CHM 106
Exam II

1. Recipes for buffer solutions of known pH can be found in many reference handbooks. One such recipe starts with two stock solutions. Solution A is made by dissolving 16.41 g of solid sodium acetate ($NaC_2H_3O_2$) in 1.00 L of water. Solution B is made by diluting 11.47 mL of glacial acetic acid ($HC_2H_3O_2$, 17.45 M) to 1.00 L. The buffer is then prepared by mixing 70.5 mL of solution A with 29.5 mL of solution B. For acetic acid, $K_a = 1.75\times10^{-5}$.

82.04

a) What is the concentration of $C_2H_3O_2^-(aq)$ in solution A?

$MW\ (NaC_2H_3O_2)$: ~~[illegible]~~ g, 1 mol

$$16.41\,g\ NaC_2H_3O_2 \cdot \frac{1\,mol\ NaC_2H_3O_2}{\underset{82.04}{\cancel{[illegible]}}\,g\ NaC_2H_3O_2} \cdot \frac{1}{1\,L} = \boxed{0.200\,\underline{M}\ C_2H_3O_2^-}$$

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b) What is the concentration of $HC_2H_3O_2(aq)$ in solution B?

$$0.01147\,L\ HC_2H_3O_2 \cdot \frac{17.45\,mol\ HC_2H_3O_2}{1\,L} \cdot \frac{1}{1\,L} = \boxed{0.200\,\underline{M}\ HC_2H_3O_2}$$

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c) What is the pH of the resulting buffer?

$$0.0705\,L\ C_2H_3O_2^- \cdot \frac{0.200\,mol\ C_2H_3O_2^-}{1\,L} \cdot \frac{1}{0.1\,L} = 0.141\,\underline{M}\ C_2H_3O_2^-$$

$$0.0295\,L\ HC_2H_3O_2 \cdot \frac{0.200\,mol\ HC_2H_3O_2}{1\,L} \cdot \frac{1}{0.1\,L} = 0.059\,\underline{M}\ HC_2H_3O_2$$

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$$pK_a = -\log K_a = 4.76$$

$$pH = pK_a + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 4.76 + \log\frac{0.141}{0.059}$$

$$= \boxed{5.14}$$

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2. Piperidine ($C_5H_{11}N$) is a weak base that can accept one hydrogen ion. Suppose a 10.00 mL aliquot of piperidine solution of unknown concentration is titrated to the equivalence point with 37.23 mL of 0.1015 M HCl.

a) Write a balanced chemical equation for this reaction. Under your equation, specify which species reacts as an acid, which species reacts as a base, which species is the conjugate acid, and which species is the conjugate base.

$$C_5H_{11}N + HCl \rightarrow C_5H_{11}NH^+ + Cl^-$$

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BASE ACID CONJ. ACID CONJ. BASE

b) What is the concentration of the piperidine solution?

$$0.03723\text{ L HCl} \cdot \frac{0.1015\text{ mol HCl}}{1\text{ L HCl}} \cdot \frac{1\text{ mol } C_5H_{11}N}{1\text{ mol HCl}} \cdot \frac{1}{0.01000\text{ L } C_5H_{11}N} = \boxed{0.3779\text{ M}}$$

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c) The pH of the original piperidine solution (before titration) is 12.338. What is the value of K_b for piperidine?

$$K_b = \frac{[C_5H_{11}NH^+][OH^-]}{[C_5H_{11}N]}$$

	$C_5H_{11}N$	$+ H_2O$	$\rightleftharpoons C_5H_{11}NH^+$	$+ OH^-$
INIT:	0.3779	-	0	0
CHANGE:	$-x$	-	$+x$	$+x$
EQ:	$0.3779-x$	-	x	x

$$K_b = \frac{x^2}{0.3779-x}$$

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$pH = -\log[H^+] = 12.338$

$pOH = 14 - pH = 1.662 = -\log[OH^-]$

$[OH^-] = 10^{-1.662} = 0.02178 = x$

$$K_b = \frac{(0.02178)^2}{0.3779-0.02178} = \boxed{1.33 \times 10^{-3}}$$

d) What is the percent dissociation of piperidine in the original solution?

$$\%\text{ DISSOCIATION} = \frac{0.02178}{0.3779} = \boxed{5.76\%}$$

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3. Lead (II) iodide is slightly soluble in water with $K_{sp} = 7.1\times10^{-9}$.

a) What is the molar solubility of lead (II) iodide?

	$PbI_2(s)$ $\rightleftharpoons$	$Pb^{2+}(aq)$ +	$2I^-(aq)$
init:	-	0	0
change:	$-x$	$+x$	$+2x$
eq:	-	x	$2x$

$K_{sp} = [Pb^{2+}][I^-]^2$

$7.1\times10^{-9} = x(2x)^2 = 4x^3$

$x = \boxed{0.0012\ M}$

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b) What is the molar solubility of lead (II) iodide in 0.10 M KI?

	PbI_2 $\rightleftharpoons$	Pb^{2+} +	$2I^-$
init:	-	0	0.10
change:	$-x$	$+x$	$+2x$
eq:	-	x	$0.10+2x$

$7.1\times10^{-9} = x(0.10+2x)^2 \approx x(0.10)$

$x = \boxed{7.1\times10^{-7}\ M}$

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c) Suppose that you slowly add KI(s) to a solution of 0.10 M $Pb(NO_3)_2$. At what concentration of iodide does lead (II) iodide precipitate?

$K_{sp} = [Pb^{2+}][I^-]^2$

$7.1\times10^{-9} = 0.10\,[I^-]^2$

$[I^-] = \boxed{2.66\times10^{-4}\ M}$

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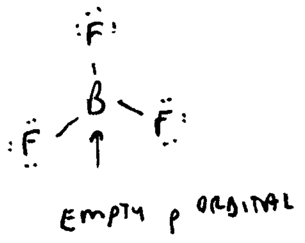
4. Explain the following phenomena.

a) The compound BF_3 reacts with bases and gives an aqueous solution with a very low pH despite the fact that there are no hydrogen atoms in its structure.



BF_3 HAS AN EMPTY p ORBITAL SO IT CAN ACCEPT AN ELECTRON PAIR. THUS, IT IS A LEWIS ACID.

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b) In the titration of a weak acid with strong base, the pH of the titration flask does not change much for a good portion of the titration before the equivalence point is reached.

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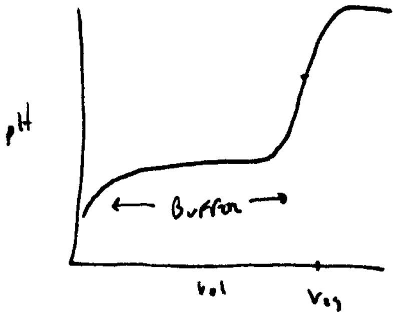

IN THE TITRATION OF A WEAK ACID, WHEN THE ACID IS PARTIALLY NEUTRALIZED, THERE IS A MIXTURE OF THE ACID AND ITS CONJUGATE, WHICH IS A BUFFER.

c) $BaCO_3$, $BaSO_3$, and $BaSO_4$ are all only slightly soluble in water, but the first two dissolve in HCl solution whereas $BaSO_4$ does not.

CO_3^{2-} AND SO_3^{2-} ARE THE CONJUGATE BASES OF WEAK ACIDS SO THEY ARE APPRECIABLY BASIC AND THUS REACT WITH HCl TO PULL THE SOLUBILITY EQUILIBRIUM RIGHT. SO_4^{2-} IS THE CONJUGATE BASE OF A STRONG ACID, SO IT IS NOT APPRECIABLY BASIC AND THUS THE SOLUBILITY OF $BaSO_3$ IS INDEPENDENT OF pH.

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5. Pivalic acid ($HC_5H_9O_2$) is a weak monoprotic acid with $K_a = 9.31 \times 10^{-6}$. Suppose that a 20.00 mL portion of 0.100 M pivalic acid is titrated with standard 0.100 M sodium hydroxide.

a) What is the pH of the pivalic acid solution before any NaOH is added?

$$HC_5H_9O_2 \rightleftharpoons H^+ + C_5H_9O_2^-$$

$$K_a = \frac{[H^+][C_5H_9O_2^-]}{[HC_5H_9O_2]}$$

	$HC_5H_9O_2$	H^+	$C_5H_9O_2^-$
INIT:	0.100	0	0
CHANGE:	$-x$	$+x$	$+x$
EQ:	$0.100 - x$	x	x

$$9.31 \times 10^{-6} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

$$x = 9.65 \times 10^{-4} M = [H^+]$$

Is it valid? $\frac{9.65 \times 10^{-4}}{0.100} = 0.962$ ✓

$$pH = -\log [H^+] = \boxed{3.016}$$

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b) What is the pH of the pivalic acid solution after 10.00 mL of NaOH is added?

$$HC_5H_9O_2 + OH^- \longrightarrow C_5H_9O_2^- + H_2O$$

	$HC_5H_9O_2$	OH^-	$C_5H_9O_2^-$	H_2O
Before:	0.002	0.001	0	–
After:	0.001	0	0.001	–

$$pK_a = -\log K_a = 5.031$$

$$[HC_5H_9O_2] = \frac{0.001 \text{ mol}}{0.02 + 0.01 \text{ L}} = 0.0333 \text{ M}$$

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$$[C_5H_9O_2^-] = \frac{0.001 \text{ mol}}{0.02 + 0.01 \text{ L}} = 0.0333 \text{ M}$$

$$pH = pK_a + \log \frac{[C_5H_9O_2^-]}{[HC_5H_9O_2]}$$

$$= 5.031 + \log \frac{0.0333}{0.0333} = \boxed{5.031}$$

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c) What is the pH at the equivalence point?

	$HC_5H_9O_2$	$+ OH^-$	$\rightarrow \cancel{H}C_5H_9O_2^-$	$+ H_2O$
Before:	0.002	0.002	0	-
After:	0	0	0.002	-

$[C_5H_9O_2^-]_0 = \frac{0.002 \text{ mol}}{0.02 + 0.02 L} = 0.050 M$

$K_b = \frac{K_w}{K_a} = \frac{1.00\times10^{-14}}{9.31\times10^{-6}} = 1.07\times10^{-9}$

	$C_5H_9O_2^-$	$+ H_2O$	$\rightleftharpoons HC_5H_9O_2$	$+ OH^-$
Init:	0.0500	-	0	0
Change:	$-x$	-	$+x$	$+x$
Eq:	$0.050 - x$	-	x	x

$K_b = \frac{[HC_5H_9O_2][OH^-]}{[C_5H_9O_2^-]}$

$1.07\times10^{-9} = \frac{x^2}{0.05 - x} \approx \frac{x^2}{0.05}$

$x = 7.328\times10^{-6} M = [OH^-]$

is it valid? $\frac{7.328\times10^{-6}}{0.05} = 0.0148$ ✓

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$pOH = -\log[OH^-] = 5.135$

$pH = 14 - pOH = \boxed{8.865}$

d) What is the pH after 40.00 mL of NaOH is added?

	$HC_5H_9O_2$	$+ OH^-$	$\rightarrow C_5H_9O_2^-$	$+ H_2O$
Before:	0.002	0.004	0	-
After:	0	0.002	0.002	

$[OH^-]$ is stronger base.

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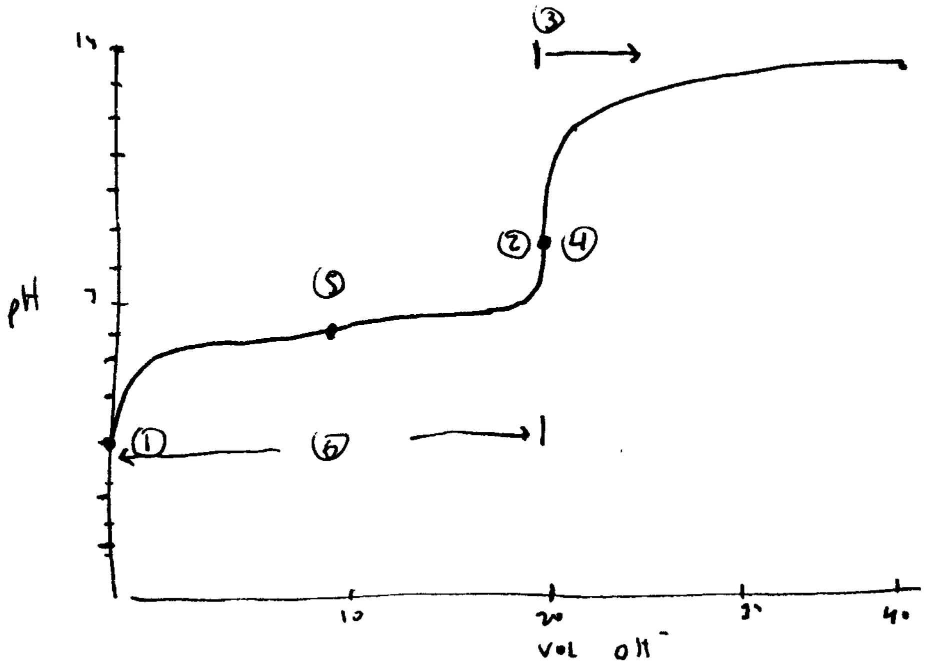
$[OH^-] = \frac{0.002 \text{ mol}}{0.02 + 0.04 L} = 0.0333 M$

$pOH = -\log[OH^-] = 1.477$

$pH = 14 - pOH = \boxed{12.523}$

e) Sketch the titration curve for this titration. In your sketch, identify the following points: (1) pH depends only on a weak acid, (2) pH depends only on the conjugate base, (3) pH depends only on the strong base hydroxide, (4) the equivalence point, (5) pH = pK_a, (6) the buffer region.



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For the remaining questions, circle the letter that corresponds to the best answer.

6. Which acid below gives the highest pH in a 0.1 M solution?

[✓ (A)] HA_1 with $K_a = 2\times10^{-5}$
(B) HA_2 with $K_a = 2\times10^{-4}$
(C) HA_3 with $K_a = 1.4\times10^{-3}$
(D) HA_4 with $K_a = 1.4\times10^{-2}$
(E) HA_5 with $K_a = 1\times10^{6}$

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7. A buffer of pH = 3.00 is desired. If the following reagents are available, which pair of reagents will make the buffer of highest capacity?

(A) $HClO_3$ (pK_a = -2.70) and $NaClO_3$
(B) HNO_2 (pK_a = 3.14) and NaN_3
(C) K_2HPO_4 (pK_a = 11.90) and K_3PO_4
[✓ (D)] HF (pK_a = 3.20) and KF
(E) NaH_2PO_4 (pK_a = 6.68) and Na_2HPO_4

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8. Hydrofluoric acid has a $K_a = 6.31\times10^{-4}$. Which of the following factors would increase the pH of a solution of 1.0 <u>M</u> HF?

I. ✗ Add some HNO_3
II. ✓ Add some KOH
III. ✓ Add some KF
IV. ✓ Add some H_2O
V. ✗ Add some KNO_3

(A) **I** and **IV**
3 (B) **II** and **III**
(C) **I** and **V**
5 [✓ (D)] **II**, **III**, and **IV**
(E) **I**, **IV**, and **V**

For questions 9-11, refer to the following table of acid and base dissociation constants and circle the letter that best describes the acid/base properties of each of the following salts.

Substance	K_a	K_b
HCN	6.17×10^{-10}	1.62×10^{-5} (CN^-)
$HC_2H_3O_3$	1.78×10^{-5}	
C_5H_5N		1.49×10^{-9}
NH_3	5.62×10^{-10} (NH_4^+)	1.78×10^{-5}

9. NH_4CN $K_b > K_a$

(A) produces and acidic solution when dissolved in water
5 [✓ (B)] produces a basic solution when dissolved in water
(C) produces a neutral solution when dissolved in water

10. $C_5H_5NHNO_3$

5 [✓ (A)] produces and acidic solution when dissolved in water
(B) produces a basic solution when dissolved in water
(C) produces a neutral solution when dissolved in water

11. $KC_2H_3O_2$

(A) produces and acidic solution when dissolved in water
5 [✓ (B)] produces a basic solution when dissolved in water
(C) produces a neutral solution when dissolved in water

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12. Which of the following statements are *true*?

I. ✗ A weak acid has a strong conjugate base.
II. ✓ Acid strength is inversely proportional to the affinity of the conjugate base for hydrogen ions.
III. ✓ A strong acid has $pK_a < 0$.
IV. ✗ As base strength increases, the conjugate acid is more willing to donate hydrogen ions.

- (A) **I** and **III**
- (B) **I** and **II**
- [✓ (C)] **II** and **III**
- (D) **I** and **IV**
- (E) **I**, **II**, and **III**

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13. If bromocresol purple (pH color range = 5.2 – 6.8) is used as an indicator when titrating a weak acid with a strong base, the volume of base needed to reach the equivalence point will be:

- (A) greatly overestimated
- (B) slightly overestimated
- [✓ (C)] underestimated
- (D) accurate
- (E) cannot be determined by the information given

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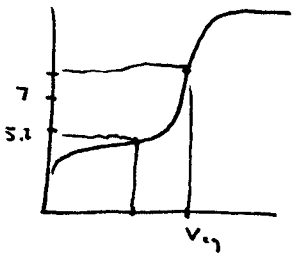

14. $Cu(OH)_2$ is a sparingly soluble salt with $K_{sp} = 2.2\times10^{-20}$. Which of the following factors will increase K_{sp} for $Cu(OH)_2$?

$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$

I. ✗ Add some $Cu(NO_3)_2$
II. ✗ Add some $Cu(OH)_2$
III. ✗ Increase pH
IV. ✗ Decrease pH

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- (A) **II** only
- (B) **IV** only
- (C) **I** and **III**
- (D) **II** and **IV**
- [✓ (E)] none of the above

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15. Solution A has a pH of 9.00 and solution B has a pH of 11.00. Which of the following statements are *true*?

I. ✗ Solution B has twice as many OH^- ions as solution A.
II. ✓ Solution B has one hundred times as many OH^- ions as solution A.
III. ✗ Solution A has one hundred times as many OH^- ions as solution B.
IV. ✓ Solution A has one hundred times as many H_3O^+ ions as solution B.
V. ✗ There are no H_3O^+ ions in either solution because they are both basic.

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(A) **I** only
(B) **III** only
(C) **II** and **III**
[✓ (D)] **II** and **IV**
(E) **III** and **IV**

Equations and Constants

$$PV = nRT$$

$$\ln [A] = -kt + \ln [A]_0$$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

$$[A] = -kt + [A]_0$$

$$K_p = K(RT)^{\Delta n}$$

$$pH = -\log [H^+]$$

$$pOH = -\log [OH^-]$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A$$

$$\ln \frac{k_1}{k_2} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$K_w = 1.00\text{x}10^{-14} = [H^+][OH^-]$$

$$pH + pOH = 14.000$$

$$K_a \cdot K_b = K_w$$

$$R = 8.314\ J / mol \cdot K = 0.0821\ L \cdot atm / mol \cdot K$$

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