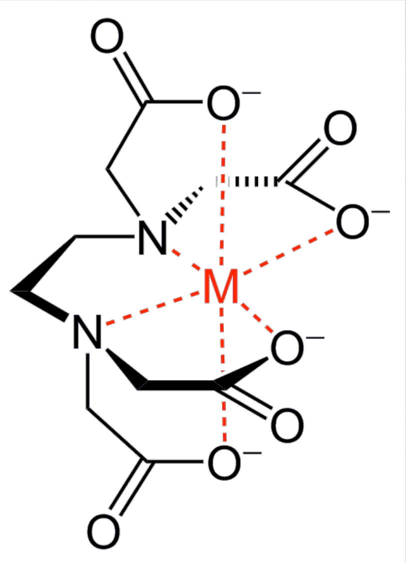
COMPLEXATION TITRATIONS

SDSU CHEM 251

CHELATING AGENTS

- Chelating agents complex metal ions
- Metal ions act as Lewis acids and can accept a pair of electrons from a donor ligand
- Chelating agents form more than one bond with a metal ion
- Bonds are typically between N or O and the metal
- Can prevent the metal from undergoing other reactions



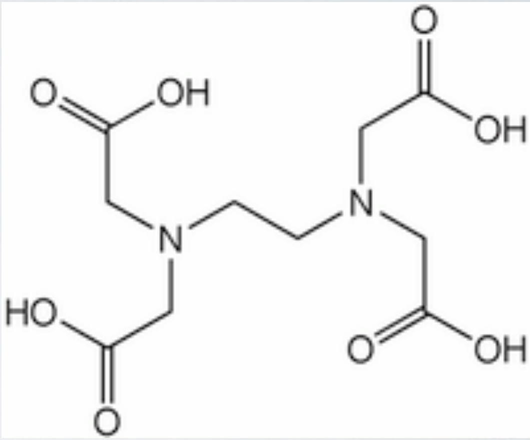
EDTA-Metal complex

COMPLEXATION TITRATIONS

- Because chelating agents can react with metal cations, they can be used to quantify the amount of a metal free in a solution.
- A common example is the titration of calcium with ethylenediaminetetraacetic (EDTA).
- The indicator is a second chelator that undergoes a color change as it loses the metal ion to the stronger EDTA chelator.

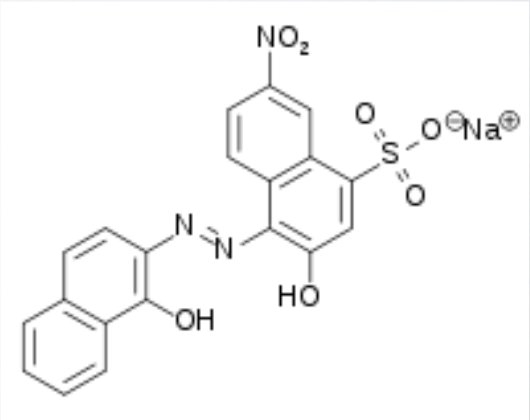
Titrant used:

EDTA



Indicator used:

Eriochrome Black T



COMPLEXATION

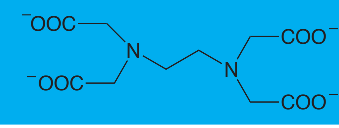
- The reaction between a metal ion (M^{n+}) and EDTA (Y^{4-}) always occurs in a 1:1 ratio.

- Only the fully deprotonated form of EDTA (Y4-) is capable of chelating the metal ions.

- The complexes are very stable and the formation constants (K_f) values are listed as the log K_f values.

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

EDTA



	log K_1
Mg^{2+} (T = 20 °C, μ = 0.1 M)	8.79
Ca^{2+} (T = 20 °C, μ = 0.1 M)	10.69
Ba^{2+} (T = 20 °C, μ = 0.1 M)	7.86
Bi^{3+} (T = 20 °C, μ = 0.1 M)	27.8
Co^{2+}+ (T = 20 °C, μ = 0.1 M)	16.31
Ni^{2+} (T = 20 °C, μ = 0.1 M)	18.62
Cu^{2+} (T = 20 °C, μ = 0.1 M)	18.80
Cr^{3+} (T = 20 °C, μ = 0.1 M)	[23.4]
Fe^{3+} (T = 20 °C, μ = 0.1 M)	25.1
Ag^{+} (T = 20 °C, μ = 0.1 M)	7.32
Zn^{2+} (T = 20 °C, μ = 0.1 M)	16.50
Cd^{2+} (T = 20 °C, μ = 0.1 M)	16.46
Hg^{2+} (T = 20 °C, μ = 0.1 M)	21.7

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$$

SOLUTION CONSIDERATIONS

- The pH of the solution has a significant impact on the formation constant.
- Only the fully deprotonated EDTA is capable of complexing metal cations.
- The proportion of EDTA that is fully deprotonated is denoted by (α_{Y4-}).
- In knowing the <u>formal concentration of EDTA</u> and the <u>pH</u> we can use the conditional formation constant (K_f') in our calculations.

Table 9.10 Values of α_{Y4-} for Selected pH Levels

pH	α_{Y4-}	pH	α_{Y4-}
1	1.9×10^{-18}	8	5.6×10^{-3}
2	3.4×10^{-14}	9	5.4×10^{-2}
3	2.6×10^{-11}	10	0.37
4	3.8×10^{-9}	11	0.85
5	3.7×10^{-7}	12	0.98
6	2.4×10^{-5}	13	1.00
7	5.0×10^{-4}	14	1.00

$$[Y^{4-}] = \alpha_{Y^{4-}} \times [EDTA]$$

$$K_f' = K_f \times \alpha_{Y^{4-}} = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]}$$

SOLUTION CONSIDERATIONS

- A further consideration of the solution conditions comes from the choice of buffers for the titration.
- Some of the buffers (required to maintain a stable pH) can complex with metal cations.
- These complexes influence the amount of free metal $[M^{n+}]$ in the equilibria, further altering the conditional formation constant (K_f'').

Table 9.12 Values of $\alpha_{M^{2+}}$ for Selected Concentrations of Ammonia

$[NH_3]$ (M)	$\alpha_{Ca^{2+}}$	$\alpha_{Cd^{2+}}$	$\alpha_{Co^{2+}}$	$\alpha_{Cu^{2+}}$	$\alpha_{Mg^{2+}}$	$\alpha_{Ni^{2+}}$
1	5.50×10^{-1}	6.09×10^{-8}	1.00×10^{-6}	3.79×10^{-14}	1.76×10^{-1}	9.20×10^{-10}
0.5	7.36×10^{-1}	1.05×10^{-6}	2.22×10^{-5}	6.86×10^{-13}	4.13×10^{-1}	3.44×10^{-8}
0.1	9.39×10^{-1}	3.51×10^{-4}	6.64×10^{-3}	4.63×10^{-10}	8.48×10^{-1}	5.12×10^{-5}
0.05	9.69×10^{-1}	2.72×10^{-3}	3.54×10^{-2}	7.17×10^{-9}	9.22×10^{-1}	6.37×10^{-4}
0.01	9.94×10^{-1}	8.81×10^{-2}	3.55×10^{-1}	3.22×10^{-6}	9.84×10^{-1}	4.32×10^{-2}
0.005	9.97×10^{-1}	2.27×10^{-1}	5.68×10^{-1}	3.62×10^{-5}	9.92×10^{-1}	1.36×10^{-1}
0.001	9.99×10^{-1}	6.09×10^{-1}	8.84×10^{-1}	4.15×10^{-3}	9.98×10^{-1}	5.76×10^{-1}

$$[M^{n+}] = \alpha_{M^{n+}} \times C_{M^{n+}}$$

$$K_f'' = K_f \times \alpha_{Y^{4-}} \times \alpha_{M^{n+}} = \frac{[MY^{n-4}]}{C_{M^{n+}}[EDTA]}$$