Your Name: Key Section:

Chemistry 31 – Quantitative Analysis Exam #2, April 18, 2012

Multiple Choice and Short Answer

Circle the one correct answer from the choices listed, enter the correct term or phrase on the blank line, or briefly answer the question as indicated.

1 **(4 points)**. As ionic strength decreases, the values of activity coefficients approach:

a. 1 b. 0
c. 2 d. there is no specific value

2 **(4 points)**. As the pK_a of weak acids get larger (value increases), the strength of their *conjugate bases* become:

a. stronger b. weaker
c. stay the same d. they cannot be compared

3 **(4 points)**. The ionic strength of a 0.012M solution of the soluble weak acid CH_3CO_2H ($K_a = 1.75 \times 10^{-5}$) is:

a. 0.024M b. 0.012M
c. 0.030M d. close to 0.000M

4 **(4 points)**. What is the charge balance for the following system of chemical equations?

$$NiCO_{3(s)} \longrightarrow Ni^{2+}_{(aq)} + CO^{2-}_{3(aq)}$$
$$CO^{2-}_{3(aq)} + H_2O_{(l)} \longleftrightarrow HCO^{-}_{3(aq)} + OH^{-}_{(aq)}$$
$$HCO^{-}_{3(aq)} + H_2O_{(l)} \longleftrightarrow H_2CO_{3(aq)} + OH^{-}_{(aq)}$$
$$H_2O_{(l)} \longleftrightarrow OH^{-}_{(aq)} + H^{+}_{(aq)}$$

a. $[Ni^{2+}]^2 + [H^+] = [CO_3^{2-}]^2 + [HCO_3^-] + [OH^-]$
b. $[Ni^{2+}] + [H^+] = [CO_3^{2-}] + [HCO_3^-] + [OH^-]$
c. $2[Ni^{2+}] + [H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] + [OH^-]$
d. $2[Ni^{2+}] + [H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-]$

5 **(4 points)**. What resolution listed below indicates baseline resolution between two peaks in a chromatograph?

a. 0.0 b. 1.5
c. 1.0 d. 0.5

6 **(4 points)**. If analyte A and analyte B have different partition coefficients with respect to a chromatography column, it is due to:

a. differential partitioning between the mobile and stationary phases
b. band broadening (diffusion) in the column
c. both a and b
d. neither a or b

7 **(4 points)**. When we cannot precisely control our sample injection volume, we should use an Internal Standard to insure a precise calibration.

8 **(4 points)**. Circle the correct answer. Does **absorption** or **emission** spectroscopy generally have lower (better) detection limits?

9 **(4 points)**. What type of mechanism of separation is most common for chromatography?

a. ion exchange
b. adsorption
c. partition (absorption)
d. molecular exclusion

Worked out Problems

It is your responsibility to work out your answers clearly. Unclear, or unreadable work will not be graded. If there is not enough space provided to show your work, continue on the back of the page and clearly mark the problem number. Be sure to show all of your work and report your final answer with the correct number of significant figures and **units**. Unless otherwise noted, an unreasonable number of significant figures in a final answer will be marked off 2 points. A correct answer without work shown will not receive credit. Circle or draw a box around your final answer.

Equations that may or may not be useful to you:

$$x = -\frac{b \pm \sqrt{b^2 - 4ac}}{2a}; \text{ where } ax^2 + bx + c = 0 \qquad \text{pH} = \text{pK}_a + \log\frac{[base]}{[acid]}$$

$$\log\gamma = \frac{-0.51 z^2 \sqrt{u}}{1 + (\alpha\sqrt{\mu}/305)} \qquad \mu = \frac{1}{2}\sum_i c_i z_i^2$$

$$\frac{I_X}{I_S} = F\frac{[X]}{[S]} \qquad \frac{[X]}{[X]+[S]} = \frac{I_X}{I_{S+X}}$$

10 **(10 points)**. You are using an internal standard to analyze toluene by gas chromatography. You are using benzene as your internal standard. Your standard solution contains: 10.0mg/mL toluene and has a GC response of 9567mV, and 10.0mg/mL of benzene that gives a GC response of 11236mV. Your unknown sample gives a toluene response of 3659mV and contains 10.0mg/mL of benzene that gives you a response of 8556mV. What is the concentration (mg/mL) of toluene in your unknown sample?

$$\frac{9567}{11236} = F \frac{10.0\,mg/mL}{10.0\,mg/mL}$$

$$F = 0.8515$$

$$\frac{3659}{8556} = (0.8515)\frac{[x]}{10.0\,mg/mL}$$

$$[x] = \boxed{5.02\,mg/mL}$$

11 **(10 points).** Accounting for ionic strength, what is the pH of a 0.100M solution of HBr? See the attached table for activity coefficients. Report your answer with 3 significant figures.

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

$$= -\log (0.100)(0.83)$$

$$\boxed{pH = 1.08}$$

Table 8-1 Activity coefficients for aqueous solutions at 25°C

Ion	Ion size (α, pm)	Ionic strength (μ, M) 0.001	0.005	0.01	0.05	0.1
Charge = ±1						
H^+	900	0.967	0.933	0.914	0.86	0.83
$(C_6H_5)_2CHCO_2^-$, $(C_3H_7)_4N^+$	800	0.966	0.931	0.912	0.85	0.82
$(O_2N)_3C_6H_2O^-$, $(C_3H_7)_3NH^+$, $CH_3OC_6H_4CO_2^-$	700	0.965	0.930	0.909	0.845	0.81
Li^+, $C_6H_5CO_2^-$, $HOC_6H_4CO_2^-$, $ClC_6H_4CO_2^-$, $C_6H_5CH_2CO_2^-$, $CH_2{=}CHCH_2CO_2^-$, $(CH_3)_2CHCH_2CO_2^-$, $(CH_3CH_2)_4N^+$, $(C_3H_7)_2NH_2^+$	600	0.965	0.929	0.907	0.835	0.80
$Cl_2CHCO_2^-$, $Cl_3CCO_2^-$, $(CH_3CH_2)_3NH^+$, $(C_3H_7)NH_3^+$	500	0.964	0.928	0.904	0.83	0.79
Na^+, $CdCl^+$, ClO_2^-, IO_3^-, HCO_3^-, $H_2PO_4^-$, HSO_3^-, $H_2AsO_4^-$, $Co(NH_3)_4(NO_2)_2^+$, $CH_3CO_2^-$, $ClCH_2CO_2^-$, $(CH_3)_4N^+$, $(CH_3CH_2)_2NH_2^+$, $H_2NCH_2CO_2^-$	450	0.964	0.928	0.902	0.82	0.775
$^+H_3NCH_2CO_2H$, $(CH_3)_3NH^+$, $CH_3CH_2NH_3^+$	400	0.964	0.927	0.901	0.815	0.77
OH^-, F^-, SCN^-, OCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-, HCO_2^-, $H_2citrate^-$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$	350	0.964	0.926	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	300	0.964	0.925	0.899	0.805	0.755
Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+	250	0.964	0.924	0.898	0.80	0.75

a. Lanthanides are elements 57–71 in the periodic table.

12 **(12 points).** What is the pH of a solution with a 0.0365M formal concentration of hydroxyacetic acid ($HOCH_2CO_2$)? The pK_a is 3.832.

$$HA \rightleftharpoons H^+ + A^- \qquad K = 10^{-3.832}$$

$$\frac{[H^+][A^-]}{[HA]} = 1.47\times10^{-4}$$

	HA	H^+	A^-
I	0.365	0	0
C	$-x$	$+x$	$+x$
E	$0.365-x$	x	x

$$\frac{x^2}{0.365-x} = 1.47\times10^{-4}$$

$$x^2 + 1.47\times10^{-4}x - 5.37\times10^{-6}$$

$$x = \frac{-1.47\times10^{-4} \pm \sqrt{(1.47\times10^{-4})^2 - 4(5.37\times10^{-6})}}{2}$$

$$\frac{-1.47\times10^{-4} \pm 4.64\times10^{-3}}{2}$$

$$x = 2.24\times10^{-3}\,M = [H^+]$$

$$\boxed{pH = 2.6}$$

13 **(16 points)**. Using the systematic method, set up the following problem for solving. Give the charge balance, mass balance, equilibrium expressions, and unknowns. Clearly label each. You do not have to solve. What is the equilibrium pH of a solution made by dissolving 0.057 moles of Na_2HPO_4 into 1.000L of pure water? Hint: there are two different mass balance equations. Consider the following chemical reactions:

$$Na_2HPO_{4(s)} \longrightarrow 2Na^+_{(aq)} + HPO^{2-}_{4(aq)}$$

$$HPO^{2-}_{4(aq)} \longleftrightarrow H^+_{(aq)} + PO^{3-}_{4(aq)} \quad K_a = 4.22x10^{-13}$$

$$HPO^{2-}_{4(aq)} + H_2O_{(l)} \longleftrightarrow H_2PO^-_{4(aq)} + OH^-_{(aq)} \quad K_b = 1.58x10^{-7}$$

$$H_2O_{(l)} \longleftrightarrow OH^-_{(aq)} + H^+_{(aq)} \quad K_w = 1.0x10^{-14}$$

charge: $[Na^+] + [H^+] = 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [H_2PO_4^-] + [OH^-]$

mass: must show 2 of the following:

$$[Na^+] = 2([HPO_4^{2-}] + [PO_4^{3-}] + [H_2PO_4^-])$$

$$[Na^+] = 2(0.057M)$$

$$[HPO_4^{2-}] + [PO_4^{3-}] + [H_2PO_4^-] = 0.057M$$

equilibrium expressions: $\dfrac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.22\times10^{-13}$

$$\frac{[OH^-][H_2PO_4^-]}{[HPO_4^{2-}]} = 1.58\times10^{-7}$$

$$[H^+][OH^-] = 1.0\times10^{-14}$$

unknowns:

$[Na^+]$, $[H^+]$, $[OH^-]$, $[PO_4^{3-}]$, $[HPO_4^{2-}]$, $[H_2PO_4^-]$

↑

not necessary if second mass balance equation is included

14 **(16 points)**. What is the equilibrium pH of a solution that is made by mixing 50.0 mL of 0.0475M $NaHCO_2$ with 75.0mL of 0.0226M H_2CO_2? The pK_a of H_2CO_2 (formic acid) is 3.744. What is the final pH of this solution if 10.0mL of 0.100M NaOH is added?

$$50.0\,mL \left| \frac{0.0475\ mmol}{1\,mL} \right| = 2.375\ mmol\ A^-$$

$$75.0\,mL \left| \frac{0.0226\ mmol}{1\,mL} \right| = 1.695\ mmol\ HA$$

$$pH = 3.744 + \log \frac{2.375}{1.695}$$

$$\boxed{pH = 3.89}$$

$$10.0\,mL \left| \frac{0.100\ mmol}{1\,mL} \right| = 1.00\ mmol\ OH^-$$

$HA + OH^- \rightarrow H_2O + A^-$

$$pH = 3.744 + \log \frac{(2.375 + 1.00)}{(1.695 - 1.00)}$$

$$\boxed{pH = 4.43}$$

15 **(Must be signed)**. I did not cheat on this test in any way. Signed _____