Chem 36: 1999 Final Exam Questions with Answers

1. a. As you all recall from lab, Aspirin is a weak acid (acetylsalicylic acid). When a 0.150 M solution of this acid is prepared, it has a pH of 4.69. Calculate the K_a for acetylsalicylic acid.

   K_a = 2.8×10^{-9}

   b. Calculate K_b for the acetylsalicylate ion.

   K_b = 3.6×10^{-6}

   c. Calculate the pH of a 0.150 M solution of sodium acetylsalicylate.

   pH = 10.87

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

   $2\,A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} D$ (fast equilibrium)

   $D + B \xrightarrow[k_2]{} E + F$ (slow)

   $F \xrightarrow[k_3]{} G$ (fast)

   a. Write a balanced equation for the overall reaction.

      2A + 2B ® G + E

   b. Write the rate law that corresponds to the preceding mechanism. Express the rate in terms of concentrations of reactants only (A, B).

      Rate = $(k_2k_1/k_{-1})[A]^2[B]^2$

   c. Identify the reactive intermediates involved in this reaction mechanism.

      Reactive Intermediates: D and F (not in overall reaction)

4. In a study of the reaction of pyridine (C_5H_5N) with methyl iodide (CH_3I) in a benzene solution, the following set of initial reaction rates was measured at 25 ^oC for different initial concentrations of the two reactants:

[Pyridine] (mol/L)	[Methyl Iodide] (mol/L)	Rate (mol/L/sec)
0.00100	0.00100	5.0×10^{-7}
0.00100	0.00200	1.0×10^{-6}
0.00200	0.00200	2.0×10^{-6}

a. Write the rate law for this reaction.

Rate = k[C_5H_5N][CH_3I]

b. Calculate the rate constant k, and give its units.

k = 5.0 x 10^{-1} L/mol-s

c. Predict the initial reaction rate for a solution in which [C_5H_5N] is 5.0×10^{-5} M and [CH_3I] is 2.0×10^{-5} M.

Rate = 5.0 x 10^{-10} mol/L-s

5. a. The reaction SO_2Cl_2 (g) $\rightarrow$ SO_2 (g) + Cl_2 (g) is first-order, with a rate constant equal to 1.7×10^{-4} s^{-1} at 550 K. If the partial pressure of SO_2Cl_2 in a sealed vessel at 550 K is 1.0 atm, how long will it take for the partial pressure of SO_2Cl_2 to fall to 0.50 atm?

4.1 x 10^3 sec

b. At a temperature of 600 K, this reaction has a rate constant of 4.8×10^{-3} s^{-1}. Calculate the activation energy (kJ/mol) for this reaction

E_a = 1.8 x 10^2 kJ/mol

6. The isotope ^{232}Th decays to ^{208}Pb by the emission of six alpha particles, with a half-life of 1.39×10^{10} years.

   a. Write a balanced reaction for this decay process.

   $$^{232}_{90}Th \rightarrow {}^{208}_{82}Pb + 6\ {}^{4}_{2}He + 4\ {}^{0}_{-1}e$$

   b. Analysis of 1.0 kg of ocean sediment show it to contain 7.4 mg of ^{232}Th and 4.9×10^{-2} cm^3 of gaseous helium at 0 ^oC and atmospheric pressure. Calculate the age of the sediment, assuming no loss or gain of thorium or helium from the sediment since its formation and assuming that the helium arose entirely from the decay of thorium.

   2.3 x 10^8 years

7. You may recall that spectacular demonstration in which the following *gas phase* acid-base reaction was performed:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

   a. 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.

   ΔS = negative

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

   b. Obviously, this reaction is spontaneous at 25 ^oC. Based on this and on your answer to *part a*, is this reaction exothermic or endothermic? Explain.

   $\Delta G = \Delta H - T\Delta S$

   If ΔS is negative, then $-T\Delta S$ will be positive. Thus, ΔH must be negative in order for the process to be spontaneous (ΔG = negative): Exothermic

c. This reaction is between a strong acid and a weak base. Ignoring all of the thermodynamic data for a moment, do you expect the equilibrium constant for this reaction to be much less than 1.0, much greater than 1.0, or about equal to 1.0. Explain.

The reaction of any strong acid with <u>any</u> base will go to completion and so <u>K >> 1</u>

d. ΔG^o for this reaction is -91.2 kJ/mol. Calculate the value of the equilibrium constant for this reaction.

<u>K = 1. x 10^{16}</u>

e. If you were to place 1.0 x 10^{-5} atm each of NH_3 (g) and HCl (g) into a 500-mL flask, how much NH_4Cl (s) will form when the system reaches equilibrium?

<u>10.9 mg</u>

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. 1.0 x 10^{-2} M Sodium Acetate (NaAc) solution (K_a (HAc) = 1.8 x 10^{-5}).

<u>Basic</u> – acetate is the conjugate base of acetic acid

b. 1.0 x 10^{-2} M $NaNO_3$ solution.

<u>Neutral</u> – water determines the pH of this solution

c. Solution obtained by mixing 20.0 mL 0.100 M HCl with 20.0 mL 0.010 M NH_3 (K_b (NH_3) = 1.8 x 10^{-5}).

<u>Acidic</u> – excess HCl

d. Solution obtained by mixing 20.0 mL 0.010 M HCl with 20.0 mL 0.100 M NH_3 (K_b (NH_3) = 1.8 x 10^{-5}).

<u>Basic</u> – buffer composed of a base and its conjugate acid

e. 1.0×10^{-2} M Na_2HPO_4 solution. (For phosphoric acid, H_3PO_4: $K_{a1} = 7.5 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$, $K_{a3} = 2.2 \times 10^{-13}$)

***Basic* – amphoteric species, but $K_b > K_a$**

f. Solution obtained by mixing 20.0 mL 0.100 M H_3PO_4 with 20.0 mL 0.300 M NaOH (see K_a values from *part e*).

***Basic* – left with PO_4^{3-} (conjugate base) after reaction**

9. An I_2 (s)||I^- (1.00 M) half-cell is connected to an $H_3O^+|H_2$ (1 atm) half-cell in which the concentration of the hydronium ion is unknown. The measured cell voltage is 0.755 volts when the I_2 (s)||I^- (1.00 M) half-cell is the cathode. What is the pH in the $H_3O^+|H_2$ (1 atm) half-cell?

pH = 3.72