

## Applications of Latimer-diagram:

The applications of the Latimer-diagram are given below :

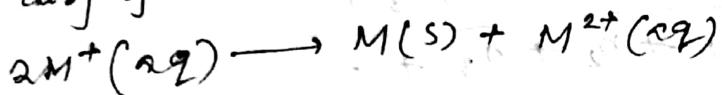
(i) It is possible to predict whether a species will disproportionate from an inspection of the Latimer-diagram covering the redox species.

If the redox potential to the right of the species is higher than the potential on the left, then the species will undergo disproportionation.

Let us consider the following case :



The disproportionation rxn will be as :



We have,  $M^+ + e \rightarrow M ; E^\circ = y \text{ volt}$



If we subtract the R.H.S potential from the L.H.S potential of the Latimer-diagram, we get the disproportionation rxn whose standard potential is given by

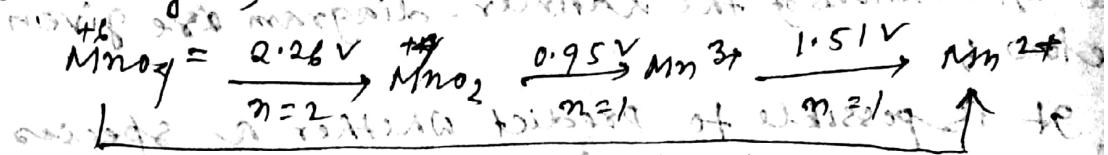
$$E^\circ = (y-x) \text{ volt.}$$

When  $(y-x)$  is positive,  $E^\circ$  is positive and  $\Delta G^\circ$  is negative and so the rxn is spontaneous i.e; the species will disproportionate.

(ii) By using the Latimer-diagram the  $E^\circ$  value of one step can be calculated. The basic principle is that  $\Delta G^\circ$  is a thermodynamic state function. Hence the total change in the Gibbs free energy does not depend on the path, through which the process is carried out and it depends only on the final and the initial states. Let us calculate the potential for  $MnO_4^- / Mn^{2+}$  couple.



Thus the process may occur in two possible pathways;



As  $\Delta E^\circ$  for both the pathways are the same  
hence we can write

$$-\Delta E^\circ = -2F(2.26) - 1.5F(0.95) - 1.5F(1.51)$$

$$\Delta E^\circ = \frac{2 \times 2.26 + 1 \times 0.95 + 1 \times 1.51}{2+1+1}$$

$$= 1.759 \text{ volt.}$$

In general we can write

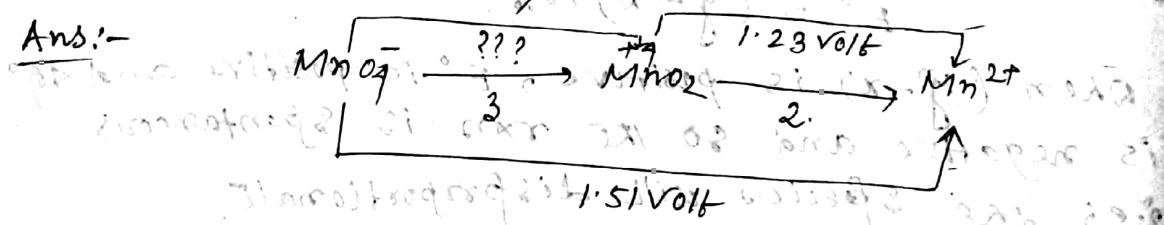
$$\boxed{\Delta E^\circ = \frac{n_1 E_1^\circ + n_2 E_2^\circ + n_3 E_3^\circ + \dots}{n_1 + n_2 + n_3 + \dots}}$$

Question: Findout the standard electrode

potential for  $\text{MnO}_4^-/\text{MnO}_2$  redox couple in acid medium.

Given  $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ volt}$  and  $E^\circ_{\text{MnO}_2/\text{Mn}^{2+}} = 1.23 \text{ volt at } 25^\circ\text{C}$

Ans:-



We know that,  $E^\circ = n_1 E_1^\circ + n_2 E_2^\circ$

From the following diagram calculate the standard potential of  $\text{MnO}_4^-/\text{Mn}^{2+}$  couple in acid medium.

Given  $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ volt}$  and  $E^\circ_{\text{MnO}_2/\text{Mn}^{2+}} = 1.23 \text{ volt}$

or,  $1.51 \text{ volt} = 3E_1^\circ + 2 \times 1.23$

or,  $3E_1^\circ + 2 \times 1.23 = 1.51 \times 5$

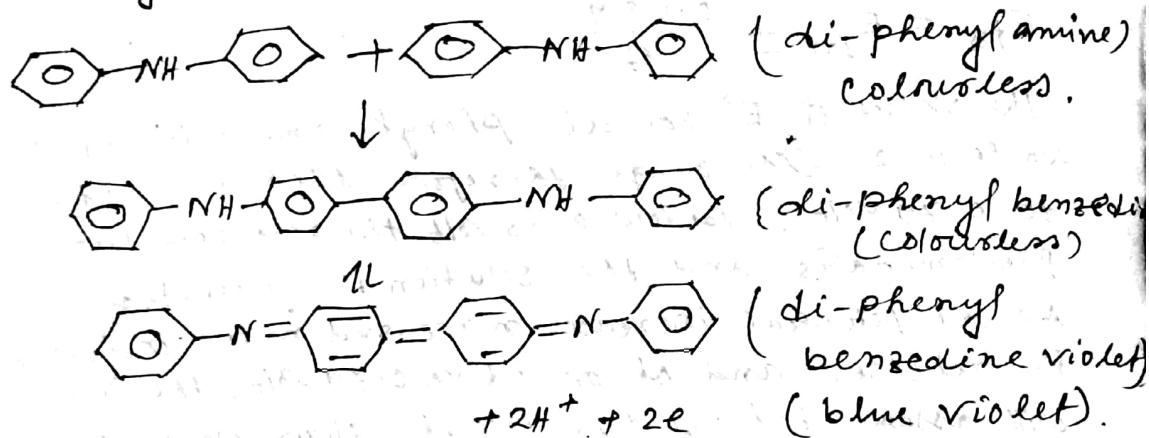
or,  $3E_1^\circ = 1.51 \times 5 - 2.46$

or,  $E_1^\circ = 1.51 \times 5 - 2.46 / 3 = 1.70 \text{ volt.}$

\* predict which species in the above diagram have tendency to disproportionate.

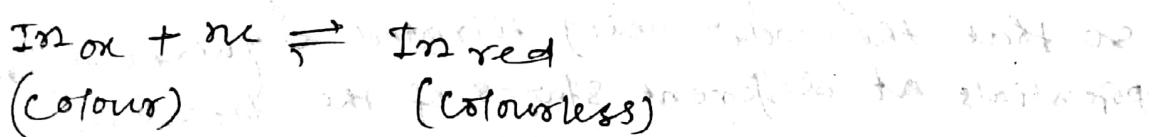
Redox indicators:  
 Indicators that change colour at a definite potential of the titrated solution in redox titration are called redox indicators. Redox potential indicators are mostly organic dyes which can undergo reversible oxidation or reduction in the titration medium giving different colour. Usually the reduced form is colourless and the oxidised form is different colour. The redox indicator for any titration is so chosen that it gets oxidised very near the equivalent points of the titration.

e.g.; colourless di-phenyl amine is oxidised to di-phenyl benzidine violet (blue violet) via di-phenyl benzidine (colourless).



Question: Di-phenyl amine ( $E^\circ = 0.76 \text{ V}$  at  $1 \text{ M}$   $\text{H}_2/\text{H}_2\text{O}$ ) is a good redox indicator. Establish its work in potential range.

The oxidised and reduced forms of a redox indicator establish a redox system with a characteristic electrode potential. If the two form are expressed as  $\text{In}_{\text{ox}}$  and  $\text{In}_{\text{red}}$  respectively, we may write



Therefore according to Nernst equation, we can write

$$E_{\text{In}} = E^\circ + \frac{0.059}{n} \log \frac{[\text{In}_{\text{ox}}]}{[\text{In}_{\text{red}}]}$$

It may be assumed that the colour of the oxidised form predominates when its concentration is 10 times that of the colourless form. So for an appreciable colour of the oxidised form we have

the condition

$$E_{In} = E_{In}^{\circ} + \frac{0.059}{n} \log \frac{I}{I_0}$$

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

Again, the soln may be consider almost colourless when the reduced form has atleast 10 times greater conc. than the oxidise form, then we may write

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

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

$$= E_{In}^{\circ} - \frac{0.059}{n}$$

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

$$E_{In} = E_{In}^{\circ} \pm \frac{0.059}{n}$$

The value of  $E^{\circ}$  for di- phenyl-amine is 0.76 V while  $n=2$ . The range therefore lies from 0.73 V to 0.79 volt. Below 0.73 volt the reduced form predominates and the solution is colourless.

As the potential increases more and more indicator is oxidised and at or above 0.79 volt, the indicator will assume intense blue violet colour which is the colour of the oxidised form.

### ④ Redox titration and its curve in redox system

The e.m.f of a half cell depends upon the conc. of different chemical species present in the system.

In any titration process, the relative amounts of the two reacting species are gradually varied so that the soln being titrated acquires different potentials at different stages of the titration. This fact may be utilised to determine the equivalence points of a titration.

Except when the titrant is itself coloured, one may use a suitable indicator which would get oxidised at the potential of the equivalence point. This method is more suitable for redox titration and the