Name ____________________________Chem 163 Section: ______ Team Number: ______

ALE 12. Equilibria of Aqueous Solutions of Weak Acids & Weak Bases

(Reference: 18.3 – 18.5 Silberberg *5th edition*)

How is the pH of a solution related to the concentration of a weak acid?

The Model: Weak Acids

When the generic ***monoprotic*** weak acid (HA) is dissolved in water, the following *reversible* reaction occurs (eqn **1a**).

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq) \qquad \textbf{(1a)}$$

Because the reaction is *understood* to be aqueous, it is often abbreviated as simply eqn **1b**.

$$HA \rightleftharpoons A^- + H^+ \qquad \textbf{(1b)}$$

The equilibrium constant for the dissociation of a weak acid is known as the acid dissociation constant, $\boldsymbol{K_a}$ (where the subscript "a" tells the reader that this constant refers to an **a**cid.)

Key Question

1. Finish the law of mass action corresponding to eqn **1b** (*i.e.*, the dissociation of the weak acid HA).

$$\boldsymbol{K_a} =$$

The Model: Weak Bases

Lithium hydroxide is an example of a metal hydroxide that is soluble in but only partially ionizes in water.

$$LiOH(aq) \rightleftharpoons Li^+(aq) + OH^-(aq) \qquad K_b = 0.6$$

(The subscript "b" tells the reader that this constant refers to a **b**ase.) Since the number of soluble "inorganic" weak bases is quite few, we focus mainly on "organic" bases (*i.e.*, amines). As presented in the last session, ammonia is a base in water. Methylamine [CH_3NH_2], dimethyl-amine [$(CH_3)_2NH$], and trimethylamine [$(CH_3)_3N$] react with water in a similar fashion (see eqns **2**, **3**, and **4**), having as conjugate acids the methylammonium cation, the dimethylammonium cation, and the trimethylammonium cation, respectively.

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq) \qquad \textbf{(2)}$$

$$(CH_3)_2NH(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH_2^+(aq) + OH^-(aq) \qquad \textbf{(3)}$$

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq) \qquad \textbf{(4)}$$

Key Questions

2 a. It is convenient to represent the a weak base as simply "B". Use eqns **2**, **3**, and **4** in the Model to finish the chemical equation for the reaction that occurs when the generic organic base is dissolved in water (*i.e.*, eqn **5**).

$$B(aq) + H_2O(l) \rightleftharpoons \qquad \textbf{(5)}$$

b. Finish the law of mass action corresponding to eqn **5** (*i.e.*, the ionization of the weak base B in water. (*Hint*: Don't forget what we learned about previously about heterogeneous equilibria and laws of mass action!)

$$\boldsymbol{K_b} = \qquad \textbf{(5a)}$$

3 a. A weak base B with ionization constant K_b has a conjugate weak acid BH^+ with ionization constant K_a. Write the reversible chemical equation that occurs when BH^+ (say, from a soluble salt in which the anion is a spectator ion) is dissolved in water (*i.e.*, eqn **6**).

$$\mathbf{BH^+}(\boldsymbol{aq}) \rightleftharpoons \qquad \textbf{(6)}$$

b. Finish the law of mass action corresponding to eqn **6** (*i.e.*, the ionization of the weak acid BH^+).

$$\boldsymbol{K_a} = \qquad \textbf{(6a)}$$

4. Use the laws of mass action you wrote in Questions 2b and 3b as substitutions to show through a step-by-step derivation that $K_a \cdot K_b = 10^{-14}$ for an acid-base conjugate pair.

$$\boldsymbol{K_a \cdot K_b} =$$

The Model: Percent Ionization of an Acid or Base

The percent ionization of an acid (HA) or organic base (B) is given by eqns **7a** and **7b**

$$\%\ \text{ionization} = \frac{[A^-]_{eq}}{[HA]_o} \times 100 \qquad \textbf{(7a)}$$

$$\%\ \text{ionization} = \frac{[BH^+]_{eq}}{[B]_o} \times 100 \qquad \textbf{(7b)}$$

where $[\ ]_{eq}$ is the equilibrium concentration of a resulting ion (provided that the acid or base was the only source of the ion!) and $[\ ]_o$ is the initial concentration of the acid or base.

Exercise

5. The K_a of hydrochloric acid has been estimated to be 10^7. In a 1 *M* HCl(*aq*) solution, the equilibrium molar concentration of undissociated HCl *molecules* is equal to 10^{-7} *M*. What is the percent ionization of a 1 *M* HCl(*aq*) solution? (① Write the law of mass action for the dissociation of HCl. ② Substitute the known values of K_a and $[HCl]_{eq}$. ③ Solve for $[Cl^-]$. *Hint*: Since HCl was the only substance dissolved in water, what is the relationship between $[H^+]$ and $[Cl^-]$? ④ Employ the definition of percent ionization of an acid.)

Key Questions

6. Exercise #5, above, hopefully served as a reminder from your General Chemistry I course as to what a strong acid is. *What is a strong acid*?

7. The K_a of nitric acid (HNO_3, a strong acid) has been estimated to be 10^4. The K_a of nitrous acid (HNO_2) is 4.5×10^{-4}. What is the relationship between the value of K_a and the strength of an acid?

8. Suppose HA and HB are two acids with ionization constants such that $K_a(HA) > K_a(HB)$.
   a. Which is the stronger acid: HA or HB? (*Circle your answer*.)
   b. Look back at Question 4. Place a "<" or a ">" in the blank that makes the inequality correct.

      $K_b(A^-)$ ___ $K_b(B^-)$

   c. Which is the stronger base: A^- or B^-? (*Circle your answer*.)

Exercises

9. A 0.10 *M* acetic acid solution is prepared. The K_a of acetic acid is 1.8×10^{-5}. ① What is the pH of this solution? (*Hints*: Set up an ICE table. Let "x' represent $[H^+]_{eq}$. Substitute the algebraic expressions into the law of mass action. Make an assumption that will simplify the algebra and solve for the variable.) ② What is the percent ionization of this solution? (*Hint*: What is the relationship between $[H^+]_{eq}$ and $[CH_3COO^-]_{eq}$?)

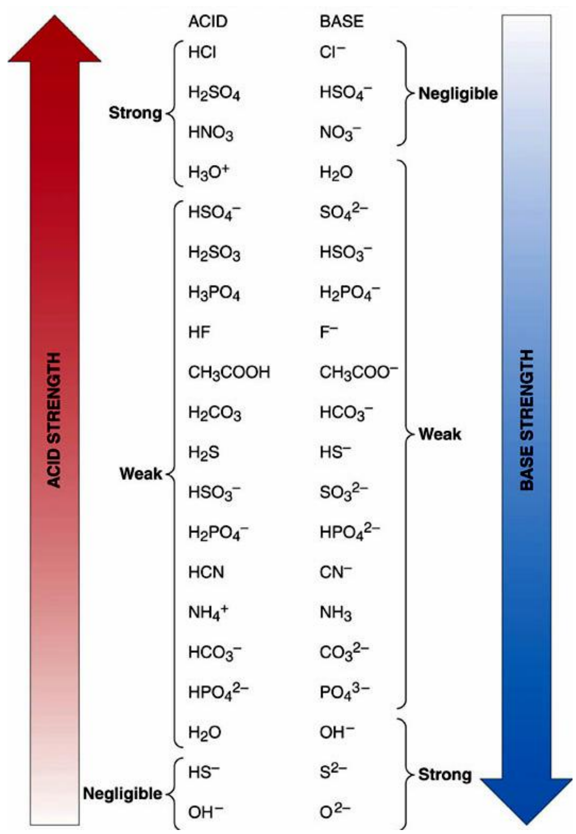
10. A 2.0 *M* $(CH_3)_3N(aq)$ solution is 0.61% ionized. What is the K_a of the trimethylammonium cation? [*Hints*: Use the definition of the percent ionization of a weak base to determine what the equilibrium concentration of the trimethylammonium cation is in a 2.0 *M* aqueous solution of trimethylamine. Use an ICE table to determine the equilibrium concentrations of $(CH_3)_3N$, OH^-, and $(CH_3)_3NH^+$ in a 2.0 *M* $(CH_3)_3N(aq)$ solution. Use the law of mass action to determine K_b for $(CH_3)_3N$. Finally determine the K_a of $(CH_3)_3NH^+$.]

11. Use the figure to the right to determine if $Kc < 1$ for each reaction below. *Explain your reasoning/show your work*.

a. $H_2PO_4^-{}_{(aq)} + F^-{}_{(aq)} \rightleftharpoons HPO_4^{2-}{}_{(aq)} + HF_{(aq)}$

b. $CH_3COO^-{}_{(aq)} + HSO_4^-{}_{(aq)} \rightleftharpoons CH_3COOH_{(aq)} + SO_4^{2-}{}_{(aq)}$

Strengths of conjugate acid-base pairs



12. A sample of 0.0001 *M* HCl has a $[H_3O^+]$ close to that of 0.1 *M* CH_3COOH. Are acetic acid and hydrochloric acid equally strong in these examples? Explain.

13. A 0.035 *M* solution of a weak acid (HA) has pH of 4.88. What is the K_a of the acid? Show your work.

14. Hydrofluoric acid, HF, has a K_a of 6.8×10^{-4}. What are $[H_3O^+]$, $[F^-]$ and $[OH^-]$ in 0.75 *M* HF? *Show your work*.

15. Hypochlorous acid, HClO, has a pK_a of 7.54. What are $[H_3O^+]$, pH, $[ClO^-]$ and [HClO] in 0.115 *M* HClO? *Show your work.* *Hint*: Just as pH is the negative log of the hydronium ion, pKa is the negative log of the K_a: $pKa = -\log K_a$

16. Write the balanced equation and K_b expression for the benzoate ion (a Bronsted-Lowry base), $C_6H_5COO^-$, in water.

$$C_6H_5COO^- (aq) + H_2O(l) \rightleftharpoons$$

$$K_b =$$

17. The K_a of benzoic acid, C_6H_5COOH, is 6.3 x 10^{-5}. Calculate the K_b of the benzoate ion, $C_6H_5COO^-$. ***Hint***: See your response to question #4!

18. Calculate the pH of 0.100 *M* sodium phenolate, $C_6H_5O^-Na^+$, the sodium salt of phenol. The K_a of phenol is 1.0 x 10^{-10}. ***Hints***: Calculate the K_b of the phenolate ion, $C_6H_5O^-$, and then set up an ICE table to calculate $[OH^-]$. Now use K_w to calculate $[H^+]$ and then calculate the pH.

$$C_6H_5O^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + C_6H_5OH(aq) \qquad K_b = ?$$