$\qquad$

## Some Useful Constants:

$\mathrm{R}=8.314 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1} 0^{\circ} \mathrm{C}=273 \mathrm{~K}$
$\mathrm{K}_{\mathrm{w}}$ (autoprotolysis constant for $\mathrm{H}_{2} \mathrm{O}$ ) $=1.0 \times 10^{-14}$
$\mathrm{h}=$ Planck's constant $=6.63 \times 10^{-34} \mathrm{~J} \cdot \mathrm{~s} ; \mathrm{c}=$ speed of light $=3.00 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}$
A. Multiple Choice/Fill in the Blank Section. Only one correct answer for multiple choice questions. (4 points for each question)

1. In the reaction: $\mathrm{Al}^{3+}(\mathrm{aq})+3 \mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}(\mathrm{aq}) \rightleftharpoons \mathrm{Al}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}{ }^{3-}(\mathrm{aq}), \mathrm{Al}^{3+}$ is a:
a) Lewis acid but not a Bronsted-Lowry acid
b) both a Lewis and a Bronsted-Lowry acid
c) neither a Lewis acid nor a Bronsted-Lowry acid
d) a Lewis base only
2. Which of the following salts is acidic?
a) $\mathrm{Mg}(\mathrm{OH})_{2}$
b) $\mathrm{CrCl}_{3}$
c) KClO
d) $\mathrm{NaNO}_{2}$
$\mathrm{K}_{\mathrm{a}}$ values for related weak acids: $\mathrm{HClO}\left(\mathrm{K}_{\mathrm{a}}=3.0 \times 10^{-8}\right) ; \mathrm{HNO}_{2}\left(\mathrm{~K}_{\mathrm{a}}=7.1 \times 10^{-4}\right)$
3. The point in a titration in which an indicator changes color (in response to a change in reactant concentration) is called:
a) the end point
b) the equilibrium point
c) the equivocate point
d) the equivalence point
4. A precipitation titration is being performed in which $\mathrm{Ag}^{+}$is added to a solution. Which of the following conditions will lead to a sharper titration in a precipitation titration?
a) a solution containing multiple anions (e.g. $\mathrm{Cl}^{-}, \mathrm{Br}^{-}$, and $\mathrm{I}^{-}$)
b) anions with a larger $\mathrm{K}_{\text {sp }}$ value
c) a solution with higher anion and $\mathrm{Ag}^{+}$concentrations
d) all of the above
5. Ultra-violet light, when absorbed by matter, causes transitions primarily in:
a) molecular rotation states
b) molecular vibration states
c) electrons in valence shell states
d) nuclear states
6. Infrared radiation is typically given in wavenumbers. A wavenumber of $1830 \mathrm{~cm}^{-1}$ corresponds to a wavelength of:
a) 1830 nm
b) $1.83 \times 10^{10} \mathrm{~nm}$
c) $5.46 \times 10^{7} \mathrm{~nm}$
d) 5460 nm
7. In gas chromatography, the analyte that elutes earliest is usually
a) the most volatile
b) has the highest boiling point temperature
c) the most polar
d) the least polar
8. It is desired to "clean up" biodiesel by removing free fatty acids in the biodiesel by extracting the diesel with water. The biodiesel is a fairly non-polar solvent. Typical free fatty acids have high octanol water partition coefficients (i.e. favor dissolution in non-polar solvents) and are weak acids. To aid the transfer to water, one could.
a) buffer the water to a high pH
b) buffer the water to a low pH
c) use a more polar solvent than water
9. List one component of a chromatograph and its purpose: (2 pts each part)

Component $\qquad$ Purpose $\qquad$
10. How would you expect the aqueous equilibrium reaction, $\mathrm{MgCO}_{3}(\mathrm{~s})+\mathrm{H}^{+} \Leftrightarrow \mathrm{Mg}^{2+}+$ $\mathrm{HCO}_{3}{ }^{-}$to shift following the addition of some NaCl , assuming the only change is the ionic strength?
a) toward reactants
b) toward products
c) no change from addition of NaCl
B. 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.

1. The concentration of iron(III) in a solution can be determined by adding $\mathrm{SCN}^{-}$to form the colored metal ligand complex, $\mathrm{FeSCN}^{2+}$. The K value for $\mathrm{Fe}^{3}+\mathrm{SCN}^{-} \leftrightarrow \mathrm{FeSCN}^{2+}$ is 1050. NaSCN is added to an $\mathrm{Fe}^{3+}$ containing sample to create the complex. If after mixing, the concentration of the complex is measured to be $3.1 \times 10^{-4} \mathrm{M}$ (based on absorption of light) and the equilibrium concentration of $\mathrm{SCN}^{-}$is 0.20 M , calculate the concentration of $\mathrm{Fe}^{3+}$ in equilibrium with $\mathrm{SCN}^{-}$and the complex. ( 8 pts )
2. Determine the percent of $\mathrm{CaCO}_{3}$ in a 1.21 g sample that is analyzed using a back titration. In the back titration, $\mathrm{CaCO}_{3}$ reacts with $\mathrm{HCl}(10.0 \mathrm{~mL}$ of 0.500 M$)$ present in excess as follows:

$$
\mathrm{CaCO}_{3}(\mathrm{~s})+2 \mathrm{HCl} \Leftrightarrow \mathrm{CaCl}_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}(\mathrm{~g})
$$

The solution is heated to remove $\mathrm{CO}_{2}(\mathrm{~g})$, and the excess HCl (that which doesn't react with $\mathrm{CaCO}_{3}$ ) requires 23.2 mL of 0.100 M NaOH . The formula weight of $\mathrm{CaCO}_{3}$ is $100.1 \mathrm{~g} / \mathrm{mol}$. (16 pts)
3. The following chromatogram and data table show the separation of linear fatty acids (C18:3, C18:2, C18:1, C16:0, C17:0, and C18:0 - where the first number gives the number of carbons in the fatty acids and number after the colon gives the number of double bonds - all in cis isomer). All of the fatty acids have $\mathrm{pK}_{\mathrm{a}}$ values of around 4.8. The separation was performed on a C18 (reversed phase) column using HPLC with an eluent of 0.001 M trifluoroacetic acid in water ( $\mathrm{pH}=3$ and $8 \%$ by volume) and $92 \%$ acetonitrile. $\mathrm{W}_{\mathrm{b}}$ in table is the baseline width.

a) Calculate the retention factor (k) of C17:0. (4 pts)
b) Based on the elution order, which compound would be considered the least polar? (4 pts)
c) What is the resolution between the two least well resolved peaks. (4 pts)

Bonus) Switching from 92\% acetonitrile to $92 \%$ methanol was found to result in smaller retention times for C18:1, C18:2, and C18:3 without affecting the C16:0, C17:0, or C18:0 retention times. Is this a good change? Explain. (3 pts)
4. A compound is known to have a molar absorbtivity of $731 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ at a wavelength of 382 nm in water (solvent). A cell with path length of 0.200 cm is filled with the compound and the absorbance is measured to be 0.103 . Determine the concentration of the compound. (8 pts)
5. It is desired to determine the solubility of $\mathrm{PbI}_{2}\left(\mathrm{~K}_{\text {sp }}=7.9 \times 10^{-9}\right)$ in a solution containing $0.0120 \mathrm{M} \mathrm{CaI}_{2}$ with the inclusion of activity in the calculation.
a) Determine the ionic strength of the $0.0120 \mathrm{M} \mathrm{CaI}_{2}$ solution. ( 6 pts)
b) Using the following table and the ionic strength from part a), determine the solubility of $\mathrm{PbI}_{2}$ in the $0.0120 \mathrm{M} \mathrm{CaI}_{2}$ solution. ( 10 pts ).

| Ionic Strength | 0.012 M | 0.030 M | 0.036 M | 0.054 M |
| :--- | :---: | :---: | :---: | :---: |
| $\gamma\left(\mathrm{Pb}^{2+}\right)$ | 0.642 | 0.523 | 0.498 | 0.444 |
| $\gamma\left(\mathrm{I}^{-}\right)$ | 0.890 | 0.840 | 0.828 | 0.801 |

Hint: Select the $\gamma$ values using the closest $\mu$ value and assume $\mathrm{PbI}_{2}$ does not provide a significant amount of $\mathrm{I}^{-}$to the solution. No iterations in this calculation are needed.

