## CHEMISTRY 31 FINAL EXAM

Dec. 12, 2016-150 points total
NAME $\qquad$
Equations:
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 $\mathrm{ax}^{2}+\mathrm{bx}+\mathrm{c}=0, \quad x=\frac{-b \pm \sqrt{b^{2}-4 a c}}{2 a}$
Constants:
$\mathrm{K}_{\mathrm{w}}\left(\right.$ autoprotolysis of $\left.\mathrm{H}_{2} \mathrm{O}\right)=1.0 \times 10^{-14} \quad \mathrm{~h}=$ Planck's constant $=6.63 \times 10^{-34} \mathrm{~J} \cdot \mathrm{~s}$
$\mathrm{c}=$ speed of light in a vacuum $=3.00 \times 10^{8} \mathrm{~m} / \mathrm{s}$
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 Mg standard used in the AA lab was $0.996 \%$ by mass. The concentration of Mg in ppm is:
Mg (atomic weight $=24.3 \mathrm{~g} \mathrm{~mol}^{-1}$ and density of solution $=1.04 \mathrm{~g} \mathrm{~mL}^{-1}$ )
a) 9.96
b) 9960
c) 415
d) 426
2. A researcher has invented a cheaper method to measure glucose in blood. She is interested in comparing the precision of her method compared to a standard method. She measures one blood sample 6 times by her method and the standard method to compare the standard deviations from the two methods. Which test is best to use to compare precision?
a) case 1 t-test
b) case 2 t-test
c) F-test
d) Grubb’s test
3. A student is analyzing a tap water sample for Mg by atomic absorption spectroscopy and has the following table of standards data:

| Conc. (ppm) | 0.20 | 0.40 | 0.70 | 1.0 |
| :--- | :---: | :---: | :---: | :---: |
| Absorbance | 0.131 | 0.255 | 0.498 | 0.641 |

She prepared 3 dilutions of her tap water (see below). Which dilution is the best to use?

| Tap Dilution ratio | $1: 4$ | $1: 20$ | $1: 50$ |
| :--- | :---: | :---: | :---: |
| Absorbance | 1.321 | 0.330 | 0.130 |

a) any value could be used with equal precision
c) the $1: 20$ dilution is best
b) the $1: 4$ dilution is best
d) the $1: 50$ dilution is best
4. Given that for $\mathrm{Hg}^{2+}+2 \mathrm{CH}_{3} \mathrm{CO}_{2}^{-} \leftrightarrow \mathrm{Hg}_{\left(\mathrm{CH}_{3} \mathrm{CO}_{2}\right)_{2}(\mathrm{aq}), \mathrm{K}=2.8 \times 10^{8} \text { and for } \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}(\mathrm{aq}) ~}^{\text {a }}$ $\leftrightarrow \mathrm{H}^{+}+\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}, \mathrm{K}=1.8 \times 10^{-5}, \mathrm{~K}$ for $\mathrm{Hg}^{2+}+2 \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}(\mathrm{aq}) \leftrightarrow \mathrm{Hg}_{\left(\mathrm{CH}_{3} \mathrm{CO}_{2}\right)}{ }_{2}(\mathrm{aq})+2 \mathrm{H}^{+}$, is:
a) $9.1 \times 10^{-2}$
b) $1.0 \times 10^{4}$
c) $2.8 \times 10^{8}$
d) $8.6 \times 10^{17}$
5. The following salts are dissolved in water. Predict which results in an acidic solution.
a) NaBr
b) $\mathrm{K}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$
c) $\mathrm{Fe}\left(\mathrm{NO}_{3}\right)_{3}$
d) $\mathrm{Ca}(\mathrm{OH})_{2}$

HBr and $\mathrm{HNO}_{3}$ are strong acids, and $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$ is a weak acid.
6. In gas chromatography, what is normally done to decrease the retention factor of an analyte:
a) Increase the column temperature
b) Use a longer column
c) Use a more polar column
d) Use a larger diameter column
7. The concentration of $\mathrm{Ag}^{+}$in an unknown solution can be determined through a precipitation titration with $\mathrm{Cl}^{-}$, $\mathrm{Br}^{-}$, or $\mathrm{I}^{-}$. Given the $\mathrm{K}_{\text {sp }}$ values, which titration gives the sharpest equivalence point?

| Salt | AgCl | AgBr | AgI |
| :--- | :--- | :--- | :--- |
| $\mathrm{K}_{\text {sp }}$ | $1.8 \times 10^{-10}$ | $5.0 \times 10^{-13}$ | $8.3 \times 10^{-17}$ |

a) $K_{\text {sp }}$ doesn't affect titration sharpness
b) $\mathrm{Cl}^{-}$titration
c) $\mathrm{Br}^{-}$titration
d) $I^{-}$titration
8. The purpose of a monochromator is to:
a) detect light transmitted through the sample in a spectrometer
b) select a single ion in an ion chromatograph
c) to detect gases leaving a gas chromatograph
d) to select a single wavelength of light in a spectrometer
9. How would the aqueous equilibrium reaction, $\mathrm{Mg}^{2+}+\mathrm{HIn}^{2-} \Leftrightarrow \mathrm{MgIn}^{-}+\mathrm{H}^{+}$shift following the addition of some NaCl , assuming the main change is the ionic strength? (In = indicator)
a) toward reactants
b) toward products
c) no change from addition of NaCl
10. In step 5 of the systematic method, everything checks out if:
a) the number of unknown species is greater than the number of equations
b) the number of unknown species is equal to or less than the number of equations
c) there are no redundant equations
d) the number of unknown species is equal to the number of equilibrium equations
11. Which of the following equal volume mixtures will make a traditional buffer solution:
a) $0.010 \mathrm{M} \mathrm{HCl}+0.010 \mathrm{M} \mathrm{NaOH}$
b) $0.010 \mathrm{M} \mathrm{HCl}+0.0050 \mathrm{M} \mathrm{NH}_{4} \mathrm{Cl}$
c) $0.030 \mathrm{M} \mathrm{HCl}+0.008 \mathrm{M} \mathrm{NaCH}_{3} \mathrm{CO}_{2}$
d) $0.0080 \mathrm{M} \mathrm{HCl}+0.0180 \mathrm{M} \mathrm{NH}_{3}$
( $\mathrm{NH}_{4}{ }^{+}$and $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$ are weak acids)
12. $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$ is a weak diprotic acid with $\mathrm{K}_{\mathrm{a} 1} \gg \mathrm{~K}_{\mathrm{a} 2} .0 .020$ moles of $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$ is dissolved in water to prepare 1.00 L of solution. To determine which of the following concentrations must the second $\mathrm{K}_{\mathrm{a}}$ reaction be considered (as opposed to just the first reaction)?
a) $\left[\mathrm{H}^{+}\right]$
b) $\left[\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}\right]$
c) $\left[\mathrm{HC}_{2} \mathrm{O}_{4}^{-}\right]$
d) $\left[\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}\right]$
13. Which of the following affects the sharpness of a strong acid - strong base titration?
a) the type of strong acid used
b) the type of strong base used
c) the concentration of the acid and base
d) the indicator chosen for the titration
14. In which of the following salts, is a diprotic acid being given in its most acidic form?
a) $\mathrm{NaHSO}_{3}$
b) $\mathrm{NaNH}_{2} \mathrm{CH}_{2} \mathrm{CO}_{2}$
c) $\mathrm{NH}_{3} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{HCl}$
d) $\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{3} \mathrm{Cl}$
$\mathrm{H}_{2} \mathrm{SO}_{3}$ is a weak acid, $\mathrm{NH}_{3} \mathrm{CH}_{2} \mathrm{CO}_{2}$ is a zwitterion at $\mathrm{pH}=7$, and $\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}$ has two base functional groups.
15. Citric acid is a triprotic acid (e.g. $\mathrm{H}_{3} \mathrm{~A}$ ) with $\mathrm{pK}_{\mathrm{a}}$ values given in the table below. Which two species should be present to make a buffer at a pH of 6.2 ?

| $\mathrm{pK}_{\mathrm{a} 1}$ | $\mathrm{pK}_{\mathrm{a} 2}$ | $\mathrm{pK}_{\mathrm{a} 3}$ |
| :---: | :---: | :---: |
| 3.13 | 4.76 | 6.40 |

a) $\mathrm{H}_{3} \mathrm{~A}+\mathrm{H}_{2} \mathrm{~A}^{-}$
b) $\mathrm{H}_{2} \mathrm{~A}^{-}+\mathrm{HA}^{2-}$
c) $\mathrm{HA}^{2-}+\mathrm{A}^{3-}$
d) $\mathrm{H}_{3} \mathrm{~A}+\mathrm{HA}^{2-}$

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 student performed the water hardness titration four times on a tap water sample, and got the following results ( ppm CaCO 3 equivalent calculated each time):

| Trial 1 | Trial 2 | Trial 3 | Trial 4 |
| :--- | :--- | :--- | :--- |
| 533 | 541 | 525 | 538 |

Calculate the 95\% confidence interval for her values using the table below for student t values. Be sure to express your answer with the correct number of significant figures. (8 pts)

| Degrees of freedom | 3 | 4 | 5 |
| :--- | :--- | :--- | :--- |
| t-value (at 95\% level) | 3.182 | 2.776 | 2.571 |

2. The $\mathrm{K}_{\mathrm{sp}}$ for $\mathrm{Mg}(\mathrm{OH})_{2}$ is $7.1 \times 10^{-12}$.
a) Without considering activity and ignoring any post-dissolution reactions (e.g. those that would require the use of the systematic method), determine the solubility of $\mathrm{Mg}(\mathrm{OH})_{2}$ in 5.0 x $10^{-3} \mathrm{M} \mathrm{NaOH}$. (7 pts)
b) Calculate the ionic strength of the saturated $\mathrm{Mg}(\mathrm{OH})_{2}$ in $5.0 \times 10^{-3} \mathrm{M} \mathrm{NaOH}$ solution described in a). (4 pts)
c) From the ionic strength in b), determine the activity coefficients for $\mathrm{Mg}^{2+}$ and $\mathrm{OH}^{-}$given that $\alpha\left(\mathrm{Mg}^{2+}\right)=800 \mathrm{pm}$ and $\alpha\left(\mathrm{OH}^{-}\right)=350 \mathrm{pm}$. (If you couldn't determine the ionic strength assume it is 0.010 M$)(8 \mathrm{pts})$
d) Using the activity coefficients in c), recalculate the solubility of $\mathrm{Mg}(\mathrm{OH})_{2}$, now accounting for activity. (You do not need to recalculate the ionic strength though. If you couldn't solve c) assume $\left.\gamma\left(\mathrm{Mg}^{2+}\right)=\gamma\left(\mathrm{OH}^{-}\right)=0.8\right)$. ( 6 pts )

BONUS - 2pts) Give the pH of the solution (using the true definition and to 4 sig figs).
3. A solution is prepared that is $0.0050 \mathrm{M} \mathrm{CdCl}_{2}$. Assuming $\mathrm{Cd}^{2+}$ can react to form the complexes $\mathrm{CdCl}^{+}$and $\mathrm{CdOH}^{+}$but no other complexes, complete the following steps in determining the concentrations of all species using the systematic method. Note that you are only asked to do specific steps. Ignore activity for this problem
a) List all of the relevant reactions for the above problem: (8 pts)
b) Give the charge balance equation for the above problem: (4 pts)
c) Give mass balance equations relating concentrations of species to the initial concentration of $\mathrm{CdCl}_{2}$. (6 pts)
d) Give the equilibrium equations. (3 pts)
4. A solution of 0.050 M NaBrO is made by dissolving NaBrO into 1.00 L of solution. The $\mathrm{K}_{\mathrm{a}}$ of HBrO (the conjugate acid of $\mathrm{BrO}^{-}$) $=2.3 \times 10^{-9}$ and $\mathrm{K}_{\mathrm{w}}=1.0 \times 10^{-14}$. Using the ICE method, determine the pH of the solution to 4 sig figs. ( 9 pts )
5. How many moles of $\mathrm{NaCH}_{3} \mathrm{CO}_{2}$ should be added to 100.0 mL of $0.150 \mathrm{M} \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$ to make a $\mathrm{pH}=5.00$ buffer. $\mathrm{pK}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}\right)=4.76$. ( 8 pts )
6. Aminobenzene is a weak base ( $\mathrm{pK} \mathrm{K}_{\mathrm{a}}$ for conjugate acid is 4.601). It is desired to analyze for it in a complex sample by reversed phase HPLC, which requires the main form of it to be in an uncharged form (not as an ion).
a) A scientist tries to analyze it using a mobile phase of methanol and water buffered with acetic acid/sodium acetate to a pH of 5.20 . Calculate the fraction of aminobenzene in the uncharged form (assuming that aminobenzene does not change the pH and that the fraction in the uncharged form is not affected by methanol). (8 pts)
b) How will an increase in the \% of methanol in the HPLC mobile phase affect retention of aminobenzene? (3 pts)

BONUS 2) In the intial analysis it turns out that aminobenzene elutes at almost the same time as another compound (call it compound X ) in the sample so the resolution is very bad ( $<1$ ). It is known that compound X has no acid or base functional groups. Suggest a change in the eluent that will allow better separation of aminobenzene and compound $X$ and describe the expected effect of the change. (3 pts)
7. A 25.0 mL aliquot of 0.0340 M NaOH is being titrated by 0.0250 M HCl . What is the pH after 30.0 mL of HCl has been added? Give answer to 5 sig figs. ( 8 pts )

