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 (ε) is **not** dependent on:

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

6 (**4 points**). To separate Cl^-, NO_3^-, and 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:

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

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

$$[H^+] = \sqrt{\frac{K_1K_2F + K_1K_w}{K_1 + F}}$$

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

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

10 (**10 points**). Accounting for ion activities, what is the solubility (moles/L) of TlCl in water with and 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}.

$$TlCl_{(s)} \rightleftharpoons Tl^+ + Cl^-$$

$$[Tl^+]\gamma_{Tl^+}[Cl^-]\gamma_{Cl^-} = 1.8\times10^{-4}$$

$$(x)\,0.750\,(x)\,0.755 = 1.8\times10^{-4}$$

$$x = \boxed{1.78\times10^{-2}\,M}$$

11 (**12 points**). Calculate the pH of a solution of 7.50×10^{-3}M of the weak acid 2,4-dinitrophenol ($C_6H_3(NO_2)_2OH$) with a pK_a of 4.11.

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

$$\frac{[H^+][A^-]}{[HA]} = 7.76\times10^{-5}$$

$$\frac{x^2}{7.50\times10^{-3} - x} = 7.76\times10^{-5}$$

should not ignore x

$$x^2 + 7.76\times10^{-5}x - 5.82\times10^{-7} = 0$$

$$x = 7.25\times10^{-4} = [H^+]$$

$$\boxed{pH = 3.14}$$

12 **(12 points).** Calculate the equivalence point (mL) and the pH at the equivalence point in the titration of 20.0mL of a 1.20×10^{-2}M solution of CH_3CO_2H by 9.50×10^{-3} M KOH. For CH_3CO_2H $pK_a = 4.757$.

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

$20.0\,mL\,HA \left| \frac{1.20\times10^{-2}\,mmol\,HA}{1\,mL\,HA} \right| \left| \frac{1\,mmol\,OH^-}{1\,mmol\,HA} \right| \left| \frac{1\,mL\,OH^-}{9.50\times10^{-3}\,mmol\,OH^-} \right| = 25.3\,mL$

at equiv. pt solution of A^- $\quad A^- + H_2O \rightleftharpoons HA + OH^-$

$20.0\,mL \left| \frac{1.20\times10^{-2}\,mmol}{1\,mL} \right| = \frac{0.24}{20+25.3\,mL} = 5.30\times10^{-3}$

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

$\frac{[HA][OH^-]}{[A^-]} = 5.71\times10^{-10}$

$\frac{x^2}{5.30\times10^{-3}} = 5.71\times10^{-10}$

$x = 1.74\times10^{-6} = [OH^-]$

$pH = 14 - \log\left(\frac{1\times10^{-14}}{1.74\times10^{-6}}\right) = 8.24$

13 **(15 points).** 15.00mL of 0.100M Na_2CO_3 is added to 33.00mL of 0.0750M HCl. What is the pH of the resulting mixed solution? For H_2CO_3, $pK_{a1} = 6.352$ and $pK_{a2} = 10.329$.

$CO_3^{2-} + H^+ \rightarrow HCO_3^-$ (1.5 mmol)

$HCO_3^- + H^+ \rightarrow H_2CO_3$

0.525 $\quad pK_{a1}$ $\quad$ 0.975

$15.00\,mL \left| \frac{0.100\,mmol}{1\,mL} \right| = 1.5\,mmol\,CO_3^{2-}$

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

$-\,1.5$

0.975 left over

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

14 **(15 points)**. Calculate the mass (g) of pure $Na_3AsO_{4(s)}$ 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 $H_2AsO_4^-{}_{(aq)}$ concentration of 0.100M. The MW of Na_3AsO_4 is 207.862g/mol and for H_3AsO_4, $pK_{a1} = 2.24$, $pK_{a2} = 6.96$, and $pK_{a3} = 11.50$.

16.92mL $A^{3-} + H^+ \rightarrow HA^{2-}$ (base → acid)

10.0mL $HA^{2-} + H^+ \rightarrow H_2A^-$

26.92mL $H_2A^- + H^+ \rightarrow H_3A$

$$6.80 = 6.96 + \log \frac{[HA^{2-}]}{0.100}$$

$$-0.16 = \log \frac{[HA^{2-}]}{0.100}$$

$$0.692 = \frac{[HA^{2-}]}{0.100}$$

$$[HA^{2-}] = 6.92 \times 10^{-2} + 0.100 = 0.1692M$$

$$100mL \left| \frac{1L}{1000mL} \right| \frac{0.1692mol}{1L} \left| \frac{207.862g}{1mol} \right| = 3.52g$$

$$100mL \left| \frac{0.100}{1mL} \right|$$

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

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