

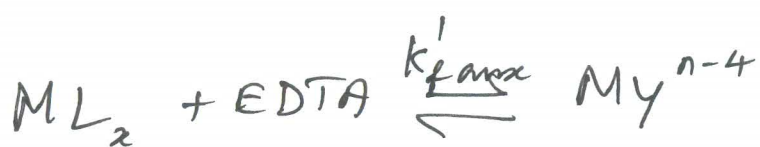
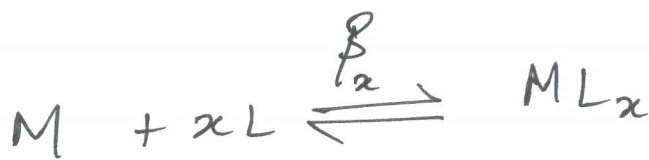
## 12-5 Auxiliary Complexing Agents:

(14)

Sometimes it is necessary to add an additional complexing agent to increase the solubility of the analyte at a particular pH.

To permit many metals to be titrated in alkaline solutions with EDTA, we use an auxiliary complexing agent.

This is a ligand that binds the metal strongly enough to prevent the hydroxide from precipitating, but weakly enough to give up the metal when EDTA is added.



$\beta_x$  must be less than  $k'_{f aux}$

Example for auxiliary complexing agent.

Ammonia, Triethanolamine, and citrate.

## Metal-Ligand Equilibria<sup>a-</sup>

Consider a metal ion that forms two complexes with the auxiliary complexing ligand L:



$$\beta_1 = \frac{[ML]}{[M][L]} \longrightarrow \textcircled{1}$$



$$\beta_2 = \frac{[ML_2]}{[M][L]^2} \longrightarrow \textcircled{2}$$

$\beta_i$  is the equilibrium constants are called overall or Cumulative formation constants.

The fraction of metal ion in the uncomplexed state,  $M$ , can be expressed as

$$\alpha_M = \frac{[M]}{\textcircled{M}_{tot}} \longrightarrow \textcircled{3}$$

where  $C_M$  refers to the total concentration of all forms of  $M$  ( $= M, ML, \& ML_2$ )

$$\therefore M_{\text{tot}} = [M] + [ML] + [ML_2]$$

From the equation ① and ②

$$[ML] = \beta_1 [M][L]$$

$$[ML_2] = \beta_2 [M][L]^2$$

$$\begin{aligned} \therefore M_{\text{tot}} &= [M] + \beta_1 [M][L] + \beta_2 [M][L]^2 \\ &= [M] \{ 1 + \beta_1 [L] + \beta_2 [L]^2 \} \rightarrow \textcircled{4} \end{aligned}$$

Substituting  $\textcircled{4}$  in  $\textcircled{3}$

$$\begin{aligned} \alpha_M &= \frac{[M]}{[M] \{ 1 + \beta_1 [L] + \beta_2 [L]^2 \}} \\ &= \frac{1}{1 + \beta_1 [L] + \beta_2 [L]^2} \end{aligned}$$

11-6

## ~~13-6~~ Metal ion Indicators:

(17)

### End-point detection methods:

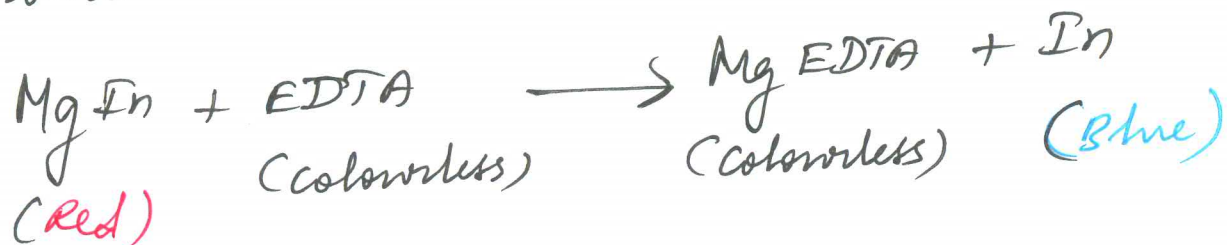
- (i) Metal ion indicators.
- (ii) Mercury electrode.
- (iii) Ion-selective electrode.
- (iv) Glass (pH) electrode.

### Metal ion Indicators :-

Metal ion indicators are compounds whose color changes when they bind to a metal ion.

Indicators must bind metal less strongly than EDTA.

Eg. Reaction of  $Mg^{2+}$  with EDTA, using Eriochrome black T as the indicator.





(18)

At the start of the experiment, a small amount of indicator (In) is added to the colourless solution of  $Mg^{2+}$  to form a red complex.

As EDTA is added, it reacts first with free, colourless  $Mg^{2+}$ . When free  $Mg^{2+}$  is used up, the last EDTA added before the equivalence point displaces indicators from the red  $MgIn$  complex.

The change from the red  $MgIn$  to blue unbound In signals the end point of the titration.

Most metal ion indicators are also called acid-base indicators, with  $pK_a$  values listed in Table 13-3 in the Book.

11-7

## ~~EDTA~~ EDTA Titration Techniques:-

(19)

### Direct Titration:-

- \* The analyte is titrated with standard EDTA.
- \* The analyte is buffered to a pH at which the conditional formation constant for the metal-EDTA complex is large and the colour of the free indicator is distinctly different from that of the metal-indicator complex.
- \* An auxiliary complexing agent - for example, ammonia, tartrate, citrate, or triethanolamine - may be employed to prevent the metal ion from precipitating in the absence of EDTA.

### Back titration:-

- \* A known excess of EDTA is added to the analyte.
- \* Then excess EDTA is then titrated with a standard solution of a second metal ion.
- \* The metal ion used in the back titration must not displace the analyte metal ion from its EDTA.

19a

Example for Direct titration:

The direct titration of  $Pb^{2+}$  is carried out in ammonia buffer at  $pH 10$  in the presence of tartrate, which complexes the metal ion and does not allow  $Pb(OH)_2$  to precipitate.

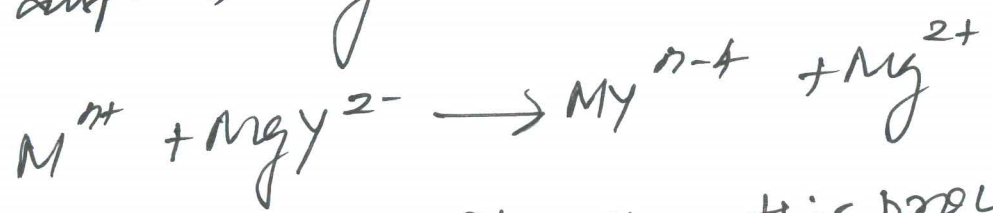
The lead-tartrate complex must be less stable than the lead-EDTA complex, or the titration would not be feasible.



\* Must use this technique when the analyte precipitates in the absence of EDTA or if the reaction with EDTA is too slow, or if the analyte blocks the indicator.

### Displacement titration :-

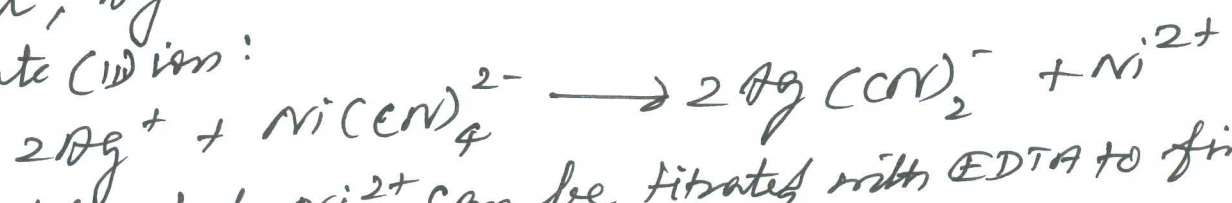
\* If there is no suitable indicator for a metal, treat the analyte with excess  $\text{Mg}(\text{EDTA})^{2-}$  to displace  $\text{Mg}^{2+}$ . Then titrate the displaced  $\text{Mg}^{2+}$  with standard EDTA.



\* Can titrate  $\text{Hg}^{2+}$  using this procedure.

\* The formation constant of  $\text{MY}^{n-4}$  must be  $>$  the formation constant of  $\text{MgY}^{2-}$ .  
Otherwise, the displacement won't happen.

Ex. There is no suitable indicator for  $\text{Ag}^+$ ,  
However,  $\text{Ag}^+$  will displace  $\text{Ni}^{2+}$  from the tetracyano-nickelate (II) ion:



The liberated  $\text{Ni}^{2+}$  can be titrated with EDTA to find out how much  $\text{Ag}^+$  was added.



## Indirect Titration :-

\* Anions that precipitate with certain metal ions can be analysed with EDTA by indirect titration.

Eg.  $\text{SO}_4^{2-}$  can be analysed by precipitation with excess  $\text{Ba}^{2+}$  at  $\text{pH} \sim 1$ .

The  $\text{BaSO}_4 (\text{s})$  is washed then boiled with excess EDTA at  $\text{pH} \sim 10$  to bring  $\text{Ba}^{2+}$  back into solution as  $\text{Ba}(\text{EDTA})^{2-}$ . The excess EDTA is back-titrated with  $\text{Mg}^{2+}$ .

Anions such as  $\text{CO}_3^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{S}^{2-}$  and  $\text{SO}_4^{2-}$  can be determined by indirect titration with EDTA.

## Masking :-

\* A masking agent is a reagent that protects some component of the analyte from reaction with EDTA.

\* Masking is used to prevent only element from interfering in the analysis of another element.

\* Masking is not restricted to EDTA titrations.

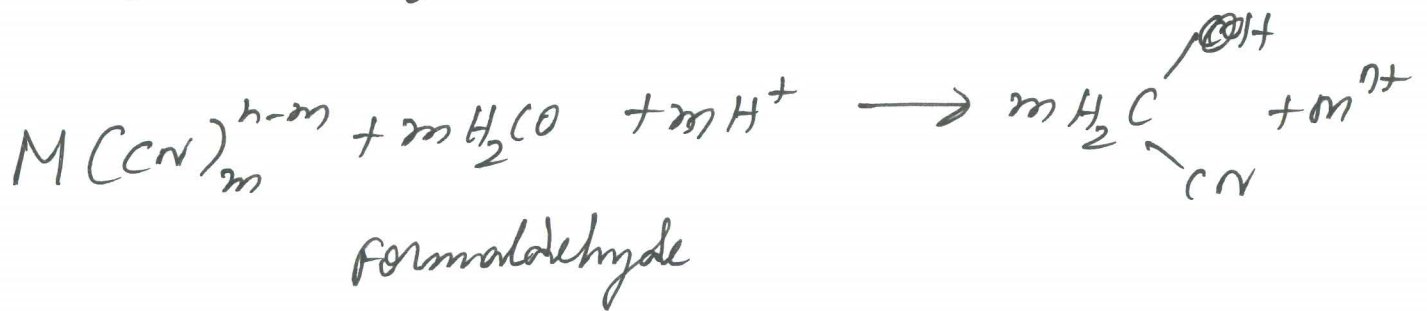
Eg.

$\text{Al}^{3+}$  in a mixture of  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  can be measured by first masking the  $\text{Al}^{3+}$  with  $\text{F}^-$ , thereby leaving only the  $\text{Mg}^{2+}$  to react with EDTA.

## Demasking :

Demasking releases metal ion from a masking agent.

Eg. \* Cyanide complexes can be demasked with formaldehyde.



Eg. \* Thiourea masks  $Cu^{2+}$  by reducing it to  $Cu^+$  and complexing the  $Cu^+$ .

Copper can be liberated from the thiourea complex as  $Cu^{2+}$  by oxidation with  $H_2O_2$ .