Skills to Develop

- Explain elementary steps.
- Write the expression for elementary steps.

## Reaction Mechanism - Elementary Process

A **mechanism** for a reaction is a collection of elementary processes (also called elementary steps or elementary reactions) that explains how the overall reaction proceeds.

A mechanism is a proposal from which you can work out a rate law that agrees with the observed rate laws. The fact that a mechanism explains the experimental results is not a proof that the mechanism is correct. A mechanism is our rationalization of a chemical reaction, and devising mechanisms is an excellent academic exercise.

The animation here shows an elementary step of two molecules colliding with each other and exchanging a hydrogen atom in the process. Since elementary processes are the language of mechanisms, let us first define elementary processes or steps.

### Elementary Processes or Steps

An **elementary process** is also called an **elementary step** or **elementary reaction**. It expresses how molecules or ions actually react with each other. The equation in an elementary step represents the reaction at the molecular level, not the overall reaction. Based on numbers of molecules involved in the elementary step, there are three kinds of elementary steps: unimolecular step (or process), bimolecular process, and trimolecular process.

An elementary step is proposed to give the reaction rate expression. The rate of an elementary step is always written according to the proposed equation. This practice is very different from the derivation of rate laws for an overall reaction.

When a molecule or ion decomposes by itself, such an elementary step is called a **unimolecular step (or process)**. A unimolecular step is always a first order reaction. The following examples are given to illustrate this point:

\[
\text{\( \ce{O3 \rightarrow O2 + O} \), \( \text{Rate} = k \ce{[O3]} \)}
\]

or in general

\[
\text{\( \ce{A \rightarrow B + C + D} \), \( \text{Rate} = k \ce{[A]} \)}
\]

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A trimolecular process involves the collision of three molecules. For example:

\[ \text{O + O}_2 + \text{N}_2 \rightarrow \text{O}_3 + \text{N}_2, \text{Rate} = k \text{[O][O}_2][\text{N}_2]\]

\[ \text{O + NO + N}_2 \rightarrow \text{NO}_2 + \text{N}_2, \text{Rate} = k \text{[O][NO][N}_2]\]

Three molecules colliding at an instant is rare, but occasionally these are some of the ways reactions take place.

Elementary processes are written to show how a chemical reaction progresses leading to an overall reaction. Such a collection is called a reaction mechanism. In a mechanism, elementary steps proceed at various speeds. The slowest step is the rate-determining step. The order for that elementary process is the order of a reaction, but the concentrations of reactants in that step must be expressed in terms of the concentrations of the reactants.

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**Deriving Rate Laws From Reaction Mechanisms**

The following example illustrates how elementary steps are used to represent a reaction mechanism. In particular, a slow step in a mechanism determines the rate of a reaction.

Example 1

If the reaction

\[ \text{2 NO}_2 + \text{F}_2 \rightarrow \text{2 NO}_2\text{F} \]

follows the mechanism

\[ \text{\[mathrm{i.}\] \text{[i]}; \text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}: (\text{slow})} \]
Work out the rate law.

**SOLUTION**

Since step i. is the rate-determining step, the rate law is

$$-rac{1}{2} \frac{\text{d}[\text{NO}_2]}{\text{dt}} = k [\text{NO}_2][\text{F}_2]$$

Addition of i. and ii. gives the overall reaction.

**DISCUSSION**

This example illustrates that the overall reaction equation has nothing to do with the order of the reaction. The elementary process in the rate-determining step determines the order.

Other possible elementary steps in this reaction are:

$$\text{F} + \text{F}_2 \rightarrow \text{F}_2 + \text{F}$$

$$\text{NO}_2\text{F} + \text{F} \rightarrow \text{F} + \text{NO}_2\text{F}$$

but they do not lead to the formation of products.

To propose a mechanism requires the knowledge of chemistry to give plausible elementary processes. A freshman in chemistry will not be asked to propose mechanisms, but you will be asked to give the rate laws from a given mechanism.

**Summary**

The number of particles involved in an elementary step is called the **molecularity**, and in general, we consider only the molecularity of 1, 2, and 3. Types of elementary steps are summarized below. In the table, \(\text{A}, \text{B}, \text{C}\) represent reactants, intermediates, or products in the elementary process.

<table>
<thead>
<tr>
<th>Molecularity</th>
<th>Elementary step</th>
<th>Rate law</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\text{A} \rightarrow \text{products})</td>
<td>(\text{rate} = k [\text{A}])</td>
</tr>
<tr>
<td>2</td>
<td>(\text{A} + \text{A} \rightarrow \text{products})</td>
<td>(\text{rate} = k [\text{A}]^2)</td>
</tr>
<tr>
<td></td>
<td>(\text{A} + \text{B} \rightarrow \text{products})</td>
<td>(\text{rate} = k [\text{A}] [\text{B}])</td>
</tr>
<tr>
<td>3</td>
<td>(\text{A} + \text{A} + \text{A} \rightarrow \text{products})</td>
<td>(\text{rate} = k [\text{A}]^3)</td>
</tr>
</tbody>
</table>
Questions

1. Which one of the following is a bimolecular process?
   a. \( \ce{A \rightarrow products} \)
   b. \( \ce{A + A \rightarrow products} \)
   c. \( \ce{A + A + A \rightarrow products} \)

   Hint: b. \( \ce{A + A \rightarrow products} \)

   Skill -
   Recognize and name all three elementary steps.

2. What is the order of a trimolecular process (or step)?

   Hint: Third order

   Skill -
   Give the order of any elementary step.

3. An excited atom or molecule loses its energy either by emitting a photon or by collision with some other molecule. For example,

   \( \text{Hg}^* \rightarrow \text{Hg} + \text{light} \)
   \( \text{Hg}^* + \text{Ar} \rightarrow \text{Hg} + \text{Ar}^* \)

   What is the order of light emission?

   Hint: First order for the light emission step.

   Skill -
   Emission of light is first order, but use a number.

Contributors

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