Your Name: Key

Chemistry 31 – Quantitative Analysis Final Exam, May 18, 2011

Multiple Choice

Circle the one correct answer from the choices listed.

1 (**3 points**). What term refers to the ability to distinguish two peaks from one another in a chromatogram?

a. partition coefficient
b. diffusion
c. capacity factor
d. resolution

2 (**3 points**). What is the major reason for using an internal standard in chromatography?

a. poor peak separation
b. sample matrix interferences
c. injection volume is imprecise
d. all of these

3 (**2 points**). (True or False) Doubling the number of repeated measurements will decrease the value of confidence intervals by a factor of two.

a. True
c. False

4 (**3 points**). What is the absolute uncertainty in the following calculation?

$$\left(\frac{4.3(\pm 2.5)}{4.6(\pm 0.5)\times 1.6(\pm 0.8)}\right)$$

a. 2.7
b. 0.5
c. 0.8
d. 4.6

5 (**3 points**). When using Beer's law for spectroscopy, the molar absorptivity (ε) multiplied by the pathlength (b) represents the ___________ of the calibration curve.

a. slope
b. x-intercept
c. y- intercept
d. none of these

6 (**3 points**). The best analytical technique to use for the separation of compounds with high boiling points is:

a. GC
b. acid/base titration
c. HPLC
d. it doesn't matter

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

a. 10
b. 100
c. 0.1
d. 0.01

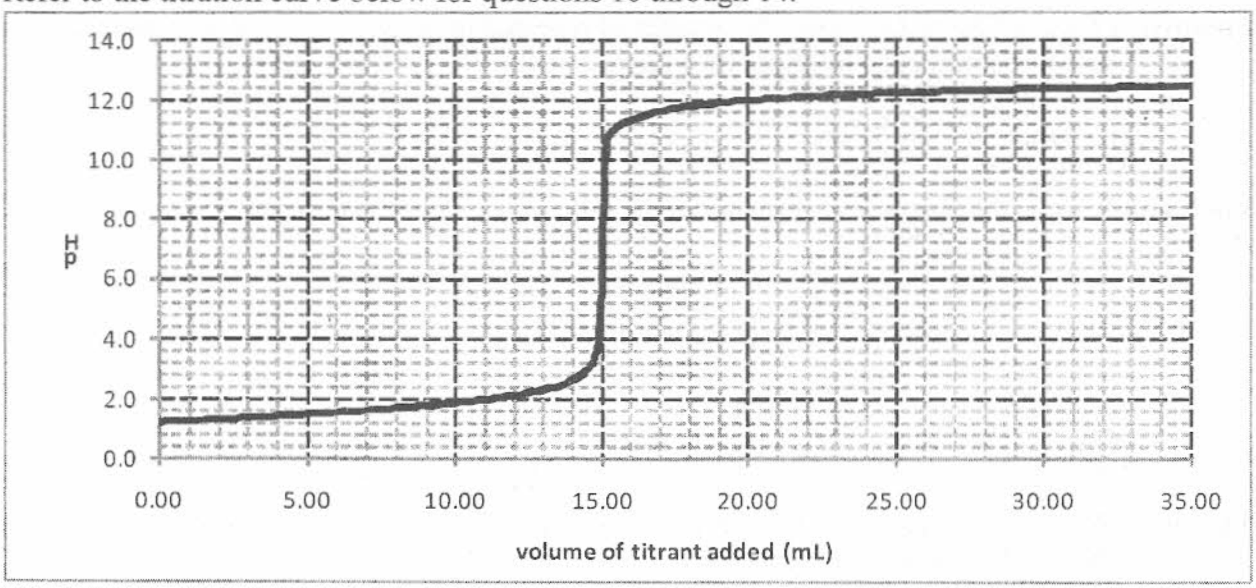
8 (2 points). The pH of a 10^{-15} M solution of the strong acid HBr is

a. 15
b. -1.0
c. 5.0
d. 7.0

9 (3 points). What is the dominant form of aspartic acid (a triprotic acid) at a pH of 1.50 (pK_{a1} = 1.990, pK_{a2} = 3.900, pK_{a3} = 10.002)?

a. H_3A and H_2A^- are equal
b. H_3A
c. H_2A^-
d. HA^{2-}

Refer to the titration curve below for questions 10 through 14.



10 (3 points). The titration curve shown above describes the:

a. titration of a strong base.
b. titration of a weak acid.
c. titration of a strong acid.
d. titration of a weak base.

11 (3 points). The equivalence point occurs at:

a. 7.50 mL titrant added.
b. 30.0 mL titrant added.
c. 15.0 mL titrant added.
d. 22.5 mL titrant added.

12 **(3 points)**. The titrant is a

a. strong acid.
b. strong base.
c. weak acid.
d. weak base.

13 **(3 points)**. What is the molarity of H^+ in solution when 0.00 mL of titrant have been added?

a. 1.2 M
b. 1.6×10^{-13} M
c. 1.0×10^{-7} M
d. 6.3×10^{-2} M

14 **(3 points)**. When more than 15.00 mL of titrant have been added in the titration curve above, the pH can be determined by assuming there is:

a. a weak base in solution.
b. a buffer with HA and A^-.
c. excess strong acid added to solution.
d. excess strong base added to solution.

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:

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

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

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

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

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

basic form

15 **(6 points)**. The fumarate ion ($CH_2(CO_2)^{2-}$) is an intermediate in the citric acid cycle. What is the equilibrium pH of a 0.0750 M solution of sodium fumarate? The pKa_1 and pKa_2 for fumaric acid are 3.02 and 4.48 respectively.

$A^{2-} + H_2O \rightleftharpoons HA^- + OH^-$

$K_{b_1} = \frac{10^{-14}}{10^{-4.48}} = 3.02 \times 10^{-10}$

$\frac{[OH^-][HA^-]}{[A^{2-}]} = 3.02 \times 10^{-10}$

	$[A^{2-}]$	$[OH^-]$	$[HA^-]$
I	0.0750	0	0
C	−x	+x	+x
E	0.0750−x	x	x

$\frac{x^2}{0.0750 - x} = 3.02 \times 10^{-10}$ (ignore)

$x = 4.76 \times 10^{-6}\ M = [OH^-]$

$pH = -\log\left(\frac{10^{-14}}{4.76 \times 10^{-6}}\right)$

pH = 8.7

16 **(12 points)**. Starting with 50.0mL of a 4.80×10^{-2}M solution of the diprotic base CO_3^{2-}, what volume of 1.20×10^{-1}M HBr must be added to reach a pH of 10.00? For H_2CO_3, $pK_{a1} = 6.351$ and $pK_{a2} = 10.329$.

$10.00 = 10.329 + \log \frac{CO_3^{2-}}{HCO_3^-}$

$50.00\,mL \left| \frac{4.80 \times 10^{-2}\,mmol}{1\,mL} \right| = 2.4\,mmol$ total

$A^{2-} + H^+ \rightarrow HA^-$
$(CO_3^{2-}) \quad\quad (HCO_3^-)$

$\frac{CO_3^{2-}}{HCO_3^-} = 0.469$

$CO_3^{2-} + HCO_3^- = 2.4\,mmol$

$0.469(HCO_3^-) + HCO_3^- = 2.4\,mmol$

$HCO_3^- = 1.63\,mmol$ = mmol H^+ necessary

$CO_3^{2-} = 0.77\,mmol$

$1.63\,mmol\ H^+ \left| \frac{mL}{1.20 \times 10^{-1}\,mmol} \right| =$ **13.6 mL**

17 **(12 points)**. Accounting for ionic strength, what is the pH of a 0.0200M solution of NaOH that also contains 0.0800M $NaNO_3$? See the table below for activity coefficients. **Circle the appropriate activity coefficient on the table below and report your answer to 3 significant figures.**

$\mu = 0.0800M + 0.0200M = 0.100M$

$[OH^-] = 0.0200$

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

$pH = -\log\left(\frac{10^{-4}}{(0.0200)(0.76)}\right)$

$= 12.2$

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.

18 **(12 points)**. What is the solubility (M) of $SrSO_4$ in a solution that already contains 0.0600 M SO_4^{2-}? The K_{sp} for $SrSO_4$ is 3.2 x 10^{-7}.

$SrSO_{4(s)} \rightleftharpoons Sr^{2+} + SO_4^{2-}$

$[SO_4^{2-}][Sr^{2+}] = 3.2 \times 10^{-7}$

	$[Sr^{2+}]$	$[SO_4^{2-}]$
I	-	0.0600
C	+x	+x
E	x	0.0600+x

$(0.0600 + x)(x) = 3.2 \times 10^{-7}$ (ignore x)

$(0.0600)(x) = 3.2 \times 10^{-7}$

$x = 5.33 \times 10^{-6} M$

19 **(12 points).** Citric acid is a triprotic acid commonly used to make buffer solutions in the lab. Its pKa values are 3.13, 4.76, and 6.40, and its molecular weight is 192.12 g/mol. What mass (g) of citric acid and what volume (mL) of 1.00 M NaOH is needed to produce 100.0 mL of a buffer with a pH of 6.5 and a weak base concentration of 0.100 M?

equilibrium

$H_3A \rightleftharpoons H_2A^- + H^+$ 3.13

$H_2A^- \rightleftharpoons HA^{2-} + H^+$ 4.76

$HA^{2-} \rightleftharpoons A^{3-} + H^+$ 6.40

weak acid, base

titration

$H_3A + OH^- \rightarrow H_2A^- + H_2O$

17.94 + $H_2A^- + OH^- \rightarrow HA^{2-} + H_2O$

17.94 + $HA^{2-} + OH^- \rightarrow A^{3-} + H_2O$

\+ 10.0 = 45.9 mmol of strong base

$\frac{45.9\ mmol}{} \Big| \frac{1\ mL}{1\ mmol} = 45.9\ mL$

$6.5 = 6.40 + \log \frac{0.100\,M \leftarrow A^{3-}}{[HA^{2-}]}$

$[HA^{2-}] = 0.0794\,M$

$\frac{100.0\ mL}{} \Big| \frac{0.100\ mmol}{1\ mL} = 10.0\ mmol\ A^{3-}$

$\frac{100.0\ mL}{} \Big| \frac{0.0794\ mmol}{1\ mL} = 7.94\ mmol\ HA^{2-}$

$\frac{17.94\ mmol}{} \Big| \frac{mol}{10^3\ mmol} \Big| \frac{192.12\ g}{1\ mol} = 3.45\ g$

20 **(6 points).** If 25.0 mL of 0.075 M HCl was added to the 100.0 mL of buffer produced through problem 19, what is the resulting pH of the solution?

$\frac{25.0\ mL}{} \Big| \frac{0.075\ mmol}{1\ mL} = 1.875\ mmol\ H^+$

$A^{3-} + H^+ \rightarrow HA^{2-}$

$pH = 6.4 + \log \frac{10.0\ mmol - 1.875\ mmol}{7.94\ mmol + 1.875\ mmol}$

$= 6.31$

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