5.1: Chemical Kinetics

A reaction mechanism describes the sequence of bond-making, bond-breaking, and intramolecular-rearrangement steps that results in the overall chemical change. These individual steps are called ***elementary reactions*** or ***elementary processes***. In an elementary reaction, no intermediate species is formed; that is, none of the arrangements of atoms that occur during the elementary reaction has a lifetime greater than the duration of a molecular vibration, which is typically from 10^{-12} to 10^{-14} seconds. We expand on this point in Section 5.6.

We can distinguish two levels of detail in a chemical reaction mechanism: The first is the series of elementary processes that occurs for a given net reaction. This is called the ***stoichiometric mechanism***. Frequently it is also possible to infer the relative positions of all of the atoms during the course of a reaction. This sort of model is called an ***intimate*** mechanism or ***detailed mechanism***.

A ***rate law*** is an equation that describes how the observed reaction rate depends on the concentrations of the species involved in the reaction. This concentration dependence can be determined experimentally. We will see that any series of elementary reactions predicts the dependence of reaction rates on concentrations, so one of the first tests of a proposed mechanism is that it be consistent with the rate law that is observed experimentally. (If the overall reaction proceeds in more than one step and the concentration of an intermediate species becomes significant, we may need more than one equation to adequately describe the rates of all of the reactions that occur.)

The rate law plays a central role in our study of reaction rates and mechanisms. We infer the rate law from experimental measurements. We must be able to prove that the experimental rate law is consistent with any mechanism that we propose. The rate law that we deduce from experimental rate data constitutes an experimental fact. Our hypothesized mechanism is a theory. We can entertain the idea that the theory may be valid only so long as its predictions about the rate law are consistent with the experimental result. We can predict rate laws for elementary processes by rather simple arguments. For a mechanism involving a series of elementary processes, we can often predict rate laws by making simplifying assumptions. When simplifying assumptions are inadequate, we can use numerical integration to test agreement between the proposed mechanism and experimental observations of the dependence of the reaction rate on the concentrations of the species involved in the reaction. We will see that a given experimental rate law may be consistent with any of several mechanisms. In such cases, we must develop additional information in order to discriminate among the several mechanisms.

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