

1st lecture

Syllabus: *Ion-electron method of balancing equation of redox reactions. Elementary idea on standard redox potentials with sign conventions, Nernst equation (without derivation). Influence of complex formation, precipitation and change of pH on redox potentials; formal potential. Feasibility of a redox titration, redox potential at the equivalence point, redox indicators. Redox potential diagram (Latimer and Frost diagrams) of common elements and their applications. Disproportionation and comproportionation reactions (typical examples). Solubility product principle, common ion effect and their applications to the precipitation and separation of common metallic ions as hydroxides, sulfides, phosphates, carbonates, sulfates and halides.*

Ion-electron method of balancing equation of redox reaction: This method is based on the electronic theory of oxidation and reduction and is limited to ionic reactions in aqueous solutions. The procedure may be summarised as follows:

Step-1: The products of the reaction are ascertained and the loss of electron by the reductant and the gain of electron by the oxidant are expressed separately by “**partial equations**”.

Step-2: The individual partial equations are balanced separately with respect to different atoms as well as with respect to the electrical charge on both sides. The following points may be used as a guideline:

(a) Since redox reactions occurred in aqueous solutions are chiefly concerned, only the species capable of appearing as ions in solution and actually taking part in oxidation-reduction should appear in such half-reactions. Substances which are either insoluble or slightly ionisable in water should appear *as such* in these equations (e.g., H_2O_2).

(b) H^+ and OH^- ions and H_2O molecules may be inserted to balance the half-reactions “atomically”.

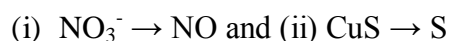
(c) For electrical balance, the total charge of all the ions appearing on the two sides of the half reactions (including those on the H^+ and OH^- ions inserted) are considered and the difference is adjusted by adding electrons (-ve charge) on the appropriate side.

Step-3: The two partial equations so obtained are multiplied by suitable factors to equalise the number of electrons in them. These are then added, the electrons cancelled and the ions are replaced by molecules by making necessary adjustments.

A few examples are given below:

Example 1: CuS dissolves in hot dilute HNO₃ forming Cu(NO₃)₂, NO and S.

Step-1: The oxidant furnishes NO₃⁻ ions which are reduced to NO. The reduction is done by the CuS. Hence, we start the partial equations by writing:

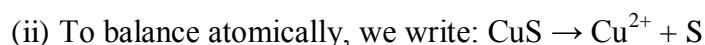
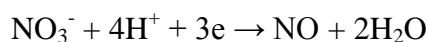


Step-2: (i) For balancing this partial equation atomically, the two extra oxygen atoms on the left are adjusted by inserting two molecules of water on the right.

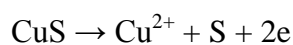


The four extra hydrogen atoms on the right are now balanced by placing four H⁺ ions on the left: NO₃⁻ + 4H⁺ → NO + 2H₂O

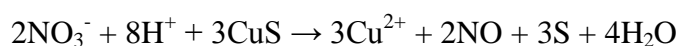
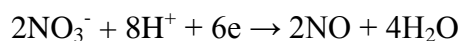
Now we have to balance the charge. The left side contains a net excess of three positive charges. So, three electrons are added to this side:



For charge balance, we are to insert two negative charges on the right:



Step-3: The number of electrons in these two partial equations are equalised by multiplying reaction (i) by 2 and reaction (ii) by 3. Subsequent addition gives:

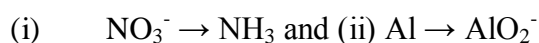


To obtain the final equation, we shall have to provide $3 \times 2 = 6$ nitrate ions for the three cupric ions when we get the total equation as:



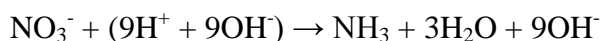
Example 2: Reduction of NaNO_3 solution by metallic aluminium in presence of NaOH .

Step-1: NO_3^- is reduced to NH_3 and Al is oxidised to AlO_2^- ion. The partial equations may be written as:

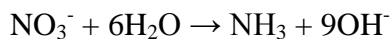


Step-2: (i) For balancing atomically, one obviously starts by writing: $\text{NO}_3^- \rightarrow \text{NH}_3 + 3\text{H}_2\text{O}$

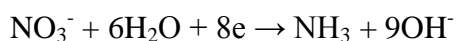
But now the nine hydrogen atoms on the right cannot be adjusted on the left by placing 9H^+ , since the medium is *alkaline*. These may be assumed to combine with nine OH^- ions from the alkaliof the medium to produce water:



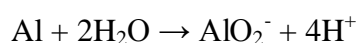
That is, we put 9OH^- ions on the right and nine H_2O on the left. Ultimately we have:



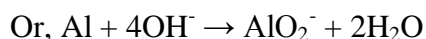
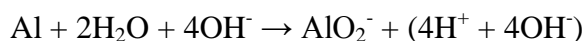
To balance electrically, we have to put eight more negative charges on the left:



(ii) For balancing atomically, one may write:

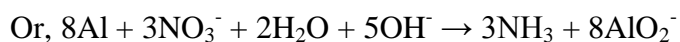
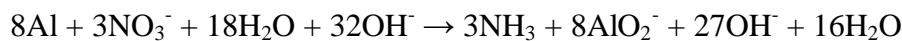
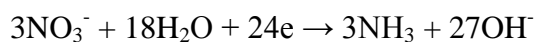


Here again, the alkalinity of the medium has to be considered:



Balancing electrically, we have, $\text{Al} + 4\text{OH}^- \rightarrow \text{AlO}_2^- + 2\text{H}_2\text{O} + 3\text{e}^-$

Step-3: We multiply the first equation by 3 and the second equation by 8 to make the number of electrons 24 in each and add the two partial equations:

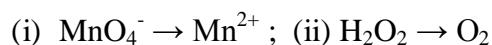


Writing NaNO_3 in place of NO_3^- , NaAlO_2 in place of AlO_2^- and NaOH in place of OH^- , the balanced equation becomes:

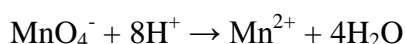


Example 3: Reduction of KMnO_4 to manganous salt by H_2O_2 in acid medium.

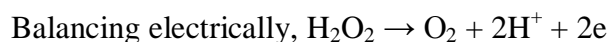
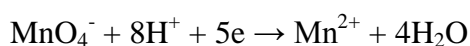
Step-1: The partial equation should be written as:



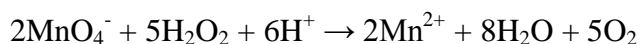
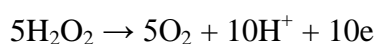
Step-2: To balance atomically, we first write four molecules of water on the right. The excess hydrogen so introduced are adjusted on the left as H^+ :



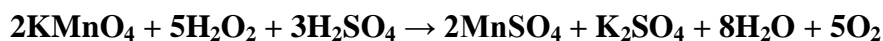
Balance of charge now gives:



Step-3: Multiplying the first equation by 2 and second one by 5 and then adding,

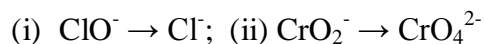


In terms of KMnO_4 and H_2SO_4 , this becomes:



Example 4: Oxidation of sodium chromite in basic solution by sodium hypochlorite.

Step-1: Sodium hypochlorite is reduced to sodium chloride and sodium chromite is oxidised to sodium chromate. Hence we write:



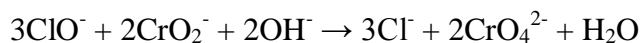
Step-2: Balancing atomically, $\text{ClO}^- + \text{H}_2\text{O} \rightarrow \text{Cl}^- + 2\text{OH}^-$ (since the medium is alkaline).

Balancing electrically, $\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cl}^- + 2\text{OH}^-$

(ii) Balancing atomically, $\text{CrO}_2^- + 4\text{OH}^- \rightarrow \text{CrO}_4^{2-} + 2\text{H}_2\text{O}$ (since the medium is alkaline).

Balancing electrically, $\text{CrO}_2^- + 4\text{OH}^- \rightarrow \text{CrO}_4^{2-} + 2\text{H}_2\text{O} + 3\text{e}^-$

Step-3: Multiplying the first equation by 3 and the second one by 2, and then adding, we get



Inserting the corresponding cations,



2nd lecture

Electrode potentials:

When a metal is immersed in water, or a solution containing its own ions, equilibrium is established between the metal and its ions. As a result, the metal has a tendency to go into the solution through the formation of M^{n+} ions by releasing n number of electrons (defined as the **oxidation potential**). Similarly, the M^{n+} ions also have a tendency to go to the M state by accepting n number of electrons (defined as the **reduction potential**). The actual nature of the electrode potential (i.e., either oxidation or reduction) depends on the nature of particular metal and the size of electrode potential (E) depends on number of electrons involved, the activity of ions in the solution and the temperature. **E^0 is the standard electrode potential, which is a constant for any particular metal and is in fact the electrode potential measured under standard conditions of temperature and with unit activity.** These terms are related by the equation:

$$E = E^0 + \frac{RT}{nF} \ln(1/a_M^{n+})$$

(Where R is the gas constant, T the absolute temperature, a_M^{n+} the activity of ions in solution, n the valency of the ion and F the Faraday). For most purpose, the activity, a_M^{n+} may be replaced by the concentration of ions in solution.

The potential of a single electrode cannot be measured, but if a second electrode of known potential is joined with this electrode, the potential difference between the two electrodes can be measured. The standard against which all electrode potentials are compared is the standard hydrogen electrode (Fig.1).

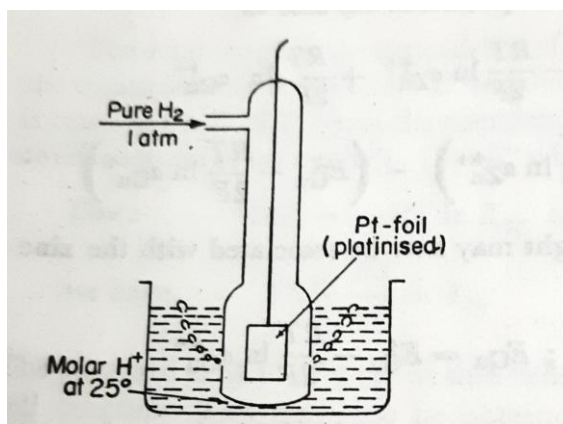


Fig.1. Standard hydrogen electrode.

A standard hydrogen electrode consists of a platinised platinum [Platinum foil coated with a fine deposit of metallic platinum (Platinum black) formed by electrolysis of a solution of chloroplatinic acid] electrode partially immersed in an acidic solution containing H^+ ions of unit activity and pure hydrogen gas at 1 atm pressure is slowly bubbled through the solution. Hydrogen gas thus surrounds the electrode and is also adsorbed by the platinised platinum. Equilibrium is established between hydrogen molecules and the H^+ ions in solution.

As per IUPAC recommendation, the electrode potential [$E^\circ_{\text{H}^+/\frac{1}{2}\text{H}_2(\text{g})}$ or $E^\circ_{\text{H}_2(\text{g})/\text{H}^+}$] of standard hydrogen electrode is arbitrarily assigned to 0 V.

Secondary Reference Electrode: The Calomel Electrode

Experimentally, it is difficult to set up a standard hydrogen electrode. So, a number of subsidiary reference electrodes have been devised. These can be easily set up with accurately known potentials with respect to the standard hydrogen electrode. The **calomel electrode** is most common among them.

The calomel electrode (Fig. 2) consists of mercury in contact with solid mercurous chloride (also called calomel) and a solution of potassium chloride (saturated with mercurous chloride). It may be represented as:

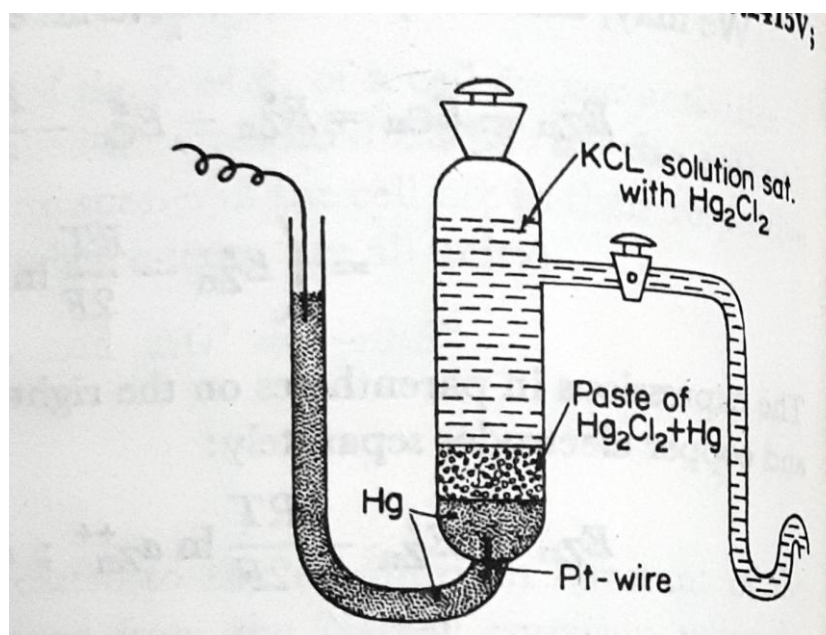
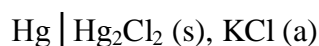
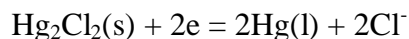


Fig. 2. The calomel electrode.

When this electrode is connected with a standard hydrogen electrode, the reaction taking place spontaneously in the electrode is:



The potential of the electrode is accordingly dependent on the activity (and hence concentration) of the KCl solution. **Three different concentrations of KCl** are generally employed with their corresponding E.M.F. values. For the cell reaction written above (reduction), the EMF's at 25 °C for various concentrations of KCl are.

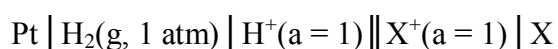
(i) For 1.0 N KCl solution: $E_{\text{Cal}} = 0.28 \text{ V}$

(ii) For 0.1 N KCl solution: $E_{\text{Cal}} = 0.33 \text{ V}$

(iii) For saturated KCl solution: $E_{\text{Cal}} = 0.24 \text{ V}$

Sign convention:

As per IUPAC recommendation, the standard electrode potential of an electrode X is the EMF of a cell in which (i) the *negative* electrode is made up of a standard hydrogen electrode, arbitrarily assigned a potential of 0 V and (ii) the *positive* electrode is made up of the electrode X, its components being maintained at *unit activity*. If the electrode X is written as X/X^+ , then its standard electrode potential is the EMF of the cell



in which the cell reaction is: $\frac{1}{2}\text{H}_2(\text{g}) + \text{X}^+(\text{a} = 1) = \text{H}^+(\text{a} = 1) + \text{X}$

According to this definition, the *sign* of the electrode potential is always the sign of the electrostatic potential *actually observed* when the electrode is coupled with a standard hydrogen electrode. The electrode potential thus becomes a *sign invariant* quantity and does not change its sign even when electrode is placed on the left of a cell and oxidation occurs in it. Thus, when a standard zinc-zinc ion electrode, $\text{Zn} \mid \text{Zn}^{2+} (\text{a} = 1)$, is combined with a standard hydrogen electrode, the experimental potential is -0.76 V. Accordingly, E°_{Zn} is assigned the value -0.76 V. Even when this electrode is as the negative electrode in some cell, E°_{Zn} will be taken as -0.76 V.

But this gives rise to certain difficulties from the thermodynamic standpoint. We know that a piece of metallic Zn reacts spontaneously with acid solution liberating hydrogen. The reaction: $\frac{1}{2}\text{Zn} + \text{H}^+ = \frac{1}{2}\text{Zn}^{2+} + \frac{1}{2}\text{H}_2$

Corresponds to the cell: $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{H}^+ \mid \text{H}_2(\text{g})$

In which Zn forms the negative electrode where oxidation takes place. ΔG° for the cell reaction should be negative as the reaction is spontaneous. Since, $\Delta G^\circ = -nFE^\circ$, one must conclude that E°_{Zn} should be positive in this case. But the definition given above sets E°_{Zn} as inherently negative, which is the experimentally obtained *electrostatic potential* of the electrode in combination with a hydrogen electrode. The thermodynamic tendency of the reaction, as given by a negative ΔG° , corresponds to an electromotive force *which is algebraically negative*, and has little to do with the ‘+’ and ‘-’ signs of electrostatics *which originated from Franklin’s accidental choice between “two kinds of electricity”*.

In order to reduce this apparent discrepancy, the IUPAC has recommended some revision of terminology. Accordingly, (a) the term Electrode Potential should refer only to the electrostatic potential, designated by V, (b) the term EMF should be used to represent the thermodynamic quantity E, where $\Delta G^\circ = -nFE^\circ$. The potential of a half-cell is then expressed in terms of its *reduction potential*.

Standard reduction potential of some common metallic and non-metallic species are given in the following Table 1.

Table 1. Standard reduction potential (volts at 25 °C) of some common species.

Li^+/Li -3.05	Fe^{2+}/Fe -0.44	$\text{H}^+/\frac{1}{2}\text{H}_2$ 0.00	$\frac{1}{2}\text{Br}_2/\text{Br}^-$ +1.07
K^+/K -2.93	Cd^{2+}/Cd -0.40	Cu^{2+}/Cu +0.35	$\frac{1}{2}\text{Cl}_2/\text{Cl}^-$ +1.36
Ca^{2+}/Ca -2.84	Co^{2+}/Co -0.27	Ag^+/Ag +0.80	$\frac{1}{2}\text{F}_2/\text{F}^-$ +2.86
Al^{3+}/Al -1.66	Ni^{2+}/Ni -0.23	Au^{3+}/Au +1.38	$\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ +1.36
Mn^{2+}/Mn -1.08	Sn^{2+}/Sn -0.14	$\frac{1}{2}\text{O}_2/\text{OH}^-$ +0.40	$\text{MnO}_4^-/\text{Mn}^{2+}$ +1.52
Zn^{2+}/Zn -0.76	Pb^{2+}/Pb -0.13	$\frac{1}{2}\text{I}_2/\text{I}^-$ +0.54	$\text{Fe}^{3+}/\text{Fe}^{2+}$ +0.77

3rd lecture

Several factors affect the value of the standard potential. The conversion of M to M^+ in aqueous solution may be considered in a series of steps:

- (i) Sublimation of a solid metal
- (ii) Ionization of a gaseous metal atom
- (iii) Hydration of a gaseous ion

These are best considered in a Born-Haber type of cycle (Fig. 1)

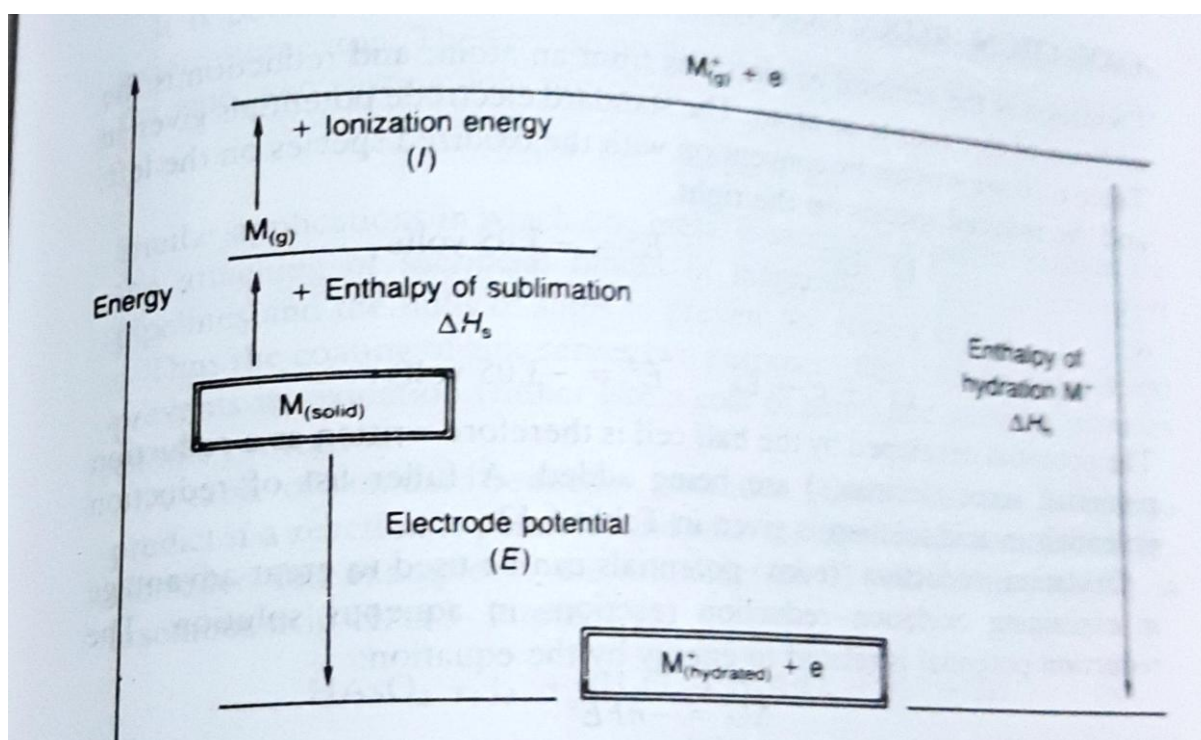


Fig. 1. Energy cycle for electrode potentials. (Strictly E is the free energy change associated with electrode potential).

The enthalpy of sublimation and the ionization energy are positive since energy must be put into the system, and the enthalpy of hydration is negative since energy is evolved. Thus,

$$E = +\Delta H_s + I - \Delta H_h$$

Consider first a transition metal. Most transition metals have high melting points: hence the enthalpy of sublimation is high. Similarly, they are fairly small atoms and have high ionization energies. Thus the value for the electrode potential E is low, and the metal has little tendency to form ions: hence it is less reactive.

In contrast, the s-block metals (Groups 1 and 2) have low melting points (hence low enthalpies of sublimation), and the atoms are large and therefore have low ionization energies. Thus the electrode potential E is high and the metals are highly reactive.

Electrons are lost when a substance is oxidized and electrons are gained when it is reduced. A reducing agent must therefore supply electrons and elements having large negative electrode potentials are strong reducing agents. The strengths of oxidizing and reducing agents may be measured by the size of the potential between solution and an inert electrode. Standard reduction potentials are obtained when the concentrations of oxidised and reduced forms are 1 M, and the potential developed is measured against standard hydrogen electrode. **The most powerful oxidizing agents have a large positive reduction potential and strong reducing agents have a large negative reduction potential.** Standard reduction potentials allow us to predict which ions should oxidize or reduce other ions. The potentials indicate if the energy changes for the process are favourable or unfavourable. It is important to realize that though the potentials may suggest that a reaction is possible, they do not give any kinetic information concerning the rate of the reaction. The rate of the reaction may be very fast or slow, and in some cases a catalyst may be required for the reaction to occur at all – for example, in the oxidation of Cr^{3+} ion by sodium or potassium persulphate, Ag^+ ion is required as catalyst.

Formal potential:

The standard potential of a half-cell refer to unit activity of the constituent species in the system. This is only an ideal and limiting situation. In actual practice, the solutions are usually quite concentrated and the activities of various species differ appreciably from respective concentrations. But we have to prepare solutions and conduct experiments mostly in terms of concentrations, not activities. So, *inferences drawn on the basis of standard potentials may often appear anomalous*. This is more important when a solution contains additional electrolytes and/or involves interactions like acid-base dissociation, complexation

etc. For these reasons, the idea of **formal potential** has been introduced to supplement the use of **standard potential** in practical cases.

The **formal potential** is the potential observed experimentally in a half cell containing oxidised and reduced species in different molar ratios. It incorporates the effects of varying ionic strength of the medium, acid-base dissociation, complexation etc. The formal potential (E) is related to the standard potential (E^0) of a half-cell by the Nernst equation as:

$$E = E^0 + (0.059/n) \log([\text{Oxidised form}]/[\text{Reduced form}])$$

(n represents the number of electron transferred)

It has already been described that the formal potential varies with electrolyte composition. Thus, the E^0 value for $\text{Fe}^{3+}/\text{Fe}^{2+}$ system is + 0.77 V; but its formal potential (E) is + 0.75 V in 1 M HClO_4 ; + 0.70 V in 1 M HCl ; + 0.68 V in 1 M H_2SO_4 and + 0.61 V in 0.5 M H_3PO_4 + 1 M H_2SO_4 . The value of E decreases as the extent of complexation of Fe^{3+} increases in the order shown.

4th lecture

Formal potential provides explanation for the observed behaviour of many redox systems which cannot be explained by *standard potential* alone. As an example, let us consider the following half-cells:



The reduction potential data suggests that iodine should oxidise ferrocyanide to ferricyanide. In fact, the reverse process takes place when the two half cells are combined; ferricyanide oxidises iodide to iodine quantitatively in 1 M HCl, H₂SO₄ or HClO₄ medium. In such acid medium, the acids H₄[Fe(CN)₆] and H₃[Fe(CN)₆] are formed, H₄[Fe(CN)₆] being the weaker one. As a result, the concentration of free [Fe(CN)₆]⁴⁻ ion in solution is largely reduced, leading to a significant increase in the formal potential of the system to ~ + 0.71 V, a value sufficient to oxidise iodide ion.

Factors affecting the E of half-cells:

(i) Effect of concentration: The concentration of the reacting species in a half-cell greatly influences the potential of a system. For any half-cell reaction, we may write:

Oxidised form + ne = Reduced form

$$E = E^0 + (0.059/n) \log([\text{oxidised form}]/[\text{reduced form}])$$

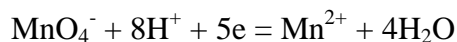
This shows that a tenfold increase in the concentration of the oxidised form will raise the half-cell potential by 0.059/n volts. Thus, for the Fe³⁺ - Fe²⁺ system, E⁰ is + 0.77 V; but when [Fe³⁺] = 1 mol/dm³ and [Fe²⁺] = 1.0 × 10⁻⁴ mol/dm³, we have,

$$E = E^0 + 0.059/1 \log([\text{Fe}^{3+}]/[\text{Fe}^{2+}]) = 0.77 + 0.059 \log(1/10^{-4}) = + 1.006 \text{ V}$$

Concentrations of different constituents of a half-cell may be largely affected by precipitation or complex formation, leading to significant change in potential.

(ii) Effect of pH: When H⁺ or OH⁻ ions are involved in a half cell reaction, their concentrations appear in the Nernst equation and accordingly the potential is influenced by the pH of the medium. This effect may be understood from the following typical example:

The standard reduction potential of the $\text{MnO}_4^-/\text{Mn}^{2+}$ system (+ 1.52 V) may at first suggest that permanganate solution would oxidise each of Cl^- , Br^- or I^- ions to the free halogens ($E^0 = + 1.36 \text{ V}$, + 1.07 V and + 0.54 V respectively). But the potential of the $\text{MnO}_4^-/\text{Mn}^{2+}$ system is greatly influenced by the pH of the medium and accordingly permanganate solution may oxidise the three halides selectively at different pH values:

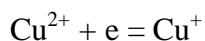


$$\begin{aligned} E &= E^0 + (0.059/5) \log([\text{MnO}_4^-] [\text{H}^+]^8 / [\text{Mn}^{2+}]) \\ &= E^0 + (0.059/5) \log[\text{H}^+]^8 + (0.059/5) \log([\text{MnO}_4^-] / [\text{Mn}^{2+}]) \\ &= 1.52 - 0.094 \times \text{pH} + (0.059/5) \log([\text{MnO}_4^-] / [\text{Mn}^{2+}]) \end{aligned}$$

At pH = 6, the reduction potential falls to + 0.96 V, below the potential of either $\text{Cl}_2 - \text{Cl}^-$ or $\text{Br}_2 - \text{Br}^-$ couples. So, permanganate can no more oxidise Br^- or Cl^- ions at this pH. At pH = 3, the reduction potential shifts to ~ + 1.24 V, when Br^- and I^- are both oxidised, but not Cl^- . Cl^- is oxidised only below pH 1.5.

(iii) Effect of Precipitation: This is another method through which the concentration of oxidised or reduced form may be changed. The concentration change follows from precipitation of one of the reaction products due to low solubility.

The $\text{Cu}^{2+} - \text{Cu}^+$ system has low reduction potential of + 0.15 V. It is not expected to oxidise iodide to iodine ($E^0_{1/2\text{I}_2/\text{I}^-} = + 0.54 \text{ V}$). However, the extremely low solubility of CuI reduces the concentration of Cu^+ ion to such an extent that reduction potential is substantially increased:



$$E = E^0 + 0.059 \log([\text{Cu}^{2+}] / [\text{Cu}^+])$$

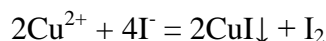
$[\text{Cu}^+]$, the concentration of cuprous ion, is determined by the solubility product (K) of CuI :

$$K = [\text{Cu}^+] \times [\text{I}^-] = 10^{-12}.$$

So, $[\text{Cu}^+] = 10^{-12} / [\text{I}^-]$; So, $E = E^0 + 0.059 \log([\text{Cu}^{2+}] \times [\text{I}^-] / 10^{-12})$

$$= + 0.15 + 12 \times 0.059 + 0.059 \log[\text{Cu}^{2+}][\text{I}^-] = + \mathbf{0.86} + \mathbf{0.059 \log[\text{Cu}^{2+}][\text{I}^-]}$$

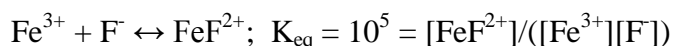
Thus, the effective potential rises above the reduction potential of the iodine – iodide system. So, iodide ion is oxidised by Cu^{2+} ion in solution. In fact, the reaction,



Proceeds almost towards right so that copper may be estimated by titrating the liberated iodine with a standard solution of sodium thiosulphate.

(iv) Effect of Complex formation:

Complex formation may also reduce the effective concentration of one of the species involved in an electrode process, thereby altering its potential. Fe^{3+} ion normally oxidises iodide to iodine in aqueous solution. But in presence of excess F^- ion, the Fe^{3+} ion is removed from the solution as the complex ion $[\text{FeF}]^{2+}$, $[\text{FeF}_2]^+$ etc.



The value of $[\text{Fe}^{3+}]$ from this relation may now be substituted in the expression for the reduction potential of the $\text{Fe}^{3+} - \text{Fe}^{2+}$ system:

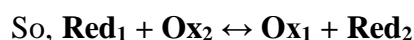
$$\begin{aligned} E &= E^0 + 0.059 \log([\text{Fe}^{3+}]/[\text{Fe}^{2+}]) \\ &= + 0.77 + 0.059 \log\{[\text{FeF}^{2+}]/(10^5 \times [\text{Fe}^{2+}] \times [\text{F}^-])\} \\ &= + 0.77 + 0.059 \log 10^{-5} + 0.059 \log\{[\text{FeF}^{2+}]/([\text{Fe}^{2+}] \times [\text{F}^-])\} \\ &= + 0.47 + 0.059 \log\{[\text{FeF}^{2+}]/([\text{Fe}^{2+}] \times [\text{F}^-])\} \end{aligned}$$

As the reduction potential decreases, the oxidising power of Fe^{3+} decreases and it can no more oxidise iodide ion. On the other hand, Cu^{2+} ion does not form any such stable complex with F^- ion. Thus Cu^{2+} may be estimated selectively in an $\text{Fe}^{3+} - \text{Cu}^{2+}$ mixture by titrating the iodine liberated from KI in presence of F^- ion.

5th lecture

Q. What will be the minimum potential difference between two red-ox couples for a quantitative red-ox reaction?

In the simplest case, the half-cell reactions for two reacting red-ox systems may be written as:



At equilibrium, the electrode potentials of the two half-cells will be equal. The reduction potentials in terms of equilibrium concentrations (25 °C) are:

$$E_1 = E_1^0 - 0.059 \log([\text{Red}_1]/[\text{Ox}_1])$$

$$E_2 = E_2^0 - 0.059 \log([\text{Red}_2]/[\text{Ox}_2])$$

Since, $E_1 = E_2$ at equilibrium, we get

$$E_2^0 - E_1^0 = 0.059 \log\{([\text{Red}_2][\text{Ox}_1])/([\text{Red}_1][\text{Ox}_2])\} = 0.059 \log K_{\text{eq}}$$

Now, for 99.9% completion of the reaction at equilibrium, $[\text{Ox}_1]/[\text{Red}_1]$ and $[\text{Red}_2]/[\text{Ox}_2]$ should be at least 1000:1.

$$\text{So, } K_{\text{eq}} (\text{minimum}) = ([\text{Red}_2][\text{Ox}_1])/([\text{Red}_1][\text{Ox}_2]) = 10^3 \times 10^3 = 10^6$$

$$\text{So, } E_2^0 - E_1^0 (\text{minimum}) = 0.059 \log 10^6 = 0.354 \text{ V}$$

Thus, Fe^{3+} cannot be estimated iodimetrically with high accuracy. From the E^0 values of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $1/2\text{I}_2/\text{I}^-$ systems, K_{eq} (at 25 °C) for the reaction $\text{Fe}^{3+} + \text{I}^- \leftrightarrow \text{Fe}^{2+} + 1/2\text{I}_2$ is given by, $\log K_{\text{eq}} = (1/0.059)(0.77 - 0.54) \approx 4$; So, **$K_{\text{eq}} = 10^4$**

This suggests that at equilibrium, a significant amount of Fe^{3+} will remain unreacted.

Now, if both the red-ox systems are of the type:

$\text{Red}_1 - ne \leftrightarrow \text{Ox}_1$ and $\text{Ox}_2 + ne \leftrightarrow \text{Red}_2$; It is easy to find that for a minimum of 10^6 for K_{eq} , $E_2^0 - E_1^0 = (0.059/n) \log K_{\text{eq}} = (0.059/n) \times 6$

When $n = 2$, $E_2^0 - E_1^0 = 0.177$

Red-ox titrations and red-ox indicators:

As a typical example, let us consider the titration of a solution of FeSO_4 by a solution of KMnO_4 , both of the order of (N/10). The relevant standard reduction potential differ widely (E^0 of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{MnO}_4^-/\text{Mn}^{2+}$ systems are respectively + 0.77 V and + 1.52 V) and the titration can be carried out in dilute H_2SO_4 medium (~ 1.5 N). H_3PO_4 is used to mask the yellow colour of ferric ion formed by complexation. In addition to that, H_3PO_4 has two another vital roles: (i) in maintaining the potential value of $\text{Fe}^{3+}/\text{Fe}^{2+}$ system at a particular value (near its standard potential value) and (ii) in maintaining the pH of the reaction medium. One drop of excess KMnO_4 solution just after the equivalence point is sufficient to develop an observable pink colour in the titrated solution which marks the end point of titration.

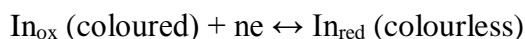
The procedure cannot be adopted in presence of substances which are also oxidised by KMnO_4 , e.g., Cl^- ion (the E^0 value of $\frac{1}{2}\text{Cl}_2/\text{Cl}^-$ system is + 1.36 V). Estimation of Fe^{2+} in presence of Cl^- may be carried out after addition of preventive solution containing MnSO_4 . The increased concentration of Mn^{2+} seems to lower the effective reduction potential of $\text{MnO}_4^-/\text{Mn}^{2+}$ system below that of $\frac{1}{2}\text{Cl}_2/\text{Cl}^-$ system.

6th lecture

Red-ox indicators:

These are mostly organic dyes which can undergo reversible oxidation or reduction in the titration medium imparting different colours. Usually the reduced form is colourless and the oxidised form is distinctly coloured. The red-ox indicator for any titration is so chosen that it get oxidised very near the equivalence point of the titration. For example, colourless diphenylamine (1% solution in conc. H_2SO_4) is oxidised to blue violet diphenyl benzidine violet via diphenyl benzidine (colourless; $E^0 = + 0.76 \text{ V}$) (Fig. 1).

The oxidised and reduced forms of a red-ox indicator establish a red-ox system with a characteristic electrode potential. If the two forms are expressed as In_{ox} and In_{red} respectively, we may write,



$$E_{\text{In}} = E^0_{\text{In}} + (0.059/n) \log([\text{In}_{\text{ox}}]/[\text{In}_{\text{red}}])$$

It may be roughly assumed that the colour of the oxidised form predominates when its concentration is **ten times** that of the colourless form (or of the colour in the reduced state, if any). So, for an appreciable colour of the oxidised form we have the condition

$$E_{\text{In}} = E^0_{\text{In}} + (0.059/n) \log(10/1) = E^0_{\text{In}} + 0.059/n$$

Again, the solution may be considered almost colourless (or of the colour in the reduced state) when the reduced form has at least **ten times** greater concentration concentrations than the oxidised form. We may write

$$E_{\text{In}} = E^0_{\text{In}} + (0.059/n) \log(1/10) = E^0_{\text{In}} - 0.059/n$$

Thus, the range of potential values across which an indicator exhibits sharp contrast of colour will be $E^0_{\text{In}} \pm 0.059/n$.

The value of E^0 for diphenylamine is + 0.76 V and n is equal to 2. The range therefore lies from + 0.73 V to + 0.79 V. Below + 0.73 V, 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 V, the indicator will assume intense blue-violet colour, the colour of the oxidised form.

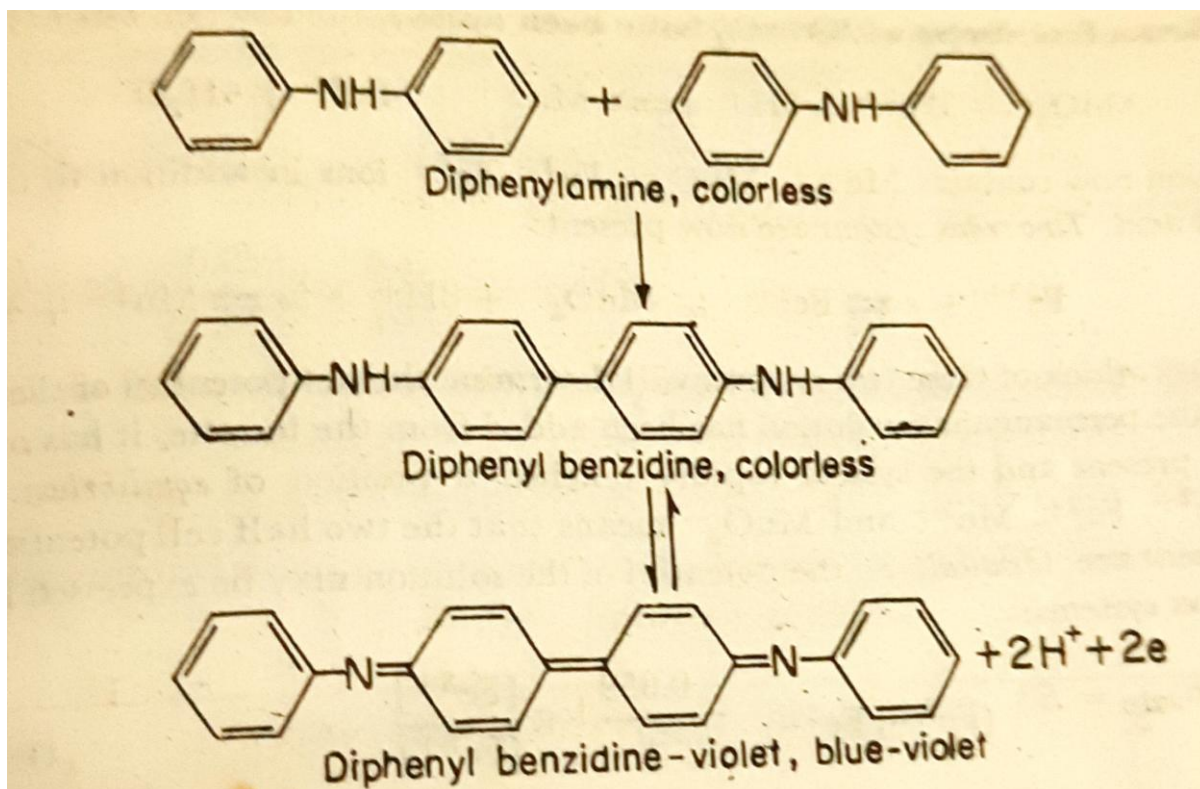


Fig.1. Structures of Diphenylamine, Diphenyl benzidine and Diphenyl benzidine-violet.

For practical purposes, the standard potential of an indicator should be intermediate between that of the solution titrated (titrate) and the titrant.

It should be noted that because of very poor solubility of diphenylamine in water, for practical purpose a water soluble form of diphenylamine, here, barium salt diphenylamine sulphonic acid (BDS) (Fig. 2) has been used. It should also be noted that due to incorporation of an electron withdrawing sulphonic acid group, the reduction potential of this indicator has been increased to + 0.86 V.

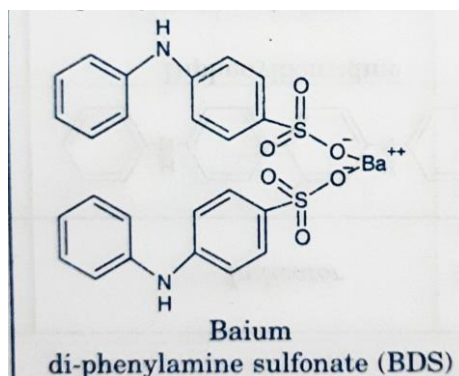


Fig. 2. Structure of Barium diphenylamine sulphonate (BDS) indicator.

Variation of potential during a red-ox titration:

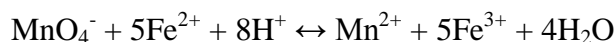
The actual situation in a red-ox titration is further complicated by the gradual change of potential of the titration system as the titration proceeds. This is not unwarranted; as the titration proceeds, the amounts of oxidant and reductant in the system change continuously, and so also the potential. Let us illustrate the situation with the titration of Fe^{2+} ion by permanganate solution in 1 M acid medium.

(a) Potential before the addition of any permanganate: Before the addition of permanganate, the solution in the conical flask contains only Fe^{2+} ion. The potential of the system will be given by that for a $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple:

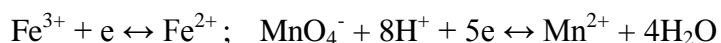
$$E = E^0 + (0.059/1) \log([\text{Fe}^{3+}]/[\text{Fe}^{2+}])$$

One should not consider $[\text{Fe}^{3+}]$ to be exactly zero; traces of impurities are sufficient to make it non zero. The potential is of course very small at the start.

(b) Potential when a few drops KMnO_4 have been added: When a few drops of KMnO_4 have been added, the reaction occurs in the medium:



The solution now contains Mn^{2+} , MnO_4^- , Fe^{2+} , Fe^{3+} ions in addition to the ions furnished by water and acid. Following two red-ox systems are now present in the solution:



One may ask which of these two systems will determine the net potential of the solution. Actually, as soon as the permanganate solution has been added from the burette, it has oxidised some of the Fe^{2+} ion present and the system rapidly reached *equilibrium*. Now equilibrium between Fe^{2+} , Fe^{3+} , Mn^{2+} and MnO_4^- means that the two half cell potentials for the two red-ox systems present are *identical*. So, the potential of the solution may be expressed in terms of either of the two red-ox systems:

$$\begin{aligned} E_{\text{soln}} &= E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} + (0.059/1) \log([\text{Fe}^{3+}]/[\text{Fe}^{2+}]) \\ &= E^0_{\text{MnO}_4^-/\text{Mn}^{2+}} + (0.059/5) \log([\text{MnO}_4^-][\text{H}^+]^8/[\text{Mn}^{2+}]) \\ &= E^0_{\text{MnO}_4^-/\text{Mn}^{2+}} + (0.059/5) \log([\text{MnO}_4^-]/[\text{Mn}^{2+}]) \quad [\text{since } [\text{H}^+] = 1 \text{ in 1 M acid}] \end{aligned}$$

The potential of the solution at any intermediate point of titration may be easily calculated from the expressions given above. As an example, we calculate the potential at a point when 90 ml of 0.1 (N) KMnO_4 has been added to 100 ml of 0.1 (N) FeSO_4 solution in 1 M acid medium at 25 °C.

$$E = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + (0.059/1) \log([\text{Fe}^{3+}]/[\text{Fe}^{2+}])$$

$$= + 0.77 + 0.059 \log(90/10) = + 0.83 \text{ V.}$$

(c) At the equivalence point: At the equivalence point, traces of Fe^{2+} will still exist as determined by the equilibrium and an exactly equivalent amount of MnO_4^- will also remain unreacted. Remembering that the mole ratios of Fe^{2+} and MnO_4^- ions in the reaction are 5:1, we shall have at equivalence point,

$$[\text{Fe}^{2+}] = 5[\text{MnO}_4^-]$$

The ratio of Fe^{3+} and Mn^{2+} ions formed will also be in the same ratio, i.e., $[\text{Fe}^{3+}] = 5[\text{Mn}^{2+}]$.

$$\text{So, we have } [\text{Fe}^{2+}]/[\text{Fe}^{3+}] = [\text{MnO}_4^-]/[\text{Mn}^{2+}]; \text{ or, } ([\text{Fe}^{3+}][\text{MnO}_4^-])/([\text{Fe}^{2+}][\text{Mn}^{2+}]) = 1$$

If E_{eq} is the potential at the equivalence point, we may write:

$$E_{\text{eq}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + (0.059/1) \log([\text{Fe}^{3+}]/[\text{Fe}^{2+}])$$

$$\text{and } E_{\text{eq}} = E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 + (0.059/5) \log([\text{MnO}_4^-]/[\text{Mn}^{2+}])$$

$$\text{or, } 5E_{\text{eq}} = 5E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 + 0.059 \log([\text{MnO}_4^-]/[\text{Mn}^{2+}])$$

$$\text{Adding, } 6E_{\text{eq}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + 5E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 + 0.059 \log([\text{Fe}^{3+}][\text{MnO}_4^-])/([\text{Fe}^{2+}][\text{Mn}^{2+}])$$

$$= E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + 5E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 \quad (\text{as } \log 1 = 0)$$

$$= 0.77 + 5 \times 1.52 = + 8.37 \text{ V}$$

$$\text{Or, } E_{\text{eq}} = + 8.37/6 \text{ V} = + 1.395 \text{ V}$$

(d) After the equivalence point: When an excess of permanganate, say 100.1 ml has been added to the above Fe^{2+} solution, the potential may be found out by the alternative expression:

$$E = E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 + (0.059/5) \log([\text{MnO}_4^-]/[\text{Mn}^{2+}])$$

$$= 1.52 + (0.059/5) \log(0.1/100) = \mathbf{1.48 \text{ V}}$$

The values of potential for different amounts of KMnO_4 solution added in the above titration are listed in Table 1.

Table 1. Variation of potential during the titration of a 100 ml (N/10) FeSO_4 solution by (N/10) KMnO_4 solution at 25 °C.

(N/10) KMnO_4 added (ml)	$[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$	$[\text{MnO}_4^-]/[\text{Mn}^{2+}]$	E (V)
50.0	50:50	-	+ 0.77
90.0	90:10	-	+ 0.83
99.0	99:1	-	+ 0.89
99.9	99.9:0.1	-	+ 0.95
100.0	-	-	+ 1.395
100.1	-	0.1:100	+ 1.47
101.0	-	1:100	+ 1.49
110	-	10:100	+ 1.50

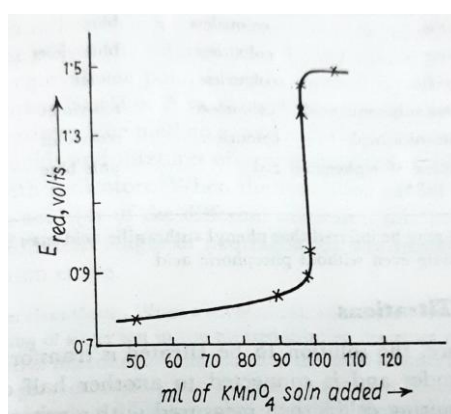


Fig. 1. Variation of potential during the titration of 100 ml (N/10) FeSO_4 solution by (N/10) KMnO_4 solution at 25 °C.

When these potentials are plotted against the volume of KMnO_4 solution added (in this case this is also the percentage of Fe^{2+} ion neutralised up to the equivalence point) a curve is obtained as shown in Fig. 1.

From the graph it is seen that there occurs a sudden rise of potential from 0.95 V for 99.9% Fe^{2+} oxidised to 1.47 V for addition of only 0.1 ml of excess KMnO_4 solution. In all red-ox titrations, there occurs such an abrupt change in potential around the equivalence point; the actual extent of this abruptness depends however on the respective potentials of the oxidant and reductant.

The nature of the curve is independent of dilution in the case discussed; but in other cases dilution may be a factor, as in the titration of Fe^{2+} ion by $\text{Cr}_2\text{O}_7^{2-}$ solution. One $\text{Cr}_2\text{O}_7^{2-}$ ion gives two Cr^{3+} ions on reduction and the potential at 1M acid solution is:

$$E = E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^0 + 0.059/6 \log([\text{Cr}_2\text{O}_7^{2-}]/[\text{Cr}^{3+}]^2)$$

If the volume is changed, the ratio of $[\text{Cr}_2\text{O}_7^{2-}]/[\text{Cr}^{3+}]^2$ changes due to the square term.

Precipitation, complex formation, pH etc. which alter the concentration of any species maintaining equilibrium will obviously change the nature of the titration curve.

7th lecture

Choice of red-ox indicator:

The choice of a red-ox indicator suitable for a particular titration should be made with reference to the titration curve (or the potential change data). It is desirable that the indicator should be oxidised as close to the equivalence point as possible, neither too early, nor too late. So the potential of the indicator, rather the range of its potential for detectable colour change, should lie within the limits of the sharp change of potential in the titration curve.

In the titration of Fe^{2+} by MnO_4^- , as shown above, the potential is + 0.77 V when only 50% of the Fe^{2+} has been oxidised. If one were to use an indicator, diphenylamine would not be the right indicator as it starts changing its colour appreciably from + 0.73 V. Diphenylamine would not be right indicator in the titration of Fe^{2+} by $\text{Cr}_2\text{O}_7^{2-}$ too, as in this case also the break in the titration curve corresponds to + 0.94 V to + 1.30 V. However, in presence of H_3PO_4 (or F^- ion), the Fe^{3+} formed is complexed and hence the potential cannot rise above + 0.71 V even when 99% of the Fe^{2+} has been oxidised. The potential crosses + 0.73 V only when “all” of the Fe^{2+} has been oxidised and the equivalence point is indicated without almost any error. A few red-ox indicators with their characteristic E^0 values are given below in Table 2.

Table 2. A few common red-ox indicators

Indicator	Colour in reduced form	Colour in oxidised form	E^0 (V) at pH = 0
Methylene blue	colourless	blue	+ 0.52
Diphenyl amine	colourless	blue-violet	+ 0.76
Diphenylbenzidine	colourless	violet	+ 0.76
Diphenyl amine sulphonic acid	colourless	red-violet	+ 0.86
N-phenylanthranilic acid	colourless	red-violet	+ 0.89
Ferroin (Fe^{2+} - o-phenanthroline complex)	red	pale blue	+ 1.06

From the Table 2, it may be inferred that N-phenylanthranilic acid may be used in the titration of Fe^{2+} ion by $\text{K}_2\text{Cr}_2\text{O}_7$ even without H_3PO_4 .

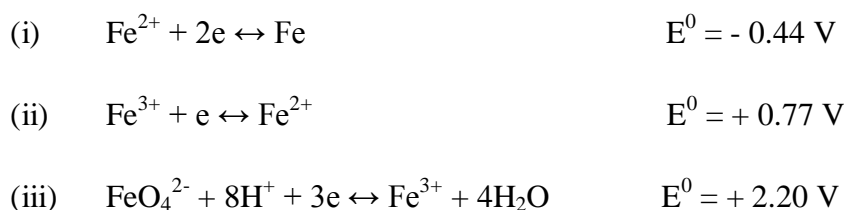
Internal red-ox indicator: The compound, added to the titrating solution which indicates the equivalence point by changing its colour very close to the equivalence point. For example, Barium diphenylamine sulphonate which is used in the titration of Fe^{2+} by $\text{K}_2\text{Cr}_2\text{O}_7$. Such compounds are considered as *internal red-ox indicators*.

External red-ox indicator: Alternatively, the equivalence point in a red-ox titration may also be located by means of an *external red-ox indicator*. This is not added to the titrating system, but is used externally. As an example, the titration of Fe^{2+} with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution may be carried out by using $\text{K}_3[\text{Fe}(\text{CN})_6]$ as external indicator. Near the equivalence point, drops of solution are removed from time to time and treated with freshly prepared solution of this indicator on a spot plate. When the drop first fails to produce a blue colour with the indicator, the end point of the titration is marked. External indicators have now been largely superseded by satisfactory internal indicators (e.g., 1,10-phenanthroline in this case).

Redox potential diagram (Latimer and Frost diagrams) of common elements and their applications:

Latimer diagram:

The relative stabilities of various oxidation states of an element are revealed by the relevant electrode potential data. Let us consider the electrode potential data of iron as an example:



The values show that $\text{FeO}_4^{2-} - \text{Fe}^{3+}$ system has the highest reduction potential value, suggesting that FeO_4^{2-} species will be strongly oxidising in nature (thereby getting reduced to Fe^{3+}). On the other hand, the standard reduction potential of $\text{Fe}^{3+} - \text{Fe}^{2+}$ system is appreciably lower than $\text{FeO}_4^{2-} - \text{Fe}^{3+}$ couple, which indicates that Fe^{2+} will be more readily oxidised to Fe^{3+} . So, Fe^{2+} will be good reducing agent. It should be noted that the standard reduction potential of $\text{Fe}^{3+} - \text{Fe}^{2+}$ couple is higher than $\text{H}^+ - \frac{1}{2}\text{H}_2(\text{g})$ couple, consequently Fe^{2+} ion

cannot reduce H^+ ion from aqueous solution. Similarly, the E^0 value for $\text{Fe}^{2+} - \text{Fe}$ couple suggests that Fe^{2+} species is a fairly stable species in aqueous solution (in absence of oxygen or other oxidising agents) and has no tendency to get reduced to Fe.

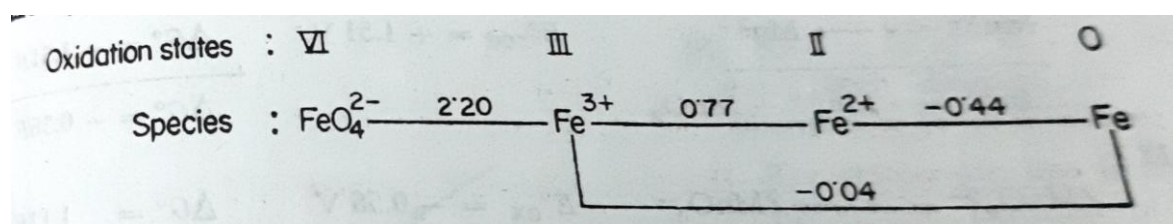
We have not considered the potential for $\text{Fe}^{3+} - \text{Fe}$ couple. The E^0_{red} for this couple is - 0.04 V; this appears anomalous at first in view of the $\text{Fe}^{2+} - \text{Fe}$ and $\text{Fe}^{3+} - \text{Fe}^{2+}$ potentials. It should be noted that in such cases, the potentials are *not additive*. It is necessary to consider the actual change in free energy according to the relation $\Delta G = - nFE$. Thus,



Adding, the total ΔG for the reaction $\text{Fe}^{3+} + 3e \rightarrow \text{Fe}$ is obtained as + 0.11F.

From the relation $\Delta G = - nFE$, $E^0(\text{Fe}^{3+}, \text{Fe}) = \Delta G / -nF = + 0.11F / (-3F) = - 0.04 \text{ V}$.

The information listed above may be summarily expressed by the following reduction potential diagram, known as **Latimer diagram**:



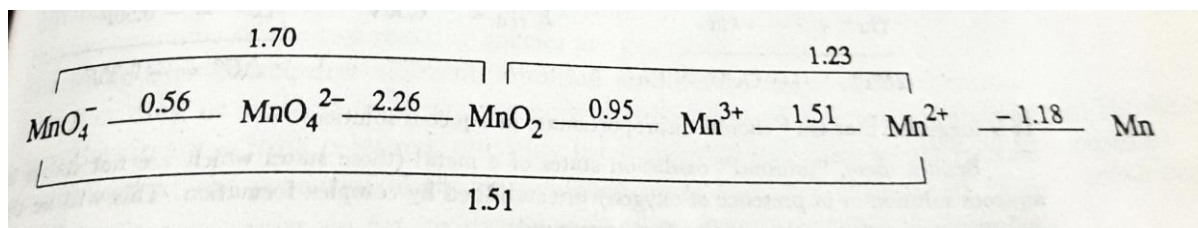
A **Latimer diagram** of a chemical element is a summary of the standard electrode potential data of that element. This type of **diagram** is named after Wendell Mitchell **Latimer**, an American chemist.

From this set of electrode potential data, a few broad generalisations may be made as follows:

In aqueous solutions, systems with negative values of E^0_{red} are more strongly *reducing* than hydrogen (e.g., Fe) while systems with positive values of E^0_{red} are more strongly *oxidising* than hydrogen (e.g., Fe^{3+} in the $\text{Fe}^{3+} - \text{Fe}^{2+}$ couple). Only the Fe^{3+} is therefore reduced by hydrogen (FeCl_3).

8th lecture

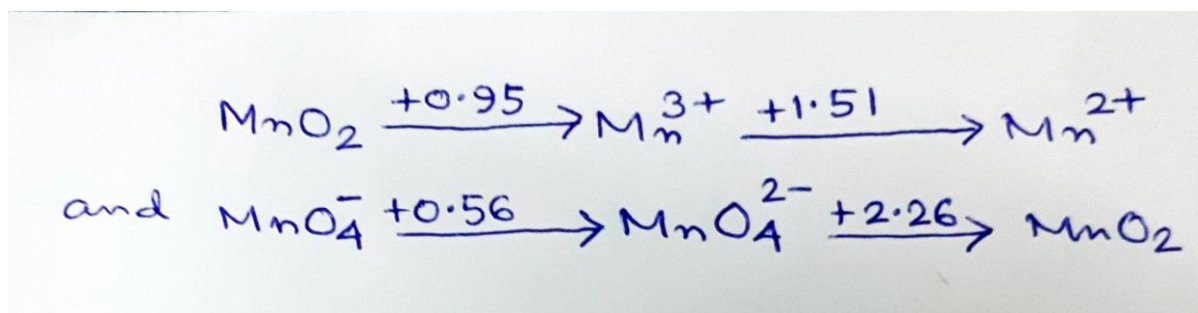
The manganese system:



The diagram shows that (i) Mn^0 will be readily oxidised to Mn^{2+} ; (ii) Mn^{3+} will be readily reduced to Mn^{2+} ; (iii) MnO_4^{2-} will be readily reduced to MnO_2 ; (iv) MnO_2 will be readily reduced to Mn^{2+} ; (v) MnO_4^- will be reduced rather to MnO_2 or Mn^{2+} than to MnO_4^{2-} .

In other words, Mn^{3+} , MnO_2 , MnO_4^{2-} and MnO_4^- - all will behave as strong oxidising agent.

Another interesting feature of the diagram is the sharp gradual decrease in E° in the two triad systems:



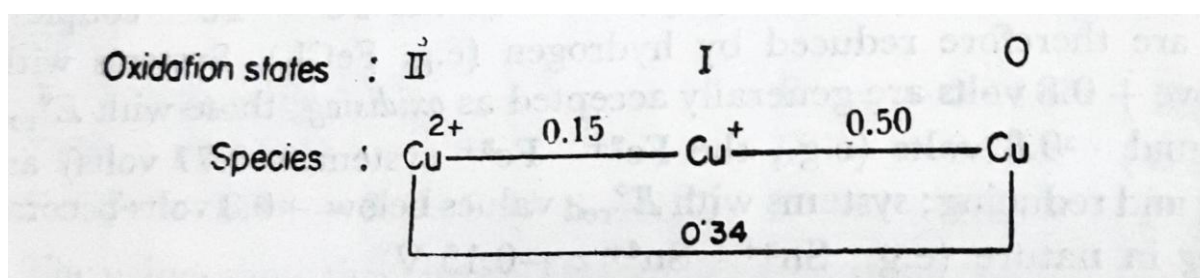
Whenever such a situation occurs, the intermediate species in each case acts itself as a self-oxidising and self-reducing agent; it is said to **disproportionate** which results in a net decrease of free energy.

Case I		
$\text{Mn}^{3+} - e \longrightarrow \text{MnO}_2$	$E^\circ_{\text{ox}} = -0.95 \text{ V}$	$\Delta G^\circ = 0.95F$
$\text{Mn}^{3+} + e \longrightarrow \text{Mn}^{2+}$	$E^\circ_{\text{red}} = +1.51 \text{ V}$	$\Delta G^\circ = -1.51F$
<hr/>		
$2\text{Mn}^{3+} \longrightarrow \text{Mn}^{2+} + \text{MnO}_2$		$\Delta G^\circ = -0.56F$
Case II		
$2\text{MnO}_4^{2-} - 2e \longrightarrow 2\text{MnO}_4^-$	$E^\circ_{\text{ox}} = -0.56 \text{ V}$	$\Delta G^\circ = 1.12F$
$\text{MnO}_4^{2-} + 2e \longrightarrow \text{MnO}_2$	$E^\circ_{\text{red}} = +2.26 \text{ V}$	$\Delta G^\circ = -4.52F$
<hr/>		
$3\text{MnO}_4^{2-} \longrightarrow \text{MnO}_2 + 2\text{MnO}_4^-$		$\Delta G^\circ = -3.40F$

$$\log_{10}K = (0.56 \text{ V} \times 96500 \text{ C mol}^{-1}) / (2.303 \times 8.314 \text{ J } ^\circ\text{K}^{-1} \text{ mol}^{-1} \times 298 \text{ K})$$

$$\text{or, } K = 10^{9.5} = 3.2 \times 10^9$$

The Copper system:


$$\begin{array}{rcl}
 \text{Cu}^+ - e \longrightarrow \text{Cu}^{2+} & E^\circ_{\text{ox}} = -0.15\text{V} & \Delta G^\circ = 0.15F \\
 \text{Cu}^+ + e \longrightarrow \text{Cu} & E^\circ_{\text{red}} = 0.50\text{V} & \Delta G^\circ = -0.50F \\
 \hline
 2\text{Cu}^+ \longrightarrow \text{Cu}^{2+} + \text{Cu} & & \Delta G^\circ = -0.35F
 \end{array}$$

Frost diagram:

$$M^{n+} + ne \leftrightarrow M^0$$

2

whereas **Frost diagram** summarizes the relative stability of different oxidation states of a substance. The diagram for manganese is shown in Fig. 1 where nE^0 ($= -\Delta G^0/F$) has been plotted against the oxidation state n . The points in the graph may be calculated from the known red-ox data, for example:

$$\begin{aligned}
 n=2 : E^0(\text{Mn}^{2+}, \text{Mn}) &= -1.18 \text{ V}; 2E^0 = -2.36 \text{ V} \\
 n=3 : E^0(\text{Mn}^{3+}, \text{Mn}^{2+}) &= 1.51 \text{ V}; E^0(\text{Mn}^{2+}, \text{Mn}) = -1.18 \text{ V}. \\
 \therefore \Delta G^0/F &= (2 \times 1.18 - 1.51) \text{ V or } 3E^0 = -0.85 \text{ V}. \\
 n=4 : E^0(\text{MnO}_2, \text{Mn}^{3+}) &= 0.95 \text{ V}; 3E^0(\text{Mn}^{3+}, \text{Mn}) = -0.85 \text{ V}. \\
 \therefore (\Delta G^0/F) &= (-0.95 + 0.85) \text{ V}; 4E^0(\text{MnO}_2, \text{Mn}) = 0.10 \text{ V}.
 \end{aligned}$$

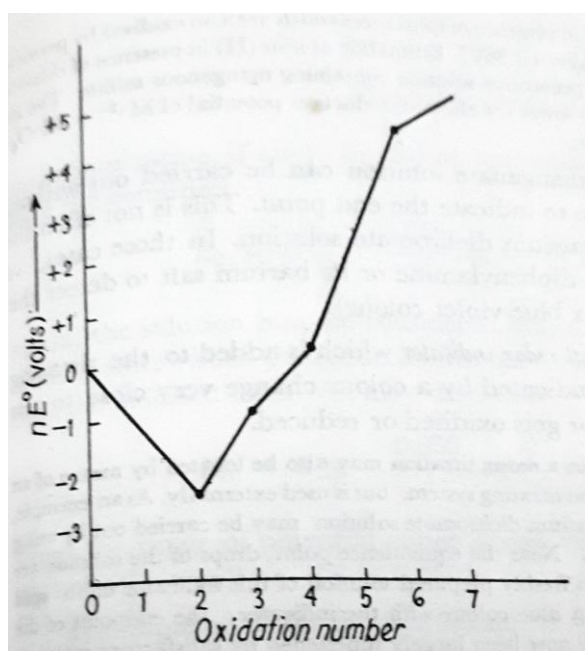


Fig.1. Plot of nE^0 vs n for Mn (n = oxidation state) (Frost diagram of Mn).

Following conclusions can be drawn from the Fig. 1:

- (i) The steeper the line joining two points, the higher the potential of the corresponding couple.
- (ii) A state is unstable with respect to disproportionation if it lies above the line connecting two adjacent oxidation states.

Thus, (a) Mn^{3+} is likely to disproportionate to Mn^{2+} and MnO_2 . Since both these products involve one electron transfer, the process is likely to be rapid.

(b) The point for Mn(VI) similarly suggests disproportionation to Mn(VII) and Mn(IV).

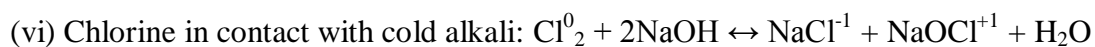
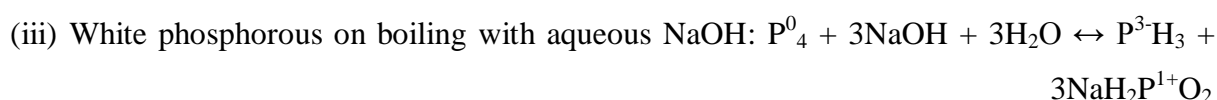
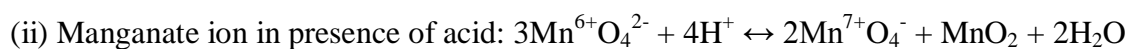
(c) MnO_2 is also a strong oxidising agent – its slope to Mn^{2+} is greater than the slopes to higher oxidation states. Most species that reduce MnO_4^- should also reduce MnO_2 .

(d) The minimum at Mn^{2+} suggests this to be the common product of reduction of MnO_4^- in acidic solution.

9th lecture

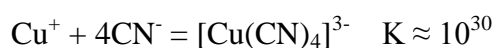
Disproportionation reaction:

The reaction in which an element with its particular oxidation state is converted into two oxidation states, one higher and another lower than its oxidation state in the reactant, is known as *disproportionation reaction*. A part of the reactant is oxidised while another part of it gets reduced and the two processes take place to equivalent extent. Few examples of such reactions are given below:



In basic solution the hypochlorite ion tends to disproportionate further as $3\text{OCl}^{-1} \leftrightarrow 2\text{Cl}^{-1} + \text{Cl}^{5+}\text{O}_3^-$. The equilibrium constant for this reaction is very high (10^{27}), but the rate is very low at room temperature. Around 75 °C and higher, the rate becomes high and chlorate is the main product.

The position of equilibrium in a disproportionation reaction may be altered by removal of reactants or products in the usual manner, e.g., neutralisation, precipitation, complex formation etc. For the disproportionation of Cu^+ in aqueous solution (reaction i), the equilibrium constant is of the order of 10^6 . In the presence of Cl^- ions, CuCl is precipitated (solubility product $\approx 10^{-7}$) and the concentration of Cu^+ ion is significantly lowered. Disproportionation is checked to cause a corresponding decrease in the concentration of Cu^{2+} ion (to maintain the equilibrium constant). Similarly, addition of CN^- ions reduces the concentration of Cu^+ ions by forming the very stable $[\text{Cu}(\text{CN})_4]^{3-}$ ion:

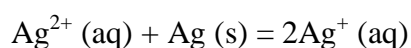


Accordingly, disproportionation is almost checked.

Disproportionation reactions involving H^+ ions are similarly influenced by the H^+ ion concentration of the medium. The disproportionation of manganate ion (reaction ii) is an example. The equilibrium constant is of the order of 10^{58} and disproportionation occurs in acid, neutral or even slightly basic solutions. It can be shown that manganate ions may exist only in strongly alkaline solutions ($pH \sim 14$).

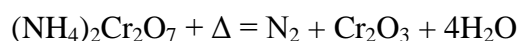
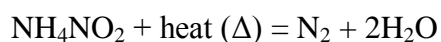
Comproportionation reaction:

Comproportionation reaction is a chemical reaction where two reactants, each containing the same element but with a different oxidation number, form a product in which the elements involved reach the same oxidation number. It is the reverse of disproportionation reaction. An example for such reaction is given below:



The E^0 value for the Ag^{2+}/Ag^+ couple is + 1.98 V while the E^0 value for the Ag^+/Ag^0 couple is + 0.80 V. So, the E^0 value of the above comproportionation reaction is +1.18 V, which is largely positive suggesting that the forward reaction will be highly favoured thermodynamically.

Decomposition of NH_4NO_2 and $(NH_4)_2Cr_2O_7$ are also examples of comproportionation reaction in which both the oxidising as well as reducing agents are present in the same molecule.



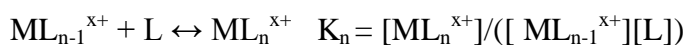
Stability constants of complexes:

The formation of a complex from an aquated metal ion in aqueous solution may be considered to take place stepwise; with a neutral unidentate ligand L, this may be represented as (the water molecules are not shown for simplicity):

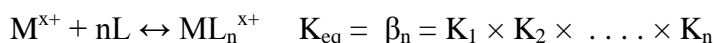




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K_1, K_2, \dots, K_n are the *stepwise* (or consecutive) *formation constants* expressed in terms of concentration. The product of the stepwise stability constants gives the cumulative or *overall stability constant* β_n :

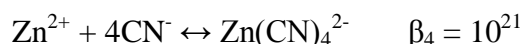


The effect of stability constants of complexes on the red-ox potential of a system may be understood from the following examples:

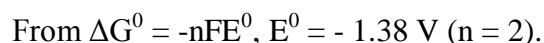
Example 1: The overall stability constant for $Zn(CN)_4^{2-}$ is 10^{21} . Calculate E^0 for the process:



Solutions: We have



We combine these reactions to suit our purpose:



Note: In a solution, initially containing C_1 molar Zn^{2+} and C_2 molar CN^- ions ($C_2 \gg C_1$), the equilibrium concentration of Zn^{2+} will be very small, as seen from the high value of the formation constant. So, the equilibrium concentration of $Zn(CN)_4^{2-}$ may be taken as nearly C_1 , while that of the CN^- ion will be $(C_2 - 4C_1)$. Hence the formal reduction potential of the system at 25 °C will be approximately given by

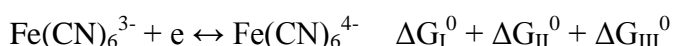
$$E = E^0 + (0.059/2) \log ([Zn(CN)_4^{2-}]/[CN^-]^4) = -1.38 + (0.059/2) \log [C_1/(C_2 - 4C_1)^4]$$

Example 2: Predict whether $[\text{Fe}(\text{CN})_6]^{3-}$ will be a stronger or weaker oxidising agent in comparison to Fe^{3+} (aq). Given $E^0 (\text{Fe}^{3+} - \text{Fe}^{2+}) = 0.77 \text{ V}$; $\log\beta_6$ of $[\text{Fe}(\text{CN})_6]^{3-} = 31.0$ and of $[\text{Fe}(\text{CN})_6]^{4-} = 24.0$.

Solution: we have to compare the standard reduction potentials for the half reactions:



We arrange the equilibrium processes of known E^0 / K_{eq} to arrive at this half-reaction:



The standard reduction potential for the overall process, E_1^0 , is related to the overall ΔG^0 as $\Delta G^0 = -FE_1^0$ and $\Delta G^0 = \Delta G_I^0 + \Delta G_{\text{II}}^0 + \Delta G_{\text{III}}^0$

$$\text{So, } -FE_1^0 = -0.77F - 2.303RT \times \log\beta_6 (\text{Fe}^{2+}) + 2.303RT \times \log\beta_6 (\text{Fe}^{3+})$$

$$= -0.77F - 2.303 \times 24RT + 2.303 \times 31RT$$

$$\text{Or, } E_1^0 = (0.77 + 0.059 \times 24 - 0.059 \times 31) \text{ V} = 0.36 \text{ V}$$

So, the standard reduction potential for $\text{Fe}^{3+} - \text{Fe}^{2+}$ system decreases significantly from the aqua species to the cyano complex (as the cyano complex of Fe^{3+} has a much higher stability than of Fe^{2+}). Hence, the oxidising power of Fe^{3+} decreases.

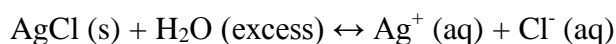
However, exceptions arise when the complex in lower oxidation state is more stable than in the higher oxidation state, as for example, for the tris (o-phenanthroline) complex of iron (o-phenanthroline is a bidentate ligand). $\log\beta_3 = 21.3$ for Fe^{2+} and 14.1 for Fe^{3+} . E^0 for the couple $\text{Fe}(\text{phen})_3^{3+} / \text{Fe}(\text{phen})_3^{2+}$ rises to $\sim 1.20 \text{ V}$ (vs 0.77 V for the aqua ions).

10th lecture

Sparingly soluble salts:

Salts having solubilities less than about 0.01 mol/dm^3 in water at ordinary temperature may be called sparingly soluble. AgCl (solubility = $1.2 \times 10^{-5} \text{ mol/dm}^3$) is an example of sparingly soluble salt.

When excess of a sparingly soluble salt is shaken up with water, part of the salt passes into solution to make it saturated at that temperature. It appears that the process of dissociation has stopped. Actually a dynamic equilibrium is established between the solid salt and the ions furnished by it in solution. Taking the example of AgCl , this may be represented, *assuming complete ionisation of AgCl in solution*, as



or conventionally as, $\text{AgCl (s)} \leftrightarrow \text{Ag}^+ + \text{Cl}^-$

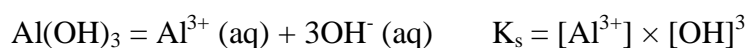
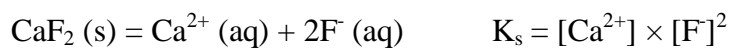
hydration being implied. At equilibrium, the rates of the forward and the backward processes become equal. Application of the law of mass action to such systems leads to the solubility product principle which is of great significance in qualitative and quantitative analysis.

Solubility product:

It was found experimentally that in saturated solutions of sparingly soluble salts, the product of the total molecular concentrations of the ions is a constant at a constant temperature. This observation was incorporated by Nernst in the **solubility product principle** (1889). This principle states that, *in a saturated solution of a sparingly soluble electrolyte, the product of the concentrations of the constituent ions is constant at a given temperature, the ion concentrations being raised to powers equal to the respective numbers of ions of each kind furnished by one molecule of the electrolyte on complete dissociation.*

Thus, for an electrolyte A_xB_y , ionising as $\text{A}_x\text{B}_y \leftrightarrow x\text{A}^+ + y\text{B}^-$, the solubility product principle states: $[\text{A}^+]^x \times [\text{B}^-]^y = \text{constant}$ at a constant temperature.

This product of the total molecular concentrations of the ions in a saturated solution of a sparingly soluble salt is termed the **solubility product** of the salt; it is often denoted by K_s . The solubility of CaF_2 and Al(OH)_3 may be taken as examples:



Solubility products of a few common sparingly soluble salts are given in Table 1.

Table 1. Solubility products at 25 °C

PbCl ₂	1.6×10^{-5}	CaC ₂ O ₄	2.1×10^{-9}
AgCl	1.0×10^{-10}	SrSO ₄	7.6×10^{-7}
AgBr	5.2×10^{-13}	BaSO ₄	1.0×10^{-10}
Mg(OH) ₂	1.1×10^{-11}	NiS	2.0×10^{-21}
Zn(OH) ₂	7.0×10^{-18}	ZnS	3.0×10^{-22}
Al(OH) ₃	2.0×10^{-32}	CdS	7.0×10^{-27}
Fe(OH) ₃	6.0×10^{-38}	CuS	8.0×10^{-36}
CaF ₂	4.9×10^{-11}	HgS	3.0×10^{-52}

The solubility product principle follows readily from an application of the law of mass action to the equilibrium established by a sparingly soluble salt in contact with its saturated solution. For simplicity, let us consider a binary electrolyte AB, ionising in solution completely to give A⁺ and B⁻ ions: AB (solid) ↔ A⁺ + B⁻

By applying the law of mass action in terms of activities (a) of respective species,

$$K_{\text{eq}} = (a_{\text{A}^{+}} \times a_{\text{B}^{-}})/a_{\text{AB}}$$

The activity of solid AB, a_{AB}, may be taken as unity since it is the pure component. So one obtains: $K_{\text{eq}} = a_{\text{A}^{+}} \times a_{\text{B}^{-}}$.

Since the solution is extremely dilute, one may reasonably replace activities by concentrations: $[\text{A}^{+}] \times [\text{B}^{-}] = \text{constant} = K_s$

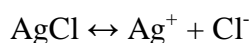
The product $a_{A^+} \times a_{B^-}$ is called the **activity solubility product** of AB which may be represented as K_s^a . It is the actual solubility product of thermodynamic significance.

Solubility products may be evaluated from the saturation solubilities of salts in pure water. The solubilities, in turn, may be obtained by direct analysis of the saturated solutions or by conductance measurements if the ion conductances (at infinite dilution) of the constituent ions of the salt are known. If Λ_0 is the equivalent conductance of an electrolyte (obtained from the individual ion conductances) and κ is its measured specific conductance in the saturated solution containing s gm-equivalents per dm^3 , then the solubility s is obtained in gm-equivalents per dm^3 from the relation:

$$\Lambda_0 = 1000 \times \kappa / s$$

Solubility products may also be obtained from the measurement of EMF of suitably devised cells.

Example 1: The solubility of AgCl is 0.0015 g/dm^3 . Calculate its solubility product.



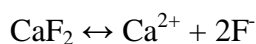
1 mol of AgCl dissolves to give 1 mol each of Ag^+ and Cl^- ions. So, solubility of AgCl in mol/dm^3 is obtained by dividing the gram-solubility by its molecular weight 143.5.

$$\text{Solubility} = 0.0015/143.5 = 1.05 \times 10^{-5} \text{ mol/dm}^3$$

$$\text{So, } [\text{Ag}^+] = [\text{Cl}^-] = 1.05 \times 10^{-5} \text{ mol/dm}^3$$

$$\text{Or, } K_s = [\text{Ag}^+] \times [\text{Cl}^-] = (1.05 \times 10^{-5})^2 = 1.1 \times 10^{-10}.$$

Example 2: The solubility product of CaF_2 is 4.9×10^{-11} . Calculate its solubility in pure water neglecting hydrolysis by the F^- ion.



For each mole of CaF_2 dissolved, we have 1 mol of Ca^{2+} ion and 2 moles of F^- ions. Let S be the solubility of CaF_2 in mol/dm^3 . Then,

$$[\text{Ca}^{2+}] = S \text{ mol/dm}^3; [\text{F}^-] = 2S \text{ mol/dm}^3$$

$$\text{Therefore, } K_s = [\text{Ca}^{2+}] \times [\text{F}^-]^2 = S \times (2S)^2 = 4S^3$$

$$\text{So, } 4S^3 = 4.9 \times 10^{-11}; \text{ or, } S = 2.3 \times 10^{-4} \text{ mol/dm}^3$$

Therefore, the solubility of CaF_2 in pure water is $2.3 \times 10^{-4} \text{ M}$.

(The solubility in gram may be obtained by multiplying this value with the molecular weight).

11th lecture

The Common Ion Effect: The constancy of the solubility product at a given temperature implies that if we change the concentration of an ion (in the saturated solution of the sparingly soluble salt), the concentration of the other ion will adjust itself to maintain the constancy of the solubility product. For example, let us take a saturated solution of AgCl. We may increase the concentration of Cl^- ion by adding say, NaCl (or any electrolyte having a common anion). If this is done, the concentration of Ag^+ ion will decrease to maintain the product $[\text{Ag}^+] \times [\text{Cl}^-]$ constant (K_s) at that temperature. This will result in a displacement of the equilibrium towards left, i.e. some Ag^+ ion will combine with Cl^- ions to precipitate AgCl. Similarly, when solid AgCl is shaken with a solution of NaCl, a very small amount of it will pass into solution which is just sufficient to maintain the constancy of the solubility product. Thus the effect of an electrolyte giving common ions in solution as those of the sparingly soluble salt is to diminish its solubility than in pure water.

The effect of common ion in lowering the solubility of a sparingly salt is in agreement with the Le Chatelier's principle. The addition of, say, NaCl to a saturated solution of AgCl in water is a "stress" applied to the equilibrium maintained by the solubility of AgCl. With the addition of Cl^- ions from NaCl, the system tends to adjust itself by way of diminishing the concentration of Cl^- ion. This results in the precipitation of solid AgCl, lowering its solubility.

Let us illustrate this point further with a few typical examples:

Problem 1: What will be the solubility of AgCl in a solution 0.1 M with respect to NaCl? ($K_s = 1.0 \times 10^{-10}$).

Solution: Let the solubility be equal to $x \text{ mol/dm}^3$. $x \text{ mol}$ of AgCl furnishes $x \text{ mol}$ of Ag^+ and $x \text{ mol}$ of Cl^- ions. But the solution contains additional Cl^- ions from the NaCl. As this is a strong electrolyte, the concentration of Cl^- ions from this is 0.1 mol/dm^3 .

So, the total concentration of Cl^- ions in solution: $[\text{Cl}^-] = x + 0.1$

Concentration of Ag^+ , i.e., $[\text{Ag}^+] = x$

Therefore, $K_s = 1.0 \times 10^{-10} = [\text{Ag}^+] \times [\text{Cl}^-] = x \times (x + 0.1)$

Remembering that x is very small in comparison to 0.1, we may avoid the quadratic equation.

Therefore, $K_s = x \times 0.1 = 1.0 \times 10^{-10}$; so, $x = 10^{-9}$

Hence, the solubility of AgCl in a 0.1 M solution of NaCl would be 10^{-9} mol/dm³.

[It should be remembered that in pure water, $K_s = 1.0 \times 10^{-10} = S^2$, where S is the solubility. This gives $S = 10^{-5}$ mol/dm³. Hence $[Ag^+]$ in pure water is 10^{-5} mol/dm³. In presence of NaCl, $[Ag^+]$ must be still less.]

Problem 2: Calculate the solubility of CaF₂ in a solution of 0.1 M Ca(NO₃)₂ salt. $K_s = 4.9 \times 10^{-11}$.

Solution: Let the solubility of CaF₂ be x mol/dm³. Since each mol of CaF₂ supplies 2 moles of F⁻ ion in solution, the concentration of F⁻ ion, $[F^-] = 2x$ mol/dm³.

The total concentration of Ca²⁺ ions in solution will be the sum of (i) Ca²⁺ ions from Ca(NO₃)₂, equal to 0.1 mol/dm³ and (ii) Ca²⁺ ions from CaF₂, equal to x mol/dm³.

Therefore, $[Ca^{2+}] = (0.1 + x)$ mol/dm³

By arguments similar to those applied in the above Example 1, $x \ll 0.1$ and we may effectively write $[Ca^{2+}] = 0.1$ mol/dm³.

Therefore, $K_s = 4.9 \times 10^{-11} = [Ca^{2+}] \times [F^-]^2 = 0.1 \times (2x)^2$

This gives, $x = 1.11 \times 10^{-5}$ mol/dm³.

Thus, the required solubility of CaF₂ is 1.11×10^{-5} mol/dm³.

Application of the solubility product principle:

The solubility product of a sparingly soluble salt sets a limit to the ultimate value of the product of the concentrations of its ions in solution at equilibrium at a given temperature. If the experimental conditions are such that the ionic product is different from the solubility product, the system will tend to adjust itself so as to equalise the two quantities. This has great bearing upon precipitation from solution, which is one of the principal operations of qualitative and quantitative analysis.

For any sparingly soluble salt AB, having solubility product K_s at a given temperature, the maximum concentrations of the ions, say, A^+ and B^- , capable of existing at equilibrium at this temperature is given by the relation $K_s = [A^+] \times [B^-]$.

If to a solution containing the ion A^+ at some arbitrary concentration (together with other ions), a large amount of the species B^- is added by some means, the solubility product principle indicates that *solid AB will be precipitated until the ionic product reaches the solubility product*. Using appropriate concentration of B^- ions, it is therefore possible to reduce the concentration of A^+ ion to a negligible value.

Let us consider a solution of $AgNO_3$ at some arbitrary concentration, say 0.01 M. To this solution we add, say, a solution of KCl , so that the concentration of Cl^- ion in the solution is momentarily raised to 0.1 M. The ionic product becomes $0.1 \times 0.01 = 10^{-3}$. This is greater than the solubility of $AgCl$ at this temperature ($\approx 10^{-10}$). In order to maintain equilibrium, the process $Ag^+ + Cl^- \rightarrow AgCl(s)$ will take place, causing precipitation of solid $AgCl$. The process will continue until the ionic product equals to the solubility product.

One may also start with a saturated solution of $AgCl$ and add a solution of KCl , in which case the concentration of Ag^+ ion in solution will be further reduced. On the other hand, if we take the final solutions in the above two cases after they have attained equilibrium and add aqueous ammonia solution to them, the concentration of Ag^+ ion will be greatly reduced owing to the formation of the complex $[Ag(NH_3)_2]^+$ ion. As a result, the system will tend to restore its equilibrium by the reverse process, i.e. $AgCl(s) \rightarrow Ag^+ + Cl^-$, resulting in dissolution of the precipitated $AgCl$. Using appropriate concentration of ammonia, the process may be carried until the entire precipitate dissolves.

A few points are to be remembered before we actually apply the solubility product principle to specific cases. (i) The solubility product defines a state of equilibrium. But it does not commit anything towards the rate at which the equilibrium will be attained. In practice, some time is always necessary to start precipitation, and then a further period of variable duration must elapse before precipitation is complete. (ii) Conditions of super saturation must be eliminated for effective precipitation. (iii) *Complete precipitation* of a sparingly soluble salt is not possible because a finite, though small, concentration of each type of ion must remain in solution to maintain the solubility product. (iv) The solubility product may somewhat vary depending upon the physical structure of the precipitate. The

solubility product of freshly precipitated NiS is 3×10^{-21} while on standing the precipitates attain lower solubility product, $\sim 10^{-26}$ or even less. (v) One should not consider that a *large excess* of the precipitant (say KCl in the precipitation of AgCl from AgNO₃ solution) will lead to nearly complete precipitation. A certain excess of the precipitant is certainly necessary for effective precipitation, but a very large excess may actually cause some of the precipitate to dissolve owing to very high ionic strength of the medium.

A few practical applications of the solubility product principle in qualitative analysis are described below:

(a) Precipitation of sulphides: For the precipitation of metal sulphide MS, the required condition is: $[M^{2+}] \times [S^{2-}] > K_s$ (M^{2+} is the metal ion).

In reality, there exists a wide range of solubility product (S. P.) among the metal sulphides. For example, at ordinary temperature,

$$\text{HgS} \approx 10^{-54}; \text{CuS} \approx 10^{-44}; \text{PbS} \approx 10^{-29}; \text{CdS} \approx 10^{-28}; \text{ZnS} \approx 10^{-23}; \text{MnS} \approx 10^{-15}$$

We notice that the S. P. Values of HgS and CuS are quite small while those of ZnS and MnS are relatively high. This suggests that if we can somehow control the concentrations of M^{2+} and S^{2-} ions in a solution containing the above metal ions, such that the ionic product exceeds the lower S. P. Values only, then HgS and CuS will be precipitated, while MnS and ZnS will remain in solution. The fate of Pb^{2+} and Cd^{2+} ions will also be determined by the relative magnitudes of their respective K_s and ionic products.

Next comes the question of how can we actually control the ionic products for each metal sulphide. The concentration of the metal ion cannot be made too small, because in qualitative analysis we require a sufficient amount of each precipitate for further tests. The usual concentration handled in most cases lies between 0.1 and 1 M. But we may considerably vary the concentration of sulphide ions. At 0.25 – 0.3 M HCl medium, dissociation of H₂S is largely checked by the common ion effect of H⁺ ions and $[S^{2-}]$ is approximately 10^{-22} . So, at this acid medium, only the S. P. of HgS, PbS, CuS and CdS are exceeded which are therefore precipitated. If the acid concentration be made much higher, $[S^{2-}]$ will be further reduced. CdS may not be precipitated in that situation.

Now if we want to precipitate MnS and ZnS from this solution, the concentration of S^{2-} ions must be increased. In a saturated aqueous solution of H_2S , $[S^{2-}]$ is nearly 10^{-15} . Precipitation of ZnS will start under this condition. But the acid produced in the reaction will soon suppress the dissociation of H_2S , and the precipitation will be incomplete. For complete precipitation, the concentration of H^+ ion has to be maintained at a steady low value. This can be achieved either by (i) using ammoniacal medium or by (ii) the addition of CH_3COONa . The acetate ion combines with H^+ ions forming weak CH_3COOH .

(b) Precipitation of hydroxides: The solubility products of some metal hydroxides show wide variation in range, e.g. $Fe(OH)_3: \approx 10^{-38}$; $Al(OH)_3: \approx 10^{-23}$; $Cr(OH)_3: \approx 10^{-29}$; $Mg(OH)_2: \approx 10^{-11}$

It is therefore reasonable to expect that some hydroxides may be selectively precipitated by controlling the OH^- ion concentration in solution. Obviously NaOH cannot be used as the precipitant in such case since it is a strong alkali and its dissociation is complete and irreversible. A weak alkali like an aqueous ammonia solution is used which dissociates only incompletely and reversibly. Further, the dissociation may be considerably influenced by the addition of NH_4^+ salts due to common ion effect of the NH_4^+ ion in suppressing the dissociation of NH_4OH . In fact, the presence of NH_4Cl , the OH^- ion concentration in dilute aqueous ammonia solution is so reduced that the $[OH^-]$ is just sufficient to exceed the S. P.'s of $Fe(OH)_3$, $Cr(OH)_3$ and $Al(OH)_3$, but not of $Co(OH)_2$, $Ni(OH)_2$, $Zn(OH)_2$, $Mn(OH)_2$ and $Mg(OH)_2$. So only the former three metal hydroxides are precipitated, offering a means of their separation from the others in qualitative analysis.

(c) Precipitation of carbonates: The solubility products of $CaCO_3$, $SrCO_3$ and $BaCO_3$ are all nearly 10^{-9} while that of $MgCO_3$ is $\approx 10^{-5}$. Selective precipitation of Ca^{2+} , Sr^{2+} and Ba^{2+} ions from solution in presence of Mg^{2+} ion can be done by carefully controlling the concentration of carbonate ion so that only the solubility products of the former are exceeded. Na_2CO_3 , a strong alkali, cannot be used in this case as the concentration CO_3^{2-} ion from it cannot be reversibly controlled. Instead, one uses a saturated solution of $(NH_4)_2CO_3$ in presence of NH_4Cl , when $[CO_3^{2-}]$ is just sufficient to precipitate Ca^{2+} , Sr^{2+} and Ba^{2+} ions and not Mg^{2+} ion.

Problem 3: A solution contains KCl and KI, both in 0.1 M concentration. $AgNO_3$ solution at 0.01 M concentration is added dropwise with stirring. (i) which will be precipitated first,

AgCl or AgI? (ii) what will be the concentration of I^- in solution when AgCl begins to precipitate? K_s for AgCl = 1.1×10^{-10} ; for AgI = 10^{-16} .

Solution: (i) Initially, we shall have to calculate the concentrations of Ag^+ ion necessary to start precipitation of AgCl and AgI.

For AgCl: $K_s = 1.1 \times 10^{-10}$; $[\text{Cl}^-] = 0.1 \text{ mol/dm}^3$

So, $[\text{Ag}^+] = K_s/[\text{Cl}^-] = 1.1 \times 10^{-9} \text{ mol/dm}^3$.

For AgI: $K_s = 1 \times 10^{-16}$; $[\text{I}^-] = 0.1 \text{ mol/dm}^3$

So, $[\text{Ag}^+] = K_s/[\text{I}^-] = 1 \times 10^{-15} \text{ mol/dm}^3$.

Since the concentration of Ag^+ ion necessary for the precipitation of AgI is smaller, AgI will be precipitated first.

(ii) $[\text{Ag}^+]$ necessary to start precipitation of AgCl is $1.1 \times 10^{-9} \text{ mol/dm}^3$. At this concentration of Ag^+ , the concentration of I^- at equilibrium will be

$$[\text{I}^-] = K_{\text{AgI}}/[\text{Ag}^+] = 10^{-16}/1.1 \times 10^{-9} = 9.09 \times 10^{-8} \text{ mol/dm}^3.$$

This shows that iodide ion may be separated from chloride ion almost completely by precipitation with AgNO_3 .