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CONCEPT: METAL-CHELATE COMPLEXES

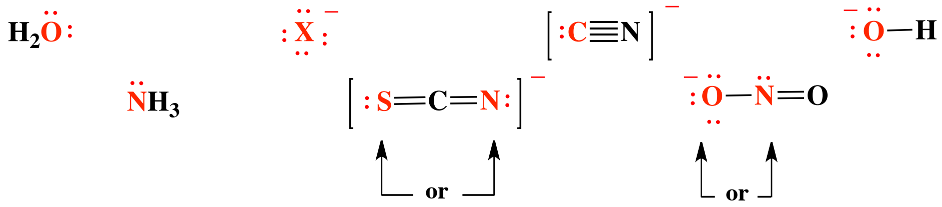
A ligand can be thought of as a ___________________ because it bonds to a central metal cation in a complex ion by using its lone pair.

Ligands are characterized by the number of elements in the molecule that can donate a lone pair.

- ____________________ agents are compounds that use their lone pairs to grab onto metal cations.

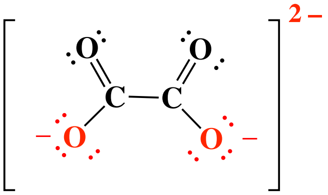
Ligands that possess only _____ element(s) able to donate a lone pair are referred to as ***monodentate ligands.***

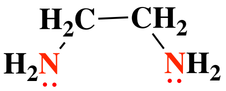
Monodentate ("One-toothed")



Ligands that possess ________________ element(s) able to donate a lone pair are referred to as ***bidentate ligands.***

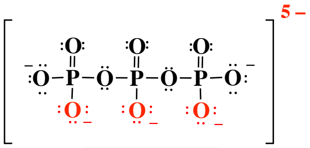
Bidentate ("Two-toothed")



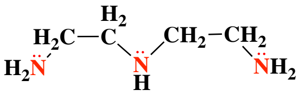


Ligands that possess ______________ element(s) able to donate a lone pair are referred to as ***polydentate ligands.***

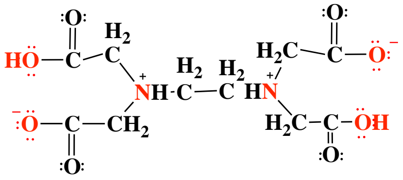
Polydentate ("Many-toothed")



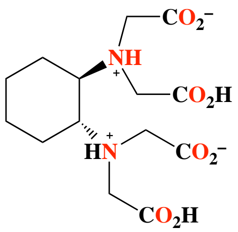
Triphosphate ion



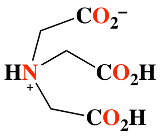
Diethylenetriamine



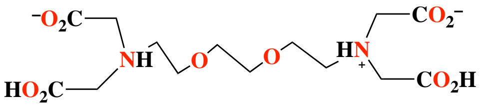
Ethylenediaminetetraacetate ion ($EDTA^{4-}$)



trans-1,2-Diaminocyclohexanetetraacetic acid (DCTA)



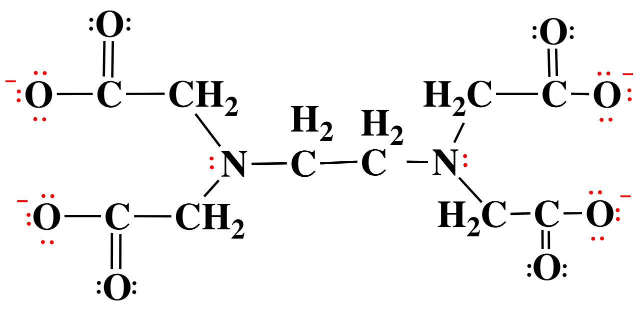
Nitrilotriacetic acid (NTA)



bis(Aminoethyl)glycolether-N,N,N',N'-tetraacetic acid (EGTA)

CONCEPT: EDTA

In its fully protonated form EDTA exists as a hexaprotic acid: ___________ .



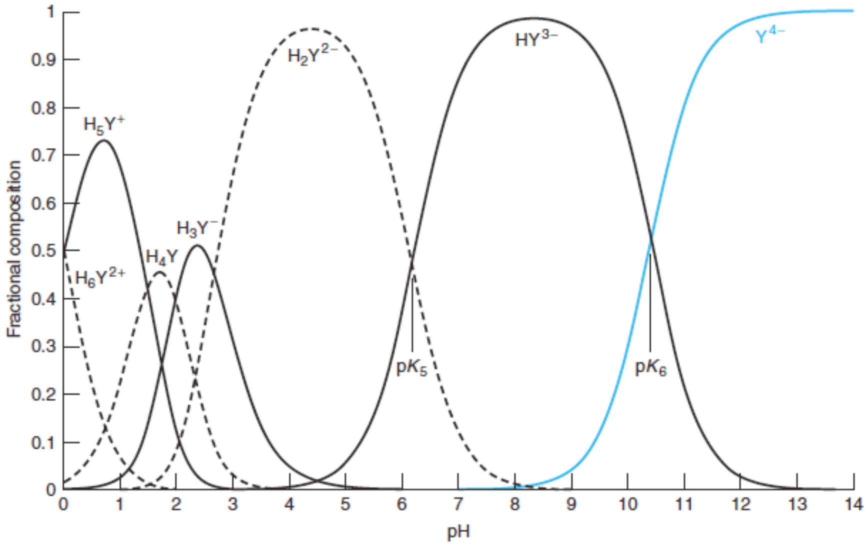
Ethylenediaminetetraacetate ion **(EDTA⁴⁻)**

$$pK_{a1} = 0.00 \qquad pK_{a4} = 2.69$$
$$pK_{a2} = 1.50 \qquad pK_{a5} = 6.13$$
$$pK_{a3} = 2.00 \qquad pK_{a6} = 10.37$$

In order to form metal-complexes these acidic hydrogens must first be lost.

- EDTA can exist in up to 7 different forms depending on the pH of the solution.

$$H_6Y^{2+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} H_5Y^{+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} H_4Y \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} H_3Y^{-} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} H_2Y^{2-} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} HY^{3-} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \boxed{Y^{4-}}$$



To calculate the fraction of EDTA in its basic form we can utilize the following equation:

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[EDTA]} = \frac{[Y^{4-}]}{[H_6Y^{2+}]+[H_5Y^{+}]+[H_4Y]+[H_3Y^{-}]+[H_2Y^{2-}]+[HY^{3-}]+[HY^{4-}]}$$

$$\alpha_{Y^{4-}} = \frac{K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}}{[H^+]^6+[H^+]^5K_{a1}+[H^+]^4K_{a1}K_{a2}+[H^+]^3K_{a1}K_{a2}K_{a3}+[H^+]^2K_{a1}K_{a2}K_{a3}K_{a4}+[H^+]K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}+K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}}$$

PRACTICE: EDTA CALCULATIONS 1

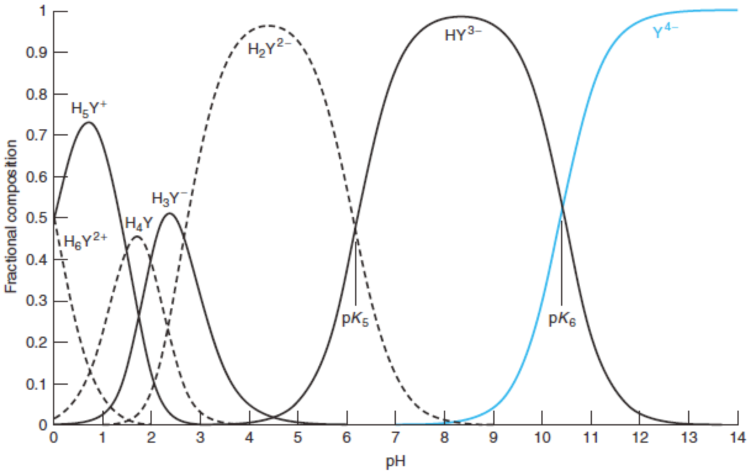
EXAMPLE 1: The formal concentration of EDTA is 1.50 mM. What is the concentration of the Y^{4-} form at a pH of 5.0?

pH	$\alpha_{Y^{4-}}$
0	1.3×10^{-23}
1	1.4×10^{-18}
2	2.6×10^{-14}
3	2.1×10^{-11}
4	3.0×10^{-9}
5	2.9×10^{-7}
6	1.8×10^{-5}
7	3.8×10^{-4}
8	4.2×10^{-3}
9	0.041
10	0.30
11	0.81
12	0.98
13	1.00
14	1.00

* 25 °C and $\mu = 0.10$ M

EXAMPLE 2: Determine the $\alpha_{Y^{4-}}$ for EDTA when the pH = 8.50.

PRACTICE: Determine the pH where $\alpha_{Y^{4-}}$ equals 0.20.

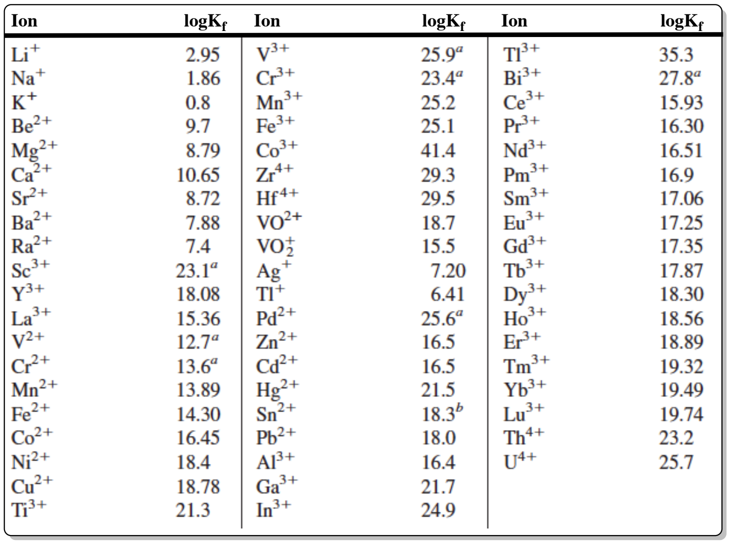


CONCEPT: EDTA COMPLEXES

The ______________________ represents the equilibrium constant for the reaction between a ligand and a metal.

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

The formation constants for metal-EDTA complexes are given below:



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		

a : 20 °C and $\mu = 0.1$ M
b : 20 °C and $\mu = 1.0$ M

Only a portion of EDTA exists in its basic form and the lower the pH the more the other forms predominate.

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

Under a fixed pH, $\alpha_{Y^{4-}}$ becomes a constant and can be used in determining the conditional formation constant because it represents the formation of MY^{n-4} at any pH value.

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

EXAMPLE: Find $[Ba^{2+}]$ in 0.10 M BaY^{2-} at pH = 10.00.

PRACTICE: EDTA COMPLEXES CALCULATIONS 1

EXAMPLE 1: Determine the conditional formation constant for $Co(EDTA)^-$ at pH = 8.00.

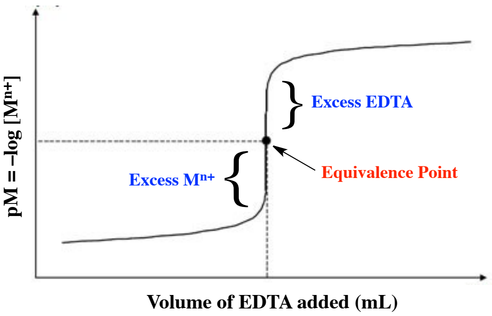
EXAMPLE 2: Find the concentration of free Sn^{2+} in 0.20 M $K_2[Sn(EDTA)]$ at pH = 9.00.

PRACTICE: Find the concentration of free Na^+ in 0.15 M $Li_3[Na(EDTA)]$ at pH = 10.00.

CONCEPT: EDTA TITRATION CURVES

The following can be used as the roadmap for determining the p[M**n+**] for a metal-EDTA Titration.

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



Equivalence Volume (V_e)

The titration of 50.0 mL of 0.100 M Ba^{2+} (buffered to 9.00) with 0.050 M EDTA

Before Equivalence Point

The titration of 50.0 mL of 0.100 M Ba^{2+} (buffered to 9.00) with 80.0 mL of 0.050 M EDTA

$$M^{n+} = \underbrace{\left(\frac{V_e - V_{EDTA}}{V_e}\right)}_{\text{Fraction of } M^{n+} \text{ remaining}}[M^{n+}]_0 \underbrace{\left(\frac{V_{\text{Initial } M^{n+}}}{V_{\text{Solution}}}\right)}_{\text{Dilution Factor}}$$

At Equivalence Point

The titration of 50.0 mL of 0.100 M Ba^{2+} (buffered to 9.00) with 100.0 mL of 0.050 M EDTA

$$[MY^{n-4}] = [M^{n+}]_0 \underbrace{\left(\frac{V_{\text{Initial } M^{n+}}}{V_{\text{Solution}}}\right)}_{\text{Dilution Factor}}$$

	M^{n+}	+	EDTA	$\rightleftharpoons$	MY^{n-4}
Initial	–		–		**$[MY^{n-4}]$**
Change	**+ x**		**+ x**		**– x**
Equilibrium	**+ x**		**+ x**		**$[MY^{n-4}]$ – x**

$$M^{n+} + EDTA \rightarrow MY^{n-4} \qquad K_f' = \alpha_{Y^{4-}} K_f$$

$$K_f' = \frac{[MY^{n-4}] - x}{[M^{n+}][EDTA]} \;\therefore\; K_f' = \frac{[MY^{2-}] - x}{x^2} \;\therefore\; x = [M^{n+}] \;\therefore\; p[M^{n+}]$$

After Equivalence Point

The titration of 50.0 mL of 0.100 M Ba^{2+} (buffered to 9.00) with 112.0 mL of 0.050 M EDTA

$$[EDTA] = [EDTA]_0\left(\frac{V_{\text{Excess EDTA}}}{V_{\text{Solution}}}\right) \qquad [MY^{n-4}] = [M^{n+}]_0\left(\frac{V_{\text{Initial } M^{n+}}}{V_{\text{Solution}}}\right) \qquad K_f' = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]}$$

PRACTICE: EDTA TITRATION CURVES CALCULATIONS 1

EXAMPLE: Calculate the pMn^{3+} for the titration of 30.0 mL of 0.0100 M EDTA with 50.0 mL of 0.0200 M $MnPO_4$ at pH = 10.00.

PRACTICE: Calculate the pNi^{2+} for the titration of 50.0 mL of 0.120 M EDTA with 15.0 mL of 0.100 M $NiCl_2$ at pH = 8.22.