## NOTES #52 Ka & Kb Values & Di/Polyprotic Acids

C.	Determining	$IH^{+}I$	and [OH-	at Equilibrium for STRO	ONG ACIDS and STRONG BAS
C.	Determining	H	and IOH	at Equilibrium for STRU	JNG ACIDS and STRONG B

\*\* These type of problems are very easy because strong acids and strong bases dissociate 100%.

(b) 
$$1.8 \times 10^{-2}$$
 M Ba(OH)<sub>2</sub> solution

- D. Determining [H<sup>+</sup>] and [OH<sup>-</sup>] at Equilibrium for WEAK ACIDS and WEAK BASES.
  - \*\* These are a little more challenging just because weak acids and bases do not dissociate 100%....
  - 1. Weak Acids and K<sub>a</sub> values.
    - a. K<sub>a</sub> value or the acid ionization constant is just the Equilibrium constant for the ionization of an acid.
      - i. Since STRONG ACIDS dissociate 100%, the reaction goes to completion. The  $K_a$  value for a STRONG ACID is said to be VERY LARGE.

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$$HCl(aq) \rightarrow H^{+}(aq) + Cl^{-}(aq)$$

$$K_a = VERY LARGE \approx 10^{20+}$$

ii. Ka values for weak acids are variable.

- HF (aq) 
$$\Rightarrow$$
 H<sup>+</sup> (aq) + F<sup>-</sup> (aq)

$$K_a = 7.1 \times 10^{-4}$$

- 
$$CH_3COOH(aq) = H^+(aq) + CH_3COO^-(aq) = 1.8 \times 10^{-5}$$

$$K_a = 1.8 \times 10^{-5}$$

$$- HCN (aq) = H^{+} (aq) + CN^{-} (aq)$$

$$K_a = 4.9 \times 10^{-10}$$

- iii. The LARGER the K<sub>a</sub>, the \_\_\_\_\_\_ the acid. (The more the H<sup>+</sup> side of the equation is favored.)
- b. Using K<sub>a</sub> to determine [H<sup>+</sup>] at Equilibrium. Use I.C.E. TABLES, just like we did in EQ

EX 2: (on a separate sheet of paper) Calculate the pH,  $[HNO_2]$ , and  $[NO_2^-]$  of a 0.50 M solution of  $HNO_2$  acid. At 25°C the Ka is 4.5 x  $10^{-4}$ .

- 1. Identify the major species that will provide  $H^+$ .

$$HNO_2 (aq) \rightleftharpoons H^+ (aq) + NO_2^- (aq)$$

$$K_a = 4.5 \times 10^{-4}$$

$$H_2O(1) \Rightarrow H^+(aq) + OH^-(aq)$$

$$K_{xy} = 1 \times 10^{-14}$$

$$K_a \times K_b = K_w$$
 So Ka for water =

- a. What species will be present in this solution,

  b. Which of the above species will provide  $H^+??$   $HNO_2$  (aq)  $\Rightarrow H^+$  (aq)  $+ NO_2^-$  (aq)  $K_a = 4.5 \times 10^{-4}$   $K_a = 4.5 \times 10^{-14}$   $K_a = 4.5 \times 10^{-14}$ \* At this point, you can single out one source of  $H^+$  can be singled out as DOMINANT. By comparing  $K_a$  for  $HNO_2$  acid and  $K_w$  for water, we see that although weak, HNO2 is a much acid than water. For the rest of the problem, we can ignore any H<sup>+</sup> contributions from the autoionization of water.
- c. Construct an I.C.E. table.
- d. Substitute Equilibrium concentrations into  $K_a$  expression.
- e. Use the Quadratic equation and solve? NO! Since  $K_a$  is so small, you can make the assumption that x will be very small and that 0.50 x = 0.50. Check to make sure that your approximation is reasonable. If your ratio of lowest initial concentration/Ka > 200, then x IS small enough and your approximation is reasonable.
- f. Solve for pH,  $[HNO_2]$  and  $[NO_2^-]$ .

## Different types of problems you will see:

EX 3: (on a separate sheet of paper) If you know the pH of a solution and the initial concentrations of a monoprotic acid, you can calculate K<sub>a</sub>. Calculate the K<sub>a</sub> of an unknown weak monoprotic acid if the pH of a 0.60 M sample is 1.87. Identify the acid from the choices in Appendix D.

- 3. WEAK BASES and K<sub>b</sub>.
  - a. The ionization of weak bases is treated the same way as we just saw with acids.
  - b.  $K_b$ , or the base ionization constant, is just a measure of how much a BASE wants to gain an H and become a + ion at equilibrium.

c. Consider the base ionization of NH <sub>3</sub> , ammonia. NH <sub>3</sub> (aq) + H <sub>2</sub> O (l) $\Leftrightarrow$ NH <sub>4</sub> <sup>+</sup> (aq) + OH <sup>-</sup> (aq) $K_b =$
d. The LARGER K <sub>b</sub> is, the the base.  Refer to Appendix D for a table of common weak Bases. What do all of these weak bases have in common???
e. Follow the same method you used for weak acids to solve for weak base problems. Just be careful in that you are dealing with [OH-] instead of [H+]
EX 4: Calculate the $K_b$ of an unknown weak base if the pH of a 0.260 M sample is 12.03. Identify the base using the $K_b$ value that you calculated. Determine the pH of a 0.50 M solution of this same base.
Diprotic and Polyprotic Acids
1. Diprotic Acids - Acids with 2 acidic protons (H <sup>+</sup> 's) to donate. EX:
Polyprotic Acids - Acids with more than 2 acid protons (H <sup>+</sup> 's) to donate. EX:
2. Diprotic and polyprotic acids ionize in a step-wise fashion, ONE $H^+$ at a time. There will be a new $K_a$ value and equilibrium expression for each ionization. REFER TO APPENDIX D IN BOOK.
$H_2SO_4 (aq) \rightarrow H^+ (aq) + HSO_4^- (aq) K_{a1} =$
$HSO_4^-(aq) \Rightarrow H^+(aq) + SO_4^{2-}(aq) K_{a2} =$
3. The first $K_a$ is always LARGER than the second $K_a$ . Why is this? It gets more difficult to remove the $H^+$ as you proceed through each ionization. In other words, it's easier to remove and $H^+$ from a neutral $H_2CO_3$ molecule than from a CHARGED $HCO_3^-$ ion. Opposites attract! $K_{a1} > K_{a2} > K_{a3}$
4. Determining [H <sup>+</sup> ] at equilibrium for a diprotic or polyprotic acid is a little tricky!
EX 1: Compare the pH of a $0.040$ M HCl solution to a $0.040$ M $H_2SO_4$ solution. Make some predictions??
1. Determine pH of the 0.040 M HCl soln. This is EASY because HCl's a STRONG acid.
2. Determine the pH of the 0.040 M $H_2SO_4$ . Watch out. You're going to need TWO I.C.E. tables
5.* Final Conclusions - Fortunately, H <sub>2</sub> SO <sub>4</sub> is really the only example of a diprotic acid with relatively large K <sub>a</sub> values. ALL the other
diprotic/polyprotic acids have really SMALL K <sub>a</sub> values which makes these calculations much easier.
EX 2: Calculate the $[C_2H_2O_4]$ , $[C_2HO_4^-]$ , $[C_2O_4^{2-}]$ , and pH of a 0.20 M oxalic acid solution. (on a separate sheet of paper)
6. Final Suggestions for handling diprotic/polyprotic acids.
a. If you're talking about a WEAK di- or polyprotic acid where $K_{a1} >> K_{a2}$ , we can make the assumption that the FIRST ionization step is the only important one. Most of the $H^+$ will come from this $1^{st}$ stepany $H^+$ contributions from the second or third ionization step will be INSIGNIFICANT!
$H_2A \Rightarrow H^+ + HA^ K_{a1} = \text{smalllike } 1.0 \times 10^{-2}$ $HA^- \Rightarrow H^+ + A^ K_{a2} = \text{very smalllike } 1.0 \times 10^{-5}$

b. The concentration of the conjugate base,  $A^-$ , will be *numerically* equal to  $K_{a2}$ . c. If you are talking about  $H_2SO_4$ , because it's a STRONG acid....no short cuts usually!  $H^+$  contributions from both ionization steps will be significant....