

### Discussion 7 Chapter 14 2018 Key:

1. 2 M of HCN has a  $K_a = 5 \cdot 10^{-10}$ . What is the pH at equilibrium and the percent reaction of the acid?

	HCN	H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>	CN <sup>-</sup>
I $Q=0 < K$	2 M		$10^{-7}$ M	0
C	-x		+x	+x
E	2 M - x $\approx$ 2M		$10^{-7} + x \approx x$	x
	$K_a \ll 1$		$K_A \gg K_w$	

$$K_a = 5 \cdot 10^{-10} = \frac{x^2}{2}$$

$$10 \cdot 10^{-10} = 1 \cdot 10^{-9} = x^2$$

$$x = 3.0 \cdot 10^{-5}$$

$$\text{pH} = -\log(3 \cdot 10^{-5}) = -\log 3.0 - \log 10^{-5} = -0.48 + 5 = 4.5$$

$$\% = \frac{3.0 \cdot 10^{-5}}{2} \cdot 100\% = 1.5 \cdot 10^{-3}\% =$$

2. A solution of 0.1M of HX in water has a pH=3.0 at room temperature.
- Based on the information given do you have a reaction of acid with water or base with water? Why? Acid pH<7
  - Write the chemical equation for the acid-base reaction that occurs in this solution. What are the conjugate acid and base pairs in the solution?  

$$\text{HX}(aq) + \text{H}_2\text{O}(l) \leftrightarrow \text{X}^-(aq) + \text{H}_3\text{O}^+(aq)$$
  - Write the expression for equilibrium constant K(does your expression represent  $K_a$  or  $K_b$ ):

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{X}^-]}{[\text{HX}]}$$

- d. Calculate equilibrium concentration of hydronium

$$[\text{H}_3\text{O}^+(aq)]_{\text{eq}} = 10^{-\text{pH}} = 1 \cdot 10^{-3} \text{ M}$$

- e. What percent of the acid reacted in solution? Is this a strong or **weak acid**?

$$(1 \cdot 10^{-3} \text{ M} / 0.1) \cdot 100\% = 1\%$$

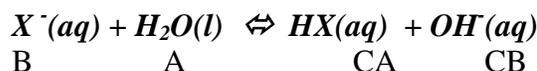
- f. Based on the information given will you expect the equilibrium constant to be: (choose one)  $K_a \ll 1$  or  $K_a \gg 1$

3. A solution of 0.1M of NaX is dissolved in pure water pH = 9.0 at room temperature.

a. Based on the information given do you have a reaction of acid with water or base with water? Why? **base with water because pH>7**

b.  $\text{NaX(s)} \rightleftharpoons \text{Na}^+(\text{aq}) + \text{X}^-(\text{aq})$

c. Write the chemical equation for the acid-base reaction that occurs in this solution. What are the conjugate acid and base pairs in the solution?



d. Write the expression for equilibrium constant  $K$  (does your expression represent  $K_a$  or  $K_b$ ):

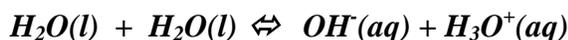
$$K_b = \frac{[\text{HX}][\text{OH}^-]}{[\text{X}^-]}$$

e. Based on the information given will you expect the equilibrium constant to be: (choose one)

$$\underline{K_b \ll 1} \quad \text{or} \quad K_b \gg 1$$

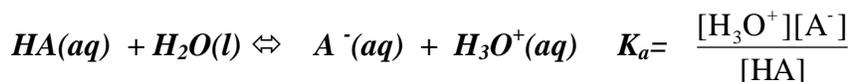
4. Using the equilibrium constants in questions 2 and 3 derive the expression for equilibrium constant for autoionization of water.

a. Write the chemical equation for autoionization of water:

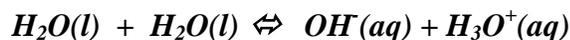
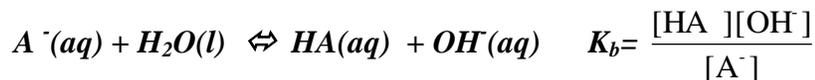


b. Write the expression for equilibrium constant  $K_w = [\text{H}_3\text{O}^+(\text{aq})][\text{OH}^-(\text{aq})]$

c. Use questions 10c and 11c to derive the expression for  $K_w$  using  $K_a$ ,  $K_b$



+



$$K_w = K_a \cdot K_b = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \cdot \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}_3\text{O}^+(\text{aq})] \cdot [\text{OH}^-(\text{aq})]$$

5. A 0.1 M solution of an acid, HB, is found to have a pH of 3.52. (This implies that it is an equilibrium pH) What is the  $K_a$ ? What was the percent reaction of the acid?

$$[\text{H}_3\text{O}^+] = 10^{-3.52} = 3.0 \times 10^{-4}$$

What is the chemical reaction?  $\text{HB}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{B}^-(\text{aq})$

What is the equilibrium expression of  $K$ :

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{B}^-]}{[\text{HB}]} \quad K_a = \frac{x^2}{0.1} = \frac{(3.0 \cdot 10^{-4})^2}{1 \cdot 10^{-1}} = \frac{9.0 \cdot 10^{-8}}{10^{-1}} = 9 \cdot 10^{-7}$$

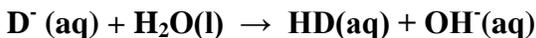
ICE table:

	HB	H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>	B <sup>-</sup>
I	0.1 M		10 <sup>-7</sup> M	0
C	-x		+x	+x
E	0.1 - x ≈ 0.1M		10 <sup>-7</sup> + x ≈ 3 · 10 <sup>-4</sup> M	x ≈ 3 · 10 <sup>-4</sup> M - 10 <sup>-7</sup> M x ≈ 3 · 10 <sup>-4</sup> M

$$\% = \frac{3.0 \cdot 10^{-4}}{0.1} \cdot 100\% = 0.3\%$$

6. 0.5 M solution of NaD (D<sup>-</sup> is a salt of the weak acid HD with the  $K_a = 2.5 \times 10^{-10}$ ).

What is the chemical reaction?



What is the equilibrium expression and the value of  $K$  for the reaction of NaD and water:

$$K_b = \frac{K_w}{K_a} = \frac{1 \cdot 10^{-14}}{2.5 \cdot 10^{-10}} = \frac{100 \cdot 10^{-16}}{25 \cdot 10^{-11}} = 4.0 \cdot 10^{-5} = \frac{[\text{OH}^-][\text{HD}]}{[\text{D}^-]}$$

ICE table:

	D <sup>-</sup>	H <sub>2</sub> O	HD	OH <sup>-</sup>
I	0.5 M		0	10 <sup>-7</sup>
C	-x		+x	+x
E	0.5 - x ≈ 0.5 M		x ≈ 4 x 10 <sup>-3</sup> M	10 <sup>-7</sup> + x ≈ 4 x 10 <sup>-3</sup> M

$$x^2 = K_b \cdot [\text{D}^-] = 4.0 \times 10^{-5} \cdot 0.5 \text{ M} = 2.0 \cdot 10^{-5} \text{ M}; \quad x = [\text{OH}^-] = 4.5 \cdot 10^{-3} \text{ M}$$

$$\text{pOH} = -\log(4.5 \times 10^{-3}) = -(\log 4.5 + \log 10^{-3}) = 2.3 \text{ or } 2.4$$

$$\text{pH} = 14 - 2.4 = 11.7 \text{ or } 11.6$$

7. **Equal volumes** of a 0.10 M solution of a weak acid, HC, with  $K_a = 1 \cdot 10^{-6}$ , and a 0.20 M solution of NaOH are combined. What is the pH of the resulting solution? (Hint: what will react first?)

**We have strongest base OH<sup>-</sup> which will react with the acid HC 100% limiting reaction**

**HC(aq) + OH<sup>-</sup>(aq) → H<sub>2</sub>O(l) + C<sup>-</sup>(aq) (let's treat this reaction as a limiting reagent reaction)**

	HC (L.R.)	OH <sup>-</sup>	Na <sup>+</sup>	C <sup>-</sup>
Initial	<b>0.1 M</b>	<b>0.2 M</b>	<b>Spectator</b>	<b>10<sup>-7</sup></b>
used	<b>-0.1 mol</b>	<b>0.1 mol</b>		<b>+0.1 mol</b>
Left	<b>0</b>	<b>0.1 mol</b>		<b>0.1 mol</b>
NewConcentration $V_{\text{new}}=2 \cdot V_{\text{old}}$	<b>0 M</b>	<b>0.1mol ÷ 2L = 0.05 M</b>		<b>0.1mol ÷ 2L = 0.05 M</b>

Equal volume hence final solution volume is doubled.

Now we have two bases available in the solution water C<sup>-</sup> and OH<sup>-</sup>

C<sup>-</sup> is a weak base  $K_b = \frac{K_w}{K_a} = 1 \cdot 10^{-8} \ll 1$ , but  $K_b \gg K_w$  it means it is stronger than water.

Hence it will react with water, but contribution will be small.

Excess of OH<sup>-</sup> at equilibrium [OH<sup>-</sup>] = 0.05 M

pOH = -log(0.05) = 1.3;    pH = 12.7

8. When 0.1mol of NaA is dissolved in 1L of pure water at room temperature, the pH is measured to be 7.0. Is HA a strong or weak acid? **Strong**

Since an A<sup>-</sup> did not change a pH of water that means it has a  $K_b \ll K_w$  it is weaker than water That means its conjugate acid HA equilibrium constant will have to be greater than 1,  $K_a > 1$  That means it is a strong Acid.

- a. Based on the information given will you expect the equilibrium constant to be: (choose one)

$K_a \ll 1$                       or                       $K_a \gg 1$

9. Rank the acids HB, HC, and HD from questions 2 through 5 in order of increasing acid strength.

**HA >> HC (1x10<sup>-6</sup>) > HB (9x10<sup>-7</sup>) > HD (4x10<sup>-10</sup>) (compare using equilibrium constants, K<sub>a</sub>)**

10. You have a 1M solution of each of the salts below. Which of the salts will give the highest pH?

Which of the salts will give the lowest pH?

$\text{NH}_4\text{CH}_3\text{COO}$  (ammonium acetate)

**NEUTRAL**

$\text{NH}_4\text{CN}$  (ammonium cyanide), **BASSIC**

$\text{NH}_4\text{HC}_2\text{O}_4$ (ammonium oxalate) **ACIDIC**

	$K_a$	$K_b$
$\text{CH}_3\text{COOH}$	$2 \cdot 10^{-5}$	$5 \cdot 10^{-10}$
$\text{HCN}$	$6 \cdot 10^{-10}$	$1.7 \cdot 10^{-5} = 2 \cdot 10^{-5}$
$\text{H}_2\text{C}_2\text{O}_4$	$6 \cdot 10^{-2}$	$1.7 \cdot 10^{-13} = 2 \cdot 10^{-13}$
$\text{NH}_3$	$5 \cdot 10^{-10}$	$2 \cdot 10^{-5}$

11. 250. mL of an 0.8 M solution of  $\text{NaD}$  ( salt of the weak acid HD with the  $K_a$  of  $2.5 \times 10^{-10}$ ) is added to 250. mL of water.

What is the Chemical Reaction?



What will be the concentration of  $\text{D}^-$  after dilution?

$$[\text{D}^-] = \frac{\left(\frac{1}{4}L \cdot 0.8 \frac{\text{mol}}{L}\right)}{0.5L} = 0.4M$$

What are the Equilibrium Expression of  $K_b$  for the reaction of  $\text{NaD}$  and water:

$$K_b = \frac{[\text{HD}][\text{OH}^-]}{[\text{D}^-]} = \frac{K_w}{K_a} = 4.0 \cdot 10^{-5}$$

$$[\text{OH}^-] = 0.004; \quad \text{pOH} = 2.4; \quad \text{pH} = 11.6$$

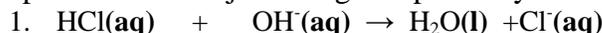
Based on the value of  $K_b$  is  $\text{D}^-$  a strong base or a weak base? **weak base**

Based on the value of  $K_a$  is HD a strong acid or a weak acid? **weak acid**

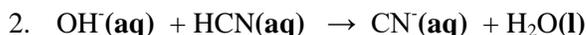
### Really Challenging problems to do at home:

13. If equal volumes of 4.4 M HCl, 4.6 M NaOH and 0.2 M HCN are mixed ( $K_a$  of HCN is  $5 \times 10^{-10}$ ), what is the pH when the resulting solution reaches equilibrium?

Must determine which reactions precede 100% and treat them as a limiting reaction problem ( in no particular order just using compounds you started with ) :



<b>Initial</b>	4.4 mol (L.R.)	4.6 mol	
Used	-4.4	-4.4mol	+4.4mol
Left:	0	0.2mol	4.4mol



Initial	0.2 mol	0.2 mol	
Used/formed	-0.2	-0.2	+0.2mol
Left:	0	0	0.2mol

New Concentration: 0.2mol ÷ 3L

$$V_{\text{new}} = 3 \cdot V_{\text{old}}$$



Equilibrium reaction; basic solution

	$\text{CN}^-$	HCN	$\text{OH}^-$
I	$(0.2 \div 3) \text{ M}$	0	$10^{-7}$
C	-x	+x	+x
E	$(0.2 \div 3) - x$	x	$10^{-7} + x$

$$K_b = \frac{10^{-14}}{5 \times 10^{-5}} = 0.2 \cdot 10^{-4} = 2 \cdot 10^{-5}$$

$$[\text{OH}^-] = \sqrt{K_b \cdot C_b} = \sqrt{\frac{2 \cdot 10^{-5} \cdot 2 \cdot 10^{-1}}{3}} = \sqrt{\frac{4}{3}} \cdot 10^{-6} = 0.00115$$

$$\text{pOH} = -\log(11.5 \cdot 10^{-4}) = 2.94$$

$$\text{pH} = 14 - 2.9 = 11.1$$

14. Determine the  $K_b$  of a base, at 25°C, if a 0.02 M aqueous solution of the base has a pH of 7.60 (This implies that it is an equilibrium pH).

$$\text{pOH} = 14 - 7.60 = 6.40$$

$$[\text{OH}^-] = 10^{-6.4} = 4.0 \times 10^{-7} \text{ M}$$

	$\text{A}^-$	$\text{H}_2\text{O}$	HA	$\text{OH}^-$
I	0.02 M		0	$10^{-7}$
C	-x		+x	+x
E	$0.02 - x \approx 0.05 \text{ M}$		x	$10^{-7} + x \approx 4.0 \times 10^{-7} \text{ M}$

$$x = 4.0 \times 10^{-7} - 10^{-7} = 3.0 \times 10^{-7}; K_b = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} = \frac{(4 \cdot 10^{-7})(3 \cdot 10^{-7})}{(2 \cdot 10^{-2})} = 6 \cdot 10^{-12}$$

**Do at home to prepare for next week's discussion section.**

1. You add HCl to a solution of equal moles of a weak acid and its conjugate base, and the number of moles of strong acid added is *smaller* than the number of moles of conjugate base initially present in the solution. Circle the correct answer(s) of the choices in the brackets.
  - a. The number of moles of  $A^-$  [decreases / increases] from the initial amount.
  - b. The number of moles of HA [decreases / increases] from the initial amount.
  - c. The number of moles of [HCl / HA /  $A^-$ ] = 0 after neutralization reaction took place but before an equilibrium is established because [HCl / HA /  $A^-$ ] is the limiting reagent and will be used up completely.
  - d. When the strong acid has completely reacted with the solution, you have a [weak acid / weak base / strong acid / both weak acid and weak base] present.
2. You add an HCl to a solution of equal moles of a weak acid and its conjugate base and the number of moles of strong acid added is *equal to* the number of moles of conjugate base initially present in the solution. Circle the correct answer(s) of the choices in the brackets:
  - a. The number of moles of  $A^-$  [decreases / increases] from the initial amount.
  - b. The number of moles of HA [decreases / increases] from the initial amount.
  - c. The number of moles of [HCl / HA /  $A^-$ ] = 0 after neutralization reaction took place but before an equilibrium is established because [HCl / HA /  $A^-$ ] is the limiting reagent and will be used up completely.
  - d. When the strong acid has completely reacted with the solution, you still have a [Weak acid / weak base / strong acid / both weak acid and weak base] present.
3. You add an HCl to a solution of equal moles of a weak acid and its conjugate base, and finally the number of moles of strong acid added is *greater than* the number of moles of conjugate base present in the solution initially. Circle the correct answer(s) of the choices in the brackets:
  - a. The number of moles of  $A^-$  [decreases / increases] from the initial amount.
  - b. The number of moles of HA [decreases / increases] from the initial amount.
  - c. The number of moles of [HCl / HA /  $A^-$ ] = 0 after neutralization reaction took place but before an equilibrium is established because [HCl / HA /  $A^-$ ] is the limiting reagent and will be used up completely.
  - d. When the HCl has completely reacted with the solution, you still have a [Weak acid / weak base / strong acid / strong base] present.

4. You add NaOH to a solution of equal moles of a weak acid and its conjugate base, and the number of moles of strong acid added is *smaller* than the number of moles of conjugate base initially present in the solution. Circle the correct answer(s) of the choices in the brackets.
- The number of moles of  $A^-$  [decreases / increases] from the initial amount.
  - The number of moles of HA [decreases / increases] from the initial amount.
  - The number of moles of [OH<sup>-</sup> / HA /  $A^-$ ] = 0 after neutralization reaction took place but before an equilibrium is established because [OH<sup>-</sup> / HA /  $A^-$ ] is the limiting reagent and will be used up completely.
  - When NaOH has completely reacted with the solution, you still have a [Weak acid / weak base / strong acid / strong base/both weak acid and weak base] present.
5. You add a NaOH to a solution of equal moles of a weak acid and its conjugate base and the number of moles of strong acid added is *equal to* the number of moles of conjugate base initially present in the solution. Circle the correct answer(s) of the choices in the brackets:
- The number of moles of  $A^-$  [decreases / increases] from the initial amount.
  - The number of moles of HA [decreases / increases] from the initial amount.
  - The number of moles of [OH<sup>-</sup> / HA /  $A^-$ ] = 0 after neutralization reaction took place but before an equilibrium is established because [OH<sup>-</sup> / HA /  $A^-$ ] is the limiting reagent and will be used up completely.
  - When NaOH has completely reacted with the solution, you still have a [weak acid / weak base / strong acid / strong base/both weak acid and weak base] present.
6. You add a NaOH to a solution of equal moles of a weak acid and its conjugate base, and finally the number of moles of strong acid added is *greater than* the number of moles of conjugate base present in the solution initially. Circle the correct answer(s) of the choices in the brackets:
- The number of moles of  $A^-$  [decreases / increases] from the initial amount.
  - The number of moles of HA [decreases / increases] from the initial amount.
  - The number of moles of [OH<sup>-</sup> / HA /  $A^-$ ] = 0 after neutralization reaction took place but before an equilibrium is established because [OH<sup>-</sup> / HA /  $A^-$ ] is the limiting reagent and will be used up completely.
  - When the NaOH has completely reacted with the solution, you still have a [weak acid / weak base / strong acid / strong base] present.

