

Name \_\_\_\_\_ KEY \_\_\_\_\_ Rec. TA/time \_\_\_\_\_

1. (3 pts) You have the following data for three weak acids.

Weak Acid	$K_a$	Concentration (M)	Percent Ionization
HA	$9.00 \times 10^{-5}$	0.100	3.0
HB	$1.10 \times 10^{-4}$	0.300	1.9
HX	$1.50 \times 10^{-5}$	0.010	3.8

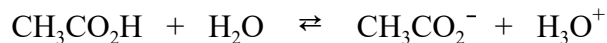
What is the correct order for the strengths of these three acids, from weakest to strongest? **Explain!**

**HX < HA < HB**

You can **NOT** use the % ionization to compare the strength of acids unless they have the same conc. The  $K_a$  tells you the strength of an acid, regardless of the conc. and the % ionization (which depends on conc. for a given acid and the acid's  $K_a$ ).

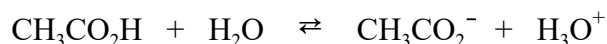
The same would apply to bases and  $K_b$ .

2. (3 pts) What change will occur for the following reaction if the acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , solution is diluted from 0.1 to 0.01 M? **Explain!**



- a) a decrease in the fraction of acid dissociated
- b)\* an increase in the fraction of acid dissociated
- c) no change in the fraction of acid dissociated

What happens when an acid is diluted? Does the reaction shift? In what direction? Does the % ionization inc. or dec.? In this problem a 0.1 M acetic acid soln. is diluted to 0.01 M. Use Le Chatelier's Principle.



As water is added the conc. of all the solute particles decrease. We can see what happens by looking at the reaction quotient and comparing it to the equil. constant. In the 0.1 M soln an equil. has been established so we can write K,

$$K = \frac{[\text{H}_3\text{O}^+]_{\text{eq},0} [\text{CH}_3\text{CO}_2^-]_{\text{eq},0}}{[\text{CH}_3\text{CO}_2\text{H}]_{\text{eq},0}}$$

These are the conc. at equil. in the original soln. Water is then added to reduce the conc. of  $\text{CH}_3\text{CO}_2\text{H}$  from 0.1 to 0.01 M. That's a reduction of 10 fold. That's like adding enough water to reduce the conc. by a factor of 10 (multiply by 1/10). We need to look at the reaction quotient, Q,

$$Q = \frac{[\text{H}_3\text{O}^+]_i [\text{CH}_3\text{CO}_2^-]_i}{[\text{CH}_3\text{CO}_2\text{H}]_i}$$

$$Q = \frac{\{(0.1) [\text{H}_3\text{O}^+]_{\text{eq},0}\} \{(0.1) [\text{CH}_3\text{CO}_2^-]_{\text{eq},0}\}}{(0.1) [\text{CH}_3\text{CO}_2\text{H}]_{\text{eq},0}}$$

$$Q = \frac{\{(0.1)(0.1)\} [\text{H}_3\text{O}^+]_{\text{eq},0} [\text{CH}_3\text{CO}_2^-]_{\text{eq},0}}{(0.1) [\text{CH}_3\text{CO}_2\text{H}]_{\text{eq},0}}$$

$$Q = 0.1 * K$$

$$Q < K$$

Not enough product and too much reactant to be at equil. The reaction shifts to the right to reach a new equil. with new equil. conc. The moles of  $\text{CH}_3\text{CO}_2\text{H}$  decreases and the moles of  $\text{H}_3\text{O}^+$  and  $\text{CH}_3\text{CO}_2^-$  inc. (the conc. of these substances are all less than before due to dilution).

This is kind of like a gas-phase rxn. When the pressure is decreased by inc. volume the reaction shifts toward more moles of gas. The same thing happens here, inc. volume of soln. by adding water, solvent, (dilution) the rxn. shifts to more moles in solution.

**Adding solvent (dilution):      Rxn shifts toward more moles in solution**

Thus, the rxn above shifts **right** and more of the acid comes apart (**inc. % ionization**). Even so, the conc of  $\text{H}_3\text{O}^+$  is less than before due to dilution. That means the resulting diluted solution won't be as acidic as before dilution (pH goes up compared to before dilution).

3. (10 pts) You have a solution of 0.20 M formic acid,  $\text{HCHO}_2$ , with  $K_a = 1.8 \times 10^{-4}$ , at  $25^\circ\text{C}$  (**Show all work, including ICE tables, assumptions & check for % error.**) **Show all work or explain!**

a) What are  $[\text{H}^+]$ ,  $[\text{OH}^-]$ , pH and pOH in this solution?

$\text{HCHO}_2$  is a weak acid - weakacid equil. problem - **Use equil. table** (in Molarity)

	$\text{HCHO}_2$	$\rightleftharpoons$	$\text{H}^+$	+	$\text{CHO}_2^-$	(or $\text{HCHO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CHO}_2^- + \text{H}_3\text{O}^+$ )
initial	0.20		0		0	
change	- x		+ x		+ x	
<hr/>						
equil	$0.20 - x$		x		x	

$$K_a = \frac{[\text{H}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]} = 1.8 \times 10^{-4} \quad \frac{x^2}{0.20 - x} = 1.8 \times 10^{-4}$$

Assume  $0.20 \gg x$ , so  $(0.20 - x) \approx 0.20$   $\frac{x^2}{0.20} = 1.8 \times 10^{-4}$  ;  $x = [\text{H}^+] = 6.0 \times 10^{-3} \text{ M}$

$$\% \text{ error} = \frac{6.0 \times 10^{-3}}{0.20} \times 100\% = 3.0 \% \text{ error (assumption above is okay)}$$

$$\text{pH} = -\log(6.0 \times 10^{-3}) = 2.22 \quad (2 \text{ s.f., the ones to the right of the decimal})$$

$$\text{pH} + \text{pOH} = \text{pK}_w = 14.00$$

$$[\text{H}^+] \times [\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

$$\text{pOH} = 14.00 - 2.22 = 11.78 \quad ("4" \text{ s.f.})$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-11.78} = 1.7 \times 10^{-12} \text{ M}$$

$$\text{or} \quad [\text{OH}^-] = \frac{1.0 \times 10^{-14}}{6.0 \times 10^{-3}} = 1.666 \times 10^{-12} \text{ M}$$

$$\text{pOH} = -\log(1.666 \times 10^{-12}) = 11.78$$

**NOTE:** The **sig. fig.** in **pH**, **pOH** and **pK** are to the **right** of the **decimal point**. While the 2.22 for pH above appears to have "3" sig. fig. in reality it only has 2, the digits to the right of the decimal. The "2" to the left of the decimal point in the 2.22 comes from the power of 10 in the  $[\text{H}^+]$ .

b) What is the **percent ionization** of  $\text{HCHO}_2$  in this solution?

$$\% \text{ ionization} = \frac{[\text{H}^+]}{[\text{HCHO}_2]_{\text{orig}}} \times 100\% = \frac{6.0 \times 10^{-3}}{0.20} \times 100\% = 3.0 \% \text{ ionized}$$

4. (11 pts) You have a solution of 0.0942 M aniline,  $\text{C}_6\text{H}_5\text{NH}_2$ , with  $K_b = 4.3 \times 10^{-10}$ , at  $25^\circ\text{C}$ . (**Show the ICE table, state any assumptions made and check your percent error.**) **Show all work or explain!**

a) What are  $[\text{H}^+]$ ,  $[\text{OH}^-]$ , pH and pOH in this solution?

$\text{C}_6\text{H}_5\text{NH}_2$  is a weak base - weak base equil. problem - **Use equil. table** (in Molarity)

	$\text{C}_6\text{H}_5\text{NH}_2$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{C}_6\text{H}_5\text{NH}_3^+$	+	$\text{OH}^-$
initial	0.0942				0		0
change	- x				+ x		+ x
equil	0.0942 - x				x		x

$$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} = 4.3 \times 10^{-10} \quad \frac{x^2}{0.0942 - x} = 4.3 \times 10^{-10}$$

Assume  $0.0942 \gg x$ , so  $(0.0942 - x) \approx 0.0942$   $\frac{x^2}{0.0942} = 4.3 \times 10^{-10}$

$$x = [\text{OH}^-] = \underline{6.36} \times 10^{-6} = \underline{6.4} \times 10^{-6} \text{ M}$$

$$\% \text{ error} = \frac{6.4 \times 10^{-6}}{0.0942} \times 100\% = 0.0068 \% \text{ error (assumption above is okay)}$$

$$\text{pOH} = -\log(6.4 \times 10^{-6}) = \underline{5.196} = \underline{5.20} \quad (2 \text{ s.f.} - 2 \text{ digits to right of decimal point})$$

$$\text{pH} + \text{pOH} = \text{pK}_w = 14.00$$

$$[\text{H}^+] \times [\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

$$\text{pH} = 14.00 - 5.20 = \underline{8.80} \quad ("2" \text{ s.f.})$$

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-8.80} = \underline{1.57} \times 10^{-9} \text{ M}$$

$$\text{or} \quad [\text{H}^+] = \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-6}} = \underline{1.571} \times 10^{-9} \text{ M}$$

$$\text{pH} = -\log(1.571 \times 10^{-9}) = 8.80$$

**NOTE:** The **significant figures** in the **pH**, **pOH** and **pK** are to the **right** of the **decimal point**.

b) What is the **percent ionization** for  $\text{C}_6\text{H}_5\text{NH}_2$  in this solution?

$$\% \text{ ionization} = \frac{[\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]_{\text{orig}}} \times 100\% = \frac{6.4 \times 10^{-6}}{0.0942} \times 100\% = \underline{0.0068} \% \text{ ionized}$$

5. (6 pts) A 0.0100 M solution of an acid is 19.0% ionized at 25 °C. **Show all work or explain!**

Want the **ionization constant**,  $K_a$ , for a weak acid given the conc. of the acid and the % ionization.

a) What are the  $[H^+]$  and **pH** of this solution?

$$\% \text{ ionization} = \frac{[H^+]_{eq}}{[HA]_{orig}} \times 100$$

$$[H^+]_{eq} = \frac{\% \text{ ionization}}{100} \times [HA]_{orig}$$

$$[H^+]_{eq} = \frac{19.0}{100} (0.0100) = 0.00190$$

$$[H^+]_{eq} = 1.90 \times 10^{-3} \text{ M} = 1.90 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log [H^+] = -\log (1.90 \times 10^{-3}) = 2.7212 = 2.721 \text{ (only 3 s.f. - to right of decimal)}$$

b) What is the  $K_a$  for the acid? **Show the ICE table.**

Technically you don't need to write out an ICE table for this but it does make the problem easier. In this case you won't be solving for  $H^+$  ( $H_3O^+$ ) but instead use it to solve for  $K_a$ .

HA is a weak acid - weak acid equil. problem - **Use equil. (ICE) table** (in Molarity)

	HA	$\rightleftharpoons$	$H^+$	+	$A^-$	(or HA + H <sub>2</sub> O $\rightleftharpoons$ A <sup>-</sup> + H <sub>3</sub> O <sup>+</sup> )
initial	0.0100		0		0	
change	- x		+ x		+ x	
equil	0.0100 - x		x		x	

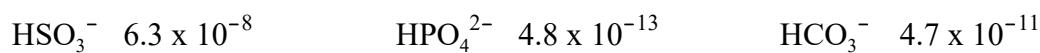
$$x = [H^+] = [H_3O^+]$$

get this from % ionized above:

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{0.0100 - x} = \frac{(0.00190)^2}{(0.0100 - 0.00190)} = 4.456 \times 10^{-4} = 4.45 \times 10^{-4}$$

Can **not** ignore the "x" in the 0.0100 - x and get the correct answer. There is no point in ignoring the "x" in this problem since you have "x" so just use it. If you did, you would get  $3.6 \times 10^{-4}$  which would be a 19% error.

6. (3 pts) Given the following  $K_a$  values, determine which species is the **strongest base**. **Explain!**



Remember:

Larger  $K_a \implies$  smaller  $\text{p}K_a \implies$  stronger acid  $\implies$  weaker conj. base

Larger  $K_b \implies$  smaller  $\text{p}K_b \implies$  stronger base  $\implies$  weaker conj. acid

For a conj. Acid-Base pair:

$$K_a \times K_b = K_w \qquad \text{and} \qquad \text{p}K_a + \text{p}K_b = \text{p}K_w$$

$$\begin{array}{cc} \text{HSO}_3^- & \text{SO}_3^{2-} \\ K_a = 6.3 \times 10^{-8} & K_b = 1.6 \times 10^{-7} \end{array}$$

$$\begin{array}{cc} \text{HPO}_4^{2-} & \text{PO}_4^{3-} \\ K_a = 4.8 \times 10^{-13} & K_b = 2.1 \times 10^{-2} \end{array}$$

$$\begin{array}{cc} \text{HCO}_3^- & \text{CO}_3^{2-} \\ K_a = 4.7 \times 10^{-11} & K_b = 2.1 \times 10^{-4} \end{array}$$

$\text{HSO}_3^-$  strongest acid (largest  $K_a$ )  $\implies$  weakest conj. base,  $\text{SO}_3^{2-}$  (smallest  $K_b$ )

$\text{HPO}_4^{2-}$  weakest acid (smallest  $K_a$ )  $\implies$  **strongest conj. base,  $\text{PO}_4^{3-}$**  (largest  $K_b$ )

7. (2 pts) The  $K_a$  of a weak acid, HX, is  $1.3 \times 10^{-6}$ . What is the  $K_b$  for its conjugate base,  $\text{X}^-$ ?

For a conjugate acid-base pair:

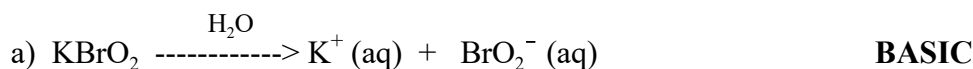
$$K_a * K_b = K_w = 1.0 \times 10^{-14} \text{ (at } 25^\circ\text{C)}$$

$$\text{p}K_a + \text{p}K_b = \text{p}K_w = 14.00 \text{ (at } 25^\circ\text{C)}$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-6}} = 7.7 \times 10^{-9}$$

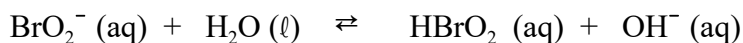
8. (2 pts) Would you expect the following solutions to be acidic, neutral, or basic? **Explain or show work!**

In general: cations  $\Rightarrow$  acidic soln (except group 1A & 2A  $\{Ca^{2+}, Sr^{2+}, Ba^{2+}\}$  cations - give neutral)  
 anions  $\Rightarrow$  basic soln (except conj. bases of strong acids;  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $NO_3^-$ ,  $ClO_3^-$ ,  $ClO_4^-$  are neutral  
 $HSO_4^-$  is acidic)  
 Also, for most amphoteric anions (like  $HCO_3^-$ ,  $HSO_3^-$ ,  $H_2PO_4^-$ , etc.) you can't tell if it's basic or acidic w/o doing calculations)



$K^+$ : group 1A cation ("conj. acid" of a strong base, KOH, and does not act as an acid) - neutral

$BrO_2^-$  is conj. base of a weak acid,  $HBrO_2$ , & acts as a **weak base**



$Cl^-$ : conj. base of a strong acid, HCl & does not act as a base - neutral

$Pb^{2+}$ : metal cation - causes soln to be **acidic**

9. (3 pts) Would you expect a solution of  $NH_4ClO$  to be acidic, neutral, or basic? ( $K_b$  for  $NH_3 = 1.8 \times 10^{-5}$  and  $K_a$  for  $HClO = 3.0 \times 10^{-8}$ ) **Explain or show work!**

$NH_4ClO$  is a salt of a weak base ( $NH_3$ ) and a weak acid ( $HClO$ ). You can't state whether the soln will be acidic, neutral or basic with just looking at the ions produced. Compare the strength of the thing that's acting as the acid to the thing that's acting as the base. Whichever is stronger determines if the solution is acidic or basic.



$NH_4^+$ : cation is conj. acid of a weak base,  $NH_3$ , & acts as a **weak acid**

$ClO^-$  is conj. base of a weak acid,  $HClO$ , & acts as a **weak base**

Compare  $K_{a,NH_4^+}$  &  $K_{b,ClO^-}$   $K_a * K_b = K_w$  for a conj. acid-base pair

If  $K_{a,acid} > K_{b,base}$  Acidic

$K_{b,base} > K_{a,acid}$  Basic

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \quad K_{a,NH_4^+} = \frac{K_w}{K_{b,NH_3}} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq) \quad K_{b,ClO^-} = \frac{K_w}{K_{a,HClO}} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-8}} = 3.3 \times 10^{-7}$$

$K_{a,NH_4^+} < K_{b,ClO^-}$   $\therefore$  **BASIC** (more  $OH^-$  produced by  $ClO^-$  than  $H^+$  produced by  $NH_4^+$ )

If  $K_{a,acid} = K_{b,base}$ , base the solution would be neutral

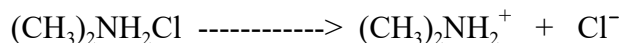
10. (8 pts) What is the **pH** of a 0.30 M  $(\text{CH}_3)_2\text{NH}_2\text{Cl}$  solution at  $25^\circ\text{C}$ ? ( $(\text{CH}_3)_2\text{NH}$ :  $K_b = 5.4 \times 10^{-4}$ , at  $25^\circ\text{C}$ ) (**Show the ICE table, state any assumptions made and check your percent error.**) **Explain or show work!**

Hydrolysis problem (salt solution- ions reacting with  $\text{H}_2\text{O}$  to make the soln acidic or basic)

**GENERALLY:**

Cations - acidic (except group 1A & 2A  $\{\text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}\}$  cations which are neutral)

Anions - basic (except conj. base of strong acids:  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$  are neutral  
 $\text{HSO}_4^-$  is acidic)



Acidic

Neutral

Solution will be acidic.

$(\text{CH}_3)_2\text{NH}_2^+$  is conj acid of weak base  $(\text{CH}_3)_2\text{NH}$  - acid equil. problem - **Use ICE (equil.) table**  
 (in Molarity)

	$(\text{CH}_3)_2\text{NH}_2^+$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$(\text{CH}_3)_2\text{NH}$	+	$\text{H}_3\text{O}^+$
initial	0.30				0		0
change	- x				+ x		+ x
<hr/>							
equil	0.30 - x				x		x

Find the pH of the solution - need the  $K_a$  for  $(\text{CH}_3)_2\text{NH}_2^+$

For a conj. acid base pair :  $K_a \cdot K_b = K_w = 1.0 \times 10^{-14}$  &  $\text{p}K_a + \text{p}K_b = \text{p}K_w = 14.00$

$$K_a = \frac{[(\text{CH}_3)_2\text{NH}][\text{H}_3\text{O}^+]}{[(\text{CH}_3)_2\text{NH}_2^+]} = \frac{x^2}{0.30 - x} = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.4 \times 10^{-4}} = 1.851 \times 10^{-11}$$

Assume  $0.30 \gg x$ , so  $(0.30 - x) \approx 0.30$   $\frac{x^2}{0.30} = 1.851 \times 10^{-11}$  ;  $x = [\text{H}_3\text{O}^+] = 2.357 \times 10^{-6}$

$$\% \text{ error} = \frac{2.35 \times 10^{-6}}{0.30} \times 100\% = 7.9 \times 10^{-4} \% \text{ error (assumption above is okay)}$$

$$\text{pH} = -\log(2.357 \times 10^{-6}) = 5.63 \text{ (only 2 s.f. - the ones to right of decimal)}$$