Your Name: Key Lab section: _____

Chemistry 31 – Quantitative Analysis Exam #2, April 20, 2011

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 the value of activity coefficients (γ) increase, solubility:

(a.) decreases
b. increases
c. stays the same
d. none of the above

2 **(4 points)**. Acid 'A' has a pK_a of 3.0. Acid 'B' has a pK_a of 5.0. Which acids' conjugate base is the stronger base?

a. A
(b.) B
c. They are equal in strength.
d. They cannot be compared.

3 **(4 points)**. What is the mass balance for the following system of chemical equations?

$$Na_2HPO_{4(s)} \longrightarrow 2Na^+_{(aq)} + HPO^{2-}_{4(aq)}$$
$$HPO^{2-}_{4(aq)} \longleftrightarrow H^+_{(aq)} + PO^{3-}_{4(aq)}$$
$$HPO^{2-}_{4(aq)} + H_2O_{(l)} \longleftrightarrow H_2PO^-_{4(aq)} + OH^-_{(aq)}$$
$$H_2O_{(l)} \longleftrightarrow OH^-_{(aq)} + H^+_{(aq)}$$

a. $2[Na^+] = [HPO_4^{2-}] + [PO_4^{3-}] + [H_2PO_4^-]$
b. $[Na^+] = [HPO_4^{2-}]$
(c.) $[Na^+] = 2([HPO_4^{2-}] + [PO_4^{3-}] + [H_2PO_4^-])$
d. $[H^+] = [OH^-] + [PO_4^{3-}]$

4 **(4 points)**. For an acid-base conjugate pair, $pK_a + pK_b =$

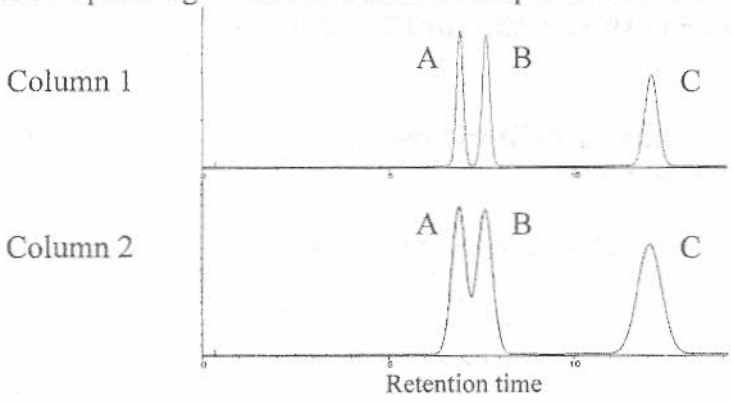
(a.) 14
b. 1
b. 1.0×10^{14}
c. 1.0×10^{-14}

5 **(4 points)**. Emission (fluorescence) spectroscopy tends to have higher sensitivity because:

a. emitted light is of a longer wavelength than absorbed light.
(b.) detection of light is on a zero background.
c. not all compounds fluoresce.
d. both a and b.

6 **(4 points)**. When matrix effects are present in our analysis, we should use the method of standard addition for calibration purposes.

Use the two chromatograms below to answer questions 7 to 10. The chromatograms were obtained from 2 columns of equal length with the same mobile phase flow rate.



7 **(3 points)**. Which column (1 or 2) gives higher resolution?

8 **(3 points)**. Which compound (A, B, or C) has the largest partition coefficient?

9 **(3 points)**. Which compound (A, B, or C) spends the most time associated with the stationary phase?

10 (**3 points**). In which column (1 or 2) does the least amount of diffusion occur?

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 <u>or may not</u> be useful to you:

$$x = -\frac{b \pm \sqrt{b^2 - 4ac}}{2a}, \text{ where } ax^2 + bx + c = 0; \qquad \text{pH} = \text{pK}_a + \log\frac{[base]}{[acid]}; \qquad \log\gamma = \frac{-0.51 z^2 \sqrt{u}}{1 + (\alpha\sqrt{\mu}/305)}$$

$$\mu = \frac{1}{2}\sum_i c_i z_i^2; \qquad M_1V_1 = M_2V_2; \qquad \frac{I_X}{I_S} = F\frac{[X]}{[S]}; \qquad \frac{[X]}{[X]+[S]} = \frac{I_X}{I_{S+X}}; \qquad A = \varepsilon bc;$$

A = 2.00-log(%T)

dilution factor = volume of original solution / total final solution volume

diluted concentration = dilution factor(original concentration)

11 **(10 points)**. You are analyzing compound 'X' using absorbance spectroscopy. A standard containing 50.0 µg/mL of 'X' gives a % transmittance of 35.6. The blank % transmittance is 97.2. What is the concentration (µg/mL) of a sample of 'X' that gives a % transmittance of 45.8?

$A_{standard} = 2.00 - \log 35.6 = 0.449 - 0.0123 = 0.437$

$A_{sample} = 0.339 - 0.0123 = 0.327$

$A_{blank} = 0.0123$

$0.437 = m(50\ \mu g/mL)$

$m = 8.74 \times 10^{-3}\ \frac{mL}{\mu g}$

$0.327 = 8.74 \times 10^{-3}\ \frac{mL}{\mu g}\ (x)$

$x = \boxed{37.4\ \mu g/mL}$

12 **(12 points)**. Accounting for activity, what is the solubility (in moles/L) of TlCl in water with an ionic strength of 0.10M? The appropriate activity coefficients are: $\gamma_{Tl} = 0.750$, and $\gamma_{Cl} = 0.755$. The K_{sp} for TlCl is 1.8×10^{-4}.

$TlCl \rightleftharpoons Tl^+ + Cl^-$

$[Tl^+]\gamma_{Tl^+}[Cl^-]\gamma_{Cl^-} = 1.8 \times 10^{-4}$

$(x)0.750(x)0.755 = 1.8 \times 10^{-4}$

	Tl	Cl
I	−	−
C	+x	+x
E	x	x

$x = \boxed{1.8 \times 10^{-2}\ mol/L}$

13 **(12 points).** What is pH of a solution with a 0.150M formal concentration of sodium acetate ($NaCH_3CO_2$) ? The pK_a of acetic acid is 4.757.

$CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$

$\frac{[OH^-][CH_3CO_2H]}{[CH_3CO_2^-]} = 5.71\times10^{-10}$

$K_b = 10^{-(14-4.757)}$

$= 5.71\times10^{-10}$

	B^-	BH	OH^-
I	0.150	–	–
C	$-x$	$+x$	$+x$
E	$0.150-x$	x	x

$\frac{x^2}{0.150-x} = 5.71\times10^{-10}$ (square)

$x = 9.25\times10^{-6} M = [OH^-]$

$pH = -\log\left(\frac{10^{-14}}{9.25\times10^{-6}}\right) = \boxed{8.97}$

14 **(14 points).** What is the pH of a 1.550×10^{-8}M solution of the strong base RbOH? Report your answer with 3 significant figures.

Rxns

$RbOH \rightarrow Rb^+ + OH^-$

$H_2O \rightleftharpoons H^+ + OH^-$

dilute strong base

mass balance

$[Rb^+] = 1.550\times10^{-8} M$

charge balance

$[Rb^+] + [H^+] = [OH^-]$

equilibrium

$[H^+][OH^-] = 10^{-14}$

unknowns

$[Rb^+]$, $[OH^-]$, $[H^+]$

3 equations

solve

$1.550\times10^{-8} + [H^+] = [OH^-]$

$1.550\times10^{-8} + [H^+] = \frac{10^{-14}}{[H^+]}$

$[H^+]^2 + 1.550\times10^{-8}[H^+] - 10^{-14} = 0$

$\frac{-1.550\times10^{-8} \pm \sqrt{(1.550\times10^{-8})^2 - 4(1)(-10^{-14})}}{2}$

$\frac{-1.55\times10^{-8} \pm \sqrt{4.02\times10^{-14}}}{2}$

$x = [H^+] = 9.25\times10^{-8}$

$\boxed{pH = 7.03}$

15 **(16 points)**. What is the final pH of a solution produced by adding the following 3 solutions together? The pK_a for acetic acid is 4.76.

75.00 mL of 0.0510 M acetic acid
20.00 mL of 0.0550 M HNO_3
50.00 mL of 0.105 M sodium acetate

$$75.00\ mL \left| \frac{0.0510\ mmol\ HA}{1\ mL} \right| = 3.825\ mmol\ HA + 1.1\ mmol$$

$$= 4.925\ mmol\ HA$$

$$50.00\ mL \left| \frac{0.105\ mmol\ A^-}{1\ mL} \right| = 5.25\ mmol\ A^- - 1.1\ mmol$$

$$= 4.15\ mmol\ A^-$$

$$20.00\ mL \left| \frac{0.0550\ mmol\ H^+}{1\ mL} \right| = 1.1\ mmol\ H^+$$

$$A^- + H^+ \rightarrow HA$$

$$pH = 4.76 + \log \frac{4.15}{4.925} = \boxed{4.69}$$