Worksheet 25 – Reaction Mechanisms and Catalysis Key

1. Define what is meant by unimolecular and bimolecular steps.

**Unimolecular steps are steps that involve only one reactant, bimolecular steps involve 2 reactants.** If the steps are elementary steps in a mechanism, the molecularity is also the reaction order for the rate. That is, a unimolecular elementary step has a first order rate.

2. Why are termolecular steps infrequently seen in chemical reactions?

**Termolecular steps involve three reactants, and its just statistically less likely that three reactants can all come together with proper orientation and energy to react.**

3. Define rate determining step.

This is the slow step in a mechanism that determines how fast or slow the overall reaction can proceed.

4. What criteria must a mechanism meet in order to be valid?

The steps in a mechanism must add up to give the overall reaction, and the rate law proposed by the mechanism (i.e., the rate of the rate determining step) must match the experimental rate law.

5. Identify the molecularity and write the rate law for each of the following elementary reactions:

   (a) \( \text{I}_2(g) \rightarrow 2\text{I}(g) \) **Unimolecular, only one species reacting, Rate = \( k [\text{I}_2] \)**

   (b) \( 2\text{NO}(g) + \text{Br}_2(g) \rightarrow 2\text{NOBr}(g) \) **Termolecular, Rate = \( k [\text{NO}]^2[\text{Br}_2] \)**

   (c) \( \text{CH}_3\text{Br}(aq) + \text{OH}^-(aq) \rightarrow \text{CH}_3\text{OH}(aq) + \text{Br}^-(aq) \) **Bimolecular, Rate = \( k [\text{CH}_3\text{Br}][\text{OH}^-] \)**

   (d) \( \text{N}_2\text{O}_5(g) \rightarrow \text{NO}_2(g) + \text{NO}_3(g) \) **Unimolecular, Rate = \( k [\text{N}_2\text{O}_5] \)**

6. The reaction \( 2 \text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g) \) exhibits the rate law

   \[ \text{Rate} = k [\text{NO}]^2[\text{O}_2]. \]

Is the following mechanisms consistent with this rate law? **NO! Rate of slow step gives rate law: rate = \( k[\text{NO}]^2 \)**

\[
\begin{align*}
2 \text{NO} & \rightarrow \text{N}_2\text{O}_2 & \text{Slow} \\
\text{N}_2\text{O}_2 + \text{O}_2 & \rightarrow \text{N}_2\text{O}_4 & \text{Fast}
\end{align*}
\]
N\textsubscript{2}O\textsubscript{4} \rightarrow 2 \text{ NO}_2 \quad \text{Fast}

List any reaction intermediates and/or catalysts \( \text{N}_2\text{O}_4 \) and \( \text{N}_2\text{O}_2 \) are intermediate

9. Define catalyst.

**A catalyst is a species that is not consumed in the overall reaction and helps to increase the rate of reaction by providing a reaction pathway with lower activation energy.**

10. Draw a rough sketch of the reaction energy diagram (potential energy profile) for an endothermic reaction with and without a catalyst, labeling \( \Delta H \), \( E_a \), reactants, transition state, and products.

![Reaction Energy Diagram]

**NOTE** that the catalyzed path should start at same energy as uncatalyzed. The major change, as shown, is that \( E_a \) is lower for the catalyzed path, so reaction proceeds faster. **NOTE** also that \( \Delta H \) is the same

11. In the upper atmosphere, chlorofluorcarbons, such as CFCl\textsubscript{3}, absorb sunlight, and subsequent fragmentation produces Cl atoms. The Cl atoms participate in the following mechanism for the destruction of ozone:

\[
\text{Cl}(g) + \text{O}_3(g) \rightarrow \text{ClO}(g) + \text{O}_2(g) \\
\text{ClO}(g) + \text{O}(g) \rightarrow \text{Cl}(g) + \text{O}_2(g)
\]

(a) Write the chemical equation for the overall reaction.

\[
\text{O}_3(g) + \text{O}(g) \rightarrow 2 \text{ O}_2(g)
\]

(b) What is the role of the Cl atoms in this reaction?
Cl atoms are used in first reaction, but regenerated in second, so overall they are not consumed – Cl atoms act as a catalyst

(c) Is ClO a catalyst or a reaction intermediate?
   ClO is a reaction intermediate

(d) What distinguishes a catalyst from an intermediate?
   A catalyst is not consumed in the overall process, whereas an intermediate is – its generated in one step and used up in the next