CHAPTER - ~~2~~ 11

EDTA Titration

Co-ordination (Complex) compound :-

Co-ordination compound is a compound formed from a Lewis acid and a Bronsted Base.

Lewis acids :-

All electron acceptors are Lewis acid.

Lewis Bases :

All electron donars are Lewis bases.

Ligand :

Ligand is an ion or a molecule capable of functioning as an electron donar. They are either neutral molecules or ions which can donate a lone pair of electrons to the central metal ion.
Ligands act as Lewis bases.

Central metal ion :-

In a complex ion, an acceptor (metal/metal ion) accepts a pair of electrons from the donar atoms.

Ex

co-ordination sphere

$K_4[Fe(CN)_6]$

Ionization sphere

Central metal atom

Ligands

Co-ordination number :-

Coordination number is defined as the number of ligands to which the metal is directly bonded.

Numerically, coordination ~~number~~ represent the total number of bonds formed between the central metal ion and ligands.

Monodentate ligand :-

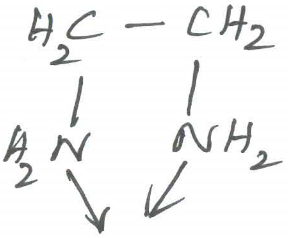
Ligands which can co-ordinate to the central metal ion through only one donar atom are known as monodentate (or) unidentate ligands.

Eg. NH_3, H_2O

Bidentate ligand :

Ligands which have two donar atoms that can Co-ordinate to the central metal ion at two positions are called bidentate ligands.

Eg. Ethylene diamine



Polydentate ligand :

The ligand occupies more co-ordination position on the same central metal ion, a close ring is formed.

Eg. EDTA

Co-ordination sphere:

The central metal ion and the ligands are enclosed with in square bracket is called Co-ordination sphere.

Positive ligands:

$H_2N-\overset{+}{N}H_3$ hydrazinium.

Negative ligand:

F^- (fluoro), Cl^- (chloro), $C_2O_4^{2-}$ (oxalato), CN^- (cyano), NO_2^- (nitro), Br^- (Bromo), SO_4^{2-} (Sulphato), CH_3COO^- (acetato), SCN^- (thiocyanato), $S_2O_3^-$ (thio sulphato).

Neutral ligands:-

H_2O (aqua), NH_3 (ammine), CO (Carbonyl), NO (nitrosyl), C_5H_5N (pyridine).

Coordination number:

Coordination number is defined as the number of ligand donor atoms to which the metal is directly bonded.

Charge on the complex ion :-

Charge on the complex ion is equal to the sum of the charges on the metal ion and their ligands.

Chelates :-

If the ligand is capable of forming more than one bond with the central metal atom (or) ion then the ring structures are produced which are known as chelates. The ligand is called chelating ligand.

Eg. $[Fe(C_2O_4)_3]^{3-}$ is a chelate in which oxalate ion act as chelating ligand.

Calculate the charge on the central metal ion present in the following complex :

$Na[B(NO_3)_4]$

Charge on Na = +1

Charge of B = x

Charge of $4NO_3^-$ = −4

−3

x − 3 = 0

x = +3

∴ Charge on central metal atom = +3

Complexometric titration :-

A titration based on complex formation is called a complexometric titration.

Chelate Effect :

The chelate effect is the ability of multidentate ligands to form more stable metal complexes than those formed by similar monodentate ligands.

Eg. A bidentate ligand forms a more stable complex than do two monodentate ligands.

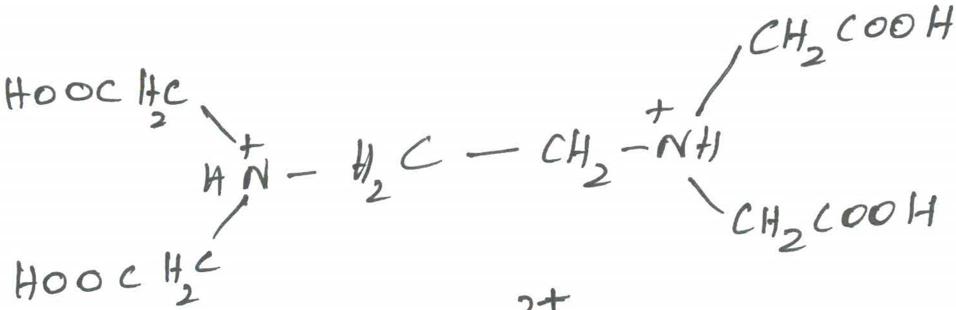
EDTA :-

EDTA is the most widely used chelator in analytical chemistry.

By direct titration or through an indirect sequence of reactions, virtually every element of the periodic table can be measured with EDTA.

1 mole of EDTA reacts with one mole of metal ion.

Acid - Base properties :



H_6Y^{2+}

$pK_1 = 0.0$

$pK_2 = 1.5$

$pK_3 = 2.0$

$pK_4 = 2.66$

$pK_5 = 6.16$

$pK_6 = 10.24$

EDTA is a hexaprotic system, designated H_6Y^{2+}.

The first 4 pK values apply to carboxyl protons, and the last two are for the ammonium protons.

The neutral acid is tetraprotic, with the formula H_4Y. A commonly used reagent is the disodium salt, $Na_2H_2Y \cdot 2H_2O$.

Fraction of EDTA in the form Y^{4-}:

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[H_6Y^{2+}] + [H_5Y^{+}] + [H_4Y] + [H_3Y^{-}] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]}$$

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[EDTA]}$$

where $[EDTA]$ = Total concentration of all free EDTA species in the solution.

" Free " means EDTA not complexed to metal ions.

$$\alpha_{Y^{4-}} = \frac{K_1K_2K_3K_4K_5K_6}{\left\{[H^+]^6 + [H^+]^5K_1 + [H^+]^4K_1K_2 + [H^+]^3K_1K_2K_3 + [H^+]^2K_1K_2K_3K_4 + [H^+]K_1K_2K_3K_4K_5 + K_1K_2K_3K_4K_5K_6\right\}}$$

EDTA Complexes :-

Formation Constant, K_f (or the stability constant):

The equilibrium constant for the reaction of a metal with a ligand is called the formation constant, K_f. or the stability constant.

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$$

$$\therefore K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]}$$

$$K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]} = \frac{[MY^{n-4}]}{[M^{n+}]\alpha_{Y^{4-}}[EDTA]}$$

$$\because \alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[EDTA]}$$

$$\therefore [Y^{4-}] = \alpha_{Y^{4-}}[EDTA]$$

Conditional formation constant :-

If the pH is fixed by a buffer, then $\alpha_{Y^{4-}}$ is constant that can be combined with K_f.

Conditional formation constant

$$K_f' = \alpha_{Y^{4-}} K_f = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]}$$

The number $K_f' = \alpha_{Y^{4-}} K_f$ is called the Conditional formation constant. (or) the effective formation constant.

The conditional formation constant allows us to look at EDTA complex formation as if the uncomplexed EDTA were all in one form:

$$M^{n+} + EDTA \overset{K_f'}{\rightleftharpoons} MY^{n-4}$$

$$\therefore K_f' = \alpha_{Y^{4-}} K_f = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]}.$$

The titration curve is a graph of $pM = -\log[M^{n+}]$ Vs the volume of added EDTA.

This curve is analogous to plotting pH versus volume of titrant in an acid-base titration.

There are three regions of the titration curve.

<u>Region 1</u>: Before the Equivalence point.

In this Region, there is excess M^{n+} left in the solution.

The Concentration of free metal ion is equal to the Concentration of excess, unreacted M^{n+}. The dissociation of MY^{n-4} is negligible.

<u>Region 2</u>:

$$MY^{n-4} \rightleftharpoons M^{n+} + EDTA$$

In this reaction, EDTA refers to the total Concentration of free EDTA in all its forms.

At the equivalence point,

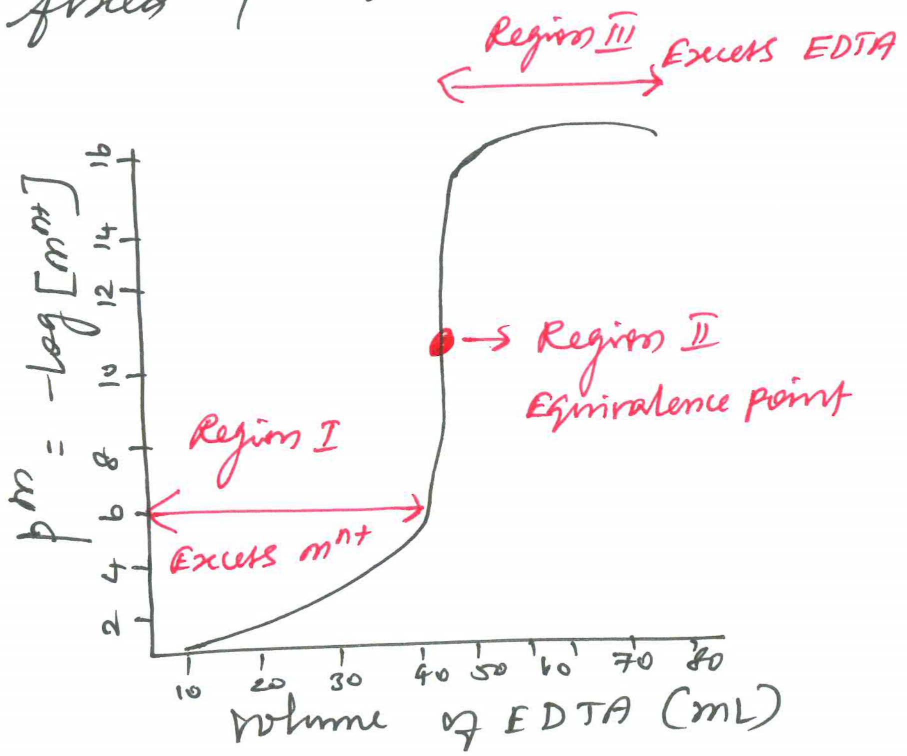
$$[M^{n+}] = [EDTA].$$

EDTA titration curves:-

using EDTA titration we can calculate the concentration of free M^{n+}.

$$M^{n+} + EDTA \rightleftharpoons MY^{n-4} \quad : K_f' = \alpha_{Y^{4-}} K_f$$

If K_f' is large, we can consider the reaction to be complete at each point in the titration. [K_f' is the effective formation constant at the fixed pH of the solution].



Region 3:

After the equivalence point, now there is excess EDTA, and virtually all the metal ion is in the form MY^{n-4}.

The concentration of free EDTA can be equated to the concentration of excess EDTA added after the equivalence point.