Complexometric Titrations!

Complexometric Titrations are titrations between metal ion and complexing agent leading to formation of a complex.

Complexation Rxn :- $\text{Metal Ion} + \underbrace{\text{Complexing Agent}}_{\text{This is also called as ligand.}} \longrightarrow \text{Complex}$.

$$\left.\begin{array}{l}\text{complexing agent} = H, Cl^-, Br^-, NH_3, H_2O, \text{etc.}\\ \text{chelating agent} = \text{EDTA, oxalato, etc.}\end{array}\right\}\text{ligand.}$$

* If the complex formed has metal ion enclosed in a ring, then the complex formed is called as chelate and the complexing agent is called chelating agent.

* For a Complexation Reaction to be used in titration, it must fulfill the following criteria :-

① Complex formed should be stoichiometric i.e. should possess definite composition.

② Complex should be soluble.

③ Complexation reaction should be rapid and should go to completion. It should possess a large equilibrium constant.

④ A suitable indicator should be available.

* **Terms :-**

① Ligand :-

an atom, molecule or ion that is capable to act as donor and form one or more co-ordinate bond with the metal ion.

② Unidentate ligand :- eg. NH_3, H_2O, Cl^-, Br^-, etc

ligand that has only one donor atom; only one co-ordinate bond with metal ion.

③ Polydentate ligand :- eg. EDTA, oxalato, etc.

ligand that has more than one donor atom; more than one co-ordinate bond with metal ion.

④ Chelons / Chelates :-

ligands that form water soluble, stable, 1:1 complex with the metal ion.

⑤ Formation Constant :-

The equilibrium constant for reaction representing the formation of complex is called as formation constant or stability constant for the complex.

⑥ Step-Wise Formation Constant :-

If the ligand (usually monodentate ligand) is able to form complex involving more than one ligand molecule, then the equilibrium constant for each step is called step-wise formation constant.

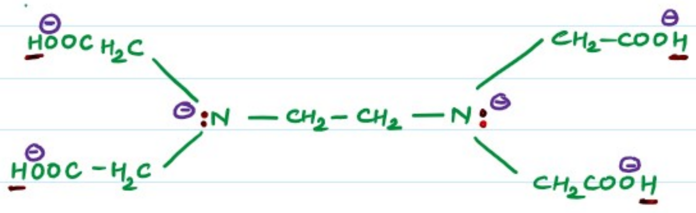
The overall formation constant for the reaction will be the product of the stepwise formation constant.

* EDTA Titrations are most common type of complexometric titration.

EDTA - Ethylene diamine tetra acetic acid.

- → Tetrabasic acid.
- → also an important complexing agent.
- → It is also represented as H_4Y
- → Y^{4-} ion is the complexing agent.
- → acid is sparingly soluble in water ⇒ Thus, we use disodium salt.

$$\underset{\text{metal}}{M^{n+}_{(aq)}} + \underset{\text{ligand}}{Y^{4-}_{(aq)}} \rightleftharpoons \underset{\text{complex}}{[MY]^{n-4}}$$

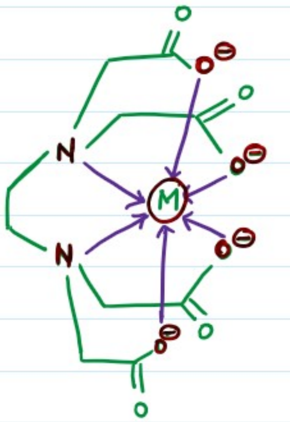


EDTA

4H - Tetrabasic Acid

⊖ → 6 point

↳ Hexadentate ligand.



$\underline{\underline{Y^{4-}}}$

M-EDTA complex.

* Advantages of EDTA :-

① It forms complex with almost all the metal ions in the periodic table.

② The complexes formed are usually very stable. The formation constant of complexes have values from 10^{10} to 10^{26}.

③ These complexes are water soluble.

④ The complexes formed with all metal ions are in the molar ratio of 1:1 irrespective of charge of metal ion.

⑤ Suitable indicators are available to signal the end point of titration.

* Absolute and Conditional Formation Constant :-

$$\left.\begin{array}{l} M^{+} + Y^{4-} \rightleftharpoons [MY]^{3-} \\ M^{2+} + Y^{4-} \rightleftharpoons [MY]^{2-} \\ M^{3+} + Y^{4-} \rightleftharpoons [MY]^{-} \\ M^{4+} + Y^{4-} \rightleftharpoons [MY] \\ \vdots \\ \boxed{M^{n+} + Y^{4-} \rightleftharpoons [MY]^{(n-4)}} \end{array}\right\}$$

The charge of the complex will vary depending on the valency of the metal ion.

$$K_{ab} = \frac{[MY]^{(n-4)}}{[M^{n+}][Y^{4-}]}$$ = (Absolute formation constant).

→ Y^{4-} is the complexing agent

→ conc. of Y^{4-} depends upon the pH of the lution. $H^{+} + {}^{-}OH \rightleftharpoons H_2O$

→ With the increase in the pH of the solution, e dissociation of the acid increases, increasing

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→ With the increase in the pH of the solution, e dissociation of the acid increases, increasing the concentration of Y^{4-} ion.

* The equilibria with dissociation of acid can shown as follows :-

$$\underline{H_4Y} + H_2O \rightleftharpoons H_3Y^- + H_3O^+ \qquad K_1 = 1.02 \times 10^{-2}$$
$$H_3Y^- + H_2O \rightleftharpoons H_2Y^{2-} + H_3O^+ \qquad K_2 = 2.14 \times 10^{-3}$$
$$H_2Y^{2-} + H_2O \rightleftharpoons HY^{3-} + H_3O^+ \qquad K_3 = 6.92 \times 10^{-7}$$
$$HY^{3-} + H_2O \rightleftharpoons Y^{4-} + H_3O^+ \qquad K_4 = 5.50 \times 10^{-11}$$

- The total concentration of EDTA $[C_T]$ will then be given by the equation,

$$[C_T] = \underline{[Y^{4-}]} + [HY^{3-}] + [H_2Y^{2-}] + \underline{[H_3Y^-]} + \underline{H_4Y}$$
$$= K_1K_2K_3K_4 + K_1K_2K_3[H^+] + K_1K_2[H^+]^2 + K_1[H^+]^3 + [H^+]^4$$

- The fraction of EDTA which will be present as Y^{4-}

$$\frac{[Y^{4-}]}{[C_T]} = \frac{K_1K_2K_3K_4}{K_1K_2K_3K_4 + K_1K_2K_3[H^+] + K_1K_2[H^+]^2 + K_1[H^+]^3 + [H^+]^4}$$

$$\alpha = \frac{[Y^{4-}]}{[C_T]}$$

$$[Y^{4-}] = \alpha[C_T] \quad — ①$$

The value of 'α' can be calculated for different pH. For a given pH, α is constant.

$$K_{ab} = \frac{[MY]^{(n-4)}}{[M^{n+}][Y^{4-}]}$$

$$K_{ab} = \frac{[MY]^{n-4}}{[M^{n+}]\,\alpha\,[C_T]} \quad —(\text{using } 1)$$

$$K_{cond.} = \alpha K_{ab} = \frac{[MY]^{n-4}}{}$$

$[M^{n+}]\,[C_T]$

Thus, EDTA titrations are carried out in buffered sol^n. This ensures that the pH remains constant and conditional formation constants can be used.

* Titration Curve :-

- plot quantity that changes during the course of titration against the volume of titrant added.

- Here, concentration of metal changes, titration curve in complexometric titration is plot of $pM = -\log[M^{n+}]$ v/s Volume of Titrant added.

* Titration of Calcium with EDTA :-

Absolute formation constant of Ca - EDTA complex $= 5 \times 10^{10}$

$\alpha = 0.35$

pH = 10.

Conditional formation constant for Ca-EDTA complex $= 1.8 \times 10^{10}$

10 mL 0.01 M Ca^{2+} sol^n is titrated against 0.01 M EDTA.

① **Case 1 :- 0 mL EDTA added.**

- only Ca^{2+} ion is present.

$$pCa = -\log[Ca] = -\log[0.01]$$
$$= 2$$

② **Case 2 :- Before equivalence point.**
'V' = Volume of EDTA added. } $V < V_{eq}$.

millimoles of Ca^{2+} originally present $= 10\,mL \times 0.01\,M = 0.1$ mmoles.

millimoles of EDTA added $= V\,mL \times 0.01\,M = (V \times 0.01)$ mmoles.

Total millimoles of Ca^{2+} remaining unreacted $= 0.1 - (V \times 0.01)$

Total volume $= (V + 10)$ mL

$$[Ca^{2+}] \times (V+10) = 0.1 - (V \times 0.01)$$

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$$[Ca^{2+}] = \frac{0.1 - (V \times 0.01)}{(V+10)}$$

Vol. of EDTA	2.0	5.0	9.0	9.5	9.9
pCa	2.18	2.48	3.28	3.60	4.30

③ Case 3: At equivalence point :-

At equivalence point, neither calcium ion nor EDTA ion are in excess.
All Ca^{2+} ions converted to complex.

conc. of complex ⇒

$$[cmplx] \times 20 = 0.01 \times 10$$

$$[complex] = 0.05 \text{ M}$$

Using conditional formation constant,

$$K_{con} = \frac{[complex]}{[Ca^{2+}][EDTA]}$$

$$1.8 \times 10^{10} = \frac{0.05}{x \cdot x}$$

[free Ca^{2+} & free EDTA will be produced in same molar ratio as cmplex formed = 1:1]

$$1.8 \times 10^{10} = \frac{0.05}{x^2}$$

$$x = 5.2 \times 10^{-7}$$

$$[Ca^{2+}] = 5.2 \times 10^{-7}$$

$$pCa = 6.28$$

④ Case 4: After equivalence point.

→ concentration of complex formed remains unchanged.
→ excess EDTA is added, conc. of EDTA increases.

V = Volume of EDTA added.
(V−10) mL = excess of EDTA.

For EDTA,

$$[EDTA] \times (V+10) = (V-10) \times 0.01$$

For complex,

$$[complex] = 0.05$$

For EDTA.,

$[EDTA] \times (V+10) = (V-10) \times 0.01$

$[EDTA] = \frac{(V-10) \times 0.01}{(V+10)}$ ✓

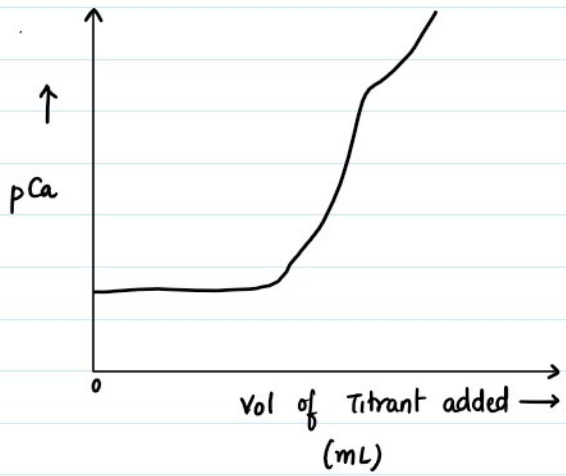
For complex,

$[complex] = 0.05$ ✓

$K_{condition} = \frac{[complex]}{[Ca^{2+}][EDTA]}$

$[Ca^{2+}] = \frac{[complex]}{K_{cond} \times [EDTA]} = \frac{0.05}{1.8 \times 10^{10} \times [EDTA]}$

Vol. of EDTA added	10.1	10.5	11	12
pCa	8.25	8.68	9	9.78



* Type of EDTA Titration :-

→ EDTA Titrations can be carried out with most metal ion.

→ EDTA Titrations are carried out in buffered solⁿ.

1) Direct Titration :-

- direct titration b/w metal ion and disodium salt of EDTA using suitable indicator.
- only those metal ions can be estimated which can
  - ↪ form stable complex with EDTA
  - ↪ reactⁿ b/w metal ion and EDTA is fast.
- suitable indicator should be available to signal the end-point.
- pH is sufficiently high to precipitate metal ion in its hydroxide form. eg. Alkaline earth

- suitable indicator should be available to signal the end-point.
- pH is sufficiently high to precipitate metal ion in its hydroxide form. eg. Alkaline earth metal ions are titrated in pH = 10–12.

  In order to prevent precipitation, we added auxillary complexing agent which forms a less stable complex than the original metal-EDTA complex. Thus, we can prevent precipitation of metal as its hydroxide.

  eg. Ammonia = commonly used auxillary complexing agent.

2) Back Titration :-

- used for metals where the reaction b/w metal and complexing agent is slow <u>OR</u> no suitable indicator is present.
- It is carried out by adding excess amt of EDTA and then this excess is titrated back with standard metal ion solⁿ like Zn (II) and Mg (II).
- Zn / Mg are choosen bcoz they form less stable complex with EDTA as compared to the original metal-EDTA complex.
- Otherwise, it will replace first metal ion from its EDTA complex before reacting with the excess EDTA.

$$M_1 + EDTA \rightleftharpoons M_1-EDTA + \boxed{\underline{\underline{EDTA_{(excess)}}}}$$

$$+\ M_2 \rightleftharpoons M_2-EDTA.$$

eg. Al, Pb, Hg, Ni, Mn, Co.

3. Substitution / Replacement / Displacement :-

- Metal ion forms stable complex but a suitable indicator may not be present.
- The solution of metal M_1, EDTA – M_2 complex is added.

  M_2-EDTA complex is less stable than M_1-EDTA complex. Excess of M_2-EDTA is added, displacement reaction takes place.

$$M_1^{n+} + M_2-EDTA \rightleftharpoons [M_1-EDTA] + M_2^{n+}$$

- liberated M_2^{n+} is titrated with EDTA using suitable indicator.
- The moles of M_2^{n+} released will be equal to moles of M_1^{n+} present.
- complexes of alkaline earth metal, Zn (II), Mg (II) are less stable than other metals.

4) Alkalimetric Titration :-

- limited solubility of EDTA is the reason why disodium salt of EDTA is used as titrant.
- Reaction b/w EDTA and metal leads to release of hydrogen ions. These hydrogen ions are consumed by the buffered solution as the titration is carried out in buffer sol^n.

$$M^{n+} + H_2Y^{2-} \rightleftharpoons [MY]^{n-4} + 2H^+.$$

- In an unbuffered sol^n, the liberated H^+ ions can be titrated against an alkali.

5) Indirect titration :-

- used when anion cannt form a complex with EDTA.

eg. solution of sulphate ion :-

react sulphate ion with excess Barium ions.
sulphate ion will be removed as $BaSO_4$ precipitate
excess Ba^{2+} can be titrated against EDTA.

* Method used to increase selectivity of EDTA as titrant :-

1. Chemical Separation :-

→ interferring ion is removed by separation technique like solvent extraction, precipitation, etc.

This method should retain the metal ion of interest.

→ Alternatively, we can also remove the ion of interest by required method and then recover and estimate.

This method should remove only the metal ion of interest.

eg. Mg (II) and Ca(II),

Mg (II) can be removed by 8 M KOH, Mg precipitates as $Mg(OH)_2$ whereas Ca(II) remains in the solution

2. Controlling pH of the solution :-

2. Controlling pH of the solution :-

- metal ions reacting with EDTA are divided into three groups based on the pH range that they are titrated.

ⓐ Alkaline earth metals, zinc :-

→ pH = 10 to 12

→ stability constant of the metal - EDTA cmplx is lowest as compared to the other metals.

→ Hence, high pH is required to provide conc. of Y^{4-} to completely convert metal into complex.

ⓑ Bivalent ions of transition metal series :-

pH = 5-7

Pb, Mn, Cd, Ni, Sn.

ⓒ High valence metals :-

acidic range 1 to 3.

Fe(III), Cr(III), Bi(III), Th(IV), Co(III)

→ If metal ions belonging to different pH groups are present, the one should start with lowest pH and gradually increase the pH.

3) Using Masking Agent :-

→ masking agent will remove metal ion from the system without its physical removal.

→ Usually, masking agent is complexing agent that forms more stable complex than the metal - EDTA complex.

eg. Usually, Cyanide is used as masking agent.

↳ It forms stable complex with Zn, Hg, Co, Ni, Cd.

↳ It doesnot form complex with alkaline earth metal, Pb, Mn.

4) Using demasking agent :-

→ process in which masked metal is brought back to solⁿ.

→ achieved by chemical reaction or physical process.

→ Usually, formaldehyde is used as demasking agent.

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$$[Zn(CN)_4]^{2-} + 4HCHO + 4H^+ \rightleftharpoons Zn^{2+} + 4HOCH_2CN.$$

5) Kinetic masking :-

→ advantage of slow reaction of EDTA with certain metal ion.

→ one metal ion reacts rapidly than other.

eg. Fe (III) and Cr(III)

At RT :- Cr - EDTA is very slow.

acidic medium & RT :- Fe(III) reacts quantitatively while Cr(III) remains in solution

At 90°C :- both ions react

Thank-You!