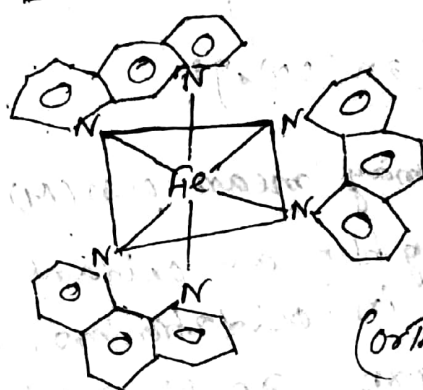


⊗⊗ Ferriin :- (A complex of ortho-phenanthroline)
 i.e; $[\text{Fe}(\text{o-phen})_3]^{2+}$ or 1,10-phenanthroline



(ortho-phenanthroline with Fe^{2+})

Question:- Redox potential of an aqueous soln. containing Fe^{3+} and Fe^{2+} at 25°C is 0.70 volt. Calculate the ratio of $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ in soln.
 given $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ volt}$.

Ans: We know that according to Nernst eqn,

$$E = E^\circ + \frac{0.059}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$\text{or, } 0.70 = 0.77 + \frac{0.059}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$\text{or, } \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = \frac{-1.186990678}{1}$$

$$\text{or, } \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = 10^{-1.186990678}$$

$$= 0.065 = \frac{65}{1000} = \frac{13}{200}$$

Therefore the ratio of $[\text{Fe}^{3+}]/[\text{Fe}^{2+}] = 13:200$. (Ans).

2009, 2008

Q:- Brass can be electrodeposited in presence of KCN or NaCN soln - explain.

Ans:- The standard reduction potential of the system Cu^{2+}/Cu is much higher (0.34V) than that of the Zn^{2+}/Zn system (-0.763V) both in aq. soln. so when an aq. soln containing Zn and Cu salts is electrolysed, Cu deposited earlier. In presence of KCN or NaCN, both Zn^{2+} and Cu^{2+} form the complexes $[\text{Zn}(\text{CN})_4]^{2-}$ and $[\text{Cu}(\text{CN})_4]^{2-}$ respectively. The later has much higher formation constant and hence the free concentration of free Cu^{2+} ion in solution is reduced to a much greater extent than for the Zn^{2+} ion. Therefore the potentials of the two couples are brought close to one another. Thus the simultaneous deposition of both Cu and Zn can be achieved. Thus brass can be electrodeposited in presence of KCN or NaCN soln.

Q. 1 (N) KMnO_4 soln may mean 0.33 (N) or 0.20 (N) KMnO_4 soln

The equivalent weight of an oxidant can be calculated from the change in oxidation no. of the reduced element in a rxn. In the reduction of KMnO_4 to a Mn^{2+} salt in an acid medium ($\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$), the change in oxidation no. of Mn = $7 - 2 = 5$.

Therefore the eqv. wt of $\text{KMnO}_4 = \frac{\text{Mol. wt of } \text{KMnO}_4}{5}$ (in acid medium)

i.e.; 1 (N) $\text{KMnO}_4 = \frac{1 (\text{M}) \text{KMnO}_4}{5} = 0.20 (\text{N}) \text{KMnO}_4$

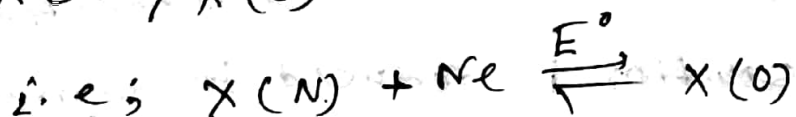
In alkaline medium, KMnO_4 is reduced to MnO_2 . The change in oxidation no. of Mn = $7 - 4 = 3$.

Hence in alkaline medium, the eqv. wt of $\text{KMnO}_4 = \frac{\text{Mol. wt of } \text{KMnO}_4}{3}$

i.e.; 1 (N) $\text{KMnO}_4 = \frac{1 (\text{M}) \text{KMnO}_4}{3} = 0.33 (\text{N}) \text{KMnO}_4$

⊗ Frost diagram ⊗

Let us consider an element 'x' capable of forming a no. of species with varying oxidation no. (N). For each species, we have a couple $\text{X}(N) / \text{X}(0)$ with a characteristic potential E° .



Frost diagram of an element is a plot of NE° against N. For different couples $\text{X}(N) / \text{X}(0)$, since n electrons are involved in the reduction we have, $-\Delta G^\circ = nFE^\circ$
or, $NE^\circ = \frac{-\Delta G^\circ}{n}$, where ΔG° = Change in Gibbs free energy.

So Frost diagram is a plot of Gibbs free energy change against oxidation no. The species representing the most stable oxidation state of an element will have the lowest -49° i.e; lowest NE° . Therefore the most stable oxidation state of an element will lie lowest in its Frost-diagram.

All Frost diagram will have an $NE^\circ = 0$ and $N=0$ plot for the elementary state.

The slope of the line joining any two points in a Frost-diagram is equal to the standard reduction potential of the couple represented by the two points.

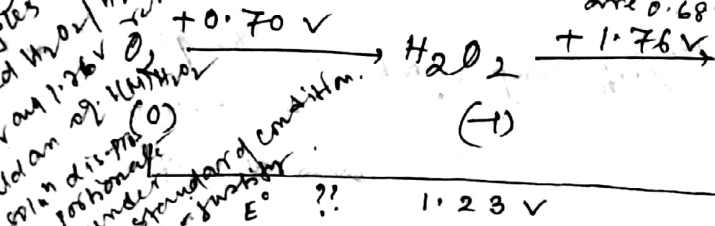
Example: — Construct the Frost diagram from the following Latimer diagram.

$$\text{Ti}^{3+} \xrightarrow{+1.25} \text{Ti}^{2+} \xrightarrow{-0.37} \text{Ti}^0$$

$$+1.23 \text{ V}$$
 show the calculations
 coordinates of each point of the plot
 let us consider the following Latimer

Latimer diagram
 for the couples
 $\text{O}_2/\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ respectively.
 are 0.70V and 1.26V
 should an $\text{O}_2/\text{H}_2\text{O}$
 couple exist
 in this
 position
 under
 standard
 condition.
 E° ??

E° values of $\text{O}_2/\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}_2/\text{H}_2\text{O}$
 are 0.68V and 1.22V respectively
 comment on the feasibility
 of the rxn
 $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
 and suggest a
 characteristic
 name to this rxn
 for answer see disprop
 rxn.



$$E^\circ = \frac{n_1 E_1^\circ + n_2 E_2^\circ}{n_1 + n_2}$$

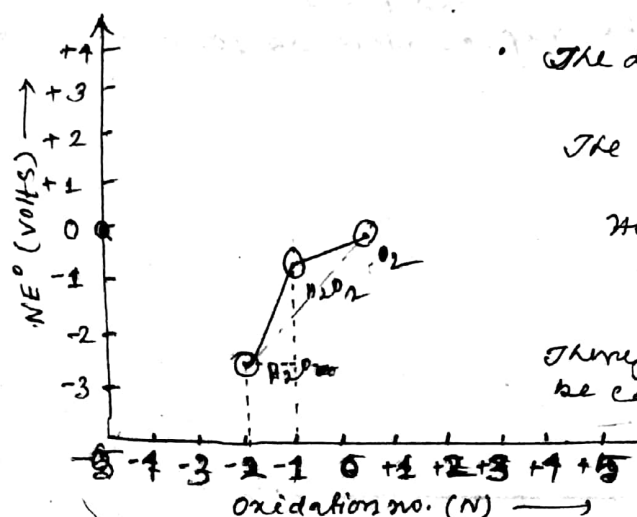
$$= \frac{1 \times 0.70 + 1 \times 1.26}{1 + 1}$$

$$= 1.23 \text{ V}$$

Case of H_2O_2 , O.N of oxygen = -1.
 Hence $NE^\circ = -1 \times 0.70 \text{ V} = -0.70 \text{ V}$

92 Case of H_2O , O.N of oxygen = -2.
 Hence $NE^\circ = -2 \times 1.23 \text{ V} = -2.46 \text{ V}$

Hence The Frost diagram can be represented as follows



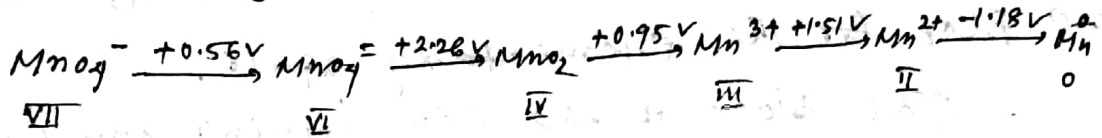
The difference of the two NE° values
 $= -0.70 - (-2.46)$
 $= 1.76 \text{ V}$
 The change in O.N of oxygen = $-1 - (-2)$
 Hence the slope = $\frac{\text{Change in } NE^\circ \text{ values}}{\text{Change in O.N (N)}}$
 $= \frac{1.76}{+1} = 1.76$

Therefore standard reduction potential can be calculated from the Frost diagram.

- A state is unstable with respect to disproportionation if it lies above the line connecting two adjacent oxidation states.

Hence, H_2O_2 disproportionate to H_2O and O_2 .

Question:
2006 Construct the Frost diagram from the following Latimer diagram.



Ans:- In case of Mn^{2+}/Mn couple, $NE^\circ = 2 \times (-1.18\text{V}) = -2.36\text{V}$

and $N = 2$.

In case of $\text{Mn}^{3+}/\text{Mn}^0$ couple, $NE^\circ = 1 \times 1.51 + (-2.36) = -0.85\text{V}$

and $N = 3$

In case of MnO_2/Mn^0 couple, $NE^\circ = 1 \times 0.95 + (-0.85) = 0.10\text{V}$

and $N = 4$

In case of $\text{MnO}_4^{2-}/\text{Mn}^0$ couple, $NE^\circ = 2 \times (2.26) + 0.10 = 4.62\text{V}$

and $N = 6$

In case of $\text{MnO}_4^-/\text{Mn}^0$ couple, $NE^\circ = 1 \times 0.56 + 4.62 = 5.18\text{V}$

and $N = 7$

The Frost diagram can be represented as follows:

