## CHEM102 Exam I (Jul 20 2009).

 $33\frac{1}{3}$  points / problem with maximum of 100 points.

1.

- a) Inspection of the first and second lines shows that  $[AgSO_4]$  quadruples and the rate goes X16. This means that it is second order with respect to AgSO<sub>4</sub>. The second and third lines show that [NaCl] doubles and the rate quadruples, which means that it is also second order with respect to NaCl. The rate law is therefore: rate =  $k[AgSO_4]^2[NaCl]^2$ .
- b) Plug in the numbers from the first line of the table into the rate law and solve for k. This gives  $k = 3.8 \times 10^5 \text{ s}^{-1} \text{M}^{-3}$  (2 sig. figs.).
- c) For elementary reactions the rate law can be read directly from the chemical equation: rate =  $k[AgSO_4][NaCl]^2$ .
- d) Starting with Arrhenius equations for two different rate constants  $k_1$  and  $k_2$  at the corresponding temperatures  $T_1$  and  $T_2$  (A is constant), the following result can be derived:  $E_a = R \ln \left(\frac{k_1}{k_2}\right) \frac{T_1 T_2}{T_1 T_2}$ . Plugging in the numbers gives  $E_a = 22.4 \text{ kJ/mol.}$

- a) 2nd order (two  $NO_2$  molecules reacting).
- b) For a second order reaction, the integrated rate law is:  $\frac{1}{[NO_2](t)} = kt + \frac{1}{[NO_2](0)}$ . Inserting t = 600 s, gives  $[NO_2](600 \text{ s}) = 0.0318 \text{ M}$ .
- c) The reaction is 2 to 1 in terms of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub>. The amount of NO<sub>2</sub> consumed is 0.200 M 0.0318 M = 0.168 M. However, only half of that amount of N<sub>2</sub>O<sub>4</sub> is produced, so 0.0841 M of N<sub>2</sub>O<sub>4</sub> has formed.
- d) The entropy should decrease as the number of gas moles is decreasing (less degrees of freedom).
- 3.
- a)  $\Delta G_{rxn}^{\circ} = \Delta H_{rxn}^{\circ} T \Delta S_{rxn}^{\circ}$ . Plugging in the values gives  $\Delta G_{rxn}^{\circ} = -660$ . kJ/mol. Yes, since this is negative, it indicates a spontaneous process.

<sup>2.</sup> 

- b)  $\Delta S_{\text{universe}}^{\circ} = \Delta S_{\text{rxn}}^{\circ} + \Delta S_{\text{surr}}^{\circ} = \Delta S_{\text{rxn}}^{\circ} \Delta H_{\text{rxn}}^{\circ}/T$ . Plugging in the numbers gives  $\Delta S_{\text{universe}}^{\circ} = 2216 \text{ J/(K mol)}$ . This is positive, which means that the process is spontaneous.
- c)  $q_{rxn} = -q_{surr}$  and  $q_{rxn} = \Delta H_{rx}^{\circ}$ . Combining these gives  $q_{rxn} = -q_{surr} = -824.2 \text{ kJ/mol}$ . Based on the signs the reaction is loosing heat and the surroundings is gaining.
- d) In general, in addition to the chemical equation, you would also need the relative standard entropies (thermodynamic table). Sometimes it is possible to predict the sign based on the change of the number of gas moles during the reaction or other structural changes (e.g., phase change).