Question 5
(8 points)

A sample of $\text{C}_2\text{H}_4(g)$ is placed in a previously evacuated, rigid 2.0 L container and heated from 300 K to 450 K. The pressure of the sample is measured and plotted in the graph below.

(a) Describe TWO reasons why the pressure changes as the temperature of the $\text{C}_2\text{H}_4(g)$ increases. Your descriptions must be in terms of what occurs at the molecular level.

Two reasons are:

1. As the temperature increases, the average speed of the molecules increases and the molecules collide more frequently with the container walls.

2. As the temperature increases, the average kinetic energy of the molecules increases and the molecules strike the walls of the container with greater force.

(b) When $\text{HCl}(g)$ is injected into the container of $\text{C}_2\text{H}_4(g)$ at 450 K, the total pressure increases. Then, as the reaction proceeds at 450 K, the total pressure decreases. Explain this decrease in total pressure in terms of what occurs at the molecular level.

C$_2$H$_4(g)$ reacts readily with HCl(g) to produce C$_2$H$_5$Cl(g), as represented by the following equation.

$$\text{C}_2\text{H}_4(g) + \text{HCl}(g) \rightarrow \text{C}_2\text{H}_5\text{Cl}(g) \quad \Delta H^\circ = -72.6 \text{ kJ/mol}_\text{rxn}$$

The decrease in pressure after the initial increase is a consequence of the reaction that produces fewer gas molecules than it consumes. When fewer gas molecules are present, there are fewer collisions with the container walls, resulting in a decrease in pressure.
Question 5 (continued)

It is proposed that the formation of $\text{C}_2\text{H}_5\text{Cl}(g)$ proceeds via the following two-step reaction mechanism.

**Step 1:** $\text{C}_2\text{H}_4(g) + \text{HCl}(g) \rightarrow \text{C}_2\text{H}_5^+(g) + \text{Cl}^-(g)$  
*rate-determining step*

**Step 2:** $\text{C}_2\text{H}_5^+(g) + \text{Cl}^-(g) \rightarrow \text{C}_2\text{H}_5\text{Cl}(g)$  
*fast step*

(c) Write the rate law for the reaction that is consistent with the reaction mechanism above.

\[
\text{rate} = k[C_2\text{H}_4][\text{HCl}]
\]

1 point is earned for the correct rate law.

(d) Identify an intermediate in the reaction mechanism above.

$\text{C}_2\text{H}_5^+(g)$ or $\text{Cl}^-(g)$  
1 point is earned for identification of either species.

(e) Using the axes provided below, draw a curve that shows the energy changes that occur during the progress of the reaction. The curve should illustrate both the proposed two-step mechanism and the enthalpy change of the reaction.

\[\text{See drawing above.}\]

1 point is earned for the potential energy of the product being lower than the potential energy of the reactants (exothermic reaction).

1 point is earned for a reaction-energy curve that reflects a two-step process.

(f) On the diagram above, clearly indicate the activation energy, $E_a$, for the rate-determining step in the reaction.

\[\text{See drawing above in part (e).}\]

1 point is earned for the correct identification of $E_a$ in Step 1.
(e) Using the axes provided below, draw a curve that shows the energy changes that occur during the progress of the reaction. The curve should illustrate both the proposed two-step mechanism and the enthalpy change of the reaction.

\[
\begin{align*}
\text{Potential Energy} \\
\hline \\
\text{Progress of Reaction} \\
\end{align*}
\]

\[\text{\text{-}72.6 = } \Delta H\]

(f) On the diagram above, clearly indicate the activation energy, \(E_a\), for the rate-determining step in the reaction.

(a) As a gas heats up, the molecules begin to move faster causing collisions to occur more frequently, which raises the pressure. A higher temperature also causes a higher average kinetic energy, which means the collisions are more forceful, which also creates a higher pressure.

(b) The reaction goes from 2 total moles to 1 total mole as the reaction occurs. The molecules collide and become one molecule which lowers the total moles and causes collisions to become less frequent.

(c) \[\text{rate} = k [C_2H_4][HCl]\]

(d) Both \(C_2H_5^+\) and \(Cl^-\) are intermediates because they are created in one step and used up in another.
(c) Using the axes provided below, draw a curve that shows the energy changes that occur during the progress of the reaction. The curve should illustrate both the proposed two-step mechanism and the enthalpy change of the reaction.

![Potential Energy vs Progress of Reaction Diagram](image)

(f) On the diagram above, clearly indicate the activation energy, $E_a$, for the rate-determining step in the reaction.

(a) When temperature is increased, the gas molecules contain more kinetic energy and move at a higher speed. As the velocity of the gas particles is increased, collisions with the container wall happen at a higher frequency; therefore the pressure increases.

(b) As the reaction proceeds, two moles of reactants are turned into only one mole of product. Since the number of moles of the gas molecules in the container is decreased, fewer numbers of collisions with the container wall occur, thus decreasing the pressure.

(c) Rate = [C$_2$H$_4$] [HCl] 

(d) C$_2$H$_5$+
(e) Using the axes provided below, draw a curve that shows the energy changes that occur during the progress of the reaction. The curve should illustrate both the proposed two-step mechanism and the enthalpy change of the reaction.

![Diagram of potential energy vs. progress of reaction]

(f) On the diagram above, clearly indicate the activation energy, $E_a$, for the rate-determining step in the reaction.

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(i) According to the gas laws, if volume is constant, the change in temperature has a direct relationship with the change in gas. As temperature rises, the molecules have more kinetic energy, so they are moving around even faster, increasing collision in a closed container, causing an increase in pressure.

(b) If it reached the vapor pressure equilibrium, so the addition of a new gas will initially increase the total pressure, but the it will try to maintain equilibrium within the container.

c. reaction $= k(C_2H_5Cl)$

d. An intermediate: $C_2H_5^+(g)$
Overview

This question assessed students’ ability to provide molecular level descriptions to explain experimental observations and examine a proposed reaction mechanism. In part (a) students applied principles of kinetic molecular theory to explain why the pressure of a gas sample increases with temperature. In part (b) students used the concept of gas stoichiometry to link the decreased number of molecules to the observed decrease in the pressure after the reaction occurs. Part (c) asked students to write a rate law that is consistent with the proposed reaction mechanism. Part (d) required students to identify the intermediates in the proposed mechanism. In parts (e) and (f), students constructed a reaction-energy profile illustrating a two-step, exothermic reaction, and labeled the $E_a$ for the first step.

Sample: 5A
Score: 8

This response addresses the question and earned 8 points. In part (a) the distinction is made between frequency of collisions and force of collisions. In part (b), the link between reaction stoichiometry and molecular-level changes is explicit. In part (d), the term “intermediate” is nicely defined, though this is not required. The graph shows a two-step reaction, with the first step having the greater $E_a$, and the labeling is precise.

Sample: 5B
Score: 6

This good response earned all but 2 points. In part (a) increased molecular speed is linked to increased frequency of collisions with the container wall, but the increased force of the collisions is not mentioned; thus only 1 point was earned. The rate law in part (c) omits the rate constant so the point was not earned.

Sample: 5C
Score: 4

This response earned 4 points. The $P/T$ argument in part (a) earned no credit (arguments based on $PV = nRT$ are at the bulk level and not the molecular level), but the response earned 1 of 2 points for correctly citing the increased number of collisions. In part (b) vapor pressure and equilibrium arguments are not pertinent so the point was not earned. The rate law in part (c) is based on the product, not the reactants so the point was not earned. In part (e), the curve reflects a one-step reaction, but earned 1 of 2 points for indicating an exothermic process, and the $E_a$ indication is precise enough to earn the point in part (f).