

CHEM 36
General Chemistry
FINAL EXAM

May 10, 2002

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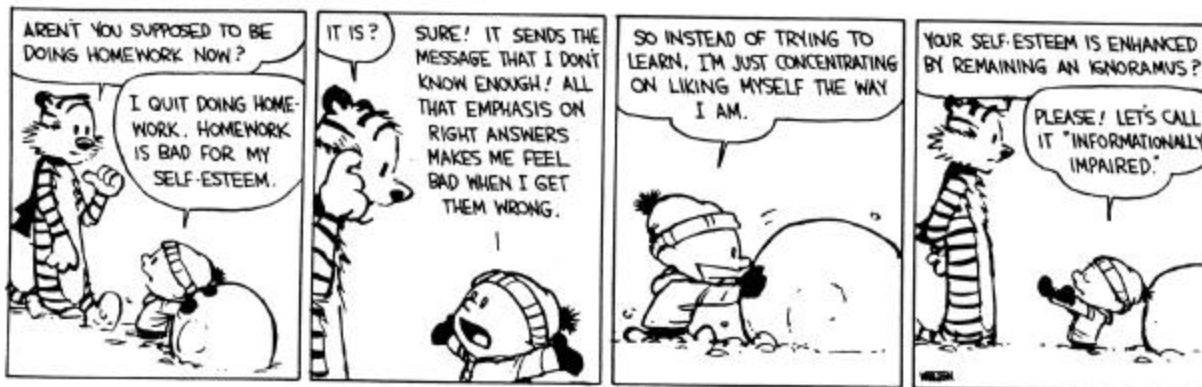
INSTRUCTIONS: Read through the entire exam before you begin. Answer all of the questions. For questions involving calculations, show **all** of your work -- **HOW** you arrived at a particular answer is **MORE** important than the answer itself!

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	25
3	15	15
4	20	20
5	20	20
6	30	30
7	20	20
8	30	30
9	25	25
10	15	15
11	20	20
12	30	30
TOTAL:	250	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 ; $K_{\text{sp}} = 1.6 \times 10^{-10}$) and with chromate (Ag_2CrO_4 ; $K_{\text{sp}} = 1.9 \times 10^{-12}$).

- 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.

We need to calculate $[\text{Ag}^+]$ at which each compound will precipitate:

$$\text{For } \underline{\text{AgCl}}: \quad [\text{Ag}^+] = K_{\text{sp}}/[\text{Cl}^-] = \frac{1.6 \times 10^{-10}}{0.0010 \text{ M}} = 1.6 \times 10^{-7} \text{ M}$$

$$\text{For } \underline{\text{Ag}_2\text{CrO}_4}: \quad [\text{Ag}^+]^2 = K_{\text{sp}}/[\text{CrO}_4^{2-}] = \frac{1.9 \times 10^{-12}}{0.100 \text{ M}}$$
$$[\text{Ag}^+] = 4.36 \times 10^{-6} \text{ M}$$

Since $[\text{Ag}^+]_{\text{AgCl}} < [\text{Ag}^+]_{\text{Ag}_2\text{CrO}_4}$, **AgCl will precipitate first**

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

From *part a*, Ag_2CrO_4 begins to precipitate when $[\text{Ag}^+] = 4.36 \times 10^{-6} \text{ M}$

So, $[\text{Cl}^-]$ when $[\text{Ag}^+] = 4.36 \times 10^{-6} \text{ M}$:

$$[\text{Cl}^-] = K_{\text{sp}}/[\text{Ag}^+] = \frac{1.6 \times 10^{-10}}{4.36 \times 10^{-6}} = 3.67 \times 10^{-5} \text{ M}$$

$$\text{Fraction Remaining} = \frac{[\text{Cl}^-]_{\text{remaining}}}{[\text{Cl}^-]_{\text{initial}}} = \frac{3.67 \times 10^{-5} \text{ M}}{0.0010 \text{ M}} = \boxed{3.7 \times 10^{-2}}$$

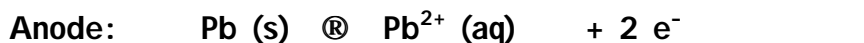
2. A student sets up the following electrochemical cell:



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



- 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° for this cell.

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{\text{AgCl}} - E^\circ_{\text{Pb}} \\ &= 0.222 - (-0.1263) = 0.3483 \text{ volts} = \underline{\underline{0.348 \text{ volts}}} \end{aligned}$$

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

Nernst! $E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0592/n)\text{Log}Q$
 $0.546 = 0.3483 - (0.0592/2)\text{Log}([\text{Pb}^{2+}][\text{Cl}^{-}]^2)$
 $0.1977 = -0.02960 \text{Log}([\text{Pb}^{2+}][\text{Cl}^{-}]^2)$
 $-6.679054 = \text{Log}([\text{Pb}^{2+}][\text{Cl}^{-}]^2)$

$$[\text{Pb}^{2+}][\text{Cl}^{-}]^2 = 2.093852 \times 10^{-7}$$
$$[\text{Pb}^{2+}] = 2.093852 \times 10^{-7}/[\text{Cl}^{-}]^2$$
$$[\text{Pb}^{2+}] = 2.093852 \times 10^{-7}/(1.00 \text{ M})^2$$
$$[\text{Pb}^{2+}] = 2.093852 \times 10^{-7} \text{ M}$$

$$[\text{Pb}^{2+}] = \boxed{2.1 \times 10^{-7} \text{ M}}$$

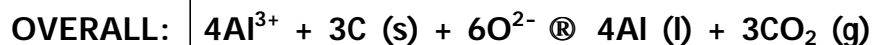
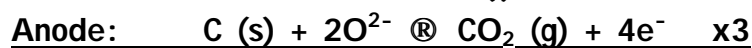
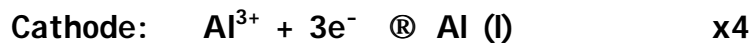
- d. **[10 pts]** Based on your above calculation(s) and the information given, calculate the K_{sp} for PbSO_4 (s).

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = (2.093852 \times 10^{-7})(0.0500)$$

$$K_{\text{sp}} = 1.046926 \times 10^{-8} = \boxed{1.0 \times 10^{-8}}$$

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.



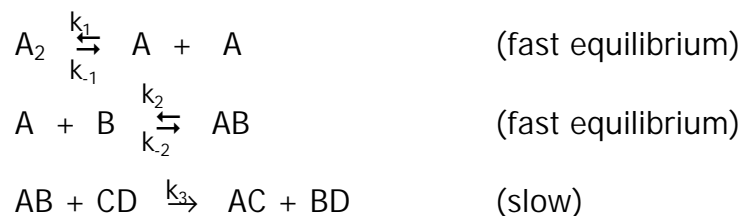
b. **[10 pts]** If a current of 100,000 amperes is passed through the cell for a period of 1.5 hours, what mass of aluminum will be recovered?

$$1.5 \text{ Hr} \times \frac{60 \text{ min}}{\text{Hr}} \times \frac{60 \text{ sec}}{\text{min}} \times \frac{100,000 \text{ C}}{\text{sec}} \times \frac{\text{mol e}^-}{96,485.31 \text{ C}} \times \frac{\text{mol Al}}{3 \text{ mol e}^-} \times \frac{26.98 \text{ g Al}}{\text{mol Al}}$$

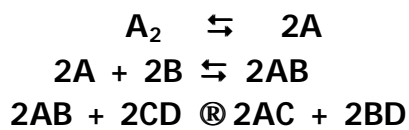
$$= 5.0333 \times 10^4 \text{ g}$$

$$= \boxed{50. \text{ kg Al}}$$

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



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).

Step 3 is rate-determining step, so: $\text{Rate} = k_3[AB][CD]$

From Step 2, we can solve for [AB]:

$$k_2[A][B] = k_{-2}[AB]$$

$$[AB] = (k_2/k_{-2})[A][B]$$

Substituting: $\text{Rate} = k_3(k_2/k_{-2})[A][B][CD]$

From Step 1, we can solve for [A]:

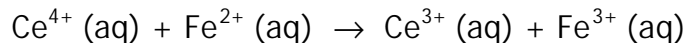
$$k_1[A_2] = k_{-1}[A]^2$$

$$[A] = \{(k_1/k_{-1})[A_2]\}^{1/2}$$

Now, the final substitution:

$$\boxed{\text{Rate} = k_3(k_2/k_{-2})(k_1/k_{-1})^{1/2}[A_2]^{1/2}[B][CD]}$$

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



is measured at several different initial concentrations of the two reactants:

$[\text{Ce}^{4+}]$ (mol/L)	$[\text{Fe}^{2+}]$ (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.

In general: Rate = $k[\text{Ce}^{4+}]^m[\text{Fe}^{2+}]^n$

To find the value of m, compare the rates for solutions 2 and 3 (constant $[\text{Fe}^{2+}]$): when $[\text{Ce}^{4+}]$ is tripled, the rate is tripled, so: $m = 1$

To find the value of n, compare the rates for solutions 1 and 2 (constant $[\text{Ce}^{4+}]$): when $[\text{Fe}^{2+}]$ is increased by 50%, the rate increases by about 50%, so: $n = 1$

Thus: $\text{Rate} = k[\text{Ce}^{4+}][\text{Fe}^{2+}]$

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

From the data for solution 1 and the rate law determined in part a:

$$k = \frac{\text{Rate}}{[\text{Ce}^{4+}][\text{Fe}^{2+}]} = \frac{2.0 \times 10^{-7} \text{ mol/L-s}}{(1.1 \times 10^{-5} \text{ mol/L})(1.8 \times 10^{-5} \text{ mol/L})}$$

$$k = 1.0101 \times 10^3 \text{ L/mol-s} = \underline{1.0 \times 10^3 \text{ L/mol-s}}$$

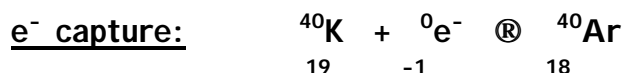
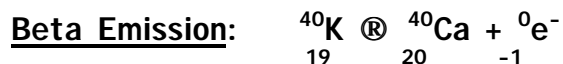
- c. **[5 pts]** Predict the initial reaction rate for a solution in which $[\text{Ce}^{4+}]$ is $2.6 \times 10^{-5} \text{ M}$ and $[\text{Fe}^{2+}]$ is $1.3 \times 10^{-5} \text{ M}$.

$$\text{Rate} = k[\text{Ce}^{4+}][\text{Fe}^{2+}] = (1.01 \times 10^3 \text{ L/mol-s})(2.6 \times 10^{-5} \text{ mol/L})(1.3 \times 10^{-5} \text{ mol/L})$$

$$\text{Rate} = 3.4141 \times 10^{-7} \text{ mol/L-s} = \underline{3.4 \times 10^{-7} \text{ mol/L-s}}$$

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 1.28×10^9 years, with 10.7% of the decay occurring 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!)

It's a first-order decay process, so we can use the integrated rate expression: $\ln(N/N_0) = -kt$

We can get k from the half-life: $k = 0.693/t_{1/2}$

$$k = 0.693/1.28 \times 10^9 \text{ yr} = \underline{5.414 \times 10^{-10} \text{ yr}^{-1}}$$

Since all species (Ar and K) have same molar mass, we can work directly in grams.

$N = 1.00 \text{ mg } ^{40}\text{K}$ (amount of ^{40}K now)

$N_0 = N + ^{40}\text{K}$ required to produce 0.42 mg ^{40}Ar via electron capture

$$0.42 \text{ mg } ^{40}\text{Ar} \times \frac{1 \text{ mg } ^{40}\text{K}_{\text{ec}}}{1 \text{ mg } ^{40}\text{Ar}} \times \frac{100 \text{ mg } ^{40}\text{K}_{\text{orig}}}{10.7 \text{ mg } ^{40}\text{K}_{\text{ec}}} = 3.9252 \text{ mg } ^{40}\text{K}_{\text{orig}}$$

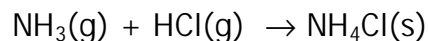
$$\text{So, } N_0 = 1.00 \text{ mg} + 3.9252 \text{ mg} = 4.9252 \text{ mg } ^{40}\text{K}$$

Substituting: $\ln(1.00/4.9252) = -(5.414 \times 10^{-10} \text{ yr}^{-1})t$

$$-1.594365 = -(5.414 \times 10^{-10} \text{ yr}^{-1})t$$

$$t = 2.94489 \times 10^9 \text{ yr} = \boxed{2.9 \times 10^9 \text{ yr}}$$

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



- 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.

DS = negative

2 mol gas @ solid, so entropy of the system will decrease as it becomes more ordered.

- 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.

DG = DH - TDS

If DS is negative, then -TDS will be positive. Thus, DH must be negative in order for the process to be spontaneous (DG = negative): Exothermic

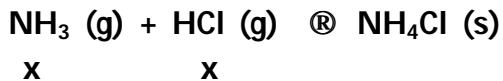
- c. **[10 pts]** ΔG° for this reaction is -91.2 kJ/mol. Calculate the value of the equilibrium constant for this reaction.

$$\Delta G^\circ = -RT \ln K$$

$$\ln K = -\Delta G^\circ / RT = \frac{-(-91.2 \times 10^3 \text{ J})}{(8.3145 \text{ J/mol-K})(298.15 \text{ K})} = 36.789500$$

$$K = 9.4946 \times 10^{15} = \boxed{9. \times 10^{15}}$$

- 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.



$$K = \frac{1}{P_{\text{NH}_3}P_{\text{HCl}}} = 9.4946 \times 10^{15}$$

$$1/x^2 = 9.4946 \times 10^{15}$$

$$x = 1.02627 \times 10^{-8} \text{ atm} = \boxed{1. \times 10^{-8} \text{ atm}}$$

- 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.

No Change. The system is "saturated" so the partial pressure of NH_3 and HCl in equilibrium with the solid NH_4Cl is independent of the amount of solid present (the only requirement is that there BE some solid present).

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]** 1.0×10^{-2} M NH_4Cl solution ($K_b(\text{NH}_3) = 1.8 \times 10^{-5}$).

Acidic. NH_4^+ is a weak acid ($K_a \gg 10^{-14}/10^{-5} = 10^{-9}$)



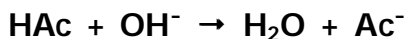
b. **[5 pts]** 1.0×10^{-2} M NaCl solution.

Neutral. Na^+ and Cl^- are conjugates of strong acids and bases, so they are weaker acids and bases than water. Thus, the autoionization of water will determine the pH (=7).

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

Basic. 20.0 mL 0.100 $\text{NaOH} = 2.00$ mmol OH^-
20.0 mL 0.010 $\text{HAc} = 0.20$ mmol HAc

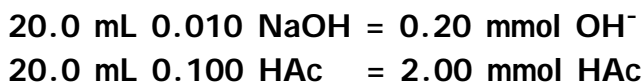
Reaction occurs until all HAc is reacted:



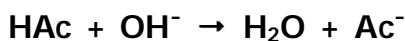
There is excess OH^- so pH is determined by the 1.8 mmol OH^- remaining: strong base = basic solution

- 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) = 1.8×10^{-5}).

Acidic.



Reaction occurs until all OH^- is reacted:



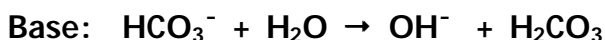
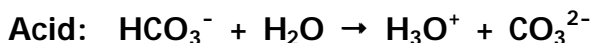
Leaves: 1.8 mmol HAc and 0.2 mmol Ac^-

Acidic Buffer: acidic solution

- e. **[10 pts]** 1.0×10^{-2} M Sodium Bicarbonate (NaHCO_3) solution. (For carbonic acid, H_2CO_3): $K_{a1} = 4.3 \times 10^{-7}$, $K_{a2} = 4.8 \times 10^{-11}$)

Basic.

Bicarbonate ion is amphoteric, so can act like an acid or as a base:



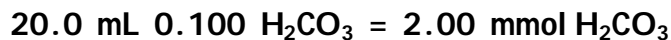
As given: $K_{a2} \gg 10^{-11}$

$K_b \gg 10^{-14}/10^{-7} = 10^{-7}$

Since $K_b > K_a$, HCO_3^- is a stronger base, than acid - basic solution

- f. **[10 pts]** Solution obtained by mixing 20.0 mL 0.100 M H_2CO_3 with 20.0 mL 0.200 M NaOH (see K_a values from part e).

Basic.



Leaves 2.00 mmol CO_3^{2-} (conj. base of H_2CO_3): basic solution

Extra Credit! -- 10 pts

About 50,000 kJ of electrical energy is required to produce 1.0 kg of Al from its $\text{Al}(\text{OH})_3$ 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.

For *newly refined Al*:

$$\frac{50,000 \times 10^3 \text{ J}}{1.0 \text{ kg Al}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{26.9815 \text{ g Al}}{\text{mol Al}} = 1.349 \times 10^6 \text{ J/mol}$$

To *recycle Al*: $10.7 \times 10^3 \text{ J/mol}$

$10.7/1,349 \times 100\% = 0.8\%$ - recycling uses less than 1% of the energy need to refine new Al