Problems for chapter - 11

EDTA:

11-1 What is the chelate effect and why does it occur?

The Chelate effect is the observation that multidentate ligands form more stable metal complexes than do similar, monodentate ligands.

This happens because the entropy change when one multidentate ligand binds to a metal is greater than the entropy when many smaller ligands are bound.

11-2. State (in words) what $\alpha_{Y^{4-}}$ means. Calculate $\alpha_{Y^{4-}}$ for EDTA at (a) pH 3.50 and (b) pH 10.50.

$\alpha_{Y^{4-}}$ give the fraction of all free EDTA in the form Y^{4-}.

(a) pH = 3.50 :-

Ans

$$\alpha_{y^{4-}} = \frac{k_1 k_2 k_3 k_4 k_5 k_6}{\left\{[H^+]^6 + [H^+]^5 k_1 + [H^+]^4 k_1 k_2 + [H^+]^3 k_1 k_2 k_3 + [H^+]^2 k_1 k_2 k_3 k_4 + [H^+] k_1 k_2 k_3 k_4 k_5 + k_1 k_2 k_3 k_4 k_5 k_6\right\}}$$

Substitute all the $[H^+]$, $k_1, k_2, k_3, k_4, k_5, k_6$ values you will get

$$\boxed{\alpha_{y^{4-}} = 3.4 \times 10^{-10}}$$

$\because$ pH = 3.50

$\therefore [H^+] = 10^{-3.50}$

$k_1 = 10^{-0.0}$

$k_2 = 10^{-1.5}$

$k_3 = 10^{-2.0}$

$k_4 = 10^{-2.66}$

$k_5 = 10^{-6.16}$

$k_6 = 10^{-10.24}$

(b) pH = 10.50

Same as above problem

at pH 10.50

$\alpha_{y^{4-}} = 0.64$

11-3. (a) Find the conditional formation constant for $Mg(EDTA)^{2-}$ at pH 9.00.

Conditional formation constant:

$$K_f' = \alpha_{Y^{4-}} K_f$$

$\log K_f$ for Mg^{2+} $= 8.79.$

$\therefore K_f = 10^{+8.79}$

Here you have to calculate $\alpha_{Y^{4-}}$ at pH 9.00.

$$\therefore K_f' = 0.054 \times 10^{8.79}$$

$$\boxed{K_f' = 3.3 \times 10^{7}}$$

(b) Find the concentration of free Mg^{2+} in 0.050 M $Na_2[Mg(EDTA)]$ at pH 9.00.

Ans

$$Mg^{2+} + EDTA \rightleftharpoons MgY^{2-}$$

$$x \qquad x \qquad 0.050 - x$$

$$\therefore K_f' = \frac{0.050 - x}{x^2}$$

$$\frac{0.050 - x}{x^2} = 3.3 \times 10^7$$

$\because k_f' = 3.3 \times 10^7$

$\therefore x = 3.9 \times 10^{-5}$ M

$\therefore x = Mg^{2+}$

$\therefore [Mg^{2+}] = 3.9 \times 10^{-5}$ M

Example 1:

What does $\alpha_{Y^{4-}}$ mean?

The fraction of all free EDTA in the form Y^{4-} is called $\alpha_{Y^{4-}}$.

At pH 6.00 at a formal concentration of 0.10M, the composition of an EDTA solution is

$[H_6Y^{2+}] = 8.4 \times 10^{-20} M$

$[H_5Y^{+}] = 8.4 \times 10^{-14} M$

$[H_4Y] = 2.7 \times 10^{-9} M$

$[H_3Y^{-}] = 2.7 \times 10^{-5} M$

$[H_2Y^{2-}] = 0.059 M$

$[HY^{3-}] = 0.041 M$

$[Y^{4-}] = 2.3 \times 10^{-6} M$

Find $\alpha_{Y^{4-}}$.

Solution:

$\alpha_{Y^{4-}}$ is the fraction in the form Y^{4-}.

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

$$= \frac{(2.3\times10^{-6})}{(8.4\times10^{-20}) + (8.4\times10^{-14}) + (2.7\times10^{-9}) + (2.7\times10^{-5}) + (0.059) + (0.041) + (2.3\times10^{-6})}$$

$$= 2.3\times10^{-5}$$

$$\therefore \boxed{\alpha_{Y^{4-}} = 2.3\times10^{-5}}$$

Example:

The formation constant for CaY^{2-} ($\log K_f = 10.69$) is $10^{10.69} = 4.9\times10^{10}$. Calculate the concentration of free Ca^{2+} in a solution of 0.10 M CaY^{2-} at pH 10.00 and at pH 6.00.

Soln

The complex formation reaction is

$$Ca^{2+} + EDTA \rightleftharpoons CaY^{2-} \qquad K_f' = \alpha_{Y^{4-}} K_f$$

where EDTA on the left side of the equation refers to all forms of unbound EDTA ($= Y^{4-}$, HY^{3-}, H_2Y^{2-}, H_3Y^{-}, etc.). using $\alpha_{Y^{4-}}$ from (Table 13-1 in book), we find.

At pH 10.00 : $K_f' = \alpha_{Y^{4-}} K_f$

$K_f' = (0.36)(4.9\times10^{10})$

∴ At pH 10.00 $\quad K_f' = 1.8\times10^{10}$

∴ At pH = 10

$\alpha_{Y^{4-}} = 0.36$

at p^H 6.00 :

$$k_f' = (2.3\times10^{-5})(4.9\times10^{10})$$

$\therefore$ at p^H 6.00 $k_f' = \underline{\underline{1.1\times10^{6}}}$

$\therefore$ at $p^H = 6.00$

$\alpha_{Y^{4-}} = 2.3\times10^{-5}$

Because dissociation of CaY^{2-} must produce equal quantities of Ca^{2+} and EDTA, we can write

	Ca^{2+}	+ EDTA	$\rightleftharpoons CaY^{2-}$
Initial Concentration (M)	0	0	0.10
Final Concentration (M)	x	x	$0.10 - x$

$$\therefore \frac{[CaY^{2-}]}{[Ca^{2+}][EDTA]} = \frac{0.10-x}{x^2} = k_f' = 1.8\times10^{10} \text{ at } p^H = 10.0$$

$$= 1.1\times10^{6} \text{ at } p^H\ 6.00$$

solving for x $(=[Ca^{2+}])$

we find $[Ca^{2+}] = 2.4\times10^{-6}$ M at p^H 10.00.

$[Ca^{2+}] = 3.0\times10^{-4}$ M at p^H 6.00.