Complex forming reactions

and complexometry

Gábor Galbács

Complex forming reactions

Mixing of salt solutions usually does not result in any observable changes. The properties of the species originally present persist and no new properties can be detected (e.g. no precipitate, no color change, etc.). Examples:

$NaCl + KNO_3$ or $ZnSO_4 + MgCl_2$

But it is not always the case… see, for instance:

$FeCl_3$ ***yellow***	+	KF ***colorless***	→	? ***colorless***
$CoCl_2$ ***pink***	+	KSCN ***colorless***	→	? ***blue***

plus, metal ions are also hidden from their usual reactions…

Complex forming reactions

In these cases, the reaction between the ions resulted in the formation of ***complex ions*** (compounds):

$$Fe^{3+} + 6\ F^- = [FeF_6]^{3-}$$

$$Co^{2+} + SCN^- = [Co(SCN)]^+$$

Complex compounds contain a ***central metal ion*** surrounded by other ion(s) or molecule(s) called ***ligands***. Ligands can be ions or neutral molecules (e.g. ammonia, water).

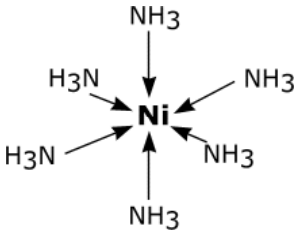
The driving force behind the formation of complex ions is that certain atoms in the ligands donate one of their free electron pairs to the central metal ion (***donor atoms***), to fill its valence shell. This is essentially an acid-base reaction according to Lewis.

This bond type is called ***coordinative bond.***

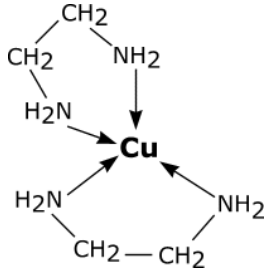
Complex forming reactions

The number of electron pairs a metal ion is capable of receiving depends on it radius and electron configuration (e.g. the M shell of Si^{4+} can accept a total of 18 electrons) and also the structure of the ligand. This number is called the ***coordination number***.

If there is only one donor atom in the ligand, it is called ***monodentate***, if two then it is ***bidentate***, etc. Examples:



coordination number: 6
monodentate ligands



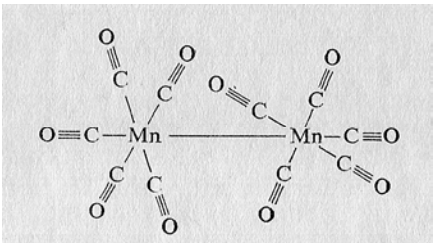
coordination number: 4
bidentate ligands

Complex forming reactions

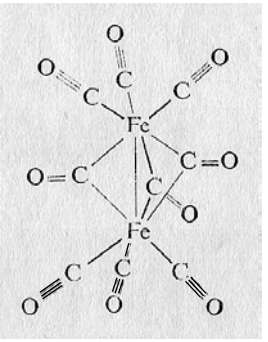
If there is more than one type of ligand present in a complex, it is called a ***mixed complex***. Example:

$$[Fe(H_2O)_4(SCN)_2]^+$$

In some complexes, there may be even more than one central metal ion; these are ***multi center complexes.*** Examples:



$Mn_2(CO)_{10}$



$Fe_2(CO)_9$

Nomenclature of complex compounds

The formula of a complex ion is put in square brackets, and it is placed at the front if its charge is positive, or at the back if negative. Examples:

$$[Co(NH_3)_6]Cl_3 \qquad K_3[Fe(CN)_6]$$

The name of ***complex cations*** starts with the greek form of the coordination number (mono-, di-, tri-, etc.), and then comes the name of the ligand (an –o tag is also appended to it if the ligand itself has charge), plus the name of the metal ion with its valence state indicated. Examples:

$[Ag(NH_3)_2]^+$	**diammine-silver (I) ion**
$[Ni(H_2O)_6]^{2+}$	**hexaaqua-nickel (II) ion**
$[CuCl_4]^{2-}$	**tetrachloro-copper (II) ion**

Nomenclature of complex compounds

Naming of ***complex anions*** is similar, but with an -ate ending added to the name of the metal ion. Examples:

$[BiI_4]^-$	**tetraiodo-bismutate (III) ion**
$[Al(OH)_4]^-$	**tetrahydroxo-aluminate (III) ion**
$[FeF_6]^-$	**hexafluoro-ferrate (III) ion**

In the case of a neutral complex:

$[HgCl_2]$	**dichloro-mercury (II)**
$[Fe(SCN)_3]$	**tri-thiocyanato-iron (III)**

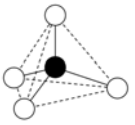
And finally, if they are written up with the counterions:

$[Cu(NH_3)_4]SO_4$	**[tetraammine-copper(II)]-sulphate**
$Na_3[Ag(S_2O_3)_2]$	**sodium-[dithiocyanato-argentate]**

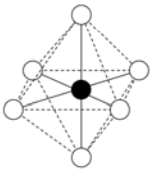
Structure of complex compounds

Coordinated ligands always try to obtain positions around the central metal ion so that the compound becomes energetically the most stable – that is the structure tends to be symmetrical. Examples:

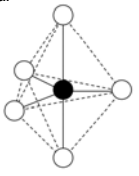
coordination number: 2
structure is linear



coordination number: 4
structure is tetrahedral



coordination number: 6
structure is octahedral



coordination number: 5
structure is trigonal-bipiramidal

Structure of complex compounds

Table 4.3-2. Most commonly observed structures of complex species

Coordination number	Hybrid orbitals	Structure	Tyical metal ion	Examples
2	*sp*	linear	H^{+}	hydrogen bond, H_2F^-
			Ag^{+}	$\{Ag_2O\}$, $Ag(CN)_2^-$, $Ag(SH)_2^-$
			Hg^{2+}	$HgCl_2$, $HgBr_2$, HgI_2, HgS_2^{2-}
			Au^{+}	$AuCl_2^-$
4	dsp^2 or sp^2d	square panar	Pd^{2+}	$Pd(H_2O)_4^{2-}$, $Pd(NH_3)_4^{2+}$
			Pt^{2+}	$PtCl_4^{2-}$
			Ni^{2+}	$Ni(CN)_4^{2-}$, Ni-dimethylglyoxime
	sp^3	tetrahedral	Fe^{3+}	$FeCl_4^-$, $FeBr_4^-$
			Tl^{3+}	$TlCl_4^-$, $TlBr_4^-$
			Co^{2+}	$CoCl_4^{2-}$, $Co(CNS)_4^{2-}$
			Li^{+}	$Li(H_2O)_4^+$
			Be^{2+}	$Be(H_2O)_4^{2+}$
			B(III)	$B(OH)_4^-$
			C(IV)	organic compounds
6	d^2sp^3 or sp^3d^2	octahedral	most metal ions	$Co(H_2O)_6^{2+}$, $Fe(H_2O)_6^{2+}$ $Fe(H_2O)_6^{3+}$, $Cr(H_2O)_6^{3+}$ $Na(H_2O)_6^+$ most EDTA complexes

Complex formation equilibria

Complex reactions always commence in a stepwise fashion. Each equilibrium is characterized by a ***stepwise formation constant*** (the example below is given for e.g. a complex with a coordination number of 4 and monodentate ligands):

$$M + L \leftrightarrow ML \qquad K_1 = \frac{[ML]}{[M]\cdot[L]}$$

$$ML + L \leftrightarrow ML_2 \qquad K_2 = \frac{[ML_2]}{[ML]\cdot[L]}$$

$$ML_2 + L \leftrightarrow ML_3 \qquad K_3 = \frac{[ML_3]}{[ML_2]\cdot[L]}$$

$$ML_3 + L \leftrightarrow ML_4 \qquad K_4 = \frac{[ML_4]}{[ML_3]\cdot[L]}$$

where usually $K_1 \geq K_2 \geq K_3 \geq K_4$.

Complex formation equilibria

The ***overall formation constant*** (K, β) for the last complex in the chain is the product of the formation constants.

$$\beta = K_1 \cdot K_2 \cdot K_3 \cdot K_4$$

$$M + n\,L \leftrightarrow ML_n \qquad \beta = \frac{[ML_n]}{[M]\cdot[L]^n}$$

Because of the parallel equilibria, there is a number of species present in a solution containing complex compounds (e.g. M, L, ML, ML_1, ML_2, ML_3, ML_4). The concentration of these species is calculable, even if in a complicated manner, using the formation constants.

One can also see that full complexation of a metal ion is only possible using a large excess of the ligand.

Conditional formation constant

The formula for the overall formation constant suggest that the complex formation is only governed by the concentration of the ligand, and the free metal ion. For a hexadentate ligand (EDTA, Y^{4-}), as an example, it is:

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

In reality, the formation equlibrium is also affected by any side reactions that influence $[Y^{4-}]$ or $[M^{n+}]$. These include:

- pH *(since protons compete with metal ions for the ligand)*
- other ligands *(as they compete with ligand for the metal ion)*

These effects can be taken into account by introducing the so called ***virtual (conditional) formation constant.*** As an illustration, we will discuss the effect of pH in the followings.

Conditional formation constant

The ligand not complexed is present in various protonated forms. If we denote the total dissolved ligand concentration by Y', then we can write

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

and we can define a proportionality factor:

$$\alpha_H = [Y']/[Y^{4-}]$$

The value for this factor is, of course, calculable based on the stepwise dissociation equilibria for H_4Y. If we do the math, we obtain:

$$\alpha_H = 1 + K_1 \cdot [H^+] + K_1 \cdot K_2 \cdot [H^+]^2 + K_1 \cdot K_2 \cdot K_3 \cdot [H^+]^3 + K_1 \cdot K_2 \cdot K_3 \cdot K_3 \cdot [H^+]^4$$

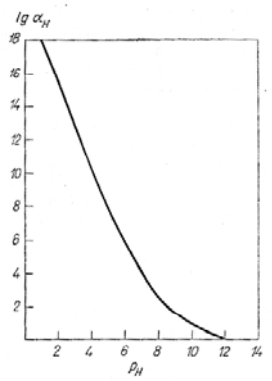
Conditional formation constant

Knowing the constants from K_1 to K_4 , the function can be plotted graphically against the pH.

Using this newly introduced factor we can write:

$$K' = \frac{[MY]}{[M][Y']} = \frac{[MY]}{[M]\alpha_H[Y^{4-}]} = \frac{K}{\alpha_H}$$

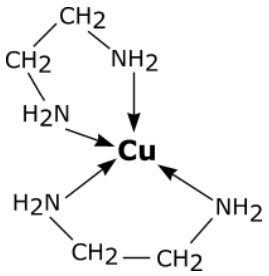
This means that we can calculate a ***conditional formation constant***, which refers to the actually present total ligand concentration, if we know α_H (as a function of pH).



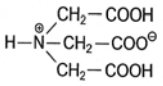
Chelate complex formation

Certain complex compounds that are formed with multidentate ligands in a way that five- or six-membered ringlike structures are created around the metal ion, are very stable (see the example below). These rings are called ***chelate rings*** and the complexes ***chelates***.

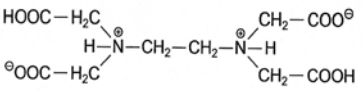
These complexes have great importance in ***complexometry***.



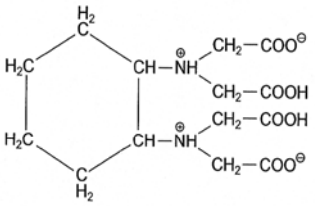
Chelate forming ligands (complexons)



nitrilo-triacetic acid (NTA)



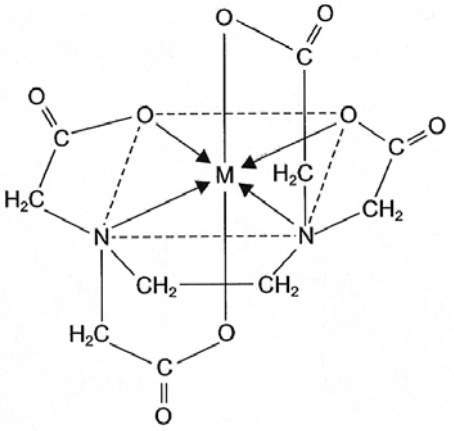
ethylene-diammine-tetraacetic acid (EDTA)



1,2-diamino-cyclohexane-tetraacetic acid (DCTA)

Comment: EDTA has four acetate groups and two amine nitrogens (all only accessible when deprotonated), which means a total of 6 binding sites (dents) Thus, EDTA is often abbreviated as Y^{4-}.

Structure of an EDTA chelate complex



Complexometry

Complexometry is a titrimetric method that is primarily used for the determination of metal ions, with the aid of complex formation (mainly chelate) reactions.

The following conditions need to be met for the successful use of a complex reaction in titrimetry:

- the complex needs to be very stable, with a high formation constant so the reaction is stochiometric (chelates)
- the solution needs to be buffered
- the complex needs to be formed in 1:1 ratio (for a sharp end-point)

There are several useful complexons, but by far the most useful is ethylene-diammine tetraacetic acid or EDTA.

Complexometry

EDTA has many features useful in complexometry:

- ***it is a versatile titrant***, as it forms highly stable 1:1 ratio chelate complexes with a number of metals
- ***its own color does not interfere with indicators***, as EDTA solution is colorless, and so are most of its complexes
- ***EDTA and also its metal complexes are water soluble***
- ***EDTA solutions are stable*** (in plastic containers)
- ***it is relatively harmless*** (non-toxic)

Versatility of EDTA complexometry

Table 12-2 Formation constants for metal-EDTA complexes

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^{+}	2.95	V^{3+}	25.9[a]	Tl^{3+}	35.3
Na^{+}	1.86	Cr^{3+}	23.4[a]	Bi^{3+}	27.8[a]
K^{+}	0.8	Mn^{3+}	25.2	Ce^{3+}	15.93
Be^{2+}	9.7	Fe^{3+}	25.1	Pr^{3+}	16.30
Mg^{2+}	8.79	Co^{3+}	41.4	Nd^{3+}	16.51
Ca^{2+}	10.65	Zr^{4+}	29.3	Pm^{3+}	16.9
Sr^{2+}	8.72	Hf^{4+}	29.5	Sm^{3+}	17.06
Ba^{2+}	7.88	VO^{2+}	18.7	Eu^{3+}	17.25
Ra^{2+}	7.4	VO_2^{+}	15.5	Gd^{3+}	17.35
Sc^{3+}	23.1[a]	Ag^{+}	7.20	Tb^{3+}	17.87
Y^{3+}	18.08	Tl^{+}	6.41	Dy^{3+}	18.30
La^{3+}	15.36	Pd^{2+}	25.6[a]	Ho^{3+}	18.56
V^{2+}	12.7[a]	Zn^{2+}	16.5	Er^{3+}	18.89
Cr^{2+}	13.6[a]	Cd^{2+}	16.5	Tm^{3+}	19.32
Mn^{2+}	13.89	Hg^{2+}	21.5	Yb^{3+}	19.49
Fe^{2+}	14.30	Sn^{2+}	18.3[b]	Lu^{3+}	19.74
Co^{2+}	16.45	Pb^{2+}	18.0	Th^{4+}	23.2
Ni^{2+}	18.4	Al^{3+}	16.4	U^{4+}	25.7
Cu^{2+}	18.78	Ga^{3+}	21.7		
Ti^{3+}	21.3	In^{3+}	24.9		

NOTE: The stability constant is the equilibrium constant for the reaction $M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$. Values in table apply at 25°C and ionic strength 0.1 M unless otherwise indicated.

Complexometric titration curves

Titration curves usually plot the pM against the added titrant (EDTA) volume. Note, that an increasing pM means strongly decreasing [M]. Points of the titration curve can be calculated using the conditional formation constant K' (at fixed pH). If K' is large, we can assume a complete reaction at each point.

Example: 50 mL 0.05 M Ca^{2+}
0.05 M EDTA (Y) titrant
$K' = 1.3 \times 10^{10}$

$M + Y \leftrightarrow MY$

Before the equivalence point:
pM is controlled by the excess, unreacted metal ion

At the equivalence point:
M is only present due to the slight dissociation of MY

After the equivalence point:
pM is controlled by the excess EDTA

Complexometric titration curves

REGION 1 - BEFORE THE EQUIVALENCE POINT

0 mL titrant added (0%):

$pM = -\lg [M] = -\lg (0.05) = 1.301$

10 mL titrant added (20%):

we can neglect the dissociation of MY

$pM = -\lg [M_{remaining}]$

$c_{M,\ remaining} = ((c_{M,\ total} \cdot V_M) - (c_{EDTA} \cdot V_{EDTA,\ added})) / V_{total}$

$pM = -\lg (0.0333) = 1.477$

25 mL titrant added (50%):

the approach is the same as above

$pM = -\lg (0.0166\ M) = 1.778$

Complexometric titration curves

REGION 2: AT THE EQUIVALENCE POINT

50 mL titrant was added (100%):

We can calculate pM like we dissolved MY $\frac{[MY]}{[M][Y]} = K'$

First, we calculate the total [MY] and then pM will be determined by the dissociation.

$[MY] = (c_{M,\,total} \cdot V_M) / V_{total} = 0.025$ M

$$\frac{0.025 - x}{x^2} = 1.3 \cdot 10^{10} \Rightarrow x = 1.38 \cdot 10^{-6} M$$

$pM = -\lg (1.38 \cdot 10^{-6}) = 5.85$

Complexometric titration curves

REGION 3: AFTER THE EQUIVALENCE POINT

75 mL titrant added (150%):

We use the equilibrium formula again, but with the actual concentrations: $\frac{[MY]}{[M][Y]} = K'$

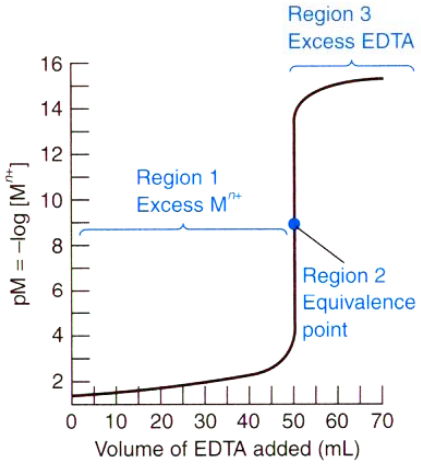
$[MY] = (c_{M,\,total} \cdot V_M) / V_{total} = 0.020$ M

$[EDTA] = (c_{EDTA} \cdot V_{EDTA,\,excess}) / V_{total} = 0.010$ M

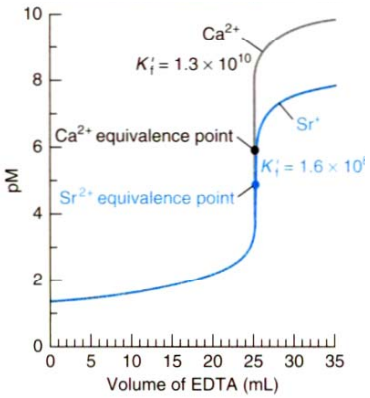
$$\frac{0.02}{[M] \cdot 0.01} = 1.3 \cdot 10^{10} \Rightarrow [M] = 1.53 \cdot 10^{-10} M$$

$pM = -\lg (1.53 \cdot 10^{-10}) = 9.81$

Complexometric titration curves

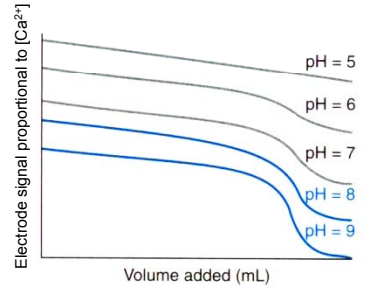


Effect of K and pH on titration curves



the larger is K, the larger is the jump on the titration curve around the EP

Simulation from Skoog CD-ROM (Part III, Module 19)



Titration of Ca^{2+} with EDTA as a function of pH. As the pH is lowered, the end point becomes less distinct.

at higher pH values, EDTA titration curves usually exhibit more distinct EP (less competition from protons), but beware of hydroxide precipitatiton…

Complexometry – auxiliary agents

Some metal ions need to be titrated at such alkaline pHs, which normally cause their hydroxide precipitate to form. To prevent this, one can add complexing agents to the sample which bring the metal ion into a weak complex. This weak complex will prevent the metal ions from forming hydroxides, but are weak enough to give up the metal ions upon the addition of EDTA.

Examples to such agents:

- ammonia
- tartarate
- citrate

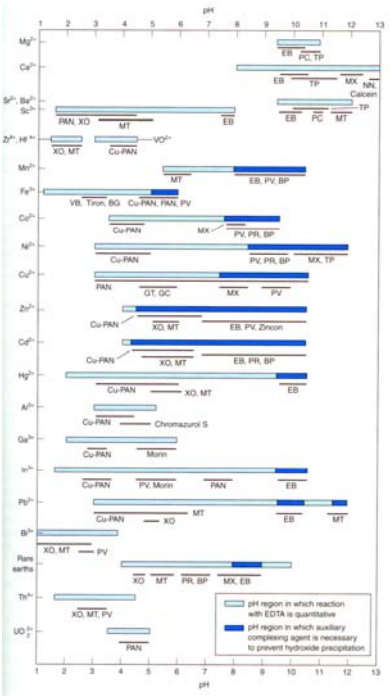


Figure 12-14 Guide to EDTA titrations of common metals. Light color shows pH region in which reaction with EDTA is quantitative. Dark color shows pH region in which auxiliary complexing agent is required to prevent metal from precipitating. Calmagite is more stable than Eriochrome black T (EB) and can be substituted for EB. *[Adapted from K. Ueno, "Guide for Selecting Conditions of EDTA Titrations," J. Chem. Ed. **1965**, 42, 432.]*

Abbreviations for indicators:

BG, Bindschedler's green leuco base
BP, Bromopyrogallol red
EB, Eriochrome black T
GC, Glycinecresol red
GT, Glycinethymol blue
MT, Methylthymol blue
MX, Murexide
NN, Patton & Reeder's dye
PAN, Pyridylazonaphthol
Cu-PAN, PAN plus Cu-EDTA
PC, o-Cresolphthalein complexone
PR, Pyrogallol red
PV, Pyrocatechol violet
TP, Thymolphthalein complexone
VB, Variamine blue B base
XO, Xylenol orange

End point indication in complexometry

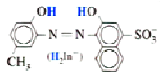
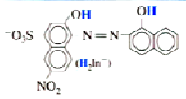
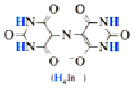
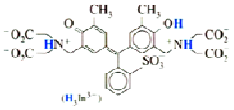
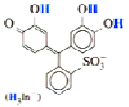
EP indication is done by weak complexing agents that change their color upon complexation (metal ion indicators). Here is what happens during titration:

- when adding the indicator, some metal ions will react with it, so color will be that of the indicator-metal complex (MIn)
- the added EDTA will react first with free metal ions
- near, but before the end-point MIn gives up its metal ion to EDTA, and the more stable EDTA-metal complex forms
- at the end-point, all MIn is broken up, so the indicator will show its free color

Of course, the indicator-EDTA push-pull reaction needs to be fast, so the end-point will not be overrun. It also follows that there is no indicator error in complexometry, thus we can use a larger amount of indicator if needed.

End point indication in complexometry

Table 12-3 Common metal ion indicators

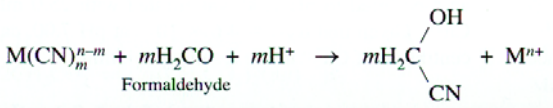
Name	Structure	pK_a	Color of free indicator	Color of metal ion complex
Calmagite		$pK_2 = 8.1$ $pK_3 = 12.4$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Eriochrome black T		$pK_2 = 6.3$ $pK_3 = 11.6$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Murexide		$pK_2 = 9.2$ $pK_3 = 10.9$	H_3In^- red-violet H_2In^{2-} violet HIn^{3-} blue	Yellow (with Co^{2+}, Ni^{2+}, Cu^{2+}); red with Ca^{2+}
Xylenol orange		$pK_2 = 2.32$ $pK_3 = 2.85$ $pK_4 = 6.70$ $pK_5 = 10.47$ $pK_6 = 12.23$	H_6In^- yellow H_5In^{2-} yellow H_4In^{3-} yellow H_3In^{4-} violet HIn^{5} violet In^{6} violet	Red
Pyrocatechol violet		$pK_1 = 0.2$ $pK_2 = 7.8$ $pK_3 = 9.8$ $pK_4 = 11.7$	H_4In red H_3In^- yellow H_2In^{2-} violet HIn^{3-} red-purple	Blue

Masking and demasking

Masking can be used to protect some component of the sample to react with EDTA. Masking agents are strong complexants. Examples:

- F^- masks Al^{3+}, Fe^{3+}, Ti^{4+}, Be^{2+}
- CN^- masks Cd^{2+}, Zn^{2+}, Co^{2+}, Ag^+, etc.
- triethanolamine masks Al^{3+}, Fe^{3+}, Mn^{2+}

If the masked component later also needs to be titrated by EDTA, it can be demasked. For ***demasking***, reagents are used that release the metal ion from a masking agent. Examples:



Preparation of the titrant solution

The titrant is usually 0.02-0.05 M EDTA solution in complexometry, prepared by the dissolution of EDTA or its Na salt.

The titrant needs to be standardized due to its high affinity towards metal ions. The standardization can be done by using e.g. a standard Zn(II) solution, either prepared from the pure metal or from its salt.

Due to metallic impurities in glass containers, plastic containers are recommended for storage.

Applications of complexometry

Complexometric applications always need a careful setting of the pH, for which one uses buffer solutions. Care must be exercised when choosing the buffer, as these contain weak bases and/or acids that may also have complexing properties (e.g. ammonia, citratic acid, acetic acid, etc.)

Direct titration of metal ions

A number of metal ions can be titrated directly. See the former tables for this.

Indirect titration

Anions that precipitate with certain metal ions can be analyzed with EDTA indirectly. For example, SO_4^{2-} can be first precipitated from the sample solution using excess Ba^{2+} as $BaSO_4$. Then the precipitate is washed and separated from the sample solution and boiled with excess EDTA at pH= 10 to bring all Ba^{2+} back into solution as $Ba(EDTA)^{2-}$. The excess of EDTA can be then titrated back using e.g. Mg^{2+}.

Applications of complexometry

Water hardness determination

Hardness is the total alkaline earth ion concentration in water (these ions form a precipitate with soap, hence the „hard water" expression). These are mainly Ca^{2+} and Mg^{2+}, so by titrating these two ions with EDTA, one can assess the hardness of a water sample.

Sample preparation: masking of minor metal ions in the sample that may also react with EDTA has to be done (ascorbic acid for Fe^{3+} reduction, CN^- for Fe^{2+}, Cu^+, etc.)

If the titration is done at pH = 10 in ammonia buffer, the result gives the total $[Ca^{2+}]+[Mg^{2+}]$. Indicator: Eriochrome Black T

Ca^{2+} can be titrated separately at pH= 13 without ammonia. At this pH, $Mg(OH)_2$ precipitates and so Mg^{2+} is inaccessible to EDTA. Indicator: Murexide

Summary of EDTA complexometry

Main use:	titrimetric determination of metal ions
Main appeal:	1) very versatile titrant 2) easily calculable, uniform stoichiometry 3) easy EP indication, largely free from error
Titrant:	0.02-0.05 M solution, needs to be standardized using metal ion solutions
Conditions:	sample has to be buffered (usually to an alkaline pH)
Indicators:	weak complexing agents (Murexide, Xylenol orange, etc.)
Applications:	e.g. direct titration of metal ions, water hardness determination, indirect sulphate determination, etc.