

Complex cation   simple anion

iii) A neutral complex , In the case of a complex compound,

$[Cr(NH_3)_6][Co(CN)_6]$, it gives both complex cation and complex anion

$[Cr(NH_3)_6][Co(CN)_6] \rightarrow [Cr(NH_3)_6]^{3+} + [Co(CN)_6]^{3-}$

complex cation   complex anion

TERMINOLOGY USED IN COORDINATION CHEMISTRY

(a) **Lewis Acid**

All electron acceptors are Lewis acids.

(b) **Lewis Base**

All electron donors are Lewis base.

(c) **Central metal ion**

In the complex ion an acceptor accepts a pair of electrons from the donor atoms. The acceptor is usually a metal / metal ion to which one (or) more of neutral molecules (or) anions are attached. The acceptor metal cation is referred to as central metal cation.

Hence, central metal cation in a complex serves as a lewis acid.

(d) **Ligand** (Latin word meaning to bind)

A ligand is an ion (or) a molecule capable of functioning as an electron donor. Therefore the neutral molecules or ions which are directly attached to the central metal ion are called as ligand (or) coordination groups. These coordination groups or ligands can donate a pair of electrons to the central metal ion (or) atom. Hence, in a complex compound ligands act as Lewis bases.

Examples:

$[Ni(NH_3)_6]^{2+}$: Ligand = NH_3 molecule and Central metal ion = Ni^{2+}

$[Co(NH_3)_5Cl]^{2+}$: Ligands = NH_3 molecule and Cl^- ion

(e) Coordination number

The total number of coordinate bonds through which the central metal ion is attached with ligand is known as coordination number. Coordination number may be two, three, four, five, six, seven, eight, nine or even higher in case of lanthanides and actinides . Coordination number depends on size, charge and electronic configuration and nature of meal/ion and ligands

For example

- large metal atoms show high CN
- bulky ligands reduce coordination number

-Lewis bases easily donate electrons to metals and metals with lesser number of electrons can easily accept electrons

Examples $K_4[Fe(CN)_6]$ the coordination number of Fe(II) is 6 and in $[Cu(NH_3)_4]SO_4$ the coordination number of Cu(II) is 4.

(f) Coordination sphere

the central metal ion and the ligands that are directly attached to it, are enclosed in a square bracket, called coordination sphere or first sphere of attraction

(g) Oxidation number or Oxidation state of central metal atom/ ion

It is the number that represent an electric charge with an atom or ion actually has or appears to have when combined with other atom

(h) Counter ions

The ions excluding the coordination sphere are called as counter ions. In $K_4[Fe(CN)_6]$ compound, K^+ is the counter ion.

Ligands and their types

The electron rich species, which may be charged species, e.g. Cl^-, CN^-, NO_2^-, etc or neutral species e.g. H_2O, NH_3, $NH_2CH_2CH_2NH_2$, CO, NO, etc., that can donate an electron pair to the metal atom/ion are called ligands.

Types of ligands

The ligands can be classified in the following ways:

Type I- Based on electron accepter/donor properties of the ligand

- σ (sigma) donor ligands are those ligands which can only donate electron pair to the meal ion, e.g. H_2O, NH_3, F^-. These ligands are also known as weak field ligands.
- σ (sigma) donor and Π (pi) accepter ligands are those ligands which can donate electron pair and also have a tendency to accept electron in their empty antibonding π molecular orbitals (MO). Such ligands can involve in

backbonding (π bond) with the metal ion. For example, CO, CN^-, NO, etc. These ligands are also known as strong field ligands.

- Π (pi) donor ligands are those ligands like benzene and ethylene, which do not have lone pair of electrons but only π electrons for donation to the metal atom/ion.

Type II- Based on the basis of number of donor atoms in the ligand

- Monodentate or unidentate ligands

The ligands that bound to a metal ion through a single donor atom are called as monodentate or unidentate ligands, e.g. Cl^-, H_2O or NH_3. These ligands can be further divided into the following subclasses on the basis of charge (Figure 1).

- Ambidentate ligands

Some ligands have two or more than two different donor atoms. These ligands can attach through any of the donor atoms. They are given different names depending upon nature of the donor atom linked to the metal atom. These ligands are known as ambidentate ligands e.g. NO_2 (donor atom may be either N or O), SCN^- (donor atom may be either S or N), CN^- (donor atom may be either C or N), $S_2O_3^{2-}$ (donor atom may be either S or N). These are also monodentate ligands.

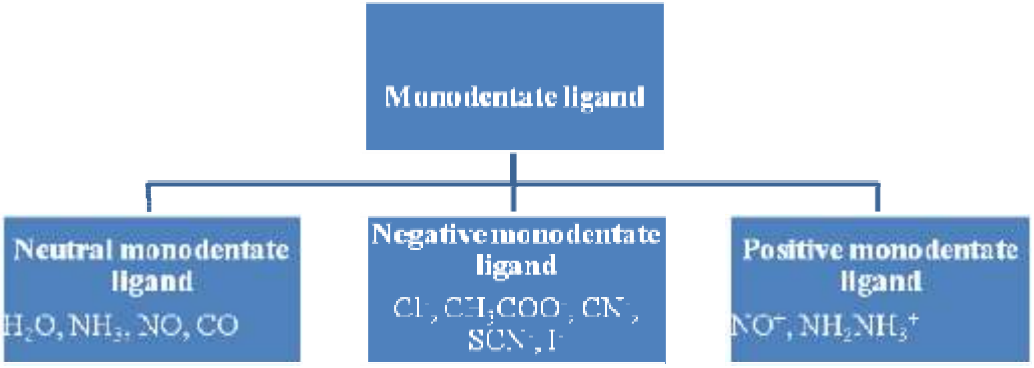


Figure1: Classification of monodentate ligands

2. WERNER’S COORDINATION THEORY AND ITS EXPERIMENTAL VERIFICATION

Alfred Werner in 1893 suggested a new theory for explaining the nature of bonding in coordination compounds known as Werner’s theory. According to this theory, there are two kinds of valences of metal atom/ion in coordination compounds: primary and secondary valences

Postulates of Werner’s theory

1) Every metal atom has two types of valencies

i) Primary valency or ionisable valency

ii) Secondary valency or non ionisable valency

2) The primary valency corresponds to the oxidation state of the metal ion. The primary valency of the metal ion is always satisfied by negative ions.

3) Secondary valency corresponds to the coordination number of the metal ion or atom. The secondary valencies may be satisfied by either negative ions or neutral molecules.

4) The molecules or ion that satisfy secondary valencies are called ligands.

5) The ligands which satisfy secondary valencies must project in definite directions in space. So the secondary valencies are directional in nature where as the primary valencies are non-directional in nature.

6) The ligands have unshared pair of electrons. These unshared pair of electrons are donated to central metal ion or atom in a compound. Such compounds are called coordination compounds.

Werner's theory can be explained on the basis of experimental evidences

- Molar conductivity measurement method

Compounds $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4Cl_2]Cl$ and $[Co(NH_3)_3Cl_3]$ show decreasing order of conductivity due to the formation of 4 ions, 3 ions, 2 ions and no ions, respectively in solution.

$[Co(NH_3)_6]Cl_3 \longrightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$ (1 complex ion + 3 chloride ions)

$[Co(NH_3)_5Cl]Cl_2 \longrightarrow [Co(NH_3)_5Cl]^{2+} + 2Cl^-$ (1complex ion +2chloride ions)

$[Co(NH_3)_4Cl_2]Cl \longrightarrow [Co(NH_3)_4Cl_2] + +Cl^-$ (1 complex ion+1chloride ion)

$[Co(NH_3)_3Cl_3] \longrightarrow [Co(NH_3)_3Cl_3]$ (No ions)

- Precipitation method

When cobalt ammine chloride complexes react with $AgNO_3$, some of the Cl^- ions get precipitated with $AgNO_3$ to form AgCl. The number of Cl^- ions that are ionisable and present outside the coordination sphere can react with $AgNO_3$. Thus, coordination compounds $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl$ react with 3, 2 and 1 mole of $AgNO_3$ to form 3, 2 and 1 mole of AgCl, respectively as there are 3, 2 and 1 ionisable Cl^- ions, respectively.

Defects of Werner’s theory

- Although the theory describes the structure of many compounds, it can’t explain the nature of bonding between metal atom/ion and ligands.
- Werner’s theory was unable to explain why 4- and 6-coordination numbers are the preferred coordination numbers.

EFFECTIVE ATOMIC NUMBER CONCEPT (EAN CONCEPT)

- This rule is given by English Chemist Nevil V. Sidgwick. Effective atomic number (EAN) is the total number of electrons in metal atom/ion (atomic number) plus the electrons gained from ligands. This EAN is the atomic number of a noble gas. Therefore, EAN decides stability of coordination compound. If a coordination compound follow EAN rule, than it is stable one.
  - EAN= Atomic number of metal atom/ion + number of e- donated by ligands or 2 x number of ligands (as each ligand can donate two electrons to metal atom/ion).
  - **For $[Co(NH_3)_6]^{3+}$**
  - Atomic number of Co=27; Atomic number of Co^{3+}=24; there are six ligands hence electrons donated by 6 ligands = 6 x 2

- EAN = 24 + (6 x 2) = 36 (atomic number of Krypton; Kr)

- **For $[Ni(CO)_4]$**
- Atomic number of Ni=28; there are four ligands hence electrons donated by 4 ligands = 4 x 2
- EAN = 28 + (4 x 2) = 36 (atomic number of Krypton; Kr)

- **For $[Fe(CN)_6]^{4-}$**
- Atomic number of Fe=26; Atomic number of Fe^{2+}=24; there are six ligands hence electrons donated 6 ligands = 6 x 2
- EAN = 24 + (6 x 2) = 36 (atomic number of Krypton;

- **For $[Ag(NH_3)_4]^+$**
  - Atomic number of Ag=47; Atomic number of Ag^+=46; there are four ligands, hence electrons donated by 4 ligands = 4 x 2
  - EAN = 46 + (4 x 2) = 54 (atomic number of Xenon; Xe)

    = 54 (atomic number of Xenon; Xe)

- **For $[V(CO)_6]^-$**
  - Atomic number of V=23; Atomic number of V^- = 24; there are six ligands hence electrons donated 6 ligands = 6 x 2
  - EAN = 24 + (6 x 2)

    = 36 (atomic number of Krypton; Kr)

- **For $[Mn(CN)_4]^{2-}$**
  - Atomic number of Mn=25; Atomic number of Mn^{2+} = 23; there are four ligands hence electrons donated 4 ligands = 4 x 2

EAN = 23 + (4 x 2) = 31

Not obeying EAN rule as 31 is not the atomic number of any noble gas

NOMENCLATURE OF COORDINATION COMPOUNDS

Rules for writing formula of coordination compounds

Formula of the cation whether simple or complex must be written first followed by anion.

The coordination sphere the sequence of symbols is :

First metal name followed by anionic ligand then neutral ligand finally cationic ligand. Ligands of same type are arranged alphabetically

Polyatomic ligands are enclosed in parentheses

e.g In $Na[PtBrCl(NO^{+2})_2NH_3(NO)]$ sequence in coordination sphere is metal atom, alphabetical sequence of anionic ligand Br^-, Cl^-, NO^{2-}, followed by neutral ligand NH_3 and then cationic ligand NO^+

IUPAC nomenclature of coordination compounds

steps suggested by IUPAC (International Union of Pure and Applied Chemistry)

The rules are outlined below:

- In naming the entire complex, the name of the cation is given first and the anion second (just as for sodium chloride), no matter whether the cation or the anion is the complex species.
- Name of non-ionic or molecular complexes are written as one word without any gap.
- In the complex ion, the name of the ligand or ligands precedes that of the central metal atom (This procedure is reversed for writing formulae).
- Ligand names generally end with ‘O’ if the ligand is negative (‘chloro’ for Cl^-, ‘cyano’ for CN^-, ‘hydrido’ for H^-) and unmodified if the ligand is neutral (‘methylamine’ for $MeNH_2$). Special ligand names are ‘aqua’ for water, ‘ammine’ for ammonia, ‘carbonyl’ for CO,ni trosyl’ for NO.

- A Greek prefix (mono, di, tri, tetra, penta, hexa, etc.) indicates the number of each ligand (mono is usually omitted for a single ligand of a given type). If the name of the ligand itself contains the terms mono, di, tri, like triphenylphosphine, ligand name is enclosed in parentheses and its number is given with the alternate prefixes bis, tris, tetrakis instead.

For example, $[Ni(PPh_3)_2Cl_2]$ is named dichlorobis(triphenylphosphine)nickel(II).

- A Roman numeral or a zero in parentheses is used to indicate the oxidation state of the central metal atom.
- If the complex ion is negative, the name of the metal ends in ‘ate’ for example, ferrate, cuprate, nickelate, cobaltate etc.
- If more than one ligand is present in the species, then the ligands are named in alphabetical order regardless of the number of each.

For example, NH_3 (ammine) would be considered as ‘a’ ligand and come before Cl^-(chloro).

- Some additional notes

Some metals in anions have special names

B Borate ,Au Aurate, Ag Argentate, Fe Ferrate, Pb Plumbate, Sn Stannate, Cu Cuprate, Ni Nickelate

- Use of brackets or enclosing marks. Square brackets are used to enclose a complex ion or neutral coordination species.

Examples

$[Co(en)_3]Cl_3$ tris(ethylenediamine)cobalt(III) chloride

$[Co(NH_3)_3(NO_2)_3]$ triamminetrinitrocobalt (III)

$K_2[CoCl_4]$ potassium tetrachlorocobaltate(II)

note that it is not necessary to enclose the halogens in brackets.

Name of Negative ligands

Ligand	Name	Ligand	Name
H^-	Hydrido	HS^-	Mercapto
O^{2-}	Oxo	NH_2^-	Amido
O_2^{2-}	Peroxo	NH^{2-}	Imido
O_2H^-	Perhydroxo	NO_3^-	Nitrato
OH^-	Hydroxo	ONO^-	Nitrito
F^-	Fluoro	NO_2^-	Nitro
Cl^-	Chloro	N^{-3}	Nitride
Br^-	Bromo	P^{3-}	Phosphido
I^-	Iodo	N_3^-	Azido
CO_3^-	Carbonato	CNO^-	Cyanato
$C_2O_4^-$	Oxalate	NCO^-	Cyanato
$CH_3CO_2^-$	Acetate	SCN^-	Thiocyanato
SO_4^{2-}	Sulphato	HCO_3^-	Hydrogencarbonato
SO_3^{2-}	Sulphito	$S_4O_6^{2-}$	Tetrathionato
S^{2-}	Sulphido	HSO_3^-	Hydrogensulphito
$NH_2CH_2CO_2^-$	glycinato	$C_5H_5^-$	Cyclopentadienyl
$(OCCH_2)_2NCH_2CH_2CH_2$ $N(CH_2CO_2^-)_2$	Ethylenediammine tetraacetato (EDTA)	$S_2O_3^{2-}$	Thiosulpahato

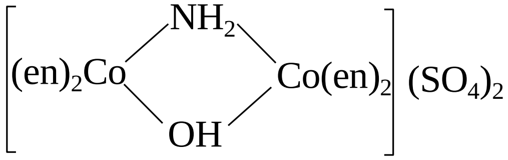
Name of neutral ligands

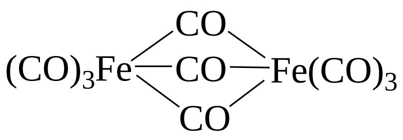
Ligand	Name	Ligand	Name
C_5H_5N (py)	pyridine	$NH_2(CH_2)_2NH_2$ (en)	ethlenediammine
NH_3	Ammine	CH_3NH_2	Methylamine
H_2O	Aqua/aquo	CO	Carbonyl
C_6H_6	Benzene	NO	Nitrosyl
N_2	Dinitrogen	CS	Thiocarbonyl
O_2	Dioxygen	NS	Thionitrosyl
Ph_3P	Triphenylphosphine	CH_3COCH_3	Acetone

Name of Positive ligands

Ligand	Name
NO^+	Nitosonium
NO_2^+	Nitronium
$NH_2NH_3^+$	hydrazinium

These rules are illustrated by the following examples:

COMPOUNDS	SYSTEMATIC NAMES
$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(II) chloride
$[Co(NH_3)_5Cl]^{2+}$	Chloropentamminecobalt(III) ion
$[Co(NH_3)_4SO_4]NO_3$	Sulphatotetramminecobalt(III) nitrate
$[Co(NH_3)_3(NO_2)_3]$	Trinitrotriamminecobalt(III)
$[Co(NH_3)_3NO_2.Cl.CN]$	Chlorocyanonitrotriamminecobalt(III)
$[Cr(en)_3]Cl_3$	Tris(ethylenediamine)chromium(III) chloride
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
$[Pt(py)_4][PtCl_4]$	Tetrapyridineplatinum(II)tetrachloroplatinate(II)
$[(NH_3)_5Co.NH.Co(NH_3)_5](NO_3)_5$	Decammine-μ-amidodicobalt(III) nitrate
	Tetrakis(ethylenediamine)-μ-amido-μ-hydroxo-dicobalt(III) sulphate



Tri-μ-carbonylbis(tricarbonyliron(III))
OR
Hexacarbonyltri-m-carbonyl-diiron(III)

$AlCl_3.(EtOH)_4$ Aluminum(III)chloride-4-ethanol.

Name the following complexes:

(a) $[Cu(NH_3)_4]SO_4$; (b) $K_2[CoCl_4]$;

(c) $Co(phen)_2Cl_2$; (d) $[Co(en)_2(H_2O)Cl]Cl_2$

ISOMERISM OF COORDINATION COMPOUNDS

INTRODUCTION

The objectives of this unit are to familiarize you with the isomerism in coordination compounds and its types. The coordination compounds which have the same chemical formula but different ways of attachment of ligands are called as isomers. These isomers have different physical and chemical properties. The phenomenon that gives rise to the isomers is known as isomerism. There are two main types of isomerism in coordination compounds; structural and stereo- isomerism. Our focus will be on both structural isomerism and stereoisomerism. Structural isomerism is due to the different bond arrangement of atoms in coordination compound around the central metal atom/ ion while stereoisomerism arises due to different three-dimensional arrangement of atoms in space.

Isomerism in coordination compounds

The coordination compounds having the same molecular formula but different arrangement of atoms/ groups around the central metal/ ion are called isomers and the phenomenon which gives rise to isomers is called as isomerism. The isomers have different physical and chemical properties.

Coordination compounds exhibit two major types of isomerism, namely

(A) structural isomerism and (B) stereoisomerism (space isomerism). Each of these is further classified as shown below.

A) Structural isomerism

i) Coordination isomerism ii) Ionization isomerism

iii) Hydrate or Solvate isomerism iv) Linkage isomerism

B) Stereoisomerism

i) Geometrical isomerism ii) Optical isomerism

A) Structural isomerism

Structural isomerism is also known as constitutional isomerism. The molecules have same number of atoms which differ in their structure or bonding. The different chemical formulae of structural isomers are either due to difference in ligands that are bonded to the central atoms or the mode of bonding of individual ligand (which atom of the ligand is bonded to the central atom). Now we will discuss the various types of structural isomerism one by one in brief.

i) Coordination isomerism

In a bimetallic complex, both complex cation and complex anion may be present. In such a case the distribution of ligands between the two coordination spheres can vary, giving rise to isomers called the coordination isomers. This phenomenon is called coordination isomerism. This isomerism is illustrated by the following pairs of complexes where the complex cation and anion contain different metal centers.

$[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6]$ $[Co(CN)_6]$

$[Pt^{II}(NH_3)_4]$ $[CuCl_4]$ and $[Cu(NH_3)_4]$ $[PtCl_4]$

$[Zn(NH_3)_4][CuCl_4]$ and $[Cu(NH_3)_4][ZnCl_4]$.

In a bimetallic complex, both complex cation and complex anion may be present. In such a case the distribution of ligands between the two coordination spheres can vary, giving rise to isomers called the coordination isomers. This phenomenon is called coordination isomerism. This isomerism is illustrated by the following pairs of complexes where the complex cation and anion contain different metal centers.

The coordination compounds in which both the cationic and anionic species are complex ions, show coordination isomerism. This isomerism occurs by the interchange of ligands in between the cationic part and the anionic part. In another words, you can define the coordination isomers as the isomers in which the complex anion and complex cation of a coordination compound exchange one or more ligands

ii) **Ionization Isomerism**

This is the phenomenon by which ligands present inside the coordination sphere and anion or neutral molecule present outside the coordination sphere can exchange their place. The central metal / ion and the other ligands except one that is exchangeable are similar in both the isomers. Thus, ionization isomerism is the exchange of ions between coordination sphere and ionization sphere. The physical and chemical properties of the two isomers are entirely different as they give different ions on dissolving in suitable solvent. Two octahedral ionization isomers will have five identical ligands while the sixth ligand will be different. In case of tetra coordinated isomers, three ligands will be identical and the fourth one will be the different one. The different ligand in one isomer may be outside of the coordination sphere in the other isomer. The oxidation state of the central ion would not be changed in the two isomers

Coordination compounds having the same molecular formula but forming different ions in solution are called ionization isomers. This property is known as ionization isomerism.

An example of this type of isomerism is furnished by the red-violet, $[Co(NH_3)_5Br]SO_4$ $[Co(NH_3)_5SO_4]Br$

The red-violet isomer yields sulphate ion and the red isomer furnishes bromide ion in solution.

$[Co(NH_3)_4Cl_2]NO_2$ and $[Co(NH_3)_4NO_2Cl]Cl$

$[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$

iii) Hydrate isomerism

In hydrate isomerism, there is exchange between water molecule inside the coordination sphere and ions present in the ionization sphere. Composition of hydrate isomers is the same but the number of water molecules inside the coordination sphere is different . For example, $CrCl_3.6H_2O$ has the following three hydrate isomers:

A. $[Cr(H_2O)_6]Cl_3$ (violet)
B. $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (blue green)
C. $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ (green)

These isomers have very different chemical properties and on reaction with $AgNO_3$ to test for Cl^- ions, would find 3,2, and 1 Cl^- ions in solution respectively.

iv) Linkage Isomerism

Complexes having ambidentate ligands like SCN^- / NCS^-, CN^-/NC^- and NO_2^-/ ONO^- (capable of coordinating in more than one way) show linkage isomerism. The two isomers differ from each other by the linkage atom attachment to the central atom/ ion. The ligand can have more than two donor atoms but should be joined to the central atom/ ion via only one atom (unidentate ligand). The formula of the compound is same but their properties are entirely different. The name of the ligands is also changed according to their donor atom. When donor atom is N, NO_2^- is called as nitro, while it is called nitrito if the donor atom is O atom.

For example

$[Co(NH_3)_5ONO]Cl_2$ the nitrito isomer -

red colour - O attached

$[Co(NH_3)_5NO_2]Cl_2$ the nitro isomer -

yellow colour - N attached

B) Stereoisomerism (space isomerism)

Consider two compounds containing the same ligands attached to the same central metal ion, but the arrangement of ligands in space about the central metal ion are different, then these two compounds are said to be stereoisomers and this phenomenon is known as stereoisomerism.

Compounds which have the same atoms/groups, same position of atoms/groups and same sets of bonds, but differ in their spatial arrangement around the central atom/ ion are called as stereoisomers and the phenomenon is known as stereoisomers

There are two different types of stereoisomerism.

i) Geometrical isomerism or ii) Optical isomerism.

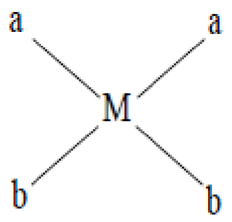
i) Geometrical isomerism (or) cis-trans isomerism

The compounds with differences in geometrical arrangement of the ligands around the central atom/ ion are known as geometrical isomers and the phenomenon as geometrical isomerism. This is also called as cis-trans isomerism. The geometrical isomers have the same empirical formula but different physical and chemical properties due to different arrangement of the ligands in space. The geometrical isomers can be easily separated from each other. When similar atoms/ groups (ligands) are adjacent to each other, the isomer is called cis-isomer (Latin, cis= same). In trans-isomer, the similar ligands are present diagonally opposite to each other (Latin, trans = across). It is common in di-substituted square planar and octahedral complexes with co-ordination number of 4 and 6, respectively. Tetrahedral (coordination number 4) complexes do not show geometrical isomerism because in this geometry, all the ligands are present in cis- position (adjacent) with respect to each other (all bond angles are same).

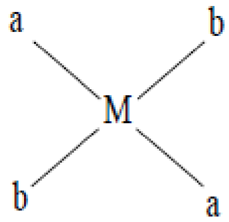
Geometrical isomerism is due to ligands occupying different position around the central ion. The ligands occupy position either adjacent to one another or opposite to one another. These are referred to as cis-form respectively. This type of isomerism is, therefore, also referred to as cis-trans isomerism. Geometric isomers are possible for both square planar and octahedral complexes, but not tetrahedral

Geometrial isomerism in 4-coordinate complex

(1) **[Ma2b2] type complexes Square planar**



cis-isomer



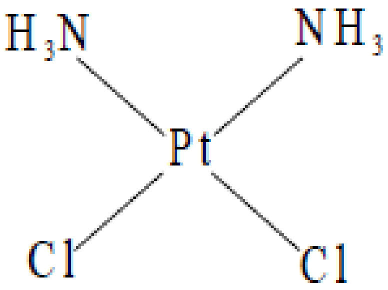
trans-isomer

In a cis-isomer two identical (or) similar groups are adjacent to each other whereas in a trans-isomer they are diametrically opposite to each other.

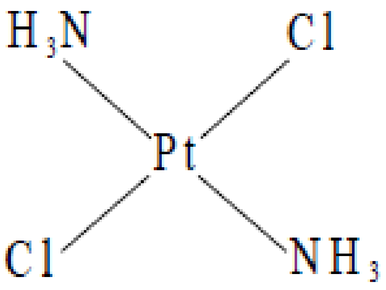
Square planar complexes of the type [Ma2b2]n+ where a and b are monodentate ligands, exist as cis and trans-isomers as shown

Example of this type of complexes are

$[Pt (NH_3)_2Cl_2]$ and $[Pd(NH_3)_2(NO_2)_2]$



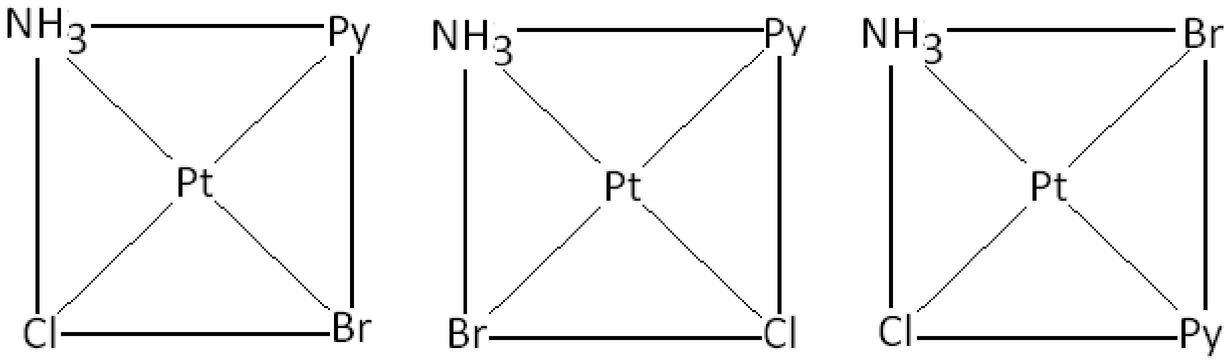
cis-isomer



trans-isomer

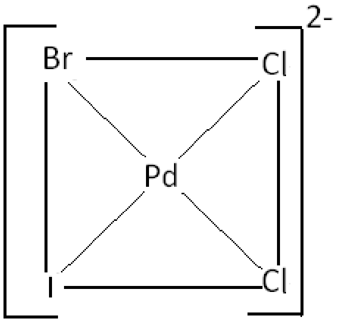
(2) [Mabcd] type complexs

Square planar complex of this type exist in three isomeric forms for example [Pt(NH_3)(Py)(Cl)(Br)] exist in the following structures

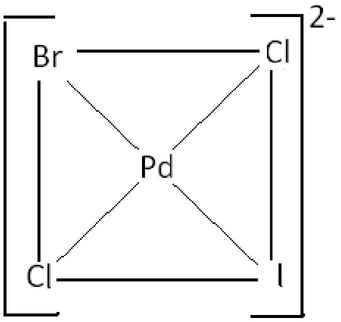


(3) [Ma2bc] type complexes

Square planar complexes of this type also shows cis-trans isomerism. For example $[Pd\,(Cl)_2BrI]^{2-}$ exists in the following cis-trans



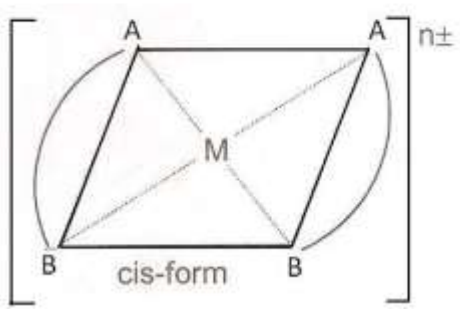
cis-isomer

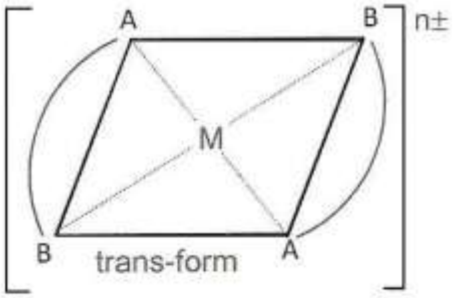


trans-isomer

(4) [M(AB)2]n± type complex

Here m is the central metal ion and (AB) represents an unsymmetrical bidentate ligand(A) and (B) arethe two ends (i.e. coordinating atoms) of the bidentates ligands such type of complexes also show trans and cis isomerism

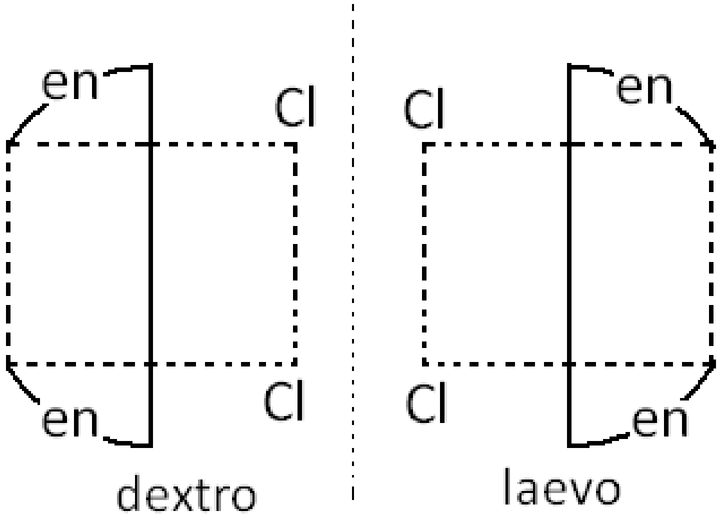




a) Optical Isomerism

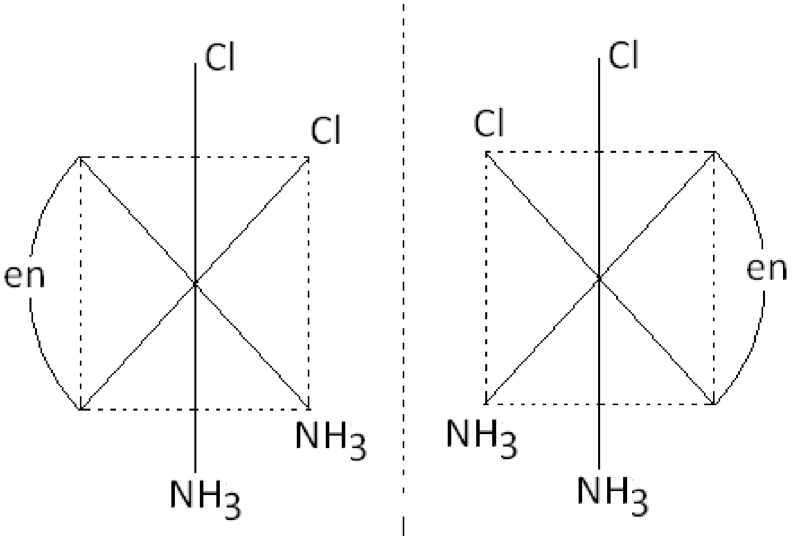
This is a phenomenon in which certain organic or inorganic compounds have the property of rotating plane polarized light. The compounds which exhibit this property are called optical isomers. The optical isomers of a compound have identical physical and chemical properties. The only distinguishing property is that the isomers rotate the plane of polarized light either to the left or right. If the rotation is on the left side, then that isomer is levo and if on right side, then isomer is dextro. The equal proportion of levo and dextro mixture is called racemic mixture

It is generally found octahedral chelate ions. The two isomers of this type of complex are mirror image of each other and cannot super impose on each other, hence they possess chirality character.



coordination compound of type $[PtCl_2(en)_2]^{2+}$ two geometrical isomers are possible. They are cis and trans. Among these two isomers, cis isomer shows optical activity because the whole molecule is asymmetric.

The optical isomers of $[CoCl_2(en)(NH_3)_2]^+$ are as follows



Importance and applications of Coordination Compounds

Coordination compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine.

These are described below:

- Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α–nitroso–β–naphthol, cupron, etc.

Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes

Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[Au(CN)_2]^-$ in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc

- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds.

For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

- Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Vitamin B12, cyanocobalamine, the anti–pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).
- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(Ph_3P)_3RhCl]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.

- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ than from a solution of simple metal ions.
- In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the un decomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.
- There is growing interest in the use of chelate therapy in medicinal chemistry.

  An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems. Thus, excess of copper and iron are removed by the chelating ligands D–penicillamine and desferrioxime B via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are: cis–platin and related compounds.

List of References:

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E.S. Gilreath

2- Coordination Compounds

S. F. A. Kettle

3- Advanced Inorganic Chemistry: A Comprehensive Text

Cotton and Wilkinson

Transition Elements

Code : 351Ch

For

3rd Students

(Zoology and Entomology group)

By

Dr. Heba Nassar Abeit

القائم بالتدريس:

د. هبه نصار عبيط محمد

Inorganic Chemistry

WHAT IS INORGANIC CHEMISTRY?

If organic chemistry is defined as the chemistry of hydrocarbon compounds and their derivatives, inorganic chemistry can be described broadly as the chemistry of "every-thing else." This includes all the remaining elements in the periodic table, as well as carbon, which plays a major role in many inorganic compounds. Organometallic chemistry, a very large and rapidly growing field, bridges both areas by considering compounds containing direct metal-carbon bonds, and includes catalysis of many organic reactions. Bioinorganic chemistry bridges biochemistry and inorganic chemistry, and environmental chemistry includes the study of both inorganic and organic compounds. As can be imagined, the inorganic realm is extremely broad, providing essentially limitless areas for investigation.

A generally-accepted definition of Inorganic Chemistry is the study of non-carbon molecules, or all the elements on the periodic table except carbon. But, this definition is not completely correct because the field of Inorganic Chemistry also includes organometallic compounds and the study of some carbon-based molecules that have properties that are familiar to metals (like conduction of electricity). This makes the field of inorganic chemistry very broad, and practically limitless.

Inorganic chemistry deals with synthesis and behavior of inorganic and organometallic compounds. This field covers chemical compounds that are not carbon-based, which are the subjects of organic chemistry. The distinction between the two disciplines is far from absolute, as there is much overlap in the sub discipline of organometallic chemistry. It has applications in every aspect of the chemical industry, including catalysis, materials science, pigments, surfactants, coatings, medications, fuels, and agriculture.

Many inorganic compounds are ionic compounds, consisting of cations and anions joined by ionic bonding. Examples of salts (which are ionic compounds) are magnesium chloride $MgCl_2$, which consists of magnesium cations Mg^{2+} and chloride anions Cl^{-}; or sodium oxide Na_2O, which consists of sodium cations Na^{+} and oxide anions O^{2-}. In any salt, the proportions of the ions are such that the electric charges cancel out, so that the bulk compound is electrically neutral. The ions are described by their oxidation state and their ease of formation can be inferred from the ionization potential (for cations) or from the electron affinity (anions) of the parent elements.

Important classes of inorganic compounds are the oxides, the carbonates, the sulfates, and the halides. Many inorganic compounds are characterized by high melting points. Inorganic salts typically are poor conductors in the solid state. Other important features include their high melting point and ease of crystallization. Where some salts (e.g., NaCl) are very soluble in water, others (e.g., FeS) are not.

The simplest inorganic reaction is double displacement when in mixing of two salts the ions are swapped without a change in oxidation state. In redox reactions one reactant, the *oxidant*, lowers its oxidation state and another reactant, the *reductant*, has its oxidation state increased. The net result is an exchange of electrons. Electron exchange can occur indirectly as well, e.g., in batteries, a key concept in electrochemistry.

When one reactant contains hydrogen atoms, a reaction can take place by exchanging protons in acid-base chemistry. In a more general definition, any chemical species capable of binding to electron pairs is called a Lewis acid; conversely any molecule that tends to donate an electron pair is referred to as a Lewis base. As a refinement of acid-base interactions, the HSAB theory takes into account polarizability and size of ions.

Inorganic compounds are found in nature as minerals. Soil may contain iron sulfide as pyrite or calcium sulfate as gypsum. Inorganic compounds are also found multitasking as biomolecules: as electrolytes (sodium chloride), in energy storage (ATP) or in construction (the polyphosphate backbone in DNA).

The first important man-made inorganic compound was ammonium nitrate for soil fertilization through the Haber process. Inorganic compounds are synthesized for use as catalysts such as vanadium(V) oxide and titanium(III) chloride, or as reagents in organic chemistry such as lithium aluminium hydride.

Subdivisions of inorganic chemistry are organometallic chemistry, industrial chemistry, coordination chemistry, transition metal compounds, cluster chemistry and bioinorganic chemistry. These fields are active areas of research in inorganic chemistry, aimed toward new catalysts, superconductors, and therapies.

Industrial inorganic chemistry

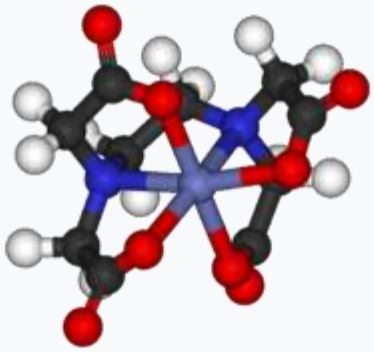
Inorganic chemistry is a highly practical area of science. Traditionally, the scale of a nation's economy could be evaluated by their productivity of sulfuric acid. The manufacturing of fertilizers, which often begins with the Haber-Bosch process, is another practical application of industrial inorganic chemistry.

Coordination compounds

Classical coordination compounds feature metals bound to "lone pairs" of electrons residing on the main group atoms of ligands such as H_2O, NH_3, Cl^-, and CN^-. In modern coordination compounds almost all organic and inorganic compounds can be used as ligands. The "metal" usually is a metal from the groups 3-13, as well as the *trans*-lanthanides and *trans*-actinides, but from a certain perspective, all chemical compounds can be described as coordination complexes.

The stereochemistry of coordination complexes can be quite rich, as hinted at by Werner's separation of two enantiomers of $[Co((OH)_2Co(NH_3)_4)_3]^{6+}$, an early demonstration that chirality is not inherent to organic compounds. A topical theme within this specialization is supramolecular coordination chemistry.[2]

Examples: $[Co(EDTA)]^-$, $[Co(NH_3)_6]^{3+}$, $TiCl_4(THF)_2$.



EDTA chelates an octahedrally coordinated Co^{3+} ion in $[Co(EDTA)]^-$

Transition metal compounds

Compounds containing metals from group 4 to 11 are considered transition metal compounds. Compounds with a metal from group 3 or 12 are sometimes also incorporated into this group, but also often classified as main group compounds.

Transition metal compounds show a rich coordination chemistry, varying from tetrahedral for titanium (e.g., $TiCl_4$) to square planar for some nickel complexes to octahedral for coordination complexes of cobalt. A range of transition metals can be found in biologically important compounds, such as iron in hemoglobin.

- Examples: iron pentacarbonyl, titanium tetrachloride, cisplatin

Periodicity

We begin this section by examining the behaviors of representative metals in relation to their positions in the periodic table. The primary focus of this section will be the application of periodicity to the representative metals.

It is possible to divide elements into groups according to their electron configurations. The **representative elements** are elements where the *s* and *p* orbitals are filling. The transition elements are elements where the *d* orbitals (groups 3–11 on the periodic table) are filling, and the inner transition metals are the elements where the *f* orbitals are filling. The *d* orbitals fill with the elements in group 11; therefore, the elements in group 12 qualify as representative elements because the last electron enters an *s* orbital. Metals among the representative elements are the **representative metals**. Metallic character results from an element's ability to lose its outer valence electrons and results in high thermal and electrical conductivity, among other physical and chemical properties. There are 20 nonradioactive representative metals in groups 1, 2, 3, 12, 13, 14, and 15 of the periodic table (in **Figure 1**). The radioactive elements copernicium, flerovium, polonium, and livermorium are also metals but are beyond the scope of this chapter.

In addition to the representative metals, some of the representative elements are metalloids. A **metalloid** is an element that has properties that are between those of metals and nonmetals; these elements are typically semiconductors.

The remaining representative elements are nonmetals. Unlike **metals**, which typically form cations and ionic compounds (containing ionic bonds), nonmetals tend to form anions or molecular compounds. In general, the combination of a metal and a nonmetal produces a salt. A salt is an ionic compound consisting of cations and anions.

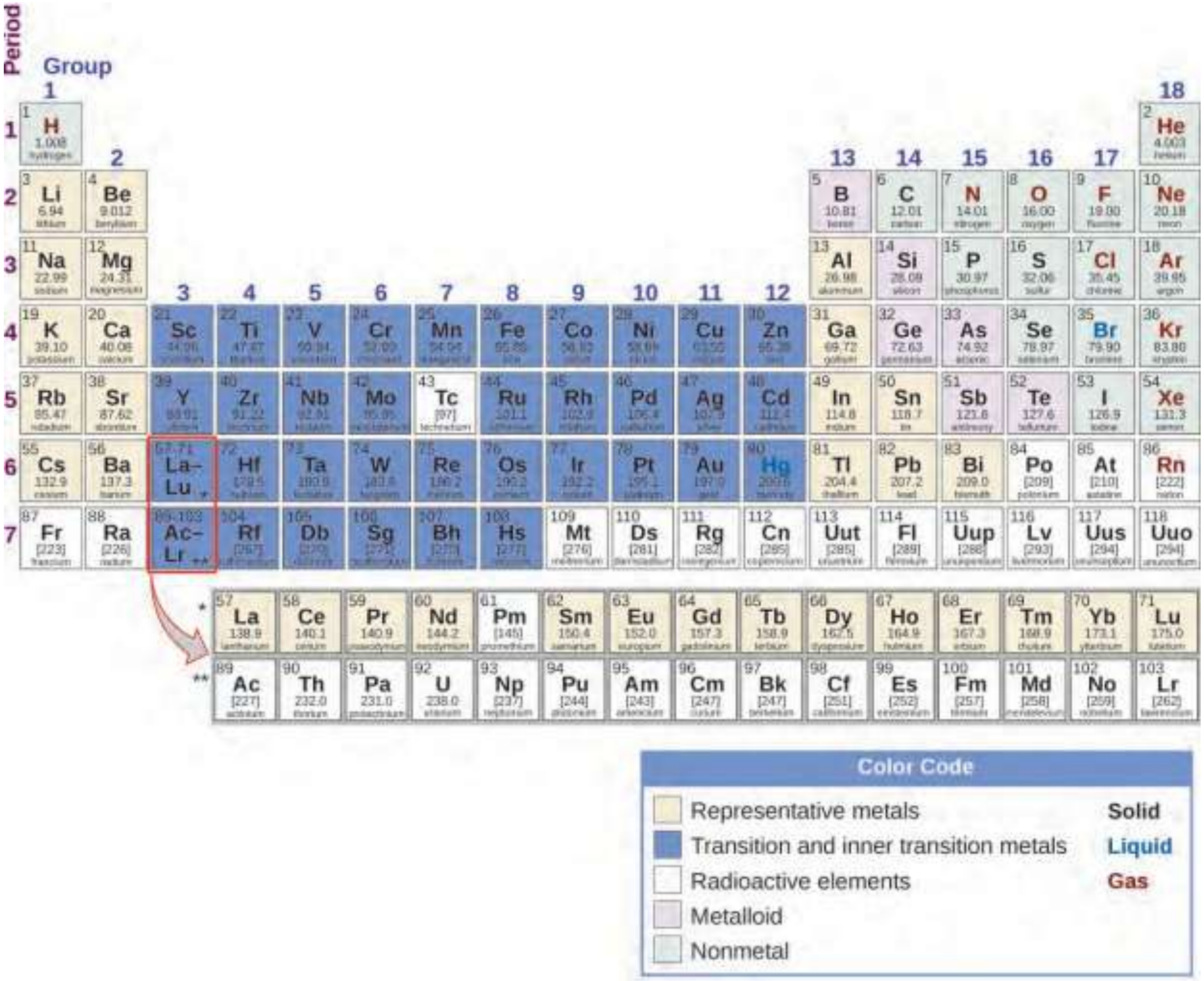


Figure 1: **The periodic table**

Group 1: The Alkali Metals

The alkali metals lithium, sodium, potassium, rubidium, cesium, and francium constitute group 1 of the periodic table. Although hydrogen is in group 1 (and also in group 17), it is a nonmetal and deserves separate consideration later in this chapter. The name alkali metal is in reference to the fact that these metals and their oxides react with water to form very basic (alkaline) solutions.

Group 2: The Alkaline Earth Metals

The **alkaline earth metals** (beryllium, magnesium, calcium, strontium, barium, and radium) constitute group 2 of the periodic table. The name alkaline metal comes from the fact that the oxides of the heavier members of the group react with water to form alkaline solutions. The nuclear charge increases when going from group 1 to group 2. Because of this charge increase, the atoms of the alkaline earth metals are smaller and have higher first ionization energies than the alkali metals within the same period. The higher ionization energy makes the alkaline earth metals less reactive than the alkali metals; however, they are still very reactive elements. Their reactivity increases, as expected, with increasing size and decreasing ionization energy. In chemical reactions, these metals readily lose both valence electrons to form compounds in which they exhibit an oxidation state of 2+. Due to their high reactivity, it is common to produce the alkaline earth metals, like the alkali metals, by electrolysis. Even though the ionization energies are low, the two metals with the highest ionization energies (beryllium and magnesium) do form compounds that exhibit some covalent characters. Like the alkali metals, the heavier alkaline earth metals impart color to a flame. As in the case of the alkali metals, this is part of the emission spectrum of these elements.

Calcium and strontium produce shades of red, whereas barium produces a green color.

Transition Metals

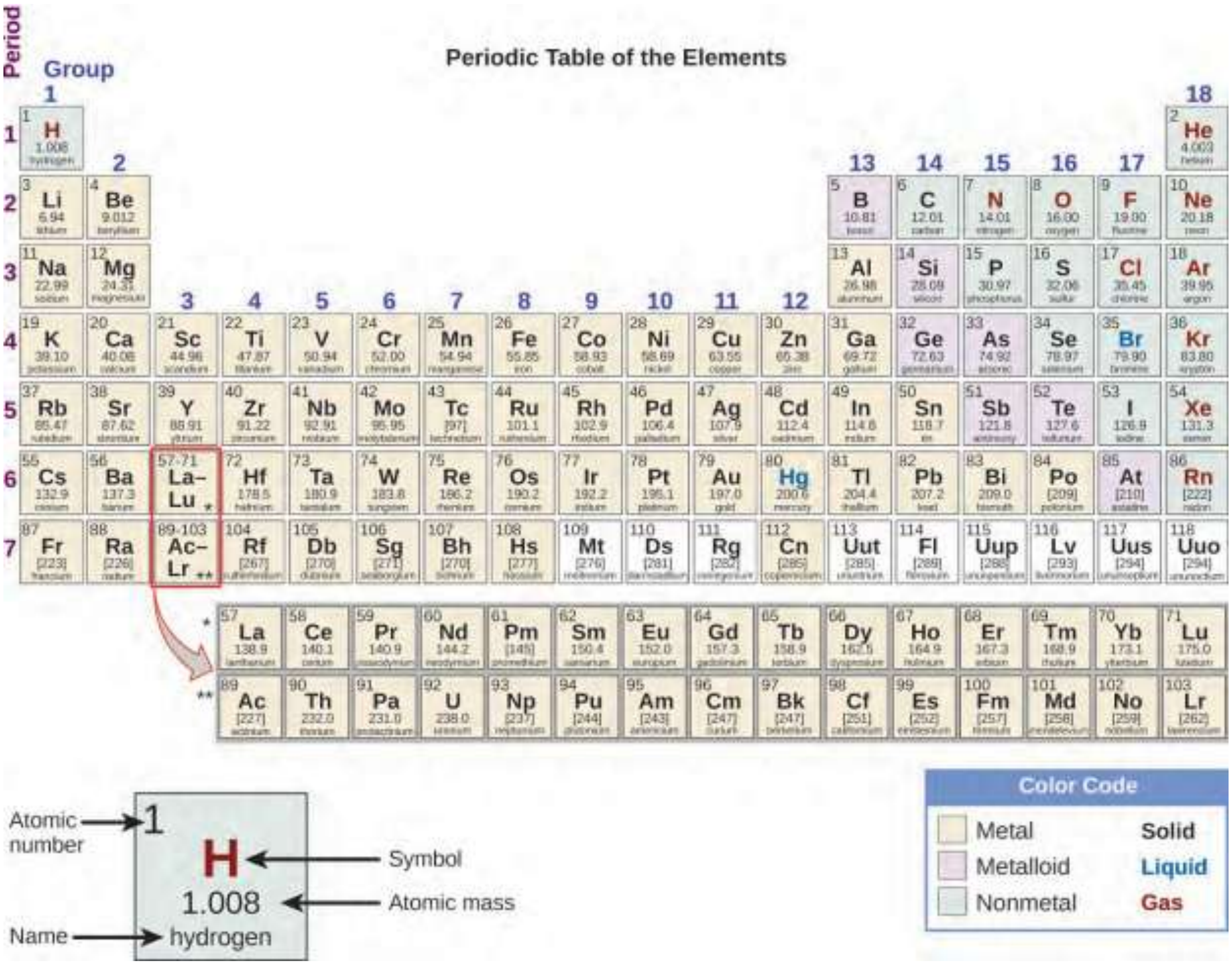
Introduction

We have daily contact with many transition metals. Iron occurs everywhere—from the rings in your spiral notebook and the cutlery in your kitchen to automobiles, ships, buildings, and in the hemoglobin in your blood. Titanium is useful in the manufacture of lightweight, durable products such as bicycle frames, artificial hips, and jewelry. Chromium is useful as a protective plating on plumbing fixtures and automotive detailing.

In addition to being used in their pure elemental forms, many compounds containing transition metals have numerous other applications. Silver nitrate is used to create mirrors, zirconium silicate provides friction in automotive brakes, and many important cancer-fighting agents, like the drug cisplatin and related species, are platinum compounds.

The variety of properties exhibited by transition metals is due to their complex valence shells. Unlike most main group metals where one oxidation state is normally observed, the valence shell structure of transition metals means that they usually occur in several different stable oxidation states. In addition, electron transitions in these elements can correspond with absorption of photons in the visible electromagnetic spectrum, leading to colored compounds. Because of these behaviors, transition metals exhibit a rich and fascinating chemistry.

Transition metals are defined as those elements that have (or readily form) partially filled *d* orbitals. As shown in **Figure 2**, the ***d*-block elements** in groups 3–11 are transition elements. The ***f*-block elements**, also called *inner transition metals* (the lanthanides and actinides), also meet this criterion because the *d* orbital is partially occupied before the *f* orbitals. The *d* orbitals fill with the copper family (group 11); for this reason, the next family (group 12) are technically not transition elements. However, the group 12 elements do display some of the same chemical properties and are commonly included in discussions of transition metals. Some chemists do treat the group 12 elements as transition metals.



Periodic Table of the Elements

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008																	2 He 4.003
2	3 Li 6.94	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc [97]	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57-71 La–Lu *	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po [209]	85 At [210]	86 Rn [222]
7	87 Fr [223]	88 Ra [226]	89-103 Ac–Lr **	104 Rf [267]	105 Db [270]	106 Sg [271]	107 Bh [270]	108 Hs [277]	109 Mt [276]	110 Ds [281]	111 Rg [282]	112 Cn [285]	113 Uut [285]	114 Fl [289]	115 Uup [288]	116 Lv [293]	117 Uus [294]	118 Uuo [294]

*	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm [145]	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.1	71 Lu 175.0
**	89 Ac [227]	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]

Color Code	
Metal	Solid
Metalloid	Liquid
Nonmetal	Gas

Figure 2: The transition metals are located in groups 3–11 of the periodic table. The inner transition metals are in the two rows below the body of the table.

The *f*-block elements are the elements Ce through Lu, which constitute the **lanthanide series** (or **lanthanoid series**), and the elements Th through Lr, which constitute the **actinide series** (or **actinoid series**). Because lanthanum behaves very much like the lanthanide elements, it is considered a lanthanide element, even though its electron configuration makes it the first member of the third transition series. Similarly, the behavior of actinium means it is part of the actinide series, although its electron configuration makes it the first member of the fourth transition series.

The d-block elements have been defined as "the elements whose atoms receive the last electron in the d-subshell belonging to the penultimate or (n-1)th shell". The d-block elements are also called the transition elements or metals. This is because they exhibit gradual transitional behaviour between highly reactive s-block

(electropositive) and p-block (electronegative) elements, i.e. their properties have been found to be intermediate between those of the s-block and p-block elements. Thus these elements are located in the middle of the periodic table and are the members of the Groups 3 to 12 (IIIB to VIII to II B) in the modern periodic table. According to IUPAC definiton, "a transition element is an element which has an incomplete d-subshell in either neutral atom or in ions in chemically significant (or common) oxidation state". According to this definition zinc (Zn), cadmium (Cd) and mercury (Hg) are excluded from the list of transition elements as they neither have partly filled d-subshell in their atoms or ions nor they show the usual properties of transition elements to an appreciable extent. Still in order to rationalize the classification of elements, they are studied along with other d-block elements.

Now according to IUPAC, transition metals are defined as metals which have incomplete *d* subshell either in neutral atom or in their ions. Zinc, cadmium and mercury of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals. However, being the end members of the 3*d*, 4*d* and 5*d* transition series, respectively, their chemistry is studied along with the chemistry of the transition metals.

The presence of partly filled *d* or *f* orbitals in their atoms makes transition elements different from that of the non-transition elements. Hence, transition elements and their compounds are studied separately. However, the usual theory of valence as applicable to the non- transition elements can be applied successfully to the transition elements also.

Various precious metals such as silver, gold and platinum and industrially important metals like iron, copper and titanium belong to the transition metals series.

In this Unit, we shall first deal with the electronic configuration, occurrence and general characteristics of transition elements with special emphasis on the trends in the properties of the first row (3*d*) transition metals along with the preparation and properties of some important compounds. This will be followed by consideration of certain general aspects such as electronic configurations, oxidation states and chemical reactivity of the inner transition metals.

The *d*-block elements are divided into the **first transition series** (the elements Sc through Cu), the **second transition series** (the elements Y through Ag), and the **third transition series** (the element La and the elements Hf through Au). Actinium, Ac, is the first member of the **fourth transition series**, which also includes Rf through Rg.

There are four series of elements which constitute the *d*-block elements. Each series comprises ten elements as given below:

1. **Elements of the First Transition series or 3d-Transition series:** The elements from scandium (Sc, Z = 21) to Zinc (Zn, Z = 30) form the 3d-series.

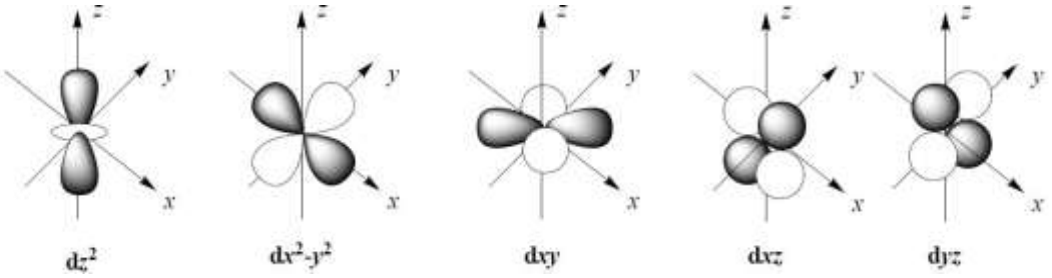
2. **Elements of the Second Transition series or 4d-Transition series:** This series consists of the elements from yttrium (Y, Z = 39) to cadmium (Cd, Z = 48).

3. **Elements of the Third Transition series or 5d-Transition series:** The elements lanthanum (La, Z= 57) and hafnium (Hf, Z= 72) to mercury (Hg, Z = 80) constitute the 5d-Transition series.

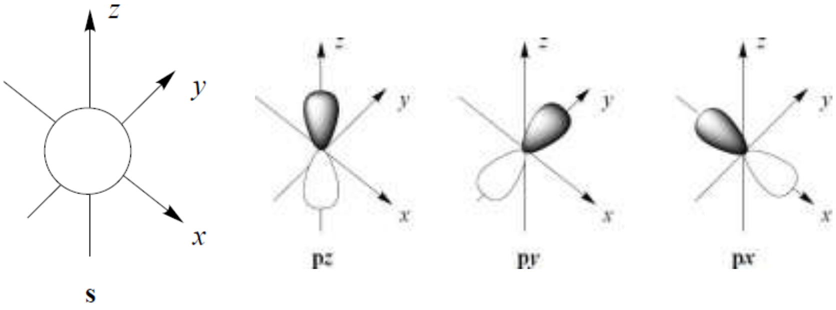
4. **Elements of the Fourth Transition series or 6d-Transition series:** The elements actinium (Ac, Z = 89) and rutherfordium (Rf, Z = 104) to copernicum (Cn, Z = 112) are the members of this series. All these elements are radipoactive and do not occur in nature. These have been artificially made in the laboratory.

Transition Metal Valence Orbitals

- *n*d orbitals



- (*n* + 1)s and (*n* + 1)p orbitals



- dx^2-dy^2 and dz^2 (e_g) lobes located on the axes
- dxy, dxz, dyz lobes (t_{2g}) located between axes

CHARACTERISTIC PROPERTIES OF D-BLOCKELEMENTS

The transition elements have several characteristic properties.

- All are metals with high tensile strength and good conductor of heat and electricity.
- All, except mercury (which is liquid at room temperature), appear as high melting point and boiling point lustrous solids. The high melting points are attributed to the involvement of greater number of electrons from (n-1) d orbitals in addition to the ns electrons in the interatomic metallic bonding. In a particular row, in general, the melting points rise to a maximum at d^5, except for anomalous values of Mn and Tc, and fall regularly as the atomic number increases .
- All have high enthalpy of atomization. The higher enthalpy values of atomization for the second and third series account for the occurrence of much more frequent metal – metal bonding in compounds of the heavy transition series.
- All form alloys with one another, and with metallic main group elements.
- Many of them are sufficiently electropositive to react with mineral acids to form salts, though some of them are rather inert in this respect.
- Most of them show more than one oxidation state (variable valence).
- Because of partly filled d orbitals some transition metal ions containing odd number ofelectrons form paramagnetic compounds.
- They have unparallel tendency to form coordination compounds with Lewis bases because of their small size, high charge and availability of low energy orbitals.
- Many form coloured compounds in one if not in all oxidation states; the absorption ofvisible light being associated with the presence of partly filled d orbitals.
- The redox behavior, magnetic and optical properties of the transition elements are importantfeatures underlying their use in innumerable applications.

Atomic Structures and Properties

- ***Electronic Configuration and Variable Oxidation States***

- **Electronic configurations**

The electronic configurations of the valence shells of the d-block elements can be given as

$(n-1)d^{1-10}$ ns^{1-2}, where (n-1) stands for the inner d orbitals (Table 1). It is observed that the electron first enters in higher principal quantum number orbital (n) rather than in unoccupied (n-1)d orbital. The reason for the preferential filling up of 4s in comparison to 3d can be understood in terms of the shielding effect and the effective nuclear charge. In fact, the relative energies of the atomic orbitals varies with increase in atomic number as shown in figure 2. In building up the elements from hydrogen (Z=1) to calcium (Z=20), the unoccupied 3d orbitals are effectively shielded from the increasing nuclear charge by the electrons of (Ar) core. As a consequence, the energy of 3d orbitals remains fairly constant. In contrast, the energies of the 4s and 4p orbitals are declining as they penetrate the (Ar) core more. However, the 3d orbitals penetrate the 4s and 4p orbitals so that after Ca a 3d electron is not fully shielded from the increasing nuclear charge by the 4s electrons. Thus, by the time Sc (Z=21) is reached the energy of 3d orbitals fall below the level of 4p orbitals and close to that of 4s orbital. The next electron therefore enters the 3d orbital. Since the d electrons shield one another rather poorly from the nuclear charge, the energy of 3d orbitals continues to fall as Z_{eff} increases. Thus, by the time Ga (Z=31) is reached, the new filled d orbitals have fallen well below the 4s and 4p orbitals in energy and are no longer part of the valence shell, but become a core. The same sequence of events follow in the case of the heavier transition metal series.

Table 1: Electronic Configurations of outer orbitals of the Transition Elements(ground state)

1st Series

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4*s*	2	2	2	1	2	2	2	2	1	2
3*d*	1	2	3	5	5	6	7	8	10	10

2nd Series

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5*s*	2	2	1	1	1	1	1	0	1	2
4*d*	1	2	4	5	6	7	8	10	10	10

3rd Series

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6*s*	2	2	2	2	2	2	2	1	1	2
5*d*	1	2	3	4	5	6	7	9	10	10

4th Series

	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
Z	89	104	105	106	107	108	109	110	111	112
7*s*	2	2	2	2	2	2	2	2	1	2
6*d*	1	2	3	4	5	6	7	8	10	10

Transition Elements	**Atomic Number**	**Electronic Configuration**
Sc	21	[Ar] $3d^1$ $4s^2$
Ti	22	[Ar] $3d^2$ $4s^2$
V	23	[Ar] $3d^3$ $4s^2$
Cr	24	[Ar] $3d^5$ $4s^1$
Mn	25	[Ar] $3d^5$ $4s^2$
Fe	26	[Ar] $3d^6$ $4s^2$
Co	27	[Ar] $3d^7$ $4s^2$
Ni	28	[Ar] $3d^8$ $4s^2$
Cu	29	[Ar] $3d^{10}$ $4s^1$
Zn	30	[Ar] $3d^{10}$ $4s^2$
Y	39	[Kr] $4d^1$ $5s^2$
Zr	40	[Kr] $4d^2$ $5s^2$
Nb	41	[Kr] $4d^4$ $5s^1$
Mo	42	[Kr] $4d^5$ $5s^1$
Tc	43	[Kr] $4d^5$ $5s^2$
Ru	44	[Kr] $4d^7$ $5s^1$
Rh	45	[Kr] $4d^8$ $5s^1$
Pd	46	[Kr] $4d^{10}$
Ag	47	[Kr] $4d^{10}$ $5s^1$
Cd	48	[Kr] $4d^{10}$ $5s^2$

- **Radii of atoms and ions**

In general, atomic radii (Table 1) of the elements show progressive decrease with increasing atomic number across a row in the transition series. This is because as the new electron enters a d orbital, each time the nuclear charge increases by unity. Since the shielding effect of a d electron is not that effective, the net electrostatic attraction between the nuclear charge and the outermost electron increases and hence a contraction in size. The same trend is observed in the ionic radii of a given series. However, the variation within a series is quite small. It may be attributed to the two opposing factors : one the increasing nuclear charge tending to decrease the size and the other electron-electron repulsion, because of addition of electrons in the same penultimate d shell, tending to increase the size.

An interesting feature emerges when atomic sizes of one series are compared with those of the corresponding elements in the other series. The data in Figure 3 show an increase from the first (3d) to the second (4d) series of the elements but the radii of the third (5d) series are virtually the same as those of the corresponding members of the second series. This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called Lanthanoid contraction which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d series exhibit similar radii (e.g. Zr 160 pm, Hf 159 pm) and have very similar physical and chemical properties much more than that expected on the basis of usual family relationship.

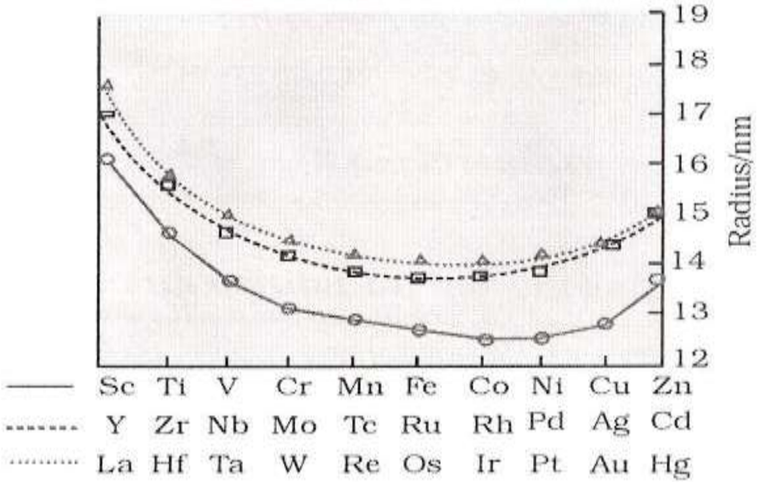


Figure3 : The variation in atomic radii of transition metals across the series

The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of these elements. Thus from titanium (Z=22) to copper (Z=29) the increase in the density is significant.

- **Ionization enthalpies**

With increasing nuclear charge, which accompanies the filling of the inner d orbitals, there is an increase in magnitude of ionization enthalpy along each series of the transition elements from left to right. However, many small variations occur. Table 1 gives the values for the first three ionization enthalpies corresponding to successive removal of electrons from outermost s orbital and d orbital of the first row elements. These values show that the successive enthalpies of these elements do not increase as steeply as in the main group elements. Although the first ionization enthalpy (removal of electron from s orbital), in general, increase, the increase in the second and third ionization enthalpies for the successive elements are not of the same magnitude. However, the trend is similar for the second ionization enthalpies, which for the most part increase smoothly as the atomic number increases; the exceptions are chromium and copper for which these values are notably larger than those of their neighbors.

The irregular trend in the first ionization enthalpy of the 3d metals, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4s and 3d orbitals. There is thus a reorganization energy accompanying ionization with some gain in exchange energy as the number of electrons increases. In general, there is an expected increasing trend in the values as the effective nuclear charge increases with the value of Cr being lower because of the absence of any change in the d configuration and the value of Zn being relatively high because of ionization from the filled 4s level. The lowest common oxidation state of these metals is +2. To form the M^{2+} ions

from the gaseous atoms, the sum of the first and second ionization energies is required in addition to the enthalpy of atomization for each element. The dominant term is the second ionization enthalpy which shows unusually high values for Cr and Cu where the d^5 and d^{10} configurations of the M^+ ions are disrupted, with considerable loss of exchange energy. The value for Zn is correspondingly low as the ionization leads to the production of the stable d10 configuration. The trend in the third ionization enthalpies is not complicated by the 4s orbital factor and shows the greater difficulty of removing an electron from the $d^5(Mn^{2+})$ and $d^{10}(Zn^{2+})$ ions superimposed upon the general increasing trend. In general, the third ionization enthalpies are quite high and there is a marked break between the values for Mn^{2+} and Fe^{2+}. Also the high values for copper, nickel and zinc indicate difficulty in obtaining oxidation state greater than two for these elements.

Although ionization enthalpies give some guidance concerning the relative stabilities of oxidation states, this problem is complicated by differing salvation (hydration) energies of different ions and, therefore not easily amenable for broad generalization .

- **Oxidation states**

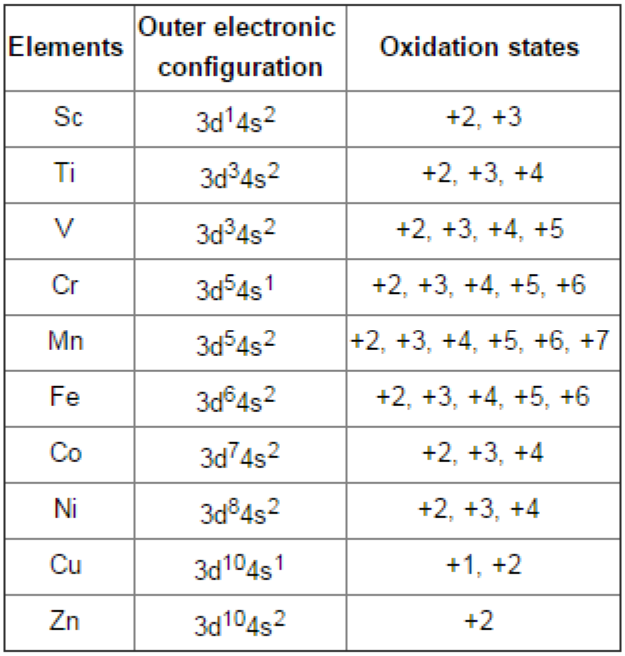
The oxidation states (or number) exhibited by the transition elements . The most common and important ones are shown in bold type. It is obvious that the transition metals exhibit a great variety of oxidation states. The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7. Ruthenium and Osmium commonly form compounds in +8 oxidation state, which is among the highest for isolable compounds. The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or too many d electrons (hence fewer orbitals available for sharing electrons with others) for higher valence (Cu, Zn.). Thus, early in the series scandium(II) is virtually unknown and titanium(IV) is more stable than Ti(III) or Ti(II). At the other end, the only oxidation state of zinc is +2 (no d electrons are involved). The maximum oxidation states of reasonable stability correspond to the sum of the s and d electrons upto manganese (TiO_2, VO^{2+}, CrO_4^{2-}, MnO_4^-) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are Fe II, III, Co II,III, Ni II, Cu I,II, Zn II. It is mainly because the latter transition metals require more energy to remove the electrons.

Most of the d-block elements show several oxidation states (variable) in their compounds due to the availability of d-electrons in the valence shell which comprises of the two subshells, viz., (n-1)d and ns whose orbitals are quite close together in energy and hence the electrons can be used from both the subshells for bonding and under different conditions different number of electrons can be used by them. The variability in the oxidation states increases towards the middle of the series from both ends, i.e. left → middle ← right. It has been observed that the d-block elements can form ionic bonds in their lower oxidation states and the ionic character of the bond decreases as well as the covalent character increases with increasing oxidation state. As a result, with decreasing ionic character the acidic character of the oxides and chlorides increases.

The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of d orbitals in such a way that their oxidation states differ from each other by unity, e.g. VII, VIII, VIV, Vv. This is in contrast with the variability of oxidation states of non-transition elements where oxidation states normally differ by units of two.

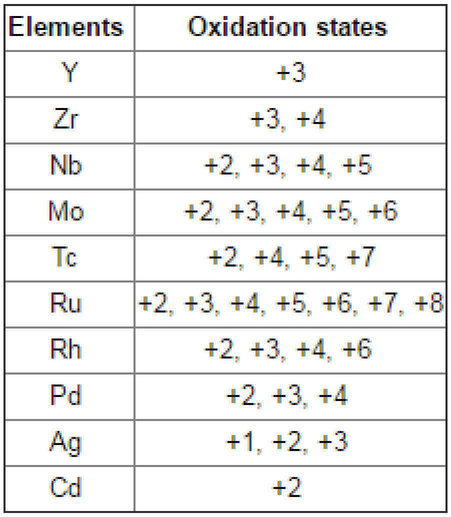
Low oxidation states are found when a complex compound has ligands capable of π–acceptor character in addition to the σ- bonding. For example in $Ni(CO)_4$ and $Fe(CO)_5$ the oxidation state of nickel and iron is zero.

Oxidation States of 3d Series



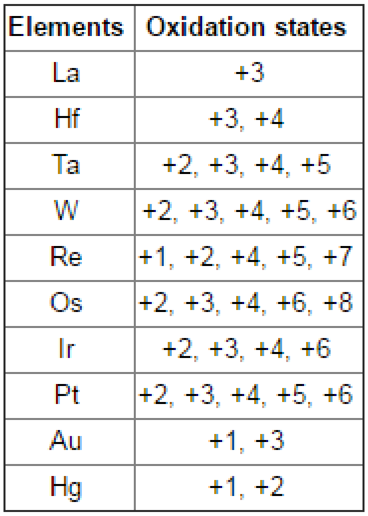
Elements	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+2, +3
Ti	$3d^3 4s^2$	+2, +3, +4
V	$3d^3 4s^2$	+2, +3, +4, +5
Cr	$3d^5 4s^1$	+2, +3, +4, +5, +6
Mn	$3d^5 4s^2$	+2, +3, +4, +5, +6, +7
Fe	$3d^6 4s^2$	+2, +3, +4, +5, +6
Co	$3d^7 4s^2$	+2, +3, +4
Ni	$3d^8 4s^2$	+2, +3, +4
Cu	$3d^{10} 4s^1$	+1, +2
Zn	$3d^{10} 4s^2$	+2

Oxidation state of 4d series



Elements	Oxidation states
Y	+3
Zr	+3, +4
Nb	+2, +3, +4, +5
Mo	+2, +3, +4, +5, +6
Tc	+2, +4, +5, +7
Ru	+2, +3, +4, +5, +6, +7, +8
Rh	+2, +3, +4, +6
Pd	+2, +3, +4
Ag	+1, +2, +3
Cd	+2

Oxidation State of 5d Series



Elements	Oxidation states
La	+3
Hf	+3, +4
Ta	+2, +3, +4, +5
W	+2, +3, +4, +5, +6
Re	+1, +2, +4, +5, +7
Os	+2, +3, +4, +6, +8
Ir	+2, +3, +4, +6
Pt	+2, +3, +4, +5, +6
Au	+1, +3
Hg	+1, +2

Cause for Variable Oxidation States

The valence electrons of the transition elements are in (n-1) d and ns orbitals which have a little distinction in energies. Both energy levels can be utilized as a part of bond development.

They demonstrate the +2 oxidation state because of the 2 electrons in ns orbitals when the electrons of (n-1) d stay unaffected.

The higher oxidation state from +3 to +7 is because of the utilization of all 4s and 3d electrons in the transition series of elements. In the excited state, the (n-1) d electrons get to be bonding and give the variable states to the iota. Subsequently, the variable

oxidation state is because of the support of both ns and (n-1) d orbitals in bonding.

- **Magnetic Properties**:

The magnetic properties of D-Block Elements are dictated by the number of unpaired electrons in it.

There are two fundamental sorts of substances.

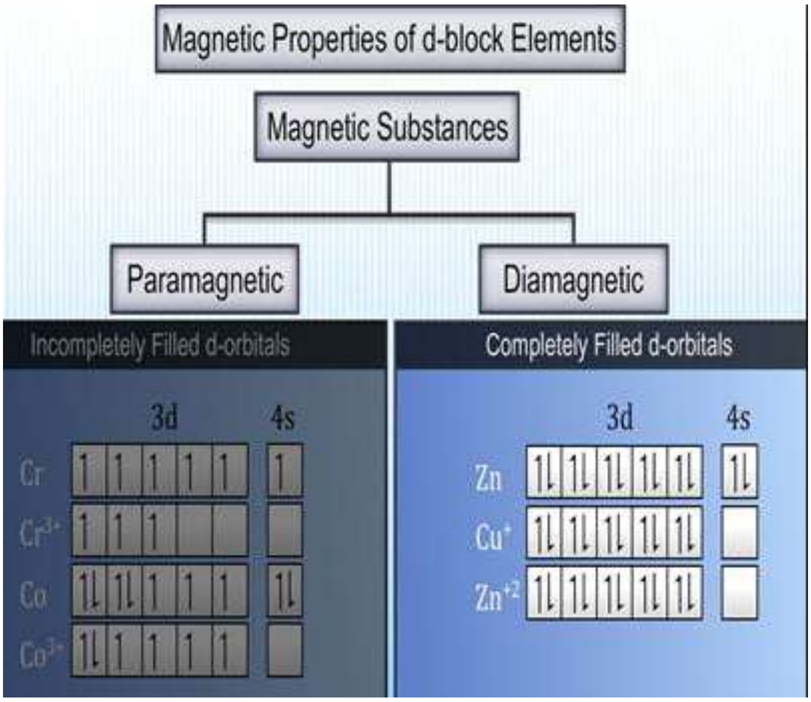
(i) Paramagnetic substances

The paramagnetic character emerges in view of the nearness of unpaired electrons. Paramagnetic substances are the substances which are pulled in by the magnetic field.

(ii) Diamagnetic Substances

Diamagnetic character emerges as a result of the nonappearance of unpaired electrons. Diamagnetic substances are the substances which are repulsed by the magnetic field.

A large portion of the transition elements and their compounds are paramagnetic and are pulled in by the magnetic field. More prominent the number of unpaired electrons in the substance more noteworthy is the paramagnetic character



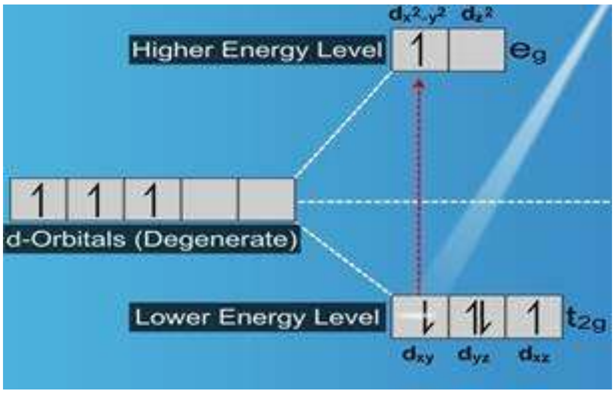
- **Formation of colored compounds:**

Most d-block metal compounds are coloured in their solid or liquid states.

In the case of transition metal ions, under the influence of ligands, the degeneracy of the 5 d-orbitals is lost and they separate into two distinct energy levels.

eg set: d x^2- y^2 and dz^2 orbitals

t2g set: dxy, dxz and dyz orbitals



When white light is incident on a transition metal ion, the electron in the lower energy d-orbital set absorbs certain radiations and gets promoted to a d-orbital set of higher energy. The transmitted radiation devoid of the absorbed radiations is the complementary colour

of the absorbed light. This complementary colour is the colour of the substance.

Colour in transition-series metal compounds is generally due to electronic transitions of two principal types.

- charge transfer transitions. An electron may jump from a predominantly ligand orbital to a predominantly metal orbital, giving rise to a ligand-to-metal charge-transfer (LMCT) transition. These can most easily occur when the metal is in a high oxidation state. For example, the colour of chromate, dichromate and permanganate ions is due to LMCT transitions. Another example is that mercuric iodide, HgI_2, is red because of a LMCT transition.

A metal-to-ligand charge transfer (MLCT) transition will be most likely when the metal is in a low oxidation state and the ligand is easily reduced.

In general charge transfer transitions result in more intense colours than d-d transitions.

- d-d transitions. An electron jumps from one d-orbital to another. In complexes of the transition metals the d orbitals do not all have the same energy. The pattern of splitting of the d orbitals can be calculated using crystal field theory. The extent of the splitting depends on the particular metal, its oxidation state and the nature of the ligands. The actual energy levels are shown on Tanabe–Sugano diagrams.

- **Catalytic Activity**

Transition metals and their compounds are often good catalysts. A few of the more obvious cases are mentioned below, but you will find catalysis explored in detail elsewhere on the site (follow the link after the examples). Transition metals and their compounds function as catalysts either because of their ability to change oxidation state or, in the case of the metals, to adsorb other substances on to their surface and activate them in the process. All this is explored in the main catalysis section.

Iron in the Haber Process

The Haber Process combines hydrogen and nitrogen to make ammonia using an iron catalyst.

Nickel in the hydrogenation of C=C bonds

This reaction is at the heart of the manufacture of margarine from vegetable oils. However, the simplest example is the reaction between ethene and hydrogen in the presence of a nickel catalyst.

Transition metal compounds as catalysts

Vanadium(V) oxide in the Contact Process

At the heart of the Contact Process is a reaction which converts Sulfur dioxide into Sulfur trioxide. Sulfur dioxide gas is passed together with air (as a source of oxygen) over a solid vanadium(V) oxide catalyst.

Iron ions in the reaction between persulfate ions and iodide ions

Persulphate ions (peroxodisulphate ions), S2O82-, are very powerful oxidizing agents. Iodide ions are very easily oxidized to iodine. And yet the reaction between them in solution in water is very slow. The reaction is catalyzed by the presence of either iron(II) or iron(III) ions.

$S_2O_8^{2-}+2I^{-}\rightarrow 2SO_4^{2-}+I_2$ (1)

- **Alloy formation**

The transition metals readily form alloys with each other because of similar radii. The alloys so formed are hard and have often high melting points. The best known are ferrous alloys; vanadium, chromium, molybdenum, tungsten and manganese are used for the production of variety of steels and stainless steel. Industrially important alloys of transition metals with non-transition metals are brass (copper-zinc), bronze (copper-tin) etc.

- **Coordination Compounds**

The transition metals and their ions have much higher tendency to from coordination compounds as compared to the s- and p- block elements. It is because of their relatively smaller sizes, higher ionic charges and the availability of d orbitals for bond formation. Coordination compounds, unlike normal compounds, retain their identity even when dissolved in water or any other suitable solvent. The properties of these compounds are totally different from those of their constituents.

Alfred Werner can be considered to be the pioneer in the field of coordination chemistry and he received Nobel Prize in 1913 in recognition of his efforts. He showed that neutral molecules were bound directly to the metal so that complex salt such as $CoCl_3.6NH_3$ is correctly formulated as $[Co(NH_3)_6]^{3+}(Cl^-)_3$. G.N. Lewis and N.V. Sidgwick proposed that a chemical bond required the sharing of an electron pair. This led to the idea that a neutral molecule with an electron pair can donate these electrons to a metal ion or other electron acceptor.

Thus, in a coordination compound, the metal species acts as electron acceptor (Lewis acid) and neutral molecule with lone pair of electrons or anion as electron donor (Lewis bases). A metal atom or ion when bonded directly to a fixed number of anions or molecules constitutes a coordination entity. For example, $[Pt(NH_3)_2Cl_2]$ is a coordination entity in which platinum(II) is surrounded by two ammonia molecules and two chloride ions. Other examples are $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_5Cl]^{2+}$, $[Ni(CO)_4]$ etc. In a coordination entity, the atom/ion to which a fixed number of ions/ groups are bound in a definite geometrical arrangement around it, is called the central atom or ion. For example, the central atom in $[Ni(NH_3)_6]^{2+}$ is Ni(II), in $[Mo(CN)_8]^{3-}$, Mo(V), and in $[Co(PR3)_3Cl]$, Co(I). The charged ions or neutral molecules bound to the central atom in the coordination entitiy are called ligands. For example, PR3 and Cl^- are ligands in $[CoCl(PR_3)_3]$. The number of ligand donor atoms directly bonded to the central atom is defined as the coordination number. For example, in the complex species $[Mo(CN)_8]^{3-}$ and $[CoCl\ (PR_3)_3]$, the coordination number of Mo and Co are 8 and 4, respectively. The central atom and the ligands bonded to it are enclosed in square bracket and is collectively termed as the coordination sphere. For example in the complex $[Ni(NH_3)_6]Cl_2$, the coordination sphere is $[Ni(NH_3)_6]^{2+}$. The spatial arrangement of the ligands around the central atom is termed as coordination polyhedron. The most common coordination polyhedra are octahedral, tetrahedral and square planar.

- **Melting and Boiling Points**

The melting and boiling points of these elements are generally very high showing that they are held by strong forces. The melting and boiling points have the highest values in the middle of the series because, perhaps these elements have the maximum number of unpaired d-electrons available for bonding, detailed account of which will be given ahead for every series.

- **Standard Electrode Potentials and Reducing Properties**

The standard reduction potential values of transition elements are generally lower (negative) than that of the standard hydrogen electrode (taken as zero). Thus they evolve H_2 gas from acids though most of them do that at low rate.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
E^o_R (volts)	-2.10	-1.60	-1.20	-0.74	-1.18	-0.41	-0.28	-0.25	+0.34	-0.76

These elements evolve H_2 from acids though at very low rate. $M + 2H^+ \rightarrow M^{2+} + H_2$ (g). Cu does not react with acids. It has the tendency to get reduced. Sometimes the metals are protected from the attack of acids by a thin impervious layer of an inert oxide, e.g. Cr. These metals are oxidized easily to their ions and hence are reducing agent though poor due to the obvious reasons given above.

Scandium

Definition

Scandium is a transition element in Group 3 (IIIB) and Period 4 with an atomic number of 21.

Chemical Properties of Scandium

Scandium is the lightest Group 3 (IIIB) element and is the lightest of the transition metals. Its atomic number (proton number) is 21, has only one long-lived isotope, and has an atomic mass of 44.95591 a.m.u. Scandium’s electronic configuration is $[Ar]4s^2 3d^1$, and only occurs in the trivalent state (Sc^{3+}) in nature. Thus, unlike most other period 4 transition metals, the geochemical behavior of scandium is not affected by redox conditions, and shows lithophile behaviour. The effective ionic radii in six- and eight-fold coordination are 74.5 and 87 pm, respectively (Shannon 1976) and its Pauling electronegativity is 1.36. Pure scandium metal has a melting point of 1541 ℃ at 1 atm. The International Union of Pure and Applied Chemistry consider Sc to be a rare earth element (REE) (Damhus et al. 2005), however, the ionic radius and electronic configuration of Sc are sufficiently different from yttrium and the lanthanides that it is generally excluded from discussions of the REE. Scandium was “discovered” by Lars Fredrik Nilson in 1879 by separation from rare earth mixtures from euxenite and gadolinite, and is named for Scandinavia.

Sources and Uses

Global production of Sc is small (~10 tonnes per year) as a by-product from mining of ores of titanium, rare earths, apatite, and uranium. Bauxites are another potential source of Sc, as it gets concentrated, along with other elements, in the “red mud” residue that results from Al processing (Deady et al. 2014). The principal uses of Sc are in Sc-Al alloys and in solid oxide fuel cells. Minor amounts of Sc are also used in variety of other applications including electronics, lasers, and lighting.

Titanium

Chemistry of Titanium

Discovered independently by William Gregor and Martin Klaproth in 1795, titanium (named for the mythological Greek Titans) was first isolated in 1910. Gregor, a Cornish vicar and amateur chemist isolated an impure oxide from ilmenite ($FeTiO_3$) by treatment with HCl and H_2SO_4 .Titanium is the second most abundant transition metal on Earth (6320 ppm) and plays a vital role as a material of construction .

For example, when it's alloyed with 6% aluminum and 4% vanadium, titanium has half the weight of steel and up to four times the strength.

Uses of titanium

Titanium is a highly corrosion-resistant metal with great tensile strength. It is ninth in abundance for elements in the earth's crust. It has a relatively low density (about 60% that of iron). It is also the tenth most commonly occurring element in the Earth's crust. That all means that titanium should be a really important metal for all sorts of engineering applications. In fact, it is very expensive and only used for rather specialized purposes.

Titanium is very expensive because it is awkward to extract from its ores - for example, from rutile, TiO_2. Whilst a biological function in man is not known, it has excellent biocompatibility--that is the ability to be ignored by the human body's immune system--and an extreme resistance to corrosion. Titanium is now the metal of choice for hip and knee replacements

Titanium Extraction

Titanium cannot be extracted by reducing the ore using carbon as a cheap reducing agent, like with iron. The problem is that titanium forms a carbide, TiC, if it is heated with carbon, so you don't get the pure metal that you need. The presence of the carbide makes the metal very brittle. That means that you have to use an alternative reducing agent. In the case of titanium, the reducing agent is either sodium or magnesium. Both of these would, of course, first have to be extracted from their ores by expensive processes.

The titanium is produced by reacting titanium(IV) chloride, $TiCl_4$ - NOT the oxide - with either sodium or magnesium. That means that you first have to convert the oxide into the chloride. That in turn means that you have the expense of the chlorine as well as the energy costs of the conversion. High temperatures are needed in both stages of the reaction.

Titanium is made by a batch process. In the production of iron, for example, there is a continuous flow through the Blast Furnace. Iron ore and coke and limestone are added to the top, and iron and slag removed from the bottom. This is a very efficient way of making something. With titanium, however, you make it one batch at a time. Titanium(IV) chloride is heated with sodium or magnesium to produce titanium. The titanium is then separated from the waste products, and an entirely new reaction is set up in the same reactor. This is a slow and inefficient way of doing things. Traces of oxygen or nitrogen in the titanium tend to make the metal brittle. The reduction has to be carried out in an inert argon atmosphere rather than in air; that also adds to costs.

Wilhelm J. Kroll developed the process in Luxemburg around the mid 1930's and then after moving to the USA extended it to enable the extraction of Zirconium as well. Titanium ores, mainly rutile (TiO_2) and ilmentite ($FeTiO_3$), are treated with carbon and chlorine gas to produce titanium tetrachloride.

$$TiO_2 + Cl_2 \rightarrow TiCl_4 + CO_2$$

Fractionation

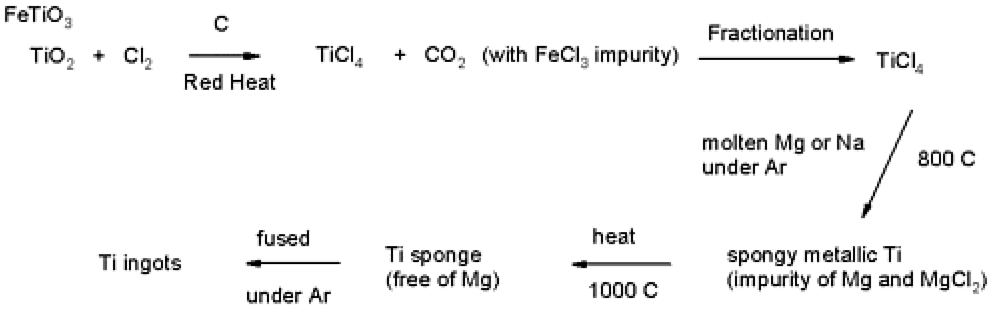
Titanium tetrachloride is purified by distillation (Boiling point of 136.4) to remove iron chloride.

Reduction

Purified titanium tetrachloride is reacted with molten magnesium under argon to produce a porous “titanium sponge”.

$$\mathbf{TiCl_4 + 2\,Mg \rightarrow Ti + 2\,MgCl_2}$$

Melting



Kroll process

Titanium Halides

- Titanium(Halides IV) TiX_4

Preparations

They can all be prepared by direct reaction of Ti with halogen gas (X_2). All are readily hydrolyzed. They are all expected to be diamagnetic.

- Titanium(III) halides TiX_3

Preparations

They can be prepared by reduction of TiX_4 with H_2. Titanium Oxides and Aqueous Chemistry

Titanium oxides

Preparations

obtained from hydrolysis of TiX_4 or Ti(III) salts. TiO_2 reacts with acids and bases.

In Acid: $TiOSO_4$ formed in H_2SO_4 (Titanyl sulfate)

In Base: $MTiO_3$ metatitanates (eg Perovskite, $CaTiO_3$ and ilmenite, $FeTiO_3$) M_2TiO_4 ortho titanates. Peroxides are highly colored and can be used for Colorimetric analysis.

$TiCl_4$ is a good Lewis acid and forms adducts on reaction with Lewis bases

$TiCl_3$ has less Lewis acid strength but can form adducts

Conversion of titanium oxide into titanium chloride

The ore rutile (impure titanium(IV) oxide) is heated with chlorine and coke at a temperature of about 900°C.

$$TiO_2 + 2Cl_2 + 2C \rightarrow TiCl_4 + 2CO$$

Other metal chlorides are formed as well because of other metal compounds in the ore. Very pure liquid titanium(IV) chloride can be separated from the other chlorides by fractional distillation under an argon or nitrogen atmosphere. Titanium(IV) chloride reacts violently with water. Handling it therefore needs care and is stored in totally dry tanks.

Reduction of the titanium chloride

Reduction by sodium: The titanium(IV) chloride is added to a reactor in which very pure sodium has been heated to about 550°C - everything being under an inert argon atmosphere. During the reaction, the temperature increases to about 1000°C.

$$TiCl_4 + 4\,Na \rightarrow Ti + 4\,NaCl \qquad (4)$$

After the reaction is complete, and everything has cooled (several days in total - an obvious inefficiency of the batch process), the mixture is crushed and washed with dilute hydrochloric acid to remove the sodium chloride.

Reduction by magnesium

This is the method used in the rest of the world. The method is similar to using sodium, but this time the reaction is:

$$TiCl_4 + 4\,Mg \rightarrow Ti + 2\,MgCl_2 \quad (5)$$

The magnesium chloride is removed from the titanium by distillation under very low pressure at a high temperature.

Vanadium

Chemistry of Vanadium

Vanadium takes its name from the Scandinavian goddess Vanadis and was discovered in 1801 by Andrés Manuel del Rio. It was isolated in 1867 by Henry Roscoe as a silvery-white metal that is somewhat heavier than aluminum but lighter than iron. It has excellent corrosion resistance at room temperature.

The history of its discovery is an interesting tale. del Rio sent his brown ore samples, containing what he thought was a new element to Paris for analysis and confirmation, along with a brief explanation that was ambiguous. The complete analysis and description of his work were lost in a shipwreck so the Paris lab saw nothing but brown powder and a brief confusing note. A second sample sent to Berlin was mislabeled lead chromate when it arrived. del Rio gave up, losing confidence in his discovery. The element was rediscovered in 1867 by Nils Sefstrôm.

Vanadium has an unusually large number of stable oxidation states (+2, +3, +4, +5)each of which is characterized by a unique color in solution. The metal is used as an alloying agent for steel. It combines with nearly all non-metals in compounds.

Vanadium(V) oxide as a Catalyst

During the *Contact Process* for manufacturing sulfuric acid, sulfur dioxide has to be converted into sulfur trioxide, which is done by passing sulfur dioxide and oxygen over a solid vanadium(V) oxide catalyst.

This is a good example of the ability of transition metals and their compounds to act as catalysts because of their ability to change their oxidation state (oxidation number). The sulfur dioxide is oxidized to sulfur trioxide by the vanadium(V) oxide. In the process, the vanadium(V) oxide is reduced to vanadium(IV) oxide.

$$SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$$

The vanadium(IV) oxide is then re-oxidized by the oxygen.

$$V_2O_4 + {}_{1/\bar{2}}O2 \rightarrow V_2O_5$$

Although the catalyst has been temporarily changed during the reaction, at the end it is chemically the same as it started.

Vanadium's oxidation states

Vanadium has oxidation states in its compounds of +5, +4, +3 and +2. This section looks at ways of changing between them. It starts with a bit of description, and then goes on to look at the reactions in terms of standard redox potentials (standard electrode potentials).

Chromium

Chromium Chemistry

History

Discovered in 1797 by the French chemist Louis Nicolas Vauquelin, it was named chromium (Greek chroma, "colour") because of the many different colours characteristic of its compounds.

Occurrence

Chromium is the earth's 21st most abundant element (about 122 ppm) and the 6th most abundant transition metal.

The principal and commercially viable ore is chromite, $FeCr_2O_4$, which is found mainly in southern Africa (with 96% of the worlds reserves), the former U.S.S.R and the Philippines. Less common sources include crocoite, $PbCrO_4$, and chrome ochre, Cr_2O_3, while the gemstones emerald and ruby owe their colours to traces of chromium.

See the International Chromium Development Association web site for more details.

Extraction

Chromite, $FeCr_2O_4$, is the most commercially useful ore, and is extensively used for extraction of chromium. Chromium is produced in two forms

Ferrochrome by the reduction of chromite with coke in an electric arc furnace. A low-carbon ferrochrome can be produced by using ferrosilicon instead of coke as the reductant. This iron/chromium alloy is used directly as an additive to produce chromium-steels which are "stainless" and hard.

Chromium metal by the reduction of Cr_2O_3. This is obtained by aerial oxidation of chromite in molten alkali to give sodium chromate, Na_2CrO_4, which is leached out with water, precipitated and then reduced to the Cr(III) oxide by carbon. The oxide can be reduced by aluminium (aluminothermic process) or silicon:

$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$ $2Cr_2O_3 + 3Si \rightarrow 4Cr + 3SiO_2$

The main use of the chromium metal so produced is in the production of nonferrous alloys, the use of pure chromium being limited because of its low ductility at ordinary temperatures. Alternatively, the Cr_2O_3 can be dissolved in sulphuric acid to give the electrolyte used to produce the ubiquitous chromium-plating which is at once both protective and decorative. The sodium chromate produced in the isolation of chromium is itself the basis for the manufacture of all industrially important chromium chemicals. World production of chromite ores approached 12 million tonnes in 1995.

Chromium Compounds

Most compounds of chromium are coloured , the most important are the chromates and dichromates of sodium and potassium and the potassium and ammonium

Chromium(III) halides

Formula	Colour	MP	M-X (pm)	μ(BM) (b)	Structure
CrF3	green	1404	190	-	-
CrCl3	red-violet	1152	238	-	CrCl3
CrBr3	green-black	1130	257	-	BiI3
CrI3	black	>500decomp	-	-	-

Chromium(II) halides

Formula	Colour	MP	μ (BM)	Structure
CrF2	green	894	4.3	distorted rutile
CrCl2	white	820-824	5.13	distorted rutile
CrBr2	white	844	-	-
CrI2	red-brown	868	-	-

Preparations:

Reduction of CrX_3 with H_2/HX gives CrX_2.

$$Cr + Cl_2 \rightarrow CrCl_3$$

$$Cr_2O_3 + C + Cl_2 \rightarrow CrCl_3$$

Oxides

Chromium oxides

Formula	Colour	Oxidation State	MP	Magnetic Moment
CrO_3	deep red	Cr^{6+}	197decomp	-
Cr_3O_8	-	intermediate	-	-
Cr_2O_5	-	-	-	-
Cr_5O_{12} etc	-	-	-	-
CrO_2	brown-black	Cr^{4+}	300decomp	-
Cr_2O_3	green	Cr^{3+}	2437	-antiferromagnetic < 35 C

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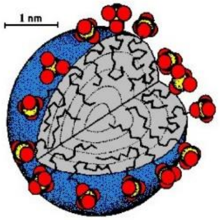
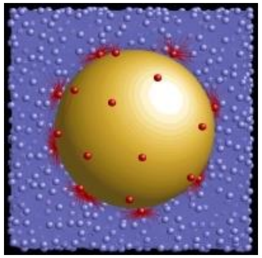
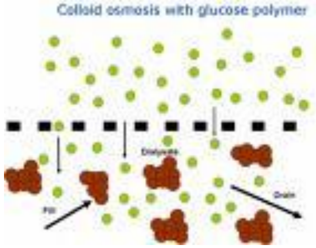
Introduction to

Colloid & Surface Chemistry



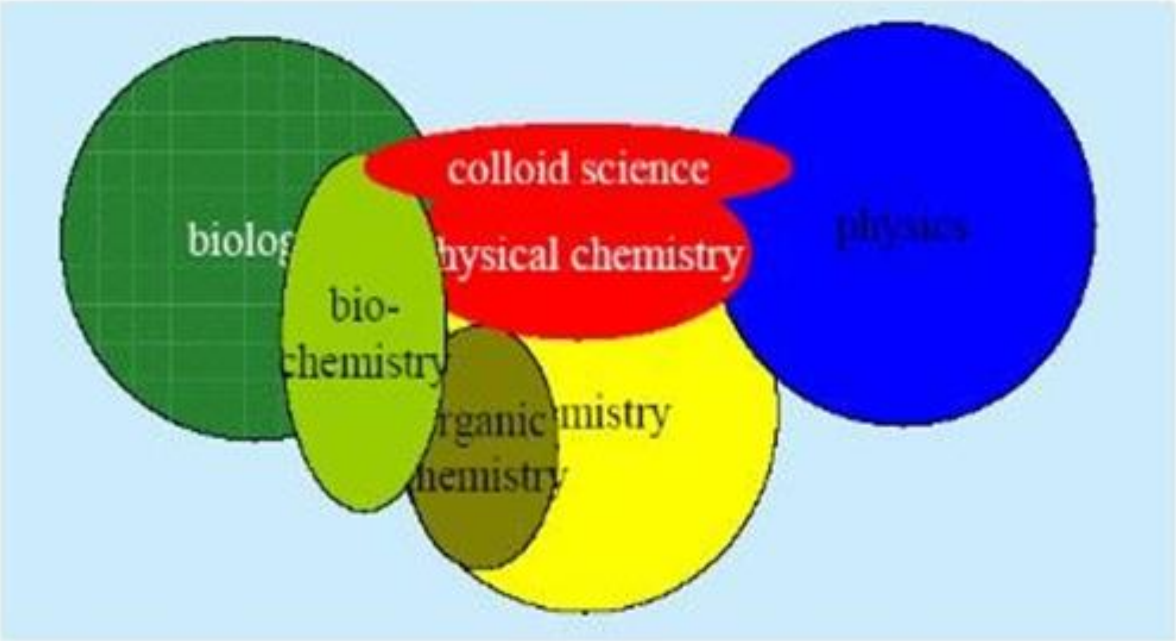




Part 1
Colloidal state

Colloid science is interdisciplinary

1. partly physical chemistry
   - it is not the chemical composition which is important
   - the state is independent of the composition
2 partly physics
   - the physical properties are of great importance
   - basic law of physics can be applied
3 partly biology
   - biological materials are colloids
   - the mechanisms of living systems are related to colloid- and interfacial chemistry



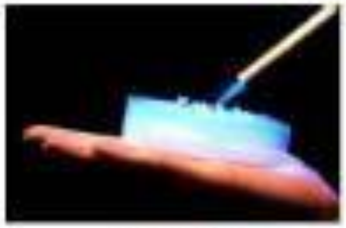
Examples of colloidal systems from daily life


Foams


Milk


Fog, smoke


Detergents


Aerogel


Blood


Paints


Cosmetics

Background (Old and new conceptions of colloids)

- In 1861, Thomas Graham divided soluble substances into two classes according to diffuse into water across a permeable membrane:
- He observed that crystalline substances such as sugar, urea, and sodium chloride passed through the membrane, while others like glue, gelatin and gum did not.

Thomas Graham

- He called the former **crystalloids** and the latter **colloids** (Greek, kolla = glue). Graham thought that the difference in the behavior of 'crystalloids' and 'colloids' was due to the particle size.

Crystalline

amorphous

Crystalloids:

Diffuse rapidly across vegetable or animal membranes such as salt, sugar and urea.

Colloids:

Exhibit little or no tendency to diffuse across vegetable or animal membranes such as gelatin, starch and gum.

Greek: *kola*= glue and *eiods*= like

Background (Old and new conceptions of colloids)

- According to Graham NaCl is crystalloid but it has been obtained in the colloidal state in benzene.

- Soap behaves as colloid in water and as crystalloid in alchohol

Later it was realized that (New conception):

►The difference in the rate of diffusion between crystalloids and colloids is due to the difference in the particle size

►Any substance, regardless of its nature, could be converted into a colloid by subdividing it into particles of colloidal size.

►We should speak of the colloidal state of matter as we speak of the gaseous, liquid or solid state of matter rather than to call a particular material as colloid or crystalloid

Nature of colloidal solutions (What are colloids)?

Sugar + water

True solution

1- 10 A^{o}

Sand + water

Suspension

>1000 A^{o}

Starch + water

Colloidal solution

10- 1000 A^{o}

Nature of colloidal solutions (What are colloids) ?

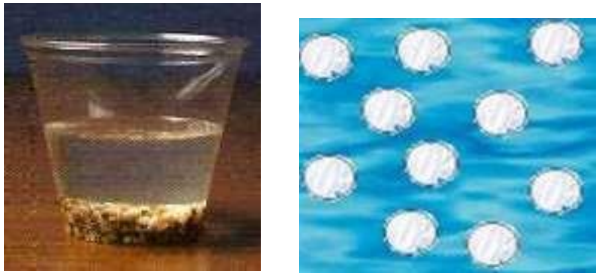
In **a true solution** as sugar or salt in water, the solute particles are dispersed in the solvent as single molecules with diameter less than 1 nm

Sugar + water (true solution(

< **1 nm**

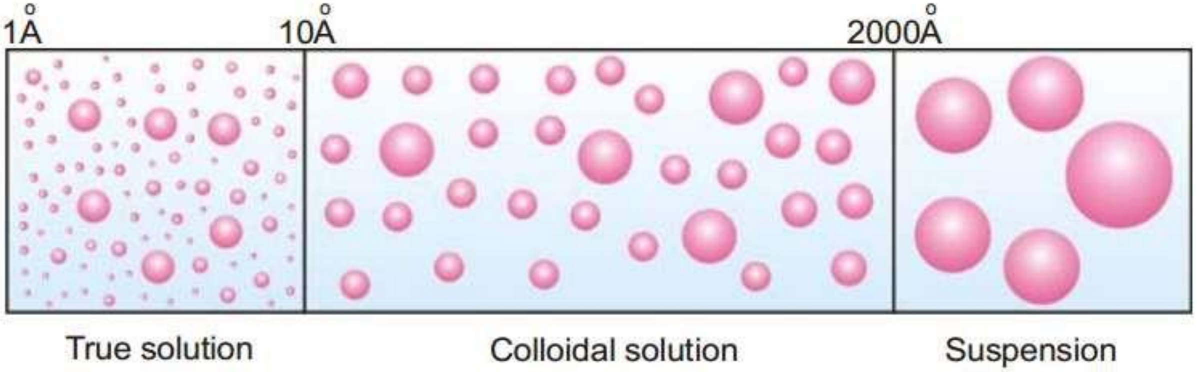
On the other hand, if **a suspension** as sand stirred into water, the dispersed particles are aggregates of millions of molecules. The diameter of these particles is of the order 1 000،Å or more

Sand + water (suspension(



<**1 000Å**

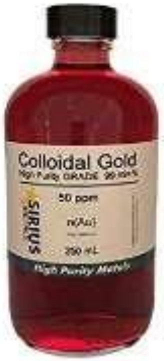
The colloidal solutions or colloidal dispersions are intermediate between true solutions and suspensions. In other words, the diameter of the dispersed particles in a colloidal dispersion is more than that of the solute particles in a true solution and smaller than that of a suspension.



Examples of colloidal solutions

Ink

Paint



Colloidal Gold

Nature of colloidal solutions (What are colloids) ?

True solution	Suspension	Colloidal solution
1- 10 A°	>1000 A°	10- 1000 A°
Transparent to light	Not transparent to light	Not transparent to light

Nature of colloidal solutions (What are colloids) ?

True solution	**Suspension**	**Colloidal solution**
1- 10 A°	>1000 A°	10- 1000 A°
Transparent to light	Not transparent to light	Not transparent to light
Can not be seen by the naked eyes or even under a microscope	Can be seen by the naked eye	Can not be seen by the naked eye or with ordinary microscope

Nature of colloidal solutions (What are colloids) ?

True solution	Suspension	Colloidal solution
1- 10 Aº	>1000 Aº	10- 1000 Aº
Transparent to light	Not transparent to light	Not transparent to light
Can not be seen by the naked eyes or even under a microscope	Can be seen by the naked eye	Can not be seen by the naked eye or with ordinary microscope
Not influenced by the gravitational pull and remain suspended in the solvent all the time	They are influenced by the gravitational pull and settle down automatically on standing	Not influenced by the gravitational pull and remain suspended in the solvent all time

Nature of colloidal solutions (What are colloids) ?

True solution	Suspension	Colloidal solution
1- 10 Aº	>1000 Aº	10- 1000 Aº
Transparent to light	Not transparent to light	Not transparent to light
Can not be seen by the naked eyes or even under a microscope	Can be seen by the naked eye	Can not be seen by the naked eye or with ordinary microscope
Not influenced by the gravitational pull and remain suspended in the solvent all the time	They are influenced by the gravitational pull and settle down automatically on standing	Not influenced by the gravitational pull and remain suspended in the solvent all time
Pass through an ordinary filter paper	Retained by an ordinary filter paper	Pass through an ordinary filter paper

Colloidal particles under microscope

Light microscope

Ultra- microscope

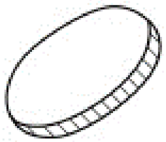
Electron microscope

The colloidal particles are smaller than the wavelength of the visible light. Thus, they are unable to reflect light and hence cannot be seen by ordinary microscope

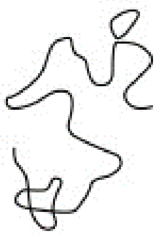
Note that

The colloidal particles are not necessarily corpuscular in shape. In fact, these may be rod-like, disc-like, thin films, or long filaments. For matter in the form of corpuscles, the diameter gives a measure of the particle size .

Rod



Disc



Random coil

However, in other cases one of the dimensions (length, width and thickness) has to be in the colloidal range for the material to be classed as colloidal .

Thus in a broader context we can say:

“A system with at least one dimension (length, width, or thickness) of the dispersed particles in the range 10 Å to 1 000‹Å, is classed as a colloidal dispersion”

Classification of colloids

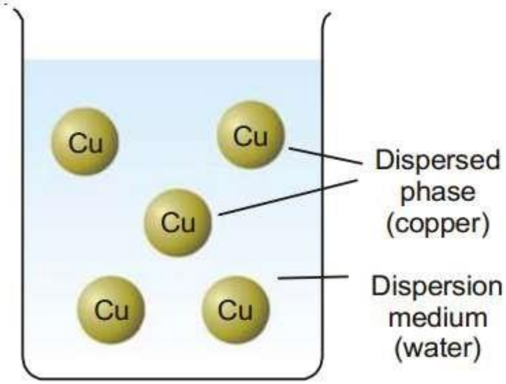
Classification is based on following criteria:

1. Physical state of dispersed phase and dispersion medium.
2. Nature of interaction between dispersed phase and dispersion medium.
3. Types of particles of the dispersed phase.

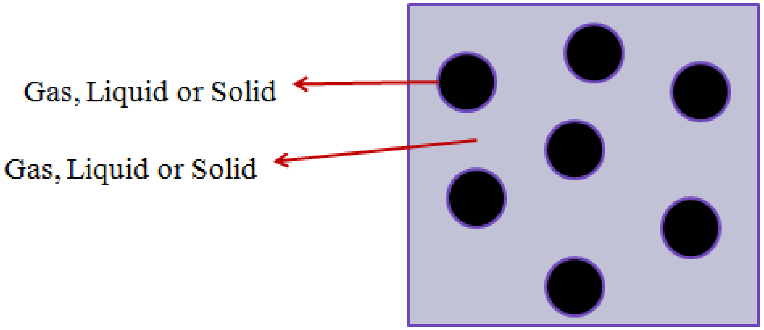
Classification based on physical state of dispersed phase and dispersion medium

Any colloidal system is made of two phases. The substance distributed as the colloidal particles is called the **Dispersed Phase** and the second continuous phase in which the colloidal particles are dispersed is called the **Dispersion Medium.**

For example, for a colloidal solution of copper in water, copper particles constitute the dispersed phase and water the dispersion medium.



Either the dispersed phase or the dispersion medium can be a gas, liquid or solid



A colloidal dispersion of one gas in another is not possible since the two gases would give a homogeneous molecular mixture. So that, there are **Eight** possible types of colloidal systems

X

Dispersed phase	Gas	Gas	Gas	Liquid	Liquid	Liquid	Solid	Solid	Solid
Dispersion medium	Gas	Liquid	Solid	Gas	Liquid	Solid	Gas	Liquid	Solid

1 Foam

Dispersed phase: **Gas** **Dispersion medium:** **Liquid**

Examples


Whipped cream


Shaving cream


Soda water


Soap Solution

2 Solid Foam

Dispersed phase: **Gas** **Dispersion medium:** **Solid**

Examples


Cork stoppers


Pumice stone


Foam rubber


Marshmallow

3 Aerosol

Dispersed phase: Liquid **Dispersion medium:** Gas

Examples


Cloud


Aerosol spray


Mist


Fog

4 Emulsion

Dispersed phase: Liquid **Dispersion medium:** Liquid

Examples


Milk

Hair cream


Mayonnaise


Emulsified water

5 Solid Emulsion (Gel)

Dispersed phase: Liquid

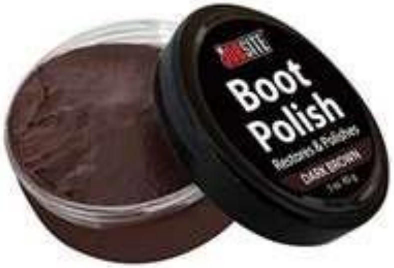
Dispersion medium: Solid

Examples


Butter


Cheese


Jelly



Boot Polish

6 Smoke

Dispersed phase: Solid **Dispersion medium:** Gas

Examples

7 Sol (Colloidal Solutions)

Dispersed phase: Solid
Dispersion medium: Liquid

Examples

Ink

Paint

Colloidal Gold

8 Solid Sol

Dispersed phase: Solid

Dispersion medium: Solid

Examples

Colored Glass

Metal Alloys

Classification of colloids

Classification is based on following criteria:

1. Physical state of dispersed phase and dispersion medium.
2. Nature of interaction between dispersed phase and dispersion medium.
3. Types of particles of the dispersed phase.

Classification based on nature of interaction

Solid dispersed in liquid (Sols(

Lyophilic (solvent-loving) **and Lyophobic** (solvent-hating) **sols**

Lyophilic sols: are those in which the dispersed phase exhibits a definite affinity for the medium or the solvent.

The examples of Lyophilic sols are dispersions of starch, gum, and protein in water.

Lyophobic sols: are those in which the dispersed phase has no attraction for the medium or the solvent.

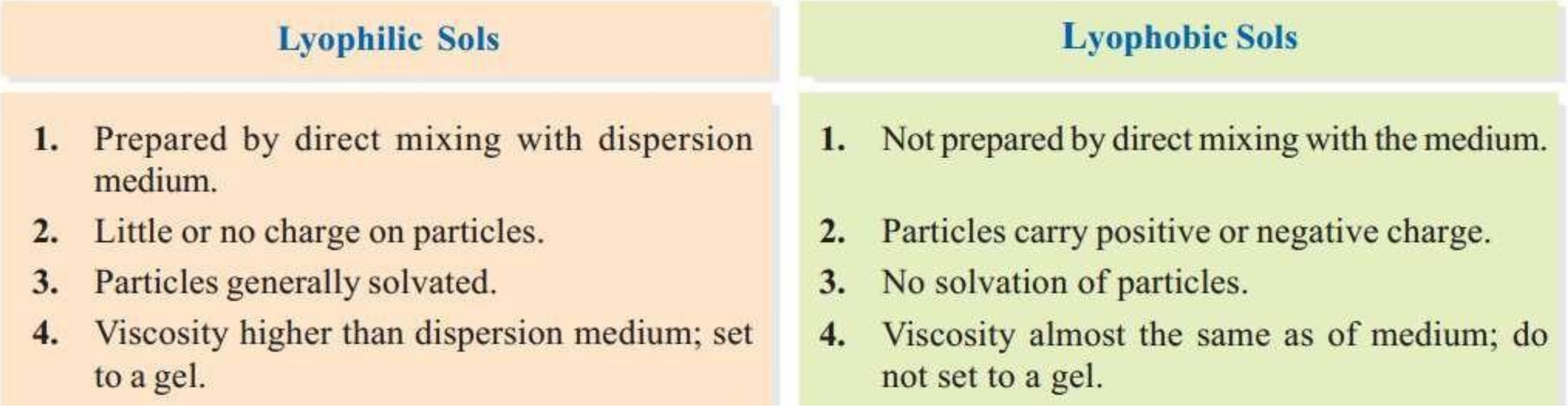
The examples of Lyophobic sols are dispersion of gold, iron (III) hydroxide and sulphur in water.

Solid dispersed in liquid (Sols(

Lyophilic (solvent-loving) **and Lyophobic** (solvent-hating) **sols**

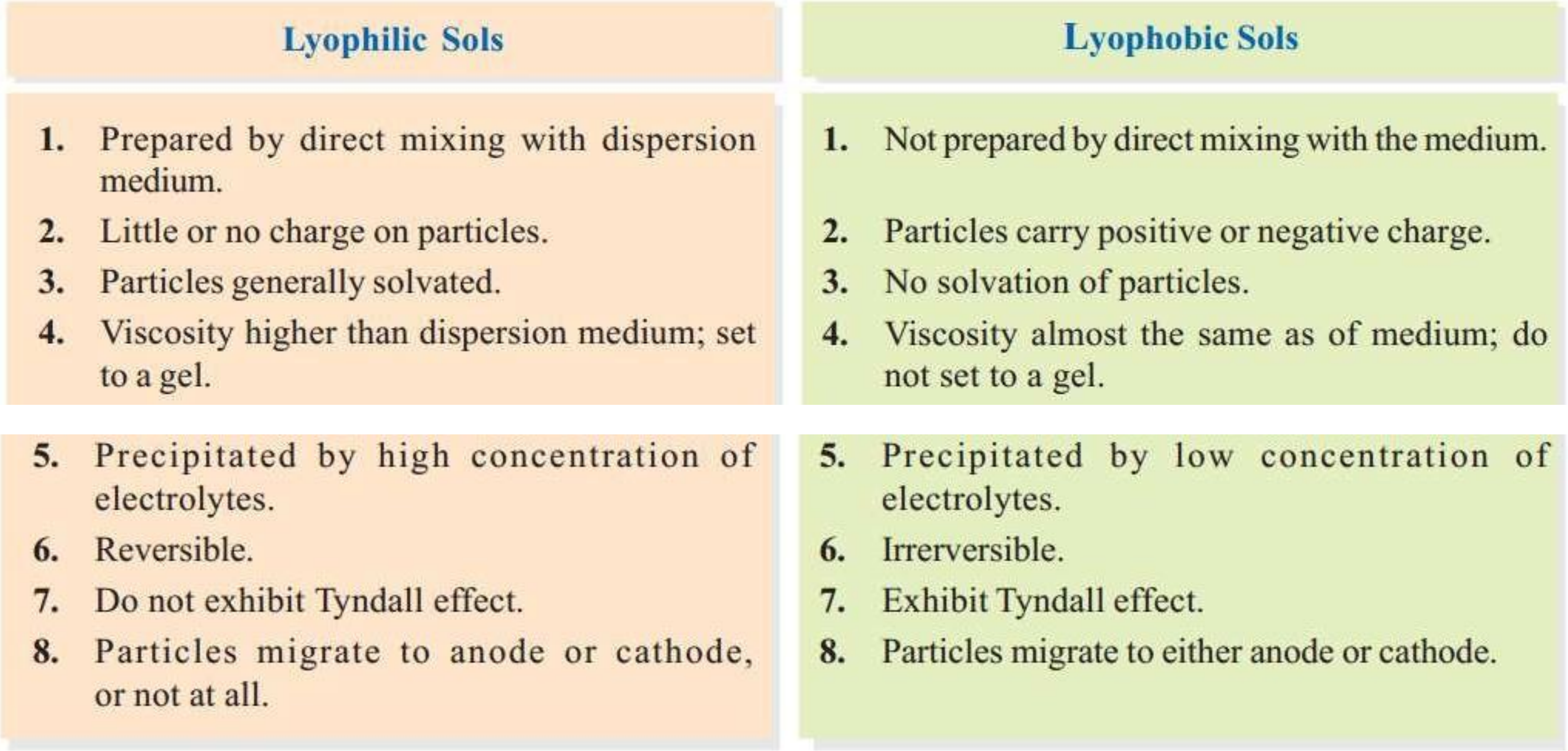
- The affinity or attraction of the sol particles for the medium, in a lyophilic sol, is due to hydrogen bonding with water .
- If the dispersed phase is a protein (as in egg) hydrogen bonding takes place between water molecules and the amino groups (–NH–, $-NH_2$) of the protein molecule.
- In a dispersion of starch in water, hydrogen bonding occurs between water molecules and the – OH groups of the starch molecule.
- There are no similar forces of attraction when sulphur or gold is dispersed in water.

Differences between lyophilic and lyophobic sols



Lyophilic Sols	Lyophobic Sols
1. Prepared by direct mixing with dispersion medium.	**1.** Not prepared by direct mixing with the medium.
2. Little or no charge on particles.	**2.** Particles carry positive or negative charge.
3. Particles generally solvated.	**3.** No solvation of particles.
4. Viscosity higher than dispersion medium; set to a gel.	**4.** Viscosity almost the same as of medium; do not set to a gel.

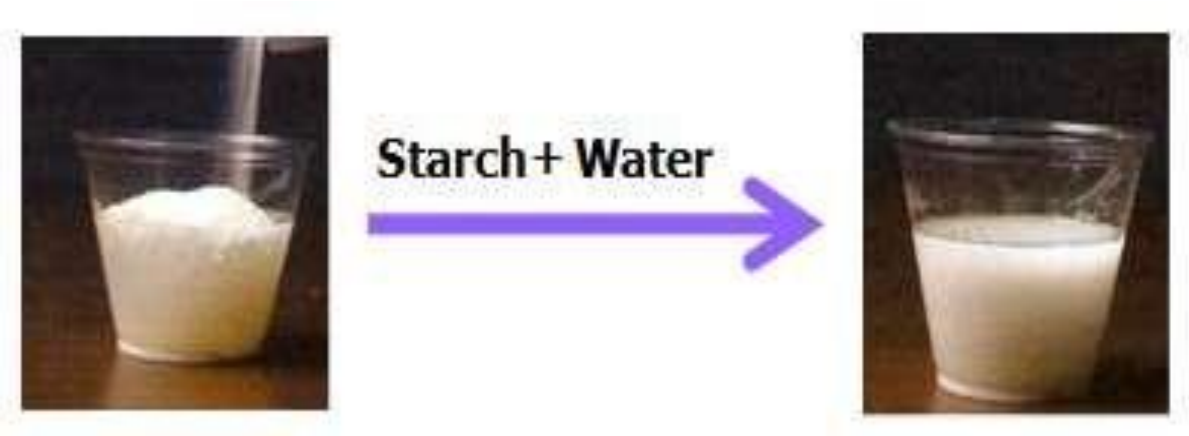
Differences between lyophilic and lyophobic sols



Lyophilic Sols	Lyophobic Sols
1. Prepared by direct mixing with dispersion medium.	1. Not prepared by direct mixing with the medium.
2. Little or no charge on particles.	2. Particles carry positive or negative charge.
3. Particles generally solvated.	3. No solvation of particles.
4. Viscosity higher than dispersion medium; set to a gel.	4. Viscosity almost the same as of medium; do not set to a gel.
5. Precipitated by high concentration of electrolytes.	5. Precipitated by low concentration of electrolytes.
6. Reversible.	6. Irrerversible.
7. Do not exhibit Tyndall effect.	7. Exhibit Tyndall effect.
8. Particles migrate to anode or cathode, or not at all.	8. Particles migrate to either anode or cathode.

Preparation of sols

Lyophilic sols may be prepared by simply warming the solid with the liquid dispersion medium e.g., starch with water.



Preparation of sols

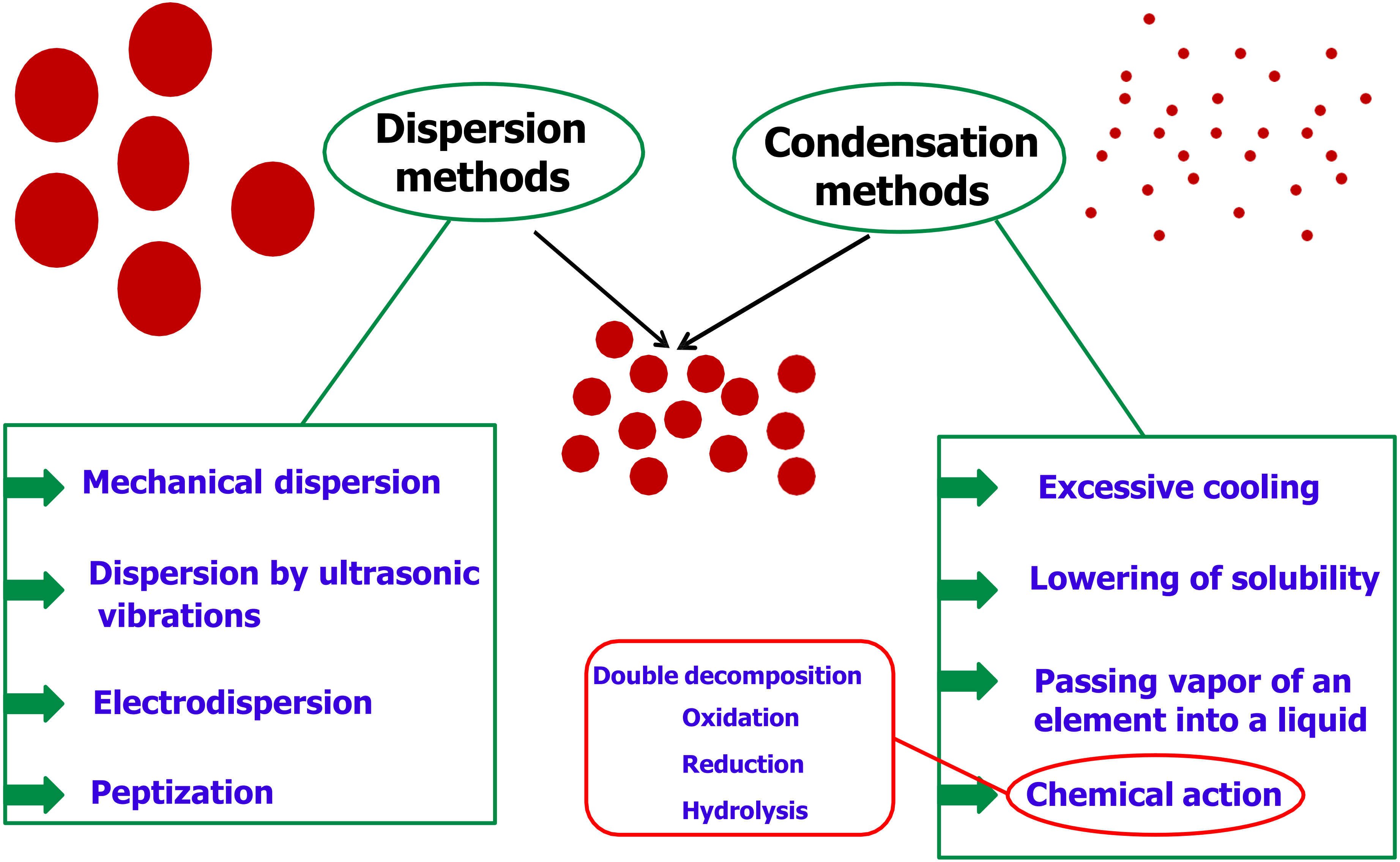
Lyophobic sols

Have to be prepared by special methods. These methods fall into two categories :

Dispersion Methods: in which larger macro-sized particles are broken down to colloidal size.

Aggregation (Condensation) Methods: in which colloidal size particles are built up by aggregating single ions or molecules of true solution

Preparation of colloidal solutions



Dispersion methods

- Mechanical dispersion
- Dispersion by ultrasonic vibrations
- Electrodispersion
- Peptization

Condensation methods

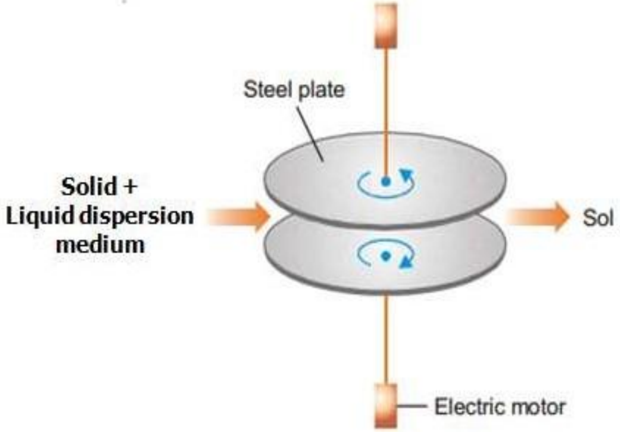
- Excessive cooling
- Lowering of solubility
- Passing vapor of an element into a liquid
- Chemical action

Double decomposition
Oxidation
Reduction
Hydrolysis

A- Dispersion Methods

-1Mechanical dispersion using colloid mill

- The solid along with the liquid dispersion medium is fed into a Colloid disk mill.
- The mill consists of two steel plates nearly touching each other and rotating in opposite directions with high speed.
- The solid particles are ground down to colloidal size and are then dispersed in the liquid to give the sol.
- Colloidal graphite and printing inks are made by this method.

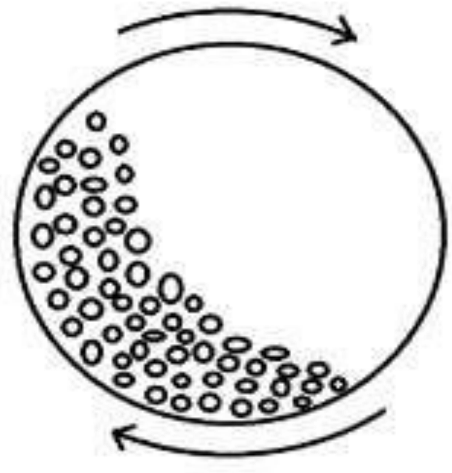


Disk mill

A- Dispersion Methods

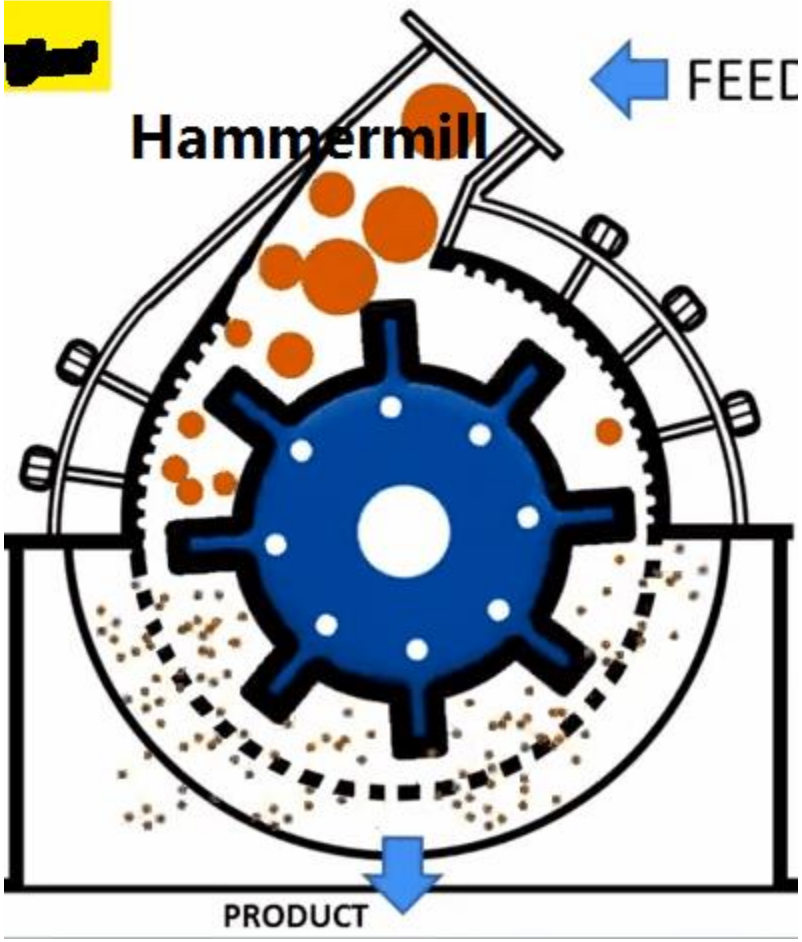
-1Mechanical dispersion using colloid mill

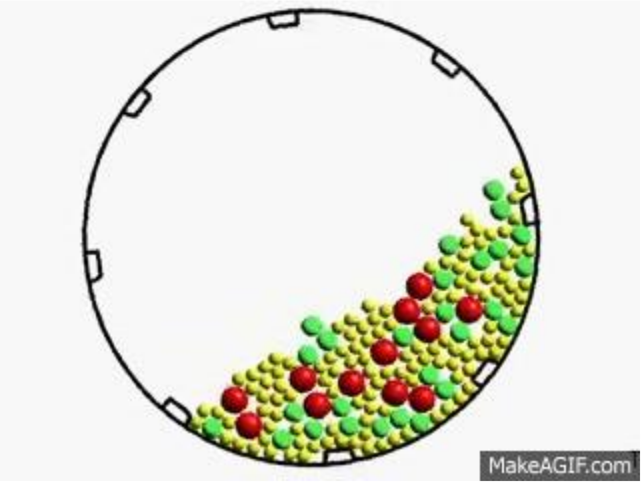
- A colloidal ball mill can also employed to obtain a colloidal solution from suspension .
- Due to the high speed rotation of the mill the coarse particles roll over one another to form fine particles of the colloidal size.



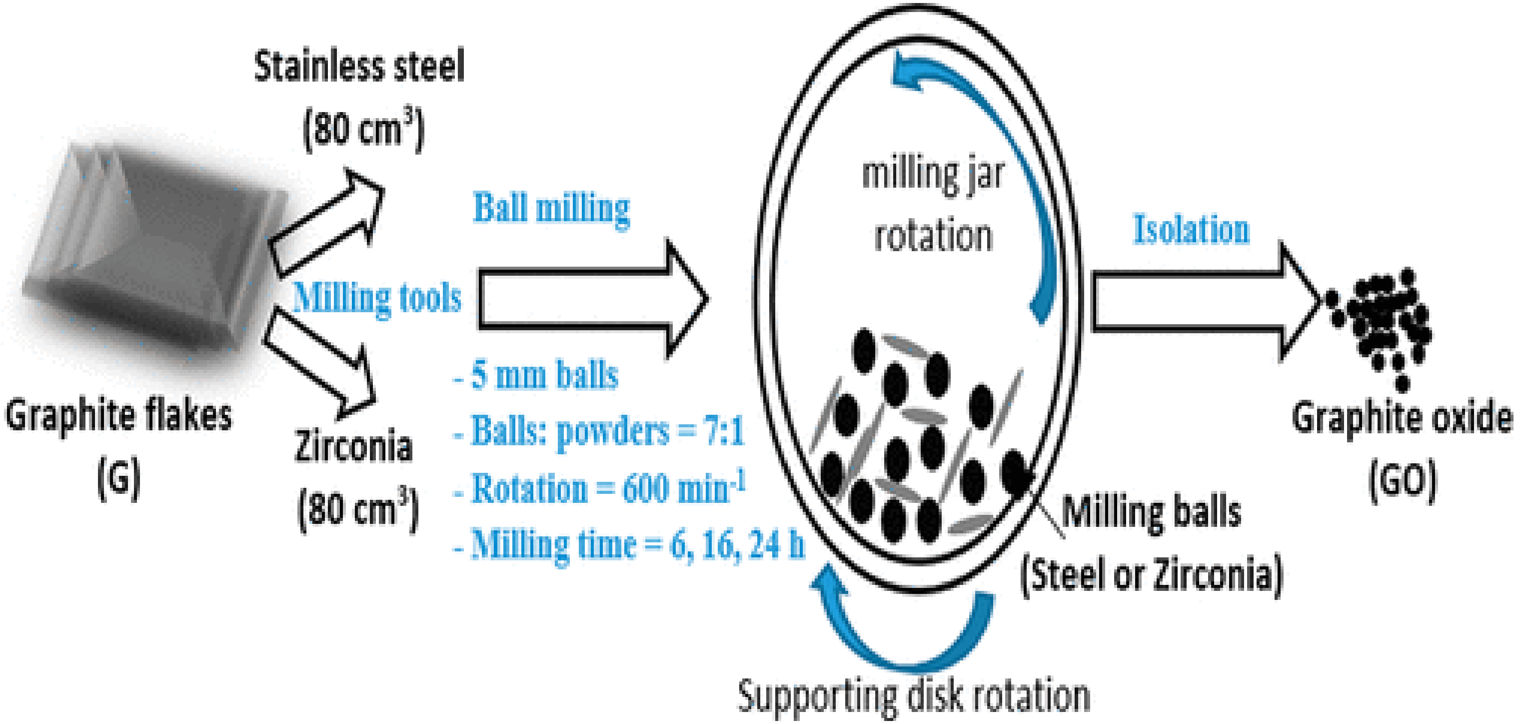
Ball mill

1- Mechanical dispersion using colloid mill





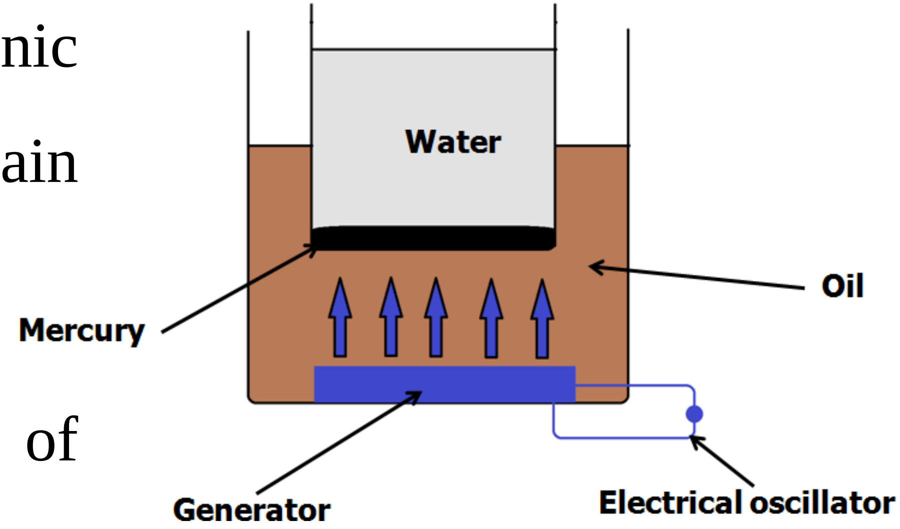
-1Mechanical dispersion using colloid mill



Ref: Sustainable Synthesis of High-Surface-Area Graphite Oxide via Dry Ball Milling, Alaa El Din Mahmoud, Achim Stolle, and Michael Stelter, *ACS Sustainable Chem. Eng.* 2018, 6, 5, 6358–6369.

-2Dispersion by ultrasonic vibrations

- In this case, the transformation of coarse particles to the colloidal size is carried out using the ultrasonic vibrations produced by a certain generator.

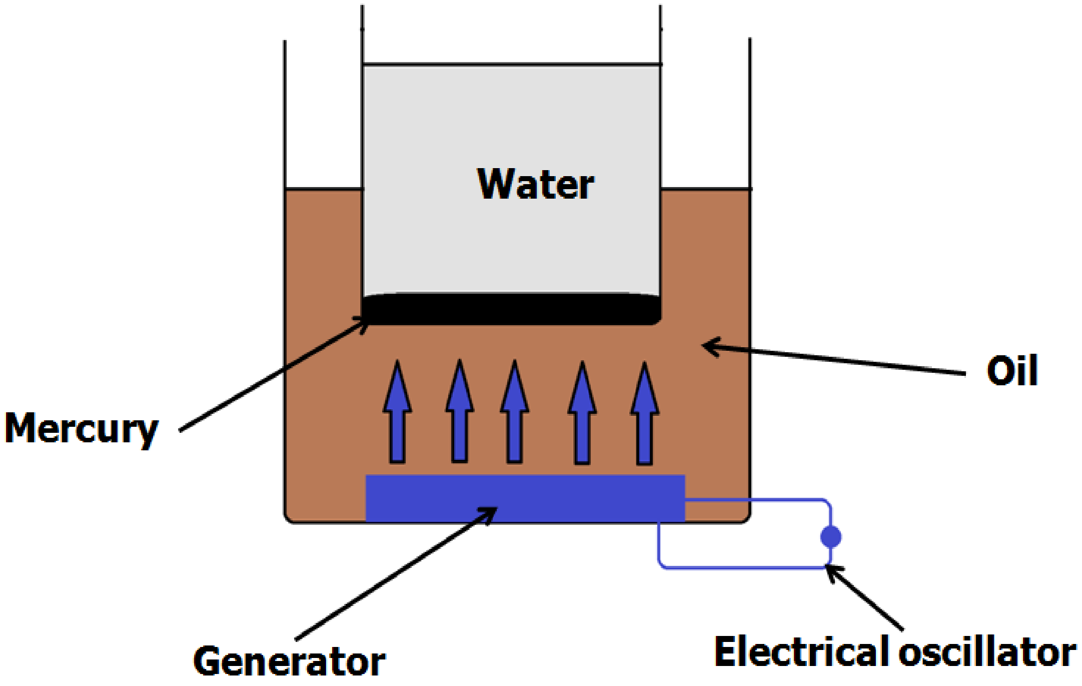


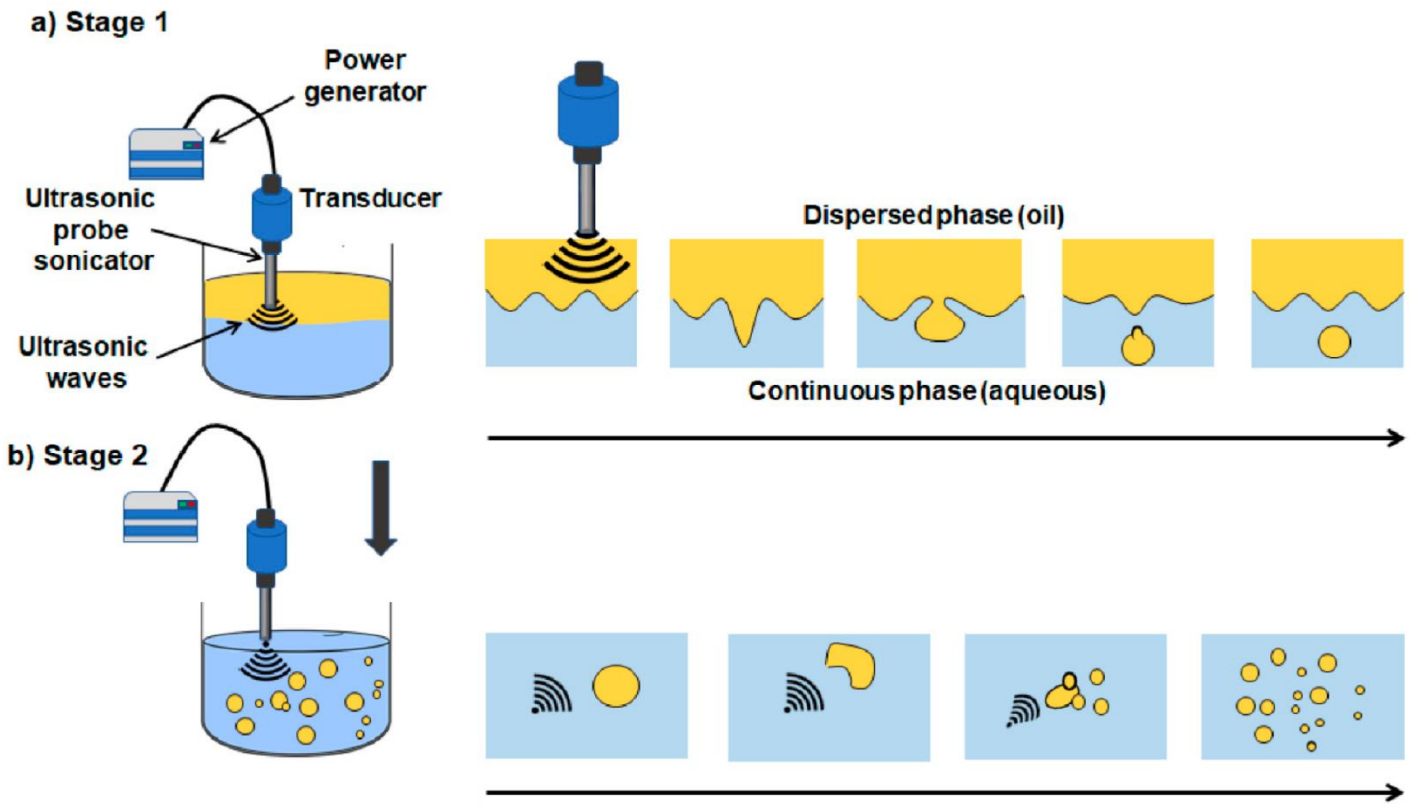
- The figure shows the formation of colloidal solution of mercury in water.

- Ultrasonic vibrations spread through the oil and hit the vessel having mercury under water .

-2Dispersion by ultrasonic vibrations

- The ultrasonic vibrations travels through the walls of the mercury container and produce clouds of mercury which form the mercury sol.





Schematic representation of ultrasonic emulsification.

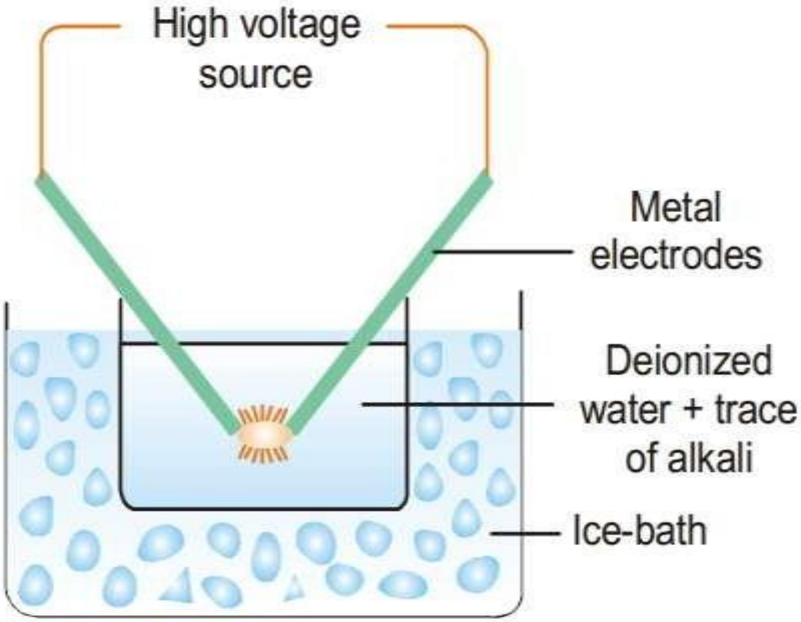
(a) The shear forces generated during acoustic cavitation near the interface between the aqueous phase and oil phase promote the eruption of large oil drops (dispersed phase) in the continuous aqueous phase.

(b) The oil droplets formed in the first stage are reduced to smaller droplets as a consequence of the shock waves generated during cavitation

(adapted from Perdih et al., 2019 and Plüisch and Wittemann, 2016).

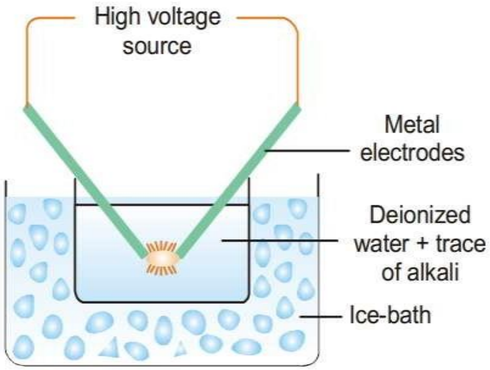
-3Bredig’s Arc Method (electrical disintegration)

- It is used for preparing hydrosols of metals e.g., silver, gold and platinum .
- An arc is struck between the two metal electrodes held close together in de- ionized water with trace of alkali .
- The water is kept cold by immersing the container in ice/water bath.
- The intense heat of the spark across the electrodes vaporizes some of the metal and the vapor condenses under water.

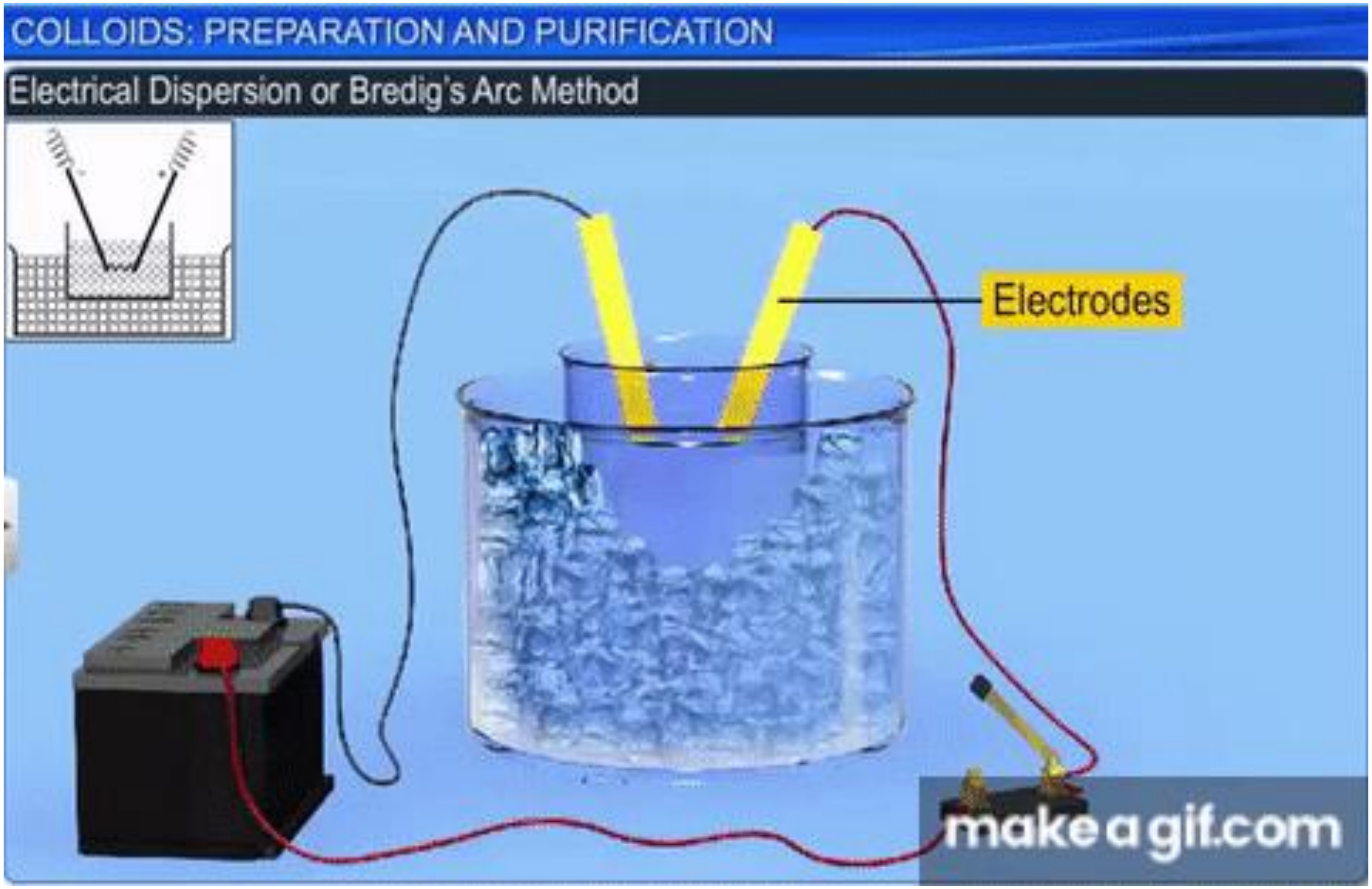


-3Bredig’s Arc Method

- Thus the atoms of the metal present in the vapour aggregate to form colloidal particles in water .
- Since the metal has been ultimately converted into sol particles (via metal vapour), this method has been treated as of dispersion method also.
- Non-metal sols can be made by suspending coarse particles of the substance in the dispersion medium and striking an arc between iron electrodes.
- This method is not suitable when the dispersion medium is an organic liquid as considerable charring occurs.



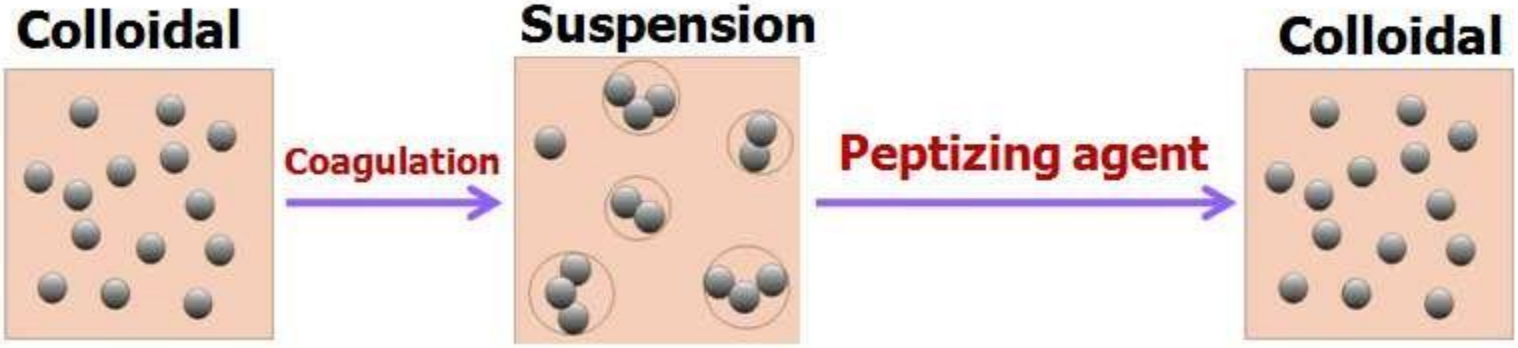
3- Bredig's Arc Method



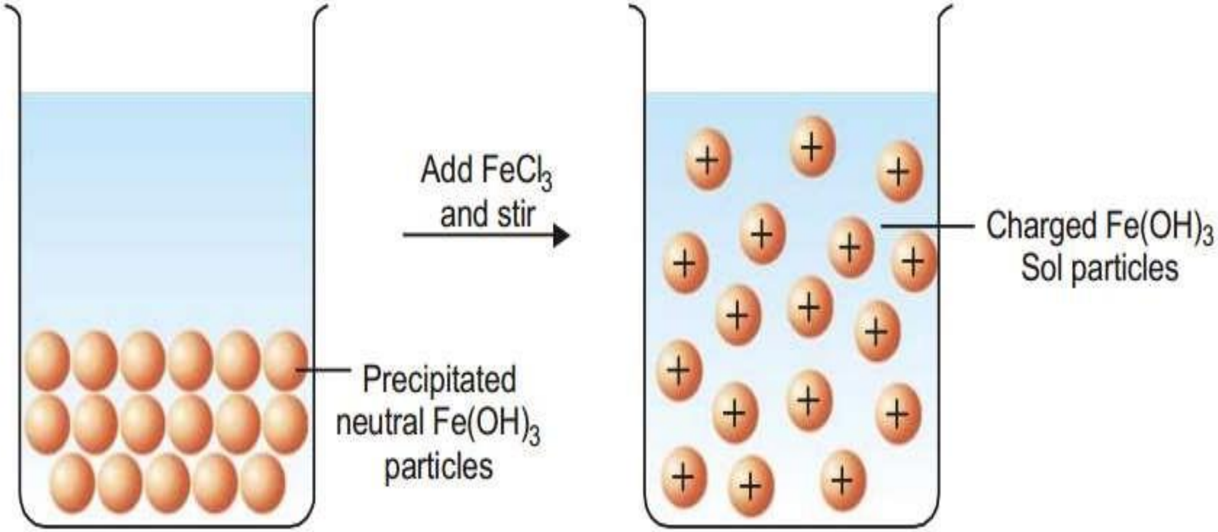
-4Peptization

- Some freshly precipitated ionic solids are dispersed into colloidal solution in water by the addition of small quantities of electrolytes, particularly those containing a common ion .

- The precipitate particles adsorbs the common ions to be electrically charged particles, then split from each other to form colloidal solution.



Sol of ferric hydroxide is obtained by stirring fresh precipitate of ferric hydroxide with a small amount of $FeCl_3$

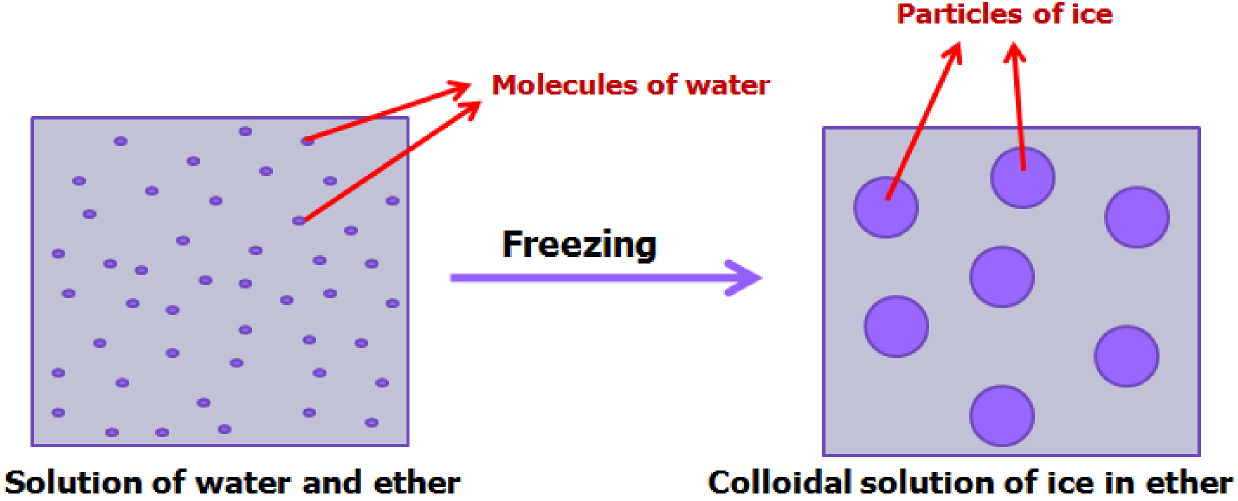


- The transformation of a precipitated material to colloidal solution by the action of an electrolyte in solution, is termed **peptization** which is the reverse of **coagulation** and the electrolyte used is called a peptizing agent.
- Another examples of preparation of sols by peptization is silver chloride, AgCl which can be converted into a sol by adding hydrochloric acid

B- Aggregation Methods

The more important aggregation methods are:

-1Extensive cooling



- The colloidal solution of ice in an organic solvent like ether is obtained by freezing a solution of water in the solvent .
- As a result of the sudden freezing of the solution, the molecules of water held together to form particles in the colloidal size dispersed in the organic solvent (ether(

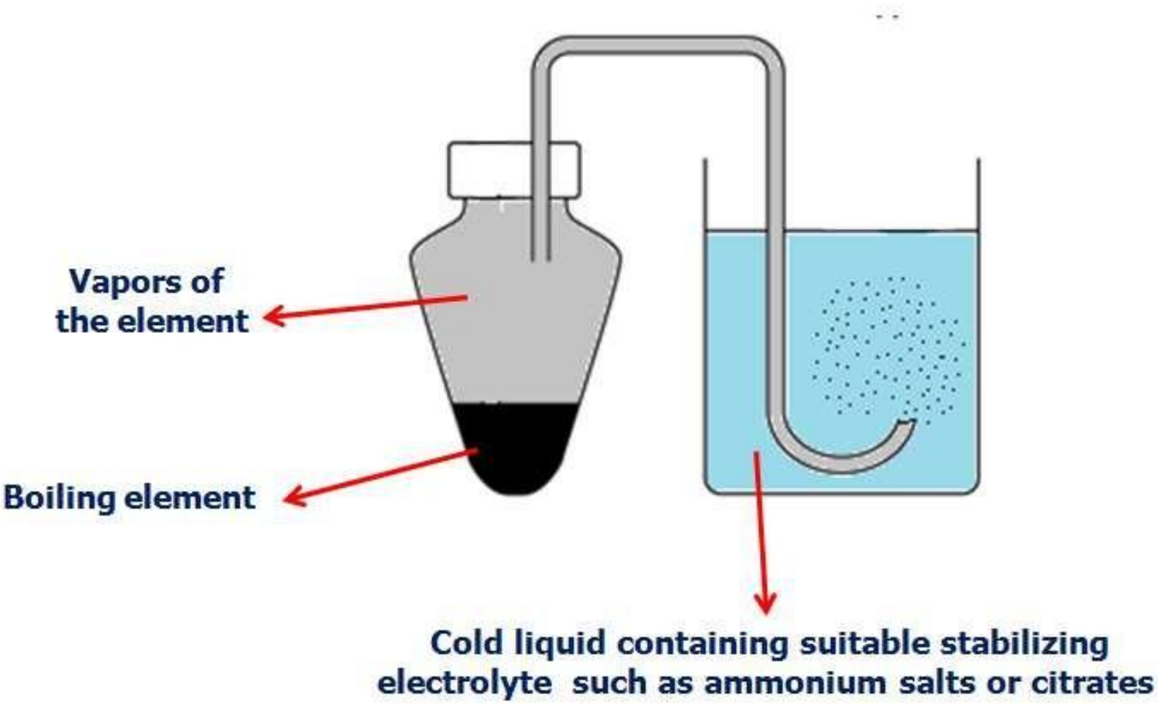
-2Lowering of solubility by exchange of solvent

- Substances like **sulphur**, **phosphorous**, etc., which are more soluble in alcohol than in water give a hydrosol by pouring a small amount of their alcoholic solution in excess of water .

- By the transference from alcohol to water, the substance is transformed from the **molecular state (true solution)** to the **colloidal state** by the coagulation of molecules together to form particles in the colloidal range.

- Phenolphthalein indicator, for example, is soluble in alcohol and not in water, so that, it is supplied to laboratory as alcoholic solution. If water is added to this solution, a milky liquid of colloidal phenolphthalein in water is produced.

-3Passing vapor of an element into a liquid



- If the vapors of a boiling element are conducted into a cold liquid, condensation takes place. Sometimes, this condensation resulted in the formation of a stable sol .
- Mercury and sulphur sols can be prepared by this method.

-4Chemical action

a- Double decomposition

- An arsenic sulphide (As_2S_3) sol is prepared by passing a slow stream of hydrogen sulphide gas through a cold solution of arsenious oxide (As$_2$O .($_3$

$$\mathbf{As_2O_3 \quad + \quad 3\,H_2S \rightarrow As_2S_{3(yellow\ sol\ )} \quad + \; 3\,H_2O}$$

- This is continued till the yellow colour of the sol attains maximum intensity.

-4Chemical action

b- Reduction

Silver sols and gold sols can be obtained by treating dilute solutions of silver nitrate or gold chloride with suitable reducing agents

$$AgNO_3 \xrightarrow{\text{Reducing agent}} \text{Ag sol}$$

$$AuCl_3 \xrightarrow{\text{Reducing agent}} \text{Au sol}$$

Reducing agents could be organic reducing agents like tannic acid or formaldehyde or others.

c- Oxidation

A sol of sulphur is produced by passing hydrogen sulphide into a solution of sulphur dioxide.

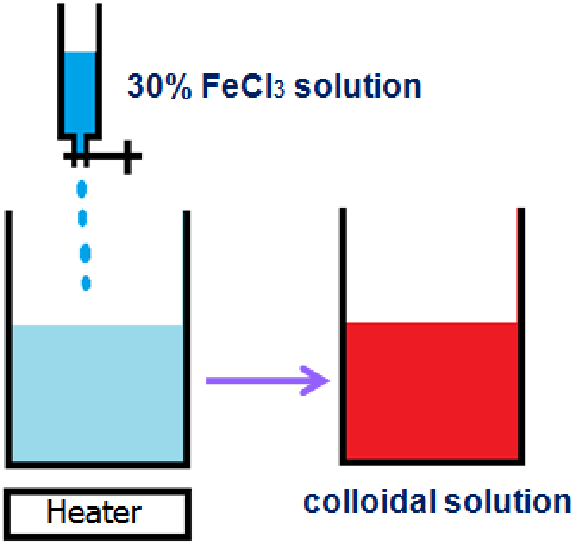
$$2H_2S + SO_2 \longrightarrow 2H_2O + S\downarrow$$

Or exploring H_2S to air for a long time

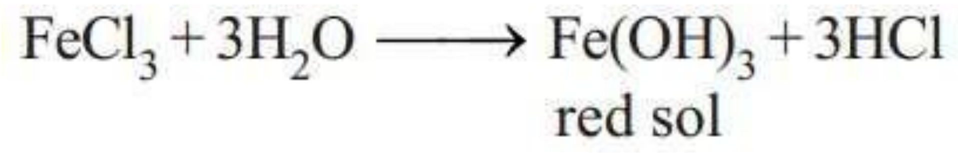
$$H_2S + O \rightarrow H_2O + S$$

d- Hydrolysis

- Sols of the hydroxides of **iron**, **chromium** and **aluminium** are readily prepared by the hydrolysis of salts of the respective metals .



- In order to obtain a red sol of ferric hydroxide, a few drops of 30% ferric chloride solution is added to a large volume of almost boiling water and stirred with a glass rod.



$$FeCl_3 + 3H_2O \longrightarrow \underset{\text{red sol}}{Fe(OH)_3} + 3HCl$$

Condensation method

Normal crystals are formed in two stages:

1. The Nucleation (formation of crystallization centers) in a supersaturated solution (like in chemical reaction that yields a slightly soluble compound.(
2. The growth of nuclei leading to the formation of sufficiently large crystals.

The nucleation rate (U) can be expressed as:

$$U= K\ (C_{sup}-C_s)/C_s$$

Condensation method

$$U = K\,(C_{sup} - C_s)/C_s$$

Where K is constant

C_{sup} = conc. of supersaturated solution

C_s = conc. of a saturated solution.

$(C_{sup}-C_s)$ is an excess of a substance which is able to form crystals, then can serve as a measure of the rate of liberation from the solution.

Cs can serve a measure of resistance to the liberation (interaction between the solute and solvent).

Condensation method

So, the grater the (C_{sup}-C_s) and the smaller Cs, the more rapidly the nuclei formed and the larger is the no. of crystallization centers, hence the smaller are colloidal particles because the liberated substance will be distributed between a large n. of crystallization centers.