

Your Name: Key

## Chemistry 31 – Quantitative Analysis Final Exam, May 16, 2012

### Multiple Choice

Circle the one correct answer from the choices listed.

1 (4 points). Emission of radiation from a molecule usually occurs at \_\_\_\_\_ absorption of radiation by the same molecule.

- a. shorter wavelengths than  
 b. longer wavelengths than  
c. the same wavelengths as  
d. emission and absorption cannot be compared

2 (4 points). What is the major reason for using the method of standard addition when calibrating an instrument's response?

- a. sample loss  
 b. sample matrix interferences  
c. variable injection volumes  
d. all of these

3 (4 points). More random errors lead to an increase in the \_\_\_\_\_ of a measurement.

- a. precision  
b. repeatability  
c. accuracy  
 d. standard deviation

4 (4 points). What is the percent relative uncertainty in the following calculation? Values in parentheses are absolute uncertainties.

$$\frac{4.6(\pm 0.5) + 1.8(\pm 0.8)}{4.3(\pm 0.5)}$$

- a. 47%  
b. 70%  
 c. 19%  
d. none of these

5 (4 points). With regards to absorption spectroscopy, molar absorptivity ( $\epsilon$ ) is **not** dependent on:

- a. wavelength.  
 b. concentration.  
c. substance.  
d. none of these.

6 (4 points). To separate  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^-$  using ion chromatography, you should use a column that contains:

- a. anion sites.  
 b. cation sites.  
c. a non-polar stationary phase.  
d. none of these.

7 (4 points). What is the ratio of  $[A^-] / [HA]$  for a buffer solution of HA with a pH of 3 if  $pK_a = 5$  for HA?

a. 10

b. 100

c. 0.1

d. 0.01

8 (4 points). The pH of a  $10^{-5}M$  solution of the strong base NaOH is

a. 3.

b. 9.

c. 5.

d. 7.

9 (4 points). What is the dominant form of citric acid (a triprotic acid) at a pH of 6.00 ( $pK_{a1} = 3.128$ ,  $pK_{a2} = 4.761$ ,  $pK_{a3} = 6.396$ )?

a.  $H_2A^-$  and  $HA^{2-}$  are equal

b.  $H_2A^-$

c.  $HA^{2-}$

d.  $A^{3-}$

### 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**. A correct answer without work shown will not receive credit, and cannot receive partial credit. Circle or draw a box around your final answer.

### Equations that may, or may not, be useful:

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

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

$$[H^+] = \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}$$

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

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

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

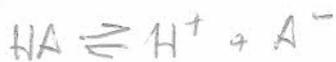


$$[\text{Tl}^+] \gamma_{\text{Tl}^+} [\text{Cl}^-] \gamma_{\text{Cl}^-} = 1.8 \times 10^{-4}$$

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

$$x = \boxed{1.78 \times 10^{-2} \text{ M}}$$

- 11 (12 points). Calculate the pH of a solution of  $7.50 \times 10^{-3}\text{M}$  of the weak acid 2,4-dinitrophenol ( $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{OH}$ ) with a  $\text{pK}_a$  of 4.11.



$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = 7.76 \times 10^{-5}$$

$$\frac{x^2}{7.50 \times 10^{-3} - x} = 7.76 \times 10^{-5}$$

should not ignore  $x$

$$x = 7.25 \times 10^{-4} = [\text{H}^+]$$

$$\boxed{\text{pH} = 3.14}$$

$$x^2 + 7.76 \times 10^{-5} x - 5.82 \times 10^{-7} = 0$$

- 12 (12 points). Calculate the equivalence point (mL) and the pH at the equivalence point in the titration of 20.0 mL of a  $1.20 \times 10^{-2} \text{ M}$  solution of  $\text{CH}_3\text{CO}_2\text{H}$  by  $9.50 \times 10^{-3} \text{ M}$  KOH. For  $\text{CH}_3\text{CO}_2\text{H}$   $\text{pK}_a = 4.757$ .



$$20.0 \text{ mL HA} \left| \frac{1.20 \times 10^{-2} \text{ mol HA}}{1 \text{ mL HA}} \right| \left| \frac{1 \text{ mL OH}^-}{9.50 \times 10^{-3} \text{ mol OH}^-} \right| = 25.3 \text{ mL}$$

at equiv. pt solution of  $\text{A}^-$  ~~at~~  $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$

$$K_b = \frac{10^{-14}}{10^{-4.757}}$$

$$x = 1.74 \times 10^{-6} = [\text{OH}^-]$$

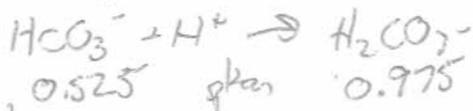
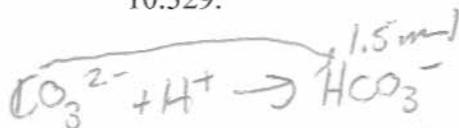
$$\frac{20.0 \text{ mL} \left| \frac{1.20 \times 10^{-2} \text{ mol}}{1 \text{ mL}} \right|}{20 + 25.3 \text{ mL}} = \frac{0.24}{45.3} = 5.30 \times 10^{-3}$$

$$\frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = 5.71 \times 10^{-10}$$

$$\frac{x^2}{5.30 \times 10^{-3}} = 5.71 \times 10^{-10}$$

$$\text{pH} = \frac{-\log(1.74 \times 10^{-6})}{1} = 5.76$$

- 13 (15 points). 15.00 mL of 0.100 M  $\text{Na}_2\text{CO}_3$  is added to 33.00 mL of 0.0750 M HCl. What is the pH of the resulting mixed solution? For  $\text{H}_2\text{CO}_3$ ,  $\text{pK}_{a1} = 6.352$  and  $\text{pK}_{a2} = 10.329$ .



$$15.00 \text{ mL} \left| \frac{0.100 \text{ mol}}{1 \text{ mL}} \right| = 1.5 \text{ mol CO}_3^{2-}$$

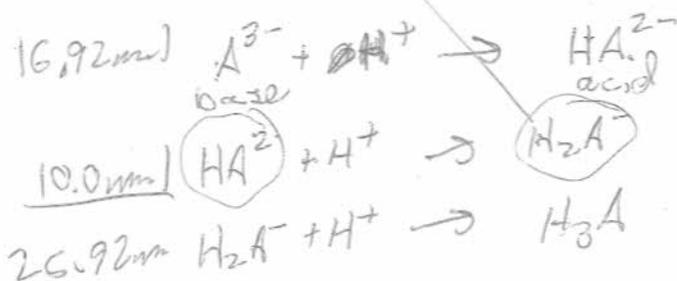
$$33.00 \text{ mL} \left| \frac{0.0750 \text{ mol}}{1 \text{ mL}} \right| = 2.475 \text{ mol H}^+$$

$$- 1.5$$

$$0.975 \text{ left over}$$

$$\text{pH} = 6.352 + \log \frac{0.525}{0.975} = 6.08$$

14 (15 points). Calculate the mass (g) of pure  $\text{Na}_3\text{AsO}_4(s)$  and volume (mL) of 1.50M HCl that are required to make 100.0mL of a buffer solution at a pH of 6.80 and an  $\text{H}_2\text{AsO}_4^-(aq)$  concentration of 0.100M. The MW of  $\text{Na}_3\text{AsO}_4$  is 207.862g/mol and for  $\text{H}_3\text{AsO}_4$ ,  $\text{pK}_{a1} = 2.24$ ,  $\text{pK}_{a2} = 6.96$ , and  $\text{pK}_{a3} = 11.50$ .



$$\begin{array}{l}
 100 \text{ mL} \left| \frac{1 \text{ L}}{1000 \text{ mL}} \right| \left| \frac{0.1692 \text{ mol}}{1 \text{ L}} \right| \left| \frac{207.862 \text{ g}}{1 \text{ mol}} \right| \\
 \boxed{3.52 \text{ g}}
 \end{array}$$

$$\frac{100 \text{ mL}}{1 \text{ mL}} \times 0.100$$

$$26.92 \text{ mL } \text{H}^+ \left| \frac{1 \text{ mL}}{1.5 \text{ mL}} \right| = \boxed{17.9 \text{ mL}}$$

$$\begin{array}{l}
 6.80 \\
 \text{pH} = 6.96 + \log \frac{[\text{HA}^{2-}]}{0.100} \\
 -0.16 = \log \frac{[\text{HA}^{2-}]}{0.100}
 \end{array}$$

$$\begin{array}{l}
 0.692 = \frac{[\text{HA}^{2-}]}{0.100} \\
 [\text{HA}^{2-}] = 6.92 \times 10^{-2} \\
 + \frac{0.100}{0.1692 \text{ M}}
 \end{array}$$

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