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Name Key
(Please print family name last; e.g., Robert Boyle)

UMB Student Number _____

Chem 104 - Section 1
Hour Examination III
May 5, 2006

This test consists of seven (7) pages, including this cover page, a table of conjugate acid-base pairs with K_a values, and a periodic table. Be sure your copy is complete before beginning your work. If this test packet is defective, ask for another one. **Feel free to detach the acid-base table and/or periodic table to use for reference or scratch paper.**

Give all numerical answers to the proper number of significant figures.

$K_w = 1.00 \times 10^{-14}$

DO NOT WRITE BELOW THIS LINE

1.

2.

3 a - e

3 f & g
+ bonus

TOTAL

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1. (12 points; 3 points each part) Complete the following table by calculating the missing entries and indicating whether the solution is acidic or basic.

$[H_3O^+]$	$[OH^-]$	pH	pOH	acidic/basic?
4.2×10^{-6}	2.4×10^{-9} M	5.38	8.62	acidic

2. (44 points; 4 points each part) Fill in the blanks.

a. For the following reaction, label the conjugate acid-base pairs (i.e., $acid_1/base_1$; $acid_2/base_2$).

$$C_4H_4O_6^{2-} + H_2AsO_4^- \rightleftharpoons HC_4H_4O_6^- + HAsO_4^{2-}$$

base$_1$ acid$_2$ acid$_1$ base$_2$

b. Write a balanced chemical equation for each of the following equilibria:

acid hydrolysis of $HC_4H_4O_6^-$ $HC_4H_4O_6^- + H_2O \rightleftharpoons C_4H_4O_6^{2-} + H_3O^+$

base hydrolysis of $HC_4H_4O_6^-$ $HC_4H_4O_6^- + H_2O \rightleftharpoons H_2C_4H_4O_6 + OH^-$

c. For the acid hydrolysis of tartaric acid, $H_2C_4H_4O_6$, $K_a = 1.0 \times 10^{-3}$. What is the value of K_b for the base hydrolysis of the hydrogen tartrate ion, $HC_4H_4O_6^-$?

$K_b =$ 1.0×10^{-11} for $HC_4H_4O_6^-$

d. For the acid hydrolysis of the hydrogen tartrate ion, $HC_4H_4O_6^-$, $K_a = 4.6 \times 10^{-5}$. Judging from this and the K_b value you just calculated in question c, would a 0.10 M solution of $NaHC_4H_4O_6(aq)$ be acidic or basic?

acidic (acidic/basic)

e. Consider a 0.10 M solution of the diprotic acid $H_2C_4H_4O_6(aq)$, for which $K_1 = 1.0 \times 10^{-3}$ and $K_2 = 4.6 \times 10^{-5}$. What is the concentration of $C_4H_4O_6^{2-}$ ion in this solution?

$[C_4H_4O_6^{2-}] =$ 4.6×10^{-5} M

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f. Refer to the Table of Conjugate Acid-Base Pairs. Which one of the following solutions when added in excess to a solution containing 1.0 mmol $Na_3PO_4(aq)$ would produce 1.0 mmol $H_2PO_4^-$ ion in solution: $HOI(aq)$, $Al(NO_3)_3(aq)$, $NH_4NO_3(aq)$?

Answer: $Al(NO_3)_3$

g. Assuming equal concentrations, which one of the following pairs would produce the more acidic solution?

$HClO_3(aq)$ or $HClO_2(aq)$ $HClO_3$

$C_6H_5CO_2H(aq)$ or $ClC_6H_4CO_2H(aq)$ $ClC_6H_4CO_2H$

h. Identify the Lewis acid and Lewis base in the following reaction

$$Fe^{3+} + 3\,C_2O_4^{2-} \rightarrow [Fe(C_2O_4)_3]^{3-}$$

acid base

i. Consider a 0.10 M solution of the weak acid HA, for which $pK_a = 4.58$. Would the expression $[H_3O^+] = \sqrt{C_{HA}K_a}$ give a reasonably accurate estimate of the hydronium ion concentration (less than 5% error)? $K_a = 2.6 \times 10^{-5}$

Answer: Yes (yes/no)

j The base B has $K_b = 1.0 \times 10^{-8}$. What is the pH of a buffer solution prepared by mixing 1.0 mol B with 1.0 mol of the salt HBCl in enough water to make a liter of solution?

pH = 6.00

k. Indicate whether 0.10 M aqueous solutions of each of the following solutions would have a pH > 7.0, pH < 7.0, or pH ≈ 7.0:

$Fe(NO_3)_3$ < 7.0 $Ba(NO_2)_2$ > 7.0

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3. (44 points) $K_a = 3.5 \times 10^{-4}$ for cyanic acid, HCNO. Consider the titration of 25.0 mL of 0.160 M HCNO solution (the analyte), with 0.100 M NaOH(*aq*) solution (the titrant):

$$HCNO(aq) + OH^-(aq) \rightarrow CNO^-(aq) + H_2O(l)$$

a. (4 points) How many milliliters of 0.100 M NaOH(*aq*) solution must be added to reach the equivalence point?

$$V_b = \frac{V_a M_a}{M_b} = \frac{(25.0\,mL)(0.160\,M)}{0.100\,M} = 40.0\,mL$$

b. (2 points) What is the total volume in the solution at the equivalence point? 65.0 mL

c. (2 points) How many millimoles of HCNO are present in the analyte sample before any titrant has been added?

millimoles HCNO = 4.00

d. (6 points) What is the initial pH of the HCNO solution, before adding any titrant?

$$[H_3O^+] = \sqrt{(0.160)(3.5\times10^{-4})} = \sqrt{5.6\times10^{-5}} = 7.4_8\times10^{-3}$$

$$pH = 2.12_{59} = 2.13$$

e. (6 points) What is the pH of the resulting solution after adding 20.0 mL of 0.100 M NaOH(*aq*) solution? [Hint: How far along in the titration is this?]

Half-titration point ⇒ equimolar buffer solution

$$pH = pK_a = -\log(3.5\times10^{-4}) = 3.45_{59} = 3.46$$

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f. (10 points) What is the pH of the resulting solution after adding 30.0 mL of 0.100 M NaOH(*aq*) solution?

mmol OH^- added = (30.0 mL)(0.100 M) = 3.00 mmol

	$HCNO$	+ OH^-	⟶ CNO^-	+ H_2O
Add	4.00	3.00		
Rxn	1.00		3.00	

$$K_a = \frac{[H_3O^+][CNO^-]}{[HCNO]} = 3.5 \times 10^{-4} = \frac{[H_3O^+](3.00)}{1.00}$$

$$[H_3O^+] = \frac{(1.00)(3.5 \times 10^{-4})}{3.00} = 1.1_{67} \times 10^{-4} \Rightarrow pH = 3.93$$

g. (14 points) What is the pH at the equivalence point?

All HCNO converted to 4.00 mmol CNO^- in 65.0 mL.

$$C_{CNO^-} = \frac{4.00 \text{ mmol}}{65.0 \text{ mL}} = 6.15_{38} \times 10^{-2} \text{ M}$$

$$K_b^{CNO^-} = \frac{K_w}{K_a^{HCNO}} = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-4}} = 2.8_{57} \times 10^{-11} = 2.9 \times 10^{-11}$$

$$[OH^-] = \sqrt{(6.15_{38} \times 10^{-2} \text{ M})(2.8_{57} \times 10^{-11})} = \sqrt{1.7_{58} \times 10^{-12}} = 1.3_{26} \times 10^{-6}$$

$$pOH = 5.88 \Rightarrow pH = 8.12$$

BONUS (5 points) What is the pH of the solution after the addition of 50.0 mL of 0.100 M NaOH solution?

mmol OH^- added = (50.0 mL)(0.100 M) = 5.00 mmol

	$HCNO$	+ OH^-	⟶ CNO^-	+ H_2O
Add	4.00	5.00		
Rxn	~0	1.00		

V = 75.0 mL

$$[OH^-] = \frac{1.00 \text{ mmol}}{75.0 \text{ mL}} = 1.33 \times 10^{-2} \Rightarrow pOH = 1.875 \Rightarrow pH = 12.125$$