125 POINTS START 8:00 am

CHM 106
Exam II

1. Imidazole ($C_3H_4N_2$) is a weak base that can accept one proton. Suppose a 20.00 mL aliquot of imidzaole solution is titrated to the equivalence point with 32.91 mL of 0.1041 M HCl.

a) Write a balanced chemical equation for the reaction taking place. Under your equation, identify 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.

$$C_3H_4N_2 + HCl \longrightarrow C_3H_4N_2H^+ + Cl^-$$

BASE ACID CONJUGATE ACID CONJUGATE BASE

5

b) What is the concentration of the imidazole solution?

$$0.03291\text{ L HCl} \cdot \frac{0.1041\text{ mol HCl}}{\text{L HCl}} \cdot \frac{1\text{ mol } C_3H_4N_2}{1\text{ mol HCl}} \cdot \frac{1}{0.02000\text{ L}} = \boxed{0.1713\text{ M } C_3H_4N_2}$$

5

c) The pH of the original imidazole solution is 10.113. What is the value of K_b for imidazole?

	$C_3H_4N_2$	$+ H_2O$	$\rightarrow C_3H_4N_2H^+$	$+ OH^-$
INIT:	0.1713		0	0
CHANGE:	$-x$		$+x$	$+x$
EQ:	$0.1713-x$		x	x

$pH = 10.113 = -\log[H^+]$

$[H^+] = 10^{-10.113} = 7.71\times10^{-11}$

$[OH^-] = \frac{1.00\times10^{-14}}{7.71\times10^{-11}} = 1.297\times10^{-4}\text{ M} = x$

$$K_b = \frac{[C_3H_4N_2H^+][OH^-]}{[C_3H_4N_2]} = \frac{x^2}{0.1713-x} = \frac{(1.297\times10^{-4})^2}{0.1713-1.297\times10^{-4}}$$

5

$$\boxed{K_b = 9.83\times10^{-8}}$$

15

2. 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 diluting 13.77 mL of concentrated (14.53 M) ammonia to 1.00 L. Solution B is made by diluting 10.699 g of solid ammonium chloride to 1.00 L. The buffer is then prepared by mixing 36.0 mL of solution A with 64.0 mL of solution B. For ammonia, $K_b = 1.762\times10^{-5}$.

a) What is the concentration of $NH_3(aq)$ in solution A?

$$0.01377\text{ L }NH_3 \cdot \frac{14.53\text{ mol }NH_3}{\text{L }NH_3} \cdot \frac{1}{1.00\text{ L}} = \boxed{0.2001\text{ M }NH_3}$$

5

b) What is the concentration of $NH_4^+(aq)$ in solution B?

MW NH_4Cl = 53.49 g/mol

5

$$10.699\text{ g }NH_4Cl \cdot \frac{1\text{ mol }NH_4Cl}{53.49\text{ g }NH_4Cl} \cdot \frac{1}{1.00\text{ L}} = \boxed{0.2000\text{ M }NH_4^+}$$

c) What is the pH of the resulting buffer?

$$[NH_3] = 0.0360\text{ L }NH_3 \cdot \frac{0.2001\text{ mol }NH_3}{\text{L}} \cdot \frac{1}{0.100\text{ L}} = 0.0720\text{ M }NH_3$$

$$[NH_4^+] = 0.0640\text{ L }NH_4^+ \cdot \frac{0.2000\text{ mol }NH_4^+}{\text{L}} \cdot \frac{1}{0.100\text{ L}} = 0.128\text{ M }NH_4^+$$

$pK_b = -\log K_b = 4.754$

$pK_a = 14 - pK_b = 9.246$

5

$$pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]}$$

$$pH = 9.246 + \log \frac{0.0720}{0.128}$$

$$\boxed{pH = 9.00}$$

15

3. Magnesium hydroxide is slightly soluble in water with $K_{sp} = 1.8\times10^{-11}$.

a) Write balanced chemical equation and an equilibrium expression for the dissolution of magnesium hydroxide.

$Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$ $\quad K_{sp} = [Mg^{2+}][OH^-]^2$

2

b) What is the molar solubility of magnesium hydroxide?

	$Mg(OH)_2$	$\rightleftharpoons$	Mg^{2+}	+	$2OH^-$
INIT:	—		0		0
CHANGE:	$-x$		$+x$		$+2x$
EQ:	—		x		$2x$

$K_{sp} = [Mg^{2+}][OH^-]^2$

$1.8\times10^{-11} = x\,(2x)^2 = 4x^3$

$x = \boxed{1.65\times10^{-4}\,M}$ = molar solubility

3

c) What is the pH of a saturated solution of magnesium hydroxide?

$[OH^-] = 2x = 2(1.65\times10^{-4}) = 3.30\times10^{-4}\,M$

$pOH = -\log[OH^-] = 3.48$

$pH = 14 - pOH = \boxed{10.52}$

3

8

1.00 L

d) Suppose that 0.50 g of $Mg(NO_3)_2$ is added to this solution. What is the molar solubiulity of magnesium hydroxide in the new solution?

	$Mg(OH)_2$	$\rightleftharpoons$ Mg^{2+}	+ $2OH^-$
INIT:	–	0.00377	0
CHANGE:	–x	+x	+2x
EQ:	–	0.00377+x	2x

$0.50 g\ Mg(NO_3)_2 \cdot \frac{1 mol\ Mg(NO_3)_2}{148.31 g\ Mg(NO_3)_2} \cdot \frac{1}{1L} = 0.00337 M$

$K_{sp} = [Mg^{2+}][OH^-]^2$

$1.8 \times 10^{-11} = (0.00377 + x)(2x)^2 \approx 0.00377(2x)^2$

$x = 3.65 \times 10^{-5} M$

IS IT VALID? $\frac{3.65 \times 10^{-5}}{0.00377} = 0.97\%$ ✓

4

MOLAR SOLUBILITY = $\boxed{3.65 \times 10^{-5} M}$

e) What is the pH of this new solution?

$[OH^-] = 2x = 2(3.65 \times 10^{-5}) = 7.31 \times 10^{-5} M$

$pOH = -\log [OH^-] = 4.14$

3 $pH = 14 - pOH = \boxed{9.86}$

4. Salts of the weak base pyridine (C_5H_5N, $K_b = 1.48\times10^{-9}$) are frequently used in organic synthesis as mild acid catalysts due to their solubility in both aqueous and organic solvents. Suppose you have an aqueous solution of 0.100 M pyridinium bromide (C_5H_5NHBr).

a) Write a chemical equation that accounts for the acidity of pyridinium bromide.

2 $C_5H_5NH^+ \rightleftharpoons H^+ + C_5H_5N$

b) In this solution, what are the concentrations of $[H^+]$, $[OH^-]$, and $[Br^-]$?

$C_5H_5NHBr(s) \xrightarrow{H_2O} C_5H_5NH^+ + Br^-$

$K_a = \frac{K_w}{K_b} = \frac{1.00\times10^{-14}}{1.48\times10^{-9}} = 6.76\times10^{-6}$

3 $\boxed{[Br^-] = 0.100\,M}$

$C_5H_5NH^+ \rightleftharpoons H^+ + C_5H_5N$

$K_a = \frac{[H^+][C_5H_5N]}{[C_5H_5NH^+]}$

	$C_5H_5NH^+$	H^+	C_5H_5N
INIT:	0.100	0	0
CHANGE:	$-x$	$+x$	$+x$
EQ:	$0.100-x$	x	x

$6.76\times10^{-6} = \frac{x^2}{0.100-x} \approx \frac{x^2}{0.100}$

$x = 8.22\times10^{-4}\,M = [H^+]$

3 $\boxed{[H^+] = 8.22\times10^{-4}\,M}$

IS IT VALID? $\frac{8.22\times10^{-4}}{0.100} = 0.82$ ✓

$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.00\times10^{-14}}{8.22\times10^{-4}}$

3 $\boxed{[OH^-] = 1.22\times10^{-11}\,M}$

c) What is the pH of this solution?

2 $pH = -\log[H^+] = \boxed{3.085}$

d) What is the percent dissociation of the pyridinium ion?

2 % DISSOCIATION $= \frac{8.22\times10^{-4}}{0.100} = \boxed{0.822\%}$

15

5. A 25.0 mL sample of a 0.100 M formic acid solution is titrated with standard 0.100 M sodium hydroxide. For formic acid, $K_a = 1.77\times10^{-4}$.

a) What is the pH of the formic acid solution before any sodium hydroxide is added?

	HA	⇌	H^+	+	A^-
INIT:	0.100		0		0
CHANGE:	$-x$		$+x$		$+x$
EQ:	$0.100-x$		x		x

$K_a = \frac{[H^+][A^-]}{[HA]}$

$1.77\times10^{-4} = \frac{x^2}{0.100-x} \approx \frac{x^2}{0.100}$

$x = 0.004210 = [H^+]$

Is it valid? $\frac{0.00421}{0.100} = 4.2\%$ ✓

$pH = -\log[H^+] = \boxed{2.376}$

3

$1.77\times10^{-5} - 1.77\times10^{-4}x - x^2 = 0$

$x = \{-0.00429, \boxed{0.00412}\}$

$pH = -\log[H^+] = \boxed{2.385}$

b) What is the pH after 12.5 mL of NaOH is added?

$0.0250\,L\ HA \cdot \frac{0.100\,mol\ HA}{L} = 0.00250\,mol\ HA$

$0.0125\,L\ OH^- \cdot \frac{0.100\,mol\ OH^-}{L} = 0.00125\,mol\ OH^-$

3

	HA	+	OH^-	→	A^-	+	H_2O
BEFORE:	0.0025		0.00125		0		–
AFTER:	0.00125		0		0.00125		–

$pK_a = -\log K_a = 3.752$

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

$pH = 3.752 + \log\frac{\cancel{0.00125}/0.0375}{\cancel{0.00125}/0.0375}$ 1

$pH = \boxed{3.752}$

6

c) What is the pH after 25.0 mL of NaOH is added?

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.77 \times 10^{-4}} = 5.65 \times 10^{-11}$$

	HA	+ OH^-	→ A^-	+ H_2O
Before:	0.0025	0.0025	0	–
After:	0	0	0.0025	–

$$[A^-]_0 = \frac{0.0025 \text{ mol } A^-}{0.050 \text{ L}} = 0.05 \text{ M}$$

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

	A^-	+ H_2O	⇌ HA	+ OH^-
Init:	0.05	–	0	0
Change:	$-x$	–	$+x$	$+x$
Eq:	$0.05-x$		x	x

3

$$5.65 \times 10^{-6} = \frac{x^2}{0.05-x} = \frac{x^2}{0.05}$$

$$x = 1.68 \times 10^{-6} \text{ M} = [OH^-]$$

$pOH = -\log[OH^-] = 5.775$

$pH = 14 - pOH = \boxed{8.225}$

d) What is the pH after 50.0 mL of NaOH is added?

	HA	+ OH^-	→ A^-	+ H_2O
Before:	0.0025	0.0050	0	–
After:	0	0.0025	0.0025	–

OH^- is stronger base so it sets pH

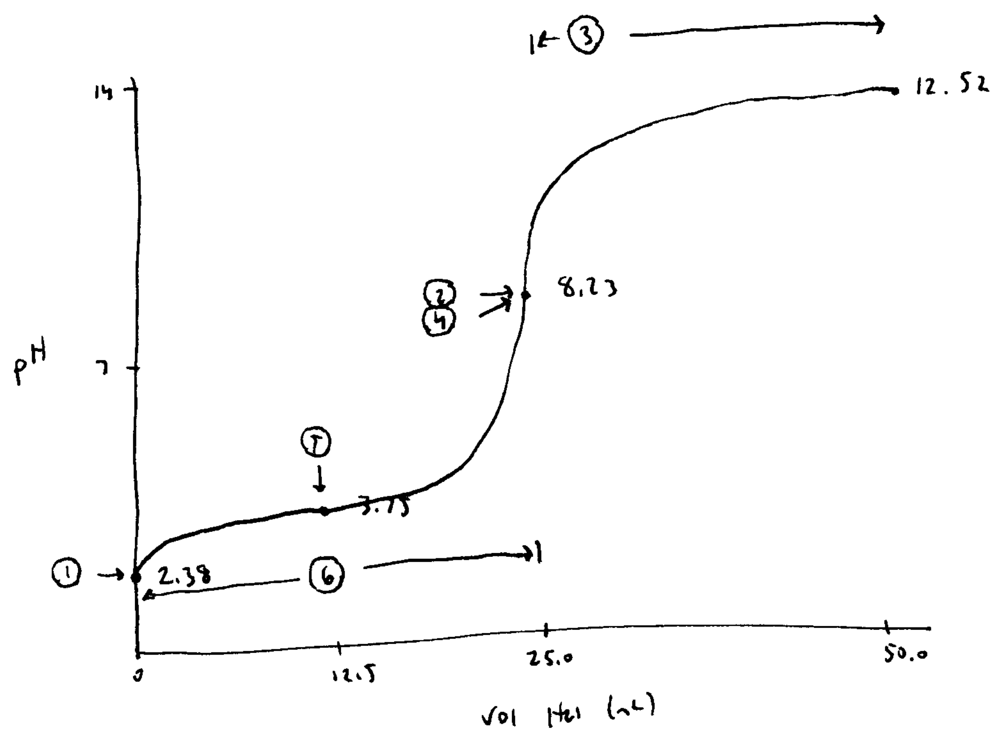
3

$$[OH^-] = \frac{0.0025 \text{ mol } OH^-}{0.025 + 0.05 \text{ L}} = 0.0333 \text{ M}$$

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

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

e) Sketch the titration curve for this titration. Label the following points: (1) pH depends only on formic acid, (2) pH depends only on the conjugate base formate, (3) pH depends only on excess base added, (4) the equivalence point, (5) pH = pK_a, (6) the buffer region.



3

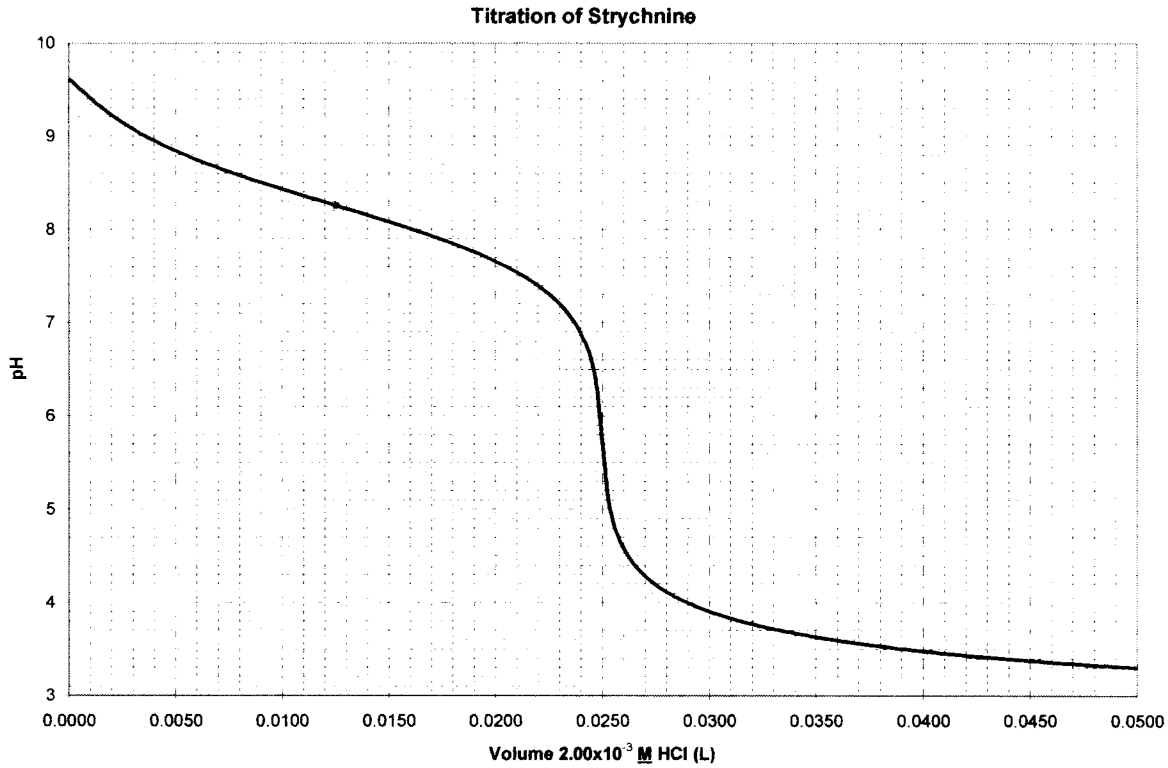
For the remaining questions, circle the letter of the answer that best satisfies the question.

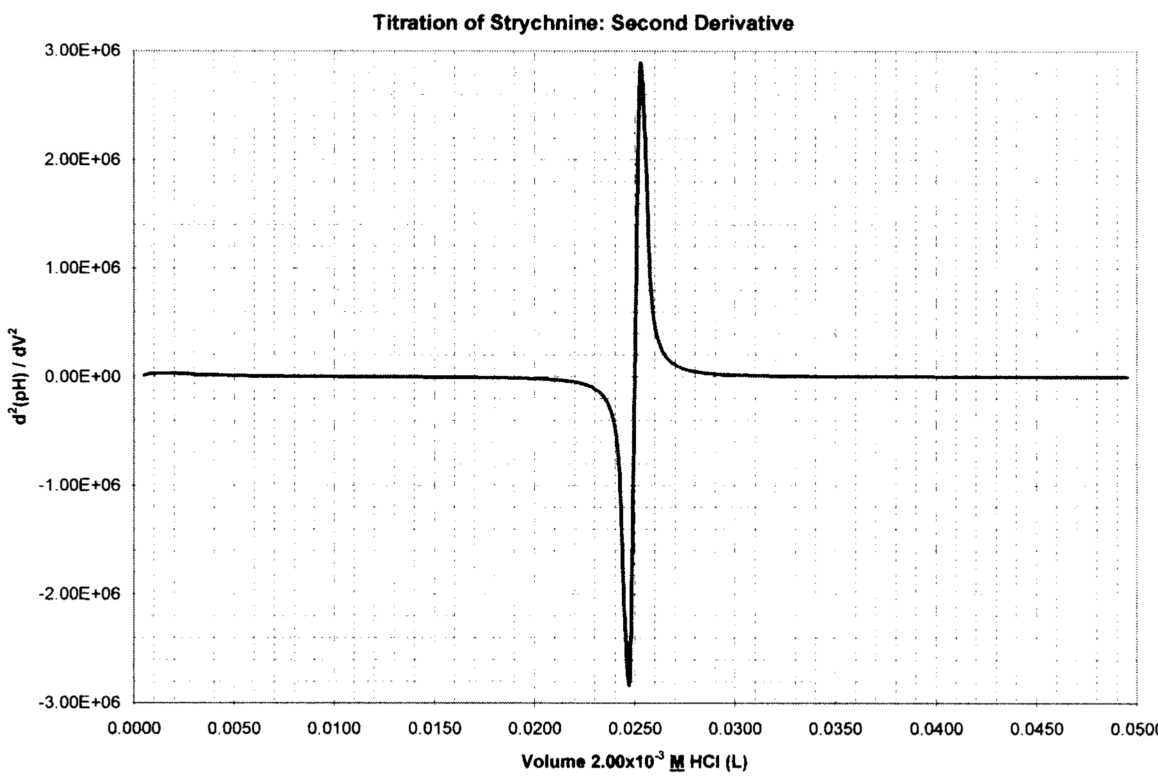
6. A buffer of pH = 3.4 is desired. If the following reagents are available, which pair of reagents will make the buffer with the highest capacity?

(A) $HClO_3$ (pK_a = -2.70) and $NaClO_3$
(B) HOCN (pK_a = 3.46) and KCl
(C) K_2HPO_4 (pK_a = 11.90) and K_3PO_4
(D) NaH_2PO_4 (pK_a = 6.68) and Na_2HPO_4
(E) H_3PO_4 (pK_a = 2.15) and KH_2PO_4

5

Problems 7 through 9 concern the following plots:





7. Strychnine ($C_{21}H_{22}N_2O_2$) is a naturally occurring weak base that can accept one proton. A 50.00 mL aliquot of strychnine solution is titrated with standard 2.00×10^{-3} M HCl. Refer to the plots on the previous page. What is the concentration of the strychnine solution?

5

(A) 5.00×10^{-4} M
(B) 1.00×10^{-3} M
(C) 2.00×10^{-3} M
(D) 4.00×10^{-3} M
(E) The concentration cannot be determined by the information given.

$0.025\ L \cdot \frac{0.002\ \text{mol HCl}}{L} \cdot \frac{1}{0.050\ L} = 0.0015$

8. Refer to the plots on the previous page. Given the information in problem 7, what is the value for the base dissociation constant K_b for strychnine?

5

(A) 5.72
(B) 8.26
(C) 1.82×10^{-6}
(D) 5.50×10^{-9}
(E) None of the above

$pK_a = 8.26$
$pK_b = 14 - pK_a = 5.74$
$K_b = 10^{-pK_b} = 1.82\times10^{-6}$

9. Refer to the plots on the previous page. Which of the following indicators would be most appropriate to use for the titration of strychnine with HCl?

5

(A) Methyl orange ($pK_a = 3.3$)
(B) Chlorophenol red ($pK_a = 6.0$)
(C) Bromothymol blue ($pK_a = 7.1$)
(D) Cresol red ($pK_a = 8.2$)
(E) Phenolphthalein ($pK_a = 9.4$)

pH = 5.7

10. Solution A has a pH of 9.00 and solution B has a pH of 10.00. Which of the following statements are *true*?

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

5

(A) **I** and **III**
(B) **I** and **IV**
(C) **II** and **III**
(D) **I, IV,** and **V**
(E) **II, III,** and **V**

For questions 11-13, 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
HF	6.31×10^{-4}	1.58×10^{-11} (F^-)
$HC_2H_3O_2$	1.78×10^{-5}	5.62×10^{-10} ($C_2H_3O_2^-$)
NH_3	5.62×10^{-10} (NH_4^+)	1.78×10^{-5}

11. NH_4F $K_a > K_b$

5

(A) produces an acidic solution when dissolved in water
(B) produces a basic solution when dissolved in water
(C) produces a neutral solution when dissolved in water

12. $NH_4C_2H_3O_2$ $K_a \approx K_b$

5

(A) produces an acidic solution when dissolved in water
(B) produces a basic solution when dissolved in water
(C) produces a neutral solution when dissolved in water

13. KF

5

(A) produces an acidic solution when dissolved in water
(B) produces a basic solution when dissolved in water
(C) produces a neutral solution when dissolved in water

14. Which of the following statements are *false*?

I. × The strength of an acid is directly proportional to the affinity of its conjugate base for hydrogen ions.
II. × A weak base has a strong conjugate acid.
III. ✓A strong base has a weak conjugate acid.
IV. ✓ As acid strength increases, the conjugate base is less willing to accept hydrogen ions.
V. × The dissociation equilibrium for a strong acid lies far to the left.

5

(A) **I and V**
(B) **III and IV**
(C) **I, II, and III**
2 (D) **II, III, and V**
(E) **I, II, and V**

20

15. Zirconium (IV) phosphate has a $K_{sp} = 1\times10^{-132}$. If the pH of a solution of zirconium phosphate is decreased. then:

(A) ✗ Nothing will happen because the salt is neither acidic nor basic.
(B) ✗ The K_{sp} for $Zr_3(PO_4)_4$ will increase because phosphate is a basic anion.
(C) ✗ The solubility equilibrium position will shift left.
5 (D) ✓The molar solubility of $Zr_3(PO_4)_4$ will increase because phosphate is the conjugate base of a weak acid.
(E) ✗ Nothing will happen because this is a heterogeneous equilibrium and $Zr_3(PO_4)_4$ is a solid.

Equations and Constants

$$PV = nRT$$

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

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

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

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

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

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

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

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

$$K_w = 1.00\times10^{-14} = [H^+][OH^-]$$

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

$$pH + pOH = 14.00$$

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

$$K_a \cdot K_b = K_w$$

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

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

5