

Your Name: Key

Chemistry 31 – Quantitative Analysis Final Exam, December ~~20~~<sup>8</sup>, 2007

Multiple Choice

Circle the one correct answer from the choices listed.

- 1 (3 points). When using standard addition as a calibration method, the identity of the standard is:
- a. different than the analyte/unknown.
  - ☒ b. the same as the analyte/unknown.
  - c. not known.
  - d. none of the above.
- 2 (3 points). In chromatography, how is it possible that two analytes can have different retention times, but still not be separated?
- a. differential partitioning
  - b. small capacity factors
  - ☒ c. analyte diffusion on the column
  - d. small peak areas
- 3 (2 points). Beer's law states that:
- a. a straight line can describe the relationship between points on a graph.
  - ☒ b. absorbance is proportional to concentration.
  - c. transmittance is proportional to concentration.
  - d. molar absorptivity is proportional to concentration.
- 4 (3 points). Report the answer to the following with the correct number of significant figures (given uncertainties are absolute):
- $11.7 \pm \sqrt{0.9^2 + 0.7^2}$   
1.1
- $25.6 (\pm 0.9) - 13.9 (\pm 0.7)$
- a.  $11.7 \pm 0.7$
  - b.  $11.70 \pm 0.06$
  - ☒ c.  $12 \pm 1$
  - d.  $11.7 \pm 1.1$
- 5 (3 points). Can a molecule that has absorbed infrared radiation subsequently emit a photon with a wavelength in the ultraviolet region as a result?
- a. yes
  - ☒ b. no
  - c. molecules cannot absorb infrared radiation
  - d. more information is necessary
- 6 (3 points). Relative to reverse phase HPLC, normal phase HPLC utilizes a stationary phase that is:
- ☒ a. polar.
  - b. non-polar.
  - c. volatile.
  - d. need more information.

7 (3 points). What is the ratio of  $[A^-] / [HA]$  for a buffer solution of HA with a pH of 9 if the  $pK_a = 7$  for HA?

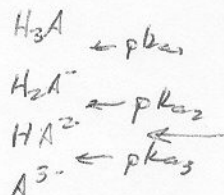
- a. 10  
☒ b. 100  
 c. 0.1  
 d. 0.01

8 (2 points). When choosing a color indicator for an acid base titration, the  $pK_a$  of the indicator should match:

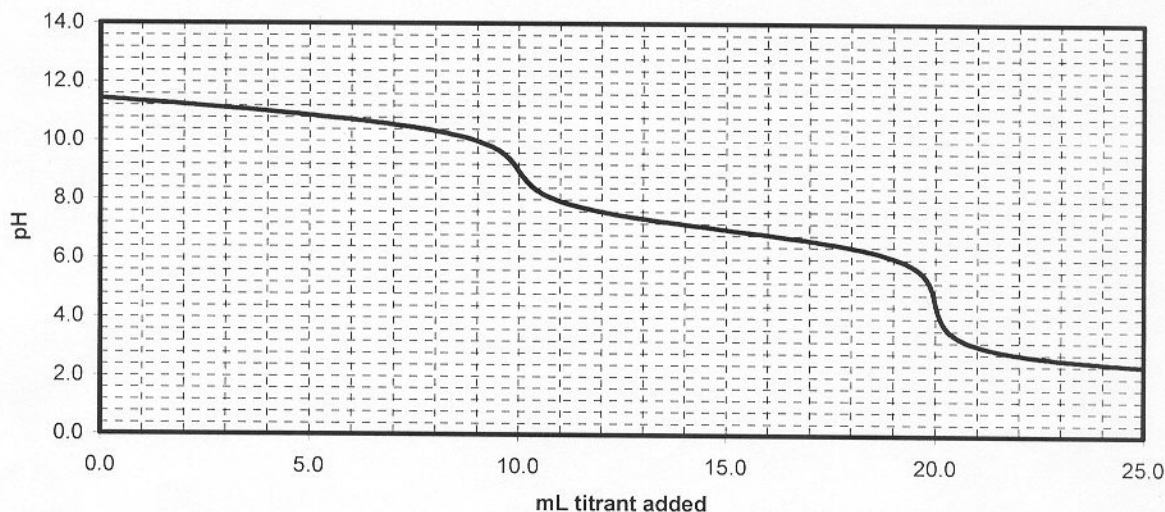
- a. the  $pK_b$  of the analyte.  
 b. the pH half way to the equivalence point.  
 c. the  $pK_a$  of the analyte.  
☒ d. the pH at the equivalence point.

9 (3 points). What is the dominant form of aspartic acid (a triprotic acid) at a pH of 5.00 ( $pK_{a1} = 1.990$ ,  $pK_{a2} = 3.900$ ,  $pK_{a3} = 10.002$ )?

- a.  $HA^{2-}$  and  $H_2A^-$  are equal  
☒ b.  $HA^{2-}$   
 c.  $H_2A^-$   
 d.  $A^{3-}$  and  $HA^{2-}$  are equal



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 diprotic acid.  
☒ b. titration of a diprotic base.  
 c. titration of a monoprotic base.  
 d. titration of a monoprotic acid.

11 (3 points). If the titration began with 100.0mL of solution (before titrant is added) and the titrant is 0.100M strong acid or base, what is the concentration of analyte in the original solution?

- a. 1.00M  
 b. 0.100M  
☒ c. 0.0100M  
 d. 0.00100M

$$\frac{10 \text{ mL} (0.1 \text{ M})}{1 \text{ mL}} = \frac{1 \text{ mmol}}{100 \text{ mL}} = 0.01 \text{ M}$$

12 (3 points). What is  $pK_{a1}$  for the conjugate acid of the base being titrated in the figure?

- ☒ a. 7.0  
b. 11.0

- c. 4.4  
d. 8.8

13 (3 points). At the first equivalence point in the titration curve above, the pH can be determined by assuming there is:

- a. a weak base in solution.  
b. a weak acid in solution.

- c. a buffer with  $HA^-$  and  $A^{2-}$ .  
☒ d. a solution of the intermediate form  $HA^-$ .

14 (3 points). When more than 20mL 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  $A^{2-}$ .

- ☒ 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:**

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

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

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

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

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



15 (6 points). What is the pH of a 0.163M solution of benzoic acid. The  $pK_a$  of benzoic acid is 4.202.



$$\frac{[H^+][A^-]}{[HA]} = 10^{-4.202} = 6.28 \times 10^{-5}$$

	HA	$A^-$	$H^+$
I	0.163	0	0
C	-x	+x	+x
E	0.163-x	x	x

$$\frac{x^2}{0.163-x} = 6.28 \times 10^{-5}$$

less than 2%  
ignore x

$$x = 3.199 \times 10^{-3} = [H^+]$$

$$pH = 2.49$$

16 (6 points). Accounting for ionic strength, what is the pH of a 0.0100M solution of NaOH that also contains 0.0900M  $NaNO_3$ ? See the table below for activity coefficients (must show the correct work to receive credit).

$$\mu = 0.05 + 0.05 = 0.1M$$

$$[H^+]_{\text{eff}} [OH^-]_{\text{eff}} = 10^{-14}$$

$$[OH^-] = 0.0100M$$

$$f_{OH^-} = 0.76$$

$$pH = -\log([H^+]_{\text{eff}}) = -\log\left(\frac{10^{-14}}{[OH^-]_{\text{eff}}}\right) = -\log\left(\frac{10^{-14}}{(0.0100)(0.76)}\right) = 11.9$$

Table 8-1 Activity coefficients for aqueous solutions at 25°C

Ion	Ion size ( $\alpha$ , pm)	Ionic strength ( $\mu$ , M)				
		0.001	0.005	0.01	0.05	0.1
Charge = $\pm 1$						
H <sup>+</sup>	900	0.967	0.933	0.914	0.86	0.83
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCO <sub>2</sub> <sup>-</sup> , (C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> N <sup>+</sup>	800	0.966	0.931	0.912	0.85	0.82
(O <sub>2</sub> N) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> O <sup>-</sup> , (C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> NH <sup>+</sup> , CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> <sup>-</sup>	700	0.965	0.930	0.909	0.845	0.81
Li <sup>+</sup> , C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> <sup>-</sup> , HOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> <sup>-</sup> , ClC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> <sup>-</sup> , C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> , CH <sub>2</sub> =CHCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> , (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> , (CH <sub>3</sub> CH <sub>2</sub> ) <sub>4</sub> N <sup>+</sup> , (C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	600	0.965	0.929	0.907	0.835	0.80
Cl <sub>2</sub> CHCO <sub>2</sub> <sup>-</sup> , Cl <sub>3</sub> CCO <sub>2</sub> <sup>-</sup> , (CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> NH <sup>+</sup> , (C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> NH <sub>2</sub> <sup>+</sup>	500	0.964	0.928	0.904	0.83	0.79
Na <sup>+</sup> , CdCl <sup>+</sup> , ClO <sub>2</sub> <sup>-</sup> , IO <sub>3</sub> <sup>-</sup> , HCO <sub>3</sub> <sup>-</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , HSO <sub>3</sub> <sup>-</sup> , H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> , Co(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub> <sup>+</sup> , CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup> , ClCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup> , (CH <sub>3</sub> ) <sub>4</sub> N <sup>+</sup> , (CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub> <sup>+</sup> , H <sub>2</sub> NCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	450	0.964	0.928	0.902	0.82	0.775
H <sub>2</sub> NCH <sub>2</sub> CO <sub>2</sub> H, (CH <sub>3</sub> ) <sub>3</sub> NH <sup>+</sup> , CH <sub>3</sub> CH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	400	0.964	0.927	0.901	0.815	0.77
OH <sup>-</sup> , F <sup>-</sup> , SCN <sup>-</sup> , OCN <sup>-</sup> , HS <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> , BrO <sub>3</sub> <sup>-</sup> , IO <sub>4</sub> <sup>-</sup> , MnO <sub>4</sub> <sup>-</sup> , HCO <sub>3</sub> <sup>-</sup> , H <sub>2</sub> citrate <sup>-</sup> , CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup> , (CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	350	0.964	0.926	0.900	0.81	0.76
K <sup>+</sup> , Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup> , CN <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup>	300	0.964	0.925	0.899	0.805	0.755
Rb <sup>+</sup> , Cs <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Tl <sup>+</sup> , Ag <sup>+</sup>	250	0.964	0.924	0.898	0.80	0.75

a. Lanthanides are elements 57-71 in the periodic table.

- 17 (12 points). Starting with 100.0 mL of a  $3.50 \times 10^{-3} \text{ M}$  solution of the diprotic maleic acid ( $\text{H}_2\text{A}$ ), what volume of  $1.20 \times 10^{-1} \text{ M}$  KOH must be added to reach a pH of 6.27? For maleic acid,  $\text{pK}_{\text{a}1} = 1.92$  and  $\text{pK}_{\text{a}2} = 6.27$ .

$$\text{pH} = 6.27 = \text{pK}_{\text{a}2} \quad \left[ \overset{\text{A}^{2-}}{\text{base}} \right] = \left[ \overset{\text{HA}^-}{\text{acid}} \right]$$

$$100.0 \text{ mL} \left| \frac{3.50 \times 10^{-3} \text{ mmol}}{1 \text{ mL}} \right| = 0.35 \text{ mmol } \text{H}_2\text{A}$$

↓ convert all  $\text{H}_2\text{A}$  to  $\text{HA}^-$  - need 0.35 mmol  $\text{OH}^-$

$$\text{HA}^-$$

↓ convert  $\frac{0.35}{2}$  mmol of  $\text{HA}^-$  to  $\text{A}^{2-}$  - need 0.175 mmol  $\text{OH}^-$

need 0.525 mmol  $\text{OH}^-$

$$0.525 \text{ mmol } \text{OH}^- \left| \frac{1 \text{ mL}}{0.120 \text{ mmol}} \right| = \boxed{4.38 \text{ mL}}$$

- 18 (12 points). Starting with 40.0 mL of a solution that contains 0.480 M  $\text{I}^-$ , what is the concentration of  $\text{I}^-$  in solution after 20.0 mL of 0.672 M  $\text{Pb}(\text{NO}_3)_2$  is added? The  $K_{\text{sp}}$  for  $\text{PbI}_2(\text{s})$  is  $7.9 \times 10^{-9}$ .  $\text{Pb}(\text{NO}_3)_2$  is completely soluble.

$$40.0 \text{ mL } \text{I}^- \left| \frac{0.480 \text{ mmol } \text{I}^-}{1 \text{ mL}} \right| = 19.2 \text{ mmol } \text{I}^- \quad \left| \frac{1 \text{ mmol } \text{Pb}^{2+}}{2 \text{ mmol } \text{I}^-} \right| = 9.60 \text{ mmol } \text{Pb}^{2+} \text{ needed to precipitate all } \text{I}^-$$

$$20 \text{ mL } \text{Pb}^{2+} \left| \frac{0.672 \text{ mmol } \text{Pb}^{2+}}{1 \text{ mL}} \right| = 13.44 \text{ mmol } \text{Pb}^{2+}$$

$$\text{PbI}_{2(\text{s})} \rightleftharpoons \text{Pb}^{2+} + 2\text{I}^-$$

	$\text{Pb}^{2+}$	$\text{I}^-$
I	0.064	0
C	+x	+2x
E	0.064+x	2x

$$= \frac{9.60}{60 \text{ mL}} = 0.16 \text{ M } \text{Pb}^{2+}$$

$$= \frac{3.84 \text{ mmol excess } \text{Pb}^{2+}}{60 \text{ mL}} = 0.064 \text{ M } \text{Pb}^{2+}$$

$$\text{PbI}_{2(\text{s})} \rightleftharpoons \text{Pb}^{2+} + 2\text{I}^-$$

ignore x

$$[\text{Pb}^{2+}][\text{I}^-]^2 = 7.9 \times 10^{-9}$$

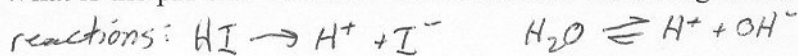
$$(0.064 + x)(2x)^2 = 7.9 \times 10^{-9}$$

$$(0.064)(4x^2) = 7.9 \times 10^{-9}$$

$$x = 1.76 \times 10^{-4}$$

$$[\text{I}^-] = 2x = \boxed{3.52 \times 10^{-4} \text{ M}}$$

19 (12 points). What is the pH of a  $7.900 \times 10^{-8} \text{ M}$  solution of the strong acid HI?



charge:

$$[\text{H}^+] = [\text{OH}^-] + [\text{I}^-]$$

mass:

$$[\text{I}^-] = 7.900 \times 10^{-8}$$

substitute:

$$[\text{H}^+][\text{H}^+] - 7.900 \times 10^{-8} = 10^{-14}$$

$$[\text{H}^+]^2 - 7.900 \times 10^{-8} [\text{H}^+] - 10^{-14} = 0$$

eqn:

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

$$\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\frac{+ 7.900 \times 10^{-8} \pm \sqrt{(7.900 \times 10^{-8})^2 + (4)(1)(10^{-14})}}{2}$$

$$\frac{7.900 \times 10^{-8} \pm 2.15 \times 10^{-7}}{2} = 1.47 \times 10^{-7} = [\text{H}^+]$$

$$\boxed{\text{pH} = 6.83}$$

20 (12 points). The acidic form of the common TRIS buffer (TRIS hydrochloride) has a molecular weight of 157.60g/mole, and a  $\text{pK}_a$  of 8.07. What mass (g) of TRIS hydrochloride and what volume (mL) of 0.100M strong base is necessary to produce 100mL of buffer at pH 7.04 and with a weak base concentration of 0.0050M?

$$7.04 = 8.07 + \log \frac{0.0050}{[\text{HA}]}$$

$$[\text{HA}] = 0.0536 \text{ M}$$

$$[\text{A}^-] = 0.0050 \text{ M}$$

$$\text{total} = 0.0586 \text{ M} (100 \text{ mL}) = 5.86 \text{ mmol} \left| \frac{157.60 \text{ g}}{1 \text{ mmol}} \right| = \boxed{0.923 \text{ g}}$$

$$100 \text{ mL} \left| \frac{0.0050 \text{ mmol A}^-}{1 \text{ mL}} \right| = 0.50 \text{ mmol A}^- \left| \frac{1 \text{ mmol OH}^-}{1 \text{ mmol A}^-} \right| \left| \frac{\text{mL}}{0.100 \text{ mmol}} \right| = \boxed{5.0 \text{ mL strong base}}$$

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