

Problems for chapter - 11

①

EDTA:

11-1 ~~Q1~~. 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 ~~Q2~~. 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

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

(b) $pH = 10.50$

same as above problem

at $pH = 10.50$

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

$pH = 3.50$

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

$k_1 = 10^{-0.0}$

$k_2 = 10^{-1.5}$

$k_3 = 10^{-2.0}$

$k_4 = 10^{-2.66}$

$k_5 = 10^{-6.16}$

$k_6 = 10^{-10.24}$

17-3. (a) Find the Conditional formation Constant for $Mg(EDTA)^{2-}$ at pH 9.00.

Conditional formation constant:

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

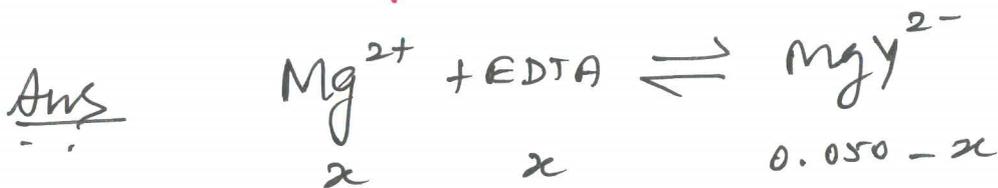
Here you have to calculate $\alpha_{Y^{4-}}$ at pH 9.00.

$$\begin{aligned} \log K_f \text{ for } Mg^{2+} &= 8.79 \\ \therefore K_f &= 10^{+8.79} \end{aligned}$$

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

$$K'_f = 3.3 \times 10^7$$

(b) Find the Concentration of free Mg^{2+} in 0.050M $Mg_2[Mg(EDTA)]$ at pH 9.00.



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

~~0~~

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

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

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

(4)

$$\therefore K_f' = 3.3 \times 10^7$$

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

(5)

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

(6)

Solution:

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

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[H_6Y^{2+}] + [H_5Y^+] + [H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]}$$
$$= \frac{(2.3 \times 10^{-6})}{(8.4 \times 10^{-20}) + (8.4 \times 10^{-14}) + (2.7 \times 10^{-9}) + (2.7 \times 10^{-5}) + (0.059) + (0.041) + (2.3 \times 10^{-6})}$$
$$= 2.3 \times 10^{-5}$$

$\therefore \alpha_{Y^{4-}} = 2.3 \times 10^{-5}$

Example:

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

Solu

The complex formation reaction is



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 $pH 10.00$:	$k_f' = \alpha_{Y^{4-}} k_f$	$\left. \begin{array}{l} \therefore \\ \text{at } pH=10 \\ \alpha_{Y^{4-}} = 0.36 \end{array} \right\}$
	$k_f' = (0.36)(4.9 \times 10^{10})$	
\therefore At $pH 10.00$	$k_f' = \underline{\underline{1.8 \times 10^{10}}}$	

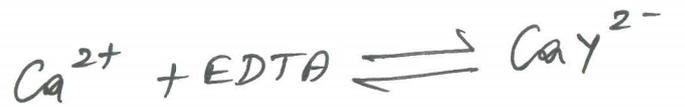
at pH 6.00 :

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

∴ at pH = 6.00
 $\alpha_{Y^{4-}} = 2.3 \times 10^{-5}$

∴ at pH 6.00 $k_f' = \underline{\underline{1.1 \times 10^6}}$

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



Initial Concentration (M)

	0	0	0.10
--	---	---	------

Final Concentration (M)

	x	x	0.10 - x
--	---	---	----------

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

$$= 1.1 \times 10^6 \text{ at } pH = 6.00$$

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

we find $[Ca^{2+}] = 2.4 \times 10^{-6} M$ at pH 10.00.

$[Ca^{2+}] = 3.0 \times 10^{-4} M$ at pH 6.00.