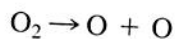
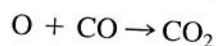


A gas that undergoes decomposition on the surface of a solid is the most common type of zero-order reaction. For example, a catalytic converter in an automobile converts carbon monoxide to carbon dioxide. Diatomic oxygen molecules are absorbed onto the metal catalyst and then converted into monatomic oxygen atoms by a zero-order reaction.



The oxygen atoms then react with carbon monoxide to produce carbon dioxide:



The **half-life** of a reaction, $t_{1/2}$, is the time required for the initial concentration of a reactant to fall to half its value.

For a first-order reaction: $t_{1/2} = 0.693/k$.

For a second-order reaction: $t_{1/2} = 1/k[A]_0$.

Notice that for a first-order reaction, the half-life is independent of the concentration of the reactant A. The half-life is inversely proportional to the rate constant.

Table 14.2 summarizes the mathematical relationships of first- and second-order reactions.

Table 14.2 Mathematical relationships of first-, second-, and zero-order kinetics.

Order of Reaction	First	Second	Zero
Differential rate law	Rate = $k[A] = -\Delta[A]/\Delta t$	Rate = $k[A]^2 = -\Delta[A]/\Delta t$	Rate = $k = -\Delta[A]/\Delta t$
Integrated rate law	$\ln[A]_t = -kt + \ln[A]_0$ or $\ln([A]_0/[A]_t) = +kt$	$1/[A]_t = kt + 1/[A]_0$	$[A]_t = -kt + [A]_0$ or $[A]_0 = +kt + [A]_t$
Half-life	$t_{1/2} = 0.693/k$	$t_{1/2} = 1/k[A]_0$	$t_{1/2} = [A]_0/2k$
Straight line plot	$\ln[A]$ versus time	$1/[A]$ versus time	$[A]$ versus time
Slope =	$-k$	k	$-kt$

Temperature and Rate Section 14.5

Generally, increasing temperature increases reaction rate. The collision model, based on kinetic-molecular theory, says that for molecules to react they must collide. Temperature increases the speed of molecules, and as molecules move faster, they collide more frequently and with more energy, increasing the fraction of molecules that have sufficient energy to react. Thus, the probability for reaction increases and so does the rate. Figure 14.4 shows that at a higher temperature, a higher fraction of molecules have sufficient energy to react than at a lower temperature.

Figure 14.9 shows how the rate constant for a chemical reaction varies with temperature. Generally, the rate constant increases with increasing temperature.

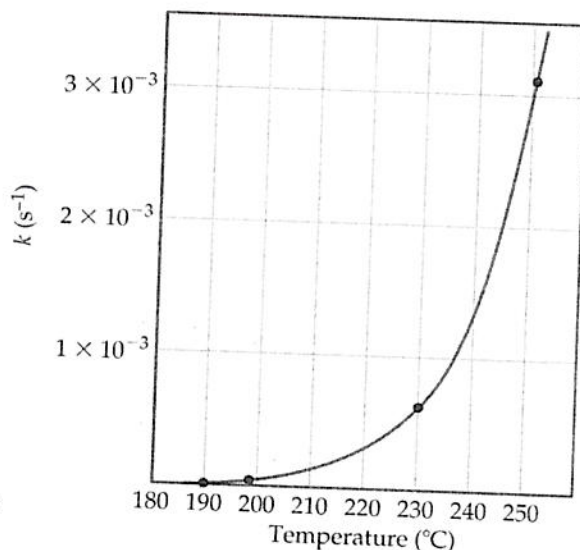


Figure 14.9 The rate constant, k , varies with temperature, T .

The algebraic equation that describes the line in Figure 14.9 relates activation energy, E_a , to the rate constant, k , at various temperatures, T .

$$\ln(k_1/k_2) = (E_a/R)(1/T_2 - 1/T_1)$$

k_1 = the rate constant at temperature T_1

k_2 = the rate constant at temperature T_2

E_a is the activation energy

(All temperatures must be expressed in Kelvin.)

$R = 8.314 \text{ J/K mol}$

Figure 14.10 shows the **energy profile** of a typical exothermic reaction. The y-axis represents relative energies of the molecules in the system. The x-axis represents the progress of the reaction as successful molecular collisions of reactants produce products.

Activation energy, E_a , is the minimum amount of energy required to initiate a chemical reaction. The activation energy can be considered to be an energy barrier that molecules must overcome before they react. On the energy profile in Figure 14.10, the activation energy is the energy difference between the reactants and the highest point of the profile.

The **enthalpy of the reaction, ΔH ,** on the reaction profile is the difference between the energy of reactants and energy of products.

The **activated complex** (also called the **transition state**) is the highest energy arrangement of molecules as they change from reactants to products. The very top of the energy profile represents the energy of the activated complex.

A **catalyst** acts to lower the activation energy of a chemical reaction and thus increases the rate of reaction.

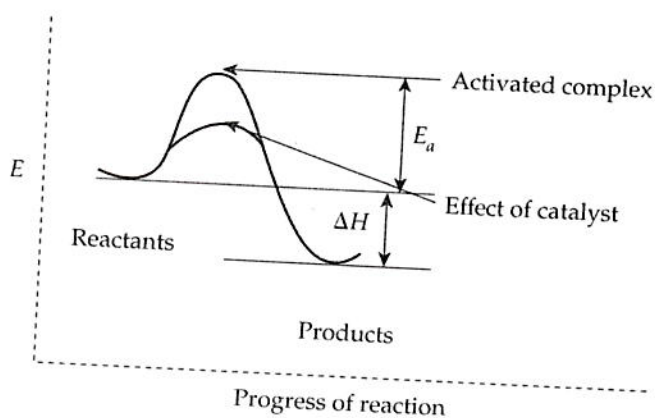


Figure 14.10 Energy profile for a typical exothermic reaction showing activation energy, E_a , change in enthalpy, ΔH , and the effect of a catalyst.

For any reaction, the higher the activation energy, the slower the rate. Very fast reactions have low activation energies and slow reactions have high activation energies. At any given temperature, only a fraction of reactant molecules have sufficient energy to react. If a reaction profile has a relatively high activation energy, relatively few molecular collisions will result in a reaction. If the activation energy is low, more collisions will produce products. Increasing the temperature of a reaction increases the fraction of molecules having sufficient activation energies to react, so the rate of the reaction increases with increasing temperature.

Figure 14.11 illustrates the relationship of activation energy to reaction rate. Profile 1 describes a reaction with the fastest rate because it has the lowest activation energy, the lowest difference between reactants and the transition state. The reaction for Profile 2 has the slowest rate because it has the highest activation energy.

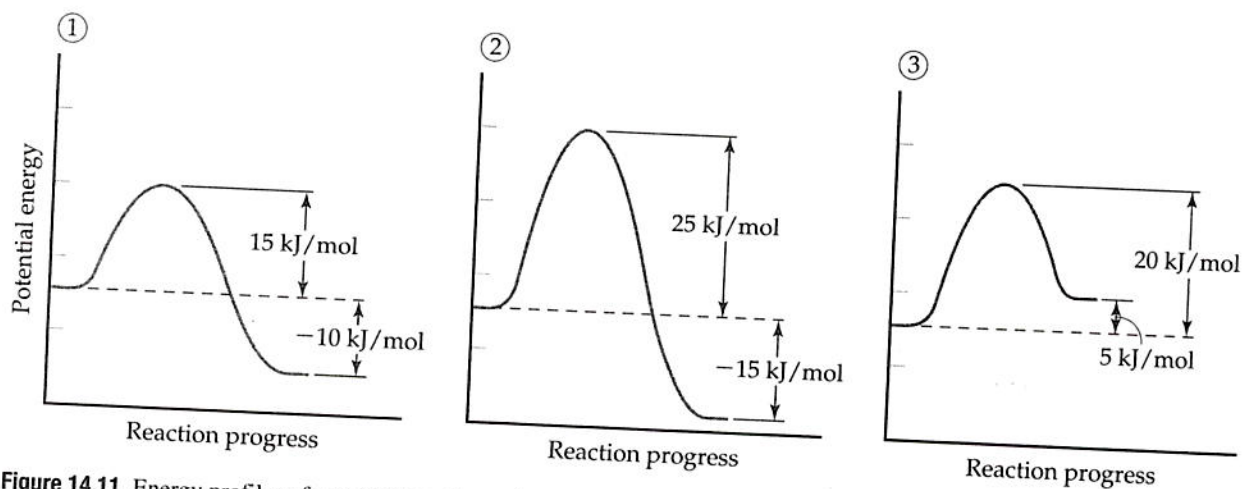


Figure 14.11 Energy profiles of two exothermic reactions and one endothermic reaction showing the activation energies. The higher the activation energy, the higher the rate of reaction.

Your Turn 14.6

- Explain using collision theory why temperature affects the rate of reaction.
- Consider the reactions shown in Figure 14.11. Rank the relative rates of the REVERSE reactions for Profiles 1, 2, and 3. Justify your answer.
- Which reaction (forward or reverse) in Figure 14.11 will have the highest temperature dependence? Why?

Write your answer in the space provided.

Section 14.6

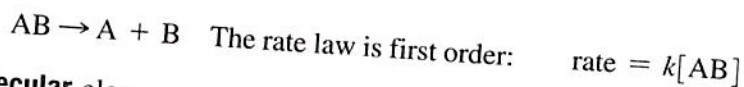
Reaction Mechanisms

A **reaction mechanism** is the step-by-step process by which a chemical reaction occurs.

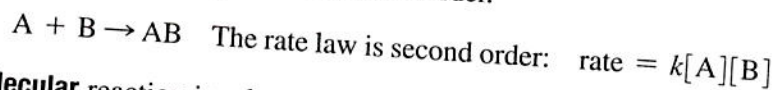
An **elementary reaction** is each single event or single step in a mechanism.

The **molecularity** of a reaction is the number of molecules that participate as reactants in an elementary reaction.

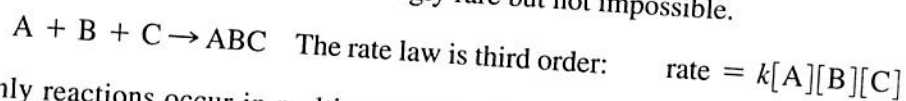
A **unimolecular** elementary reaction involves one reactant molecule. It is first order, meaning that only one reactant molecule participates. That molecule is likely activated by collisions with the solvent.



A **bimolecular** elementary reaction involves the direct collision of two reactant molecules. A bimolecular process is second order.



A **termolecular** reaction involves the simultaneous collision of three reactant molecules. A termolecular reaction is exceedingly rare but not impossible.

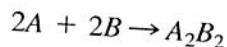


Commonly reactions occur in multistep mechanisms. Each individual step is an elementary reaction and the sum of the individual steps gives the balanced chemical

equation for the overall process. Usually, we write each elementary step in a mechanism to be a unimolecular or bimolecular process because termolecular processes are rare.

Example:

Consider the following overall process and write a mechanism that can explain how reactants A and B become the product A_2B_2 . Write the rate law for each elementary step.



Solution:

By invoking only unimolecular and bimolecular elementary steps, a possible mechanism is:

Elementary step	Rate law for each elementary step
1. $A + A \rightarrow A_2$	$\text{Rate} = k[A]^2$
2. $A_2 + B \rightarrow A_2B$	$\text{Rate} = k[A_2][B]$
3. $A_2B + B \rightarrow A_2B_2$	$\text{Rate} = k[A_2B][B]$
$2A + 2B \rightarrow A_2B_2$	

Notice that the sum of the elementary steps of a mechanism gives the chemical equation for the overall process.

An **intermediate** is a chemical species that is formed in one elementary step of a multistep mechanism and consumed in another. In the above mechanism, A_2 and A_2B are intermediates. An intermediate is neither a reactant nor a product of the overall reaction. Intermediates never appear in the rate law for the overall reaction.

Chemists often seek to detect intermediates in a reaction mixture to obtain clues about the mechanism of the reaction.

The **rate-determining step** is the slowest step of a multistep mechanism and governs the rate of the overall reaction.

The slowest step in a multistep mechanism is reflected in the rate law. The rate law includes only those reactant molecules that react during and before the rate-determining step. Therefore, the rate law must be determined experimentally and cannot be determined from the overall balanced equation.

For example, if Step 1 in the above mechanism is the slowest step, the rate law is $\text{rate} = k[A]^2$, because two molecules of A and zero molecules of B have taken part in the mechanism up to this step.

If Step 2 is slowest, the rate law will be $\text{rate} = k[\text{A}]^2[\text{B}]$, because two molecules of A and one molecule of B have taken part through Step 2 of the mechanism.

If Step 3 is slowest, the rate law will include two molecules of A and two molecules of B, because they all have taken part through Step 3 of the mechanism: $\text{rate} = k[\text{A}]^2[\text{B}]^2$.



Common misconception: A rate law that is third order or higher does not mean that the mechanism involves a three-molecule collision of reactants. Most often it involves a series of unimolecular and bimolecular elementary steps, the sum of which add to the overall balanced equation as shown in the example above.

Your Turn 14.7

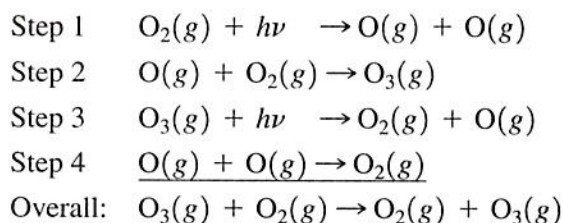
Propose an alternate mechanism for the overall reaction: $2\text{A} + 2\text{B} = \text{A}_2\text{B}_2$.
Identify any intermediates involved. Write your answer in the space provided.

Section 14.7

Catalysis

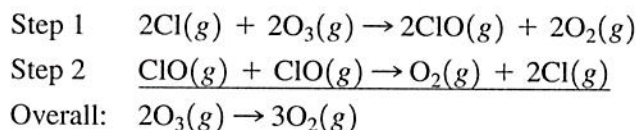
A **catalyst** is a substance that increases the rate of a chemical reaction without undergoing a permanent change in the process. Generally, catalysts act by changing the mechanism of a reaction, so that the slowest step in the uncatalyzed reaction does not exist in the catalyzed process. The effect of a catalyst is to lower the activation energy of the overall process by replacing the slowest step with one or more faster steps having activation energies lower than that of the uncatalyzed rate-determining step.

To illustrate the action of a catalyst that changes the reaction mechanism, consider the ozone cycle, the process that cycles diatomic oxygen to ozone and back to diatomic oxygen in the upper atmosphere. In its simplest form, the mechanism might look something like this:



Steps 1–4 continually repeat, producing and destroying ozone at the same rate while absorbing harmful ultraviolet radiation ($h\nu$) from the sun.

It has been shown that chlorine atoms from chlorofluorocarbons released to the atmosphere catalyze the $\text{O}_3 \rightarrow \text{O}_2$ reaction. The net result is that ozone is depleted faster than it is generated by the natural cycle. Thus, chlorine atoms from chlorofluorocarbons catalytically deplete ozone in the stratosphere. In its simplest form, the mechanism that catalyzes O_3 to O_2 is:



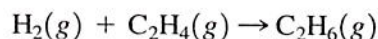
Notice that $\text{ClO}(g)$ is an intermediate. $\text{ClO}(g)$ is generated as a product in one elementary step and is consumed as a reactant in another later elementary step. Experimental detection of intermediates is an important means to study reaction mechanisms.

By contrast, Cl is a catalyst. It is consumed as a reactant in one elementary step and is regenerated as a product in a later step. A catalyst increases the rate of a chemical reaction without undergoing a permanent change. A catalyst acts by providing a different mechanism for the reaction, one that has a lower activation energy.

A catalyst is present at the start of a reaction, whereas an intermediate is formed as the reaction progresses.

(For more detailed information about the natural ozone cycle and its catalytic depletion by chlorofluorocarbons, see Section 18.2 of *Chemistry: The Central Science*.)

A catalyst can act by stabilizing the transition state, therefore lowering the activation energy. For example, the uncatalyzed reaction of hydrogen gas with ethene to produce ethane is not likely to occur by way of simple bimolecular collisions because the activation energy to break the $\text{H}-\text{H}$ bonds is too high.



However, Figure 14.12 shows that at the surface of a metal catalyst, the $\text{H}-\text{H}$ bonds readily break and the hydrogen atoms attach easily to the ethane molecule.

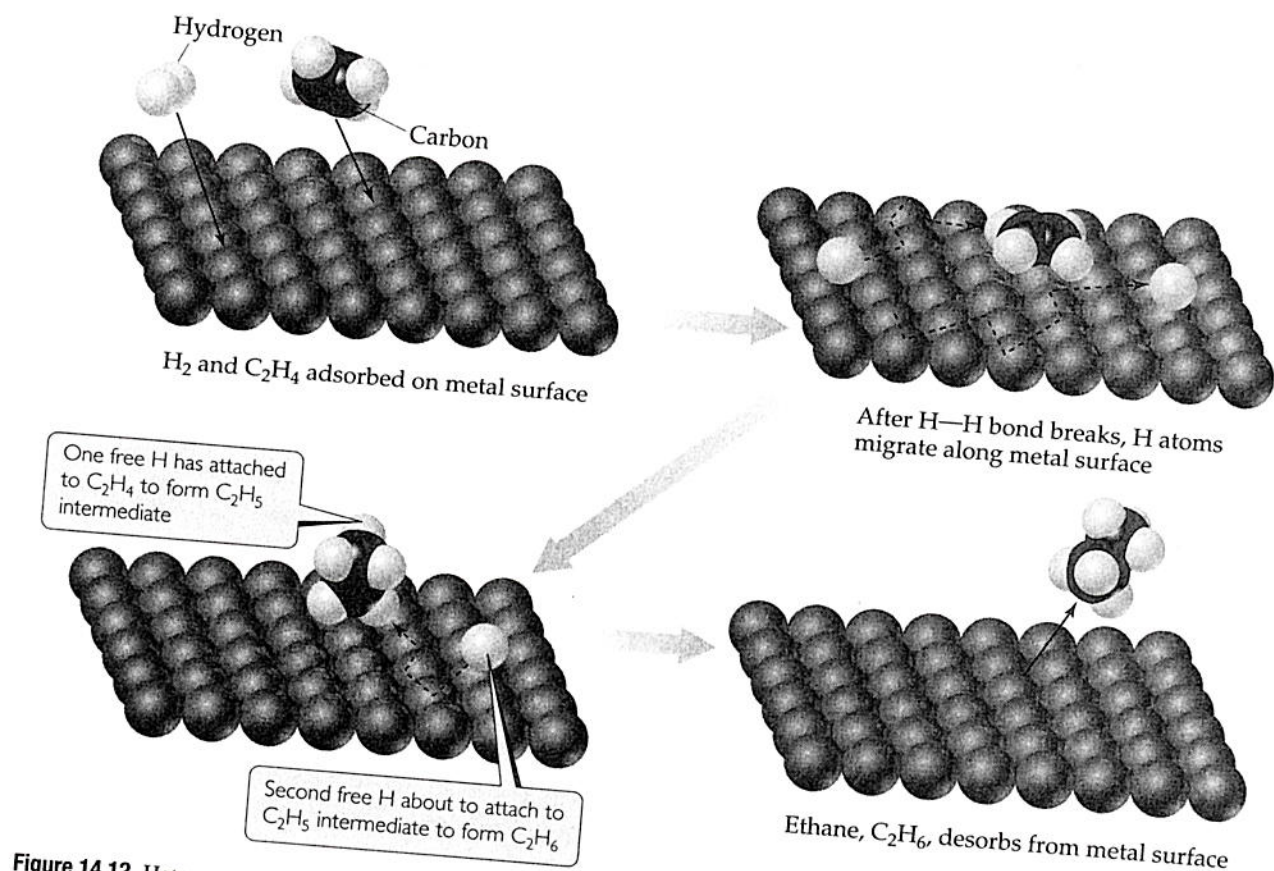


Figure 14.12 Heterogeneous catalysis. Mechanism for reaction of ethylene with hydrogen on a catalytic surface.

An **enzyme** is a large biomolecule called a protein that acts to catalyze specific biochemical reactions. Figure 14.13 shows the oversimplified lock-and-key model for enzyme catalysis. A smaller molecule called a substrate fits neatly into and binds with a geometric active site on the enzyme. The binding of this enzyme-substrate complex is accomplished by hydrogen bonding, dipole-dipole interactions, and dispersion forces. Upon binding, the electronic environment of the substrate molecule is changed causing it to break apart to form products. The enzyme acts to greatly lower the activation energy of an otherwise improbable reaction.

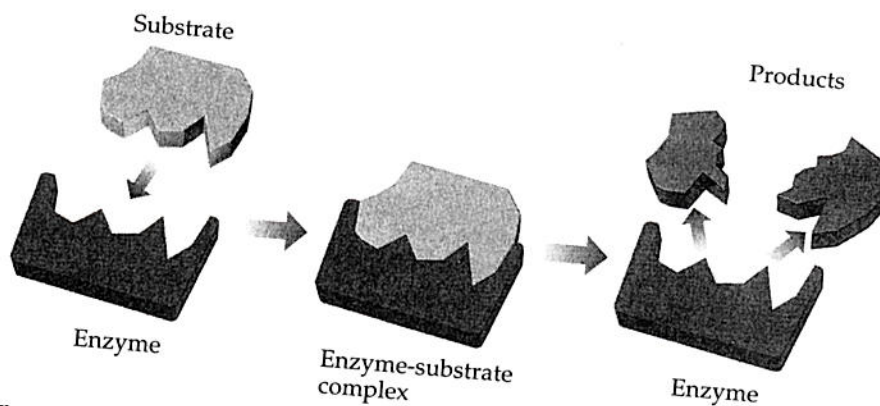


Figure 14.13 Lock-and-key model for enzyme action.

Multiple Choice Questions

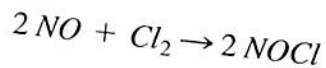
1. Which of these change with time for a first-order reaction?
 - I. rate of reaction
 - II. rate constant
 - III. half-life
 - IV. concentration of reactant
 - A) I only
 - B) III only
 - C) I and II only
 - D) II and III only
 - E) I and IV only
2. Under certain conditions, the average rate of appearance of oxygen gas in the reaction:
$$2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$$
is 6.0 torr s^{-1} . What is the average rate expressed in units of torr s^{-1} for the disappearance of O_3 ?
 - A) 9.0
 - B) 6.0
 - C) 4.0
 - D) 3.0
 - E) 1.2
3. For irreversible chemical reactions, the rate will be affected by changes in all of these factors EXCEPT
 - A) temperature.
 - B) concentration of reactants.
 - C) presence of a catalyst.
 - D) concentration of products.
 - E) surface area of solid reactant.
4. The rate expression for a third-order reaction could be:
 - A) $\text{rate} = k[\text{X}]$
 - B) $\text{rate} = k[\text{X}]^2[\text{Y}]$
 - C) $\text{rate} = k[\text{X}][\text{Y}]$
 - D) $\text{rate} = k[\text{X}]^2[\text{Y}]^2$
 - E) $\text{rate} = k[\text{X}]^2$

5. The slowest step of a reaction mechanism is called the
- A) elementary step.
 - B) inhibitor.
 - C) rate law.
 - D) rate-determining step.
 - E) catalyst.
6. The dissociation of XY molecules, as shown below, occurs at a temperature of 800 K. The rate constant $k = 6.0 \times 10^{-3} \text{ s}^{-1}$.
- $$2XY(g) \rightarrow X_2(g) + Y_2(g)$$
- What is the reaction order?
- A) 0
 - B) 1
 - C) 2
 - D) 3
 - E) 4
7. The rate law of a certain reaction is $\text{rate} = k[X][Y]$. The units of k , with time measured in seconds, is
- A) s^{-1} .
 - B) $\text{M}^{-1}\text{s}^{-2}$.
 - C) $\text{M}^{-2}\text{s}^{-1}$.
 - D) M^{-1} .
 - E) $\text{M}^{-1}\text{s}^{-1}$.
8. For a first-order reaction of half-life 75 min, what is the rate constant in min^{-1} ?
- A) $(0.693)/75$
 - B) $(0.693)/1.25$
 - C) $(0.693)(75)$
 - D) $75/(0.693)$
 - E) 0.693
9. The half-life of ^{14}C is 5730 years. Approximately how many years will it take for 94% of a sample to decay?
- A) 5730
 - B) 2×5730
 - C) 3×5730
 - D) 4×5730
 - E) 5×5730

10. A reaction between X_2 and Y was found to be described by the rate equation:
 $\text{rate} = k[X_2][Y]^2$. What can be said about the process?
- A) The balanced chemical equation for the reaction is $X_2 + 2Y \rightarrow X_2Y_2$.
 - B) The rate-determining step must be a three-atom collision.
 - C) The rate-determining step must be the first step of a multistep mechanism.
 - D) The mechanism is most likely to be multistep.
 - E) The mechanism must consist of just one elementary step.

Free Response Questions

1. The overall chemical equation for the reaction of nitrogen oxide, NO , with chlorine, Cl_2 , is:



The initial rates of reaction for various concentrations of the reactants were measured and recorded at constant temperature as follows:

Experiment	$[NO](M)$	$[Cl_2](M)$	$-\Delta[Cl_2]/\Delta t (M/h)$
1	0.25	0.50	0.75
2	0.25	1.00	3.02
3	0.50	2.00	24.10

- a. Determine the rate law for this reaction.
 - b. Calculate the numerical value for the rate constant and specify the units.
 - c. What is the order of this reaction with respect to each reactant and what is the overall order of the reaction?
 - d. What is the rate of disappearance of Cl_2 when the initial concentrations of the reactants are $[NO] = 0.50 M$ and $[Cl_2] = 0.10 M$?
 - e. When Cl_2 is disappearing at $4.5 M/h$, what is the rate of appearance of $NOCl$?
 - f. What is the rate of appearance of $NOCl$ when the initial concentrations of the reactants are $[NO] = 0.20 M$ and $[Cl_2] = 0.30 M$?
2. Consider the proposed mechanism for the reaction between nitrogen monoxide and hydrogen gas. Assume the mechanism is correct.
- Step 1: $2NO \rightarrow N_2O_2$
- Step 2: $N_2O_2 + H_2 \rightarrow N_2O + H_2O$
- Step 3: $N_2O + H_2 \rightarrow N_2 + H_2O$
- a. Use the steps in the mechanism to determine the overall balanced equation for the reaction. Clearly show your method.
 - b. If Step 2 is the rate-determining step, write the rate law for the reaction. Explain your answer.

- c. If the observed rate law is $\text{rate} = k[\text{NO}]^2[\text{H}_2]^2$, which step is rate determining? Explain your reasoning.
 - d. Identify all the intermediates in the mechanism.
 - e. If the first step is the rate-determining step, what is the order of the reaction with respect to each reactant?
3. Consider the exothermic reaction between nitrogen monoxide and ozone to form nitrogen dioxide and diatomic oxygen.
- a. Write and balance a chemical equation.
 - b. Convert the chemical equation into a particle view of the molecules.
 - c. Sketch an energy profile for the reaction and use particle views to label the reactants and products. Show the effect a catalyst might have on the energy profile.
 - d. Draw a possible transition state for the bimolecular reaction. Use dashed lines to represent the bonds that break and those that form.