CHEM 130 **Name** _____
Quiz 9 – November 18, 2016

Complete the following problems. Write your final answers in the blanks provided.

For problems 1 and 2, consider the mechanism below that has been proposed for the spontaneous gas phase reaction of chlorine gas with chloroform ($CHCl_3$) to produce carbon tetrachloride (CCl_4) and hydrogen chloride (HCl).

$$Cl_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cl(g) \qquad \text{Fast equilibrium}$$

$$Cl(g) + CHCl_3 \xrightarrow{k_2} HCl(g) + CCl_3(g) \qquad \text{Slow}$$

$$CCl_3(g) + Cl(g) \xrightarrow{k_3} CCl_4(g) \qquad \text{Fast}$$

1. If the experimentally-determined rate law is: **Rate = $k[Cl_2]^{1/2}[CHCl_3]$**, is this an acceptable mechanism? (9 points)

   Your first step would be to check that the stoichiometry for the sum of the elementary steps matches that for the overall reaction. In this case, it does.

   Then, determine the rate law for this mechanism, starting with the rate law for the slow step, which is the rate-determining step.

   $$\text{Rate} = k_2[Cl][CHCl_3]$$

   Since Cl is an intermediate, we need to find an expression for it in terms of reactants. Because step 1 is an equilibrium, the rate of the forward and reverse reactions are equal

   $$k_1[Cl_2] = k_{-1}[Cl]^2$$

   Solving for [Cl]:

   $$(k_1[Cl_2])/k_{-1} = [Cl]^2$$
   $$[Cl] = ((k_1[Cl_2])/k_{-1})^{1/2} = k[Cl_2]^{1/2}$$

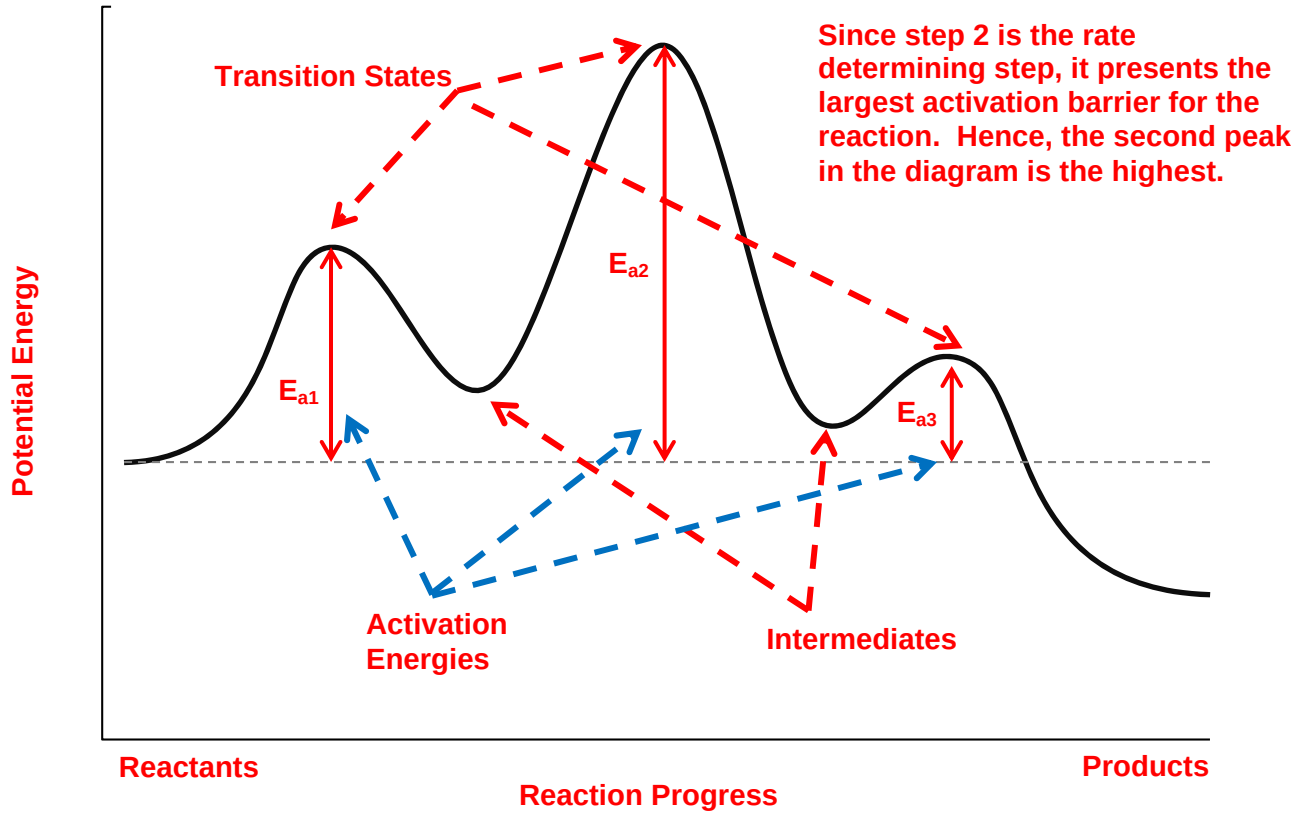
   Inserting this into the original rate law gives us

   $$\text{Rate} = k_2(k[Cl_2]^{1/2})[CHCl_3]$$
   $$\text{Rate} = k[Cl_2]^{1/2}[CHCl_3]$$

   This does match the experimental rate law, indicating that the mechanism is reasonable, assuming the experimentally-determined rate law is valid.

   Note that since the third step is fast, it does not contribute to the overall rate law for the reaction because the kinetics are dominated by the rate-determining step.

2. Regardless of your answer for part 1, draw a reaction coordinate diagram corresponding to the proposed mechanism. Label the axes of your diagram, as well as reactants, products, transition states, and intermediates. Identify the activation energies for each step. (9 points)



3. In no more than four sentences, explain how a catalyst increases the rate of a chemical reaction while not changing the enthalpy of the reaction. (7 points)

The catalyst provides an alternate, lower activation energy mechanism for the reaction that allows the reaction to proceed more rapidly. The identities of the reactants and products, as well as the stoichiometry remains the same, to the thermodynamics of the reaction are unchanged.

Possibly Useful Information

rate = $k[A]^0$	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$
rate = $k[A]^1$	$\ln[A]_t = -kt + \ln[A]_0$	$t_{1/2} = 0.693/k$
rate = $k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$t_{1/2} = 1/(k[A]_0)$