→ Oxidation and Reduction :→

① Oxidation :→

- Oxidation can be defined in a number of ways as shown below:-

(i) Classical concept :→

ⓐ Addition of oxygen (O) or electronegative element.

ⓑ Removal of hydrogen (H) or elecropositive element.

(ii) Electronic concept (Modern concept) :→

ⓐ oxidation number of an element increases.

ⓑ An atom or ion loses one or more electron thus the valency of the atom or ion is increases.

ⓒ An atom or ion loses one or more electron and changed into more electropositive or less electronegative state.

- Since electrons are lost in oxidation, so oxidation is also called de-electronation.

② Reduction :→

- Reduction can be defined in a number of ways as shown below:-

(i) classical concept :→

ⓐ Addition of hydrogen (H) or electropositive element.

ⓑ Removal of oxygen (O) or electropositive element.

(ii) Electronic concept (Modern concept):→

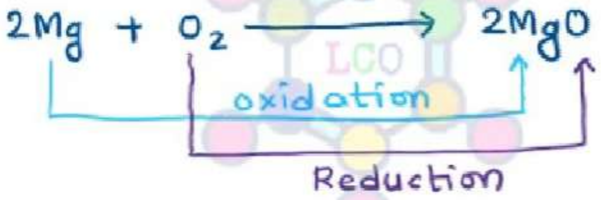
ⓐ Oxidation number of an element decreases.

ⓑ An atom or ion gains one or more electrons and thus the valency of the atom or ion is decreased.

ⓒ An atom or ion gains one or more electrons and changed into less electropositive or more electronegative element.

- since electrons gained in reduction, so reduction is also called electronation.

Example:-



$$2Mg + O_2 \longrightarrow 2MgO$$

- This reaction can be represented as half reaction.

$$2Mg \longrightarrow 2Mg^{+2} + 4e^-$$ oxidation (loss of e⁻)

$$O_2 + 4e^- \longrightarrow 2O^{-2}$$ reduction (gain of e⁻)

→ oxidising agent or oxidant :→

- An oxidising agent is a substance which is an e^- acceptor or removes electrons from other specipes or gives O or electronegative element to other substance.

→ Reducing agent or reductant :→

- An reducing agent is a substance with is an e^- donor or supplies electrons to other species or gives H or electropositive element to other substance.

Example :-

$$3CuO + 2NH_3 \longrightarrow 3Cu + N_2 + 3H_2O$$

Cu = +2   N = −3   Cu = 0   N = 0

oxidation

Reduction

CuO → oxidising agent (e^- acceptor)

NH_3 → reducing agent (e^- donor)

→ Electrode potential :→

- when a metal rod is partially immersed in the solution of its salts, there are two possibilities.

ⓐ Metal is oxidised and metal ion formed leave the rod and pass into solution. thus e^- released by metal makes metal rod negative.

ⓑ Metal ion from solution deposit on the metal rod by gaining electrons. hence makes metal rod positive.

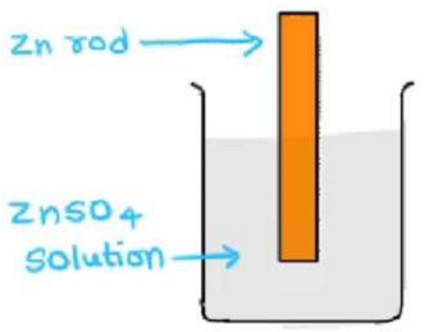


fig:- Zn electrode

- When equilibrium is stabilised between metal and metal ions, some potential differenc develops between them. This potential difference is called electrode potential.
- The tendency of an electrode to lose or gain electrons when it is in contact with its own ion in solution, is called electrode potential.
- The tendency to gain e^- is called reduction potential and tendency to lose e^- is called oxidation potential. oxidation potential is reverse to reduction potential.
- When metal rode is immersed in its solution of salts, metal is oxidised or metal is reduced. so electrode potential is also called oxidation-reduction potential (ORP) or redox potential.

- The redox potential is the tendency of a redox couple or redox pair to donate or accept electrons.
- It is not possible to determine experimentally the potential of single electrode i.e. electrode potential or redox potential.
- In order to determine signle eletrode potential of an electrode, electrode must be coupled with standard hydrogen electrode (SHE), which have zero electrode potential. The value of electrode potential determined is called standard electrode potential (E°) or standard reduction potential or standard redox potential.
- The electrode potential of an electrode depends on conc^n of the solution at given temp. During measurement of standard electrode potential, the conc^n of solution taken as unity at 25°c.

→ Electrochemical series :→

- The values of Standard electrode potential of atom or ion are arranged in decreasing order or series. This series is called Electrochemical series.

Electrode	Electrode Reaction	E°_{rd} (volts)
$F_2(g); 2F^-$	$F_2 + 2e^- \rightleftharpoons 2F^-$	+2·87
$Co^{3+}, Co^{2+}; Pt$	$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1·82
$Ce^{4+}, Ce^{3+}; Pt$	$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	+1·61
$Mn^{2+}, MnO_4^-; Pt$	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1·51
Au^{3+}, Au	$Au^{3+} + 3e^- \rightleftharpoons Au$	+1·50
$Cl_2(g), 2Cl^-; Pt$	$Cl_2(g, 1\ atm) + 2e^- \rightleftharpoons 2Cl^-$	+1·36
$Cr^{3+}, Cr_2O_7^{2-}$	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1·33
Tl^{3+}, Tl^+	$Tl^{3+} + 2e^- \rightleftharpoons Tl^+$	+1·25
$Br_2(l), 2Br^-; Pt$	$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1·06
$Hg^{2+}, Hg_2^{2+}; Pt$	$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$	+0·92
$Ag^+; Ag$	$Ag^+ + e^- \rightleftharpoons Ag$	+0·80
$Fe^{3+}, Fe^{2+}; Pt$	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0·77
$Hg_2SO_4(s), SO_4^{2-}; Hg$	$Hg_2SO_4(s) + e^- \rightleftharpoons 2Hg + SO_4^{2-}$	+0·61
$I_2(s); 2I^-; Pt$	$I_2(s) + 2e^- \rightleftharpoons 2I^-$	+0·53
Cu^+, Cu	$Cu^+ + e^- \rightleftharpoons Cu$	+0·52
Cu^{2+}, Cu	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0·34
$Hg_2Cl_2(s), Cl^-; Hg$	$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg + 2Cl^-$	+0·28
$AgCl(s), Cl^-; Ag$	$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+0·22
$Sn^{4+}, Sn^{2+}; Pt$	$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0·15
Cu^{2+}, Cu^+	$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0·15
$Hg_2Br_2(s), Br^-; Hg$	$Hg_2Br_2(s) + 2e^- \rightleftharpoons 2Hg + 2Br^-$	+0·13
$AgBr(s), Br^-; Ag$	$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-$	+0·07
$2H^+, H_2(g); Pt$	$2H^+ + 2e^- \rightleftharpoons H_2(g, 1\ atm)$	0·00
Pb^{2+}, Pb	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0·13
Sn^{2+}, Sn	$Sn^{2+} + 2e^- \rightleftharpoons Sn$	−0·15
$AgI(s), I^-; Ag$	$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	−0·15
Ni^{2+}, Ni	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−0·24
Co^{2+}, Co	$Co^{2+} + 2e^- \rightleftharpoons Co$	−0·27
Tl^+, Tl	$Tl^+ + e^- \rightleftharpoons Tl$	−0·34
Cd^{2+}, Cd	$Cd^{2+} + 2e^- \rightleftharpoons Cd$	−0·40
Fe^{2+}, Fe	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0·44
Cr^{3+}, Cr	$Cr^{3+} + 3e^- \rightleftharpoons Cr$	−0·74
Zn^{2+}, Zn	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0·76
Mn^{2+}, Mn	$Mn^{2+} + 2e^- \rightleftharpoons Mn$	−1·18
Al^{3+}, Al	$Al^{3+} + 3e^- \rightleftharpoons Al$	−1·66
Mg^{2+}, Mg	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2·52
Na^+, Na	$Na^+ + e^- \rightleftharpoons Na$	−2·71
Ca^{2+}, Ca	$Ca^{2+} + 2e^- \rightleftharpoons Ca$	−2·87
Ba^{2+}, Ba	$Ba^{2+} + 2e^- \rightleftharpoons Ba$	−2·90
K^+, K	$K^+ + e^- \rightleftharpoons K$	−2·92
Li^+, Li	$Li^+ + e^- \rightleftharpoons Li$	−3·04

↑ oxidising power increasing

↓ Reducing power increasing

→ −ve E° means that the redox couple is a stronger reducing agent than H^+/H_2 couple

→ +ve E° means that the redox couple is a weaker reducing agent than H^+/H_2 couple.

→ Use of Redox potential data :→

① Calculation of standard e.m.f. of a Galvanic cell (E°_{cell}) :→

- The value of E°_{cell} can be calculated using following relation -

$$\boxed{E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}} \quad \text{OR} \quad \boxed{E^\circ_{cell} = E^\circ_{Right} - E^\circ_{Left}}$$

- Since E°_{cell} is positive, $E^\circ_{cathode}$ should be greater than E°_{anode}

$$\boxed{E^\circ_{cell} = E^\circ_{higher} - E^\circ_{lower}}$$

<u>Example</u> :- A Galvanic cell is composed of Zn and Cu electrodes having $Zn^{+2}/Zn = -0.763\,V$ and $Cu^{+2}/Cu = +0.337\,V$. Calculate the value of E°_{cell}.

$$E^\circ_{cell} = E^\circ_{higher} - E^\circ_{lower}$$

$$E^\circ_{cell} = E^\circ_{Cu^{+2}/Cu} - E^\circ_{Zn^{+2}/Zn}$$

$$E^\circ_{cell} = 0.337 - (-0.763)\,V$$

$$E^\circ_{cell} = 1.1 \text{ Volt}$$

② To predict the feasibility of a redox reaction:→

- If $E^\circ_{reaction}$ = +ve , then the reaction proceed from left to right i.e. forward direction.
- If $E^\circ_{reaction}$ = −ve, then the reaction proceed from right to left i.e. backward direction.

③ To predict the feasibility of a metal displacement reaction :→

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

Displacing metal (RA) $E^\circ = -0.76\,V$

Displaced metal (OA) $E^\circ = +0.34\,V$

- The above reaction will take place spontaneously , if one of the following conditions is fullfilled -

ⓐ $E^\circ_{RA} < E^\circ_{OA}$

ⓑ $E^\circ_{displacing\ metal} < E^\circ_{displaced\ metal}$

ⓒ $E^\circ_{OA} - E^\circ_{RA}$ = positive quantity

④ $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ = positive quantity.

④ oxidising power of oxidants and Reducing power of reductant :→

- Decrease in E° Values ⇒ the tendency of oxidants to accept electrons decreases and hence oxidising power of oxidats decreases.
- Decrease in E° Values ⇒ the tendency of reductants to donate electron increases and hence reducing power of reductants increases.

Example:→ Reduction potential of some half reactions are given below.

$$Mg^{+2} + 2e^- \longrightarrow Mg, \quad E^\circ = -2.37\,V$$

$$Ag^+ + e^- \longrightarrow Ag, \quad E^\circ = +0.799\,V$$

$$Cd^{+2} + 2e^- \longrightarrow Cd, \quad E^\circ = -0.403\,V$$

$$Mn^{+2} + 2e^- \longrightarrow Mn, \quad E^\circ = -1.18\,V$$

which metal can reduce Cd^{+2} to Cd metal ?

Ans:- Mn and Mg both can reduce Cd^{+2} to Cd.

⑤ Calculation of equilibrium constant (K) of a redox reaction :→

- Standard free energy change (ΔG°) for a reaction is given by

$$\Delta G^\circ = -nE^\circ F \quad \text{——} \; ①$$

here n = no. of electrons involved in redox reaction
E° = Standard potential for the reaction
F = Faraday constant = 96500 coulombs

- Relationship between ΔG° and equilibrium constant (K) is given by-

$$\Delta G^\circ = -RT\ln K \text{ — ②}$$

here R = Gas constant = 8.314 $JK^{-1}mol^{-}$

T = Temp. = 298 K

on comparing eq. ① and ②

$$-nE^\circ F = -RT\ln K$$

$$nE^\circ = \frac{RT}{F}\ln K$$

or $$nE^\circ = \frac{2.303RT}{F}\log K$$

on substituting values of R, T and F, we get

$$nE^\circ = 0.0591 \log K$$

or $$\boxed{\log K = \frac{nE^\circ}{0.0591}} \text{ — ③}$$

Example:- Calculate the value of equilibrium constant (K) of the following redox reaction.

$$Ni^{+2} + Co \rightleftharpoons Ni + Co^{+2} \quad (E^\circ = 0.027\ V,\ n=2)$$

Answer:- $\log K = \frac{nE^\circ}{0.0591}$, $\log K = \frac{2 \times 0.027}{0.0591} = 0.915$, $K = 8.22$

⑥ Standard electrode potential and Metal extraction procedures:→

- On the basis of value of standard electrode potential, we can select suitable procedure for metal extraction.

ⓐ Metal ion couple with potential more negative than −1.5 V → Electrolysis is used

ⓑ Metal ion couple with negative potential in the range −1.5 to −0.75 V → Oxygen is used to reduce the metal oxide.

ⓒ Metal ion couple with negative potential in the range −0.75 to 0.0 V → Carbon reduction method is used.

ⓓ Metal ion couple with potential more positive than 0.0 V → simple heating is used.

→ Analysis of Redox cycle :→

- Redox cycle involves enthalpy change (ΔH) and energy absorbed and evolved in various steps-

① oxidation cycle of alkali metals :→

- The oxidation of alkali metals in aqueous solution can be represented as-

$$M + aq. \xrightarrow{\text{oxidation}} M^+(aq.) + e^- \quad E = E^\circ_{ox} \text{ — } ①$$

E = Measure of reducing property

- The oxidation reaction ① given above takes place through the following steps:-

ⓐ Sublimation of M(s) to M(g) :→

$$M(s) \xrightarrow{\text{Sublimation}} M(g), \ \Delta H = +\Delta H_{sub} = \text{Enthalpy of sublimation}$$

ⓑ Ionisation of M(g) to $M^+(g)$:→

$$M(g) \xrightarrow{\text{Ionisation}} M^+(g) + e^-, \ \Delta H = +IE = \text{Ionisation energy}$$

+ve = Energy absorbed

-ve = Energy released

ⓒ Hydration of $M^+(g)$ to $M^+(aq.)$:→

$$M^+(g) + aq. \xrightarrow{\text{hydration}} M^+(aq.) , \quad \Delta H = -\Delta H_{hyd} = \text{Enthalpy of hydration}$$

- On adding equations given in step (a), (b) and (c)

$$M(s) + aq \xrightarrow[\text{aq. solution}]{\text{oxidation in}} M^+(aq) + e^- \quad \Delta H = +\Delta H_{sub} + IE - \Delta H_{hyd} \text{ — ②}$$

Since reaction ② is same as reaction ①, E°_{ox} is given by

$$\boxed{E = E^\circ_{ox} = \Delta H_{sub} + IE - \Delta H_{hyd}}$$

- The value of E for Li is highest among alkali metals. so Li has highest value of E°_{ox}. Although Li has highest IE among all alkali metals but it is compensated by enthalply of hydration (ΔH_{hyd}) of $Li^+(aq.)$
- In other words, among alkali metals, Li(s) is most easily oxidised to $Li^+(aq.)$ in aqueous solution and hence Li(s) in aqueous solution act as strongest reducing agent.
- The above three steps can be shown in form of a cycle (Born-Haber cycle). This cycle is called oxidation cycle of alkali metals.

$$\begin{tikzcd}[column sep=huge, row sep=huge]
M(s) + aq \arrow[r, "\text{Oxidation in}", "\text{aq. solution}"'] \arrow[d, "\text{(a) Sublimation } (+\Delta H_{sub})"'] & M^+(aq.) + e^- \\
M(g) \arrow[r, "\text{(b) Ionisation } (-e^-)\ (+IE)"'] & M^+(g) + e^- \arrow[u, "\text{(c) Hydration } (-\Delta H_{hyd})"']
\end{tikzcd}$$

fig :- oxidation cycle of alkali metals

② Reduction cycle of Halogens :→

- The reduction of halogen in aqueous solution can be represented as :-

$$\frac{1}{2}X_2\,(s, l \text{ or } g) + e^- + aq. \xrightarrow[\text{aq. solution}]{\text{Reduction in}} X^-(aq.) \quad \Delta H = \Delta E$$

ΔE = Measure of oxidising strength.

- In the above reaction, if halogen is a solid, then the above reaction is written as :-

$$\frac{1}{2}X_2\,(s) + e^- + aq. \xrightarrow[\text{aq. solution}]{\text{Reduction in}} X^-(aq.),\ \Delta H = \Delta E \quad \text{——} \ ③$$

- Reaction ③ takes place through the following steps:-

ⓐ conversion of $\frac{1}{2}x_2(s)$ to $\frac{1}{2}x_2(l)$:→

$$\frac{1}{2}x_2(s) \xrightarrow{\text{Fusion}} \frac{1}{2}x_2(l) \quad \Delta H = +\frac{1}{2}\Delta H_f = \text{Enthalply of fusion}$$

ⓑ Conversion of $\frac{1}{2}x_2(l)$ to $\frac{1}{2}x_2(g)$:→

$$\frac{1}{2}x_2(l) \xrightarrow{\text{Vaporisation}} \frac{1}{2}x_2(g) \quad \Delta H = +\frac{1}{2}\Delta H_v = \text{Enthalpy of vaporisation}$$

ⓒ Conversion of $\frac{1}{2}x_2(g)$ to $x(g)$:→

$$\frac{1}{2}x_2(g) \xrightarrow{\text{Dissociation}} x(g) \quad \Delta H = +\frac{1}{2}\Delta H_d = \text{Enthalpy of dissociation}$$

ⓓ Conversion of $x(g)$ to $x^-(g)$:→

$$x(g) + e^- \xrightarrow{\text{Electron affinity}} x^-(g) \quad \Delta H = -EA = \text{Electron affinity}$$

ⓔ conversion of $x^-(g)$ to $x^-(aq.)$:→

$$x^-(g) + aq. \xrightarrow{\text{Hydration}} x^-(aq.) \quad \Delta H = -\Delta H_{hyd} = \text{Enthalpy of hydration}$$

- on adding reaction ⓐ, ⓑ, ⓒ, ⓓ and ⓔ

$$\frac{1}{2}x_2(s) + e^- + aq. \longrightarrow x^-(aq.) \quad \Delta H = +\frac{1}{2}\Delta H_f + \frac{1}{2}\Delta H_v + \frac{1}{2}\Delta H_d - EA - \Delta H_{hyd} \quad \text{—— ④}$$

- Since reaction ④ is the same as reaction ③, ΔE should be given by

$$\boxed{\Delta E = \frac{1}{2}\Delta H_f + \frac{1}{2}\Delta H_v + \frac{1}{2}\Delta H_d - EA - \Delta H_{hyd}}$$

- The above steps can be shown in the form of cycle. This cycle is called reduction cycle of halogens.

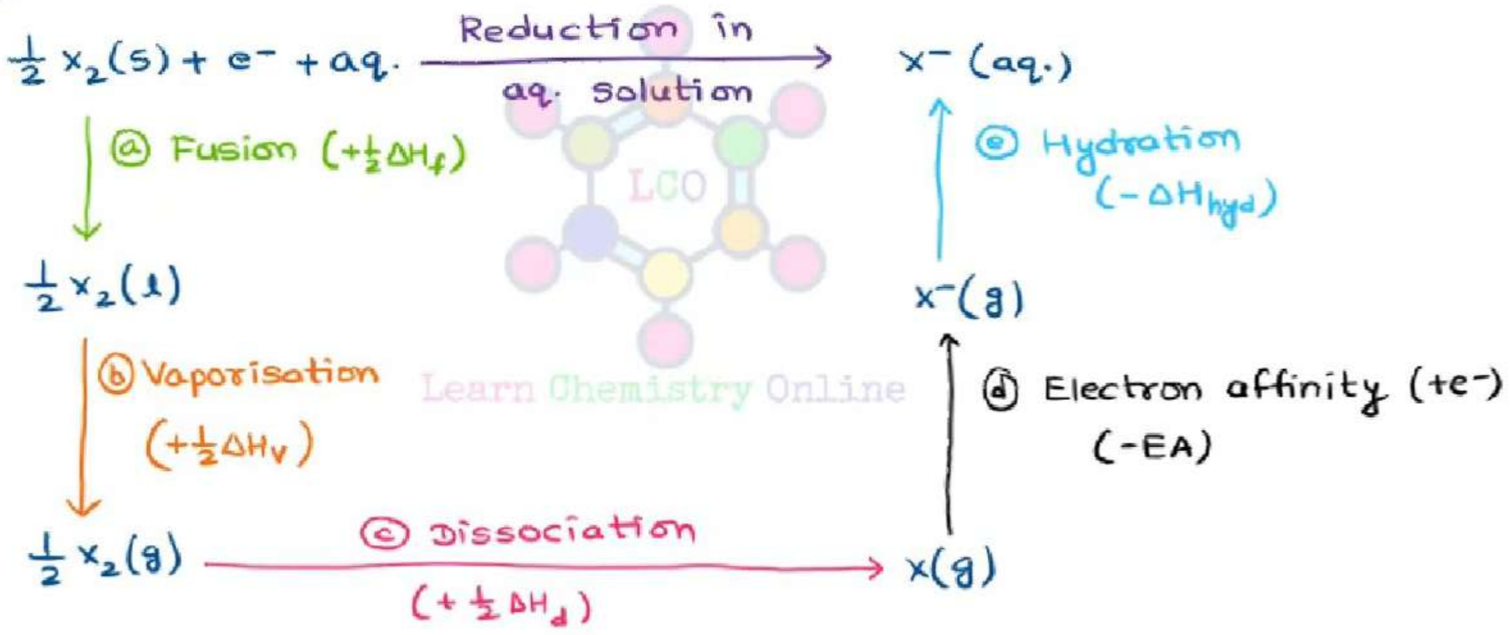


fig:- Reduction cycle of Halogen

- Since F_2 and Cl_2 are gases at room temp, ΔH_f and ΔH_v are omitted. Br_2 is a liquid, ΔH_f is omitted.
- The ΔE Value order of halogen is $F_2 > Cl_2 > Br_2 > I_2$
- F_2 has maximum value of ΔE and hence strongest oxidising agent.
- Althougth Cl_2 has highest value of EA, it is not the strongest oxidising agent. This is because of fact that Cl_2 does not have the maximum value of ΔE.
- Thus oxidising power of halogen does not depends on EA, but depends of ΔE.

$\Delta E \propto$ Oxidising power of halogens

→ Redox stability in water:→

- Ther are many species which are stable in water since these species neither oxidise or reduce water nor undergo disproportionation in water.
- On the other hand, there are compounds which are unstable in water, since these compounds undergo any of the following reactions in water-

① Water as an oxidant (oxidation of substance by H_2O and Reduction of H_2O to H_2):-

- When H_2O or H^+ ion act as an oxidant, it is reduced to H_2

$$\underset{(H=+1)}{2H_2O} + 2e^- \xrightarrow{\text{Reduction}} \underset{(H=0)}{H_2} + 2\,OH^-$$

- As a matter of fact the reduction of H_2O means the reduction of $H^+(aq.)$ ion to H_2.

$$H^+(aq.) + e^- \longrightarrow \frac{1}{2}H_2(g). \quad , \quad E^\circ_{H^+/\frac{1}{2}H_2} \text{ or } E^\circ_{red} = 0$$

- For this reduction half cell reaction, electrode potential is given by (Nernst equation)

$$E_{H^+/\frac{1}{2}H_2} = E^\circ_{H^+/\frac{1}{2}H_2} + 0.0591 \log \frac{1}{[H^+]}$$

or $$E_{H^+/\frac{1}{2}H_2} = 0 - 0.0591 \log [H^+]$$

or $$\boxed{E_{H^+/\frac{1}{2}H_2} = -0.0591\,pH} \text{ — ① } \quad (\text{at } 298\,K) \quad (\because pH = -\log[H^+])$$

- When H_2O or H^+ ions react with alkali metals or alkaline earth metals (except Be), metals are oxidised to hydroxides and H_2O or H^+ ions reduced to $H_2(g)$.

$$\underset{(M=0)}{M} + \underset{(H=+1)}{H_2O} \longrightarrow \underset{(M=+1)}{MOH} + \underset{(H=0)}{\tfrac{1}{2}H_2(g)}$$

$$\text{or} \quad M + H^+(aq.) \longrightarrow M^+ + \tfrac{1}{2}H_2(g)$$

- H_2O or H^+ ions also oxidise elements of first transition series.

$$Sc + 3H^+ \longrightarrow Sc^{+3} + \tfrac{3}{2}H_2$$

② Water as reductant (Reduction of substance by H_2O and oxidation of H_2O to O_2).

- When H_2O act as a reductant, it is oxidised to O_2

$$\underset{(O=-2)}{2H_2O} \xrightarrow{\text{oxidation}} 4H^+ + \underset{(O=0)}{O_2} + 4e^- , \quad E^0_{ox} = -1.23\ V$$

- If this oxidation half reaction is written as reduction half reaction, then we get.

$$4H^+ + O_2 + 4e^- \xrightarrow{\text{Reduction}} 2H_2O , \quad E^0_{Red} = +1.23\ V$$

- For this reduction half reaction, electrode potential is given by

$$E = E^{\circ}_{red} - 0.0591\ pH$$

$$E = 1.23 - 0.0591\ pH$$

If $pH = 0$

$$E = 1.23\ V$$

- When F_2 reacts with H_2O, F_2 is reduced to F^- ion and H_2O is oxidised to O_2

$$\underset{(F=0)}{2F_2} + \underset{(O=-2)}{2H_2O} \longrightarrow \underset{(F=-1)}{4F^-} + 4H^+ + \underset{(O=0)}{O_2}$$

- H_2O also reduces Co^{+3} to Co^{+2} and Ce^{+4} to Ce^{+3}

$$4Co^{+3} + 2H_2O \longrightarrow 4Co^{+2} + 4H^+ + O_2$$

$$4Ce^{+4} + 2H_2O \longrightarrow 4Ce^{+3} + 4H^+ + O_2$$

③ Disproportionation :→

- It is a redox reaction in which oxidation number of an element increases as well as decreases simultaneously. i.e. oxidation and reduction takes place simultaneousy of an element.
- In other words, the species which undergoes disproportionation acts as an oxidant as well as a reductant.

$$\underset{(Cu=+1)}{2Cu^{+}} \longrightarrow \underset{(Cu=+2)}{Cu^{+2}} + \underset{(Cu=0)}{Cu} \qquad E^{\circ}_{redox} = +0.36\,V$$

- If E°_{redox} is positive, the disproportionation reaction is spontaneous.

→ Redox stability field of natural water:→

- A curve obtained by plotting standard reduction potential of H^+ ion to given H_2 and standard oxidation potential of H_2O to give O_2 with the change in pH of solution is shown in figure.
- The shaded area of figure shows the range of value of E° and pH in which water is thermo-dynamically stable towards oxidation & reduction. This area or field is called redox stability field of natural water.
- Thus the redox stability field of water is the region of pH and redox potential in which water is stable towards both oxidation and reduction.
- Redox stability field lies b/w pH 4 to 9 and slopping line AB (upper) and CD (lower)

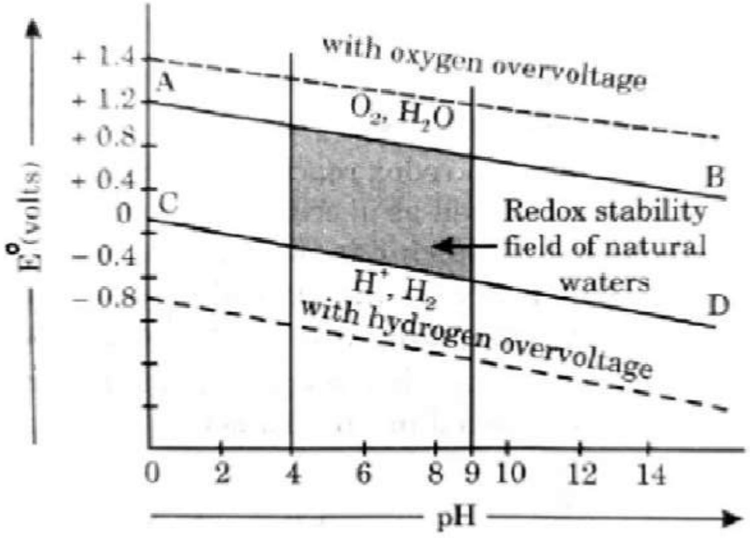


fig : Redox stability field of natural water

- Oxidising agents whose redox potential lie above line AB can oxidise H_2O and the reducing agents whose redox potential lie below line CD can reduce H_2O.

- Comproportionation Reactions:→

- Reverse of disproportionation.
- In these reactions an element in its two different oxidation states combine together to form a product which has the element in itermediate oxidation state,

$$\underset{(Cu=0)}{Cu} + \underset{(Cu=+2)}{Cu^{+2}} \longrightarrow \underset{(Cu=+1)}{2Cu^{+}} \qquad E^{\circ} = -0.37V \text{ non spontaneous reaction}$$

- If E^{0} is positive, the comproportionation is spontaneous.

- Auto oxidation:→

- It is process in which a substance undergoes oxidation and reduction both by itself.
- In disproportionation same thing happens but in case of auto-oxidation this reaction occurs slowly without the action of heat, light or electricity.

$$\underset{(N=+3)}{3HNO_2} \longrightarrow \underset{(N=+5)}{HNO_3} + \underset{(N=+2)}{2NO}$$

→ Latimer diagrams: →

- Also called Reduction potential diagrams.
- Latimer diagrams of an element presents the standard reduction potential ($E°$) values for a series of compounds of that element in which the element is in different oxidation state.
- Different species given in the Latimer diagrams have arrow between them and $E°$ values involving in two adjacent species are written over the arrow.
- The oxidation state of element concerned is written under the species.
- The species having highest oxidation state is written on left and species having lowest oxidation state is written on right. Thus, on proceeding from left to right in a Latimer diagram oxidation state of concerned elements decreases.
- Latimer diagram contains the notations for the reduction half reactions.
- In a given adjacent pair of species, the left hand species is reduced to right hand species.

- **Example** :- ① Latimer diagram for chlorine in acidic solution.

$$ClO_4^- \xrightarrow{+1.2V} ClO_3^- \xrightarrow{+1.18V} HClO_2 \xrightarrow{+1.65V} HClO \xrightarrow{+1.67V} Cl_2 \xrightarrow{+1.36V} Cl^-$$

$Cl = +7$ $\quad +5 \quad +3 \quad +1 \quad 0 \quad -1$

- Reduction half-reactions for different notation (change) show in this diagram are given below.

$$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + H_2O, \quad E^\circ = +1.20V$$

$$ClO_3^- + 3H^+ + 2e^- \longrightarrow HClO_2 + H_2O, \quad E^\circ = +1.18V$$

$$HClO_2 + 2H^+ + 2e^- \longrightarrow HClO + H_2O, \quad E^\circ = +1.65V$$

$$2HClO + 2H^+ + 2e^- \longrightarrow Cl_2 + 2H_2O, \quad E^\circ = +1.67V$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^-, \quad E^\circ = +1.36V$$

② Latimer diagram for oxygen

$$O_2 \xrightarrow{0.70V} H_2O_2 \xrightarrow{+1.76V} H_2O$$

$O = 0$ $\quad -1 \quad -2$

- Reduction half-reactions are

$$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2, \quad E^\circ = +0.70V$$

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O, \quad E^\circ = +1.76V$$

→ Applications of Latimer diagram :→

① To predict the feasibility of disproportionation reaction:→

- consider a Latimer diagram of Metal (M)

$$M^{+2} \longrightarrow M^{+} \longrightarrow M^{0}$$

$$M = +2 \qquad +1 \qquad 0$$

with the help of Latimer diagram we can predict that M^+ will disproportionat into M^{+2} and M^0 or not.

Disproportionation of M^+ into M^{+2} and M^0 can be written as.

$$2M^{+} \longrightarrow M^{+2} + M^{0} \text{ ——— } ①$$

$$M = +1 \qquad +2 \qquad 0$$

- The half reaction of Latimer diagrams is given below

$$M^{+2} + e^- \longrightarrow M^+ , \; E^\circ = E_1^\circ \text{ — } ②$$

$$M^{+} + e^- \longrightarrow M^0 , \; E^\circ = E_2^\circ \text{ — } ③$$

reaction ① can be obtained by substracting reaction ② from reaction ③

$$(M^+ + e^-) - (M^{+2} + e^-) = M^0 - M^+ \; , E^\circ = E_2^\circ - E_1^\circ$$

or $$M^+ + e^- - M^{+2} - e^- = M^0 - M^+ \; , E^\circ = E_2^\circ - E_1^\circ$$

or $$2M^+ = M^0 + M^{+2} \; , E^\circ = E_2^\circ - E_1^\circ \text{ — } ④$$

- Disproportionation reaction ④ is only feasible when $(E_2^\circ - E_1^\circ)$ is positive and $(E_2^\circ - E_1^\circ)$ will be positive only when

$$E_2^\circ > E_1^\circ \quad \text{or} \quad E^\circ_{M^+/M^0} > E^\circ_{M^{+2}/M^+}$$

- This discussion shows that a species given in a Lotimer diagram will disproportionate into its two adjacent neighbours, if E° value of right side species is higher than E° value of left side species.

② To calculate E° value for any non-adjacent couple :→

- This can be understand on the basis of following example-

ⓐ Calculate value of E° for the reduction Fe^{+3} to Fe° using following latimer diagram.

$$Fe^{+3} \xrightarrow{+0.771V} Fe^{2+} \xrightarrow{-0.44V} Fe^0$$

$Fe = +3 \qquad +2 \qquad 0$

Solution:- The given diagram can be shown as

$$\begin{tikzcd}[column sep=huge]
Fe^{+3} \arrow[r, "+0.771V", "{\Delta G_1^\circ = -n_1FE_1^\circ \quad n=1}"'] \arrow[rr, bend right, "{\Delta G^\circ = -(n_1+n_2)FE^\circ}"'] & Fe^{2+} \arrow[r, "-0.44V", "{\Delta G_2^\circ = -n_2FE_2^\circ \quad n=2}"'] & Fe^\circ
\end{tikzcd}$$

ΔG_1°, ΔG_2° & ΔG° = standard free energy change for different half reactions

n_1 & n_2 = no. of e- involved in half reactions.

- The value of ΔG° is the sum of ΔG_1° and ΔG_2°

$$\Delta G^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

or $-(n_1+n_2)FE^\circ = -n_1FE_1^\circ + (-n_2FE_2^\circ)$

or $-(n_1+n_2)FE^\circ = -n_1FE_1^\circ - n_2FE_2^\circ$

or $-(n_1+n_2)FE^\circ = -F(n_1E_1^\circ + n_2E_2^\circ)$

or $(n_1+n_2)E^\circ = n_1E_1^\circ + n_2E_2^\circ$

$$\boxed{E^\circ = \frac{n_1E_1^\circ + n_2E_2^\circ}{n_1+n_2}}$$

on putting values of n_1, n_2, E_1° and E_2°, we get

$$E^\circ = \frac{1 \times 0.771 + 2 \times (-0.44)}{1+2} = \frac{0.771 - 0.880}{3} = \frac{-0.109}{3} = -0.036\ V$$

→ Frost Diagram :→

- Frost diagram also known as an oxidation state diagram or Frost-Ebsworth diagrams.
- Frost diagram depict whether a particular species is a good oxidising agent or reducing agent. The diagram also explains that the oxidation state of an element is stable or unstable.
- Consider a half reaction in which a species X with oxidation number N is converted into its elemental form i.e. in zero oxidation state (0)

$$X(N) + Ne^- \longrightarrow X(0)$$

The redox couple for this reduction half reaction is written as $X(N)/X(0)$.

- The Frost diagram of an element X is the plot of NE° (product of O.N. & Red. pote. E°) for the couple $X(N)/X(0)$ against the oxidation number, N, of the element X.
- We know that

$$\Delta G^\circ = -NFE^\circ \quad \text{—— ①}$$

here ΔG° = std Gibbs free energy F = Faraday constant, E° standard electrode potential

N = Oxidation number of an element X.

$$\text{or} \quad \boxed{-\frac{\Delta G^\circ}{F} = NE^\circ} \text{ — ②}$$

- Because NE° is proportional to the standard Gibbs free energy for the conversion of the species $X(N)$ to the element i.e. $X(0)$. So the Frost diagram can also be regarded as a plot of standard Gibbs free energy against oxidation number.

<u>Example:</u>→ Draw the frost diagram from the following latimer diagram.

$$\underset{O=0}{O_2} \xrightarrow{+0.70V} \underset{-1}{H_2O_2} \xrightarrow{+1.76V} \underset{-2}{H_2O}$$

- Calculate E° for all couples

① $E^\circ_{O_2/H_2O_2} \Rightarrow +0.70V$ (Given) ② $E^\circ_{H_2O_2/H_2O} = +1.76V$ (Given)

③ $$E^\circ_{O_2/H_2O} = \frac{n_1E_1^\circ + n_2E_2^\circ}{n_1+n_2} = \frac{2\times0.70 + 2\times1.76}{2+2} = +1.23V$$

- Calculate NE° for the following couples

X(N)/X(0) couple	N	E°	NE°
O_2/O_2	0	0	0
H_2O_2/O_2	−1	+0.70V	−0.70V
H_2O/O_2	−2	+1.23V	−2.46V

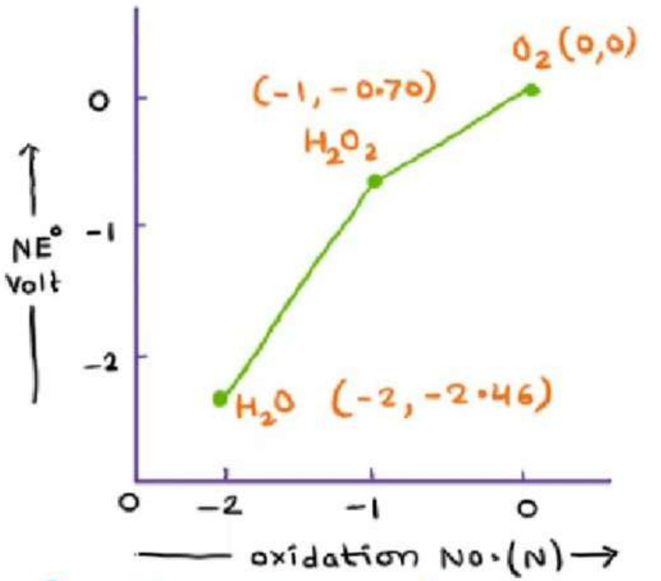


fig:- Forst diagram for oxygen in acidic medium

→ Interpretation of Frost diagram:→

① The element has most stable oxidation state in that species which occupies lowest position in Frost diagram. (fig. 1)

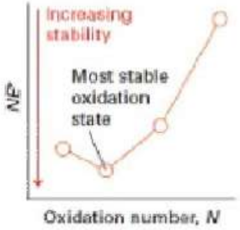


fig. 1

② The slope of the line joining any two points in a Frost diagram is equal to the standard potential of the couple formed by the two species that the point represents. (fig 2)

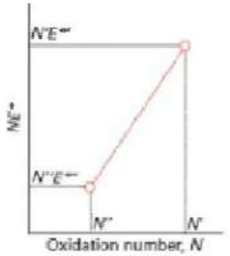


fig. 2

③ The steeper the line joining two points (from left to right) in a Frost diagram, the higher the standard potential of the corresponding curve (fig. 3)

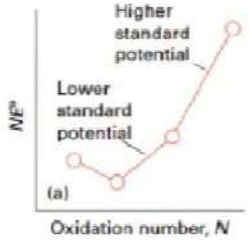


fig. 3

④ The oxidising agent in the couple is with more postive slope (more positive E°) is liable to undergo reduction and The reducing agent of the couple with less positive slope (the most negative E°) is liable to undergo oxidation. (fig 4)

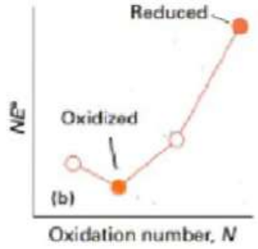
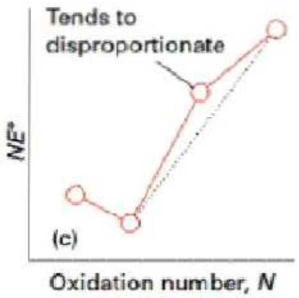


fig. 4

⑤ A species in a Frost diagram is unstable with respect to disproportionation if its point lies above the line connecting the two adjacent species. (on a convex curve). (fig.5,6)

fig. 5



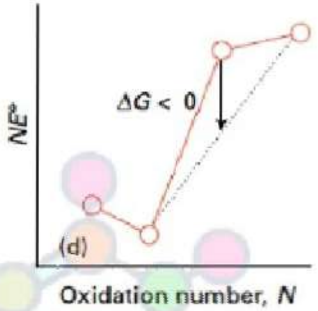
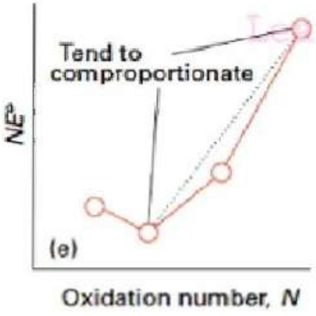


fig. 6

⑥ The two species will tend to comproportionate into an intermediate species that lies below the straight line joining the terminal species. (on a concave curve.) (fig.7,8).

fig. 7



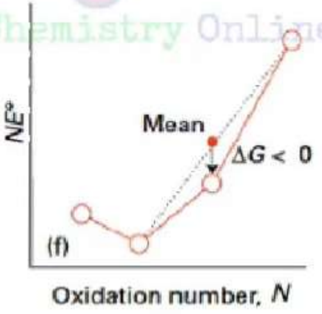


fig. 8

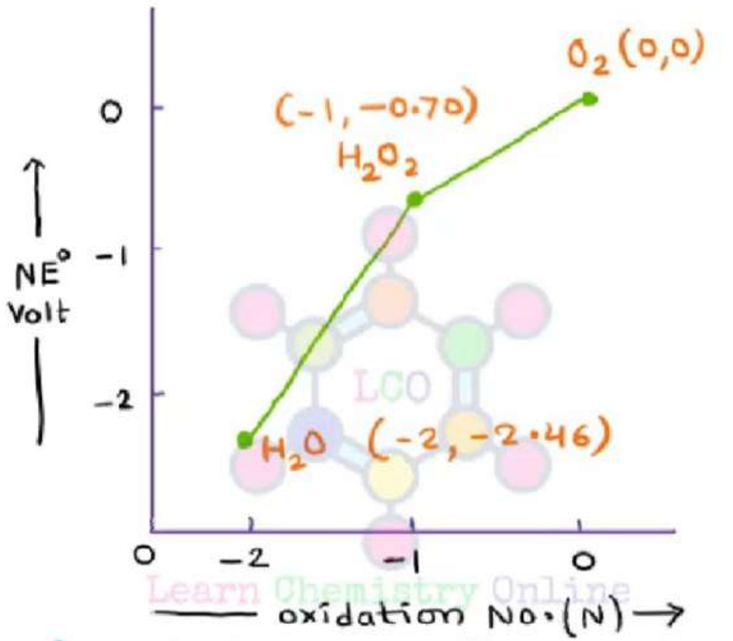


fig:- Forst diagram for oxygen in acidic medium

→ Pourbaix diagram :→

- Pourbaix diagram is also Known as E-pH diagram or Potential-pH or Predominance area diagram.
- The diagrams were introduced by Marcel Pourbaix in 1938 as a convenient way of discussing the chemical properties of species in natural waters and they are particularly useful in environmental and corrosion science.
- A Pourbaix diagram indicates the conditions of pH and potential (E) under which a species is thermodynamically stable.
- A Pourbaix diagram has potential or electrode potential (E values) on y-axis (ordinate) and pH on x - axis (abscissa).
- Positive values of potential indicates strong oxidising agent and negative value of potential indicates strong reducing agent.
- strong acids are to the left (low pH) and strong bases are to the right (high pH) of x - axis.

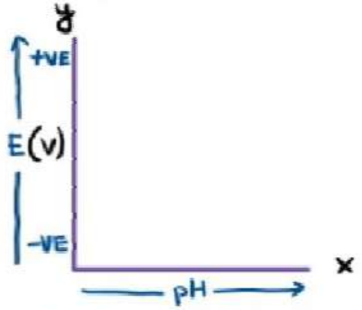


fig:- Pourbaix diagram

→ Pourbaix diagram of Iron:→

- The Pourbaix diagram of iron represents the stability ranges in terms of potential and pH for species such as Fe^{+3}, Fe^{+2}, $Fe(OH)_3$, $Fe(OH)_2$ etc. found in natural waters.

- Some reactions of iron occuring in natural waters are dissused below

① The following reduction half reaction can be considered -

$$Fe^{+3}(aq.) + e^{-} \longrightarrow Fe^{+2}(aq), \ E^{\circ} = +0.77\,V$$ (Redox reaction)

Since this reaction does not involve H+ ions, so the potential of this reaction does not depends on pH and hence corresponds to Horizontal line AB in the diagram. This line is the boundary line for above which Fe^{+3} are major species and below which Fe^{+2} are major species.

② The Following reaction may be considered -

$$\underset{Fe=+3}{Fe^{+3}(aq.)} + \underset{H=+1}{3H_2O(l)} \longrightarrow \underset{Fe=+3}{Fe(OH)_3(s)} + \underset{H=+1}{3H^{+}(aq.)}$$ (acid-base reaction)

This reaction is not a redox reaction (there is no change in oxidation number of any element), so this reaction is potential independent and therefore is represented by vertical line BC in the diagram. However this boundary does depend on pH because reaction involves H+ ions. $Fe^{+3}(aq)$ fovored by low pH and $Fe(OH)_3(s)$ is favoured by high pH. In other words, to the left side of vertical line $Fe^{+3}(aq.)$ ions are major species and to the right side of vertical $Fe(OH)_3(s)$ is the main species.

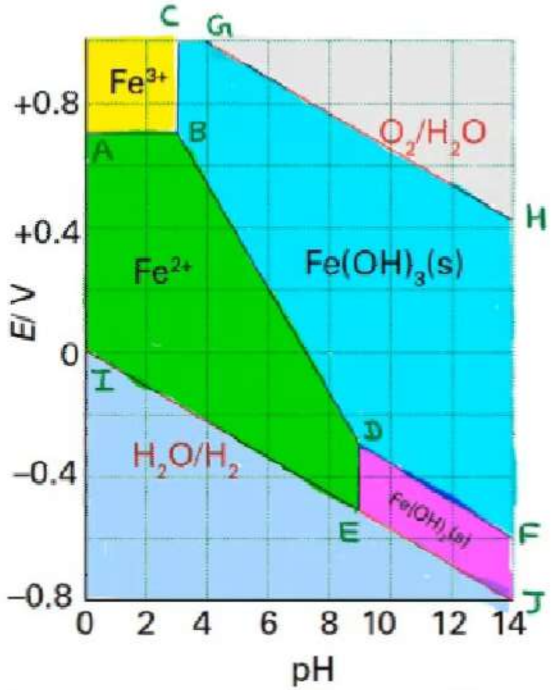


Fig:- Pourbaix diagram for iron species in natural waters

③ Reduction of $Fe(OH)_3(s)$ to $Fe^{+2}(aq.)$ can be considered as

$$Fe(OH)_3(s) + 3H^+ + e^- \longrightarrow Fe^{+2}(aq.) + 3H_2O(l) \left[\begin{array}{c}\text{combination}\\ \text{of redox+}\\ \text{Acid base}\end{array}\right]$$

This reaction is pH dependent. As pH increases the potential continue to drop. The slopy line BD is boundary line for $Fe^{+2}(aq.)$ and $Fe(OH)_3(s)$.

④ Let us consider the following reaction.

$$Fe^{+2}(aq.) + 2H_2O(l) \longrightarrow Fe(OH)_2(s) + 2H^+(aq.) \text{ (acid-base reaction)}$$

This reaction is pH-dependent but not a redox reaction. The vertical line DE is boundary line for $Fe^{+2}(aq.)$ and $Fe(OH)_2(s)$.

⑤ We may consider the following reaction.

$$Fe(OH)_3(s) + H^+(aq.) + e^- \longrightarrow Fe(OH)_2(s) + H_2O(l) \left[\begin{array}{c}\text{combination}\\ \text{of redox+}\\ \text{Acid base}\end{array}\right]$$

This is pH-dependent reaction. separtion of these two species is given by line DF.

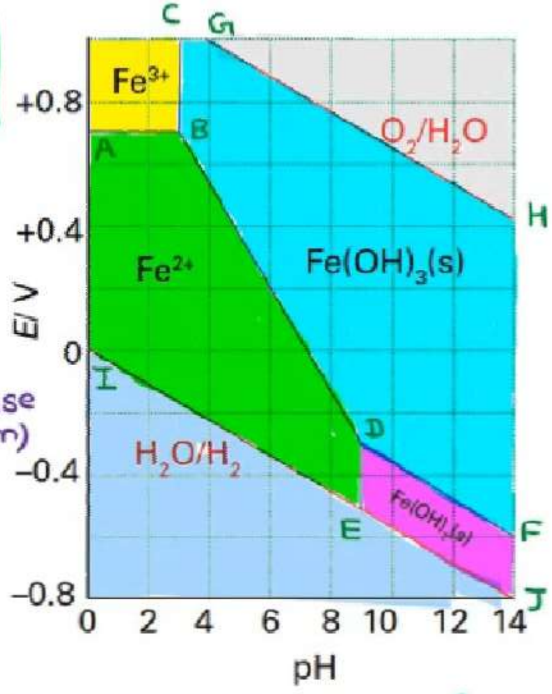


Fig:- Pourbaix diagram for Iron species in natural waters

- Two sloppling line GH (upper line) and IJ (lower line) indicate boundaries for the stability field of water. If E value is more positive than upper line then H_2O will be oxidised to O_2. On the other hand, if E is less than the lower line then H_2O will be reduced to H_2.
- It is clear that all couple representing redox reaction in water fall within the stability field of water, i.e. no species can oxidise or reduce H_2O.

→ Principles involved in the extraction of the elements :→

- The methods used for the extraction of elements from their ores depends mainly on the properties of the elements to be extracted and chemical composition of the ores.
- The ores which are mostly used are oxides, carbonates, sulphides, sulphates, halides etc. The metallurgical principles for the extraction of metal from above said ores are given below –

① Oxide ore :→ Metals like Fe, Zn, Sn, Bi, Cr, Mn etc can occur as oxides in nature. These metals are obtained by reducing their oxides ore by suitable reducing agents.

(i)

$$Fe_2O_3 + 3C \text{ (Charcoal)} \xrightarrow{\Delta} 2Fe + 3CO$$

$$ZnO + C \xrightarrow{\Delta} Zn + CO$$

$$SnO_2 + 2C \xrightarrow{\Delta} Sn + 2CO$$

$$Bi_2O_3 + 3C \xrightarrow{\Delta} 2Bi + 3CO$$

(ii) Gold - Schmidth - Thermite process :→ The metals which are reacts with carbon at reduction temp. are obtained by reducing their oxides with Al powder.

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$$

$$3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3$$

(iii) Al can be obtained by electrolytic reduction of alumina.

$$Al_2O_3 \text{ (solution)} \xrightarrow{\text{Ionisation}} 2Al^{+3} + 3O^{-2}$$

At cathode $2Al^{+3} + 6e^- \xrightarrow{\text{Reduction}} 2Al$

At Anode $3O^{-2} \xrightarrow{\text{Oxidation}} \frac{3}{2}O_2 + 6e^-$

② Carbonate ore :→

Carbonate ore first heated to convert them into oxides. Oxides thus formed are reduced to metal using above discussed method.

$$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$$

$$PbCO_3 \xrightarrow{\Delta} PbO + CO_2$$

$$FeCO_3 \xrightarrow{\Delta} FeO + CO_2$$

③ Sulphide ore :→

Sulphide ores generally have impurities of S, As, Sb etc. such ore are heated in air to convert them into oxides which is then reduced to get metal.

Example

(i) ZnS (Zinc blende) is heated in supply of air

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

$$ZnO + C \rightarrow Zn + CO$$

(ii) $CuFeS_2$ (copper pyrites) :→

$$2CuFeS_2 + O_2 \xrightarrow[\text{(oxidation)}]{\text{Roasting}} \underbrace{2FeS + Cu_2S}_{\text{mixture}} + SO_2$$

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

FeO is removed by forming ferrous silicate by reacting with silica

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

Cu_2O reacts with unreacted (unroasted) Cu_2S to give Cu metal

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

Cu_2O can also reduced to Cu by Carbon

$$Cu_2O + C \longrightarrow 2Cu + CO$$

(iii) HgS (cinnabar) is heated in air to get Hg.

$$HgS + O_2 \xrightarrow{\Delta} Hg + SO_2$$

④ Halide ore :→

(i) Water soluble alkali metal and alkaline earth metal haides are very stable. such halides are electrolysed to get metal.

$$2NaCl \xrightarrow{\text{Ionisation}} 2Na^+ + 2Cl^-$$

At anode $2Cl^- \xrightarrow{\text{oxidation}} Cl_2 + 2e^-$

At cathode $2Na^+ + 2e^- \xrightarrow{\text{Reduction}} 2Na$

(ii) Horn silver ($AgCl$, insoluble) is treated first with $NaCN$ to obtain a soluble complex.

$$AgCl + 2NaCN \longrightarrow \underset{\text{soluble complex}}{Na[Ag(CN)_2]} + NaCl$$

soluble complex is treated with Zn to get silver metal.

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$$