

6.4: The Effect of Temperature on Reaction Rate

Skills to Develop

The Learning Objective of this Module is to understand why and how chemical reactions occur.

It is possible to use kinetics studies of a chemical system, such as the effect of changes in reactant concentrations, to deduce events that occur on a microscopic scale, such as collisions between individual particles. Such studies have led to the collision model of chemical kinetics, which is a useful tool for understanding the behavior of reacting chemical species. According to the collision model, a chemical reaction can occur only when the reactant molecules, atoms, or ions collide with more than a certain amount of kinetic energy and in the proper orientation. The collision model explains why, for example, most collisions between molecules do not result in a chemical reaction. Nitrogen and oxygen molecules in a single liter of air at room temperature and 1 atm of pressure collide about 10^{30} times per second. If every collision produced two molecules of NO, the atmosphere would have been converted to NO and then NO₂ a long time ago. Instead, in most collisions, the molecules simply bounce off one another without reacting, much as marbles bounce off each other when they collide. The collision model also explains why such chemical reactions occur more rapidly at higher temperatures. For example, the reaction rates of many reactions that occur at room temperature approximately double with a temperature increase of only 10°C. In this section, we will use the collision model to analyze this relationship between temperature and reaction rates.

Activation Energy

Previously, we discussed that the average kinetic energy of the particles of a gas increases with increasing temperature. Because the speed of a particle is proportional to the square root of its kinetic energy, increasing the temperature will also increase the number of collisions between molecules per unit time. The simple observation that the molecules travel faster as they get warmer does not explain why the reaction rate of most reactions approximately doubles with a 10°C temperature increase. This result is surprisingly large considering that a 10°C increase in the temperature of a gas from 300 K to 310 K increases the kinetic energy of the particles by only about 4%, leading to an increase in molecular speed of only about 2% and a correspondingly small increase in the number of bimolecular collisions per unit time.

The collision model of chemical kinetics explains this behavior by introducing the concept of **activation energy (E_a)**. We will define this concept using the reaction of NO with ozone, which plays an important role in the depletion of ozone in the ozone layer:



Increasing the temperature from 200 K to 350 K causes the rate constant for this particular reaction to increase by a factor of more than 10, whereas the increase in the frequency of bimolecular collisions over this temperature range is only 30%. Thus something other than an increase in the collision rate must be affecting the reaction rate.

The reaction rate, not the rate constant, will vary with concentration. The rate constant, however, does vary with temperature. Figure **Table 6.4.1** shows a plot of the rate constant of the reaction of NO with O₃ at various temperatures. The relationship is not linear but instead resembles the relationships seen in graphs of vapor pressure versus temperature. In all three cases, the shape of the plots results from a distribution of kinetic energy over a population of particles (electrons in the case of conductivity; molecules in the case of vapor pressure; and molecules, atoms, or ions in the case of reaction rates). Only a fraction of the particles have sufficient energy to overcome an energy barrier.

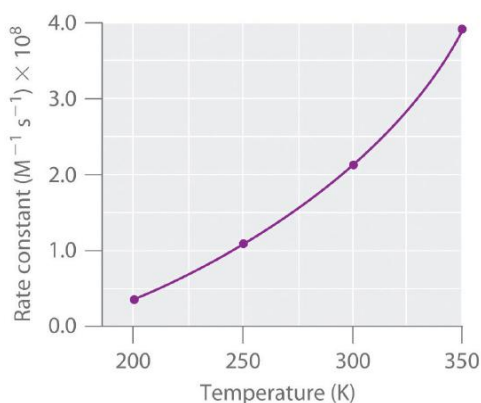


Figure 6.4.1: Rate Constant versus Temperature for the Reaction of NO with O_3 . The nonlinear shape of the curve is caused by a distribution of kinetic energy over a population of molecules. Only a fraction of the particles have enough energy to overcome an energy barrier, but as the temperature is increased, the size of that fraction increases.

In the case of vapor pressure, particles must overcome an energy barrier to escape from the liquid phase to the gas phase. This barrier corresponds to the energy of the intermolecular forces that hold the molecules together in the liquid. In conductivity, the barrier is the energy gap between the filled and empty bands. In chemical reactions, the energy barrier corresponds to the amount of energy the particles must have to react when they collide. This energy threshold, called the activation energy, was first postulated in 1888 by the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry 1903). It is the minimum amount of energy needed for a reaction to occur. Reacting molecules must have enough energy to overcome electrostatic repulsion, and a minimum amount of energy is required to break chemical bonds so that new ones may be formed. Molecules that collide with less than the threshold energy bounce off one another chemically unchanged, with only their direction of travel and their speed altered by the collision. Molecules that are able to overcome the energy barrier are able to react and form an arrangement of atoms called the **activated complex** or the **transition state** of the reaction. The activated complex is not a reaction intermediate; it does not last long enough to be detected readily.

Any phenomenon that depends on the distribution of thermal energy in a population of particles has a nonlinear temperature dependence.

Graphing Energy Changes during a Reaction

We can graph the energy of a reaction by plotting the potential energy of the system as the reaction progresses. Figure 6.4.2 shows a plot for the $\text{NO}-\text{O}_3$ system, in which the vertical axis is potential energy and the horizontal axis is the reaction coordinate, which indicates the progress of the reaction with time. The activated complex is shown in brackets with an asterisk. The overall change in potential energy for the reaction (ΔH , if the reaction is carried out at constant pressure) is negative, which means that the reaction releases energy. (In this case, ΔH is -200.8 kJ/mol .) To react, however, the molecules must overcome the energy barrier to reaction (E_a is 9.6 kJ/mol). That is, 9.6 kJ/mol must be put into the system as the activation energy. Below this threshold, the particles do not have enough energy for the reaction to occur.

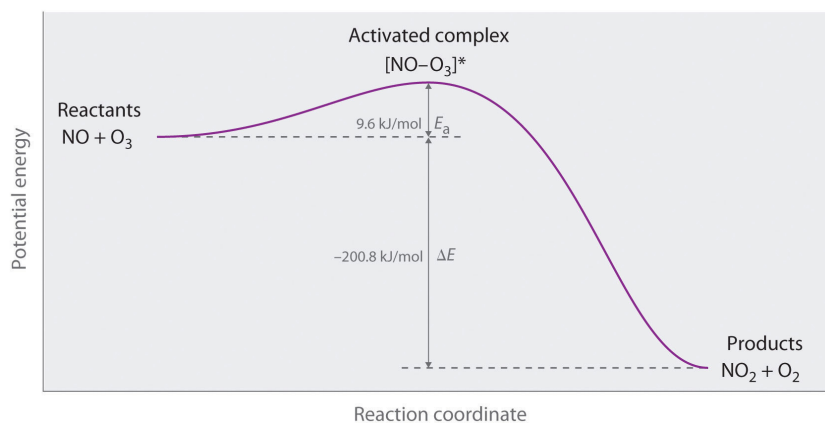


Figure 6.4.2: Energy of the Activated Complex for the NO–O₃ System. The diagram shows how the energy of this system varies as the reaction proceeds from reactants to products. Note the initial increase in energy required to form the activated complex.

Part (a) in Figure 6.4.3 illustrates the general situation in which the products have a lower potential energy than the reactants. In contrast, part (b) in Figure 6.4.3 illustrates the case in which the products have a higher potential energy than the reactants, so the overall reaction requires an input of energy; that is, it is energetically uphill, and $\Delta H > 0$. Although the energy changes that result from a reaction can be positive, negative, or even zero, in all cases an energy barrier must be overcome before a reaction can occur. This means that the activation energy is always positive.

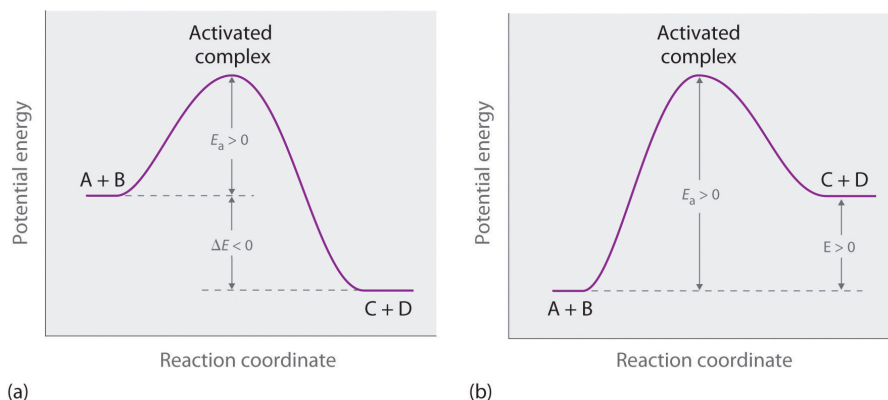


Figure 6.4.3: Differentiating between E_a and ΔH . The potential energy diagrams for a reaction with (a) $\Delta H < 0$ and (b) $\Delta H > 0$ illustrate the change in the potential energy of the system as reactants are converted to products. E_a is always positive. For a reaction such as the one shown in (b), E_a must be greater than ΔH .

For similar reactions under comparable conditions, the one with the smallest E_a will occur most rapidly.

Whereas ΔH is related to the tendency of a reaction to occur spontaneously, E_a gives us information about the reaction rate and how rapidly the reaction rate changes with temperature. For two similar reactions under comparable conditions, the reaction with the smallest E_a will occur more rapidly.

Even when the energy of collisions between two reactant species is greater than E_a , however, most collisions do not produce a reaction. The probability of a reaction occurring depends not only on the collision energy but also on the spatial orientation of the molecules when they collide. For NO and O₃ to produce NO₂ and O₂, a terminal oxygen atom of O₃ must collide with the nitrogen atom of NO at an angle that allows O₃ to transfer an oxygen atom to NO to produce NO₂ (Figure 6.4.4). All other collisions produce no reaction. Because fewer than 1% of all possible orientations of NO and O₃ result in a reaction at kinetic energies greater than E_a , most collisions of NO and O₃ are unproductive. The fraction of orientations that result in a reaction is called the **steric factor** (p), and, in general, its value can range from 0 (no orientations of molecules result in reaction) to 1 (all orientations result in reaction).

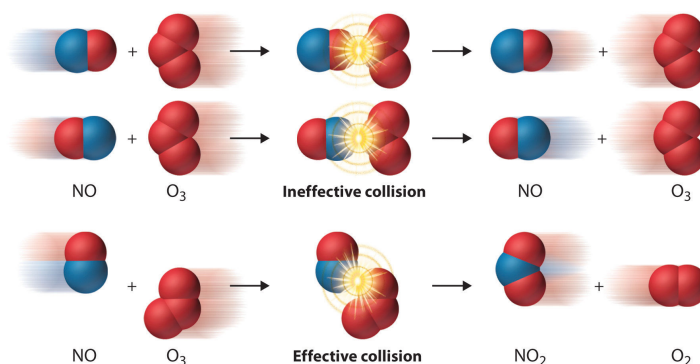


Figure 6.4.4: The Effect of Molecular Orientation on the Reaction of NO and O₃. Most collisions of NO and O₃ molecules occur with an incorrect orientation for a reaction to occur. Only those collisions in which the N atom of NO collides with one of the

terminal O atoms of O_3 are likely to produce NO_2 and O_2 , even if the molecules collide with $E > E_a$.

The Arrhenius Equation

Figure 14.5.5 shows both the kinetic energy distributions and a potential energy diagram for a reaction. The shaded areas show that at the lower temperature (300 K), only a small fraction of molecules collide with kinetic energy greater than E_a ; however, at the higher temperature (500 K) a much larger fraction of molecules collide with kinetic energy greater than E_a . Consequently, the reaction rate is much slower at the lower temperature because only a relatively few molecules collide with enough energy to overcome the potential energy barrier.

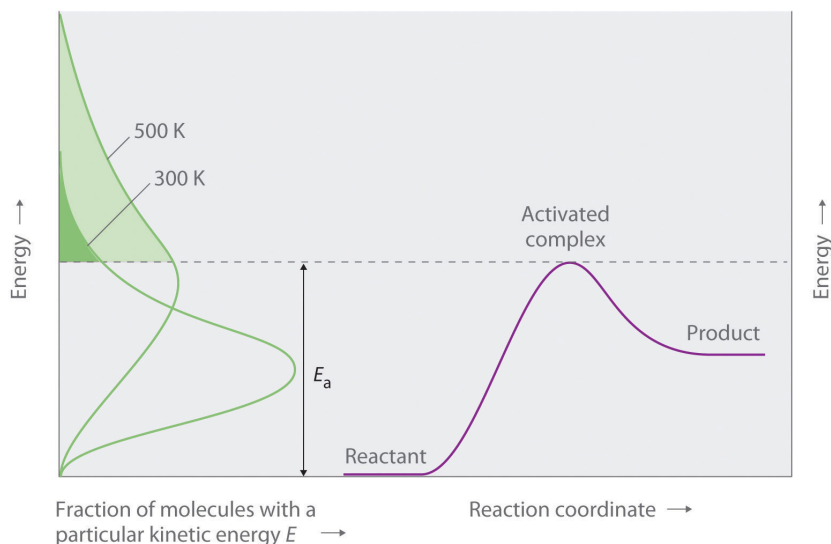


Figure 6.4.5: Surmounting the Energy Barrier to a Reaction. This chart juxtaposes the energy distributions of lower-temperature (300 K) and higher-temperature (500 K) samples of a gas against the potential energy diagram for a reaction. Only those molecules in the shaded region of the energy distribution curve have $E > E_a$ and are therefore able to cross the energy barrier separating reactants and products. The fraction of molecules with $E > E_a$ is much greater at 500 K than at 300 K, so the reaction will occur much more rapidly at 500 K.

For an $A + B$ elementary reaction, all the factors that affect the reaction rate can be summarized in a single series of relationships:

$$\text{rate} = (\text{collision frequency})(\text{steric factor})(\text{fraction of collisions with } E > E_a)$$

where

$$\text{rate} = k[A][B] \quad (6.4.2)$$

Arrhenius used these relationships to arrive at an equation that relates the magnitude of the rate constant for a reaction to the temperature, the activation energy, and the constant, A , called the **frequency factor**:

$$k = Ae^{-E_a/RT} \quad (6.4.3)$$

The frequency factor is used to convert concentrations to collisions per second. Because the frequency of collisions depends on the temperature, A is actually not constant. Instead, A increases slightly with temperature as the increased kinetic energy of molecules at higher temperatures causes them to move slightly faster and thus undergo more collisions per unit time. Equation 6.4.3 is known as the **Arrhenius equation** and summarizes the collision model of chemical kinetics, where T is the absolute temperature (in K) and R is the ideal gas constant [8.314 J/(K·mol)]. E_a indicates the sensitivity of the reaction to changes in temperature. The reaction rate with a large E_a increases rapidly with increasing temperature, whereas the reaction rate with a smaller E_a increases much more slowly with increasing temperature.

If we know the reaction rate at various temperatures, we can use the Arrhenius equation to calculate the activation energy. Taking the natural logarithm of both sides of Equation 6.4.3,

$$\ln k = \ln A + \left(-\frac{E_a}{RT}\right) = \ln A + \left[\left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right)\right] \quad (6.4.4)$$

Equation 6.4.4 is the equation of a straight line, $y = mx + b$, where $y = \ln k$ and $x = 1/T$. This means that a plot of $\ln k$ versus $1/T$ is a straight line with a slope of $-E_a/R$ and an intercept of $\ln A$. In fact, we need to measure the reaction rate at only two temperatures to estimate E_a .

Knowing the E_a at one temperature allows us to predict the reaction rate at other temperatures. This is important in cooking and food preservation, for example, as well as in controlling industrial reactions to prevent potential disasters.

Summary

For a chemical reaction to occur, an energy threshold must be overcome, and the reacting species must also have the correct spatial orientation. A minimum energy (activation energy, E_a) is required for a collision between molecules to result in a chemical reaction. Plots of potential energy for a system versus the reaction coordinate show an energy barrier that must be overcome for the reaction to occur. The arrangement of atoms at the highest point of this barrier is the activated complex, or transition state, of the reaction. At a given temperature, the higher the E_a , the slower the reaction. The fraction of orientations that result in a reaction is the steric factor. The frequency factor, steric factor, and activation energy are related to the rate constant in the Arrhenius equation: $k = Ae^{-E_a/RT}$.

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