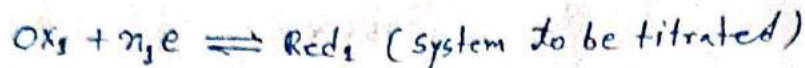


REDOX TITRATION °

Titration involving the reaction of standard solution of oxidant with reductant or standard solution of reductant with oxidant in presence of an indicator called redox titration. The indicator used here is called redox indicator.

In a redox titration two redox couple are involved —



So, net reaction is — $n_1 \text{Ox}_2 + n_2 \text{Red}_1 \rightleftharpoons n_2 \text{Ox}_1 + n_1 \text{Red}_2$

Before the equivalence point the potential of the system is governed by Ox_1/Red_1 couple (system), while after the equivalence point, potential of the medium gets controlled by the titrant system, i.e. Ox_2/Red_2 . At the equivalence point, both the systems are at equilibrium. Hence the potential of each of the systems at the equivalence point must be same i.e.

$$E_{ep} = E_1^\circ + \frac{0.059}{n_1} \log \frac{[\text{Ox}_1]}{[\text{Red}_1]} ; E_{ep} = E_2^\circ + \frac{0.059}{n_2} \log \frac{[\text{Ox}_2]}{[\text{Red}_2]}$$

By adding two equations

$$n_1 E_{ep} + n_2 E_{ep} = n_1 E_1^\circ + n_2 E_2^\circ + 0.059 \log \frac{[\text{Ox}_1] [\text{Ox}_2]}{[\text{Red}_1] [\text{Red}_2]}$$

At equivalence point $\frac{[\text{Ox}_1] [\text{Ox}_2]}{[\text{Red}_1] [\text{Red}_2]} = 1$

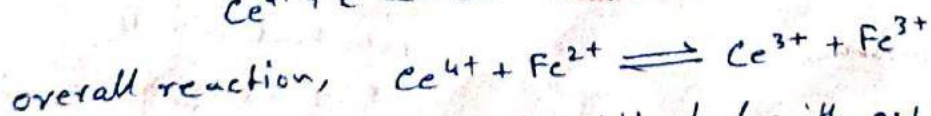
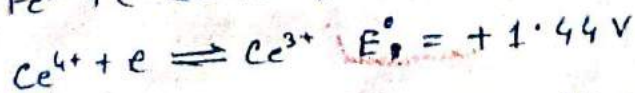
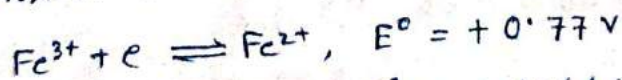
From reaction stoichiometry we get moles $[\text{Ox}_1] = \text{moles} [\text{Red}_2]$ and similarly moles $[\text{Ox}_2] = \text{moles} [\text{Red}_1]$
 $\therefore \frac{[\text{Ox}_1]}{[\text{Red}_1]} = \frac{[\text{Red}_2]}{[\text{Ox}_2]}$

$$\text{So, } E_{ep} (n_1 + n_2) = n_1 E_1^\circ + n_2 E_2^\circ$$

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

• Example-1

Now, Let us consider an example — titration of Fe^{2+} by Ce^{4+} in H_2SO_4 .



Consider 100 ml 0.1 N Fe^{2+} solution titrated with 0.1 N Ce^{4+} solution

(i) At the beginning (Before addition of Ce^{4+})

The solution contain only Fe^{2+} ion, the potential of the system will be given by $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple.

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

one should not consider $[Fe^{3+}]$ to be exactly zero, trace of impurities (airial oxidation) are sufficient to make it nonzero. Let only 0.1% of iron is oxidised to Fe^{3+} due to aerial oxidation, so,

$$E = E^{\circ} + 0.059 \log \frac{1}{1000} \\ = 0.77 + 0.059 \log \frac{1}{1000} = 0.56 \text{ V}$$

(ii) when 30 ml Ce^{4+} added: The solution contains Fe^{2+} , Fe^{3+} and Ce^{3+} with a negligible amount of Ce^{4+} . Therefore potential will be calculated w.r.t Fe^{3+}/Fe^{2+} system not Ce^{4+}/Ce^{3+} system.

$$E = 0.77 + 0.059 \log \frac{30}{10} \\ = 0.83 \text{ V}$$

(iii) At the equivalence point: The equivalence point potential for any redox system given by the expression

$$E_{ep} = \frac{n_1 E_1^{\circ} + n_2 E_2^{\circ}}{n_1 + n_2} \quad \left[\text{Where } n_1 \text{ and } n_2 \text{ are the number of electron involved in respective half-cell reaction having standard potential } E_1^{\circ} \text{ and } E_2^{\circ} \right]$$

$$\text{So, } E_{ep} = \frac{0.77 + 1.44}{1+1} = 1.10 \text{ V}$$

(iv) Beyond the equivalence point: After the equivalence point addition of Ce^{4+} ion simply increase the $[Ce^{4+}]/[Ce^{3+}]$ ratio and the potential calculation has to take into account this ratio along with standard potential +1.44 V. The $[Fe^{3+}]/[Fe^{2+}]$ ratio need not be considered since there is no practically Fe^{2+} ion.

$$E = E^{\circ} + 0.059 \log \frac{[Ce^{4+}]}{[Ce^{3+}]} \\ = 1.44 + 0.059 \log \frac{0.1}{100} \\ = 1.26 \text{ V}$$

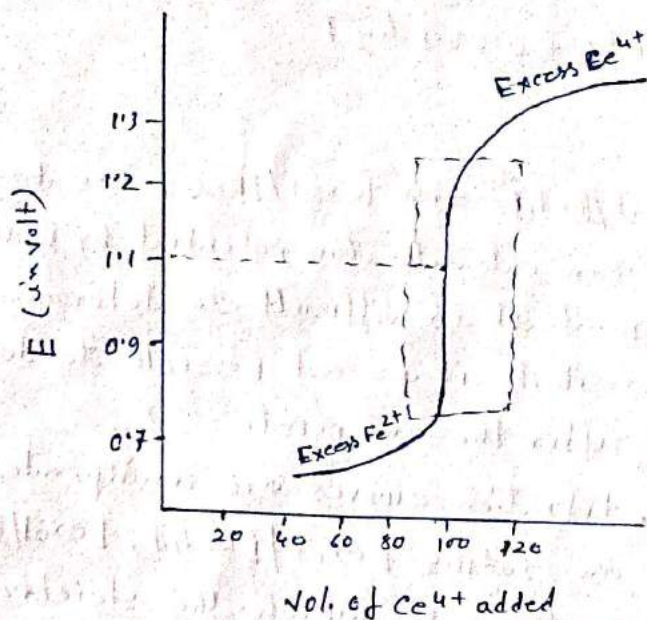
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Vol. of Ce^{4+} solution

0 ml
50 ml
99.9 ml
100 ml
100.1 ml

Potential in Volt

$$E = E^{\circ} + 0.059 \log \frac{1}{1000} = 0.56 \text{ V} \\ E = 0.77 + 0.059 \log \frac{30}{50} = 0.77 \text{ V} \\ E = 0.77 + 0.059 \log \frac{99.9}{0.1} = 0.95 \text{ V} \\ E = \frac{0.77 + 1.44}{2} = 1.10 \text{ V} \\ E = 1.44 + 0.059 \log \frac{0.1}{100} = 1.26 \text{ V}$$



• Example-2

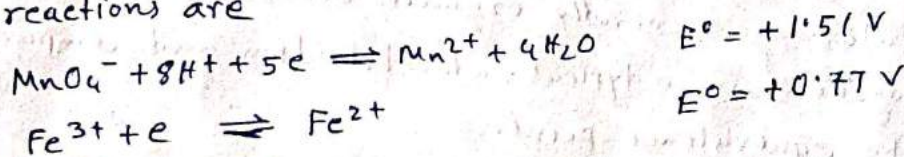
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Titration Fe^{2+} by MnO_4^-

At equivalence point trace of Fe^{2+} will still exist and exactly equivalent amount of MnO_4^- will also remain unreacted. The involved overall reaction -



The half cell reactions are



At equivalence point

$$E = E^0 + 0.059 \log \frac{[Fe^{3+}]}{[Fe^{2+}]} = 0.77 + 0.059 \log \frac{[Fe^{3+}]}{[Fe^{2+}]} \quad \dots \textcircled{1}$$

$$\text{and } E = E^0 + \frac{0.059}{5} \log \frac{[MnO_4^-] [H^+]^8}{[Mn^{2+}]} = 1.51 + \frac{0.059}{5} \log \frac{[MnO_4^-]}{[Mn^{2+}]} \quad \dots \textcircled{2}$$

[as $[H^+] = 1 \text{ mole/lit}$]

$$\text{or } 5E = 5 \times 1.51 + 0.059 \log \frac{[MnO_4^-]}{[Mn^{2+}]}$$

by adding we get (1+2)

$$6E = 0.77 + 5 \times 1.51 + 0.059 \log \frac{[Fe^{3+}][MnO_4^-]}{[Fe^{2+}][Mn^{2+}]}$$

The mole ratio of Fe^{2+} and MnO_4^- ion in the reaction are 5:1, so, at equivalence point $[Fe^{2+}] = 5[MnO_4^-]$ similarly $[Fe^{3+}] = 5[Mn^{2+}]$

$$\therefore \frac{[Fe^{2+}]}{[Fe^{3+}]} = \frac{[MnO_4^-]}{[Mn^{2+}]} \quad \text{i.e.} \quad \frac{[Fe^{3+}][MnO_4^-]}{[Fe^{2+}][Mn^{2+}]} = 1$$

$$\therefore E = 0.77 + 5 \times 1.51 + 0.059 \log 1$$

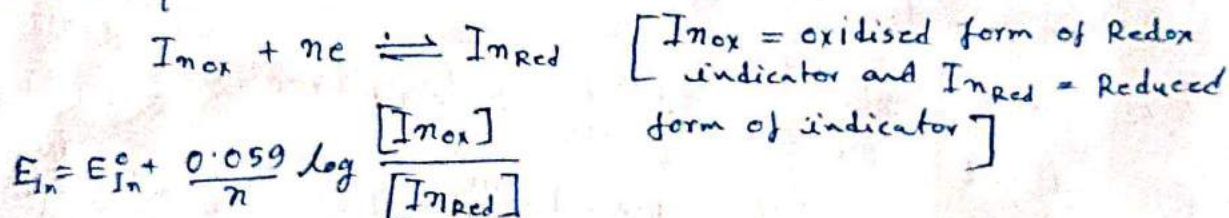
$$\therefore E = 1.387 \text{ V}$$

In fact if the ratio of $[OX_1]/[Red_1]$ and $[OX_2]/[Red_2]$ are known throughout the titration process, we can calculate the potential by using any single couple. But before the endpoint it is difficult to determine the exact ratio $[OX_2]/[Red_2]$ and similarly it is not possible to determine the exact ratio $[OX_1]/[Red_1]$ after the endpoint.

Generally redox titration curves are independent of dilution as the potential depend on ratios $[OX_1]/[Red_1]$, $[OX_2]/[Red_2]$. In fact it remain true for the systems for which the stoichiometric coefficient of oxidant and reductant in a particular system are equal. But for the system like $Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O$, the ratio $[Cr_2O_7^{2-}]/[Cr^{3+}]$ changes with dilution. If it is diluted to double then ratio also gets doubled.

REDOX INDICATOR : Dr. Sandip Mondal

Redox indicator are generally organic dyes, which can undergo reversible oxidation-reduction in a typical redox titration and impart different colours to detect the equivalence point.



The colour of oxidised form predominates when its concentration is 10 times that of the reduced form and vice-versa. So, for an appreciable colour of the oxidised form

$$E_{In} = E_{In}^{\circ} + \frac{0.059}{n} \log \frac{10}{1} = E_{In}^{\circ} + \frac{0.059}{n}$$

again, for an appreciable colour of reduced form

$$E_{In} = E_{In}^{\circ} + \frac{0.059}{n} \log \frac{1}{10} = E_{In}^{\circ} - \frac{0.059}{n}$$

Thus the range of potential values across which an indicator exhibits sharp contrast of colour will be

$$E_{EP} = E_{In}^{\circ} \pm \frac{0.059}{n} \quad (E_{EP} = \text{transition potential})$$

• Some common redox Indicators —

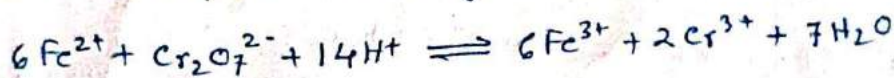
Indicators	colour:		E° (V)
	I_{ox}	I_{red}	
i) Methylene blue	Blue	Colourless	0.53
ii) Diphenylamine	Blue-violet	Colourless	0.76
iii) Diphenylamine-sulfonic acid	Red-violet	Colourless	0.85
iv) Ferroin	Pale-Blue	Red	1.14

For the above titration i.e. $Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+}$

$$E_{ep} = \frac{1.44 + 0.77}{2} = 1.10 \text{ V}$$

In fact end point lies in the range 1.0 V to 1.20 V in aqueous H_2SO_4 media. The suitable indicator is ferroin having $E_{ep} = 1.14 \pm 0.05$.

For the estimation of Fe^{2+} with $K_2Cr_2O_7$ the equivalence point lies in the range 0.95 V to 1.30 V. Hence the indicator to be taken must have the E_{ep} in this range.

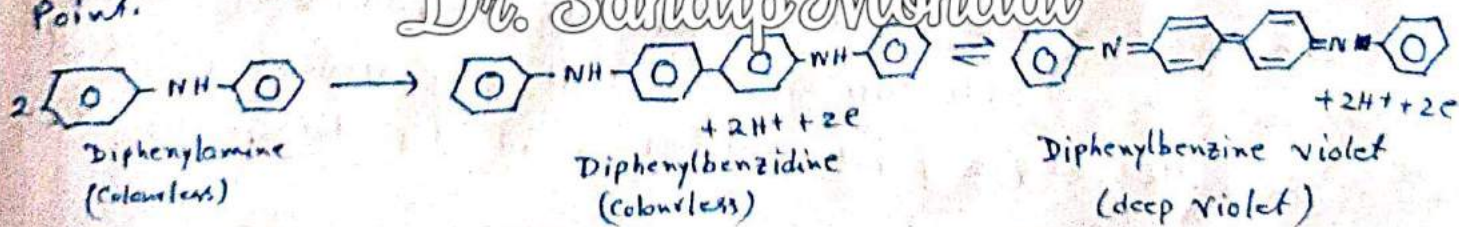


$$E_{ep} = \frac{1}{7} (6E_{Cr_2O_7^{2-}/Cr^{3+}}^{\circ} + E_{Fe^{3+}/Fe^{2+}}^{\circ})$$

$$= \frac{1}{7} (6 \times 1.33 + 0.77) = 1.25 \text{ V}$$

Thus the indicator such as diphenylamine ($E^{\circ} = 0.76 \text{ V}$) or diphenylaminesulfonic acid ($E^{\circ} = 0.85 \text{ V}$) cannot be used, as these will show the change in colour before the equivalence point. But in presence of H_3PO_4 , due to complexation with Fe^{3+} ion the formal potential of the couple Fe^{3+}/Fe^{2+} will get lowered, and before the end point, the Fe^{2+} ion is first oxidised to Fe^{3+} and at the end point the indicator reduced form will be oxidised and we get the colour change (violet) at the equivalence point.

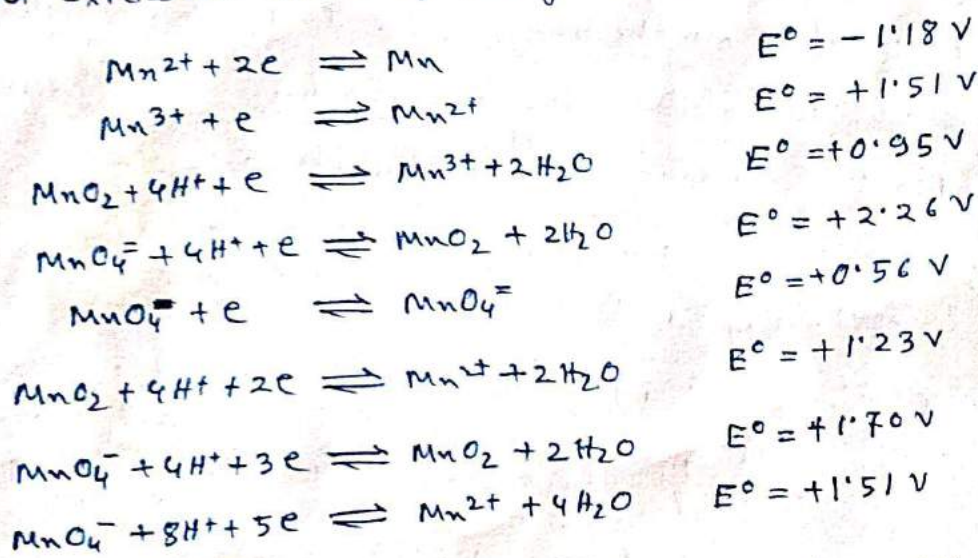
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EMF DIAGRAM :

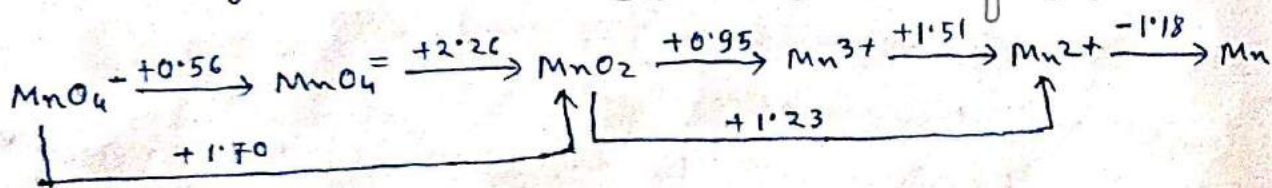
When an element exists in different oxidation states, the relative thermodynamic stability of different species can be represented in a diagrammatic way indicating the reduction potential of each species, which is known as EMF diagram. The redox potential for particular element can be summarised in the ~~emp~~ EMF diagram. There are several EMF diagrams namely, Latimer diagram, Frost diagram, Pourbaix diagram, Ellingham diagram etc.

• **LATIMER DIAGRAM :** Let us consider the reduction potential (E°) for different oxidation states of manganese in acid medium.



Wendell Latimer introduced a method for connecting E° values which is written over a horizontal arrow line with the species of an element in different oxidation states. The higher oxidation state is written on the left and successive lower oxidation states are depicted to the right, i.e. the whole information is summarised in the following EMF diagram.

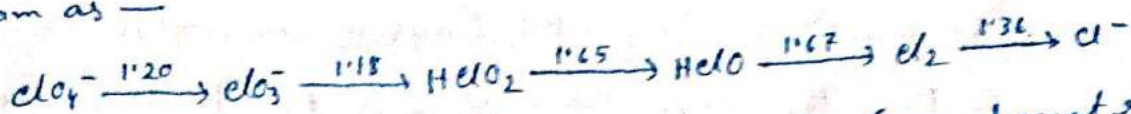
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The couple such as $\text{MnO}_4^-/\text{Mn}^{2+}$, MnO_4^-/Mn , $\text{MnO}_2/\text{Mn}^{2+}$ are referred to as "skip-step" couple and the corresponding potentials are called skip-step potentials. The word skip-step implies that

in carrying out the change in oxidation state, as if the process is being carried out without involvement of intermediate oxidation state.

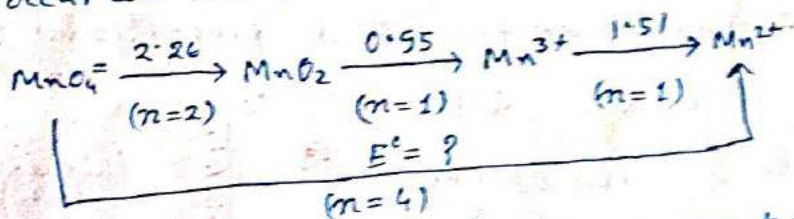
• Similarly the different species of chlorine is depicted in the Latimer diagram as —



• By using Latimer diagram, the E° value of any step (non-adjacent species) can be calculated. The basic principle is that $\Delta G^\circ (= -nFE^\circ)$ is a thermodynamic function, does not depend on the path but depend only initial and final state. (ΔG° is a state function not path function)

Let us consider the potential for the skip-step couple $\text{MnO}_4^{2-}/\text{Mn}^{2+}$ i.e. $\text{MnO}_4^- + 8\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$, then what will be the E° value for $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$?

The process may occur in two possible way —



To calculate E° value of any composite process, we have to convert the individual E° values to ΔG° values by multiplication with $-nF$ factor and add them together. The overall ΔG° value for successive steps is the sum of the individual values. i.e.

$$\Delta G^\circ = \Delta G_1^\circ + \Delta G_2^\circ + \Delta G_3^\circ + \dots$$

$$-nFE^\circ = -n_1FE_1^\circ - n_2FE_2^\circ - n_3FE_3^\circ - \dots$$

So, For the above process ΔG° of two path are same —

$$-4FE^\circ = -F(2 \times 2.26 + 1 \times 0.95 + 1 \times 1.51)$$

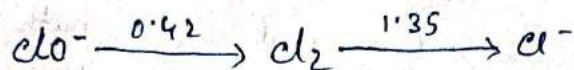
$$\therefore E^\circ = \frac{2 \times 2.26 + 1 \times 0.95 + 1 \times 1.51}{4} = 1.74 \text{ volt}$$

In general we can write

$$E^\circ = \frac{n_1E_1^\circ + n_2E_2^\circ + n_3E_3^\circ + \dots}{n_1 + n_2 + n_3 + \dots}$$

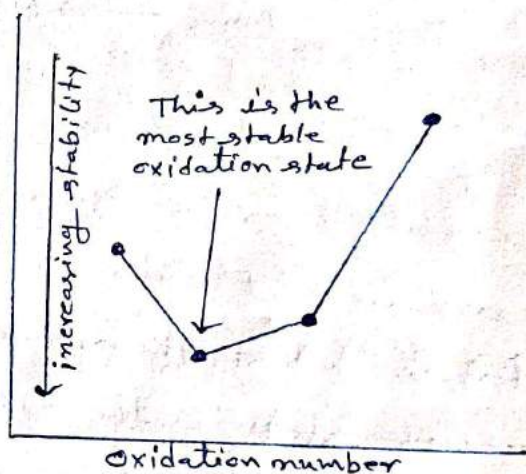
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- This diagram can be used to judge whether disproportionation of a species will occur or not. A species has a tendency to disproportionate to its nearest neighbours if the potential of the right hand species in the diagram is higher than the potential of the left. Thus Cl_2 has a tendency to disproportionate in alkaline medium due to the following



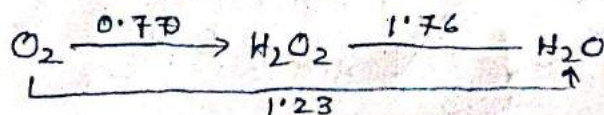
FROST DIAGRAMS: Dr. Sandip Mondal

Let an element X exist in different oxidation number X^n to X^0 . The Frost diagram of an element X is a plot of nE° versus the various oxidation number of the element. We know $\Delta G^\circ = -nFE^\circ$, so that $nE^\circ = -\Delta G^\circ/F$ and hence the nE° is proportional to the standard free energy change for the formation of the species of the element concerned in the 'n' oxidation number. Therefore the plot of nE° against 'n' can also be considered as the plot of ΔG° against 'n'. Therefore the most stable oxidation state of the element which have the position lowest to the Frost diagram.



The Frost diagram is a ready record for quick qualitative idea about the variation of redox properties of an element in different oxidation state. The following features of the Frost diagram indicate some special utility —

i) Consider the Latimer diagram of O_2



The oxidation number of oxygen in the said diagram are 0, -1 and -2 respectively. For conversion of O_2 to H_2O_2 the change in oxidation number is from 0 to -1. Here $E^\circ = +0.70V$ and $n = -1$, so $nE^\circ = -0.70$. The change in oxidation number O_2 to H_2O is from 0 to -2 and $E^\circ = +1.23V$

and hence $nE^\circ = -2 \times 1.23 = -2.46V$,

so that difference of the values is $-1.76V$ and change in oxidation number of two system is -1 .

Therefore the slope of the line is

$$\frac{-1.76}{-1} = +1.76V \text{ which is in}$$

agreement with that of the value

for the H_2O_2/H_2O couple in Latimer

diagram.

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ii) In Frost diagram steeper the line joining two points, higher is the potential of the corresponding couple. The CD line is more steeper than BC line and thus the couple

corresponding to point c and D will have higher reduction potential

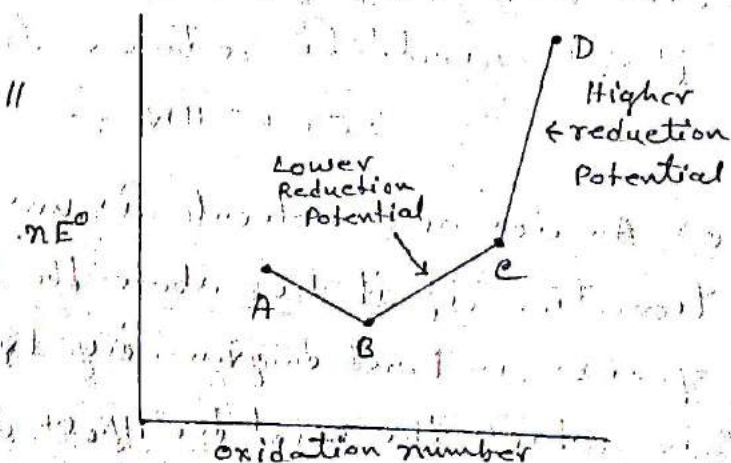
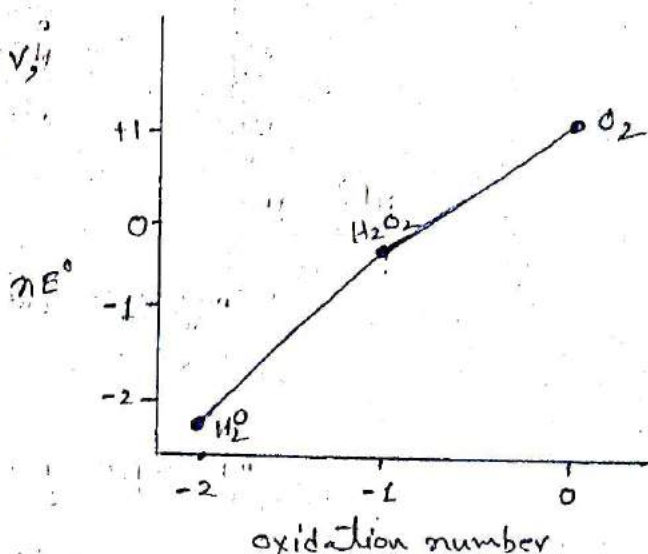
compared to that of the couple formed by B and c point. Thus

the spontaneity of the redox reaction between two points

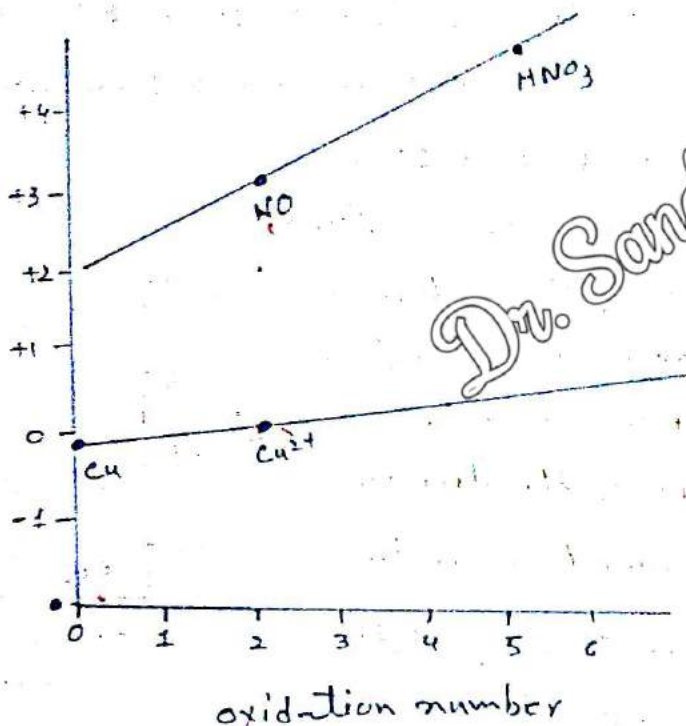
can be judged by comparing the slopes of the corresponding

line. Thus species represented by the point D would undergo reduction, while the species B would be labile to spontaneous oxidation.

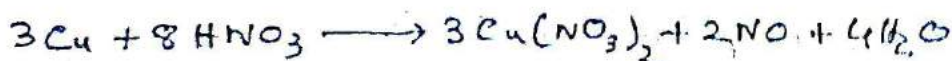
The diagram can be utilised to predict whether a particular oxidant will oxidise a particular species or not. The judgement can be made by observing that an oxidant with more positive slope



in nE° vs. oxidation number plot would easily oxidise a species, occupying the position in the said plot having less positive slope,



In the above diagram nE° vs. oxidation number plot of $\text{HNO}_3 - \text{NO}$ line has more greater positive slope than that of $\text{Cu} - \text{Cu}^{2+}$ line and hence HNO_3 would easily oxidise Cu to Cu^{2+} and itself would be reduced to NO , i.e.



c) An ion or a molecule is unstable with respect to disproportionation if it lies above the line connecting two adjacent species in Frost diagram. Eg. Frost diagram of nitrogen compounds in which the point for $\text{H}_2\text{N}_2\text{OH}$ lies above the line connecting

points for NH_3 and N_2 and hence $\text{H}_2\text{N}_2\text{OH}$ is thermodynamically less stable than NH_3 and N_2 so that $\text{H}_2\text{N}_2\text{OH}$ is liable to disproportionate into NH_3 and N_2 .

