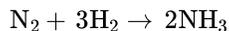


18.1: Prelude to Kinetics

Chemical kinetics is concerned with the rates of chemical reactions, that is, whether reactions proceed quickly or slowly. As we have already mentioned, some spontaneous reactions are extremely slow. An example is the Haber-process synthesis of ammonia:



with $\Delta G_m^\circ(298 \text{ K}) = -33.27 \text{ kJ mol}^{-1}$

Even though a negative ΔG_m° predicts that this reaction can occur at room temperature, it is of little value unless chemists can find some way to speed it up. On the other hand we often want to slow down undesirable reactions, such as spoilage of food or decomposition of wood. Hence it is quite useful to know how factors such as temperature, concentrations of reactants and products, and catalysts will affect the rates of reactions. Moreover, studying these factors gives valuable information about the sequence of microscopic events by which a reaction occurs. Knowledge of when and where bonds are formed and broken as well as how molecular structures change during a reaction can be very useful in helping us to devise ways to speed up or slow down that reaction.

Chemical kinetics is concerned with the rates of chemical reactions, the dependence of those rates on temperature, concentration, and catalysts, and the microscopic mechanisms by which reactions occur. The [rate of a reaction](#) is defined in terms of the change in concentration of a reactant or product per unit time, and it usually decreases as the reaction progresses. The reaction rate ordinarily is proportional to the concentrations of reactants and/or products, each raised to a power called the order with respect to that reactant or product. When the concentration of a species which is not a reactant or product in the overall reaction affects the rate, that species is called a catalyst. An equation expressing the dependence of reaction rate on concentrations is called a [rate equation](#) or rate law.

On a [microscopic level](#), a reaction usually involves [unimolecular processes](#), in which a single molecule changes structure, or [bimolecular processes](#), in which two molecules collide. One determinant of rate in this situation is frequency of collisions as seen in the animation on this page. Collision of [three or more molecules simultaneously](#) is much less probable. In both uni- and bimolecular elementary processes an activation energy barrier must be surmounted before product molecules can be produced. The species at the top of a graph of energy versus reaction coordinate is called the activated complex or transition state. Because of this energy barrier only a small fraction of the molecules are energetic enough to reach the transition state, but that fraction increases rapidly as temperature increases, and so reaction rates are strongly dependent on temperature. The [temperature dependence](#) of the rate constant can be used to obtain the activation energy by means of [an Arrhenius plot](#).

This animation displays the number of collisions that occur between the dark blue particle and a set of lighter blue particles. When hit, a lighter blue particle changes to black. A second hit changes a black particle to a red particle, so that the number of collisions can be easily counted. The frequency at which the dark blue particles hits light blue particles is an important determinant of how quickly a reaction will go.

Most reactions occur in two or more steps. Such a sequence of elementary processes is called a [reaction mechanism](#), and the overall rate is determined by the slowest, or rate-limiting, step. The experimental rate law tells us the composition of the activated complex for the rate-limiting step, but often several mechanisms are possible which agree with the rate law. Other evidence must then be used to decide among these mechanisms.

A [catalyst](#) speeds up a reaction by changing the mechanism so that the activation energy is lowered. Many [heterogeneous catalysts](#) are of great industrial importance, but the most efficient catalysts known are the enzymes in living organisms. An enzyme operates by adsorbing a substrate molecule at an active site whose structure is exactly right to stretch bonds which are to be broken or to hold atoms in position while new bonds form. This almost ideal structure of the active site makes enzymes highly specific and extremely efficient catalysts.

Contributors

- Ed Vitz (Kutztown University), [John W. Moore](#) (UW-Madison), [Justin Shorb](#) (Hope College), [Xavier Prat-Resina](#) (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.

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