Reaction Mechanisms

Although a balanced equation indicates the substances present at the beginning and end of a chemical reaction, it does not indicate the actual details of the reaction. The rearrangement of atoms that takes place during a chemical reaction is often a complicated process. In fact, most chemical reactions occur as the result of several steps, each of which consists of a simple chemical reaction.

A series of steps that leads from reactants to products is called a **reaction mechanism**. A detailed reaction mechanism describes the order in which bonds break and atoms rearrange throughout the course of a chemical reaction. Each individual step in a reaction mechanism is called an **elementary step**.

Consider the following reaction.

$$2NO(g) + F_2(g) \rightarrow 2NOF(g)$$

Although the reaction seems simple from the equation, this is not the case. Chemists have found that this reaction involves two elementary steps.

Step 1: $NO(g) + F_2(g) \rightarrow NOF_2(g)$

The product of this first step then becomes a reactant in the second elementary step.

Step 2: $NOF_2(g) + NO(g) \rightarrow 2NOF(g)$

If you write an equation that shows all the reactants and products from both the elementary steps, you will see that the sum of the two equations gives the general equation for the reaction.

$$NO(g) + F_2(g) + NOF_2(g) + NO(g) \rightarrow NOF_2(g) + 2NOF(g)$$

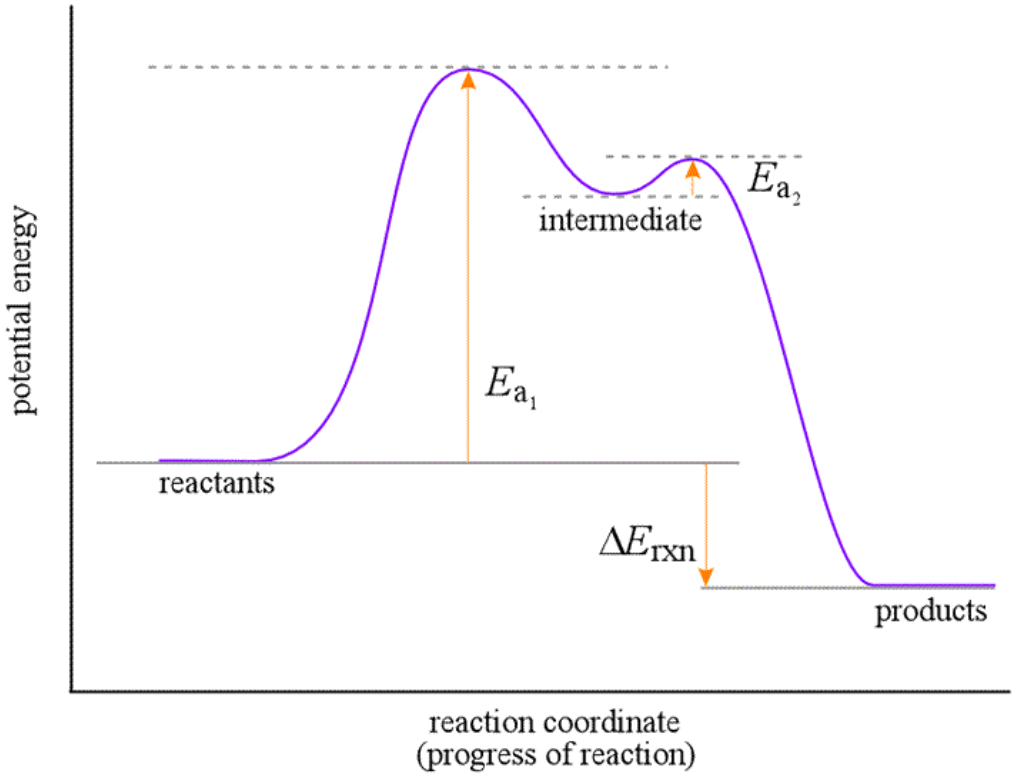
$$2NO(g) + F_2(g) \rightarrow 2NOF(g)$$

Notice that NOF_2 does not appear as either a reactant of product in the overall equation. This is because, although it is produced in the first elementary step, it is consumed in the second. Substances that are produced in one step of a reaction but consumed in a later step are called intermediate products, or **intermediates**.

Each elementary step in a reaction mechanism proceeds at its own rate. One step might proceed quickly while another might proceed slowly. The rate of the overall reaction is limited by the rate of the slowest elementary step. For this reason, the slowest elementary step is called the **rate-determining step**.

Energy Diagram of a Reaction Mechanism

The diagram below illustrates the energy changes that take place during a sample reaction mechanism.



This particular reaction mechanism consists of two elementary steps, indicated by the two peaks on the reaction pathway. Each step has a corresponding activation energy, as indicated. The step with the largest activation energy is the rate-determining step.

The enthalpy of the first elementary step is the energy difference between the intermediate and the reactants.

$$\Delta H_1 = H_{intermediate} - H_{reactants}$$

The enthalpy of the second elementary step is the difference between the energy of the products and the energy of the intermediate.

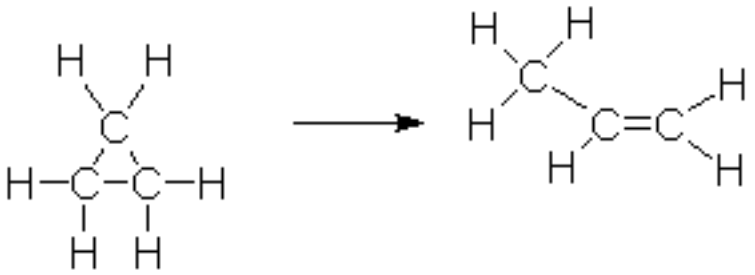
$$\Delta H_2 = H_{products} - H_{intermediate}$$

The enthalpy of the overall reaction is the difference between the energy of the product(s) and the energy of the reactants, but may also be calculated by adding the enthalpies of the elementary steps.

$$\Delta H = \Delta H_1 + \Delta H_2$$

Molecularity

In chemistry, **molecularity** refers to the number of colliding particles (reactant particles) involved in an elementary step. An elementary step involving a single particle is called **unimolecular**.



An elementary step involving two particles is called **bimolecular**. In the reaction that we considered at the start of this lesson, both elementary steps were bimolecular.

$$NO(g) + F_2(g) \rightarrow NOF_2(g)$$

$$NOF_2(g) + NO(g) \rightarrow 2NOF(g)$$

An elementary step involving three particles is called **termolecular**. Termolecular reactions are very rare, due to the extreme unlikelihood of three particles colliding with the correct orientation and sufficient energy.

Worksheet

1. What is a reaction mechanism? An intermediate?

2. The reaction $2HBr(g) + NO_2(g) \rightarrow H_2O(g) + NO(g) + Br_2(g)$ is thought to occur by the following mechanism:

   Step 1: $HBr(g) + NO_2(g) \rightarrow HOBr(g) + NO(g)$ $\Delta H_1 = 4.2\ kJ$ (slow)

   Step 2: $HBr(g) + HOBr(g) \rightarrow H_2O(g) + Br_2(g)$ $\Delta H_2 = -86.2\ kJ$ (fast)

   a) Draw the energy diagram that depicts this reaction mechanism. Your diagram should accurately show the relative energies of the reactants, intermediate, and products. It should also show the relative activation energies of the two elementary steps.

   b) Are there any intermediates in this reaction mechanism? Explain why or why not. If any intermediates exist, what are their formulas?

3. It is believed that the following two elementary steps make up the mechanism for the reaction between nitrogen monoxide and chlorine gas:

   Step 1: $NO(g) + Cl_2(g) \rightarrow NOCl_2(g)$

   Step 2: $NOCl_2(g) + NO(g) \rightarrow 2NOCl(g)$

   Write the equation for the overall reaction and identify any intermediates in the reaction mechanism.