

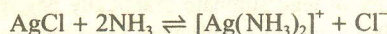
## 2 Solution reactions: fundamental theory

which has a value of  $1.0 \times 10^{-21} \text{ mol}^2 \text{ L}^{-2}$  at the ordinary temperature. By inspection of this expression, and bearing in mind that excess cyanide ion is present, it is evident the silver ion concentration must be very small, so small in fact that the solubility product of silver cyanide is not exceeded.

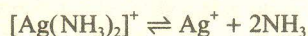
The inverse of equation (2.31) gives us the stability constant or formation constant of the complex ion

$$K = \frac{[\{\text{Ag}(\text{CN})_2\}^-]}{[\text{Ag}^+][\text{CN}^-]^2} = 10^{21} \text{ mol}^{-2} \text{ L}^2 \quad (2.32)$$

Consider now a somewhat different type of complex ion formation, namely the production of a complex ion with constituents other than the common ion present in the solution. This is exemplified by the solubility of silver chloride in ammonia solution. The reaction is



Here again electrolysis, or treatment with hydrogen sulphide, shows that silver ions are present in solution. The dissociation of the complex ion is represented by



and the dissociation constant is given by

$$K_{\text{diss}} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\{\text{Ag}(\text{NH}_3)_2\}^+]} = 6.8 \times 10^{-8} \text{ mol}^2 \text{ L}^{-2}$$

The stability constant  $K = 1/K_{\text{diss}} = 1.5 \times 10^7 \text{ mol}^{-2} \text{ L}^2$

The magnitude of the dissociation constant clearly shows that only a very small silver ion concentration is produced by the dissociation of the complex ion.

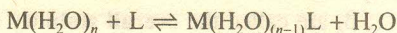
The stability of complex ions varies within very wide limits. It is quantitatively expressed by means of the **stability constant**. The more stable the complex, the greater the stability constant, i.e. the smaller the tendency of the complex ion to dissociate into its constituent ions. When the complex ion is very stable, e.g. the hexacyanoferrate(II) ion  $[\text{Fe}(\text{CN})_6]^{4-}$ , the ordinary ionic reactions of the components are not shown.

The application of complex ion formation in chemical separations depends upon the fact that one component may be transformed into a complex ion which no longer reacts with a given reagent, whereas another component does react. One example concerns the separation of cadmium and copper. Excess of potassium cyanide solution is added to the solution containing the two salts when the complex ions  $[\text{Cd}(\text{CN})_4]^{2-}$  and  $[\text{Cu}(\text{CN})_4]^{3-}$  are formed. Upon passing hydrogen sulphide into the solution containing excess of  $\text{CN}^-$  ions, a precipitate of cadmium sulphide is produced. Despite the higher solubility product of  $\text{CdS}$  ( $1.4 \times 10^{-28} \text{ mol}^2 \text{ L}^{-2}$  as against  $6.5 \times 10^{-45} \text{ mol}^2 \text{ L}^{-2}$  for copper(II) sulphide), the  $\text{CdS}$  is precipitated because the complex cyanocuprate(I) ion has a greater stability constant ( $2 \times 10^{27} \text{ mol}^{-4} \text{ L}^4$  as compared with  $7 \times 10^{10} \text{ mol}^{-4} \text{ L}^4$  for the cadmium complex).

### 2.22 Complexation

The processes of complex ion formation can be described by the general term **complexation**. A complexation reaction with a metal ion involves the replacement of one or more of the coordinated solvent molecules by other nucleophilic groups. The groups bound to the central ion are called ligands and in aqueous solution the reaction can be represented by the equation





Here the ligand (L) can be either a neutral molecule or a charged ion, and successive replacement of water molecules by other ligand groups can occur until the complex  $ML_n$  is formed;  $n$  is the coordination number of the metal ion and represents the maximum number of monodentate ligands that can be bound to it.

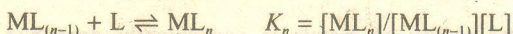
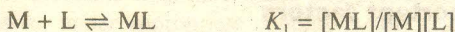
Ligands may be conveniently classified on the basis of the number of points of attachment to the metal ion. Thus simple ligands, such as halide ions or the molecules  $H_2O$  or  $NH_3$ , are **monodentate**, i.e. the ligand is bound to the metal ion at only one point by the donation of a lone pair of electrons to the metal. But when the ligand molecule or ion has two atoms, each of which has a lone pair of electrons, then the molecule has two donor atoms and it may be possible to form two coordinate bonds with the same metal ion; this is called a **bidentate** ligand. An example is the tris(ethylenediamine)cobalt(III) complex,  $[Co(en)_3]^{3+}$ . In this six-coordinate octahedral complex of cobalt(III), each of the bidentate ethylenediamine (1,2-diaminoethane) molecules is bound to the metal ion through the lone pair electrons of the two nitrogen atoms. This results in the formation of three five-membered rings, each including the metal ion; the process of ring formation is called **chelation**.

A **multidentate** ligand contains more than two coordinating atoms per molecule; for example, 1,2-diaminoethanetetra-acetic acid (ethylenediaminetetra-acetic acid, EDTA)\* has two donor nitrogen atoms and four donor oxygen atoms in the molecule, so it can be hexadentate.

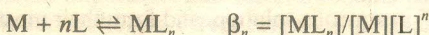
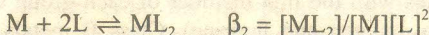
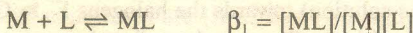
It has been assumed that the complex species does not contain more than one metal ion, but under appropriate conditions it is possible to form a binuclear complex, i.e. one containing two metal ions, or even a polynuclear complex, containing more than two metal ions. Thus interaction between  $Zn^{2+}$  and  $Cl^-$  ions may result in the formation of binuclear complexes, e.g.  $[Zn_2Cl_6]^{2-}$ , in addition to simple species such as  $ZnCl_2$  and  $ZnCl_4^{2-}$ . The formation of bi- and polynuclear complexes will clearly be favoured by a high concentration of the metal ion; if the metal ion is present as a trace constituent of a solution, polynuclear complexes are unlikely to be formed.

## 2.23 Stability of complexes

The thermodynamic stability of a species is a measure of the extent to which this species will be formed from other species under certain conditions, provided that the system is allowed to reach equilibrium. Consider a metal ion M in solution together with a monodentate ligand L, then the system may be described by the following stepwise equilibria; for convenience, coordinated water molecules are not shown.



The equilibrium constants  $K_1, K_2, \dots, K_n$  are called **stepwise stability constants**. An alternative way of expressing the equilibria is as follows:



\* 1,2-Bis[bis(carboxymethyl)amino]ethane.



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The equilibrium constants  $\beta_1, \beta_2, \dots, \beta_n$  are called the **overall stability constants** and are related to the stepwise stability constants by the general expression

$$\beta_n = K_1 K_2 \dots K_n$$

In the above equilibria it has been assumed that no insoluble products are formed nor any polynuclear species.

A knowledge of stability constant values is of considerable importance in analytical chemistry, since they provide information about the concentrations of the various complexes formed by a metal in specified equilibrium mixtures; this is invaluable in the study of complexometry and various analytical separation procedures such as solvent extraction, ion exchange and chromatography.<sup>2,3</sup>

### 2.24 Metal ion buffers

Consider the equation for complex formation



and assume that ML is the only complex to be formed by the particular system. The equilibrium constant expression can be rearranged to give

$$[M] = (1/K)[ML]/[L]$$

$$\log [M] = \log (1/K) + \log \frac{[ML]}{[L]}$$

$$pM = \log K - \log \frac{[ML]}{[L]}$$

This shows that the pM value of the solution is fixed by the value of  $K$  and the ratio of complex ion concentration to that of the free ligand. If more of  $M$  is added to the solution, more complex will be formed and the value of pM will not change appreciably. Likewise, if  $M$  is removed from the solution by some reaction, some of the complex will dissociate to restore the value of pM. This recalls the behaviour of buffer solutions encountered with acids and bases (Section 2.11), and by analogy, the complex–ligand system may be called a **metal ion buffer**.

### 2.25 Complex stability: important factors

#### Complexing ability of metals

The relative complexing ability of metals is conveniently described in terms of the **Schwarzenbach classification**, which is broadly based upon the division of metals into class A and class B Lewis acids, i.e. electron acceptors. Class A metals are distinguished by an order of affinity (in aqueous solution) towards the halogens  $F^- \gg Cl^- > Br^- > I^-$ , and form their most stable complexes with the first member of each group of donor atoms in the periodic table (i.e. nitrogen, oxygen and fluorine). Class B metals coordinate much more readily with  $I^-$  than with  $F^-$  in aqueous solution, and form their most stable complexes with the second (or heavier) donor atom from each group (i.e. P, S, Cl). The Schwarzenbach classification defines three categories of metal ion acceptors:



**Cations with noble gas configurations** The alkali metals, alkaline earths and aluminium belong to this group which exhibit class A acceptor properties. Electrostatic forces predominate in complex formation, so interactions between small ions of high charge are particularly strong and lead to stable complexes.

**Cations with completely filled d subshells** Typical of this group are copper(I), silver(I) and gold(I), which exhibit class B acceptor properties. These ions have high polarising power and the bonds formed in their complexes have appreciable covalent character.

**Transition metal ions with incomplete d subshells** In this group both class A and class B tendencies can be distinguished. The elements with class B characteristics form a roughly triangular group within the periodic table, with the apex at copper and the base extending from rhenium to bismuth. To the left of this group, elements in their higher oxidation states tend to exhibit class A properties; whereas to the right of the group, the higher oxidation states of a given element have a greater class B character.

The concept of **hard and soft acids and bases** is useful in characterising the behaviour of class A and class B acceptors. A soft base may be defined as one in which the donor atom is of high polarisability and low electronegativity, is easily oxidised, or is associated with vacant, low-lying orbitals. These terms describe, in different ways, a base in which the donor atom electrons are not tightly held, but are easily distorted or removed. Hard bases have the opposite properties, i.e. the donor atom is of low polarisability and high electronegativity, is difficult to reduce, and is associated with vacant orbitals of high energy which are inaccessible.

On this basis, class A acceptors prefer to bind to hard bases, e.g. with N, O and F donor atoms, whereas class B acceptors prefer to bind to the softer bases, e.g. P, As, S, Se, Cl, Br, I donor atoms. Examination of the class A acceptors shows them to have the following distinguishing features: small size, high positive oxidation state, and the absence of outer electrons which are easily excited to higher states. These are all factors which lead to low polarisability, and such acceptors are called hard acids. Class B acceptors have one or more of the following properties: low positive or zero oxidation state, large size, and several easily excited outer electrons (for metals these are the d electrons). These are all factors which lead to high polarisability, and class B acids may be called soft acids.

Here is a general principle for correlating the complexing ability of metals: hard acids tend to associate with hard bases and soft acids with soft bases. But do not regard it as exclusive; under appropriate conditions soft acids may complex with hard bases or hard acids with soft bases.

### Characteristics of the ligand

Some characteristics of the ligand which are generally recognised as influencing the stability of its complexes are (i) its basic strength, (ii) its chelating properties (if any) and (iii) steric effects. From the viewpoint of analytical applications, the chelating effect is of paramount importance and therefore merits particular attention.

The term **chelate effect** refers to the fact that a chelated complex, i.e. one formed by a bidentate or a multidentate ligand, is more stable than the **corresponding** complex with monodentate ligands: the greater the number of points of attachment of ligand to the metal ion, the greater the stability of the complex. Thus the complexes



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formed by the nickel(II) ion with (a) the monodentate  $\text{NH}_3$  molecule, (b) the bidentate ethylenediamine (1,2-diaminoethane), and (c) the hexadentate ligand 'penten'  $\{(\text{H}_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2)_2\}$  show an overall stability constant of  $3.1 \times 10^8$  for the complex of ligand (a), which is increased by a factor of about  $10^{10}$  for the complex of ligand (b), and is approximately 10 times greater still for the complex of ligand (c). The most common steric effect is inhibition of complex formation owing to the presence of a large group either attached to or in close proximity to the donor atom.

A further factor which must also be taken into consideration from the viewpoint of the analytical applications of complexes and of complex formation reactions is the rate of reaction. To be analytically useful, the reaction should usually be rapid. An important classification into labile and inert is based upon the rate at which complexes undergo substitution reactions. A **labile** complex completes nucleophilic substitution within the time required to mix the reagents. For example, when excess aqueous ammonia is added to an aqueous solution of copper(II) sulphate, the change in colour from pale blue to deep blue is instantaneous; the rapid replacement of water molecules by ammonia indicates that the  $\text{Cu(II)}$  ion forms kinetically labile complexes. An **inert** complex undergoes slow substitution reactions, i.e. reactions with half-times of the order of hours or even days at room temperature. Thus the  $\text{Cr(III)}$  ion forms kinetically inert complexes, so that the replacement of water molecules coordinated to  $\text{Cr(III)}$  by other ligands is a very slow process at room temperature.

Kinetic inertness or lability is influenced by many factors, but the following general observations form a convenient guide to the behaviour of the complexes of various elements:

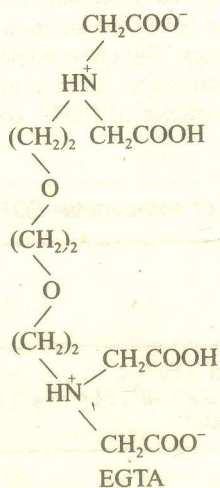
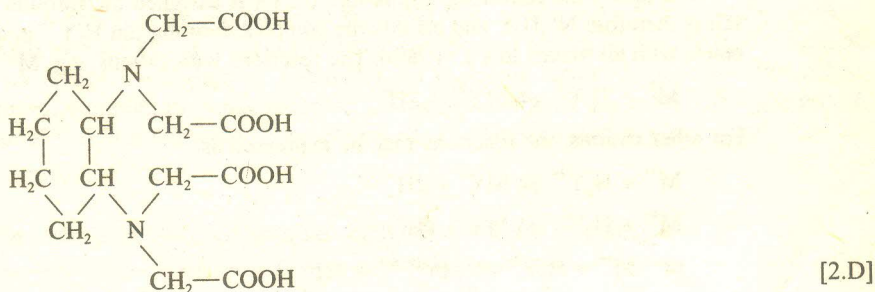
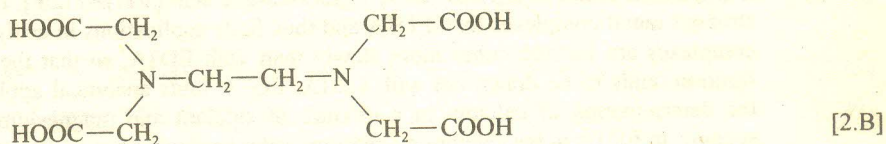
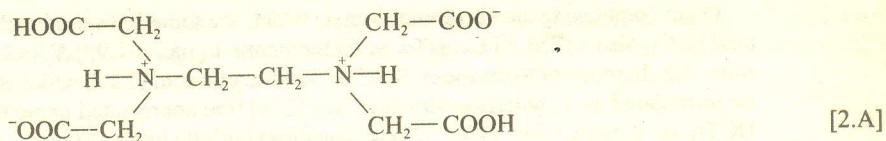
1. Main group elements usually form labile complexes.
2. With the exception of  $\text{Cr(III)}$  and  $\text{Co(III)}$ , most first-row transition elements form labile complexes.
3. Second- and third-row transition elements tend to form inert complexes.

For a full discussion of the topics introduced in this section, consult a textbook of inorganic chemistry<sup>[4]</sup> or a textbook dealing with complexes.<sup>[2]</sup>

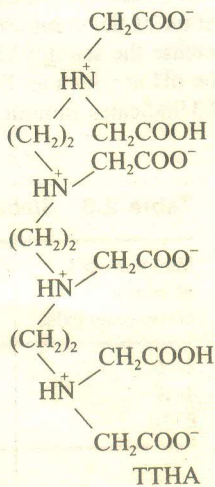
### 2.26 Complexones

Formation of a single complex species rather than the stepwise production of several species will clearly simplify complexometric titrations and facilitate the detection of end points. Schwarzenbach<sup>[2]</sup> realised that the ethanoate ion is able to form ethanoato complexes of low stability with nearly all polyvalent cations, and that if this property could be reinforced by the chelate effect, then much stronger complexes would be formed by most metal cations. He found that the aminopolycarboxylic acids are excellent complexing agents; the most important of them is 1,2-diaminoethanetetra-acetic acid (ethylenediaminetetra-acetic acid). Formula [2.A] is preferred to formula [2.B] since it has been shown from measurements of the dissociation constants that two hydrogen atoms are probably held in the form of zwitterions. The values of  $\text{p}K$  are respectively  $\text{p}K_1 = 2.0$ ,  $\text{p}K_2 = 2.7$ ,  $\text{p}K_3 = 6.2$ , and  $\text{p}K_4 = 10.3$  at  $20^\circ\text{C}$ . These values suggest that it behaves as a dicarboxylic acid with two strongly acidic groups and that there are two ammonium protons; the first of them ionises in the pH region of about 6.3 and the second of them at a pH of about 11.5. Various trivial names are used for ethylenediaminetetra-acetic acid and its sodium salts, and these include Trilon B, Complexone III, Sequestrene, Versene and Chelation 3; the disodium salt is most widely employed in titrimetric analysis. To avoid the constant use of the long name, the abbreviation EDTA is used for the disodium salt.





[2.E]



[2.F]

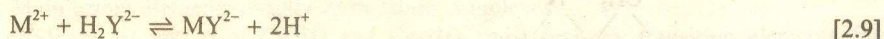


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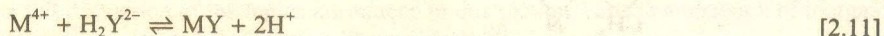
Other complexing agents (complexones) which are sometimes used include nitrilotriacetic acid [2.C], also called NITA, NTA or Complexone I ( $pK_1 = 1.9$ ,  $pK_2 = 2.5$  and  $pK_3 = 9.7$ ); *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetra-acetic acid (2.D), which should presumably be formulated as a zwitterion structure like [2.A] (the abbreviated name is CDTA, DCyTA, DCTA or Complexone IV); 2,2'-ethylenedioxybis{ethyliminodi(acetic acid)} [2.E], also known as ethylene glycolbis(2-aminoethyl ether)-*N,N,N',N'*-tetra-acetic acid (EGTA); and triethylenetetramine-*N,N,N',N'',N''',N'''*-hexa-acetic acid (TTHA) [2.F]. CDTA often forms stronger metal complexes than EDTA and thus finds applications in analysis, but the metal complexes are formed rather more slowly than with EDTA, so that the end point of the titration tends to be drawn out with CDTA. EGTA finds analytical application mainly in the determination of calcium in a mixture of calcium and magnesium and is probably superior to EDTA in the calcium/magnesium water hardness titration (Section 10.76). TTHA forms 1 : 2 complexes with many trivalent cations and with some divalent metals, and can be used for determining the components of mixtures of certain ions without the use of masking agents (Section 10.64).

However, EDTA has the widest general application in analysis because of its powerful complexing action and commercial availability. The spatial structure of its anion, which has six donor atoms, enables it to satisfy the coordination number of 6 frequently encountered among the metal ions and to form strainless five-membered rings on chelation. The resulting complexes have similar structures but differ from one another in the charge they carry.

To simplify the following discussion, EDTA is assigned the formula  $H_4Y$ ; the disodium salt is therefore  $Na_2H_2Y$  and affords the complex-forming ion  $H_2Y^{2-}$  in aqueous solution; it reacts with all metals in a 1 : 1 ratio. The reactions with cations, e.g.  $M^{2+}$ , may be written as



For other cations, the reactions may be expressed as



One mole of the complex-forming  $H_2Y^{2-}$  reacts in all cases with one mole of the metal ion, and in each case two moles of hydrogen ion are formed. Reaction [2.12] shows that the dissociation of the complex will be governed by the pH of the solution; lowering the pH will decrease the stability of the metal-EDTA complex. The more stable the complex, the lower the pH at which an EDTA titration of the metal ion in question may be carried out. Table 2.3 indicates minimum pH values for the existence of EDTA complexes of some

**Table 2.3** Stability with respect to pH of some metal-EDTA complexes

Minimum pH at which complexes exist	Selected metals
1-3	$Zr^{4+}$ , $Hf^{4+}$ , $Th^{4+}$ , $Bi^{3+}$ , $Fe^{3+}$
4-6	$Pb^{2+}$ , $Cu^{2+}$ , $Zn^{2+}$ , $Co^{2+}$ , $Ni^{2+}$ , $Mn^{2+}$ , $Fe^{2+}$ , $Al^{3+}$ , $Cd^{2+}$ , $Sn^{2+}$
8-10	$Ca^{2+}$ , $Sr^{2+}$ , $Ba^{2+}$ , $Mg^{2+}$



selected metals. In general, EDTA complexes with metal ions of the charge number 2 are stable in alkaline or slightly acidic solution, whereas complexes with ions of charge numbers 3 or 4 may exist in solutions of much higher acidity.

## 2.27 Stability constants of EDTA complexes

The stability of a complex is characterised by the stability constant (or formation constant)  $K$ :



$$K = [(MY)^{(n-4)+}] / [M^{n+}][Y^{4-}] \quad (2.33)$$

Some values for the stability constants (expressed as  $\log K$ ) of metal-EDTA complexes are collected in Table 2.4; they apply to a medium of ionic strength  $I = 0.1$  at  $20^\circ\text{C}$ . In equation (2.33) only the fully ionised form of EDTA, i.e. the ion  $Y^{4-}$ , has been taken into account, but at low pH values the species  $HY^{3-}$ ,  $H_2Y^{2-}$ ,  $H_3Y^{-}$  and even undissociated  $H_4Y$  may well be present; in other words, only a part of the EDTA uncombined with metal may be present as  $Y^{4-}$ . Furthermore, in equation (2.33) the metal ion  $M^{n+}$  is assumed to be uncomplexed, i.e. in aqueous solution it is simply present as the hydrated ion. If, however, the solution also contains substances other than EDTA which can complex with the metal ion, then the whole of this ion uncombined with EDTA may no longer be present as the simple hydrated ion. Thus, in practice, the stability of metal-EDTA complexes may be altered (a) by variation in pH and (b) by the presence of other complexing agents. The stability constant of the EDTA complex will then be different from the value recorded for a specified pH in pure aqueous solution; the value recorded for the new conditions is called the **apparent** or **conditional stability constant**. Their effects need to be examined in some detail.

**Table 2.4** Stability constants (as  $\log K$ ) of metal-EDTA complexes

Mg <sup>2+</sup>	8.7	Zn <sup>2+</sup>	16.7	La <sup>3+</sup>	15.7
Ca <sup>2+</sup>	10.7	Cd <sup>2+</sup>	16.6	Lu <sup>3+</sup>	20.0
Sr <sup>2+</sup>	8.6	Hg <sup>2+</sup>	21.9	Sc <sup>3+</sup>	23.1
Ba <sup>2+</sup>	7.8	Pb <sup>2+</sup>	18.0	Ga <sup>3+</sup>	20.5
Mn <sup>2+</sup>	13.8	Al <sup>3+</sup>	16.3	In <sup>3+</sup>	24.9
Fe <sup>2+</sup>	14.3	Fe <sup>3+</sup>	25.1	Th <sup>4+</sup>	23.2
Co <sup>2+</sup>	16.3	Y <sup>3+</sup>	18.2	Ag <sup>+</sup>	7.3
Ni <sup>2+</sup>	18.6	Cr <sup>3+</sup>	24.0	Li <sup>+</sup>	2.8
Cu <sup>2+</sup>	18.8	Ce <sup>3+</sup>	15.9	Na <sup>+</sup>	1.7

### pH effect

The apparent stability constant at a given pH may be calculated from the ratio  $K/\alpha$ , where  $\alpha$  is the ratio of the total uncombined EDTA (in all forms) to the form  $Y^{4-}$ . Thus  $K_H$ , the apparent stability constant for the metal-EDTA complex at a given pH, can be calculated from the expression

$$\log K_H = \log K - \log \alpha \quad (2.34)$$



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The factor  $\alpha$  can be calculated from the known dissociation constants of EDTA, and since the proportions of the various ionic species derived from EDTA will depend upon the pH of the solution,  $\alpha$  will also vary with pH. A plot of  $\log \alpha$  against pH shows a variation of  $\log \alpha = 18$  at pH = 1 to  $\log \alpha = 0$  at pH = 12; such a curve is very useful for dealing with calculations of apparent stability constants. Thus, from Table 2.4  $\log K$  of the EDTA complex of the  $\text{Pb}^{2+}$  ion is 18.0, and from a graph of  $\log \alpha$  against pH it is found that  $\log \alpha = 7$  at a pH of 5.0. Hence, from equation (2.34), at a pH of 5.0 the lead-EDTA complex has an apparent stability constant given by

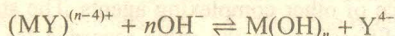
$$\log K_H = 18.0 - 7.0 = 11.0$$

Carrying out a similar calculation for the EDTA complex of the  $\text{Mg}^{2+}$  ion ( $\log K = 8.7$ ), for the same pH (5.0), it is found that

$$\log K_H(\text{Mg(II)-EDTA}) = 8.7 - 7.0 = 1.7$$

These results imply that, at the specified pH, the magnesium complex is appreciably dissociated whereas the lead complex is stable; so titration of an  $\text{Mg(II)}$  solution with EDTA at this pH will be unsatisfactory, but titration of the lead solution under the same conditions will be quite feasible. In practice, for a metal ion to be titrated with EDTA at a stipulated pH, the value of  $\log K_H$  should be greater than 8 when a metallochromic indicator is used.

The value of  $\log \alpha$  is small at high pH values, hence the larger values of  $\log K_H$  are found with increasing pH. However, increasing the pH of the solution will increase the tendency to form slightly soluble metallic hydroxides:



The extent of hydrolysis of  $(\text{MY})^{(n-4)+}$  depends upon the characteristics of the metal ion; it is largely controlled by the solubility product of the metallic hydroxide and, of course, the stability constant of the complex. Thus iron(III) is precipitated as hydroxide ( $K_{\text{sol}} = 1 \times 10^{-36}$ ) in basic solution; but nickel(II), for which the relevant solubility product is  $6.5 \times 10^{-18}$ , remains complexed. Clearly the use of excess EDTA will tend to reduce the effect of hydrolysis in basic solutions. It follows that, for each metal ion, there exists an optimum pH which will give rise to a maximum value for the apparent stability constant.

### The effect of other complexing agents

If another complexing agent (say  $\text{NH}_3$ ) is also present in the solution then in equation (2.33) the concentration  $[\text{M}^{n+}]$  will be reduced, owing to complexation of the metal ions with ammonia molecules. It is convenient to indicate this reduction in effective concentration by introducing a factor  $\beta$ , defined as the ratio of the sum of the concentrations of all forms of the metal ion not complexed with EDTA to the concentration of the simple (hydrated) ion. The apparent stability constant of the metal-EDTA complex, taking into account the effects of both pH and the presence of other complexing agents, is then given by

$$\log K_{\text{HZ}} = \log K - \log \alpha - \log \beta \quad (2.35)$$

## 2.28 Electrode potentials

When a metal is immersed in a solution containing its own ions, say, zinc in zinc sulphate solution, a potential difference is established between the metal and the solution. The potential difference  $E$  for an electrode reaction

