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_2O	H_3O^+	CN^-
I Q=0<K	**2 M**		**10^{-7} M**	**0**
C	**-x**		**+x**	**+x**
E	**2 M - x ≈ 2M**		**10^{-7} + x ≈ x**	**x**
	K_a << 1		**K_A >> K_w**	

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

$10\cdot 10^{-10} = 1\cdot 10^{-9} = x^2$
$x = 3.0 \cdot 10^{-5}$
$pH = -\log(3 \cdot 10^{-5}) = -\log 3.0 - \log 10^{-5} = -0.48 + 5 = 4.5$

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

2. A solution of 0.1M of HX in water has a pH=3.0 at room temperature.

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

   b. 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?
   $HX(aq) + H_2O(l) \Leftrightarrow X^-(aq) + H_3O^+(aq)$

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

   $$K_a = \frac{[H_3O^+][X^-]}{[HX]}$$

   d. Calculate equilibrium concentration of hydronium
   $[H_3O^+(aq)]_{eq} = 10^{-pH} = 1\cdot 10^{-3}$M

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

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

   f. Based on the information given will you expect the equilibrium constant to be: (choose one) ***K_a<<1*** or *K_a >>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. $NaX(s) \Leftrightarrow Na^{+}(aq) + X^{-}(aq)$

   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?

   $$X^{-}(aq) + H_2O(l) \Leftrightarrow HX(aq) + OH^{-}(aq)$$

   B A CA CB

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

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

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

   <u>K_b<<1</u> or $K_b >> 1$

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:

   $$H_2O(l) + H_2O(l) \Leftrightarrow OH^{-}(aq) + H_3O^{+}(aq)$$

   b. Write the expression for equilibrium constant $K_w = [H_3O^+(aq)][OH^-(aq)]$

   c. Use questions10c and 11c to derive the expression for K_w using K_a, K_b

   $$HA(aq) + H_2O(l) \Leftrightarrow A^{-}(aq) + H_3O^{+}(aq) \quad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

   +

   $$A^{-}(aq) + H_2O(l) \Leftrightarrow HA(aq) + OH^{-}(aq) \quad K_b = \frac{[HA][OH^-]}{[A^-]}$$

   $$H_2O(l) + H_2O(l) \Leftrightarrow OH^{-}(aq) + H_3O^{+}(aq)$$

   $$K_w = K_a \cdot K_b = \frac{[H_3O^+][A^-]}{[HA]} \cdot \frac{[HA][OH^-]}{[A^-]} = [H_3O^+(aq)] \cdot [OH^-(aq)]$$

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?

$[H_3O^+] = 10^{-3.52} = 3.0 \times 10^{-4}$

What is the chemical reaction? **$HB(aq) + H_2O(l) \rightarrow H_3O^+(aq) + B^-(aq)$**

What is the equilibrium **expression** of ***K***:

$$K_a = \frac{[H_3O^+][B^-]}{[HB]} \qquad K_a = \frac{x^2}{0.1} = \frac{(3.0\cdot10^{-4})^2}{1\cdot10^{-1}} = \frac{9.0\cdot10^{-8}}{10^{-1}} = 9\cdot10^{-7}$$

ICE table:

	HB	H_2O	H_3O^+	B^-
I	**0.1 M**		**10^{-7} M**	**0**
C	**-x**		**+x**	**+x**
E	**0.1 - x ≈ 0.1M**		**$10^{-7} + x \approx 3\cdot10^{-4}$ M**	**$x \approx 3 \cdot 10^{-4}$ M-10^{-7} M** **$x \approx 3 \cdot 10^{-4}$ M**

$$\% = \frac{3.0\cdot10^{-4}}{0.1}\cdot 100\% = 0.3\%$$

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

What is the chemical reaction?

$D^-(aq) + H_2O(l) \rightarrow HD(aq) + OH^-(aq)$

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

$$K_b = \frac{K_w}{K_a} = \frac{1\cdot10^{-14}}{2.5\cdot10^{-10}} = \frac{100\cdot10^{-16}}{25\cdot10^{-11}} = 4.0\cdot10^{-5} = \frac{[OH^{-1}][HD]}{[D^-]}$$

ICE table:

	D^-	H_2O	HD	OH^-
I	**0.5 M**		**0**	**10^{-7}**
C	**-x**		**+x**	**+x**
E	**0.5 - x ≈ 0.5 M**		**$x \approx 4 \times 10^{-3}$ M**	**$10^{-7} + x \approx 4 \times 10^{-3}$ M**

$x^2 = K_b \cdot [D^-] = 4.0 \times 10^{-5} \cdot 0.5\ M = 2.0\cdot10^{-5}$ M; $x = [OH^-] = 4.5 \cdot 10^{-3}$ M

$pOH = -\log(4.5 \times 10^{-3}) = -(\log 4.5 + \log 10^{-3}) = 2.3$ or 2.4
$pH = 14 - 2.4 = 11.7$ 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^- which will react with the acid HC 100% limiting reaction

   $HC(aq) + OH^-(aq) \rightarrow H_2O(l) + C^-(aq)$ (let's treat this reaction as a limiting reagent reaction)

	HC (L.R.)	OH^-	Na^+	C^-
Initial	**0.1 M**	**0.2 M**	**Spectator**	**10^{-7}**
used	**-0.1 mol**	**0.1 mol**		**+0.1 mol**
Left	**0**	**0.1 mol**		**0.1 mol**
NewConcentration $V_{new}=2\cdot\mathbf{V_{old}}$	**0 M**	**0.1mol÷2L= 0.05 M**		**0.1mol÷2L = 0.05 M**

Equal volume hence final solution volume is doubled.

Now we have two basses available in the solution water C^- and OH^-

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

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

Excess of OH^- at equilibrium $[OH^-] = 0.05$ 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? <u>**Strong**</u>

   Since an A^- did not change a pH of water that means it has a $K_b << K_w$ it is weaker than water
   That means its conjugate acid HA equilibrium constant will have to be greater than 1, Ka>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<<1   **or**   <u>***K_a >>1***</u>

9. Rank the acids HB, HC, and HD from questions 2 through 5 in order of increasing acid strength.
   HA>> HC ($1x10^{-6}$) > HB ($9x10^{-7}$) > HD ($4x10^{-10}$) (compare using equilibrium constants, K_a)

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?

	K_a	K_b
CH_3COOH	$2\cdot10^{-5}$	$5\cdot10^{-10}$
HCN	$6\cdot10^{-10}$	$1.7\cdot10^{-5} = 2\cdot10^{-5}$
$H_2C_2O_4$	$6\cdot10^{-2}$	$1.7\cdot10^{-13} = 2\cdot10^{-13}$
NH_3	$5\cdot10^{-10}$	$2\cdot10^{-5}$

NH_4CH_3COO (ammonium acetate) **NEUTRAL**
NH_4CN (ammonium cyanide), **BASSIC**
$NH_4HC_2O_4$(ammonium oxalate) **ACIDIC**

11. 250. mL of an 0.8 M solution of NaD (salt of the weak acid HD with the K_a of $2.5x10^{-10}$) is added to 250. mL of water.

What is the Chemical Reaction?

$$D^-(aq) + H_2O(l) \Leftrightarrow HD(aq) + OH^-(aq)$$

What will be the concentration of D^- after dilution?

$$[D^-] = \frac{\left(\frac{1}{4}L\cdot0.8\frac{mol}{L}\right)}{0.5L} = 0.4M$$

What are the Equilibrium Expression of K_b for the reaction of NaD and water:

$$K_b = \frac{[HD][OH^-]}{[D^-]} = \frac{K_w}{K_a} = 4.0\cdot10^{-5}$$

$[OH^-]=0.004$; pOH=2.4; pH=11.6

Based on the value of K_b is 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 5×10^{-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) :

1. $HCl\mathbf{(aq)} + OH^-\mathbf{(aq)} \rightarrow H_2O\mathbf{(l)} + Cl^-\mathbf{(aq)}$

	HCl	OH⁻	Cl⁻
Initial	4.4 mol (L.R.)	4.6 mol	
Used	-4.4	-4.4mol	+4.4mol
Left:	0	0.2mol	4.4mol

2. $OH^-\mathbf{(aq)} + HCN\mathbf{(aq)} \rightarrow CN^-\mathbf{(aq)} + H_2O\mathbf{(l)}$

	OH⁻	HCN	CN⁻
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

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

3) Equilibrium reaction: $CN^- + H_2O \rightarrow HCN + OH^-$
Equilibrium reaction; basic solution

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

$$K_b = \frac{10^{-14}}{5x10^{-5}} = 0.2\cdot10^{-4} = 2\cdot10^{-5}$$

$$[OH^-] = \sqrt{K_b \cdot C_b} = \sqrt{\frac{2\cdot10^{-5}\cdot2\cdot10^{-1}}{3}} = \sqrt{\frac{4}{3}\cdot10^{-6}} = 0.00115$$

pOH = -log($11.5\cdot10^{-4}$) =2.94
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).

pOH = 14 - 7.60 = 6.40
$[OH^-] = 10^{-6.4} = 4.0 \times 10^{-7}$ M

	A^-	H_2O	HA	OH^-
I	0.02 M		0	10^{-7}
C	-x		+x	+x
E	0.02 - x ≈ 0.05 M		x	$10^{-7} + x \approx 4.0 \times 10^{-7}$ M

$$x = 4.0 \times 10^{-7} - 10^{-7} = 3.0 \times 10^{-7};\ K_b = \frac{[OH^-][HA]}{[A^-]} = \frac{(4\cdot10^{-7})(3\cdot10^{-7})}{(2\cdot10^{-2})} = 6\cdot10^{-12}$$

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.

    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 [OH^- / HA / A^-] = 0 after neutralization reaction took place but before an equilibrium is established because [OH^- / HA / A^-] is the limiting reagent and will be used up completely.

    d. 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:

    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 [OH^- / HA / A^-] = 0 after neutralization reaction took place but before an equilibrium is established because [OH^- / HA / A^-] is the limiting reagent and will be used up completely.

    d. 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:

    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 [OH^- / HA / A^-] = 0 after neutralization reaction took place but before an equilibrium is established because [OH^- / HA / A^-] is the limiting reagent and will be used up completely.

    d. When the NaOH has completely reacted with the solution, you still have a

    [weak acid / weak base / strong acid / strong base] present.