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.

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.

3. If I prepare a saturated silver chloride (K_{sp} = 1.8 x 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.

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*.

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

Do <u>three</u> 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.

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.

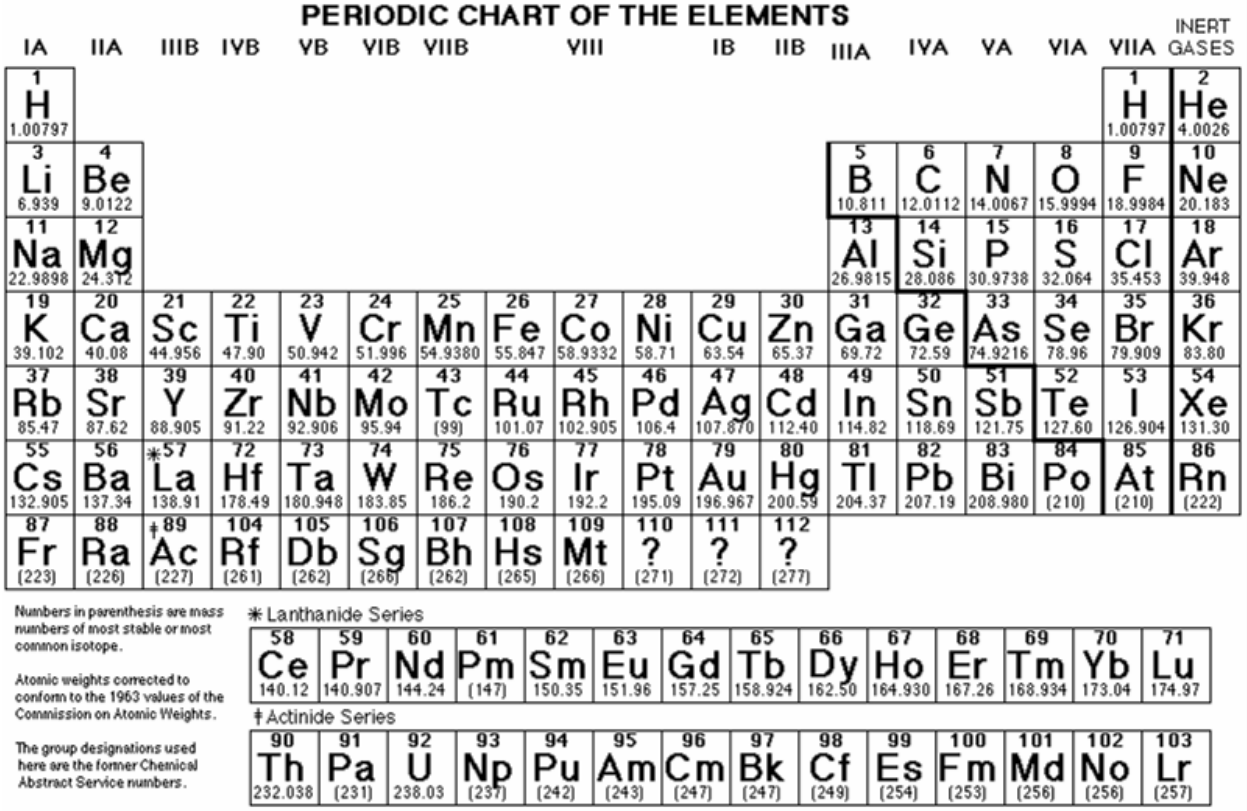
7. Is it possible to perform a 99.9 % complete separation of barium and silver by precipitation with chromate if both Ba^{2+} and Ag^{+} are present initially at 0.010 M? *Ignore activities.*

$BaCrO_4 = Ba^{2+} + CrO_4^{2-}$ $\quad K_{sp} = 2.1 \times 10^{-10}$

$Ag_2CrO_4 = 2Ag^{+} + CrO_4^{2-}$ $\quad K_{sp} = 1.2 \times 10^{-12}$

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 $[OH^-]$.

Blank Space if You Need Extra Room



Possibly Useful Information

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

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.