1. (5 pts) The activation energy for the isomerization of CH₃NC to CH₃CN is 160 kJ/mol. (a) Calculate the fraction of CH₃NC molecules that have an energy in excess of 160 kJ at 610 K. 

\[ \text{fraction} = e^{-\frac{E_a}{RT}} \]

\[ \frac{E_a}{RT} = \frac{-160,000 \text{J/mol}}{(8.314 \text{ J/mol} \cdot \text{K}^{-1}) \cdot (610 \text{ K})} \]

\[ = -31.55 \times e^{-31.55} = 1.99 \times 10^{-14} \]

(b) Likewise with 620 K

\[ e^{-31.04} = 3.31 \times 10^{-14} \]

2. (7 pts) The NYTimes stated that a drop of 36 °F (20 °C) would lower the reaction rate fortyfold for the breakdown of cellulose and starch.

a) Calculate the activation energy associated with this observation.

b) Use this activation energy and assume the rate of breakdown is a first-order process with a half-life of 2.7 years at 25 °C. Calculate the half-life at -15 °C.

3. (8 pts) The following mechanism has been proposed for the gas-phase reaction of H₂ and ICl:

\[ \text{H}_2(\text{g}) + \text{ICl}(\text{g}) \rightarrow \text{HI}(\text{g}) + \text{HCl}(\text{g}) \]  

(1)

\[ \text{HI}(\text{g}) + \text{ICl}(\text{g}) \rightarrow \text{I}_2(\text{g}) + \text{HCl}(\text{g}) \]  

(2)

a) Write the balanced equation for the overall reaction.

\[ \text{H}_2 + 2 \text{ICl} \rightarrow \text{I}_2 + 2 \text{HCl} \]

b) Identify any intermediates in the reaction and state whether or not they are catalysts.

\[ \text{HI} \quad \text{mo}-\text{t} \text{i} \text{~do} \text{~not} \text{~re} \text{~c} \text{~l} \text{~e} \text{~m} \text{~a} \text{~i} \text{~n} \text{~e} \text{~t} \text{~s} \text{~s} \]

c) Write rate laws for each of the elementary steps of the mechanism.

\[ \text{Rate}_1 = k_1 [\text{H}_2][\text{ICl}] \]

\[ \text{Rate}_2 = k_2 [\text{HI}][\text{ICl}] \]

d) If reaction (1) is slow and (2) is fast, what is the predicted rate law for the overall reaction?
1. (6 pts) Consider the reaction $\text{N}_2\text{O}_4 (g) \rightarrow 2 \text{NO}_2 (g)$, which has $\Delta H^\circ = +57 \text{ kJ}$ for the forward reaction and an activation energy for the reverse reaction of 23 kJ/mol.
   a) Sketch and label the potential-energy diagram.

   b) Calculate the activation energy for the forward reaction.

   $$
   (E_a)_f = (E_a)_r + \Delta H
   = (23 \text{kJ}) + (57 \text{kJ}) = 80 \text{kJ}
   $$

2. (6 pts) The activation energy for a particular reaction is 75 kJ/mol. How many times faster is the reaction at 50 °C than at 10 °C?

   $$
   \ln \left( \frac{n_k_2}{n_k_1} \right) = \ln \left( \frac{n_k}{n_k_1} \right) = -\frac{75,000 \text{J}}{(8.315 \text{J/mole} \cdot \text{K}) \cdot (50 + 273)} = -\frac{1}{283} = +3.948 = \ln \frac{n_k}{n_k_1}
   $$

   $$
   \frac{n_k}{n_k_1} = e^{-3.948} \approx 0.052
   $$

3. (8 pts) The gas-phase reaction $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$ seems to be explained by the following mechanism.

   $$
   \text{NO} + \text{Cl}_2 \rightarrow \text{NOCl}_2 \quad \text{(1)}
   $$

   $$
   \text{NOCl}_2 + \text{NO} \rightarrow 2\text{NOCl} \quad \text{(2)}
   $$

   a) What would be the rate law if the first step were the slow one?

   $$
   \text{Rate} = \text{Rate}_1 = k_1 [\text{NO}] [\text{Cl}_2]
   $$

   b) What would be the rate law if the second step were the slow one?

   $$
   \text{Rate} = \text{Rate}_2 = k_2 [\text{NOCl}_2] [\text{NO}] = k [\text{NO}]^2 [\text{Cl}_2]
   $$

   c) Do the elementary steps add up to the overall reaction? What is the significance of NOCl$_2$?

   $$
   2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl} \quad \text{OK}
   $$

   NOCl$_2$ is an intermediate.