

## 5.7: Rate Laws for Elementary Processes

### Bimolecular Elementary Processes

If we think about an elementary bimolecular reaction rate law between molecules  $A$  and  $B$ , we recognize that the reaction can occur only when the molecules come into contact. They must collide before they can react. So the probability that they react must be proportional to the probability that they collide, and the number of molecules of product formed per unit time must be proportional to the number of  $A - B$  collisions that occur in unit time. In our development of the collision theory for bimolecular reactions in the gas phase, (§4-12 to §4-16), we find that the number of such collisions is proportional to the concentration of each reactant. It is clear that this conclusion must apply to any bimolecular reaction.

If we have a vessel containing some concentration of  $A$  molecules and some concentration of  $B$  molecules, the collection experiences some number of  $A - B$  collisions per unit time. If we double the concentration of  $B$  molecules, each  $A$  molecule is twice as likely as before to encounter a  $B$  molecule. Indeed, for any increase in the concentration of  $B$  molecules, the number of collisions of an  $A$  molecule with  $B$  molecules increases in the same proportion. The number of  $A - B$  collisions must be proportional to the concentration of  $B$  molecules. Likewise, increasing the concentration of  $A$  molecules must increase the number of  $A - B$  collisions proportionately; the number of  $A - B$  collisions must also be proportional to the concentration of  $A$  molecules. We conclude that the rate for any bimolecular reaction between molecular substances  $A$  and  $B$  is described by the equations

$$R = \frac{1}{V} \frac{dn_A}{dt} = \frac{1}{V} \frac{dn_B}{dt} = -k_2 [A] [B]$$

This is a second-order rate law, and the proportionality constant,  $k_2$ , is called a second-order rate constant.

In Section 5.4-5.16, we derive an equation for the frequency with which a type 1 molecule collides with type 2 molecules in the gas phase when the concentration of type 2 molecules is  $N_2$  and the kinetic energy along the line of centers exceeds a threshold value,  $\epsilon_a$  per molecule, or  $E_a$  per mole. The rate at which such collisions occur is

$$\rho_{12}(\epsilon_a) = N_1 N_2 \sigma_{12}^2 \left( \frac{8\pi kT}{\mu} \right)^{1/2} \exp \left( \frac{-\epsilon_a}{kT} \right)$$

which is just  $\exp(-\epsilon_a/kT)$  times the rate at which collisions of any energy occur between molecules of type 1 and molecules of type 2. If reaction occurs at every collision between a molecule 1 and a molecule 2 in which the kinetic energy along the line of centers exceeds  $\epsilon_a$ , the collision rate,  $\rho_{12}(\epsilon_a)$ , equals the reaction rate. We have  $R = \rho_{12}(\epsilon_a)$ .

If the temperature-dependence of the rate constant is given by the Arrhenius equation, the rate of the bimolecular reaction between species 1 and species 2 is

$$R = k_2 N_1 N_2 = \left[ A \exp \left( \frac{-E_a}{RT} \right) \right] N_1 N_2$$

where  $A$  is independent of temperature and  $E_a = \bar{N}\epsilon_a$ . The collision-theory model for the bimolecular reaction is almost the same; the difference being a factor of  $T^{1/2}$  in the pre-exponential factor,  $\sigma_{12}^2(8\pi kT/\mu)^{1/2}$ . The effect of the  $T^{1/2}$  term is usually small in comparison to the effect of temperature in the exponential term. Thus, the temperature dependence predicted by collision theory, which is a highly simplified theoretical model, and that predicted by the Arrhenius equation, which is an empirical generalization usually used to describe data taken over a limited temperature range, are in substantial agreement.

Experimentally determined values of the pre-exponential factor for gas-phase bimolecular reactions can approach the value calculated from collision theory. However, particularly for reactions between polyatomic molecules, the experimental value is often much smaller than the calculated collision frequency. We rationalize this observation by recognizing that our colliding-spheres model provides no role for the effect of molecular structures. When the colliding molecules are not spherical, the collision angle is an incomplete description of their relative orientation. If the relative orientation of two colliding molecules is unfavorable to reaction, it is entirely plausible that they can fail to react no matter how energetic their collision. To recognize this effect, we suppose that the reaction rate is proportional to a **steric factor**,  $\gamma$ , where  $\gamma$  represents the probability that a colliding pair of molecules have the relative orientation that is necessary for reaction to occur. Of course,  $\gamma$  must be less than one. Taking this amplification of the collision model into account, the relationship between the reaction rate and the collision frequency becomes

$$\frac{d\xi}{dt} = \gamma \rho_{12}(\varepsilon_a)$$

When we consider reactions in solution, we recognize that there are usually many more solvent molecules than reactant molecules. As a result, collisions of a reactant molecule with solvent molecules are much more frequent than collisions of a molecule of one reactant with a molecule of another reactant. The high frequency of collisions with solvent molecules means that the net distance moved by a reactant molecule in unit time is much less in solution than in a gas. This decreases the probability that two reactant molecules will meet. On the other hand, once two reactant molecules near one another, the solvent molecules tend to keep them together, and they are likely to collide with one another many times before they finally drift apart. (This is known as the [solvent-cage effect](#).) We can expect these effects to roughly offset one another.

## Termolecular Elementary Processes

A termolecular elementary process is a reaction in which three reactant molecules collide. For this to happen, an  $A$  molecule and a  $B$  molecule must be very close to one another at exactly the time that a  $C$  molecule encounters the pair of them. If the reactants are not very concentrated, the probability that a given  $A$  molecule is very close to a  $B$  molecule during any short time interval is small. The probability that this  $A$  molecule will be hit by a  $C$  molecule during the same time interval is also very small. The probability that all three species will collide at the same time is the product of two small probabilities; under any given set of conditions, the number of collisions involving three molecules is smaller than the number of collisions between two molecules. The probability of a termolecular collision and hence the rate of a termolecular elementary process is proportional to the concentrations of all three reacting species

$$R = \frac{1}{V} \frac{dn_A}{dt} = \frac{1}{V} \frac{dn_B}{dt} = \frac{1}{V} \frac{dn_C}{dt} = -k_2 [A] [B] [C]$$

However, the low probability of a termolecular collision means that we can expect the termolecular rate constant,  $k_3$ , to be very small. If termolecular mechanisms are rare, higher-molecularity mechanisms must be exceedingly rare, if, indeed, any occur at all. For most chemical reactions, the mechanism is a series of unimolecular and bimolecular elementary reactions.

## Unimolecular Elementary Processes

A unimolecular elementary process is one in which a molecule spontaneously undergoes a chemical change. If we suppose that there is a constant probability that any given  $A$  molecule undergoes reaction in unit time, then the total number reacting in unit time is proportional to the number of  $A$  molecules present. Let the average number of moles reacting in unit time be  $\overline{\Delta n_A}$ , the number of molecules in the system be  $n_A$ , and the proportionality constant be  $k$ . (We choose a unit of time that is small enough to insure that  $\overline{\Delta n_A} \ll n_A$ .) If the probability of reaction is constant, we have  $\overline{\Delta n_A} = -kn_A$ . Since  $\overline{\Delta n_A}$  is the number of moles that react in unit time, the number of moles that react in time  $\Delta t$  is  $\Delta n_A = \overline{\Delta n_A} \Delta t$ , so that

$$\overline{\Delta n_A} = \frac{\Delta n_A}{\Delta t} = -kn_A$$

Dividing by the volume of the system, we have

$$\frac{1}{V} \frac{\Delta n_A}{\Delta t} = -k \frac{n_A}{V}$$

In the limit that  $\Delta t \rightarrow 0$ , the term on the left becomes the reaction rate,  $R = V^{-1} (dn_A/dt)$ , and since  $n_A/V = [A]$ , we have

$$R = \frac{1}{V} \frac{dn_A}{dt} = -k [A]$$

Thus, a constant reaction probability implies that a unimolecular reaction has a first-order rate law. If the volume is constant, we have

$$\frac{d[A]}{dt} = -k [A]$$

The idea that a unimolecular reaction corresponds to a constant reaction probability can be rationalized by introducing a simple model of the reaction process. This model assumes that reactant molecules have a distribution of energies, that only molecules whose energies exceed some minimum can react, and that this excess energy must be in some specific internal motion before the

reaction can occur. Molecules exchange energy by colliding with one another. When a molecule acquires excess energy as the result of a collision, redistribution of this energy among the motions available to the molecule is not instantaneous. A characteristic length of time is required for excess energy to reach the specific internal motion that leads to reaction. Any given molecule can retain excess energy only for the short time between two collisions. The molecule gains excess energy in one collision and loses it in a subsequent one. Reaction can occur only if the excess energy reaches the specific internal motion before the molecule undergoes a deactivating collision. (We return to these ideas in §14 and §15.)

In summary, only two kinds of elementary processes are needed to develop a mechanism for nearly any chemical change. These elementary processes and their rate laws are:

**Unimolecular**  $A \rightarrow$

$$\frac{d[A]}{dt} = -k[A]$$

**Bimolecular**  $A + B \rightarrow$

$$\frac{d[A]}{dt} = -k[A][B]$$

Finally, we should note that we develop these rate laws for elementary processes under the assumption that the rate at which molecules collide is proportional to the concentrations of the colliding species. In doing so, we implicitly assume that intermolecular forces of attraction or repulsion have no effect on this rate. When our goal is to predict rate laws from reaction mechanisms, this assumption is almost always an adequate approximation. However, when we study chemical equilibria, we often find that we must allow for the effects of intermolecular forces in order to obtain an adequate description. In chemical thermodynamics, we provide for the effects of such forces by introducing the idea of a **chemical activity**. The underlying idea is that the chemical activity of a compound is the effective concentration of the compound—we can view it as the concentration “corrected” for the effects of intermolecular forces.

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