

Chemistry 31 – Quantitative Analysis Exam #2, November 26, 2008Multiple 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 increases, the values of activity coefficients:

- a. change randomly b. increase
☒ c. decrease d. do not change

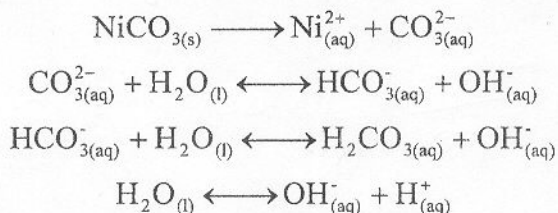
2 (4 points). What is the pH of a solution with $[HA] = 0.01M$ and $[A^-] = 0.01M$, when $pK_a = 5.2$? (Assume HA and A^- are conjugates.)

- ☒ a. 5.2 b. 4.2
 c. 6.2 d. 7.0

3 (4 points). Which solution has a higher ionic strength? A 0.500M solution of $NaCl$ or a 0.500M solution of $Ca(NO_3)_2$? (Both salts are fully soluble.)

- a. Solution of $NaCl$. ☒ b. Solution of $Ca(NO_3)_2$.
 c. Equal ionic strengths. d. Cannot be determined.

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



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

5 (4 points). Of the 4 options listed below, which is the most common mechanism of separation for chromatography?

- a. adsorption b. ion-exchange
☒ d. partition (absorption)

6 (4 points). Analyte separation in chromatography is affected by which of the following:

- 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). Standard addition should be used when:

- a. the volume of the analyzed sample cannot be controlled.
- ☒ b. matrix effects are present.
- c. analyte concentrations are too small to measure.
- d. only when using gas chromatography.

8 (4 points). Circle the correct answer (in bold). Does **absorption** or **emission** of a photon from the same molecule require/produce more energy?

9 (4 points). Fill in the blank. Beer's Law allows quantitative measurements using absorption spectroscopy.

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:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}; \text{ where } ax^2 + bx + c = 0$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

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

$$\mu = \frac{1}{2} \sum_i c_i z_i^2$$

$$M_1V_1 = M_2V_2$$

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

diluted concentration = dilution factor(original concentration)

$$\frac{I_x}{I_s} = F \frac{[X]}{[S]}$$

$$\frac{[X]}{[X] + [S]} = \frac{I_x}{I_{s+x}}$$

10 (10 points). You are using the method of standard addition to analyze the quantity of unknown A in an unknown sample. Two solutions are prepared for analysis.

Solution 1 contains 5.00 mL of unknown sample diluted to a total of 10.00 mL, and gives an instrument response of 3589.

Solution 2 contains 5.00 mL of unknown sample, 3.00 mL of standard (containing 200.0 $\mu\text{g/L}$ of A), is diluted to a total of 10.00 mL, and gives an instrument response of 9618.

What is the concentration ($\mu\text{g/L}$) of unknown A in the *original* unknown sample?

$$\text{Solution 1: unknown dilution factor} = \frac{5}{10} = 0.5$$

$$\text{Solution 2: unknown dilution factor} = \frac{5}{10} = 0.5$$

$$\text{standard dilution factor} = \frac{3}{10} \times 200 \mu\text{g/L} = 60 \mu\text{g/L}$$

$$\frac{[x]}{[x] + 60 \mu\text{g/L}} = \frac{3589}{9618}$$

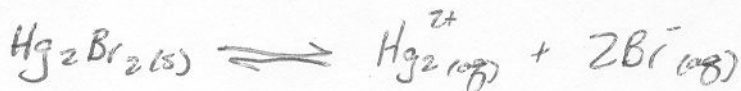
$$9618[x] = 3589[x] + 215340 \mu\text{g/L}$$

$$6029[x] = 215340 \mu\text{g/L}$$

$$[x] = \frac{35.7 \mu\text{g/L}}{0.5} = \boxed{71.4 \mu\text{g/L}}$$

unknown
dilution
factor

- 11 (10 points). Accounting for ionic strength, what is $[\text{Hg}_2^{2+}]$ in a saturated solution of $\text{Hg}_2\text{Br}_{2(s)}$ that also is 0.00500M in NaBr. The K_{sp} for Hg_2Br_2 is 5.6×10^{-23} . The appropriate activity coefficients are: $\gamma_{\text{Hg}_2^{2+}} = 0.740$, and $\gamma_{\text{Br}^-} = 0.925$.



$$[\text{Hg}_2^{2+}] \gamma_{\text{Hg}_2^{2+}} [\text{Br}^-]^2 \gamma_{\text{Br}^-}^2 = 5.6 \times 10^{-23}$$

$$X(0.740)(0.005 + 2x)^2 (0.925)^2 = 5.6 \times 10^{-23}$$

ignore 2x

$$1.58 \times 10^{-5} X = 5.6 \times 10^{-23}$$

$$X = 3.5 \times 10^{-18} \text{ M} = [\text{Hg}_2^{2+}]$$

	Hg_2^{2+}	Br^-
I	0	0.005

$$C \quad +x \quad +2x$$

$$E \quad x \quad 0.005 + 2x$$

- 12 (12 points). What is the pH of a solution with a 0.0365M formal concentration of the base hydroxyacetate ($\text{HOCH}_2\text{CO}_2^-$)? The $\text{p}K_a$ for hydroxyacetic acid is 3.832.



$$\frac{[\text{OH}^-][\text{HOCH}_2\text{CO}_2\text{H}]}{[\text{HOCH}_2\text{CO}_2^-]} = 6.79 \times 10^{-11}$$

$$\text{p}K_b = 14 - 3.832 = 10.168$$

$$K_b = 6.79 \times 10^{-11}$$

$$\frac{x^2}{0.0365 - x} = 6.79 \times 10^{-11}$$

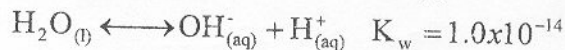
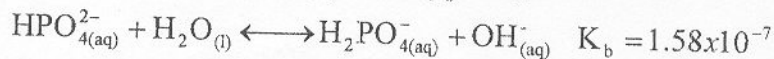
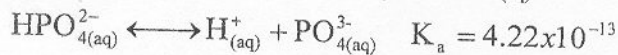
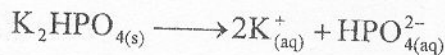
ignore x

$$x = 1.57 \times 10^{-6} = [\text{OH}^-]$$

$$\text{pH} = -\log\left(\frac{10^{-14}}{1.57 \times 10^{-6}}\right) = 8.2$$

	$\text{HOCH}_2\text{CO}_2^-$	OH^-	$\text{HOCH}_2\text{CO}_2\text{H}$
I	0.0365M	0	0
C	-x	+x	+x
E	0.0365 -x	x	x

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 should not solve.** What is the equilibrium pH of a solution made by dissolving 0.067 moles of K_2HPO_4 into 1.000L of pure water? Hint: there are two different mass balance equations. Consider the following chemical reactions ($K_2HPO_{4(s)}$ is completely soluble):



charge

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

mass

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

$$0.067M = [HPO_4^{2-}] + [PO_4^{3-}] + [H_2PO_4^-]$$

$$2(0.067M) = [K^+]$$

} need 2 out of 3

equil. expressions

$$\frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = K_a$$

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

$$\frac{[OH^-][H_2PO_4^-]}{[HPO_4^{2-}]} = K_b$$

unknowns

$$[K^+], [HPO_4^{2-}], [PO_4^{3-}], [H_2PO_4^-], [H^+], [OH^-] = 6$$

14 (16 points). What is the equilibrium pH of a solution that is made by adding 50.0 mL of 0.0475M NaHCO₂ to 75.0mL of 0.0226M H₂CO₂? The pK_a of H₂CO₂ (formic acid) is 3.744. What is the final pH of this solution if 10.0mL of 0.100M HCl is added?

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

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

$$pH = 3.744 + \log \frac{2.375}{1.695} = \boxed{3.89}$$

$$10.0 \text{ mL } H^+ \left| \frac{0.100 \text{ mmol } H^+}{1 \text{ mL}} \right| = 1 \text{ mmol} \quad A^- + H^+ \rightarrow HA$$

$$2.375 \text{ mmol } A^- - 1 \text{ mmol} = 1.375 \text{ mmol } A^-$$

$$1.695 \text{ mmol } HA + 1 \text{ mmol} = 2.695 \text{ mmol } HA$$

$$pH = 3.744 + \log \frac{1.375}{2.695} = \boxed{3.45}$$