Objectives

At the end of this unit the student is expected to be able to :

1-Define complex formation reactions.

2- Differentiate between uni- and polydentate complexing agents.

3- Understand the mechanism of complex formation reaction and the methods used for equivalent point detection .

4- realize the effect of pH on the formation of metal ions complexes .

5- distinguish between simple complexes and chelates .

6- derive the complex formation titration curve .

7- the importance of EDTA particularly in the determination of water hardness .

8- know the applications of complex formation reactions in analytical chemistry .

Introduction

Complex formation reactions are very important in chemistry . Many of the chelate complexes of metal ions are insoluble in water , therefore , it can be used for the separation or the gravimetric determination of these metal ions .

Many of the chelate complexes of metal ions are colored and can be used for the qualitative and quantitative analysis of the metals (spectrophotometry) . Complexometry play important role in the masking of Interferences , for example Co^{2+} can be detected by SCN^- where a red complex $[Co(SCN)_4]^{2-}$ is formed . But Fe^{3+} will interfere in this test because it also forms a red complex $[Fe(SCN)_4]^-$. To prevent Fe^{3+} from interfering with Co^{2+} we add F^- as a masking agent where it forms with Fe^{3+} a stable complex $[FeF_6]^{3-}$ and prevents it from reacting with SCN^- . Note that F^- does not react with Co^{2+} .

Many of the separation methods such as extraction and ion – exchange chromatography depend on the complex formation reactions . Titration of metal ions with a standard solution of a suitable ligand will be the subject of this unit .

Complex Formation Reaction

Complexes are compounds formed from combination of metal ions with ligands (complexing agents). A metal is an electron deficient species while a ligand is an electron rich, and thus, electron donating species. A metal will thus accept electrons from a ligand where coordination bonds are formed. Electrons forming coordination bonds come solely from ligands . The result complexes are called Coordination Complexes .

Ligands :

All ligands are electron pairs donors. In other words, all ligands function as *Lewis bases*. However , they differ in the number of electron pairs in one molecule of the ligand .

## Complex Formation Reaction

Unidentate ligands :

A **ligand** is called a unidentate if it donates a single pair of electrons (like **:**Cl$^-$) i.e each ligand only forms one bond with the central metal ion to give the complex ion . That means it only has one tooth i.e it only has one pair of electrons that it can use to bond to the metal ion .

Simple ligands include water, ammonia and chloride ions . What all these have got in common is active one pairs of electrons in the outer energy level. These are used to form co-ordinate bonds with the metal ion. The complexes formed are not very stable and it's application in analytical chemistry is limited compared to chelate complexes as we will see later .

Complex Formation Reaction

The number of electron pairs (bonds) that a metal ion can accept is called the co-ordination number of the metal ion . This number can be 2 or 4 or 6 or 8 but usually 4 and 6 are the most common for metals .

The following example is a complex formed by reacting Cu^{2+} which has 4 co-ordination number (4 bonds) with :Cl^- which has one active pairs of electrons (unidentate ligand) . That means , each chloride ion can form only one co-ordination bond , therefore each one copper ion needs 4 chloride ions to form the complex :

Complex Formation Reaction
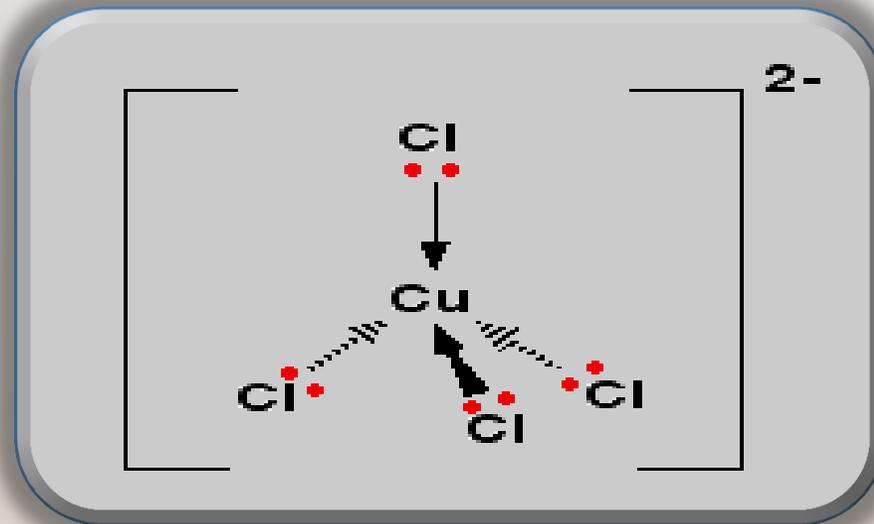
Some of the other common unidentate ligands are :

Br^- , F^- , I^- , CN^- , RNH_2 , $RCOO^-$
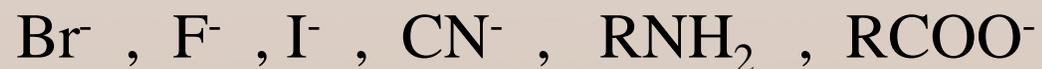
Bidentate ligands :

Bidentate ligands have two electron pairs, both of which can bond to the central metal ion.

Complex Formation Reaction

The two commonly used examples are ethylenediamine and oxalate :
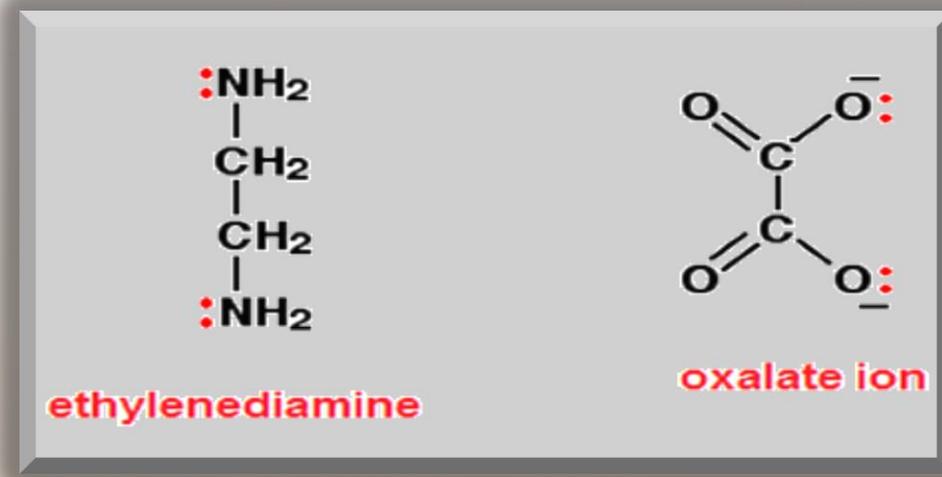
In oxalate ion, there are lots more electron pairs than the two shown, but these are the only ones we are interested in.

Complex Formation Reaction

You can think of these bidentate ligands rather as if they were a pair of headphones, carrying electron pairs on each of the "ear pieces". These will then fit around a metal ion.

These can both be used to form co-ordinate bonds with the same metal ion.
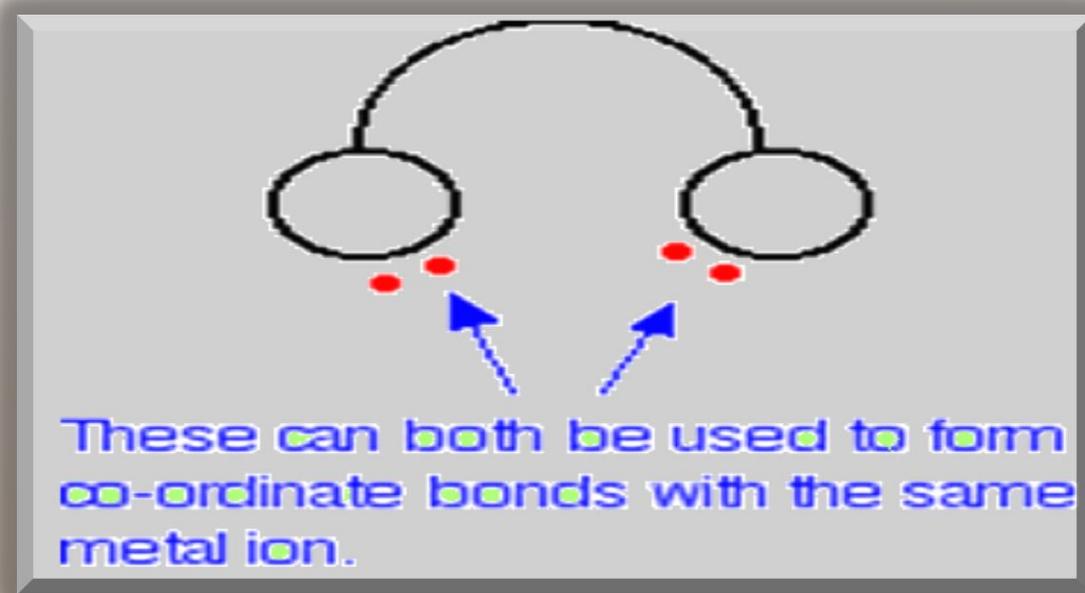
Complex Formation Reaction

Cr (C$_2$O$_4$)$_3$ $^{3-}$: This is the complex ion formed by attaching 3 oxalate ions to a chromium(III) ion. The original chromium ion carried 3+ charges, and each oxalate ion carried 2-. (3+) + (3 x 2-) = 3-.The structure of the ion complex looks like this:
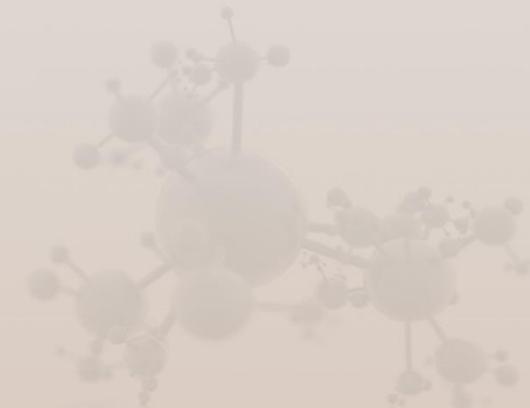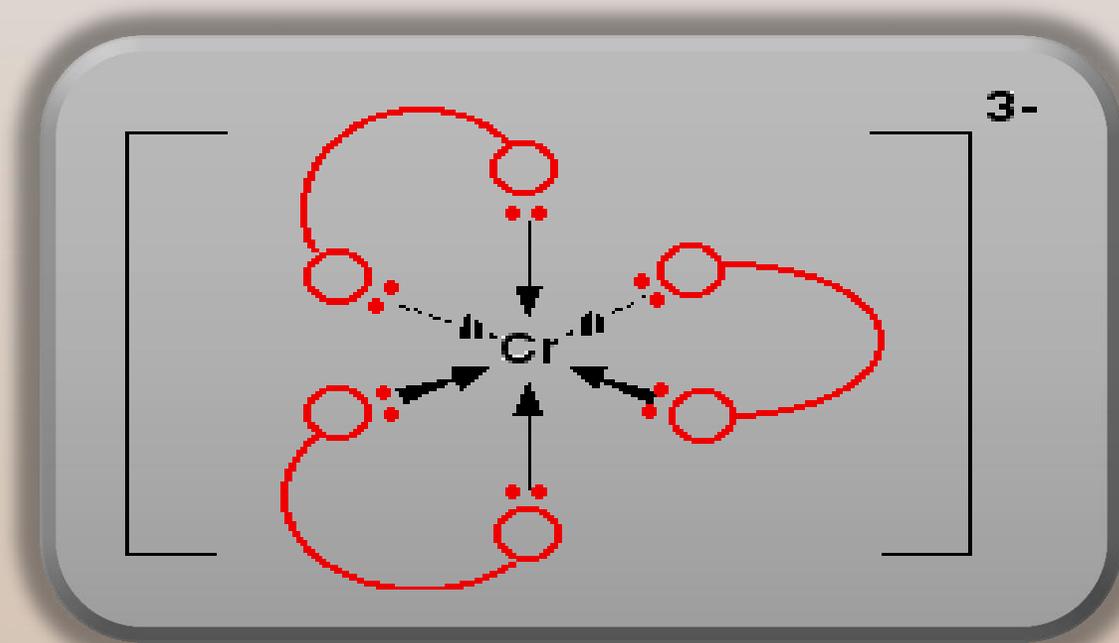
Complex Formation Reaction

Note that the co-ordination number for chromium is 6 .The structure of the **Ni (NH$_2$CH$_2$CH$_2$NH$_2$)$_3$ $^{2+}$** complex looks like this
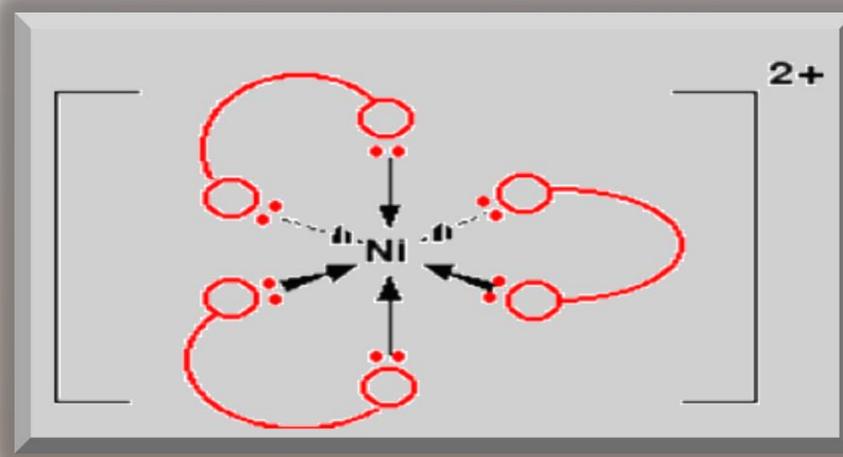

In this case, the "ear pieces" are the nitrogen atoms of the NH$_2$ groups - and the "bit that goes over your head " is the -CH$_2$CH$_2$- group. The shape of the complex is exactly the same as the previous chromium complex. The only real difference is the number of charges.

Complex Formation Reaction

Because the nickel is forming 6 co-ordinate bonds, the co-ordination number of this ion is 6, despite the fact that it is only joined to 3 ligands. Co-ordination number counts the number of bonds, not the number of ligands.

Another example is the complex between Zn^{2+} (co-ordination number = 4) and 8-hydroxylquinolate as bidantate ligands . Note that the complex is neutral .

8-hydroxyquinolate
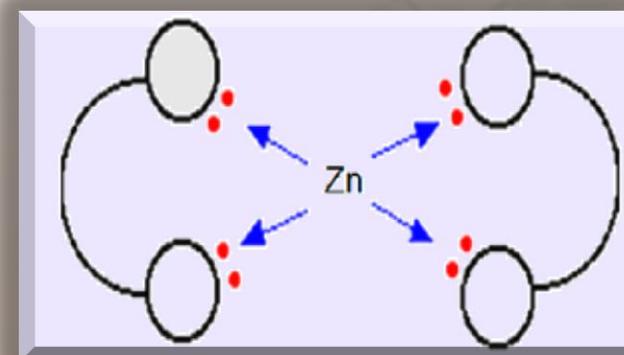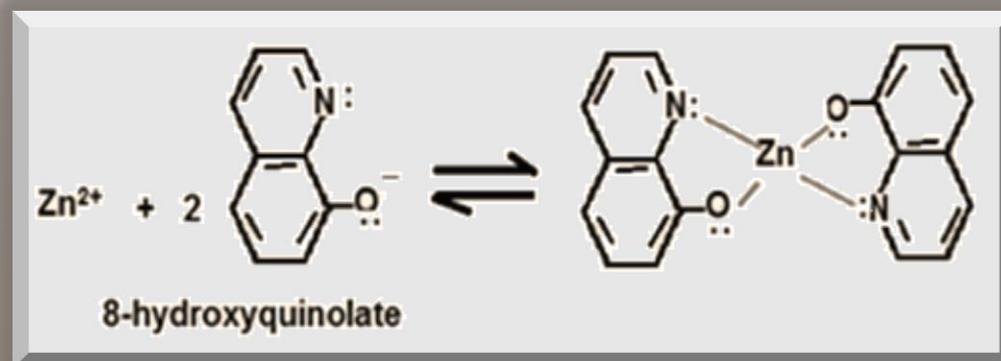
Complex Formation Reaction

polydentate ligands :

A polydentate ligand has more than two ion pairs of electrons - all of which can form co-ordinate bonds with the same metal ion. The best example is EDTA (hexaprotic acid H_4Y) . EDTA is a hexadentate ligand used as a negative ion Y^{4-}. The diagram shows the structure of the ion with the important atoms and ione pairs picked out . The EDTA ion entirely wraps up a metal ion using all 6 of the positions as shown in the figure on your right.
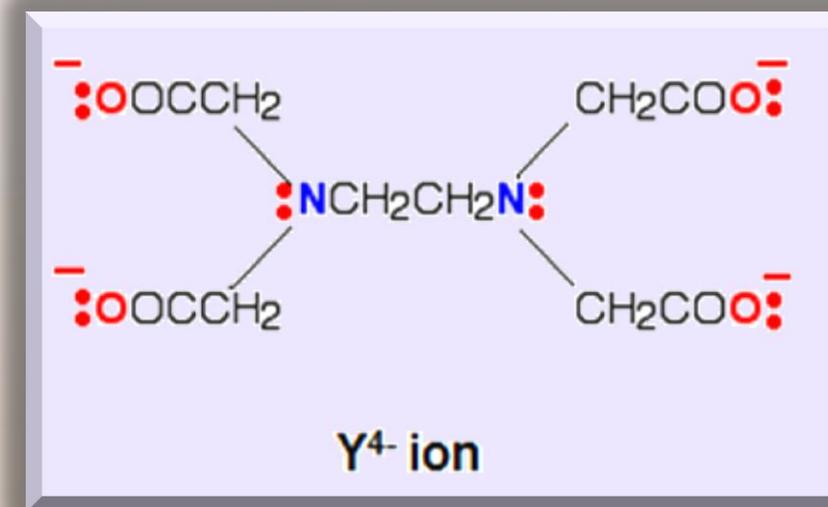
Complex Formation Reaction

The co-ordination number is again 6 because of the 6 co-ordinate bonds being formed by the central metal ion. The diagram below shows this happening with a copper(II) ion.

the CuY^{2-} complex ion
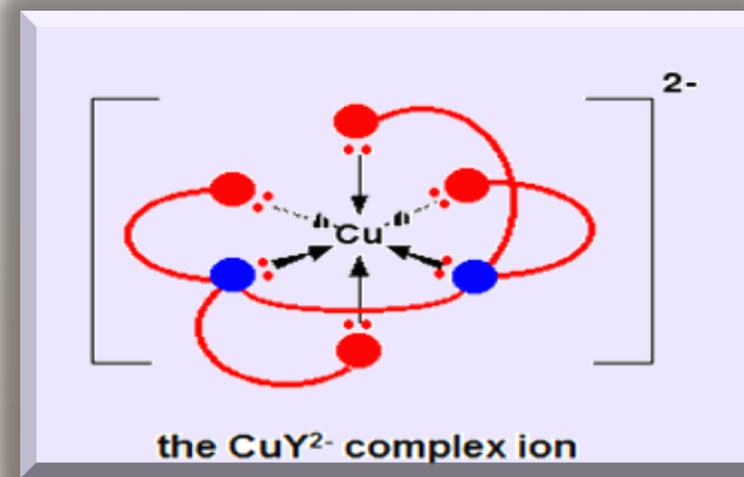
The overall charge, of course, comes from the 2+ on the original copper(II) ion and the 4- on the Y^{4-} ion. You did notice that the complexes can be positive or negative or neutral depending on the charge on the metal ion and on the ligand .

Complex Formation Reaction

For organic compounds, we can determine the number of free electrons pairs in the molecule by counting the number of atoms of each of O, S, N and halides X in that molecule. It should be noted here that in the carboxyl group RCOO- although there is two atoms of oxygen each of them having a pair of free electrons, but only one atom can participate in a bond with a metal ion because the two atoms are very near to each other which makes it difficult for both atoms to be linked to the metal ion .

Complex Formation Reaction

Chelate complexes : Complexes involving metal ion and unidentate ligands are described as co-ordination compounds . A complex of a metal ion with any ligand which has two electron pairs or more is called a chelate or a chelate complex . The stability and selectivity of a chelate is usually much greater than that of corresponding unidentate metal complex , for this reason , the former is more important in analytical chemistry applications . Ligands having more than one electron pair are called **chelating agents .**

Complex Formation Reaction

Complex – formation reaction equilibrium :

There are two common equilibrium constants used in complex formation reaction . Let us take the complex between Cu^{2+} and NH_3 as an example :

1- Formation Constant (K_f) :

$$Cu^{2+} + 4\,NH_3 \leftrightarrow Cu(NH_3)_4{}^{2+} \qquad\qquad K_f = \dfrac{[Cu(NH_3)_4{}^{2+}]}{[Cu^{2+}][NH_3]^4}$$

2- Dissociation constant (K_d) :

$$Cu(NH_3)_4{}^{2+} \leftrightarrow Cu^{2+} + 4NH_3 \qquad\qquad K_d = \dfrac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4{}^{2+}]}$$
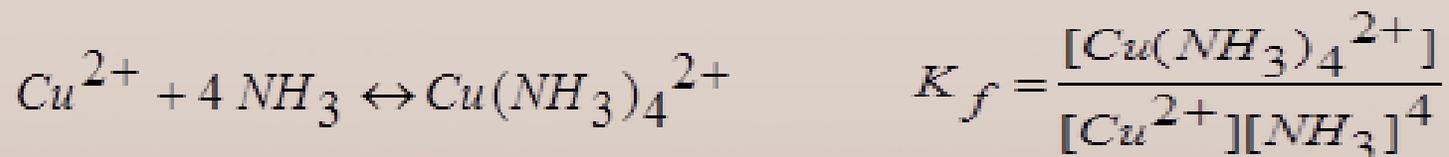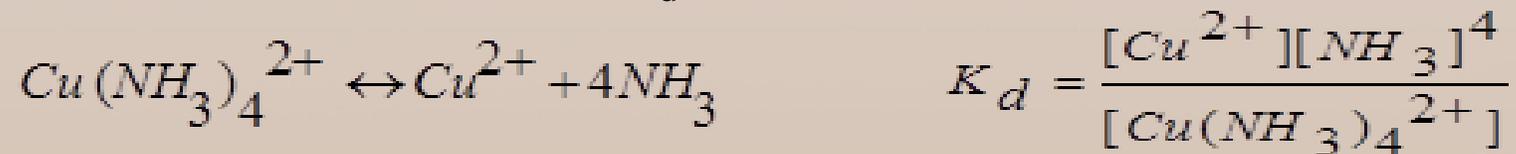
Complex Formation Reaction

You may have noticed that the K_d (sometimes called instability constant) is inverted of K_f (sometimes called stability constant) . This means that whenever the value of K_f large and the value of K_d is small whenever the complex is stronger and more stable and vice versa .

Example : Calculate the molar concentration of [CN$^-$] in a solution of Cu(CN)$_4^{2-}$ (K_d = 5.2 X 10^{-28}) prepared by dissolving 0.05 mole of the complex in water and completing the volume to one liter ?

Complex Formation Reaction

Solution :

$$Cu(CN)_4^{2-} \leftrightarrow Cu^{2+} + 4CN^-$$

$$0.05 - x \qquad\qquad x \qquad\quad 4x \qquad\qquad (at\,equilibrium)$$

$$K_d = 5.2\,X\,10^{-28} = \frac{x(4x)^4}{0.05 - x}$$

$$x = 6.3\,X\,10^{-7}\,M$$
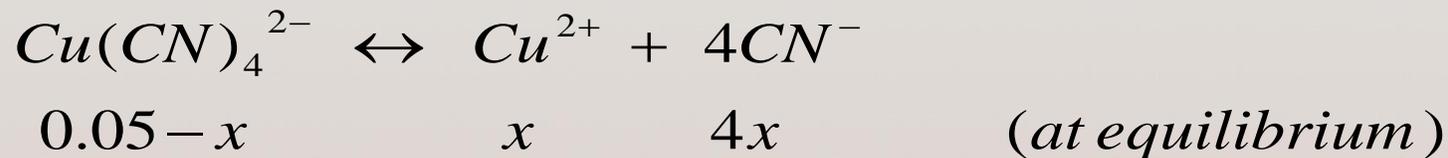
$$[CN] = 4X\,x = 4\,X\,6.3\,X\,10^{-7} = 2.52\,X\,10^{-5}\,M$$

Example : 0.05 moles of $Hg(SCN)_4^{2-}$ is dissolved in water and the volume is completed to one liter .If the concentration of $[Hg^{2+}]$ in this solution is 7.2 x 10^{-6} M , calculate , K_f and K_d for the complex ?

Complex Formation Reaction

Solution :

$$Hg(SCN)_4^{2-} \leftrightarrow Hg^{2+} + 4SCN^-$$

$$\left(0.05 - 7.2 X 10^{-6}\right) \quad (7.2 X 10^{-6}) \quad (4x7.2 X 10^{-6})$$

$$K_d = \frac{(7.2 X 10^{-6})(4x7.2 X 10^{-6})^4}{(0.05 - 7.2 X 10^{-6})} = 9.9 X 10^{-23}$$
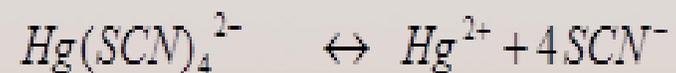
$$K_f = \frac{1}{9.9 X 10^{-23}} \approx 1.0 X 10^{22}$$

Selecting a ligand for the titration of a metal ion

The suitable ligand for the titration of a metal ion should :

1- form a stable (large K_f value) , colorless (to allow indicator color change to be seen) and water soluble (most metal titrations are in aqueous solution) complex with the metal ion .

2- React with metal ion in 1:1 stoichiometric ratio i.e in one step . Look at the graph on your right and review our discussion in unit 7.

Titration curves for the titration of a metal ion having 4 co-ordination number with :

(A) : hexadentate ligand (1:1 molar ratio , one step reaction) such as EDTA .

(B) : bidentate ligand (1:2 molar ratio , two steps reaction)

(C) : unidentate ligand (1:4 molar ratio , 4 steps reaction)

pM
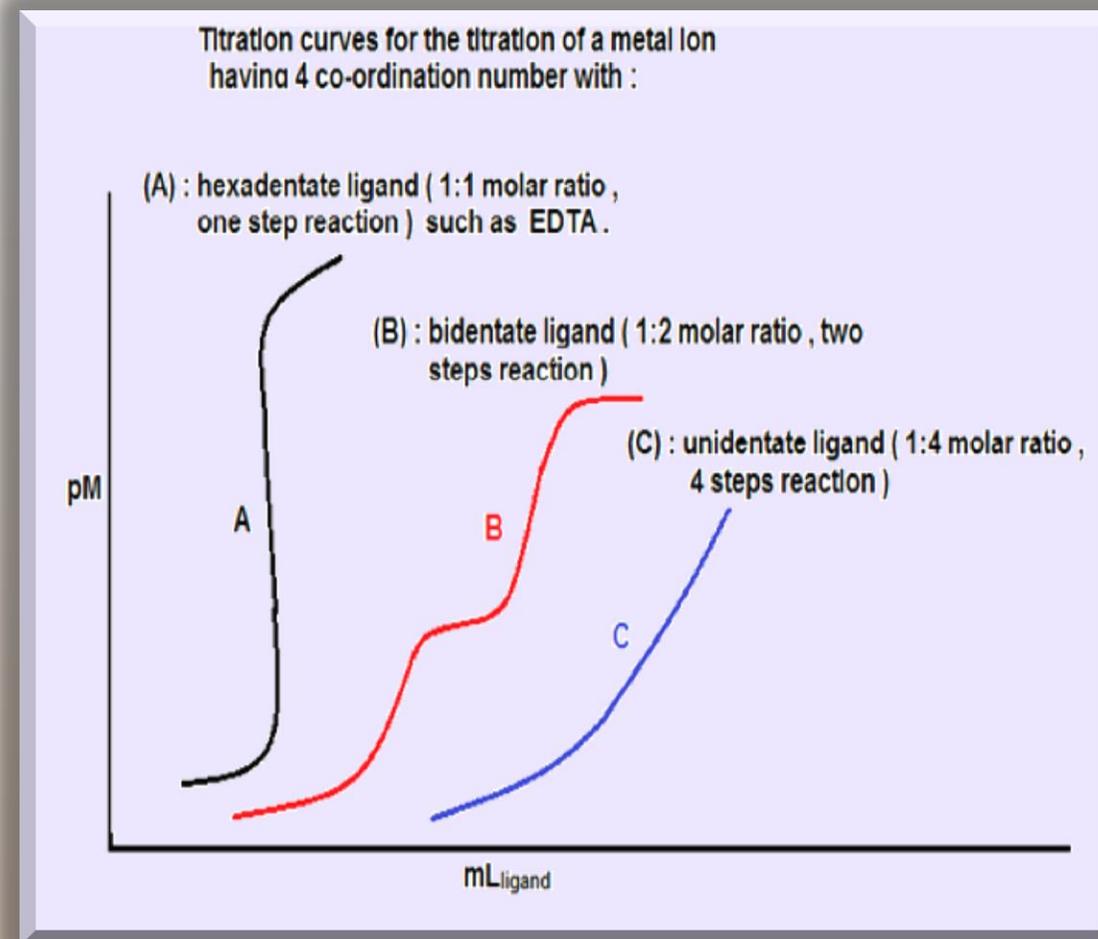
mL$_{ligand}$

Titration of metal ions by EDTA

EDTA probably the most suitable ligand for titrating metal ions for several reasons :

1- EDTA forms water soluble , colorless and stable complexes with most metal ions except alkali metals .

2- Because it is hexadentate ligand (four carboxyl groups and two amine groups that can act as electron pair donors,) it reacts with most metal ions in one step (1:1 molar ratio) . Note , the co-ordination number for most metals is 4 or 6.

3- EDTA has low price .

H_4Y and NaH_3Y salt do not dissolve in water but Na_2H_2Y salt does , therefore , the last salt is the mostly used for the preparation of EDTA solutions .

Titration of metal ions by EDTA

Effect of pH on the composition of EDTA solution :

EDTA can be regarded as polyprotic weak acid H_4Y where in solution we will have, in addition to H_4Y, the following species: H_3Y^-, H_2Y^{2-}, HY^{3-}, and Y^{4-}. Which one of these five species is the predominant depend on the pH of the solution . At very low pH (very acidic conditions) the H_4Y form predominates, whereas at very high pH (very basic condition) , the Y^{4-} form is prevalent.

Titration of metal ions by EDTA

$$\alpha_0 = \frac{[H_4Y]}{T} \; , \; \alpha_1 = \frac{[H_3Y^-]}{T} \; , \; \alpha_2 = \frac{[H_2Y^{2-}]}{T} \; , \; \alpha_3 = \frac{[HY^{3-}]}{T} \; , \; \alpha_4 = \frac{[Y^{4-}]}{T}$$

$$T = [H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]$$

$$H_4Y \leftrightarrow H^+ + H_3Y^- \; , \quad K_{a1} = \frac{[H^+][H_3Y^-]}{[H_4Y]} = 1 X 10^{-2}$$

$$H_3Y^- \leftrightarrow H^+ + H_2Y^{2-} , \quad K_{a2} = \frac{[H^+][H_2Y^{2-}]}{[H_3Y^-]} = 2.2 X 10^{-3}$$

$$H_2Y^{2-} \leftrightarrow H^+ + HY^{3-} \; , \quad K_{a3} = \frac{[H^+][HY^{3-}]}{[H_2Y^{2-}]} = 6.9 X 19^{-7}$$

$$HY^{3-} \leftrightarrow H^+ + Y^{4-} \quad , \quad K_{a4} = \frac{[H^+][Y^{4-}]}{[HY^{3-}]} = 5.5 X 10^{-11}$$
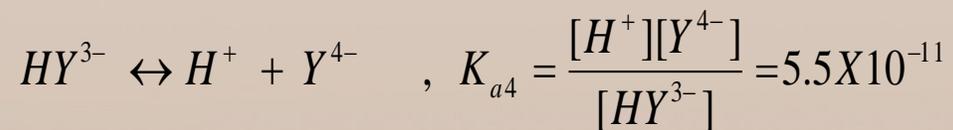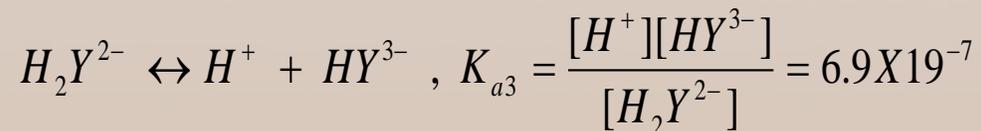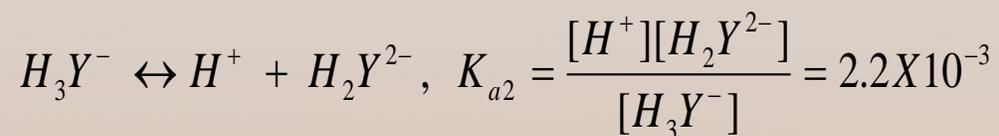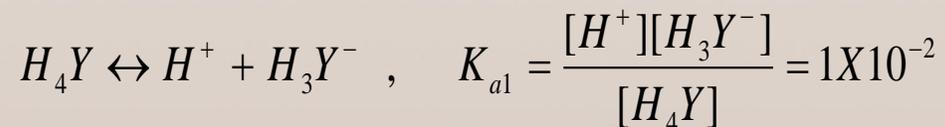
Titration of metal ions by EDTA

Where α_4 is the fraction of EDTA present as Y^{4-} . The species Y^{4-} is the ligand species in EDTA titrations and thus should be looked at carefully . At very strong basic conditions :

$$\alpha_4 = \frac{[Y^{4-}]}{T} = 1$$

By substituting in the above equation for T from the dissociation constants K_{a1} , K_{a2} , K_{a3} and K_{a4} we obtain the following equation (see ref. 1 and 5) :

$$\frac{1}{\alpha_4} = \frac{[H^+]^4}{K_{a1}.K_{a2}.K_{a3}.K_{a4}} + \frac{[H^+]^3}{K_{a2}.K_{a3}.K_{a4}} + \frac{[H^+]^2}{K_{a3}.K_{a4}} = \frac{[H^+]}{K_{a4}}$$

Titration of metal ions by EDTA

From this equation we can calculate α_4 if we know the pH of the solution and the dissociation constants values . Like wise , α_0 , α_3 , α_2 , α_1
Can be calculated in the same way , but they are not relevant in this course .The graph on your right shows the effect of pH on the composition of EDTA solution .

From this graph we can see that at pH = 0 all EDTA is turned to H_4Y.
That means :

$$\alpha_0 = \frac{[H_4Y]}{T} \approx 1$$

Effect of pH on the composition of an EDTA solution.
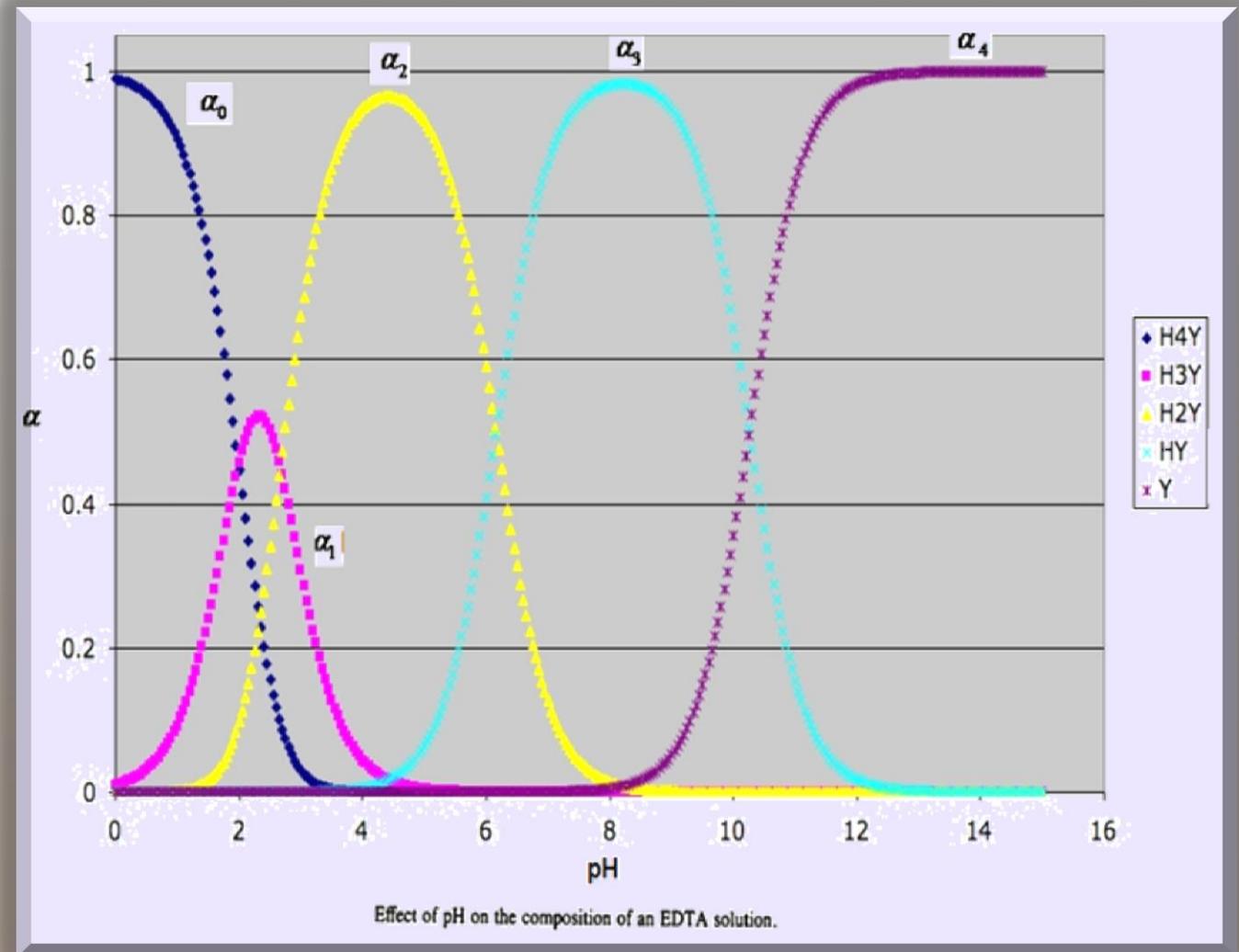
Titration of metal ions by EDTA

and at pH = 14 all EDTA is turned to Y^{4-} .This means : $\alpha_4 = \dfrac{[Y^{4-}]}{T} = 1$

Example : Calculate the fraction of EDTA present as Y^{4-} :

   (1) at pH = 8   (2) at pH = 11 ?

Solution :

   (1) at pH = 8 :

$$[H^+] = 1 \times 10^{-8} \; ; \; [H^+]^2 = 10^{-16} \; ; \; [H^+]^3 = 1 \times 10^{-24} \; ; \; [H^+]^4 = 1 \times 10^{-32}$$

$$K_{a4} = 5.5 \times 10^{-11}$$

$$K_{a3} . K_{a4} = 3.8 \times 10^{-17}$$

$$K_{a2} . K_{a3} . K_{a4} = 8.4 \times 10^{-20}$$

$$K_{a1} . K_{a2} . K_{a3} . K_{a4} = 8.4 \times 10^{-22}$$

Titration of metal ions by EDTA

Applying the above equation for α_4 we get : $\alpha_4 = 5.5 \, X \, 10^{-3}$

(2) Like wise at pH = 11 : $\alpha_4 = 0.85$

The results mean that at pH = 8, in every 1000 parts of the EDTA there are 5.5 parts present as Y4- and the rest 994.5 parts present as the other four species . But at pH = 11, in every 100 parts of the EDTA there are 85 parts presents as Y^{4-} and the rest 15 parts exist as the other four specie .Note that α_0 , α_1 , α_2 and α_3 can be calculated in a similar manner .

Titration of metal ions by EDTA

Stability of metal – EDTA complexes :

It is Preferable to conduct the titration of metals with EDTA in alkaline medium(pH $\geq$ 10) . And it is advisable to avoid an acid environment because H^+ compete with metal ion M^{2+} on the EDTA ion Y^{4-} and especially for metals that form weak complexes with EDTA thus :
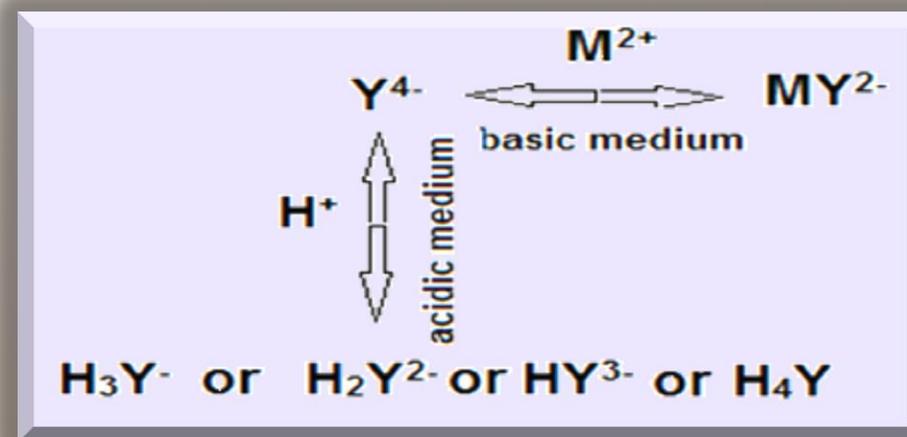
Titration of metal ions by EDTA

In other words, the H^+ in the acid environment will react with Y^{4-} to form one of the other four EDTA species at the expense of metal – EDTA complex (MY^{2-}) where this complex dissociates in an acid environment. Also it is easier for M^{2+} to react with Y^{4-} than with H_3Y^- or H_4Y because the latter requires an effort to replace H^+ by M^{2+}. The effect of pH on the titration of metal ions by EDTA is obvious with metal ions that form weak complexes with EDTA such as calcium .

The following graph shows the effect of pH on the accuracy of the calcium titration where it is clear that the higher the pH the more accurate the titration .

Titration of metal ions by EDTA
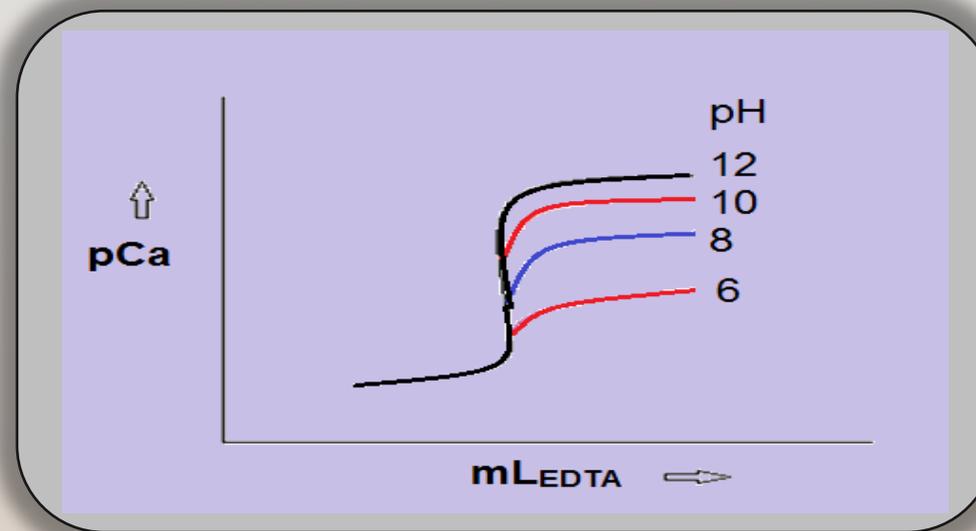
It can be concluded from the above discussion that metals which form weak complexes with the EDTA (small K_f values) can be titrated only in basic medium while the metals that form strong complexes can be titrated in an acidic or basic environment. That's why we use the buffer solution to fix the pH to suit the titrated metal . The following is the order of some metal ions on the basis of the value of K_f (the stability of their EDTA complexes) .

$$Fe^{3+} > Ni^{2+} > Zn^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$$

Titration of metal ions by EDTA

The graph on your right shows the least pH that a metal ion can be titrated i.e under this pH , the metal ion can not be titrated . For example Fe^{3+} under pH $\cong$ 2 can not be titrated while Mg^{2+} can not be titrated under pH $\cong$ 10 and so on .

Conditional Formation Constant :

$$\alpha_4 = \frac{[Y^{4-}]}{[T]} \qquad (1)$$

When metal ion M^{n+} reacts with EDTA ion Y^{4-} :
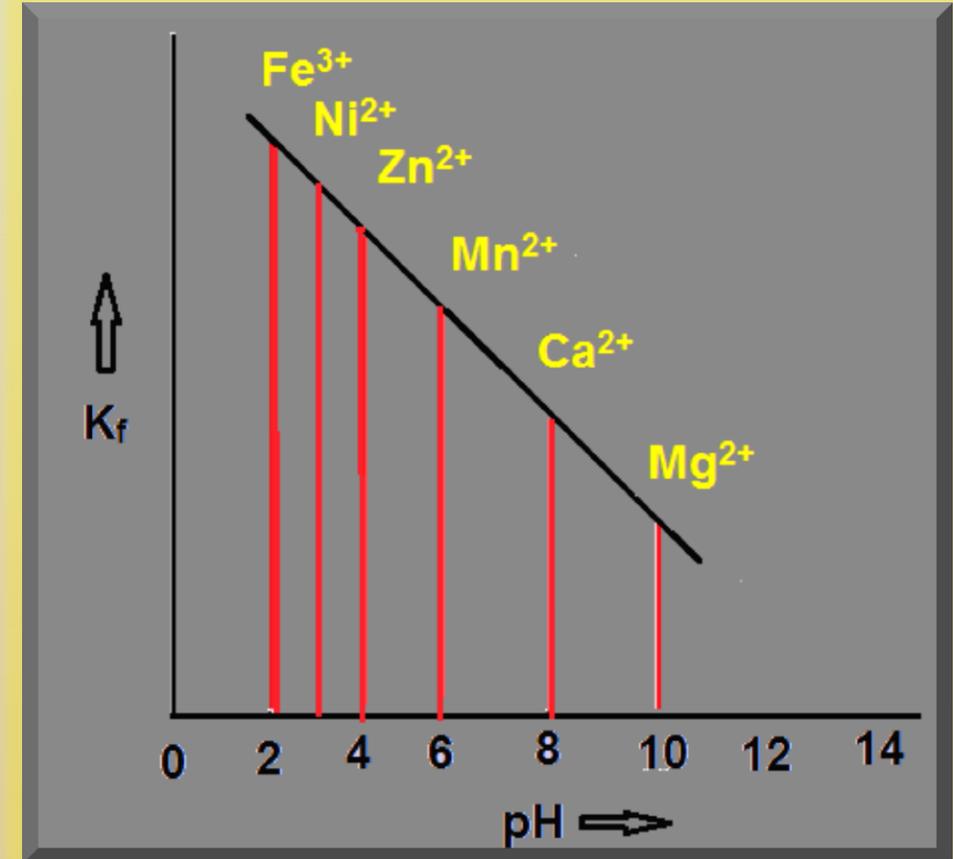
$$M^{n+} + Y^{4-} \leftrightarrow MY^{(n-4)}$$

Titration of metal ions by EDTA

The formation constant K_f can be expressed as such :

$$K_{MY^{(n-4)}} = \frac{[MY^{(n-4)}]}{[M^{n+}][Y^{4-}]} \qquad (2)$$

Substituting for $[Y^{4-}]$ from (1) in (2) we get :

$$K_{MY^{(n-4)}} = \frac{[MY^{(n-4)}]}{[M^{n+}].\alpha_4[T]}$$

By arranging the last equation we get the conditional formation constant $K^{\bullet}_{MY}{}^{(n-4)}$ like this :

$$K_{MY^{(n-4)}} \cdot \alpha_4 = K^{\bullet}_{MY^{(n-4)}} = \frac{[MY^{(n-4)}]}{[M^{n+}][T]}$$

Titration of metal ions by EDTA

This constant is named conditional because it changes with the pH (pH dependent) as noted above. It is used for the calculation of the concentration of the metal ions in the conical flask during titration with EDTA . In other words, it is used for the derivatization of the titration curve of the metal ion by EDTA as we shall see now.

Titration of metal ions by EDTA

Derivatization of titration curve :

The titration curve can be derived by drawing the relationship between the volume of EDTA added from the burett (x – axis) and pM (y – axis) .

Example : Derive the titration curve for the titration of 10 mL 0.1 M Ca^{2+} by 0.2 M EDTA at pH = 10 ? At pH = 10 ,

$$\alpha_4 = 0.35 \ , \ K_{CaY^{2-}} = 5 \times 10^{10}$$

Solution : First we calculate the Conditional Formation Constant :

$$K^*_{CaY^{2-}} = 5 \times 10^{10} \ \times \ 0.35 \approx 1.8 \times 10^{10}$$

Titration of metal ions by EDTA

Then we calculate the volume of EDTA at equivalent point $mL_{eq.p}$:

$mL_{eq.p}$ = (10 X 0.1) / 0.2 = 5 mL

Before the equivalent point : let us say after adding 3 mL of EDTA solution :

$$[Ca^{2+}] = \frac{(10 \ X \ 0.1) - (3 \ X \ 0.2)}{(10 + 3)} = 0.03 \ M$$

$$pCa = -\log 0.03 = 1.5$$

Titration of metal ions by EDTA

At the equivalent point : i.e after adding 5 mL
of EDTA solution :

$$[CaY^{2-}] = \frac{(10 \ X \ 0.1)}{10 + 5} = 0.07 M$$

Note that at equivalent point , the source of T and
Ca^{2+} is the dissociation of the complex CaY^{2-} ,
therefore they are equal (1 : 1 reaction) :

$$T = [Ca^{2+}]$$

$$Ca^{2+} + T \leftrightarrow CaY^{2-}$$

$$K^{\circ}_{CaY^{2-}} = 1.8 \ X 10^{10} = \frac{0.07}{[Ca^{2+}][T]} = \frac{0.07}{[Ca^{2+}]^2}$$

$$[Ca^{2+}] \approx 2 \ X 10^{-5} \ M \ , \ pCa = 4.7$$
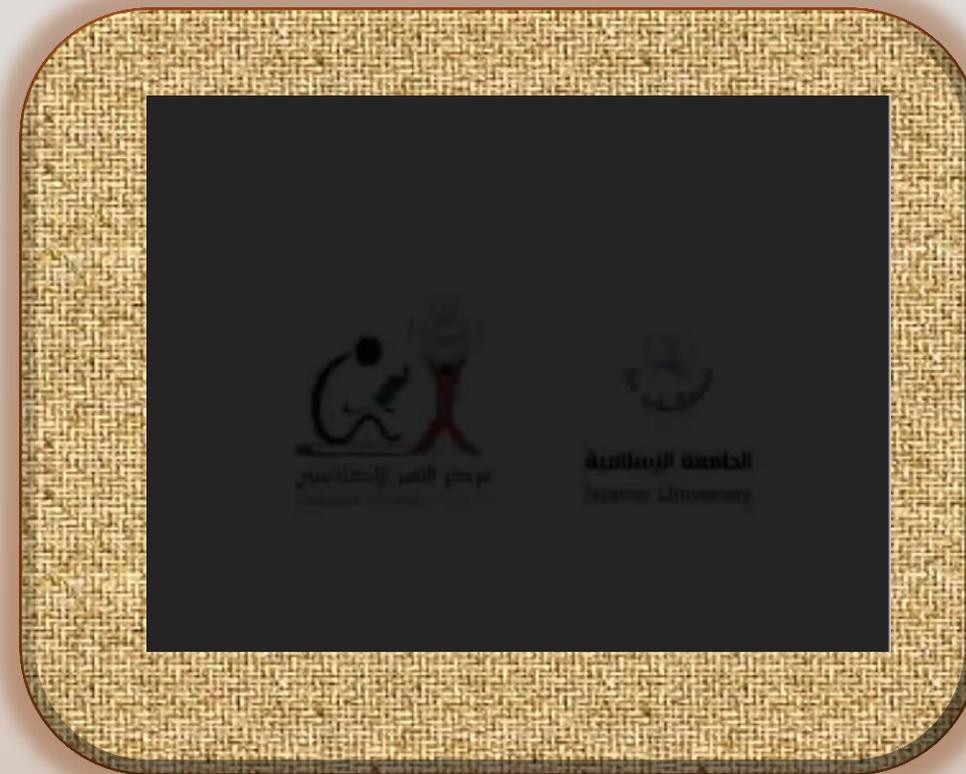
Titration of metal ions by EDTA

After equivalent point : let us say after adding 8 mL of EDTA solution :

$$[CaY^{2-}] = \frac{(10 \, X \, 0.1)}{(10+8)} = 0.06 M \quad , \quad [T] = \frac{(8 \, X \, 0.2) - (10 \, X \, 0.1)}{(10+8)} = 0.03 M$$

$$K^{\circ}{}_{CaY^{2-}} = 1.8 \, X \, 10^{10} = \frac{0.06}{[Ca^{2+}] \, X \, 0.03}$$

$$[Ca^{2+}] = 1.1 X 10^{-11} \, X \, 10^{-11} \, M \quad \therefore \quad pCa \approx 10.0$$

VIDEO
You Tube

Titration of metal ions by EDTA

Effect of auxiliary complexing agent :

We have understood from what previously stated that the titration of metal ions that form weak complexes with the EDTA has to be in basic medium . The problem is that some of these metal ions may precipitate in basic medium as hydroxides. To avoid that we add to the solution of the metal ion a suitable auxiliary complexing agent such as NH_3 . This auxiliary agent forms a complex with the metal ion and prevents its precipitation in the basic medium .

Titration of metal ions by EDTA

The most requirement for the auxiliary agent is that its complex with the metal ion is strong enough to prevent metal precipitation but not stronger than the metal – EDTA complex in order for the following titration reaction to take place :

$$M(NH_3)_4^{2+} \;+\; Y^{4-} \;\leftrightarrow\; MY^{2-} \;+\; 4\;NH_3$$

It is easier for the Y^{4-} to react with free metal ion M^{2+} than to replace NH_3 , therefore , the use of auxiliary complexing agent will slow the reaction between Y^{4-} and $M(NH_3)_4^{2+}$ and makes it less complete .

Titration of metal ions by EDTA

The graph on your right shows this effect which makes the change in pM in the region near the equivalent point small and thereby limit the sharpness of the titration curve . The solution to this problem is to use an amount of the auxiliary agent as little as possible .

Factors affecting titration curve :

The end point is affected by three major factors, the stability constant of the metal ion-EDTA complex , the concentrations of the metal ion and EDTA and the pH of the solution .

pZn

[NH$_3$]

1.0 M

0.1 M

0.001 M

mL$_{EDTA}$

Note the effect of NH$_3$ concentration on magnitude of the change of pZn near the equivalent point of the titration of Zn^{2+} by EDTA using NH$_3$ as auxilary agent
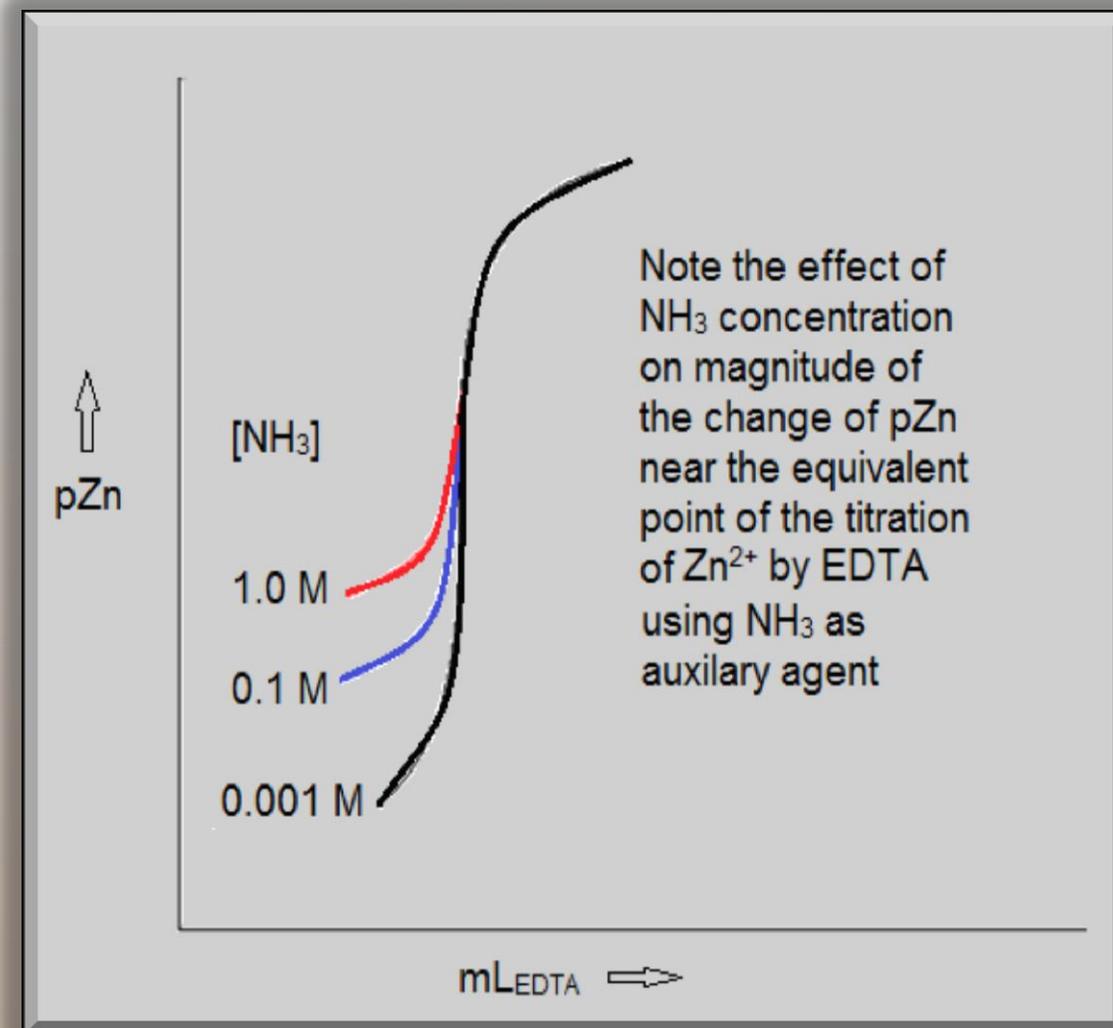
Titration of metal ions by EDTA

As these factors increased , sharper end points are achieved. If either of the three factors has a low value, end points of less sharpness result. For very low stability constants diffuse end points are observed and large errors should be expected . In order to get sharp endpoints, solutions are typically buffered at basic conditions (i.e. pH ≈ 10) . Higher pH is desirable for sharp endpoints and formation of stable metal-EDTA complexes . The graph on your right shows the effect of both the formation constant and the concentration on the shape of the metal- EDTA titration curve .
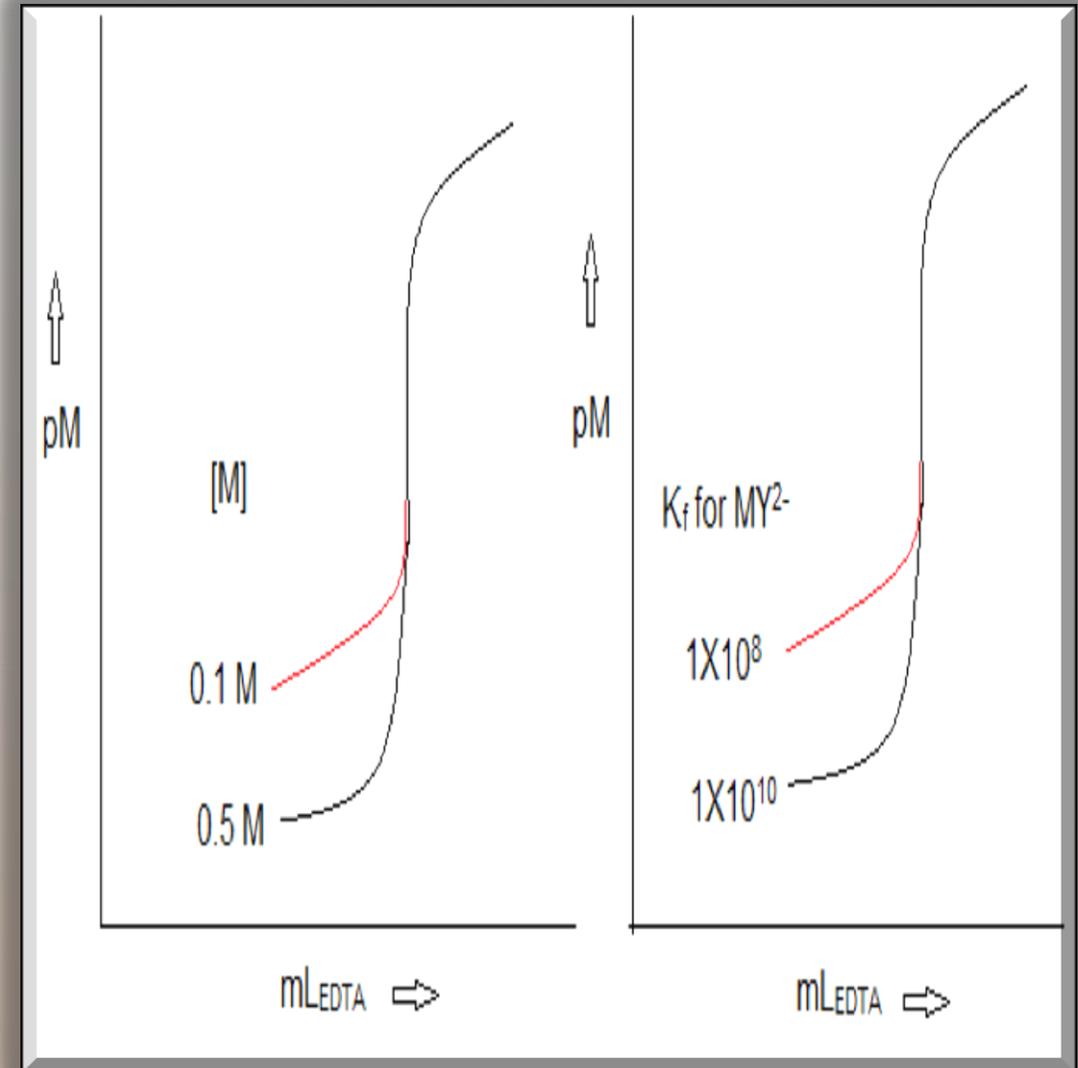
Titration of metal ions by EDTA

Indicators for EDTA Titrations :

The metal indicator is a dye that can act as a complexing agent to complex the metal ion being titrated. The color of the indicator depends on whether it is attached to the metal ion or free.

At the beginning of a titration, little of the analyte metal ion is complexed by the indicator :

$$M \ + \ In \quad \leftrightarrow \ MIn$$

As EDTA is added from burette, the free metal ion M^{n+} concentration decreases but some metal ion

Titration of metal ions by EDTA

remains complexed by the indicator MIn . At the equivalence point the EDTA (Y) has complexed all of the free metal ion and then replaces the indicator from the metal -indicator complex MIn :

$$MIn + Y \rightarrow MY + In$$

Where MIn and In have different colors .
For this reaction to occur the following requirement must meet :

$$K_f (MY) > (10 - 100) \, X \, K_f (MIn)$$
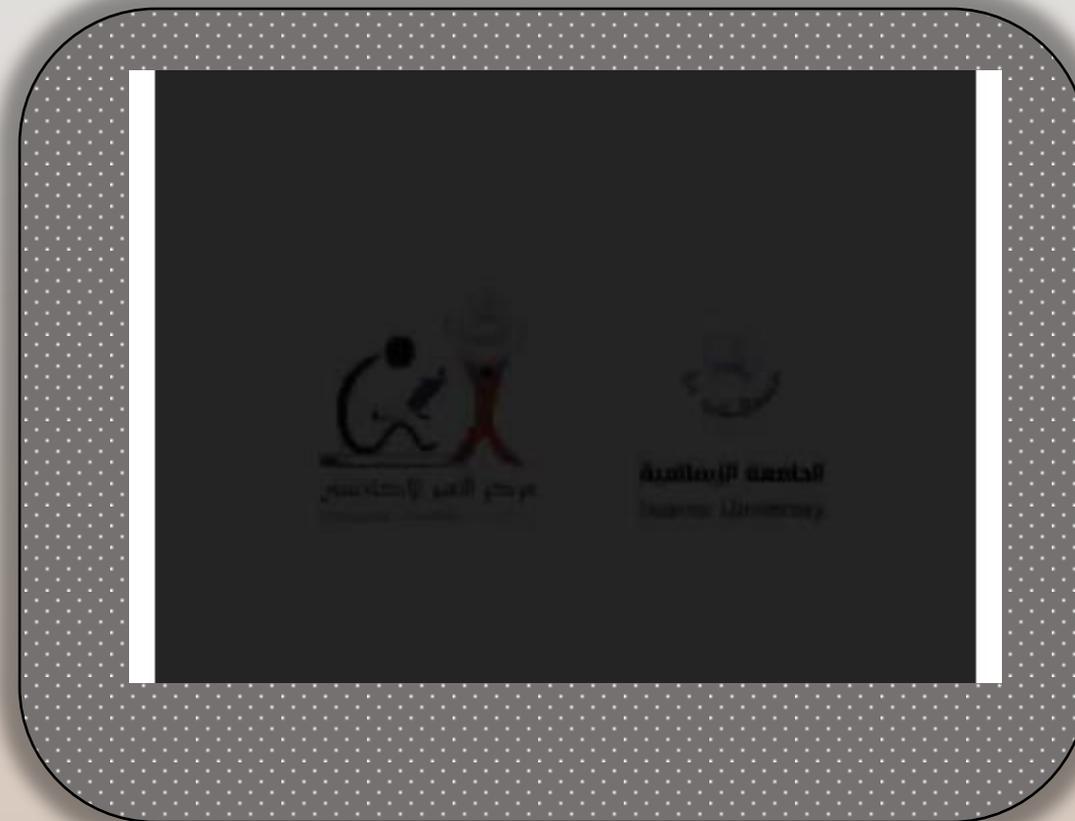
VIDEO
You Tube

Titration of metal ions by EDTA

If >> 100 this may Leeds to earlier equivalent point but if << 10 this may result in late equivalent point . Most metal indicators are also acid-base indicators; the color of the free indicator depends on the pH .

Among the very important indicators that are routinely used, you will encounter two indicators namely Muroxide and Eriochrome Black T (EBT) because of their high selectivity towards specific metal ions.

The rang at which the indicator change its color is the same as discussed with acid – base indicators as we will see in the following example.

Titration of metal ions by EDTA

Example : In the titration of Ni^{2+} by EDTA , calculate the range of the change in the pNi needed to change the color of indicator In. And if pNi = 7.2 at equivalent point does this indicator suit this titration or not ?

$$K^{*}_{NiIn} = 1x10^{8}$$

Solution : As we mentioned in the acid base indicators , the human eye will usually distinguish the change in color when the $\frac{[NiIn]}{[T_{In}]}$ ratio is changed from $\frac{10}{1}$ to $\frac{1}{10}$ thus :

$$K^{*}_{NiIn} = \frac{[NiIn]}{[Ni^{2+}][T_{In}]} = \frac{10}{[Ni^{2+}]X\,1} = 1\,X\,10^{8}$$

Titration of metal ions by EDTA

From this equation we can say that the NiIn color will be predominant when :

$$pNi \leq 7$$

Also :

$$K^*_{NiIn} = \frac{[NiIn]}{[Ni^{2+}][T_{In}]} = \frac{1}{[Ni^{2+}] \, X \, 10} = 1 X 10^8$$

Therefore, the color of In will be predominant when :

$$pNi \geq 9$$

Since at equivalent pNi = 7.2 which is within the range of the indicator (7 – 9) therefore , this indicator is suitable for this titration . Note that pNi is increasing during titration so if pNi at equivalent point is less than 7 , then the indicator will give late equivalent point but if it is more than 9 it will show earlier equivalent point .

Titration of metal ions by EDTA

EDTA Techniques :

EDTA titrations can be performed in many ways :

Direct Titrations :

In direct titrations you simply add an indicator to a solution of the metal ion which is in the conical flask and titrate with EDTA from burette . Before you start the titration you need to check that the pH of the solution gives a good K_f for the metal ion – EDTA complex .You may need to add a suitable auxiliary complexing agent such as ammonia, tartrate, or citrate to block formation of insoluble metal hydroxides . The stability of the metal-auxiliary complex must be less than that of the metal-EDTA complex .

Titration of metal ions by EDTA

Back Titrations :

In a back titration an excess of EDTA is added to the metal ion solution, and the excess EDTA is titrated with a known concentration of a second metal ion (such as Mg).

$$M \; + \; Excess \; Y \; \leftrightarrow \; MY$$

$$Excess \; Y \; + \; Mg \; \leftrightarrow \; MgY$$

The second metal ion must form a weaker complex with EDTA than the analyte ion in order not to displace the analyte ion from its complex with EDTA . For this reason we choose Mg which forms a weak complex with EDTA (K_f MY > K_f MgY) . Back titration are used when the metal ion blocks the indicator or when the metal-EDTA complex reaction is slow , or when the metal precipitates in the absence of EDTA .

Titration of metal ions by EDTA

Displacement Titrations

This is suitable for metal ions that do not have a good indicator . The analyte is treated with an excess of a second metal -EDTA complex e.g MgY complex . The analyte ion (M) displaces the second metal from it's EDTA complex (MgY) and then the liberated second metal is titrated with EDTA .

$$MgY + M \leftrightarrow MY + Mg$$

$$Mg + Y \leftrightarrow MgY$$
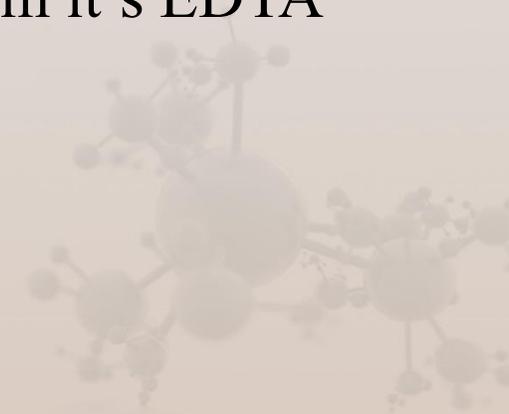
Titration of metal ions by EDTA

A typical displacement titration is the titration of Ag^+ :

$$2\,Ag^+ \;+\; excess\ Ni(CN)_4^{2-} \quad \leftrightarrow \quad 2\,Ag(CN)_2^- \;+\; Ni^{2+}$$

The liberated Ni^{2+} is titrated with EDTA . Note that $Ni(CN)_4^{2-}$ should be stronger than Ni-EDTA complex .

Indirect Titrations
EDTA can be used as a titrant for anions like SO_4^{2-} Where we
add excess Ba^{2+} to SO_4^{2-} solution . The precipitate $BaSO_4$ is filter
and wash .The precipitate , then is boiled in excess EDTA to complex
all the Ba. Back titrate the excess EDTA to determine how much Ba
you have, and that, in turn, tells you how much SO_4^{2-} you have .

Titration of metal ions by EDTA

$$BaSO_4 + \text{known excess } Y^{4-} \leftrightarrow BaY^{2-} + SO_4^{2-}$$

excess Y^{4-} + Mg^{2+} ↔ MgY^{2-}

Or titrate the excess Ba in the filtrate with EDTA .

$$SO_4^{2-} + \text{known excess } Ba^{2+} \leftrightarrow BaSO_4$$

$$\text{excess } Ba^{2+} + Y^{4-} \leftrightarrow BaY^2$$
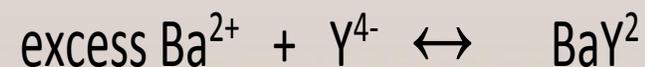
Also CN^- can be indirectly titrated by adding known excess of Ni^{2+} and titrating the excess with EDTA .

known excess Ni^{2+} + 4 CN^- ↔ $Ni(CN)_4^{2-}$

Excess Ni^{2+} + EDTA ↔ Ni-EDTA complex

Note that $Ni(CN)_4^{2-}$ must be stronger than Ni-EDTA complex

.

Titration of metal ions by EDTA

Selectivity of EDTA :

EDTA is not selective ligand where it forms complexes with many metals . However , its selectivity can be improved by :

1- Using chemical masking and demasking agents :

Some metal ions that interfere in EDTA titrations can be masked by addition of a suitable masking agent . For example, cyanide ion can be used to mask certain metals that interfere in the titration of Ca^{2+} or Mg^{2+} with EDTA. In the absence of cyanide, transition metals such as Zn^{2+} and Cd^{2+} interfere by reacting simultaneously with the EDTA. When cyanide ion is added, these cations form stable complexes with cyanide and are prevented from reacting with the EDTA . Note that cyanide does not react with Ca^{2+} or Mg^{2+}.

Titration of metal ions by EDTA

if desired a demasking agent can be added to free the previously masked metal ions so that they can be determined by EDTA. Cd and Zn ions can be demasked by the addition of a mixture consisting from formaldehyde and acetic acid (3 : 1) .

2- pH control : It is possible to titrate two metal ions in the same solution by EDTA if one metal forms with EDTA a stronger complex K_{f1} than the other K_{f2} so the following requirement is met :

$$\frac{K_{f1}}{K_{f2}} \geq 1x10^8$$

Titration of metal ions by EDTA

For example , Fe^{3+} and Ca^{2+} can be both titrated in one solution .The pH is fixed at about 4 or 5 where Fe^{3+} reacts with EDTA but not Ca^{2+} . Then , the pH is raised to 10 , and Ca^{2+} reacts with EDTA.

3- Changing the oxidation state of the metal ion . For example if Fe^{3+} does interfere but not Fe^{2+} , then we can avoid interferences by reducing Fe^{3+} to Fe^{2+} .

4- **Using selective metal indicator .**

5- **Classical separation** by precipitation or extraction …etc.

Titration of metal ions by EDTA

Water Hardens :

Hardness is defined as the concentrations of calcium and magnesium ions expressed in terms of calcium carbonate . These minerals in water can cause some everyday problems. They react with soap and produce a deposit called *soap curd* that remains on the skin and clothes . Hard water may also shorten the life of plumbing and water heaters . When water containing calcium carbonate is heated, a hard scale is formed that can plug pipes and coat heating elements. Scale is also a poor heat conductor. With increased deposits on the unit, heat is not transmitted to the water fast enough and overheating of the metal causes failure . Build-up of deposits will also reduce the efficiency of the heating unit, increasing the cost of fuel.

Water Hardness Scale	
mg/L & ppm	Classification
Less than 17.1	Soft
17.1 - 60	Slightly Hard
60 - 120	Moderately Hard
120 - 180	Hard
Over 180	Very Hard

Titration of metal ions by EDTA

There are two types of water hardness, temporary and permanent . Temporary Hardness is due to the bicarbonate ion, HCO_3^-, being present in the water. This type of hardness can be removed by boiling the water to expel the CO_2, as indicated by the following equation:

$$Ca(HCO_3)_2 \rightarrow \leftarrow CaCO_3 + CO_2 + H_2O$$

Permanent hardness is due to calcium and magnesium nitrates, sulphates, and chlorides etc. This type of hardness cannot be eliminated by boiling.
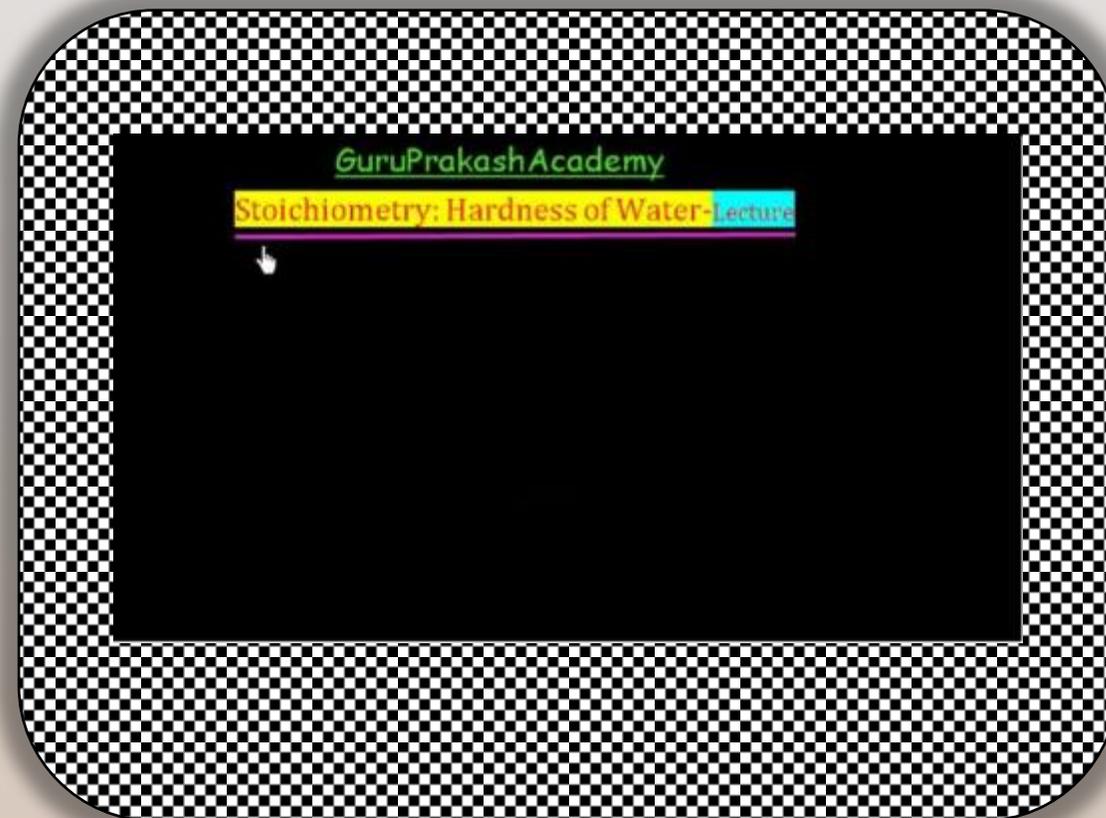

VIDEO
You Tube

Titration of metal ions by EDTA

Estimation of water hardness using EDTA : The Ca - EDTA complex is stronger (higher K_f value) than Mg- EDTA complex but $K_{fCa\ /}\ K_{fMg}\ <<\ 1X10^8$) therefore Ca and Mg can not be titrated in the same solution by EDTA .When adding EDTA from burette to water sample in the conical flask it will react first with Ca and later with Mg .For this reason we use EBT indicator (In) to form a red complex with Mg . At the equivalent point , EDTA (Y) replaces In producing blue color :

$$MgIn\ +\ Y\ \leftrightarrow\ MgY\ +\ In$$

red   blue
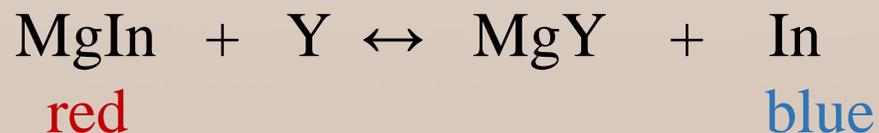
The volume of EDTA in this case will be equivalent to (Ca + Mg) .

Exp. 15: Volumetric Analysis: Total Hardness of Water by EDTA
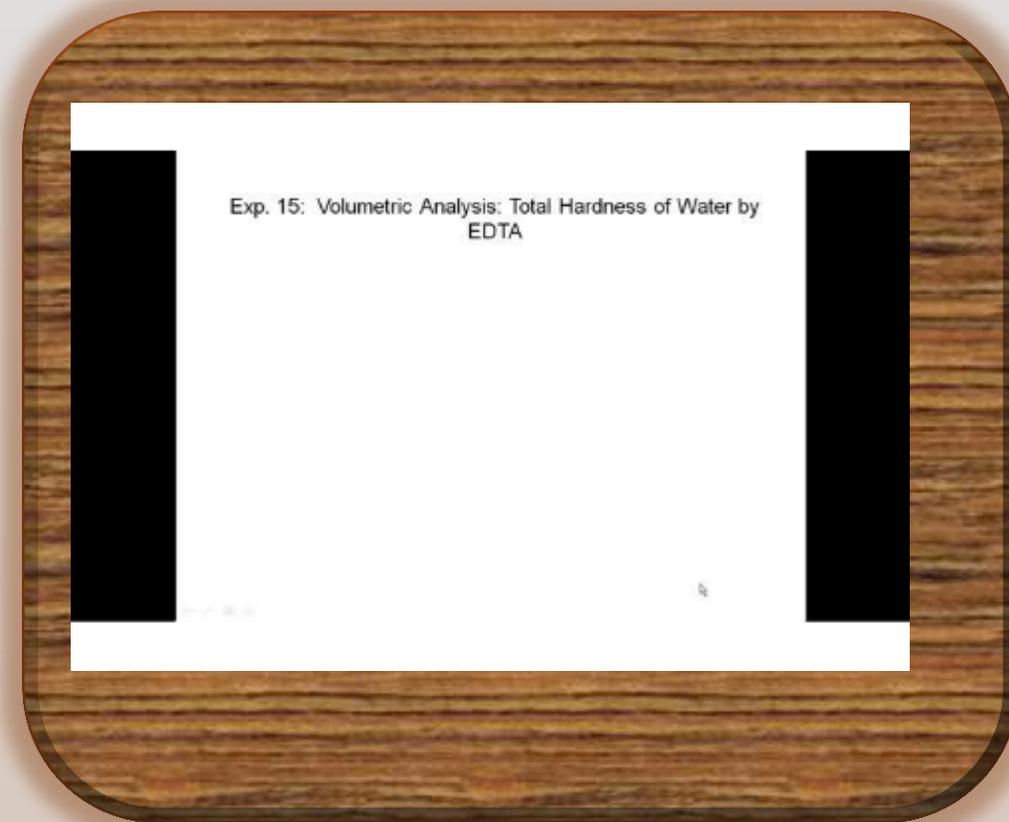
Titration of metal ions by EDTA

Example : 50 mL of water sample is transferred into a conical flask . The pH is fixed at pH = 10 using a suitable buffer solution and some drops of EBT indicator are added . This solution is titrated with 0.01 M EDTA . The blue color appears after adding 30 mL of EDTA solution . Calculate the total hardness as ppm $CaCO_3$?

Solution : The Ca – EDTA and Mg-EDTA reactions both are 1 : 1 so :

(mmoles Ca + mmoles Mg) = mmoles EDTA

Assume that only Ca is present :

mmoles Ca = mmoles EDTA

mmoles Ca = mmoles $CaCO_3$

mmoles $CaCO_3$ = mmoles EDTA

Titration of metal ions by EDTA

$$\frac{Wt._{CaCO_3}\,(mg)}{mw_{CaCO_3}} = \frac{Wt._{CaCO_3}\,(mg)}{100.1} = 30\;X\;0.01 = 0.30$$

$$Wt._{CaCO_3}\,(mg) = 30.03\;(mg\;in\;50\;mL)$$

$$ppm\;CaCO_3 = \frac{30.03\,(mg)}{50\;mL\,X\,10^{-3}\,(L)} = 600.06\;(mg/L)$$

The result indicates that the hardness of this sample of water is very hard .

Introduction

| Why? | How? |
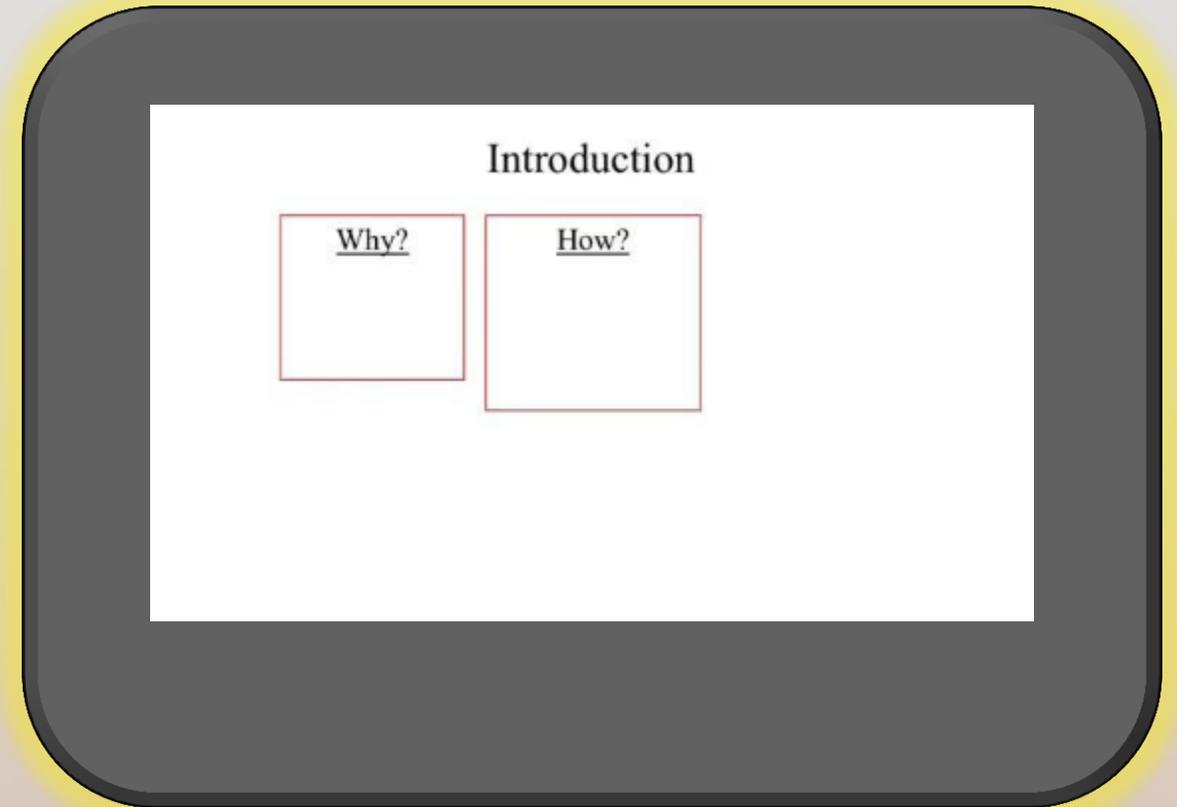
VIDEO
You Tube

Titration of metal ions by EDTA

Example : 100 mL of water sample is transferred into a conical flask . The pH is fixed at 10 and some drops of EBT are added . This solution is titrated with 0.02 M EDTA and the volume at the equivalent point is 35 mL (this volume is equivalent to Ca + Mg) . Another 100 mL of the water sample is transferred into the conical flask and the pH is fixed at 12 where $Mg(OH)_2$ is precipitated . A suitable indicator for Ca is added and the solution is titrated with EDTA solution . The volume of EDTA at the equivalent point is 28 mL (this equivalent to only Ca) . Calculate both ppm $CaCO_3$ and ppm $MgCO_3$?

Titration of metal ions by EDTA

Solution :

$$mmoles \ CaCO_3 \ = \ mmoles \ EDTA \quad (\ R=1/1)$$

$$\frac{Wt_{-CaCO_3}}{mw_{CaCO_3}} = \frac{Wt_{-CaCO_3}}{100.1} = 28 \ X \ 0.02 = 0.56$$

$$Wt_{-CaCO_3} = 56.06 \ (mg \ in \ 100 \ mL \ )$$

$$ppm \ CaCO_3 \ = \ \frac{56.06 \ (mg)}{100 \ X \ 10^{-3} \ (L} = 56.06 \ (mg \ / L)$$

$$mmoles \ MgCO_3 \ = \ mmoles \ EDTA$$

$$\frac{Wt_{-MgCO_3}}{mw_{MgCO_3}} = \frac{Wt_{-MgCO_3}}{84.3} = (\ 35 - 28\ ) \ X \ 0.02 = 0.14$$

$$Wt_{-MgCO_3} = 11.80 \ (mg \ in \ 100 \ mL \ )$$

$$ppm \ MgCO_3 \ = \ \frac{11.80 \ (mg)}{100 \ X \ 10^{-3} \ (L)} = 118 \ (mg \ / L \ )$$

Summary

In this unit we defined the complex formation reactions , discussed the types of ligands particularly of those of chelating agents and review the mechanism of complex formation reactions . The use of EDTA for the titration of metal ions is the core of this unit . We studied the EDTA titration curve calculations and the equivalent point detection . We also investigated the application of EDTA in the determination of water hardness . We hope that the provided pictures , graphs and videos help in understanding the fundamentals of this unit .

Tutorial

Exercise 1 : 50.0 mL 0.0500 M EDTA are added to 50.0 mL 0.030 M Ni^{2+} solution buffered at pH 3.0 .Calculate the molar concentration of Ni^{2+} ? $K_{NiY} = 4.2 \times 10^{18}$; $a_4 = 2.5 \times 10^{-11}$ at pH = 3.0

Answer :

Homework

Answer 1 : Assume very little Ni is uncomplexed:

[NiY] = (50.0 mL x 0.030M) /100.0mL = 0.015M

[excess EDTA] = ((50.0 x 0.050) – (50.0 x 0.030))/100.0 = 0.010 M

$K^*_{NiY} = a_4 K_{NiY} = 4.2 \times 10^{18} \times 2.5 \times 10^{-11} = [NiY]/[Ni][0.010] = 0.015/[Ni][0.010]$

$[Ni] = 1.4 \times 10^{-8}M$

Tutorial

Exercise 2 : When 20 mL 0.1 M of EDTA is added to 50 mL 0.05 M Ca^{2+} , calculate the molar concentration of Ca^{2+} in final solution ? The conditional formation constant for $CaY = 1.8X10^{10}$

Answer :

Our answer next slide

Tutorial

Answer 2 :

$$Ca^{2+} \quad + \quad Y^{4-} \quad \leftrightarrow \quad CaY^{2-} \quad , K^{\bullet}_f = 1.8 X 10^{10}$$

$50 X 0.o5 = 2.5$	$20 X 0.1 = 2.0$	0 (mmole)(I)
0.5	0	2.0 (mmole)(C)
$(0.5 + x)$	x	$(2.0 - x)$ (mmole)(E)
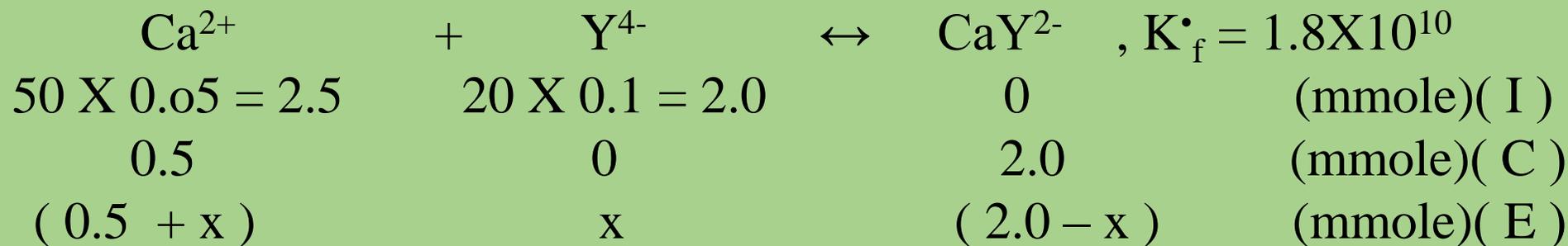
$$K^*f \;=\; 1.8\,X\,10^{10} \;=\; \frac{\dfrac{(2.0 - x)}{(50 + 20)}}{\dfrac{(0.5 + x)}{(50+20)}\,X\,\dfrac{x}{(50+20)}} \;\approx\; \frac{\dfrac{2.0}{70}}{\dfrac{0.5}{70}\,X\,\dfrac{x}{70}}$$

$$\therefore \quad x = 1.6\ X\ 10^{-8}\ mole$$

$$[Ca^{2+}] = \frac{(0.5 + 1.6\,X\,10^{-8})}{70} = 7.1\ X\ 10^{-3}\ M$$

Tutorial

Exercise 3 : 100 mL water sample is transferred into a conical flask . After fixing the pH at 10 and adding EBT indicator, the solution is titrated with 0.1 M EDTA . If the volume of EDTA at the equivalent point is 20 mL , calculate the total hardness of the water sample as ppm $CaCO_3$ (mw = 100) ?

Your answer :

**Our answer
next slide**

Tutorial

Answer 3 :

Note that almost all EDTA reactions with metal ions are I : 1 ratio :

mmoles $CaCO_3$ = mmoles Ca

mmoles Ca = mmoles EDTA = 20 X 0.1 = 2.0 mmoles

mmoles $CaCO_3$ = 2.0 mmoles

$$\frac{Wt.CaCO_3\ (mg)}{mw_{CaCO_3}} = \frac{Wt.CaCO_3\ (mg)}{100} = 2.0\,mmoles$$

$$\therefore \quad wt.CaCO_3\ (mg) = 200\ mg$$

$$ppm = \frac{200\ (mg)}{100\,mL\,X10^{-3}\,(L)} = 2000\ mg/L$$

Tutorial

Exercise 4 : 100 mL of a paint sample containing Ni^{2+} (aw = 58.7) is diluted with a buffer solution pH = 10 . Then 50 mL of 0.05 M EDTA is added . The excess EDTA is titrated with 0.01 M Mg^{2+} solution using EBT indicator . If the volume of Mg^{2+} solution at the equivalent point is 5 mL calculate the concentration of Ni^{2+} in the paint sample in g Ni / L ?

Answer :

Our answer next slide

Tutorial

Answer 4 : This is an example of back titration :

mmoles Ni^{2+} = total mmoles EDTA - excess mmoles EDTA

= total mmoles EDTA – mmoles Mg^2

=   50 x 0.05   -   5 X 0.01   = 2.45 mmoles

$$g \ Ni \ / \ L = \frac{2.45 \, X \, 58.7 \ (mg) \ X \ 10^{-3} \ (g)}{100 \ (mL) \ X \ 10^{-3} \ (L)} = 1.4 \ g \, Ni \ / \ L$$

Tutorial

Exercise 5 : 20 mL of 0.01 M Ca^{2+} is titrated with 0.02 M EDTA solution . Calculate the concentration of Ca^{2+} in the conical flask after adding 5 mL of EDTA solution ? The conditional formation constant for CaY = 1.8 X 10^{10} ?

Answer :

Our answer next slide

Tutorial

Answer 5 : Before the equivalent point :

$V_{eq.p.} = (\ 20\ X\ 0.01\ )\ /\ 0.02\ =\ 10\ mL$

Since the formation constant is very high and this point is before the equivalent point therefore we will assume complete reaction :

$$Ca^{2+}\quad +\quad EDTA\quad \leftrightarrow \quad Ca-EDTA\ \ complex$$

Ca^{2+}	+	EDTA	$\leftrightarrow$	Ca – EDTA complex	
20 X 0.01 = 0.2		5 X 0.02 = 0.1		0	(mmole) (I)
0.1		0		0.1	(mmole)(C)
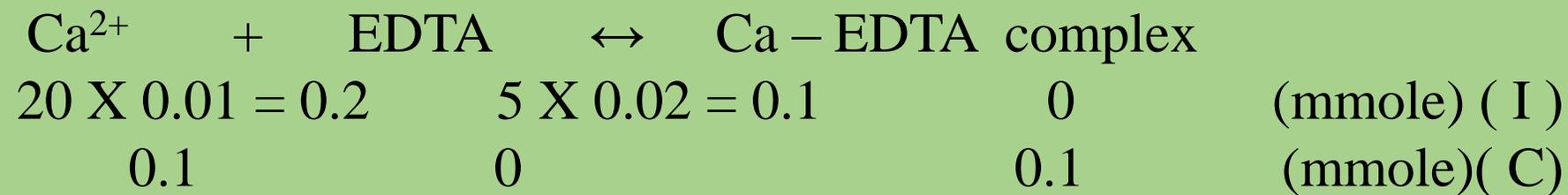
$$[Ca^{2+}]\ =\ \frac{no.of\ \ mmoles}{V_{mL}}\ =\ \frac{0.1}{5+20\ (mL)}\ =\ 4\,X\,10^{-3}\ M$$

Tutorial

Exercise 6 : 20 mL of 0.01 M Ca^{2+} is titrated with 0.02 M EDTA solution . Calculate the concentration of Ca^{2+} in the conical flask after adding 10 mL of EDTA solution ? The conditional formation constant for CaY = 1.8 X 10^{10} ?

Answer :

Our answer next slide

Tutorial

Answer 6 : At the equivalent point :

$$Ca^{2+} \quad + \quad EDTA \quad \leftrightarrow \quad Ca-EDTA \ complex$$

20 X 0.01 = 0.2	10 X 0.02 = 0.2	0	(mmole) (I)
0	0	0.2	(mmole) (C)
x	x	0.2 – x	(mmole) (E)
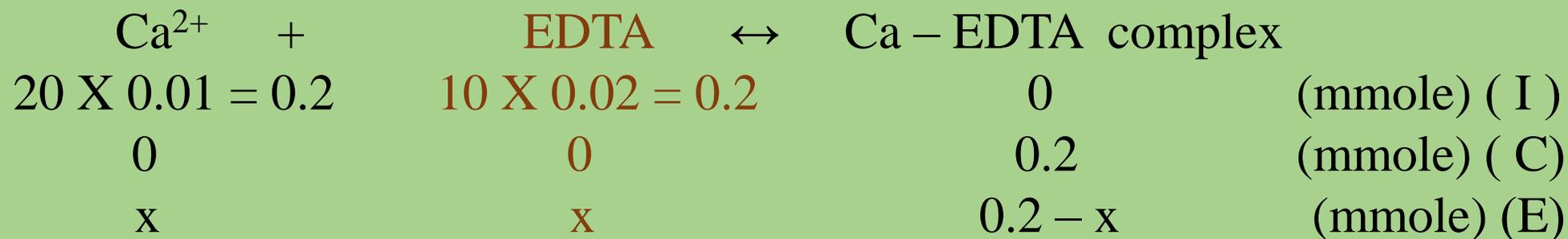
$$K_f = 1.8\,X\,10^{10} = \dfrac{\dfrac{(0.2-x)}{(20+10)}}{\dfrac{x}{(20+10)}\,X\,\dfrac{x}{(20+10)}} \approx \dfrac{\dfrac{(0.2)}{(20+10)}}{\dfrac{x}{(20+10)}\,X\,\dfrac{x}{(20+10)}}$$

$$= \dfrac{6}{x^2} \quad \therefore \quad x = \sqrt{\dfrac{6}{1.8\ X\ 10^{10}}} \approx 1.8\,X\,10^{-5}\ mmole$$

$$[Ca^{2+}] = \dfrac{1.8\ X\ 10^{-5}}{20+10} \approx 6.0\,X\,10^{-7}\ M$$

Tutorial

Exercise 7 : 20 mL of 0.01 M Ca^{2+} is titrated with 0.02 M EDTA solution . Calculate the concentration of Ca^{2+} in the conical flask after adding 20 mL of EDTA solution ? The conditional formation constant for $CaY = 1.8 \times 10^{10}$?

Answer :

Tutorial

Answer 7 : After the equivalent point :

$$Ca^{2+} \quad + \quad EDTA \quad \leftrightarrow \quad Ca-EDTA \text{ complex}$$

20 x 0.01 = 0.2	20 x 0.02 = 0.4	0 (mmole) (I)
0	0.2	0.2 (mmole) (C)
x	0.2 + x	0.2 – x (mmole) (E)
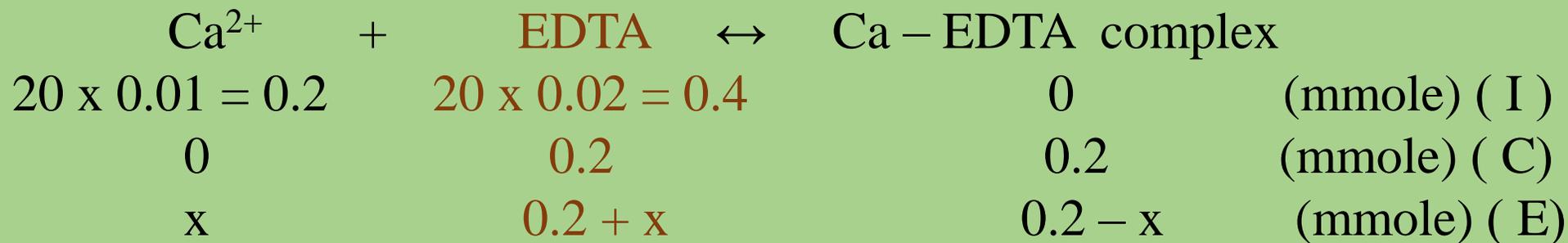
$$K_f = 1.8 \, X \, 10^{10} = \dfrac{\dfrac{(0.2-x)}{(20+20)}}{\dfrac{x}{(20+20)} \, X \, \dfrac{(0.2+x)}{(20+20)}}$$

$$\approx \dfrac{\dfrac{(0.2)}{(20+20)}}{\dfrac{x}{(20+20)} \, X \, \dfrac{(0.2)}{(20+20)}} \qquad \therefore \quad x \approx 2.2 \, X \, 10^{-9} \; mmole$$

$$[Ca^{2+}] = \dfrac{2.2 \, X \, 10^{-9}}{20+20} \approx 5.6 \, X \, 10^{-11} \; M$$

على الراغبين الاستماع الى محاضرات الاستاذ الدكتور/ ابراهيم زامل الزامل باللغة العربية عن هذا الموضوع الرجوع الى الروابط التالية :

المعايرات التي تتضمن تكون مركب معقد

المعايرات التي تتضمن تكون مركب معقد ٢