CHEM 36
General Chemistry
## FINAL EXAM

May 10, 2002

Name:

 INSTRUCTIONS: Read through the entire exam before you begin. Answer all of the questions. For questions involving calculations, show **all** of your work -- **HOW** you arrived at a particular answer is **MORE** important than the answer itself!

If you are working a multipart question that uses your response from a __previous__ question that you did not know how to answer, use a fabricated value for the missing data (and state so explicitly).

PLEASE circle your final answer to all numerical questions.

Page	Possible Points	*Points Earned*
2	25	
3	15	
4	20	
5	20	
6	30	
7	20	
8	30	
9	25	
10	15	
11	20	
12	30	
TOTAL:	*250*	

The entire exam is worth a total of 250 points. Attached are a periodic table and a formula sheet jam-packed with useful stuff. Good Luck!
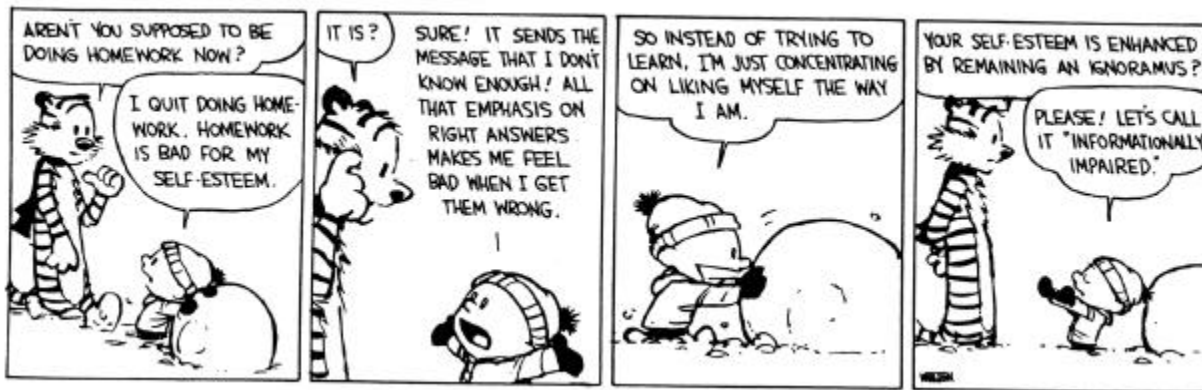
1. Silver can form a precipitate by reaction with chloride (AgCl; K_{sp} = 1.6 x 10^{-10}) and with chromate (Ag_2CrO_4; K_{sp} = 1.9 x 10^{-12}).

   a. *[10 pts]* Suppose we have a solution that is 0.0010 *M* in Cl^- and 0.100 *M* in CrO_4^{2-}. If we add 0.100 *M* $AgNO_3$ solution drop by drop, will AgCl or Ag_2CrO_4 precipitate first? Justify your answer with a calculation.

   b. *[15 pts]* When the *second* precipitate first appears, what fraction of the *first precipitating anion* (identified in your answer in *part a*) remains?

2. A student sets up the following electrochemical cell:

$$Pb|PbSO_4|SO_4^{2-} \text{ (aq, 0.0500 M)}||Cl^- \text{ (aq, 1.00 M)}|AgCl|Ag$$

At 25 $^\circ$C, she measures a cell voltage of 0.546 volts. For the two half-cells, the following standard reduction reaction/potentials are applicable:

$AgCl(s) + e^- \rightarrow Ag\ (s) + Cl^-\ (aq)$ $E^o = 0.222$ volts

$Pb^{2+}\ (aq) + 2\ e^- \rightarrow Pb\ (s)$ $E^o = -0.1263$ volts

  a. *[10 pts]* Write the overall reaction for the cell and indicate which reaction takes place at the anode and which takes place at the cathode.
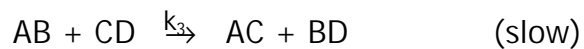
  b. *[5 pts]* Based on the standard reduction potentials provided above, calculate E^o for this cell.

c. ***[10 pts]*** Calculate the molar concentration of Pb^{2+} in the Pb half-cell.

d. ***[10 pts]*** Based on your above calculation(s) and the information given, calcuate the K_{sp} for $PbSO_4$ (s).

3. In the Hall-Heroult process for the electrolytic production of aluminum, Al^{3+} ions from the Al_2O_3 dissolved in molten cryolite (Na_3AlF_6) are reduced to Al (l) while carbon (graphite) is oxidized to CO_2 by reaction with the oxide ions.

   a. *[10 pts]* Write balanced equations for the half-reactions at the anode and at the cathode and for the overall cell reaction.

   b. *[10 pts]* If a current of 100,000 amperes is passed through the cell for a period of 1.5 hours, what mass of aluminum will be recovered?

4. The following reaction mechanism has been proposed for a chemical reaction:

$$A_2 \; \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \; A \; + \; A \qquad\qquad \text{(fast equilibrium)}$$

$$A \; + \; B \; \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \; AB \qquad\qquad \text{(fast equilibrium)}$$

$$AB + CD \; \overset{k_3}{\rightarrow} \; AC + BD \qquad\quad \text{(slow)}$$

a. **[10 pts]** Write a balanced equation for the overall reaction.

b. **[20 pts]** Write the rate expression that corresponds to the preceding mechanism. Express the rate in terms of concentrations of reactants only (A_2, B, CD).

5. The rate for the oxidation of iron(II) by cerium(IV):

$$Ce^{4+} (aq) + Fe^{2+} (aq) \rightarrow Ce^{3+} (aq) + Fe^{3+} (aq)$$
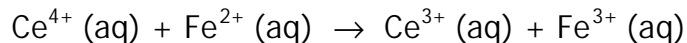
is measured at several different initial concentrations of the two reactants:

| $[Ce^{4+}]$ (mol/L)	$[Fe^{2+}]$ (mol/L)	Rate (mol/L-s)
1.1×10^{-5}	1.8×10^{-5}	2.0×10^{-7}
1.1×10^{-5}	2.8×10^{-5}	3.1×10^{-7}
3.4×10^{-5}	2.8×10^{-5}	9.5×10^{-7}

a. **[10 pts]** Write the rate law for this reaction, including numerical values for the reaction order with respect to both of the reactants.

b. **[5 pts]** Calculate the value of the rate constant k, and give its units.

c. **[5 pts]** Predict the initial reaction rate for a solution in which $[Ce^{4+}]$ is 2.6×10^{-5} M and $[Fe^{2+}]$ is 1.3×10^{-5} M.

6. ^{40}K is radioactive and can decay either by beta emission (to ^{40}Ca) or by electron capture (to ^{40}Ar). The half-life for both processes is 1.28 x 10^9 years, with 10.7% of the decay occuring via electron capture and the remaining 89.3% via beta emission.

    a. *[15 pts]* Write balanced equations for the two ^{40}K radioactive decay processes.

    b. *[15 pts]* Analysis of a rock sample shows that it contains 0.42 mg of ^{40}Ar for every 1.00 mg of ^{40}K. Assuming that all of the argon resulted from the decay of the potassium and that neither element has left or entered the rock since its formation, calculate the age of the rock. (Remember: not all of the potassium decays to argon!)

7. The following acid-base reaction occurs spontaneously in the *gas phase*:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$
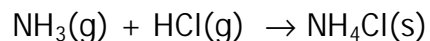
a. *[5 pts]* Would you expect the entropy change associated with this reaction to be positive or negative? (No calculations, just base your answer on inspection of the reaction equation.) Briefly explain.

b. *[10 pts]* This reaction is spontaneous at 25 °C. Based on this and on your answer to *part a*, is this reaction exothermic or endothermic? Explain.

c. *[10 pts]* ΔG^o for this reaction is -91.2 kJ/mol. Calculate the value of the equilibrium constant for this reaction.

d. *[10 pts]* If you were to place 10.0 grams of NH_4Cl (s) into a 250-mL flask, calculate the partial pressures (in atm) of NH_3 (g) and HCl(g) after the system reaches equilibrium.

e. *[5 pts]* If you were to add more NH_4Cl(s) to the flask, how would the NH_3 (g) and HCl(g) partial pressures be affected (i.e., increase, decrease, no change)? Explain.

8. Indicate whether the aqueous solutions described in each instance below are acidic, basic, or neutral (pH=7). Either show your work or explain your reasoning.

   a. **[5 pts]** 1.0 x 10^{-2} M NH$_4$Cl solution (K$_b$ (NH$_3$) = 1.8 x 10^{-5}).

   b. **[5 pts]** 1.0 x 10^{-2} M NaCl solution.

   c. **[10 pts]** Solution obtained by mixing 20.0 mL 0.100 M NaOH with 20.0 mL 0.010 M Acetic Acid (K$_a$ (Acetic Acid) = 1.8 x 10^{-5}).

d. **[10 pts]** Solution obtained by mixing 20.0 mL 0.010 M NaOH with 20.0 mL 0.100 M Acetic Acid (K_a (Acetic Acid) = 1.8 x 10^{-5}).

e. **[10 pts]** 1.0 x 10^{-2} M Sodium Bicarbonate (NaHCO$_3$) solution. (For carbonic acid, H$_2$CO$_3$): K_{a1} = 4.3 x 10^{-7}, K_{a2} = 4.8 x 10^{-11})

f. **[10 pts]** Solution obtained by mixing 20.0 mL 0.100 M H$_2$CO$_3$ with 20.0 mL 0.200 M NaOH (see K_a values from *part e*).

Extra Credit! -- 10 pts

About 50,000 kJ of electrical energy is required to produce 1.0 kg of Al from its $Al(OH)_3$ ore. The major energy cost in recycling aluminum cans is the melting of aluminum. The enthalpy of fusion of Al(s) is 10.7 kJ/mol. Compare the energy cost for making new aluminum with that for recycling.