Chemistry 222 **Name**____
Fall 2010
Exam 2: Chapters 5,6,7
80 Points

Complete two (2) of problems 1-3, problem 4, and three (3) of problems 5-8. CLEARLY mark the problems you do not want graded. You must show your work to receive credit for problems requiring math. Report your answers with the appropriate number of significant figures.

Do <u>two</u> of problems 1-3. Clearly mark the problem you do not want graded. (10 pts each)

1. A *real* solution at equilibrium will likely contain several equilibrium reactions. The statement "***all equilibrium conditions must be satisfied simultaneously***" is often used in describing these systems. Clearly describe the chemical significance of this statement, especially as it pertains to an ion or molecule that may appear in more than one equilibrium in the same solution.

   There can only be *one* concentration of each species in solution. To reach equilibrium, all equilibria must adjust to this single equilibrium concentration. The concentration of each species must satisfy the equilibrium constant expressions for all equilibria.

2. In determining activity coefficients, there are three primary factors that play a role. Briefly describe the impact of these factors on the activity of an ion.

   Each affect has an impact on the tendency for an ion to interact with other charged species in solution. Your description should illustrate this.

   1. Hydrated diameter (α): The more strongly solvated the ion is (larger α), the less likely it is to interact with other ions in solution (smaller γ).
   2. Ionic charge (z): The larger the charge, the greater the electrostatic interaction with other ions.
   3. Ionic strength (μ): The greater the effective concentration of ions in solution, the more opportunities for the ion of interest to interact with another species.

3. If I prepare a saturated silver chloride ($K_{sp} = 1.8 \times 10^{-10}$) solution by putting 100 g of AgCl in *10 mL* of water and you prepare a saturated silver chloride solution by putting 100 g of AgCl in *100 mL* of water, what is the relative concentration of Ag^+ in your solution compared to mine? Clearly explain your reasoning.

Since both solutions are saturated, the silver ion concentrations are identical.
$[Ag^+] = (K_{sp})^{1/2}$

You <u>MUST</u> do problem 4. (15 points)

4. Consider a solution saturated with lanthanum oxalate. Set up the equations necessary to determine the solubility of lanthanum oxalate, considering the equilibria below. You must write the charge balance expression and at least one mass balance. *Give enough independent equations to solve for the unknowns, a numerical answer is not necessary*.

$$La_2(C_2O_4)_3(s) = 2\,La^{3+} + 3\,C_2O_4^{2-} \qquad K_{sp} = 1.0 \times 10^{-25}$$
$$H_2C_2O_4 = HC_2O_4^- + H^+ \qquad K_{a1} = 5.62 \times 10^{-2}$$
$$HC_2O_4^- = C_2O_4^{2-} + H^+ \qquad K_{a2} = 5.42 \times 10^{-5}$$
$$H_2O = H^+ + OH^- \qquad K_w = 1.0 \times 10^{-14}$$

6 unknowns, need 6 equations

$$La_2(C_2O_4)_3(s) = 2\,La^{3+} + 3\,C_2O_4^{2-} \qquad K_{sp} = [La^{3+}]^2[C_2O_4^{2-}]^3$$
$$H_2C_2O_4 = HC_2O_4^- + H^+ \qquad K_{a1} = [HC_2O_4^-][H^+]/[H_2C_2O_4]$$
$$HC_2O_4^- = C_2O_4^{2-} + H^+ \qquad K_{a2} = [C_2O_4^{2-}][H^+]/[HC_2O_4^-]$$
$$H_2O = H^+ + OH^- \qquad K_w = [H^+][OH^-]$$

Charge Balance:

$$3[La^{3+}] + [H^+] = [OH^-] + [HC_2O_4^-] + 2[C_2O_4^{2-}]$$

Mass Balance:

$$3[La]_{total} = 2[C_2O_4]_{total}$$
$$3[La^{3+}] = 2([H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}])$$

Do three of problems 5-8. Clearly mark the problem you do not want graded. (15 pts each)

5. Clearly describe the case when it is preferable to use internal standards, rather than a traditional calibration curve for an analysis. Include an example of how you would run the experiment and extract an unknown concentration from your data.

Internal standards are useful when variable sample sizes are used or when instrument fluctuations prevent the reliable use of a calibration curve.

First, determine the response factor (F) for the analyte relative to a standard of different identity by running a mixture of known concentration of both the standard and the analyte and determine F below:

$$\frac{R_{unknown}}{[unknown]} = \frac{F(R_{standard})}{[standard]}$$

Second, run an unknown sample spiked with standard at a known concentration and calculate the unknown concentration as below:

$$[unknown] = \frac{R_{unknown}[standard]}{F(R_{standard})}$$

Take care to account for any dilutions that occur during sample prep.

6. Calculate the pH of a solution 25.0 mL of 0.100 M acetic acid with 10.0 mL of 0.0644 M NaOH. The pK_a for acetic acid (a weak monoprotic acid) is 4.76.

To deal with this problem, we first must determine what's left after the strong base NaOH reacts with our acetic acid (HA)

	HA	+	OH^-	⇄	A^-	+	H_2O
Start	2.5 mmol		0.644 mmol		0		--
End	1.856 mmol		0		0.644 mmol		--
Concentrations	1.856mmol/35 mL		0		0.644 mmol/35 mL		--
	= 0.0530_3 M		0		= 0.0184_0 M		

Now solve the equilibrium:

	HA	⇄	H^+	+	A^-
I	0.0530_3 M		0		0.0184_0 M
C	-x		+x		+x
E	0.0530-x		x		0.0184 +x

$$K_a = (x)(0.0184+x)/(0.0530-x)$$
$$0.0530K_a-K_ax = 0.184x + x^2$$
$$0 = x^2+(0.0184+K_ax)- 0.0530K_a$$
$$x = 4.99 \times 10^{-5}M, -1.85x10^{-2}M$$

Since a negative value for x makes no chemical sense, the appropriate solution is:

$x = 4.99 \times 10^{-5}M = [H^+]$, or $pH = -\log[H^+] = 4.30$

Note: Making the assumption that x<<0.0184 M turns out to be reasonable and simplifies the math, while giving the same pH.

7. Is it possible to perform a 99.9 % complete separation of barium and silver by precipitation with chromate if both Ba^{2+} and Ag^+ are present initially at 0.010 M? *Ignore activities.*

$$BaCrO_4 = Ba^{2+} + CrO_4^{2-} \qquad K_{sp} = 2.1 \times 10^{-10}$$
$$Ag_2CrO_4 = 2Ag^+ + CrO_4^{2-} \qquad K_{sp} = 1.2 \times 10^{-12}$$

What $[CrO_4^{2-}]$ is required to reduce each ion to 0.1% of its initial value?
0.1% of 0.010 = 0.00001 M

Ba:
$BaCrO_4 = Ba^{2+} + CrO_4^{2-}$ $\qquad K_{sp} = [Ba^{2+}][CrO_4^{2-}] = 2.1 \times 10^{-10} = (1.0 \times 10^{-5})[CrO_4^{2-}]$
$[CrO_4^{2-}] = 2.1 \times 10^{-5}$ M

Ag:
$Ag_2CrO_4 = 2Ag^+ + CrO_4^{2-}$ $\qquad K_{sp} = [Ag^+]^2[CrO_4^{2-}] = 1.2 \times 10^{-12} = (1.0 \times 10^{-5})^2[CrO_4^{2-}]$
$[CrO_4^{2-}] = 1.2 \times 10^{-2}$ M

So, $BaCrO_4$ will precipitate first. Will Ag_2CrO_4 also precipitate if $[CrO_4^{2-}] = 2.1 \times 10^{-5}$ M?

$Q = [Ag^+]^2[CrO_4^{2-}] = (0.0100\text{ M})^2(2.1 \times 10^{-5}\text{ M}) = 2.1 \times 10^{-9}$

$Q > K_{sp}$ for Ag_2CrO_4**, so a precipitate will form and a 99.9% complete separation is NOT possible.**

8. *Using activities*, show how to calculate the hydroxide concentration in a saturated solution of iron (II) hydroxide in 0.010 F magnesium nitrate. The K_{sp} for $Fe(OH)_2$ is 7.9×10^{-16}, assume that $Mg(NO_3)_2$ dissociates completely. You do not need a numerical solution for $[OH^-]$, just determine the value for the activity coefficients and generate an expression that could be solved for $[OH^-]$.

	$Fe(OH)_2$ =	Fe^{2+}	+	$2OH^-$
I	--	0		0
C	--	+x		+2x
E	--	x		2x

$K_{sp} = A_{Fe2+}(A_{OH-})^2 = \gamma_{Fe2+}[Ca^{2+}](\gamma_{OH-}[OH^-])^2 = \gamma_{Fe2+}x(\gamma_{OH-}2x)^2 = \gamma_{Fe2+}(\gamma_{OH-})^2 4x^3$

Since K_{sp} is so small, little dissolution of $Fe(OH)_2$ will occur, and the ionic strength will be determined by the concentration of $Mg(NO_3)_2$.

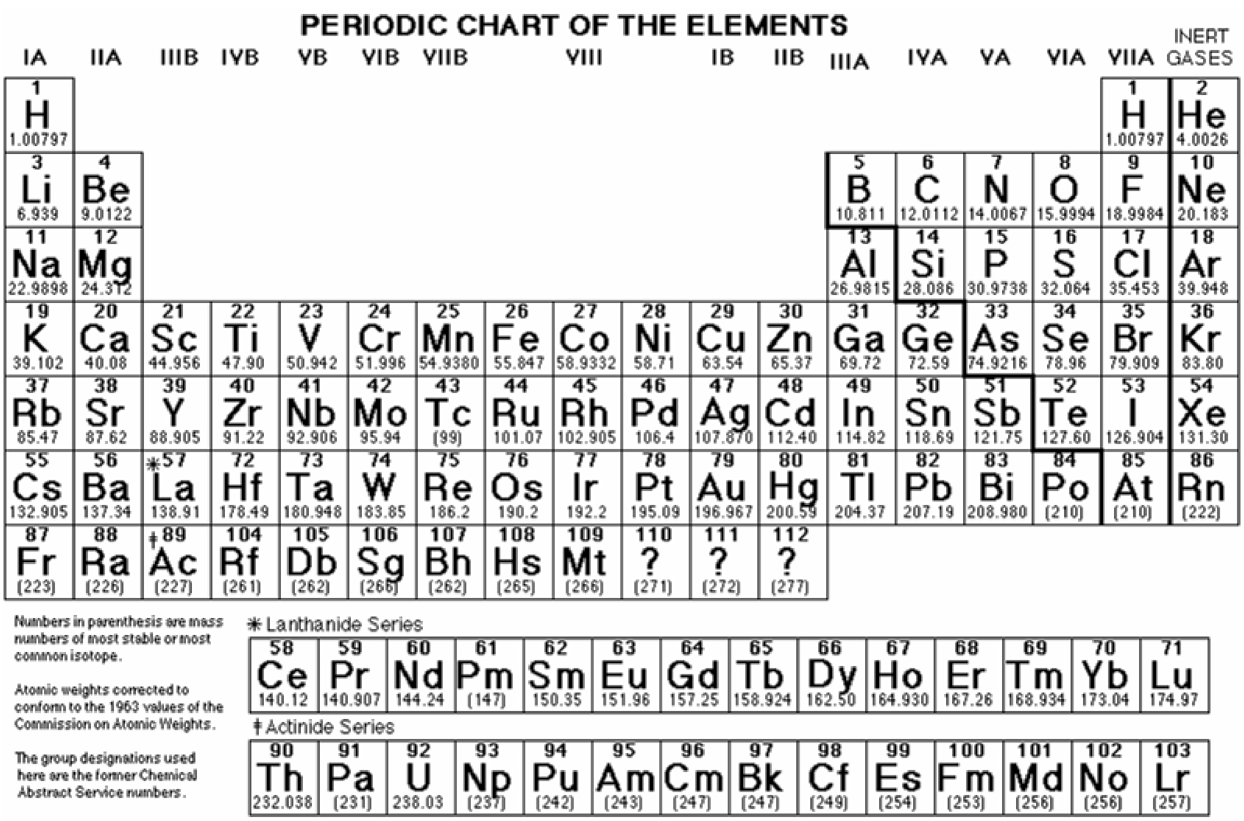
$\mu = 1/2\{[Mg^{2+}](+2)^2 + [NO_3^-](-1)^2\} = 1/2(0.0100M(4) + 0.020\text{ M}(1)) = 0.030\text{ M}$

Using the Debye-Huckel equation at this ionic strength, $\gamma_{Fe2+} = 0.545$, $\gamma_{OH-} = 0.844$.
(Interpolation from the table of activity coefficients gives similar values.)

Therefore, the expression to solve is: $7.9 \times 10^{-16} = (0.545)(0.844)^2 4x^3$

(Given these values, and solving for x, $x = 7.98 \times 10^{-6}$ M, **$[OH^-] = 2x = 1.60 \times 10^{-5}$ M**)

Blank Space if You Need Extra Room



Possibly Useful Information

$K_aK_b = K_W = 1.0 \times 10^{-14}$	$pH = -\log [H^+]$
$\log\gamma = \dfrac{-0.51z^2\sqrt{\mu}}{1+\left(\alpha\sqrt{\mu}/305\right)}$ (with α in pm)	$\mu = \dfrac{1}{2}\sum_i c_i z_i^2$
$\Delta G = \Delta H - T\Delta S = -RT\ln K$	$x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
$\dfrac{I_x}{I_{s+x}} = \dfrac{k[x]_i}{k([s]_f + [x]_f)} = \dfrac{[x]_i}{[s]_f + [x]_f}$	$\dfrac{\text{Analyte Signal}}{\text{Analyte Concentration}} = F\left(\dfrac{\text{Standard Signal}}{\text{Standard Concentration}}\right)$

Activity coefficients for aqueous solutions at 25°C

Ion	Ion size (α, pm)	Ionic strength (μ, M) 0.001	0.005	0.01	0.05	0.1
CHARGE = ±1						
H^+	900	0.967	0.933	0.914	0.86	0.83
$(C_6H_5)_2CHCO_2^-$, $(C_3H_7)_4N^+$	800	0.966	0.931	0.912	0.85	0.82
$(O_2N)_3C_6H_2O^-$, $(C_3H_7)_3NH^+$, $CH_3OC_6H_4CO_2^-$	700	0.965	0.930	0.909	0.845	0.81
Li^+, $C_6H_5CO_2^-$, $HOC_6H_4CO_2^-$, $ClC_6H_4CO_2^-$, $C_6H_5CH_2CO_2^-$, $CH_2{=}CHCH_2CO_2^-$, $(CH_3)_2CHCH_2CO_2^-$, $(CH_3CH_2)_4N^+$, $(C_3H_7)_2NH_2^+$	600	0.965	0.929	0.907	0.835	0.80
$Cl_2CHCO_2^-$, $Cl_3CCO_2^-$, $(CH_3CH_2)_3NH^+$, $(C_3H_7)NH_3^+$	500	0.964	0.928	0.904	0.83	0.79
Na^+, $CdCl^+$, ClO_2^-, IO_3^-, HCO_3^-, $H_2PO_4^-$, HSO_3^-, $H_2AsO_4^-$, $Co(NH_3)_4(NO_2)_2^+$, $CH_3CO_2^-$, $ClCH_2CO_2^-$, $(CH_3)_4N^+$, $(CH_3CH_2)_2NH_2^+$, $H_2NCH_2CO_2^-$	450	0.964	0.928	0.902	0.82	0.775
$^+H_3NCH_2CO_2H$, $(CH_3)_3NH^+$, $CH_3CH_2NH_3^+$	400	0.964	0.927	0.901	0.815	0.77
OH^-, F^-, SCN^-, OCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-, HCO_2^-, $H_2citrate^-$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$	350	0.964	0.926	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	300	0.964	0.925	0.899	0.805	0.755
Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+	250	0.964	0.924	0.898	0.80	0.75
CHARGE = ±2						
Mg^{2+}, Be^{2+}	800	0.872	0.755	0.69	0.52	0.45
$CH_2(CH_2CH_2CO_2^-)_2$, $(CH_2CH_2CH_2CO_2^-)_2$	700	0.872	0.755	0.685	0.50	0.425
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, $C_6H_4(CO_2^-)_2$, $H_2C(CH_2CO_2^-)_2$, $(CH_2CH_2CO_2^-)_2$	600	0.870	0.749	0.675	0.485	0.405
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, $S_2O_4^{2-}$, WO_4^{2-}, $H_2C(CO_2^-)_2$, $(CH_2CO_2^-)_2$, $(CHOHCO_2^-)_2$	500	0.868	0.744	0.67	0.465	0.38
Pb^{2+}, CO_3^{2-}, SO_3^{2-}, MoO_4^{2-}, $Co(NH_3)_5Cl^{2+}$, $Fe(CN)_5NO^{2-}$, $C_2O_4^{2-}$, $Hcitrate^{2-}$	450	0.867	0.742	0.665	0.455	0.37
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_2O_8^{2-}$, SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}	400	0.867	0.740	0.660	0.445	0.355
CHARGE = ±3						
Al^{3+}, Fe^{3+}, Cr^{3+}, Sc^{3+}, Y^{3+}, In^{3+}, lanthanides[a]	900	0.738	0.54	0.445	0.245	0.18
$citrate^{3-}$	500	0.728	0.51	0.405	0.18	0.115
PO_4^{3-}, $Fe(CN)_6^{3-}$, $Cr(NH_3)_6^{3+}$, $Co(NH_3)_6^{3+}$, $Co(NH_3)_5H_2O^{3+}$	400	0.725	0.505	0.395	0.16	0.095
CHARGE = ±4						
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	1 100	0.588	0.35	0.255	0.10	0.065
$Fe(CN)_6^{4-}$	500	0.57	0.31	0.20	0.048	0.021

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

SOURCE: J. Kielland, *J. Am. Chem. Soc.* **1937**, *59*, 1675.