## CHEMISTRY 31 FINAL EXAM May 15, 2017 - 150 points total

NAME \_\_\_\_\_

Lab Sect.

Debye-Hückel Equation:

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

Where:  $\gamma$  = activity coefficient,  $\mu$  = ionic strength,  $\alpha$  = hydrated ion radius, and z = ion charge

Quadratic Equation: for  $ax^2 + bx + c = 0$ ,  $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ Constants:  $K_w$  (autoprotolysis of H<sub>2</sub>O) = 1.0 x 10<sup>-14</sup> h = Planck's constant = 6.63 x 10<sup>-34</sup> J·s c = speed of light in a vacuum = 3.00 x 10<sup>8</sup> m/s

**A. Multiple Choice and Short answer Section.** Circle the letter corresponding to the best answer (only one) or fill in the blank (4 points for each question).

1.	The number	0.030020	has how	many sigr	ificant figures?
a)	2	b) 4		c) 5	d) 6

2. A test sample is analyzed for testosterone using a new method. The measured value is 38.11 ± 0.02 mg/L (±standard deviation) vs. a true value of 27.1 mg/L. It is desired to have % errors under 5% and % relative standard deviations under 2%. Thus, the measurement is:
a) precise but not accurate
b) precise and accurate
c) accurate but not precise
d) neither precise nor accurate

3. An instrument is expected to give a linear calibration. When a set of standards have been analyzed (responses measured), a linear least squares analysis is performed. What quantities are determined by the least squares analysis that define the calibration line? Quantities: \_\_\_\_\_\_ and \_\_\_\_\_\_. (Give names or equation symbols)

4. Which of the following combination produces a "traditional" buffer? a)  $0.0100 \text{ M NH}_4\text{Cl} + 0.0050 \text{ M HCl}$  b)  $0.0100 \text{ M NH}_4\text{Cl} + 0.0050 \text{ M NaOH}$ c)  $0.0100 \text{ M NaCH}_3\text{CO}_2 + 0.0070 \text{ M NaOH}$  d)  $0.0100 \text{ M NaCH}_3\text{CO}_2 + 0.0200 \text{ M HCl}$ NH<sub>3</sub> is a weak base and CH<sub>3</sub>CO<sub>2</sub>H is a weak acid

5. In a precipitation titration,  $Ba^{2+}$  is added out of a buret to a flask containing  $SO_4^{2-}$  forming solid BaSO<sub>4</sub>. The concentration of initial ions and volume of  $SO_4^{2-}$  solution is known. In order to determine [Ba<sup>2+</sup>] at a point before the equivalence point where the volume of Ba<sup>2+</sup> added is measured, you want to first calculate:

a) the initial  $[Ba^{2+}]$  in the buret

c) the mass of solid BaSO<sub>4</sub> in the flask

b) the excess  $[Ba^{2+}]$  in the flask d) the excess  $[SO_4^{2-}]$  in the flask

6.	Which	of the	followin	g salts	is	acidic?	
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a)  $Mg(OH)_2$  b)  $CrCl_3$  c) KClO d)  $NaNO_2$ K<sub>a</sub> values for related weak acids: HClO (K<sub>a</sub> = 3.0 x 10<sup>-8</sup>); HNO<sub>2</sub> (K<sub>a</sub> = 7.1 x 10<sup>-4</sup>)

7. Infrared radiation is typically given in wavenumbers. A wavenumber of  $1830 \text{ cm}^{-1}$  corresponds to a wavelength of: a) 1830 nm b)  $1.83 \times 10^{10} \text{ nm}$  c)  $5.46 \times 10^7 \text{ nm}$  d) 5460 nm

8. A separation is occurring in normal phase liquid chromatography with a 85% hexane 15% 2-propanol (more polar solvent) and is taking too long. What is normally done to decrease the retention time of an analyte:

a) Increase the column temperature	b) Increase the % hexane
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c) Increase the % 2-propanol

d) Use a longer column

9. In chromatography, the sample is introduced into the chromatograph using the:

a) injector b) mobile phase reservoir c) fraction collector d) detector

10. Lead iodide, PbI<sub>2</sub>, is a sparingly soluble salt. Following dissolution through a secondary reaction, Pb<sup>2+</sup> can react with OH<sup>-</sup> to form PbOH<sup>+</sup> in significant quantities. HI is a strong acid, and ignore any other Pb complexes. This secondary reaction results in:
a) increased solubility and a basic solution
b) decreased solubility and a basic solution
c) increased solubility and a neutral solution
d) increased solubility and an acidic solution

11. A strong base is prepared from NaOH in which prepared concentration is known. The equilibrium concentration of  $OH^-$ ,  $[OH^-] = [NaOH]_0$  (initial prepared concentration) is valid in all cases **except when**:

a) $[Na^+] < [H^+]$	b) [OH <sup>-</sup> ] from water is negligible
c) $[Na^+] = [OH^-]$	d) activity is considered

12. A student is solving a problem to determine the pH of a 2.0 x 10<sup>-6</sup> M NH<sub>4</sub>Cl solution and correctly using the ICE method determines that the pH is 7.47. This result indicates:
a) the ICE method is NOT valid because a strongly basic solution is expected
b) the ICE method is NOT valid because a strongly acidic solution is expected
c) the ICE method is valid because a weakly basic solution is expected
d) the ICE method is NOT valid because a weakly basic solution is expected

13. Given are the following 4 compounds shown in their most basic (basic pH) form. All of these compounds exist in an acidic, an intermediate, and a basic form. Which of these compounds forms a plus 2 cation in the most acidic form? a)  $CO_3^{2^-}$  b)  $NH_2CH_2CO_2^{-}$  c)  $NH_2CH_2NH_2$  d)  $NH_2C_6H_4O^{-}$ 

14. It is desired to use the amino acid phenylalanine,  ${}^{+}NH_{3}CHRCO_{2}{}^{-}$ , where  $R = -CH_{2}C_{6}H_{5}$ , to make a pH = 8.80 buffer. Phenylalanine has  $pK_{a1} = 2.20$  and  $pK_{a2} = 9.31$ . What can be added to make the buffer?

a) HCl b) NaOH c)  $^{+}NH_{3}CHRCO_{2}HCl^{-}$  d) none of the above

15. Cysteine,  ${}^{+}NH_{3}CHRCO_{2}^{-}$ , where R = -CH<sub>2</sub>SH, has two acidic functional groups and one base functional group. How many forms can it be present in (if the pH is varied from 1 to 13)? a) 1 b) 2 c) 3 d) 4

**Problem Section.** Show all needed calculations to receive full credit. The number of points are shown in parentheses. Use the back side of the page if needed. Activity only needs to be considered for the parts of problem 2 where it is mentioned and the systematic method only needs to be used for problem 3.

1. A tap water sample is analyzed for Mg by atomic absorption spectroscopy. Using calibration standards between 0.2 and 1.0 ppm, a student finds the equation for the calibration line as: A = 0.431C - 0.011 where A = absorbance and C = concentration (in ppm). The tap water is prepared by transferring 5.00 mL of tap water to a 100.0 mL volumetric flask and diluting to the line.

a) If the diluted tap water sample is found to give an absorbance of 0.107, calculate the concentration of Mg in the diluted tap water. (6 pts)

b) What was the concentration of Mg in the original tap water sample (in ppm)? (6 pts)

Bonus 1) Was the diluted tap water in the best range for determining its concentration? If not suggest a better dilution ratio (2 pts)

2. What is the pH of a 2.0 x  $10^{-3}$  M NH<sub>2</sub>OH solution? NH<sub>2</sub>OH is a weak base with a conjugate acid K<sub>a</sub> = 1.10 x  $10^{-6}$  (activity can be ignored) (10 pts)

3. A standard of MTBE (methyl tertiary butyl ether) in gasoline, was analyzed 4 times to test a method. The measured values were: 0.81 wt %, 0.68 wt %, 0.73 wt %, and 0.79 %.a) Using the table below, give the 95% confidence value about the mean using the correct number of significant figures. (8 pts)

Degrees of freedom	3	4	5
t-value (at 95% level)	3.18	2.776	2.571

b) If the true percent of MTBE in the gasoline standard is known, what specific type of statistical test should be used to check for systematic errors? (3 pts)

4. Calcium fluoride is a sparingly soluble salt that dissociates in water as:

 $CaF_2(s) \leftrightarrow Ca^{2+} + 2F$ . The K<sub>sp</sub> for this reaction is 3.9 x 10<sup>-11</sup>. Assume F<sup>-</sup> and Ca<sup>2+</sup> do NOT significantly react with water or form an ion pair. Determine the solubility of calcium fluoride in 0.050 M KNO<sub>3</sub> if the activity coefficients,  $\gamma(Ca^{2+})$  and  $\gamma(F^-)$ , are 0.485 and 0.81, respectively, in the KNO<sub>3</sub> solution. Assume the only effect of the KNO<sub>3</sub> solution is through an ionic strength change. (12 pts)

5. The following chromatogram and table shows the separation of 2-propanol from 2, 5dimethylfuran. The separation was by gas chromatography with a 2 m x 2 mm packed at 95°C.



Compound	Retention time (min)	Peak Area	Peak width* (min)
solvent (unretained)	0.99	63,102	NA
2-propanol	2.31	5,771	0.198
2, 5-dimethylfuran	5.92	10,039	0.481

\* baseline width

a) Calculate the retention factor of 2-propanol. (5 pts)

b) Calculate the column plate number (N). (5 pts)

c) Which quantity from the table should be used for quantifying the concentration of 2, 5dimethylfuran (assuming you also have data from standards). (4 pts)

bonus #2) What is non-optimal about the separation? and what change could improve it? (2 pts)

6. A solution is prepared in which 0.0020 moles of FeCl<sub>3</sub> is dissolved completely in water making a 1.000 L solution. The Fe<sup>3+</sup> ion is known to form the following complexes (and assume no other complexes form): FeOH<sup>2+</sup> and Fe(OH)<sub>2</sub><sup>+</sup>. (15 pts)

a) Write out all of the relevant reactions needed if one is solving this problem using the systematic method

- b) Give a charge balance equation.
- c) Give two mass balance equations based on the listed reactions and the initial concentration of the dissolved ionic compound.

7. Phthalic acid,  $HO_2CC_6H_4CO_2H$ , is an acid readily available in its intermediate form as KHP (postassium hydrogen phthalate or K<sup>+</sup>HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub><sup>-</sup>). If phthalic acid's pK<sub>a1</sub> and pK<sub>a2</sub> are 2.95 and 5.41, respectively, calculate the mass of NaOH (FW = 40.00 g/mol) should be added to 500.0 mL of 0.0080 M KHP to get a pH = 6.00 buffer solution. (activity can be ignored) (10 pts)

8. Hydrogen cyanide gas can be generated when the  $CN^{-}$  ion is placed in an acidic solution because HCN is a weak acid (pK = 9.21). Calculate the fraction of  $CN^{-}$  that is in the HCN form in a pH = 7.00 buffer solution. (activity can be ignored) (6 pts)