

## 16: Reaction Rates

### Foundation

We will assume an understanding of the postulates of the **Kinetic Molecular Theory** and of the energetics of chemical reactions. We will also assume an understanding of phase equilibrium and reaction equilibrium, including the temperature dependence of equilibrium constants.

### Goals

We have carefully examined the observation that chemical reactions come to equilibrium. Depending on the reaction, the equilibrium conditions can be such that there is a mixture of reactants and products, or virtually all products, or virtually all reactants. We have not considered the time scale for the reaction to achieve these conditions, however. In many cases, the speed of the reaction might be of more interest than the final equilibrium conditions of the reaction. Some reactions proceed so slowly towards equilibrium as to appear not to occur at all. For example, metallic iron will eventually oxidize in the presence of aqueous salt solutions, but the time is sufficiently long for this process that we can reasonably expect to build a boat out of iron. On the other hand, some reactions may be so rapid as to pose a hazard. For example, hydrogen gas will react with oxygen gas so rapidly as to cause an explosion. In addition, the time scale for a reaction can depend very strongly on the amounts of reactants and their temperature.

In this concept development study, we seek an understanding of the rates of chemical reactions. We will define and measure reaction rates and develop a quantitative analysis of the dependence of the reaction rates on the conditions of the reaction, including concentration of reactants and temperature. This quantitative analysis will provide us insight into the process of a chemical reaction and thus lead us to develop a model to provide an understanding of the significance of reactant concentration and temperature.

We will find that many reactions proceed quite simply, with reactant molecules colliding and exchanging atoms. In other cases, we will find that the process of reaction can be quite complicated, involving many molecular collisions and rearrangements leading from reactant molecules to product molecules. The rate of the chemical reaction is determined by these steps.

### Observation 1: Reaction Rates

We begin by considering a fairly simple reaction on a rather elegant molecule. One oxidized form of buckminsterfullerene,  $C_{60}O_3$ , with a three oxygen bridge as shown in Figure 16.1.



**Figure 16.1:** Oxidized buckminsterfullerene

$C_{60}O_3$  is prepared from  $C_{60}$  dissolved in toluene solution at temperatures of  $0^\circ\text{C}$  or below. When the solution is warmed,  $C_{60}O_3$  decomposes, releasing  $O_2$  and creating  $C_{60}O$  in a reaction which goes essentially to completion. We can actually watch this process happen in time by measuring the amount of light of a specific frequency absorbed by the  $C_{60}O_3$  molecules, called the **absorbance**. The absorbance is proportional to the concentration of the  $C_{60}O_3$  in the toluene solution, so observing the absorbance as a function of time is essentially the same as observing the concentration as a function of time. One such set of data is given in Table 16.1, and is shown in the graph in Figure 16.2.

Table 16.1: Oxidized Buckminsterfullerene Absorbance during Thermal Decomposition at  $23^\circ\text{C}$

Time (minutes)	$C_{60}O_3$ absorbance
3	0.04241
9	0.03634
15	0.03121
21	0.02680
27	0.02311
33	0.01992
39	0.01721

Time (minutes)	C <sub>60</sub> O <sub>3</sub> absorbance
45	0.01484
51	0.01286
57	0.01106
63	0.00955
69	0.00827
75	0.00710
81	0.00616
87	0.00534
93	0.00461
99	0.00395



**Figure 16.2:** Oxidized Buckminsterfullerene Absorbance

The rate at which the decomposition reaction is occurring is clearly related to the rate of change of the concentration [C<sub>60</sub>O<sub>3</sub>], which is proportional to the slope of the graph in Figure 16.2. Therefore, we define the rate of this reaction as

$$\text{Rate} = -\frac{d[\text{C}_{60}\text{O}_3]}{dt} \cong -\frac{\Delta[\text{C}_{60}\text{O}_3]}{\Delta t} \quad (16.1)$$

We want the rate of reaction to be positive, since the reaction is proceeding forward. However, because we are measuring the rate of disappearance of the reactant in this case, that rate is negative. We include a negative sign in this definition of rate so that the rate in the equation is a positive number. Note also that the slope of the graph in Figure 16.2 should be taken as the derivative of the graph, since the graph is not a straight line. We will approximate that derivative by estimating the slope at each time in the data, taking the change in the absorbance of the C<sub>60</sub>O<sub>3</sub> divided by the change in time at each time step. The rate, calculated in this way, is plotted as a function of time in Figure 16.3.



**Figure 16.3:** Rate of Decomposition of C<sub>60</sub>O<sub>3</sub>

It is clear that the slope of the graph in Figure 16.2 changes over the course of time. Correspondingly, Figure 16.3 shows that the rate of the reaction decreases as the reaction proceeds. The reaction is at first very fast but then slows considerably as the reactant C<sub>60</sub>O<sub>3</sub> is depleted.

The shape of the graph for rate versus time (Figure 16.3) is very similar to the shape of the graph for concentration versus time (Figure 16.2). This suggests that the rate of the reaction is related to the concentration of C<sub>60</sub>O<sub>3</sub> at each time. Therefore, in Figure 16.4, we plot the rate of the reaction, defined in the equation above and shown in Figure 16.3, versus the absorbance of the C<sub>60</sub>O<sub>3</sub>.



**Figure 16.4:** Rate versus Concentration for C<sub>60</sub>O<sub>3</sub> Decomposition

We find that there is a very simple proportional relationship between the rate of the reaction and the concentration of the reactant. Therefore we can write

$$\text{Rate} = -\frac{d[\text{C}_{60}\text{O}_3]}{dt} \quad (16.2)$$

$$= k[\text{C}_{60}\text{O}_3] \quad (16.3)$$

where  $k$  is a proportionality constant. This equation shows that, early in the reaction when [C<sub>60</sub>O<sub>3</sub>] is large, the reaction proceeds rapidly, and that as C<sub>60</sub>O<sub>3</sub> is consumed, the reaction slows down. The rate equation above is an example of a **rate law**, expressing

the relationship between the rate of a reaction and the concentrations of the reactant or reactants. Rate laws are expressions of the relationship between experimentally observed rates and concentrations.

As a second example of a reaction rate, we consider the dimerization reaction of butadiene gas,  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ . Two butadiene molecules can combine to form vinylcyclohexene, shown in Figure 16.5.



**Figure 16.5:** Dimerization of Butadiene to Vinylcyclohexene

Table 16.2 provides experimental data on the gas phase concentration of butadiene  $[\text{C}_4\text{H}_6]$  as a function of time at  $T = 250^\circ\text{C}$ .

Table 16.2: Dimerization of Butadiene at  $250^\circ\text{C}$

Time (s)	$[\text{C}_4\text{H}_6]$ (M)	Rate (M/s)	$\frac{\text{Rate}}{[\text{C}_4\text{H}_6]}$	$\frac{\text{Rate}}{[\text{C}_4\text{H}_6]^2}$
0	0.0917	$9.48 \times 10^{-6}$	$1.03 \times 10^{-4}$	$1.13 \times 10^{-3}$
500	0.0870	$8.55 \times 10^{-6}$	$9.84 \times 10^{-5}$	$1.13 \times 10^{-3}$
1000	0.0827	$7.75 \times 10^{-6}$	$9.37 \times 10^{-5}$	$1.13 \times 10^{-3}$
1500	0.0788	$7.05 \times 10^{-6}$	$8.95 \times 10^{-5}$	$1.14 \times 10^{-3}$
2000	0.0753	$6.45 \times 10^{-6}$	$8.57 \times 10^{-5}$	$1.14 \times 10^{-3}$
2500	0.0720	$5.92 \times 10^{-6}$	$8.22 \times 10^{-5}$	$1.14 \times 10^{-3}$
3000	0.0691	$5.45 \times 10^{-6}$	$7.90 \times 10^{-5}$	$1.14 \times 10^{-3}$
3500	0.0664	$5.04 \times 10^{-6}$	$7.60 \times 10^{-5}$	$1.14 \times 10^{-3}$
4000	0.0638	$4.67 \times 10^{-6}$	$7.32 \times 10^{-5}$	$1.15 \times 10^{-3}$

We can estimate the rate of reaction at each time step as in the rate equation shown earlier, and these data are presented in Table 16.2 as well. Again we see that the rate of reaction decreases as the concentration of butadiene decreases. This suggests that the rate is given by an expression like the rate law. To test this, we calculate  $\frac{\text{Rate}}{[\text{C}_4\text{H}_6]}$  in Table 16.2 for each time step. We note that this is **not** a constant, so the rate law above does not describe the relationship between the rate of reaction and the concentration of butadiene. Instead we calculate  $\frac{\text{Rate}}{[\text{C}_4\text{H}_6]^2}$  in Table 16.2. We discover that this ratio is a constant throughout the reaction. Therefore, the relationship between the rate of the reaction and the concentration of the reactant in this case is given by

$$\text{Rate} = -\frac{d[\text{C}_4\text{H}_6]}{dt} \quad (16.4)$$

$$= k[\text{C}_4\text{H}_6]^2 \quad (16.5)$$

which is the rate law for the reaction in Figure 16.5. This is a very interesting result when compared to the rate law given above. In both cases, the results demonstrate that the rate of reaction depends on the concentration of the reactant. However, we now also know that the way in which the rate varies with the concentration depends on what the reaction is. Each reaction has its own rate law, observed experimentally.

## Observation 2: Rate Laws and the Order of Reaction

We would like to understand what determines the specific dependence of the reaction rate on concentration in each reaction. In the first case considered above, the rate depends on the concentration of the reactant to the first power. We refer to this as a **first order reaction**. In the second case above, the rate depends on the concentration of the reactant to the second power, so this is called a second order reaction. There are also **third order reactions**, and even **zeroth order reactions** whose rates do not depend on the amount of the reactant. We need more observations of rate laws for different reactions.

The approach used in the previous section to determine a reaction's rate law is fairly clumsy and at this point difficult to apply. We consider here a more systematic approach. First, consider the decomposition of  $\text{N}_2\text{O}_5$  (g).



We can create an initial concentration of  $\text{N}_2\text{O}_5$  in a flask and measure the rate at which the  $\text{N}_2\text{O}_5$  first decomposes. We can then create a different initial concentration of  $\text{N}_2\text{O}_5$  and measure the new rate at which the  $\text{N}_2\text{O}_5$  decomposes. By comparing these rates, we can find the order of the decomposition reaction. The rate law for decomposition of  $\text{N}_2\text{O}_5(g)$  is of the general form:

$$\text{Rate} = k[\text{N}_2\text{O}_5]^m \quad (16.7)$$

so we need to determine the exponent  $m$ . For example, at  $25^\circ\text{C}$  we observe that the rate of decomposition is  $1.4 \times 10^{-3} \frac{\text{M}}{\text{s}}$  when the concentration of  $\text{N}_2\text{O}_5$  is 0.020 M. If instead we begin with  $[\text{N}_2\text{O}_5] = 0.010 \text{ M}$ , we observe that the rate of decomposition is  $7.0 \times 10^{-4} \frac{\text{M}}{\text{s}}$ . We can compare the rate from the first measurement, Rate 1, to the rate from the second measurement, Rate 2. From the equation above, we can write that

$$\frac{\text{Rate 1}}{\text{Rate 2}} = \frac{k[\text{N}_2\text{O}_5]_1^m}{k[\text{N}_2\text{O}_5]_2^m} \quad (16.8)$$

$$= \frac{1.4 \times 10^{-3} \frac{\text{M}}{\text{s}}}{7.0 \times 10^{-4} \frac{\text{M}}{\text{s}}} \quad (16.9)$$

$$= \frac{k(0.020 \text{ M})^m}{k(0.010 \text{ M})^m} \quad (16.10)$$

This can be simplified on both sides of the equation to give

$$2.0 = 2.0^m \quad (16.11)$$

Clearly, then,  $m = 1$  and the decomposition is a first order reaction. We can also then find the first order rate constant  $k$  for this reaction by simply plugging in one of the initial rate measurements to the rate law equation. We find that  $k = 0.070 \text{ s}^{-1}$ .

This approach to finding reaction order is called the method of initial rates, since it relies on fixing the concentration at specific initial values and measuring the initial rate associated with each concentration.

So far we have considered only reactions which have a single reactant. Consider a second example of the method of initial rates involving the reaction of hydrogen gas and iodine gas:



In this case, we expect to find that the rate of the reaction depends on the concentrations for both reactants. As such, we need more initial rate observations to determine the rate law. In Table 16.3, observations are reported for the initial rate for three sets of initial concentrations of  $\text{H}_2$  and  $\text{I}_2$ .

Table 16.3: Hydrogen Gas and Iodine Gas Initial Rate Data at 700 K

Experiment	$[\text{H}_2]_0$ (M)	$[\text{I}_2]_0$ (M)	Rate (M/s)
1	0.10	0.10	$3.00 \times 10^{-4}$
2	0.20	0.10	$6.00 \times 10^{-4}$
3	0.20	0.20	$1.19 \times 10^{-3}$

Following the same process we used in the  $\text{N}_2\text{O}_5$  example, we write the general rate law for the reaction as

$$\text{Rate} = k[\text{H}_2]^n[\text{I}_2]^m \quad (16.13)$$

By comparing Experiment 1 to Experiment 2, we can write

$$\frac{\text{Rate 1}}{\text{Rate 2}} = \frac{k[\text{H}_2]_1^n[\text{I}_2]_1^m}{k[\text{H}_2]_2^n[\text{I}_2]_2^m} \quad (16.14)$$

$$= \frac{3.00 \times 10^{-4} \frac{\text{M}}{\text{s}}}{6.00 \times 10^{-4} \frac{\text{M}}{\text{s}}} \quad (16.15)$$

$$= \frac{k(0.10 \text{ M})^n(0.10 \text{ M})^m}{k(0.20 \text{ M})^n(0.10 \text{ M})^m} \quad (16.16)$$

This simplifies to

$$0.50 = 0.50^m 1.00^n \quad (16.17)$$

from which it is clear that  $m = 1$ . Similarly, we can find that  $n = 1$ . The reaction is therefore first order in each reactant and is second order overall.

$$\text{Rate} = k [\text{H}_2] [\text{I}_2] \quad (16.18)$$

Once we know the rate law, we can use any of the data from Table 16.3 to determine the rate constant, simply by plugging in concentrations and rate into the rate law equation. We find that  $k = 3.00 \times 10^{-2} \frac{1}{\text{Ms}}$ .

This procedure can be applied to any number of reactions. The challenge is preparing the initial conditions and measuring the initial change in concentration precisely versus time. Table 16.4 provides an overview of the rate laws for several reactions. A variety of reaction orders are observed, and they cannot be easily correlated with the stoichiometry of the reaction.

Table 16.4: Rate Laws for Various Reactions

Reaction	Rate Law
$2\text{NO} (g) + \text{O}_2 (g) \rightarrow 2\text{NO}_2 (g)$	$\text{Rate} = k [\text{NO}]^2 [\text{O}_2]$
$2\text{NO} (g) + 2\text{H}_2 (g) \rightarrow 2\text{N}_2 (g) + 2\text{H}_2\text{O} (g)$	$\text{Rate} = k [\text{NO}]^2 [\text{H}_2]$
$2\text{ICl} (g) + \text{H}_2 (g) \rightarrow 2\text{HCl} (g) + \text{I}_2 (g)$	$\text{Rate} = k [\text{ICl}] [\text{H}_2]$
$2\text{N}_2\text{O}_5 (g) \rightarrow 4\text{NO}_2 (g) + \text{O}_2 (g)$	$\text{Rate} = k [\text{N}_2\text{O}_5]$
$2\text{NO}_2 (g) + \text{F}_2 (g) \rightarrow 2\text{NO}_2\text{F} (g)$	$\text{Rate} = k [\text{NO}_2] [\text{F}_2]$
$2\text{H}_2\text{O}_2 (aq) \rightarrow 2\text{H}_2\text{O} (l) + \text{O}_2 (g)$	$\text{Rate} = k [\text{H}_2\text{O}_2]$
$\text{H}_2 (g) + \text{Br}_2 (g) \rightarrow 2\text{HBr} (g)$	$\text{Rate} = k [\text{H}_2] [\text{Br}_2]^{\frac{1}{2}}$
$\text{O}_3 (g) + \text{Cl} (g) \rightarrow \text{O}_2 (g) + \text{ClO} (g)$	$\text{Rate} = k [\text{O}_3] [\text{Cl}]$

## Concentrations as a Function of Time and the Reaction Half-life

Once we know the rate law for a reaction, we should be able to predict how fast a reaction will proceed. From this, we should also be able to predict how much reactant remains or how much product has been produced at any given time in the reaction. We will focus on the reactions with a single reactant to illustrate these ideas.

Consider a first order reaction like  $\text{A} \rightarrow \text{products}$ , for which the rate law must be

$$\begin{aligned} \text{Rate} &= -\frac{d\text{A}}{dt} \\ &= k [\text{A}] \end{aligned} \quad \begin{aligned} (16.19) \\ (16.20) \end{aligned}$$

From calculus, it is possible to use the above equation to find the function  $[\text{A}] (t)$  which tells us the concentration  $[\text{A}]$  as a function of time. The result is

$$[\text{A}] = [\text{A}]_0 e^{-kt} \quad (16.21)$$

or equivalently

$$\ln ([\text{A}]) = \ln ([\text{A}]_0) - kt \quad (16.22)$$

The above equation reveals that, if a reaction is first order, we can plot  $\ln ([\text{A}]_0)$  versus time and get a straight line with slope equal to  $-k$ . Moreover, if we know the rate constant and the initial concentration, we can predict the concentration at any time during the reaction.

An interesting point in the reaction is the time at which exactly half of the original concentration of A has been consumed. We call this time the **half life** of the reaction and denote it as  $t_{\frac{1}{2}}$ . At that time,  $[\text{A}] = \frac{1}{2} [\text{A}]_0$ . From the above equation and using the properties of logarithms, we find that, for a first order reaction

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k} \quad (16.23)$$

This equation tells us that the half-life of a first order reaction does not depend on how much material we start with. It takes exactly the same amount of time for the reaction to proceed from all of the starting material to half of the starting material as it does to proceed from half of the starting material to one-fourth of the starting material. In each case, we halve the remaining material in time equal to the constant half-life shown in the equation above.

These conclusions are only valid for first order reactions. Consider then a second order reaction, such as the butadiene dimerization discussed above. The general second order reaction  $A \rightarrow \text{products}$  has the rate law

$$\text{Rate} = -\frac{d[A]}{dt} \quad (16.24)$$

$$= k[A]^2 \quad (16.25)$$

Again, we can use calculus to find the function  $[A](t)$  from the above equation. The result is most easily written as

$$\frac{1}{[A]} = \frac{1}{[A]_0} + k(t) \quad (16.26)$$

Note that, as  $t$  increases,  $\frac{1}{[A]}$  increases, so  $[A]$  decreases. The equation reveals that, for a reaction which is second order in the reactant  $A$ , we can plot  $\frac{1}{[A]}$  as a function of time to get a straight line with slope equal to  $k$ . Again, if we know the rate constant and the initial concentration, we can find the concentration  $[A]$  at any time of interest during the reaction.

The half-life of a second order reaction differs from the half-life of a first order reaction. From the above equation, if we take  $[A] = \frac{1}{2}[A]_0$ , we get

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0} \quad (16.27)$$

This shows that, unlike a first order reaction, the half-life for a second order reaction depends on how much material we start with. From this equation, the more concentrated the reactant is, the shorter the half-life.

### Observation 3: Temperature Dependence of Reaction Rates

It is a common observation that reactions tend to proceed more rapidly with increasing temperature. Similarly, cooling reactants can have the effect of slowing a reaction to a near halt. How is this change in rate reflected in the rate law equation? One possibility is that there is a slight dependence on temperature of the concentrations, since volumes do vary with temperature. However, this is insufficient to account for the dramatic changes in rate typically observed. Therefore, the temperature dependence of reaction rate is primarily found in the rate constant,  $k$ .

Consider for example the reaction of hydrogen gas with iodine gas at high temperatures. The rate constant of this reaction at each temperature can be found using the method of initial rates, as discussed above, and we find in Table 16.5 that the rate constant increases dramatically as the temperature increases.

Table 16.5: Rate Constant for Hydrogen Gas and Iodine Gas

$T$ (K)	$k$ ( $\frac{1}{\text{Ms}}$ )
667	$6.80 \times 10^{-3}$
675	$9.87 \times 10^{-3}$
700	$3.00 \times 10^{-2}$
725	$8.43 \times 10^{-2}$
750	$2.21 \times 10^{-1}$
775	$5.46 \times 10^{-1}$
800	1.27

As shown in Figure 16.6, the rate constant appears to increase exponentially with temperature. After a little experimentation with the data, we find in Figure 16.7 that there is a simple linear relationship between  $\ln(k)$  and  $\frac{1}{T}$ .



**Figure 16.6:** Rate constant vs. Temperature for reaction of  $\text{H}_2$  and  $\text{I}_2$  **Figure 16.7:** Rate constant vs. Inverse Temperature for reaction of  $\text{H}_2$  and  $\text{I}_2$

From Figure 16.7, we can see that the data in Table 16.5 fit the equation

$$\ln(k) = a \frac{1}{T} + b \quad (16.28)$$

where  $a$  and  $b$  are constant for this reaction. It turns out that, for our purposes, all reactions have rate constants which fit this equation, but with different constants  $a$  and  $b$  for each reaction. Figure 16.7 is referred to as an **Arrhenius plot**, after Svante Arrhenius.

It is very important to note that the form of the above equation and the appearance of Figure 16.7 are both the same as the equations and graphs for the temperature dependence of the equilibrium constant for an endothermic reaction. This suggests a model to account for the temperature dependence of the rate constant, based on the energetics of the reaction. In particular, it appears that the reaction rate is related to the amount of energy required for the reaction to occur. We will develop this further in the next section.

## Collision Model for Reaction Rates

At this point, we have only observed the dependence of reaction rates on concentration of reactants and on temperature, and we have fit these data to equations called rate laws. Although this is very convenient, it does not provide us insight into why a particular reaction has a specific rate law or why the temperature dependence should obey the equation shown above. Nor does it provide any physical insights into the order of the reaction or the meaning of the constants  $a$  and  $b$  in the equation.

We begin by asking why the reaction rate should depend on the concentration of the reactants. To answer this, we consider a simple reaction between two molecules in which atoms are transferred between the molecules during the reaction. For example, a reaction important in the decomposition of ozone  $\text{O}_3$  by aerosols is



What must happen for a reaction to occur between an  $\text{O}_3$  molecule and a  $\text{Cl}$  atom? Obviously, for these two particles to react, they must come into close proximity to one another so that an  $\text{O}$  atom can be transferred from one to the other. In general, two molecules cannot trade atoms to produce new molecules unless they are close together for the atoms of the two molecules to interact. This requires a collision between molecules.

The rate of collisions depends on the concentrations of the reactants, since the more molecules there are in a confined space, the more likely they are to run into each other. To write this relationship in an equation, we can think in terms of probability, and we consider the reaction above. The probability for an  $\text{O}_3$  molecule to be near a specific point increases with the number of  $\text{O}_3$  molecules, and therefore increases with the concentration of  $\text{O}_3$  molecules. The probability for a  $\text{Cl}$  atom to be near that specific point is also proportional to the concentration of  $\text{Cl}$  atoms. Therefore, the probability for an  $\text{O}_3$  molecule and a  $\text{Cl}$  atom to be in close proximity to the same specific point at the same time is proportional to the  $[\text{O}_3]$  times  $[\text{Cl}]$ .

It is important to remember that not all collisions between  $\text{O}_3$  molecules and  $\text{Cl}$  atoms will result in a reaction. There are other factors to consider including how the molecules approach one another. The atoms may not be positioned properly to exchange between molecules, in which case the molecules will simply bounce off of one another without reacting. For example, if the  $\text{Cl}$  atom approaches the center  $\text{O}$  atom of the  $\text{O}_3$  molecule, that  $\text{O}$  atom will not transfer. Another factor is energy associated with the reaction. Clearly, though, a collision must occur for the reaction to occur, and therefore the rate of the reaction can be no faster than the rate of collisions between the reactant molecules.

Therefore, we can say that, in a **bimolecular reaction**, where two molecules collide and react, the rate of the reaction will be proportional to the product of the concentrations of the reactants. For the reaction of  $\text{O}_3$  with  $\text{Cl}$ , the rate must therefore be proportional to  $[\text{O}_3][\text{Cl}]$ , and we observe this in the experimental rate law in Table 16.4. Thus, it appears that we can understand the rate law by understanding the collisions which must occur for the reaction to take place.

We also need our model to account for the temperature dependence of the rate constant. As noted at the end of the last section, the temperature dependence of the rate constant is the same as the temperature dependence of the equilibrium constant for an

endothermic reaction. This suggests that the temperature dependence is due to an energetic factor required for the reaction to occur. However, we find experimentally that the rate constant equation describes the rate constant temperature dependence regardless of whether the reaction is endothermic or exothermic. Therefore, whatever the energetic factor is that is required for the reaction to occur, it is not just the endothermicity of the reaction. It must be that all reactions, regardless of the overall change in energy, require energy to occur.

A model to account for this is the concept of **activation energy**. For a reaction to occur, at least some bonds in the reactant molecule must be broken, so that atoms can rearrange and new bonds can be created. At the time of collision, bonds are stretched and broken as new bonds are made. Breaking these bonds and rearranging the atoms during the collision requires the input of energy. The minimum amount of energy required for the reaction to occur is called the activation energy,  $E_a$ . This is illustrated in Figure 16.8, showing conceptually how the energy of the reactants varies as the reaction proceeds. In Figure 16.8a, the energy is low early in the reaction, when the molecules are still arranged as reactants. As the molecules approach and begin to rearrange, the energy rises sharply, rising to a maximum in the middle of the reaction. This sharp rise in energy is the activation energy, as illustrated. After the middle of the reaction has passed and the molecules are arranged more as products than reactants, the energy begins to fall again. However, the energy does not fall to its original value, so this is an endothermic reaction.

Figure 16.8b shows the analogous situation for an exothermic reaction. Again, as the reactants approach one another, the energy rises as the atoms begin to rearrange. At the middle of the collision, the energy maximizes and then falls as the product molecules form. In an exothermic reaction, the product energy is lower than the reactant energy.

Figure 16.8 thus shows that an energy barrier must be surmounted for the reaction to occur, regardless of whether the energy of the products is greater than (Figure 16.8a) or less than (Figure 16.8b) the energy of the reactants. This barrier accounts for the temperature dependence of the reaction rate. We know from the kinetic molecular theory that as temperature increases the average energy of the molecules in a sample increases. Therefore, as temperature increases, the fraction of molecules with sufficient energy to surmount the reaction activation barrier increases.

a.   
b.

**Figure 16.8:** Reaction energy for (a) an endothermic reaction and (b) an exothermic reaction.

Although we will not show it here, kinetic molecular theory shows that the fraction of molecules with energy greater than  $E_a$  at temperature  $T$  is proportional to  $e^{-\frac{E_a}{RT}}$ . This means that the reaction rate and therefore also the rate constant must be proportional to  $e^{-\frac{E_a}{RT}}$ . Therefore we can write

$$k(T) = Ae^{-\frac{E_a}{RT}} \quad (16.30)$$

where  $A$  is a proportionality constant. If we take the logarithm of both sides of the equation, we find that

$$\ln(k(T)) = -\frac{E_a}{RT} + \ln(A) \quad (16.31)$$

This equation matches the experimentally observed equation. We recall that a graph of  $\ln(k)$  versus  $\frac{1}{T}$  is observed to be linear. Now we can see that the slope of that graph is equal to  $-\frac{E_a}{R}$ .

As a final note on the above equation, the constant  $A$  must have some physical significance. We have accounted for the probability of collision between two molecules and we have accounted for the energetic requirement for a successful reactive collision. We have not accounted for the probability that a collision will have the appropriate orientation of reactant molecules during the collision. Moreover, not every collision which occurs with proper orientation and sufficient energy will actually result in a reaction. There are other random factors relating to the internal structure of each molecule at the instant of collision. The factor  $A$  takes account for all of these factors, and is essentially the probability that a collision with sufficient energy for reaction will indeed lead to reaction.  $A$  is commonly called the **frequency factor**.

#### Observation 4: Rate Laws for More Complicated Reaction Processes

Our collision model in the previous section accounts for the concentration and temperature dependence of the reaction rate, as expressed by the rate law. The concentration dependence arises from calculating the probability of the reactant molecules being in the same vicinity at the same instant. Therefore, we should be able to predict the rate law for any reaction by simply multiplying



together the concentrations of all reactant molecules in the balanced stoichiometric equation. The order of the reaction should therefore be simply related to the stoichiometric coefficients in the reaction. However, Table 16.4 shows that this is incorrect for many reactions.

Consider for example the apparently simple reaction



Based on the collision model, we would assume that the reaction occurs by 2ICl molecules colliding with a single H<sub>2</sub> molecule. The probability for such a collision should be proportional to [ICl]<sup>2</sup> [H<sub>2</sub>]. However, experimentally we observe (see Table 16.4) that the rate law for this reaction is

$$\text{Rate} = k [\text{ICl}] [\text{H}_2] \quad (16.33)$$

As a second example, consider the reaction



It would seem reasonable to assume that this reaction occurs as a single collision in which an oxygen atom is exchanged between the two molecules. However, the experimentally observed rate law for this reaction is

$$\text{Rate} = k[\text{NO}_2]^2 \quad (16.35)$$

In this case, the [CO] concentration does not affect the rate of the reaction at all, and the [NO<sub>2</sub>] concentration is squared. These examples demonstrate that the rate law for a reaction cannot be predicted from the stoichiometric coefficients and therefore that the collision model does not account for the rate of the reaction. There must be something seriously incomplete with the collision model.

The key assumption of the collision model is that the reaction occurs by a single collision. Since this assumption leads to incorrect predictions of rate laws in some cases, the assumption must be invalid in at least those cases. It may well be that reactions require more than a single collision to occur, even in reactions involving just two types of molecules. Moreover, if more than two molecules are involved, the chance of a single collision involving all of the reactive molecules becomes very small. We conclude that many reactions must occur as a result of several collisions occurring in sequence, rather than a single collision. The rate of the chemical reaction must be determined by the rates of the individual steps in the reaction.

Each step in a complex reaction is a single collision, often referred to as an **elementary process**. In a single collision process step, our collision model should correctly predict the rate of that step. The sequence of such elementary processes leading to the overall reaction is referred to as the **reaction mechanism**. Determining the mechanism for a reaction can require gaining substantially more information than simply the rate data we have considered here. However, we can gain some progress just from the rate law.

Consider for example the reaction of nitrogen dioxide and carbon monoxide. Since the rate law involved [NO<sub>2</sub>]<sup>2</sup>, one step in the reaction mechanism must involve the collision of two NO<sub>2</sub> molecules. Furthermore, this step must determine the rate of the overall reaction. Why would that be? In any multi-step process, if one step is considerably slower than all of the other steps, the rate of the multi-step process is determined entirely by that slowest step, because the overall process cannot go any faster than the slowest step. It does not matter how rapidly the rapid steps occur. Therefore, the slowest step in a multi-step process is thus called the **rate determining** or **rate limiting** step.

This argument suggests that the reaction proceeds via a slow step in which two NO<sub>2</sub> molecules collide, followed by at least one other rapid step leading to the products. A possible mechanism is therefore

Step 1



Step 2



If Step 1 is much slower than Step 2, the rate of the reaction is entirely determined by the rate of Step 1. From our collision model, the rate law for Step 1 must be  $k[\text{NO}_2]^2$ , which is consistent with the experimentally observed rate law for the overall reaction. This suggests that the mechanism is the correct description of the reaction process, with the first step as the rate determining step.

There are a few important notes about the mechanism. First, one product of the reactions is produced in the first step, and the other is produced in the second step. Therefore, the mechanism does lead to the overall reaction, consuming the correct amount of reactants and producing the correct amount of products. Second, the first reaction produces a new molecule,  $\text{NO}_3$ , which is neither a reactant nor a product. The second step then consumes that molecule, and  $\text{NO}_3$  therefore does not appear in the overall reaction. As such,  $\text{NO}_3$  is called a **reaction intermediate**. Intermediates play important roles in the rates of many reactions.

If the first step in a mechanism is rate determining as in this case, it is easy to find the rate law for the overall expression from the mechanism. If the second step or later steps are rate determining, determining the rate law is slightly more involved.

## Review and Discussion Questions

When  $\text{C}_{60}\text{O}_3$  in toluene solution decomposes,  $\text{O}_2$  is released leaving  $\text{C}_{60}\text{O}$  in solution. Based on the data in Figure 16.2 and Figure 16.3, plot the concentration of  $\text{C}_{60}\text{O}$  as a function of time.

How would you define the rate of the reaction in terms of the slope of the graph from Figure 16.3? How is the rate of appearance of  $\text{C}_{60}\text{O}$  related to the rate of disappearance of  $\text{C}_{60}\text{O}_3$ ? Based on this, plot the rate of appearance of  $\text{C}_{60}\text{O}$  as a function of time.

The reaction  $2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g)$  was found in this study to have rate law given by  $\text{Rate} = k[\text{N}_2\text{O}_5]$  with  $k = 0.070 \text{ s}^{-1}$ . How is the rate of appearance of  $\text{NO}_2$  related to the rate of disappearance of  $\text{N}_2\text{O}_5$ ? Which rate is larger? Based on the rate law and rate constant, sketch a plot of  $[\text{N}_2\text{O}_5]$ ,  $[\text{NO}_2]$ , and  $[\text{O}_2]$  versus time all on the same graph.

For which of the reactions listed in Table 16.4 can you be certain that the reaction does not occur as a single step collision? Explain your reasoning.

Consider two decomposition reactions for two hypothetical materials, A and B. The decomposition of A is found to be first order, and the decomposition of B is found to be second order. Assuming that the two reactions have the same rate constant at the same temperature, sketch  $[\text{A}]$  and  $[\text{B}]$  versus time on the same graph for the same initial conditions, i.e.  $[\text{A}]_0 = [\text{B}]_0$ . Compare the half-lives of the two reactions. Under what conditions will the half-life of B be less than the half-life of A? Under what conditions will the half-life of B be greater than the half-life of A?

A graph of the logarithm of the equilibrium constant for a reaction versus  $\frac{1}{T}$  is linear but can have either a negative slope or a positive slope, depending on the reaction. However, the graph of the logarithm of the rate constant for a reaction versus  $\frac{1}{T}$  has a negative slope for essentially every reaction. Using equilibrium arguments, explain why the graph for the rate constant must have a negative slope.

Using the rate constant equation involving activation energy and the data in Table 16.5, determine the activation energy for the reaction  $\text{H}_2(g) + \text{I}_2(g) \rightarrow 2\text{HI}(g)$ .

We found that the rate law for the reaction  $\text{H}_2(g) + \text{I}_2(g) \rightarrow 2\text{HI}(g)$  is  $\text{Rate} = k[\text{H}_2][\text{I}_2]$ . Therefore, the reaction is **second order** overall but **first order** in  $\text{H}_2$ . Imagine that we start with  $[\text{H}_2]_0 = [\text{I}_2]_0$  and we measure  $[\text{H}_2]$  versus time. Will a graph of  $\ln([\text{H}_2])$  versus time be linear or will a graph of  $\frac{1}{[\text{H}_2]}$  versus time be linear? Explain your reasoning.

As a rough estimate, chemists often assume a **rule of thumb** that the rate of any reaction will double when the temperature is increased by  $10^\circ\text{C}$ . What does this suggest about the activation energies of reactions? Using the rate constant equation involving activation energy, calculate the activation energy of a reaction whose rate doubles when the temperature is raised from  $25^\circ\text{C}$  to  $35^\circ\text{C}$ . Does this rule of thumb estimate depend on the temperature range? To find out, calculate the factor by which the rate constant increases when the temperature is raised from  $100^\circ\text{C}$  to  $110^\circ\text{C}$ , assuming the same activation energy you found above. Does the rate double in this case?

Consider a very simple hypothetical reaction  $\text{A} + \text{B} \leftrightarrow 2\text{C}$  which comes to equilibrium. At equilibrium, what must be the relationship between the rate of the forward reaction,  $\text{A} + \text{B} \rightarrow 2\text{C}$  and the reverse reaction  $2\text{C} \rightarrow \text{A} + \text{B}$ ? Assume that both the forward and reverse reactions are elementary processes occurring by a single collision. What is the rate law for the forward reaction? What is the rate law for the reverse reaction? Using these results, show that the equilibrium constant for this reaction can be calculated from  $K_c = \frac{k_f}{k_r}$ , where  $k_f$  is the rate constant for the forward reaction and  $k_r$  is the rate constant for the reverse reaction.

Consider a very simple hypothetical reaction  $\text{A} + \text{B} \leftrightarrow \text{C} + \text{D}$ . By examining Figure 16.8, provide and explain the relationship between the activation energy in the forward direction,  $E_{a,f}$ , and in the reverse direction,  $E_{a,r}$ . Does this relationship depend on whether the reaction is endothermic (Figure 16.8a) or exothermic (Figure 16.8b)? Explain.

For the reaction  $\text{H}_2(g) + \text{I}_2(g) \rightarrow 2\text{HI}(g)$ , the rate law is  $\text{Rate} = k[\text{H}_2][\text{I}_2]$ . Although this suggests that the reaction is a one-step elementary process, there is evidence that the reaction occurs in two steps, and the second step is the rate determining step:

Step 1



Step 2



Where Step 1 is fast and Step 2 is slow. If both the forward and reverse reactions in Step 1 are much faster than Step 2, explain why Step 1 can be considered to be at equilibrium. What is the rate law for the rate determining step? Since this rate law depends on the concentration of an intermediate I, we need to find that intermediate. Calculate  $[\text{I}]$  from Step 1, assuming that Step 1 is at equilibrium. Substitute  $[\text{I}]$  into the rate law found previously to find the overall rate law for the reaction. Is this result consistent with the experimental observation?

### Contributors and Attributions

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