More Review Problems (Chapters 16-17)

1. Morpholine, $O(CH_2CH_2)_2NH$ (87.12 g/mole), call it R_2NH for short, is a weak base with $pK_b = 5.508$. A 2.505-g sample of morpholine was dissolved in enough water to make 250.0 mL of solution. A 50.00-mL portion of this solution was then titrated with 0.150 M HCl.

(a) What volume of HCl is required to reach the end-point?

Initial moles of R_2NH?

(2.505 g) (1 mole / 87.12 g) = 0.02875 mole R_2NH

molarity of R_2NH?

(0.02875 mole) / 0.250 L = 0.115 M

moles R_2NH = moles HCl

(0.0500 L) (0.115 mole/L) = 0.00575 moles

mL of HCl?

(0.00575 moles) (1000 mL / 0.150 mole)

= 38.33 mL

(b) Determine the pH of the solution:
- before any HCl is added

Solution just contains the weak base, R_2NH

$$R_2NH + H_2O \rightleftharpoons R_2NH_2^+ + OH^-$$
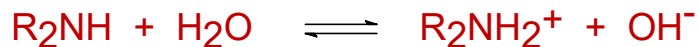
$K_b = 10^{-5.508} = 3.10 \times 10^{-6} = x^2 / [R_2NH]$

$3.10 \times 10^{-6} = x^2 / [R_2NH] = x^2 / 0.115$

$x = [OH^-] = 5.97 \times 10^{-4}$

pOH = 3.22   and   pH = 10.78

- after 25.00 mL of HCl is added

Initial moles of R_2NH?

(50.00 mL) (0.115 mole / 1000 mL) = 0.00575 mole

Moles HCl added?

(25.00 mL) (0.150 mole / 1000 mL) = 0.00375 mole

Neutralization Rx: R_2NH + H^+ $\longrightarrow$ $R_2NH_2^+$

R_2NH left?

= 0.00575 - 0.00375 = 0.00200 moles

$R_2NH_2^+$ formed?

= 0.00375 moles

Mixture now contains $R_2NH_2^+$ (a weak acid)

and R_2NH (it's conjugate base)

$\therefore$ a buffer solution!

Major Equilibrium is K_a for the weak acid:

$R_2NH_2^+$ $\rightleftharpoons$ H^+ + R_2NH
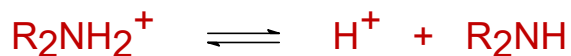
K_a = K_w / K_b = $(10^{-14}) / (3.10 \times 10^{-6})$

= 3.23×10^{-9}

$[H^+]$ = $K_a [R_2NH_2^+] / [R_2NH]$

= K_a (moles $R_2NH_2^+$) / (moles R_2NH)
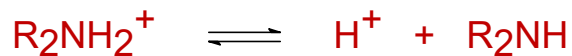
= (3.23×10^{-9}) (0.00375) / (0.00200)

= 6.05×10^{-9}

$\therefore$ pH = 8.22

- at the equivalence point

All R_2NH has been converted to $R_2NH_2^+$ (a weak acid!)

Major Equilibrium is K_a for the weak acid:

$$R_2NH_2^+ \; \rightleftharpoons \; H^+ \; + \; R_2NH$$

$$K_a \; = \; 3.23 \times 10^{-9} \qquad \text{(as above)}$$

$$K_a \; = \; [H^+][R_2NH] / [R_2NH_2^+] \; = \; x^2 / [R_2NH_2^+]$$

$[R_2NH_2^+]$ = moles $R_2NH_2^+$ / volume of solution

moles $R_2NH_2^+$ = initial moles R_2NH = 0.00575 mole

volume = 50.00 mL + 38.33 mL = 88.33 mL

$$= \; 0.08833 \text{ L}$$

$[R_2NH_2^+]$ = (0.00575 mole) / (0.08833 L) = 0.0651 M

so, now:

$$3.23 \times 10^{-9} \; = \; x^2 / 0.0651$$

$$x \; = \; [H^+] \; = \; 1.45 \times 10^{-5} \qquad \qquad \therefore \; pH \; = \; 4.84$$

2. A 0.625-gram sample of an unknown weak acid (call it HA for short) is dissolved in enough water to make 25.0 mL of solution. This weak acid solution is then titrated with 0.100 M NaOH and 45.0 mL of the NaOH solution is required to reach the equivalence point. The pH of the solution at the equivalence point is found to be 8.25.

(a) Determine the molecular mass of the unknown acid.

moles HA = moles NaOH = (0.045 L) (0.10 mole/L)

= 0.0045 moles

molar mass = 0.625 g / 0.0045 mole = 139 g/mole

(b) Determine the pKa value of the unknown acid.

At the equivalence point -- solution contains NaA:

K_b: A^- + H_2O HA + OH^-

M_{A^-} = 0.0045 mole / 0.070 L = 0.0643 M

pOH = 14 - 8.25 = 5.75 $[OH^-]$ = $[HA]$ = $10^{-5.75}$

K_b = $[OH^-] [HA] / [A^-]$ = $(10^{-5.75})^2$ / 0.0643

K_b = 4.92 x 10^{-11} pK_b = 10.31 pK_a = 3.69

3. For $Fe(OH)_3$, $K_{sp} = 1.6 \times 10^{-39}$. For $Fe(CN)_6{}^{3-}$, $K_f = 1.0 \times 10^{31}$.

(a) Determine the molar solubility of $Fe(OH)_3$ in water.
   (*Hint*: It's even LESS soluble than you may first think!)

$$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3\ OH^-$$
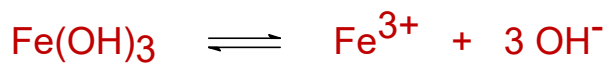
$$K_{sp} = [Fe^{3+}]\,[OH^-]^3 = 1.6 \times 10^{-39}$$

Since K_{sp} is so VERY small, the amount of OH^- in water must be considered!

let x = molar solubility of $Fe(OH)_3$

then, $[Fe^{3+}] = x$

and $[OH^-] = 10^{-7} + 3x \approx 10^{-7}$

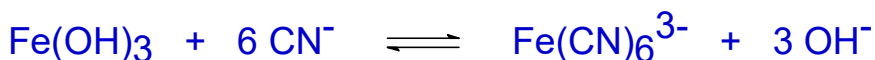$$1.6 \times 10^{-39} = (x)(10^{-7} + 3x)^3 \approx (x)(10^{-7})^3$$

(since K_{sp} is VERY small, assume $3x << 10^{-7}$)

$x \approx 1.6 \times 10^{-18}$ (assumption is OK!)

(b) Determine molar solubility of $Fe(OH)_3$ in 1.0 M NaCN.

Must consider both K_{sp} and K_f equilibria!

Net Reaction:

$$Fe(OH)_3 + 6\ CN^- \rightleftharpoons Fe(CN)_6{}^{3-} + 3\ OH^-$$

$$K_{net} = K_{sp}\,K_f = (1.6 \times 10^{-39})(1.0 \times 10^{31})$$

$$K_{net} = 1.6 \times 10^{-8} \qquad \text{(still quite small)}$$

From a concentration table:

$$1.6 \times 10^{-8} = (x)(3x)^3 / (1.0 - 6x)^6$$

assume $6x << 1.0$

$$1.6 \times 10^{-8} \approx 27x^4 / (1.0)^6$$

$x \approx 4.9 \times 10^{-3}$ M

4. The pK_a of cyanic acid, HOCN, is 3.46. Calculate the volume (in mL) of 2.00 M NaOH that must be added to 500 mL of 0.300 M HOCN in order to yield a buffer solution with a pH equal to 4.00.

NaOH will neutralize some HOCN to form some OCN^-

(Must be **excess acid** since final solution is still acidic, pH = 4.00)

initial moles HOCN = (0.50 L) (0.30 mole/L)

$\qquad\qquad$ = 0.150 moles

let moles NaOH added = X

moles HOCN after neutralization?

$\quad$ 0.150 moles total - X

$\quad$ = 0.150 - X

moles OCN^- = moles NaOH added = X

major equilibrium in the buffer solution:

$\quad$ HOCN $\quad\rightleftharpoons\quad$ H^+ + OCN^-

$\qquad K_a$ = $10^{-3.46}$ = 3.47 x 10^{-4}
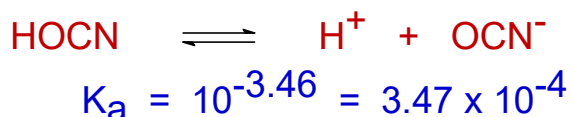
$\qquad [H^+]$ = K_a (moles HOCN) / (moles OCN^-)

$\qquad 10^{-4.00}$ = (3.47 x 10^{-4}) / (0.150 - X) / (X)

$\qquad$ 0.288 = (0.150 - X) / (X)

$\qquad\qquad$ X = 0.116 moles OH^- added

Volume of NaOH = (0.116 moles) (1000 mL / 2.00 moles)

$\qquad\qquad$ = 58.0 mL

5. Consider an aqueous solution that is 0.20 M NH_4CN.

   (a) First, write balanced ionic equations for the ***three*** important equilibrium reactions that are occurring in this solution. Second, use numerical values of the appropriate equilibrium constants to predict whether this solution should be acidic, basic, or neutral. Briefly explain your reasoning (in 30 words or less!)

   NH_4^+ is a weak acid: $NH_4^+ \rightleftharpoons NH_3 + H^+$

   $\quad\quad K_a = K_w / K_b$ (for NH_3) $= 5.68 \times 10^{-10}$

   CN^- is a weak base: $CN^- + H_2O \rightleftharpoons HCN + OH^-$

   $\quad\quad K_b = K_w / K_a$ (for HCN) $= 2.04 \times 10^{-5}$

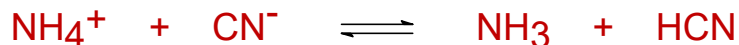   Ionization of water: $H_2O \rightleftharpoons H^+ + OH^-$
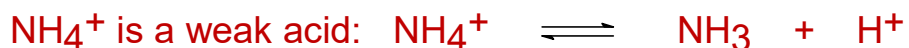
   $\quad\quad K_w = 1.0 \times 10^{-14}$

   K_b for $CN^- >> K_a$ for NH_4^+ $\quad \therefore$ the solution should be basic!

(b) Determine the pH of this 0.20 M NH_4CN solution.
    (**Think** carefully! The pH is lower than you might first expect!)

In addition to the above equilibria, the acid NH_4^+ and the base CN^- can undergo neutralization to some extent as follows.

$$NH_4^+ \; + \; CN^- \; \rightleftharpoons \; NH_3 \; + \; HCN$$

Note that this reaction is the net result of adding the first two reactions above with the reverse of the K_W reaction.

$K_{net} \; = \; K_a \, K_b \, / \, K_W$

$K_{net} \; = \; (5.68 \times 10^{-10}) \, (2.04 \times 10^{-5}) \, / \, (1.0 \times 10^{-14})$

$K_{net} \; = \; 1.16 \; = \; [NH_3] \, [HCN] \, / \, [NH_4^+] \, [CN^-]$

$\quad\quad 1.16 \; = \; x^2 \, / \, (0.20 - x)^2 \quad\quad$ (take square root of both sides)

$\quad\quad 1.08 \; = \; x \, / \, (0.20 - x)$

$\quad\quad x \; = \; [NH_3] \; = \; [HCN] \; = \; 0.104$

$\quad\quad [NH_4^+] \; = \; [CN^-] \; = \; 0.20 - x \; = \; 0.096$

Substitute these values into either the K_a or K_b expression above.

$K_a \; = \; 5.68 \times 10^{-10} \; = \; [NH_3] \, [H^+] \, / \, [NH_4^+]$

$\quad\quad = \; (0.104) \, [H^+]/(0.096)$

$\quad\quad \therefore \; [H^+] \; = \; 5.24 \times 10^{-10} \quad\quad pH \; = \; 9.28$

Note that if only the above K_b reaction was occuring, the pH would be 11.24!