12.1: Reaction Mechanisms

A **reaction mechanism** is a set of **elementary reactions** steps, that when taken in aggregate define a chemical pathway that connects reactants to products. An elementary reaction is one that proceeds by a single process, such a molecular (or atomic) decomposition or a molecular collision. Typically, elementary reactions only come in **unimolecular**

$$A \rightarrow products$$

and **bimolecular**

$$A + B \rightarrow products$$

form. Occasionally, an elementary step that is **termolecular**

$$A + B + C \rightarrow products$$

(involved the simultaneous collision of three atoms or molecules) but it is generally a pair of bimolecular steps acting in rapid succession, the first forming an activated complex, and the second stabilizing that complex chemically or physically.

$$A + B \rightarrow AB^*$$

$$AB^* + C \rightarrow AB + C^*$$

The wonderful property of elementary reactions is that the **molecularity** defines the order of the rate law for the reaction step.

The Requirements of a Reaction Mechanism

A valid reaction mechanism must satisfy three important criteria:

1. The sum of the steps must yield the overall stoichiometry of the reaction.
2. The mechanism must be consistent with the observed kinetics for the overall reaction.
3. The mechanism must account for the possibility of any observed side products formed in the reaction.

Example 12.1.1:

For the reaction

$$A + B \rightarrow C$$

is the following proposed mechanism valid?

$$A + A \xrightarrow{k_1} A_2$$

$$A_2 + B \xrightarrow{k_1} C + A$$

Solution

Adding both proposed reactions gives

$$2A + A_2 + B \rightarrow A_2 + C + A$$

Canceling those species that appear on both sides of the arrow leaves

$$A + B \rightarrow C$$

which is the reaction, so the mechanism is at least stoichiometrically valid. However, it would still have to be consistent with the observed kinetics for the reaction and account for any side-products that are observed.

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