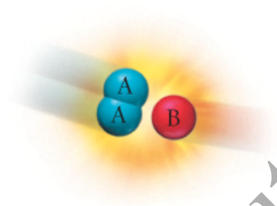
14.2: Rates of Reaction and the Particulate Nature of Matter

We have seen throughout this book that matter is composed of particles (atoms, ions, and molecules). The simplest way to begin to understand the factors that influence a reaction rate is to think of a chemical reaction as the result of a collision between these particles. This is the basis of *the collision model*, which we cover in more detail in Section 14.6. For example, consider the following simple generic reaction occurring in the gaseous state:

$$A - A + B \rightarrow A - B + A$$

According to the collision model, the reaction occurs as a result of a collision between A-A particles and B particles.



The rate at which the reaction occurs—that is, how many particles react per unit time—depends on several factors: (a) the concentration of the reacting particles; (b) the temperature; and (c) the structure and relative orientation of the reacting particles. We examine each of these individually.

The Concentration of the Reactant Particles

We saw in Chapter 10 that we can model a gas as a collection of particles in constant motion. The particles frequently collide with one another and with the walls of their container. The greater the number of particles in a given volume—that is, the greater their *concentration*—the greater the number of collisions per unit time. Since a chemical reaction requires a collision between particles, the rate of the reaction depends on the concentration of the particles.

The first person to accurately measure this effect was Ludwig Wilhelmy (1812–1864). In 1850, he measured how fast sucrose, upon treatment with acid, hydrolyzed (broke apart) into glucose and fructose. This reaction occurred over several hours, and Wilhelmy was able to show how the rate depended on the initial amount of sugar present—the greater the initial amount, the faster the initial rate. We more thoroughly examine the relationship between reaction rate and reactant concentration in Section 14.4.

The Temperature of the Reactant Mixture

We saw in Section 14.1 that chemical reactions generally occur faster with increasing temperature. We can understand this behavior based on particle collisions. Let's return to our simple generic reaction:

$$A - A + B \rightarrow A - B + A$$

When B reacts with A-A, the A-A bond breaks and a new bond forms between A and B. *The initial breaking of the A-A bond, however, requires energy*, and even though the forming of A-B gives off energy, some energy, called the *activation energy*, is required to get the reaction started. The energy needed to begin to break the A-A bond can come from the kinetic energy of the colliding particles. In other words, the reaction between A-A and B can occur if there is enough energy in the collision to begin to break the A-A bond.

Recall from Section 10.2 that the average kinetic energy of a gas increases with increasing temperature. At low temperatures, very few of the particle collisions occur with enough energy to begin to break the A-A bond, so the reaction rate is slow. At high temperatures, many particle collisions occur with enough energy to begin to break the A-A bond, and the reaction rate is fast. Therefore, reaction rate increases with increasing temperature. We more thoroughly examine the relationship between reaction rate and temperature in Section 14.6.

The Structure and Orientation of the Colliding Particles

The rates of chemical reactions also depend on the *structure* and relative *orientation* of the colliding particles. We can understand this behavior by comparing two simple reactions:

$$\begin{aligned} A - A + B &\rightarrow A - B + A \\ A - X + B &\rightarrow A - B + X \end{aligned}$$

In the first reaction, B can collide with A-A from either side and result in a reaction. In the second reaction, however, B must collide with A-X only from one side (the A side). If B collides with A-X on the X side, the reaction cannot occur because B must form a bond with A, not X. As a result, in the second reaction many of the collisions that occur, even if they occur with enough kinetic energy, will not result in a reaction because the orientation of the colliding particles is not correct. In this way, the structure of the reactant particles influences the rate of the reaction. All other factors being equal, we expect the first reaction to occur with a faster rate than the second one. We examine examples of the structure dependence of reaction rates in Section 14.6.

Conceptual Connection 14.1 Particle Collisions and Reaction Rates

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