Question 2 (7 points)

Consider the following mechanism:

$$NO_2ClG) \longrightarrow NO_2(g) + Cl(g) \qquad \textit{slow}$$

$$NO_2Cl(g) + Cl(g) \longrightarrow NO_2(g) + Cl_2(g) \qquad \textit{fast}$$

(a) Write the overall reaction that is occurring.

(b) If for this mechanism there are two energy of activation values (E_a), 23 kJ/mol of reaction and 96 kJ/mol of reaction, and that enthalpy or $\triangle H$ = -114 kJ/mol of reaction , make a clean sketch of the reaction energy diagram for this mechanism. You may assume all intermediates are more unstable than reactants or products. Your sketch does not need an accurate "energy scale" but does need to indicate energy values and their relative size. Make sure your sketch includes:

- the labels for any axes
- Identifies $\triangle H$
- Identifies where the given E_a values can be found
- Identifies the chemical species present at the start, at any intermediate stage and at the finish of the mechanism.
- Identifies where the transition state, for any reaction, may be studied.

(c) If liquid NO_2Cl were used instead of gaseous NO_2Cl (see the mechanism below), a fellow student proposes that the $\triangle H$ of the reaction would decrease in magnitude, ie, become a less negative value. Is the student correct? Explain why or why not.

$$NO_2Cl(l) \longrightarrow NO_2(g) + Cl(g) \qquad \textit{slow}$$

$$NO_2Cl(l) + Cl(g) \longrightarrow NO_2(g) + Cl_2(g) \qquad \textit{fast}$$

Question 4 (3 points)

A student performs a pseudo order kinetics experiment for the reaction

$$H_2(g) + 2ICl(g) \longrightarrow I_2(g) + 2HCl(g) \quad \text{Rate} = k[H_2]^x[ICl]^y$$

They use the initial concentrations of 3.6×10^{-4} M for H_2 and 3.1 M for ICl. .

(a) Why did they use a [ICl] so much larger than the $[H_2]$? Your answer should include how the rate law changes given the concentrations above.

(b) If the order with respect to H_2 is 2, sketch the plot that you would use to confirm this order and explain how you would use the plot to determine a value for the pseudo rate constant in the rate law you gave in (a).

(c) If the plot in (b) yields a pseudo rate constant for the rate law in (a) of 5.8 $M^{-1}s^{-1}$ AND the reaction is first order in ICl what would the rate constant, k, be for the rate law given with the reaction equation above?

All questions that follow relate to the reaction

$$2A(g) \longrightarrow X(g).$$

To answer the questions that follow you will need to know that the rate constant is $k = 1.10\ M^{-1}s^{-1}$ at 275 K.

Question 1 (1 point)

What would be the form of the integrated rate law that you would use to further study the reaction given above ?

- $t_{1/2} = \frac{[A]_0}{2k}$
- $\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$
- $[A]_t = -kt + [A]_0$
- $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$

Question 2 (1 point)

How long it will take (in minutes) to reach a final concentration of A of 0.0011 M if the reaction above is carried out at 275 K, with an initial concentration of A of 0.25 M?

Question 3 (1 point)

This reaction is known to occur via a series of steps. A proposed mechanism is:

$$2A(g) \longrightarrow B(g) + C(g) \qquad \textit{slow}$$

$$B(g) \longrightarrow D(g) \qquad \textit{fast}$$

$$D(g) + C(g) \longrightarrow X(g) \qquad \textit{fast}$$

What is the rate law for this mechanism?

Question 4 (2 points)

Explain whether the mechanism from the previous question (shown again below) is valid or not for the reaction being studied.

$$2A(g) \longrightarrow B(g) + C(g) \qquad \textit{slow}$$

$$B(g) \longrightarrow D(g) \qquad \textit{fast}$$

$$D(g) + C(g) \longrightarrow X(g) \qquad \textit{fast}$$

Question 2 (4.5 points)

Consider the reaction: $NaOH(aq) + HCl(aq) \rightleftharpoons NaCl(aq) + H_2O(l)$ *exothermic*

Refer to this reaction when completing (a) through (c) below.

(a) Sketch the curve for the reaction coordinate using the axes given.
Your curve must identify where to find:
- ΔH
- E_a
- Products and Reactants

(b) Write out the expression for the equilibrium constant.

(c) Explain how an increase in temperature changes both the speed and yield.