CHEMISTRY 31 EXAM 2
April 19, 2017
SOLUTIONS

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: Al^{3+} (aq) + $3C_2O_4^{2-}$(aq) $\rightleftharpoons$ $Al(C_2O_4)_3^{3-}$ (aq), 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) $Mg(OH)_2$ b) $CrCl_3$ c) KClO d) $NaNO_2$
K_a values for related weak acids: HClO ($K_a = 3.0 \times 10^{-8}$); HNO_2 ($K_a = 7.1 \times 10^{-4}$)
[all others are strong or weak bases; Cr^{3+} is acidic because it is a metal outside group I/II]

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 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. Cl^-, Br^-, and I^-)
b) anions with a larger K_{sp} value
c) a solution with higher anion and 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 cm^{-1} corresponds to a wavelength of:
a) 1830 nm b) 1.83×10^{10} nm c) 5.46×10^7 nm d) 5460 nm
$\lambda = (\text{wavenumber})^{-1} = 1/(1830\ cm^{-1}) = (5.46 \times 10^{-4}\ cm)(1\ m/100\ cm)(10^9\ nm/1\ m) =$

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
[high pH means low [H$^+$], which shifts reaction to anion or HA ⇔ H$^+$ + A$^-$ and anion partitions to water phase]

9. List one component of a chromatograph and its purpose: (2 pts each part)
Component _1) mobile phase reservoir, 2) flow control, 3) injector, 4) column, 5) detector, 6) data processor_
Purpose _1) hold mobile phase, 2) control flow, 3) put sample into flow stream, 4) separate compounds, 5) detect analytes, 6) collect, store and process data ______

10. How would you expect the aqueous equilibrium reaction, $MgCO_3(s) + H^+ \Leftrightarrow Mg^{2+} + HCO_3^-$ 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 SCN^- to form the colored metal ligand complex, $FeSCN^{2+}$. The K value for $Fe^3 + SCN^- \leftrightarrow FeSCN^{2+}$ is 1050. NaSCN is added to an Fe^{3+} containing sample to create the complex. If after mixing, the concentration of the complex is measured to be 3.1 x 10^{-4} M (based on absorption of light) and the equilibrium concentration of SCN^- is 0.20 M, calculate the concentration of Fe^{3+} in equilibrium with SCN^- and the complex. (8 pts)

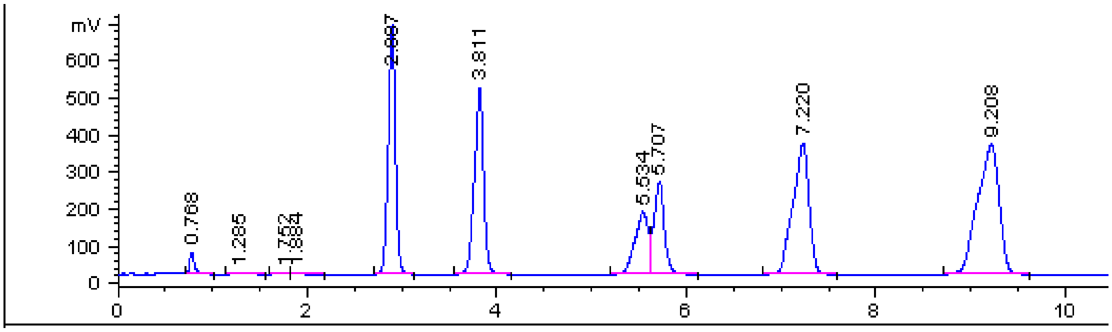
K_f (f for formation of complex) = 1050 = $[FeSCN^{2+}]/[Fe^{3+}][SCN^-]$
= (3.1 x 10^{-4} M)/{$[Fe^{3+}]$(0.20 M)} or $[Fe^{3+}]$ = (3.1 x 10^{-4} M)/[(1050)(0.20)] = ***1.5 x 10^{-6} M***

2. Determine the **percent of $CaCO_3$** in a 1.21 g sample that is analyzed using a back titration. In the back titration, $CaCO_3$ reacts with HCl (10.0 mL of 0.500 M) present in excess as follows:

$$CaCO_3(s) + 2HCl \Leftrightarrow CaCl_2(aq) + H_2O + CO_2(g)$$

The solution is heated to remove CO_2(g), and the excess HCl (that which doesn't react with $CaCO_3$) requires 23.2 mL of 0.100 M NaOH. The formula weight of $CaCO_3$ is 100.1 g/mol. (16 pts)
n_{added}(HCl) = $n_{reacted}$(HCl) + n_{excess}(HCl) or $n_{reacted}$(HCl) = n_{added}(HCl) – n_{excess}(HCl)
and n_{excess}(HCl) = $n_{backtitration}$(NaOH) = (0.0232 L)(0.100 mol/L) = 0.000232 mol
n_{added}(HCl) = (0.0100 L)(0.500 mol/L) = 0.00500 mol
n_{added}(HCl) = 0.00500 mol – 0.000232 mol = 0.00268 mol
From the reaction with $CaCO_3$, $n(CaCO_3)/n_{reacted}$(HCl) = 1/2
$n(CaCO_3)$ = 0.5(0.00268 mol) = 0.00134 mol*
*mass % = (0.00134 mol)(100.1 g/mol)*100/1.21 g sample =* ***11.1%***

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 pK_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 (pH = 3 and 8% by volume) and 92% acetonitrile. W_b in table is the baseline width.



Compound	Retention (min.)	Area	W_b (min.)
Unretained	0.768	NA	NA
C18:3	2.887	3611.5	0.127
C18:2	3.811	3389.3	0.156
C18:1	5.534	1656	0.222
C16:0	5.707	1908.9	0.180
C17:0	7.22	4182.1	0.266
C18:0	9.208	5552.7	0.358

a) Calculate the retention factor (k) of C17:0. (4 pts)

*$k = (t_r - t_m)/t_m = (7.22 - 0.768)/0.768 =$ **8.4** (see values in yellow above)*

b) Based on the elution order, which compound would be considered the least polar? (4 pts)

*Since reversed phase HPLC has a non-polar stationary phase, the least polar compound will elute last (spend the most time in the non-polar stationary phase). That is **C18:0**.*

c) What is the resolution between the two least well resolved peaks. (4 pts)

Peaks with most overlap are the least well resolved (so C18:1 and C16:0). Resolution = $\Delta t/w_{ave}$
*Resolution = (5.707 – 5.534)/[0.5(0.222 + 0.180)] = **0.86***

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)

***This is good.** The biggest problem with the chromatogram shown is poor C18:1/C16:0 resolution. By eluting C18:1 earlier, the separation (α value) will improve.*

4. A compound is known to have a molar absorbtivity of 731 M^{-1} 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)

$A = \varepsilon bC$ or $C = A/\varepsilon b = 0.103/(731\ M^{-1}\ cm^{-1})(0.200\ cm) = \mathbf{7.05 \times 10^{-4}\ M}$

5. It is desired to determine the solubility of PbI_2 ($K_{sp} = 7.9 \times 10^{-9}$) in a solution containing 0.0120 M CaI_2 with the inclusion of activity in the calculation.

a) Determine the ionic strength of the 0.0120 M CaI_2 solution. (6 pts)

concentrations of 0.0120 M CaI_2 solution: $[Ca^{2+}] = 0.0120\ M$; $[I^-] = 2(0.0120\ M)\ 0.0240\ M$

$\mu = 0.5\{[Ca^{2+}](+2)^2 + [I^-](-1)^2\} = 0.5[(0.0120)(4) + 0.0240] = \mathbf{0.0360\ M}$

b) Using the following table and the ionic strength from part a), determine the solubility of PbI_2 in the 0.0120 M CaI_2 solution. (10 pts).

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

Hint: Select the γ values using the closest μ value and assume PbI_2 does not provide a significant amount of I^- to the solution. No iterations in this calculation are needed.

ICE table to solve part b:

	$PbI_2(s) \Leftrightarrow$	$Pb^{2+}(aq)$ +	$2I^-(aq)$
Initial		0	0.024 M
Change		+x	+2x
Equilibrium		x	0.024 + 2x (hint says 0.024 >> 2x)

$K_{sp} = 7.9 \times 10^{-9} = \gamma(Pb^{2+})[Pb^{2+}]\{\gamma(I^-)[I^-]\}^2 = (0.498)x[(0.828)(0.024)]^2$

$x = 7.9 \times 10^{-9}/[(0.498)(0.828)^2(0.024)^2] = \mathbf{3.4 \times 10^{-5}\ M}$ (note: that $2x = 0.00007 << 0.0240$)