RATE OF REACTIONS

FACTORS THAT AFFECT REACTION RATES

The physical state of the reactants: Reactants must come together to react. The more readily molecules collide with each other, the more rapidly they react. Most reactions are homogeneous (same phases). When reactants are in different phases (e.g. solid and gas), the reaction is limited to their area of contact. Therefore, reactions that involve solids proceed faster if the surface area of the solid is increased.

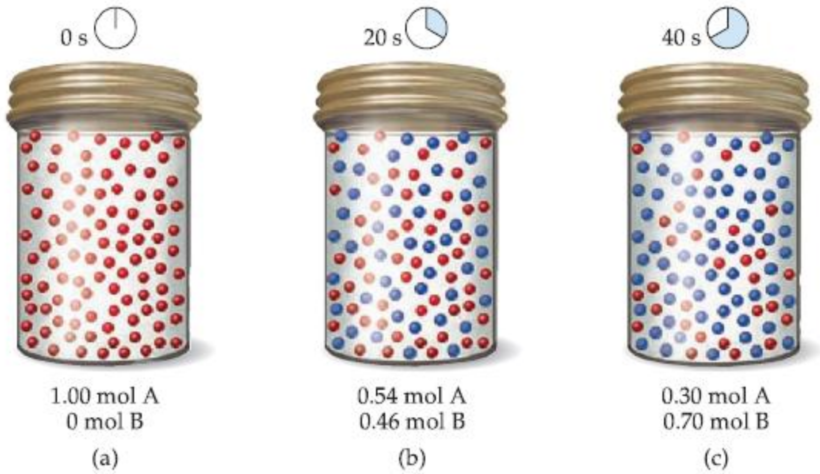
The concentration of the reactants: most chemical reactions proceed faster if the concentration of one or more of the reactants is increased. For example, steel wool burns difficulty in air (20% O_2) but bursts into a brilliant white flame in pure oxygen. As concentration increases, the frequency with which the reactant molecules collide increases, leading to increased rates.

The temperature at which the reaction occurs: the rates of chemical reactions increase as temperature is increased. Increasing temperatures increases the kinetic energies of molecules. As molecules move more rapidly, they collide more frequently and also with higher energy, leading to increased reaction rates. For example, in milk, the bacterial reactions that lead to the spoiling of milk proceed much more rapidly at room temperature than they do at the lower temperature of a refrigerator.

The presence of a catalyst: catalysts are agents that increase reaction rates without being used up. They affect the kinds of collisions (the mechanism) that lead to reaction. For example, the physiology of most living species depend on enzymes (protein molecules that act as catalyst) increasing the rates of biochemical reactions.

REACTION RATES

The speed of a chemical reaction – its reaction rate – is the change in the concentration of reactants or products per unit time. The units are usually molarity per second (M/s). Consider as simple hypothetical reaction $A \rightarrow B$ as shown below:



Each red sphere represents 0.01 mol of A, each blue sphere represents 0.01 mol of B, and the container has a volume of 1.00 L. At the beginning of the reaction there is 1.00 mol of A, so the concentration is 1.00 mol/L. After 20s, the concentration of A has fallen to 0.54 M, where as the concentration of B has risen to 0.46 M. The sum of the concentrations is still 1.00 M because 1 mol of B is produced for each mole of A that reacts. After 40s the concentration of A is 0.30 M and that of B is 0.70 M.

The rate of this reaction can be expressed either as the rate of disappearance of reactant A or as the rate of appearance of product B. The average rate of appearance of B over a particular time interval is given by the change in concentration of B divided by the change in time:

$$\text{Average rate of apperance of B} = \frac{\text{change in concentration of B}}{\text{change in time}}$$

$$\frac{[\mathrm{B}]\text{at } t_2 - [\mathrm{B}]\text{at } t_1}{t_2 - t_1} = \frac{\Delta[\mathrm{B}]}{\Delta t}$$

Brackets around a chemical formula, as in [B], indicate the concentration of the substance in molarity. The Greek letter delta, Δ, is read ‘change in’ and is always equal to the final quantity minus the initial quantity. The average rate of appearance of B over the 20 s interval from the beginning of the reaction (t_1 = 0 s to t_2 = 20 s) is given by:

$$\text{Average rate} = \frac{0.46\text{M} - 0.00\text{M}}{20\text{s} - 0\text{s}} = 2.3 \times 10^{-2}\ \text{M/s}$$

We could equally express the rate of reaction with respect to the change of concentration of the reactant, A. In this case we would be describing the rate of disappearance of A, which we express as:

$$\text{Average rate of disappearance of A} = -\frac{\Delta[\text{A}]}{\Delta \text{t}}$$

Notice the minus sign in this equation. By convention, rates are always expressed as positive quantities. Because [A] is decreasing with time, Δ[A] is a negative number. We use the negative sign to convert the negative Δ[A] to a positive rate.

Because one molecule of A is consumed for every molecule of B that forms, the average rate of disappearance of A equals the average rate of appearance of B, as calculation shows:

$$\text{Average rate} = -\frac{\Delta[\text{A}]}{\Delta \text{t}} = -\frac{0.54\text{M} - 1.00\text{M}}{20\text{s} - 0\text{s}} = 2.3 \times 10^{-2}\ \text{M/s}$$

Problem

Given that the concentration of A at 20 s is 0.54 M and at 40 s is 0.30 M. Calculate the average rate of reaction at which A disappears.

Solution

$$\text{Average rate} = -\frac{\Delta[\text{A}]}{\Delta \text{t}} = -\frac{0.30\text{M} - 0.54\text{M}}{40\text{s} - 20\text{s}} = 1.2 \times 10^{-2}\ \text{M/s}$$

CHANGE OF RATE WITH TIME

Consider an actual chemical reaction, one that occurs when butyl chloride, C_4H_9Cl is placed in water. The products formed are butyl alcohol and hydrochloric acid:

$$C_4H_9Cl\ (aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + HCl(aq)$$

Suppose we prepare a 0.100M aqueous solution of C_4H_9Cl and then measure the concentration of C_4H_9Cl at various times after time zero (the time the reactants are mixed, thereby initiating the reaction). The resultant data are shown below:

TABLE 14.1 ■ Rate Data for Reaction of C_4H_9Cl with Water

Time, t(s)	$[C_4H_9Cl](M)$	Average Rate (M/s)
0.0	0.1000	1.9×10^{-4}
50.0	0.0905	1.7×10^{-4}
100.0	0.0820	1.6×10^{-4}
150.0	0.0741	1.4×10^{-4}
200.0	0.0671	1.22×10^{-4}
300.0	0.0549	1.01×10^{-4}
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

We can use these data to calculate the average rate of disappearance of C_4H_9Cl over the time intervals between measurements; these rates are given in the third column. Notice that the average rate decreases over each 50s interval for the first several measurements and continues to decrease over larger intervals through the remaining measurements. It is typical for rates to decrease as a reaction proceeds, because the concentration of reactants decreases. The change in rate as the reaction proceeds is given by the following graph (notice how the slope of the curve decreases with time, indicating a decreasing rate of reaction).

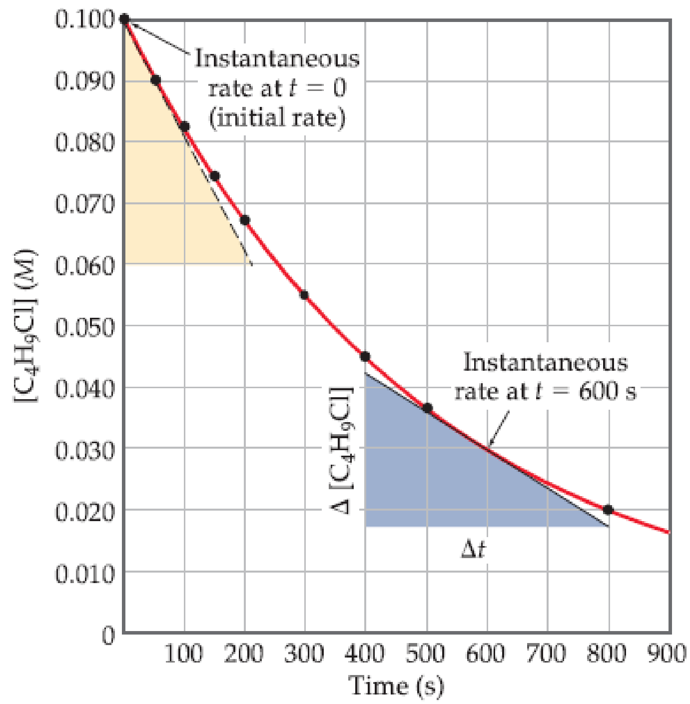


Figure 1

INSTANTANEOUS RATE

Graphs showing how the concentration of a reactant or product changes with time allow us to evaluate the instantaneous rate, the rate at a particular moment in the reaction. The instantaneous rate is determined from the slope (or tangent) of this curve at the point of interest. The graph above shows two tangents, one at t = 0s and the other at t = 600s. The slopes of these tangents give the instantaneous rates at these times. For example, to determine the instantaneous rate at 600s, we draw the tangent to the curve at this time, then construct a horizontal and vertical lines to form the right triangle shown. The slope is the ratio of the height of the vertical side to the length of the horizontal side:

$$\text{Instantaneous rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = -\frac{(0.017 - 0.042)M}{(800 - 400)s} = 6.3 \times 10^{-5}\,\frac{M}{s}$$

Problem

Using the graph, calculate the instantaneous rate of disappearance of C_4H_9Cl at t = 0 (initial rate).

Solution

$$\text{Rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = -\frac{(0.060 - 0.100)M}{(210 - 0)s} = 1.9 \times 10^{-4}\frac{M}{s}$$

Practice Problem

Using the graph, determine the instantaneous rate of disappearance of C_4H_9Cl at t = 300s (**Answer**: 1.1 $\times 10^{-4}$ M/s).

REACTION RATES AND STOICHIOMETRY

ONE TO ONE STOICHIOMETRY

Reconsider the hypothetical reaction A ⟶ B, we saw that the stoichiometry requires that the rate of disappearance of A equals the rate of appearance of B. Likewise, the stoichiometry of the following reaction indicates that 1 mol of C_4H_9OH is produced for each mole of C_4H_9Cl consumed.

$$C_4H_9Cl\,(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + HCl(aq)$$

Therefore, the rate of appearance of C_4H_9OH equals the rate of disappearance of C_4H_9Cl:

$$\text{Rate} = -\frac{\Delta[C_4H_9OH]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

NOT ONE TO ONE STOICHIOMETRY

Consider the reaction:

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

We can measure the rate of disappearance of HI or the rate of appearance of either H_2 or I_2. Because 2 mol of HI disappear for each mole of H_2 or I_2 that forms, the rate of disappearance of HI is twice the rate of appearance of either H_2 or I_2. To equate the rates, we must therefore divide the rate of disappearance of HI by 2 (its coefficient in the balanced chemical equation):

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[\text{HI}]}{\Delta t} = \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t}$$

In general, for the reaction:

$$\text{aA} + \text{bB} \rightarrow \text{cC} + \text{dD}$$

The rate is given by:

$$\text{Rate} = -\frac{1}{a}\frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{c}\frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d}\frac{\Delta[\text{D}]}{\Delta t}$$

When we speak of the rate of a reaction without specifying a particular reactant or product, we will mean it in this sense.

Problem

(a) How is the rate at which ozone disappears related to the rate at which oxygen appears in the reaction $2\text{O}_3(g) \rightarrow 3\text{O}_2(g)$?

(b) If the rate at which O2 appears, $\frac{\Delta[\text{O}_2]}{\Delta t} = 6.0 \times 10^{-5}$ M/s at a particular instant, at what rate is O_3 disappearing at this same time.

Solution

(a) Using the coefficients in the balanced equation:

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[\text{O}_3]}{\Delta t} = \frac{1}{3}\frac{\Delta[\text{O}_2]}{\Delta t}$$

(b) Solving the equation from part (a) for the rate at which O_3 disappears:

$$-\frac{\Delta[O_3]}{\Delta t} = \frac{2}{3}\frac{\Delta[O_2]}{\Delta t} = \frac{2}{3}\left(6.0 \times 10^{-5}\,\frac{M}{s}\right) = 4.0\ \times 10^{-5}\,\frac{M}{s}$$

Practice Problem

The decomposition of N_2O_5 proceeds according to the following equation:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

If the rate of decomposition of N_2O_5 at a particular instant in a reaction vessel is 4.2 x 10^{-7} M/s, what is the rate of appearance of (a) NO_2 and (b) O_2? (**Answers**: (a) 8.4 x 10^{-7} M/s (b) 2.1 x 10^{-7} M/s)

THE RATE LAW: THE EFFECT OF CONCENTRATION ON RATE

One way of studying the effect of concentration on reaction rate is to determine the way in which the rate at the beginning of a reaction (the initial rate) depends on the starting concentrations. Consider the following reaction:

$$NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$$

We might study the rate of this reaction by measuring the concentration of NH_4^+ or NO_2^- as a function of time or by measuring the volume of N_2 collected. Because the stoichiometric coefficients on NH_4^+, NO_2^- and N_2 are all the same, all of these rates will be equal.

The following table shows the initial rate for various starting concentrations of NH_4^+ and NO_2^-. These data indicate that changing either $[NH_4^+]$ or $[NO_2^-]$ changes the reaction rate.

TABLE 14.2 ■ Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25 °C

Experiment Number	Initial NH_4^+ Concentration (*M*)	Initial NO_2^- Concentration (*M*)	Observed Initial Rate (*M*/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.200	0.0202	10.8×10^{-7}
5	0.200	0.0404	21.6×10^{-7}
6	0.200	0.0808	43.3×10^{-7}

Table 1

Notice that if we double $[NH_4^+]$ while holding $[NO_2^-]$ constant, the rate doubles (compare experiments 1 and 2). If $[NH_4^+]$ is increased by a factor of 4 with $[NO_2^-]$ left unchanged (compare experiments 1 and 3) the rate changes by a factor of 4, and so forth. These results indicate that the rate is proportional to $[NH_4^+]$. When $[NO_2^-]$ is similarly varied while $[NH_4^+]$ is held constant, the rate is affected in the same manner. Thus, the rate is also directly proportional to the concentration of NO_2^-. We can express the way in which the rate depends on the concentrations of the reactants, NH_4^+ and $[NO_2^-]$, in terms of the following equation:

$$\text{Rate} = k[NH_4^+][NO_2^-]$$

The above equation is called a rate law, which shows how the rate depends on the concentrations of reactants. For a general reaction,

$$aA + bB \rightarrow cC + dD$$

The rate law generally has the form:

$$\text{Rate} = k[A]^m[B]^n$$

The constant k in the rate law is called the rate constant. The magnitude of k changes with temperature and therefore determines how temperature affects rate. The exponents '*m*' and '*n*' are typically small whole numbers (usually 0, 1, or 2).

If we know the rate law for a reaction and its rate for a set of reactant concentrations, we can calculate the value of the rate constant, *k*. For example, using the data in Table 1 and the results from experiment 1, we can have:

$$\text{Rate} = \text{k}[\text{NH}_4^+][\text{NO}_2^-]$$

$$5.4 \times 10^{-7} = \text{k}(0.0100\text{M})(0.200\text{M})$$

Solving for *k* gives:

$$k = \frac{(5.4 \times 10^{-7}\text{M/s})}{(0.0100\text{M})(0.200\text{M})} = 2.7 \times 10^{-4}\ \text{M}^{-1}\text{s}^{-1}$$

Once we have both the rate law and the value of the rate constant for a reaction, we can calculate the rate of reaction for any set of concentrations. For example, we can calculate the rate for $[\text{NH}_4^+] = 0.100\text{M}$ and $[\text{NO}_2^-] = 0.100\text{M}$:

$$\text{Rate} = (2.7 \times 10^{-4}\ \text{M}^{-1}\text{s}^{-1})(0.100\text{M})(0.100\text{M}) = 2.7 \times 10^{-6}\ \text{M/s}$$

REACTION ORDERS: THE EXPONENTS IN THE RATE LAW

The rate laws for most reactions have the general form:

$$\text{Rate} = \text{k}[\text{reactant 1}]^{\text{m}}[\text{reactant 2}]^{\text{n}} \ldots$$

The exponents '*m*' and '*n*' in a rate law are called reaction orders. For example, consider again the rate law for the reaction of NH_4^+ with NO_2^-:

$$\text{Rate} = \text{k}[\text{NH}_4^+][\text{NO}_2^-]$$

Because the exponent of $[\text{NH}_4^+]$ is 1, the rate is first order in NH_4^+. The rate is also first order in NO_2^-. The exponent 1 is not shown explicitly in rate laws. The overall reaction order is the sum of the orders with respect to each reactant in the rate law. Thus the rate law has an overall reaction order of 1+1=2, and the reaction is second order overall.

The exponents in a rate law indicate how the rate is affected by the concentration of each reactant. Because the rate at which NH_4^+ reacts with NO_2^- depends on $[NH_4^+]$ raised to the first power, the rate doubles when $[NH_4^+]$ doubles, triples when $[NH_4^+]$ triples, and so forth. Doubling or tripling $[NO_2^-]$ likewise doubles or triples the rate. If a rate law is second order with respect to a reactant, $[A]^2$, then doubling the concentration of that substance causes the reaction rate to quadruple ($[2]^2 = 4$), whereas tripling the concentration causes the rate to increase nine fold ($[3]^2 = 9$).

The following are some additional examples of rate laws:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g) \quad \text{Rate} = k[N_2O_5]$$

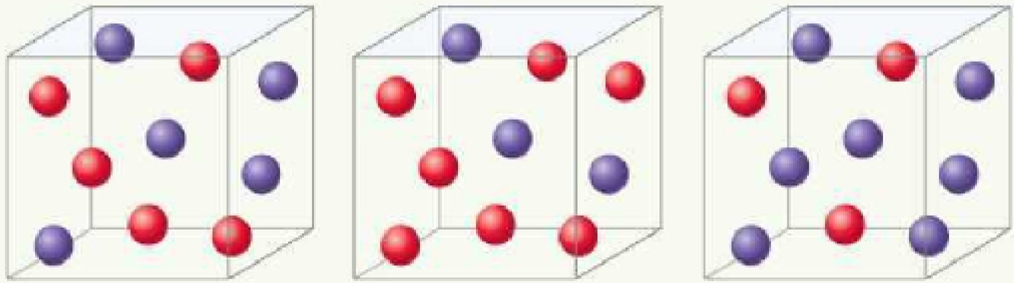
$$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g) \quad \text{Rate} = k[CHCl_3][Cl_2]^{\frac{1}{2}}$$

$$H_2(g) + I_2(g) \rightarrow 2HI(g) \quad \text{Rate} = k[H_2][I_2]$$

Although the exponents in a rate law are sometimes the same as the coefficients in the balanced equation, this is not necessarily the case. The values of these exponents must be determined experimentally. In most rate laws, the reaction orders are 0, 1, or 2. However, we also occasionally encounter rate laws in which the reaction order is fractional or even negative.

SAMPLE EXERCISE 14.4 | Relating a Rate Law to the Effect of Concentration on Rate

Consider a reaction $A + B \longrightarrow C$ for which rate $= k[A][B]^2$. Each of the following boxes represents a reaction mixture in which A is shown as red spheres and B as purple ones. Rank these mixtures in order of increasing rate of reaction.



(1) (2) (3)

SOLUTION

Analyze: We are given three boxes containing different numbers of spheres representing mixtures containing different reactant concentrations. We are asked to use the given rate law and the compositions of the boxes to rank the mixtures in order of increasing reaction rates.

Plan: Because all three boxes have the same volume, we can put the number of spheres of each kind into the rate law and calculate the rate for each box.

Solve: Box 1 contains 5 red spheres and 5 purple spheres, giving the following rate:

$$\text{Box 1: Rate} = k(5)(5)^2 = 125k$$

Box 2 contains 7 red spheres and 3 purple spheres:

$$\text{Box 2: Rate} = k(7)(3)^2 = 63k$$

Box 3 contains 3 red spheres and 7 purple spheres:

$$\text{Box 3: Rate} = k(3)(7)^2 = 147k$$

The slowest rate is $63k$ (box 2), and the highest is $147k$ (box 3). Thus, the rates vary in the order $2 < 1 < 3$.

Check: Each box contains 10 spheres. The rate law indicates that in this case [B] has a greater influence on rate than [A] because B has a higher reaction order. Hence, the mixture with the highest concentration of B (most purple spheres) should react fastest. This analysis confirms the order $2 < 1 < 3$.

PRACTICE EXERCISE

Assuming that rate $= k[A][B]$, rank the mixtures represented in this Sample Exercise in order of increasing rate.

Answer: $2 = 3 < 1$

UNITS OF RATE CONSTANTS

The units of the rate constant depend on the several reaction order of the rate law. In a reaction that is second order overall, for example, the units of the rate constant must satisfy the equation:

$$\text{Units of Rate} = (\text{Units of Rate Constant})(\text{Units of Concentration})^2$$

Hence, in our usual units of concentration and time:

$$\text{Units of Rate Constant} = \frac{\text{Units of Rate}}{(\text{Units of Concentration})^2} = \frac{\text{M/s}}{\text{M}^2} = \text{M}^{-1}\ \text{s}^{-1}$$

DETERMINING REACTION ORDERS AND UNITS FOR RATE CONSTANTS

Problem

(a) What are the overall reaction orders for the following reactions?

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g) \quad \text{Rate} = k[N_2O_5]$$

$$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g) \quad \text{Rate} = k[CHCl_3][Cl_2]^{\frac{1}{2}}$$

(b) What are the units of the rate constant for the rate law in the following reaction?

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g) \quad \text{Rate} = k[N_2O_5]$$

Solution

(a) For the first reaction, the overall order is 1.

For the second reaction, the overall order is 3/2 (first order with respect to $CHCl_3$ and one-half order with respect to Cl_2)

(b) $k = \frac{\text{Rate}}{[N_2O_5]} = \frac{(\text{M/s})}{\text{M}} = \text{s}^{-1}$

Practice Problem

(a) What is the reaction order of the reactant H_2 in the following equation?

$$H_2(g) + I_2(g) \rightarrow 2HI(g) \quad Rate = k[H_2][I_2]$$

(b) What are the units of the rate constant for the following equation?

$$H_2(g) + I_2(g) \rightarrow 2HI(g) \quad Rate = k[H_2][I_2]$$

Answers: (a) 1 (b) M^{-1} s^{-1}

USING INITIAL RATES TO DETERMINE RATE LAWS

The rate law for any chemical reaction must be determined experimentally; it cannot be predicted by merely looking at the chemical equation. We normally determine the rate law for a reaction by observing the effect of changing the initial concentrations of the reactants on the initial rate of the reaction.

We have seen that the rate laws for most reactions have the general form:

$$Rate = k[reactant\ 1]^m[reactant\ 2]^n \ldots$$

Thus, the task of determining the rate law becomes one of determining the reaction orders, m and n. IN most reactions the reactions orders are 0, 1 or 2. If a reaction is zero order in a particular reactant, changing its concentration will have no effect on rate (as long as some of the reactant is present) because any concentration raised to the zero power equals 1. On the other hand, we have seen that when a reaction is first order in a reactant, changes in the concentration of that reactant will produce proportional changes in the rate. Thus doubling the concentration will double the rate, and so forth. Finally, when the rate law is second order in a particular reactant, doubling its concentration increases the rate by a factor 2^2 = 4, tripling its concentration causes the rate to increase by a factor of 3^2 = 0 and so forth.

In working with rate laws, it is important to realize that the rate of a reaction depends on concentration, but the rate constant does not.

Problem

The initial rate of a reaction $A + B \rightarrow C$ was measured for several different starting concentrations of A and B, are as follows:

Experiment Number	[A] (*M*)	[B] (*M*)	Initial Rate (*M*/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

Using these data, determine (a) the rate law for the reaction, (b) the rate constant, (c) the rate of the reaction when [A] = 0.050 M and [B] = 0.100M.

Solution

(a) The Rate Law

$$\text{Rate} = k[A]^m[B]^n$$

Consider experiments 1 and 2 where [A] is constant and [B] is doubled. Thus this pair of experiments show how [B] affects the rate, allowing us to deduce the order of the rate law with respect to B. Because the rate remains the same when [B] is doubled, the concentration has no effect on the rate. The rate law is therefore zero order with respect to B (that is n=0).

Consider experiments 1 and 3 where [B] is constant and [A] is double. It can be seen that the rate increases four fold. This indicates that the rate is proportional to $[A]^2$ (that is the reaction is second order in A).

Therefore, the rate law is:

$$\text{Rate} = k[A]^2[B]^0 = k[A]^2$$

Alternatively:

Consider experiments 1 and 2:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[A]_2{}^m [B]_2{}^n}{k[A]_1{}^m [B]_1{}^n}$$

$$\frac{(4.0 \times 10^{-5}\text{M/s})}{(4.0 \times 10^{-5}\text{M/s})} = \frac{k[0.100\text{M})^m [0.200\text{M}]^n}{k[0.100\text{M}]^m [0.100\text{M}]^n}$$

$$1 = \frac{[0.200]^n}{[0.100]^n} = 2^n$$

Taking logs:

$$\log(1) = \log(2^n) = n\log(2)$$

$$n = \frac{\log(1)}{\log(2)} = 0$$

Consider experiments 1 and 3:

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k[A]_3{}^m [B]_3{}^n}{k[A]_1{}^m [B]_1{}^n}$$

$$\frac{(16.0 \times 10^{-5}\text{M/s})}{(4.0 \times 10^{-5}\text{M/s})} = \frac{k[0.200\text{M})^m [0.100\text{M}]^n}{k[0.100\text{M}]^m [0.100\text{M}]^n}$$

$$4 = \frac{[0.200]^m}{[0.100]^m} = 2^m$$

$$\log(4) = mlog(2)$$

$$n = \frac{\log(4)}{\log(2)} = 2$$

Therefore the rate law is:

$$\text{Rate} = \text{k}[\text{A}]^2[\text{B}]^0 = \text{k}[\text{A}]^2$$

(b) The rate constant

$$\text{Rate} = \text{k}[\text{A}]^2$$

Using any experiment:

$$4.0 \times 10^{-5}\ \text{M/s} = \text{k}[0.100]^2$$

$$\rightarrow \frac{(4.0 \times 10^{-5}\ \text{M/s})}{[0.100\ \text{M}]^2} = \text{k}$$

$$\therefore k = 4.0 \times 10^{-3}\ \text{M}^{-1}\ \text{s}^{-1}$$

(c) The Rate Law When [A] = 0.050 M and [B] = 0.100M

$$\text{Rate} = \text{k}[\text{A}]^2 = (4.0 \times 10^{-3}\ \text{M}^{-1}\ \text{s}^{-1})(0.050)^2 = 1.0 \times 10^{-5}\ \text{M/s}$$

Practice Problem

The following data were measured for the reaction of nitric oxide with hydrogen:

$$2\,NO(g) + 2\,H_2(g) \longrightarrow N_2(g) + 2\,H_2O(g)$$

Experiment Number	[NO] (*M*)	$[H_2]$ (*M*)	Initial Rate (*M*/s)
1	0.10	0.10	1.23×10^{-3}
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

(a) Determine the rate law for this reaction. **(b)** Calculate the rate constant. **(c)** Calculate the rate when [NO] = 0.050 *M* and $[H_2]$ = 0.150 *M*

Answers: **(a)** rate = $k[NO]^2[H_2]$; **(b)** $k = 1.2\ M^{-2}\ s^{-1}$; **(c)** rate = $4.5 \times 10^{-4}\ M/s$

THE CHANGE OF CONCENTRATION WITH TIME

FIRST ORDER REACTIONS

A first order reaction is one whose rate depends on the concentration of a single reactant raised to the first power. For a reaction of the type $A \rightarrow product$ the rate law may be first order:

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta \text{t}} = \text{k}[\text{A}]$$

The form of a rate law, which expresses how rate depends on concentration, is called the differential rate law. Using an operation from calculus called integration, this relationship can be transformed into an equation that relates the concentration of A at the start of the reaction, $[A]_0$, to its concentration at any other time t, $[A]_t$:

$$\ln[\text{A}]_\text{t} - \ln[\text{A}]_0 = -\text{kt}$$

$$\rightarrow \ln\frac{[\text{A}]_\text{t}}{[\text{A}]_0} = -\text{kt}$$

This form of the rate law is called the integrated rate law. The function 'ln' is the natural logarithm. From the above equation, we can have:

$$\ln[A]_t = -kt + \ln[A]_0$$

These equations can be used with any concentration units, as long as the units are the same for both $[A]_t$ and $[A]_0$. These equations can be used to determine (1) the concentration of a reactant remaining at any time after the reaction has started, (2) the time required for a given fraction of a sample to react, or (3) the time required for a reactant concentration to fall to a certain level.

SAMPLE EXERCISE 14.7 | Using the Integrated First-Order Rate Law

The decomposition of a certain insecticide in water follows first-order kinetics with a rate constant of 1.45 yr^{-1} at 12 °C. A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of 5.0×10^{-7} g/cm^3. Assume that the average temperature of the lake is 12 °C. **(a)** What is the concentration of the insecticide on June 1 of the following year? **(b)** How long will it take for the concentration of the insecticide to decrease to 3.0×10^{-7} g/cm^3?

Problem

The decomposition of a certain insecticide in water follows first order kinetics with a rate constant of 1.45 yr^{-1} at 12 ^{o}C. A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of 5.0×10^{-7} g/cm^3. Assume that the average temperature of the lake is 12 ^{o}C. (a) What is the concentration of the insecticide on June 1 of the following year? (b) How long will it take for the concentration of the insecticide to decrease to 3.0×10^{-7} g/cm^3?

Solution

Practice Problem

The decomposition of dimethyl ether, $(CH_3)_2O$, at 510 °C is a first-order process with a rate constant of $6.8 \times 10^{-4}\ s^{-1}$:

$$(CH_3)_2O(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

If the initial pressure of $(CH_3)_2O$ is 135 torr, what is its pressure after 1420 s?
Answer: 51 torr

The following equation can be used to verify whether a reaction is first order and to determine its rate constant. This equation has the form of the general equation for a straight line, y = mx + b, in which m is the slope and b is the y-intercept of the line:

$$\ln[A]_t = -k \cdot t + \ln[A]_0$$

$$y = m \cdot x + b$$

For a first order reaction, therefore a graph of $\ln[A]_t$ versus time gives a straight line with a slope of $-k$ and a y-intercept of $\ln[A]_0$. A reaction that is not first order will not yield a straight line. As an example consider the conversion of methyl isonitrile (CH_3NC) to acetonitrile (CH_3CN). Because experiments show that the reaction is first order, we can write the rate equation:

$$\ln[CH_3NC]_t = -kt + \ln[CH_3NC]_0$$

Figure 2(a) shows how pressure of methyl isonitrile varies with time as it rearranges in the gas phase at 198.9 °C. We can use the pressure as a unit of concentration for a gas because from the ideal gas law, the pressure is directly proportional to the number of moles per unit volume. Figure 2(b) shows a plot of the natural logarithm of the pressure versus time, a plot that yields a straight line. The slope of this line is -5 x 10^{-5} s^{-1}. Because the slope of the line is –*k*, the rate constant for this reaction is +5.1 x 10^{-5} s^{-1}.

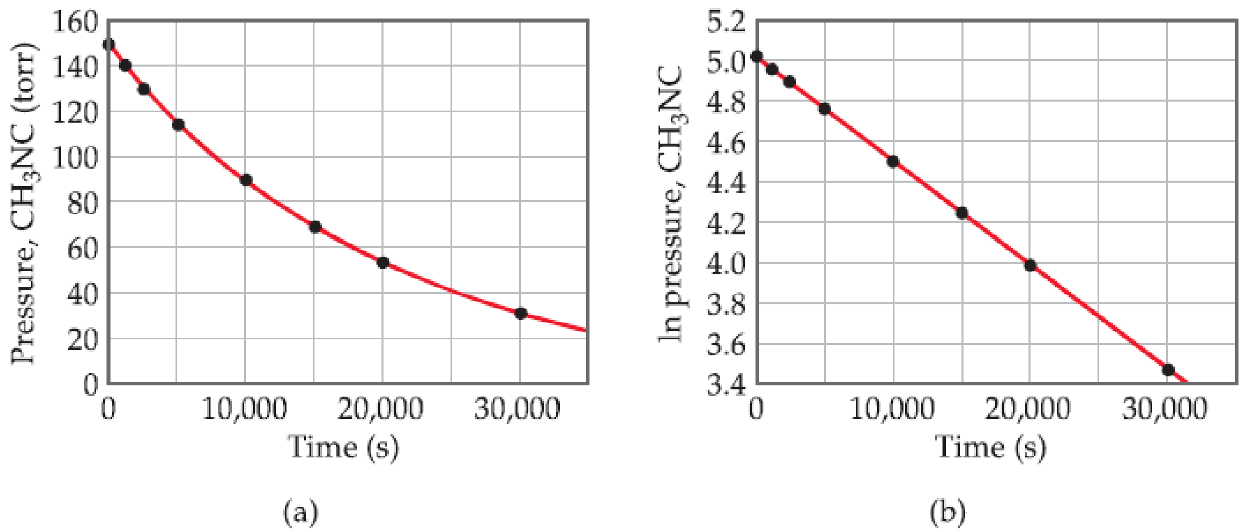


Figure 2

FIRST ORDER REACTIONS

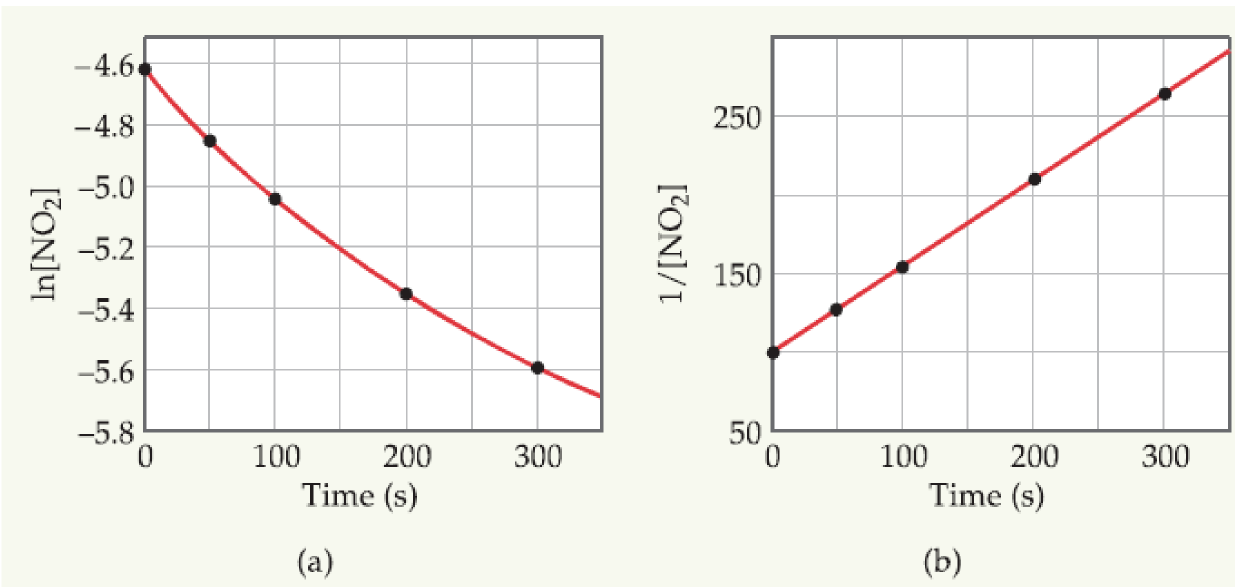
A second order reaction is one whose rate depends on the reactant concentration raised to the second power or on the concentrations of two different reactants, each raised to the first power. For simplicity, let's consider reactions of the type A → products or A + B → products that are second order in just one reactant, A:

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta \text{t}} = k[\text{A}]^2$$

With the use of calculation, this differential rate law can be used to derive the following integrated rate law:

$$\frac{1}{[\text{A}]_\text{t}} = k\text{t} + \frac{1}{[\text{A}]_0}$$

The above equation also has the form of a straight line (y = mx + b). If the reaction is second order, a plot of $1/[A]_t$ versus t will yield a straight line with a slope of k and a y-intercept equal to $1/[A]_0$. One way to distinguish between first and second order rate laws is to graph both $\ln[A]_t$ and $1/[A]_t$ against *t*. If the $\ln[A]_t$ plot is linear, the reaction is first order; if the $1/[A]_t$ plot is linear, the reaction is second order.



HALF LIFE

The half life of a reaction, $t_{1/2}$ is the time required for the concentration of a reactant to reach one half its initial value, $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$. The half-life is a convenient way to describe how fast a reaction occurs, especially if it's a first order process. A fast reaction will have a short half life.

The first order reaction has the following integrated rate law:

$$\ln\frac{[A]_t}{[A]_0} = -kt$$

Subsituting $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$ into the above equation gives.

$$\ln \frac{\frac{1}{2}[A]_0}{[A]_0} = -kt_{\frac{1}{2}}$$

$$\ln\left(\frac{1}{2}\right) = -kt_{\frac{1}{2}}$$

Transposing for $t_{\frac{1}{2}}$:

$$t_{\frac{1}{2}} = -\frac{\ln\left(\frac{1}{2}\right)}{k} = +\frac{\ln\left(\frac{1}{2}\right)^{-1}}{k} = \frac{\ln(2)}{k} = \frac{0.693}{k}$$

Note: sign change from – to +!

From the above equation we see that $t_{\frac{1}{2}}$ for a first order rate law does not depend on the starting concentration. Consequently, the half life remains constant throughout the reaction. If, for example, the concentration of the reactant is 0.120 M at some moment in the reaction, it will be ½ (0.120M) = 0.060 M after one half life. After one more half-life passes, the concentration will drop to 0.030 M, and so on. The equation also indicates that we can calculate the half life for a first order reaction if k is known, or k is the half life is known.

The change in concentration over time for the first order rearrangement of methyl isonitrile at 198.9 oC is graphed in Figure 3:

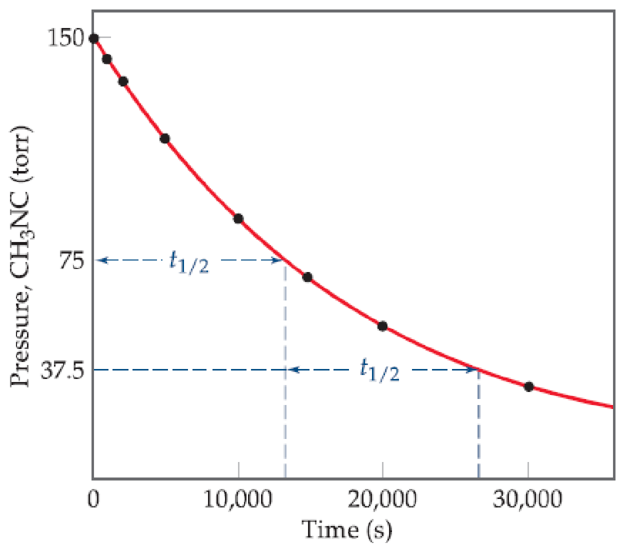


Figure 3

The first half life is shown at 13, 600 s (that is, 3.78 h). At a time 13, 600 s later, the isonitrile concentration has decreased to one half of one half or one fourth the original concentration. In a first order reaction, the concentration of the reactant decreases by ½ in each of a series of regularly spaced time intervals, namely, $t_{½}$. The concept of half life is widely used in describing radioactive decay.

Problem

Determining the Half Life of a First Order Reaction

The reaction of C_4H_9Cl with water is a first order reaction. Figure 1 shows how the concentration of C_4H_9Cl changes with time at a particular temperature. (a) From that graph, estimate the half life for this reaction. (b) Use the half life from (a) to calculate the rate constant.

Solution

(a) From the graph (Figure 1), we see that the initial value of $[C_4H_9Cl]$ is 0.100 M. The half life for this first order reaction is the time required for $[C_4H_9Cl]$ to decrease to 0.050 M, which can read of the graph. This point occurs at approximately 340 s.

(b) For t = 340 s:

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$\rightarrow k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{340\ s} = 2.0 \times 10^{-3}\ s^{-1}$$

Practice Problem

(a) Using Equation 14.15, calculate $t_{1/2}$ for the decomposition of the insecticide described in Sample Exercise 14.7. **(b)** How long does it take for the concentration of the insecticide to reach one-quarter of the initial value?
Answers: **(a)** 0.478 yr $= 1.51 \times 10^7$ s; **(b)** it takes two half-lives, 2(0.478 yr) = 0.956 yr

In contrast to the behavior of first order reactions, the half life for second order and other reactions depends on reactant concentrations and therefore changes as the reaction progresses. Using the integrated law for a second order reaction as shown below:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

We find that the half life of a second order reaction (using the same substitution for the first order reaction and transposing for $t_{½}$):

$$\frac{1}{\frac{1}{2}[A]_0} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}$$

$$kt_{\frac{1}{2}} = \frac{1}{[A]_0}$$

$$\rightarrow t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

In this case, the half life depends on the initial concentration of the reactant – the lower the initial concentration the greater the half life!

TEMPERATURE AND RATE

The rates of most chemical reactions increase as the temperature rises. For example, dough rises faster at room temperature than when refrigerated, and plants grow more rapidly in warm weather than in cold. We can literally see the effect of temperature on reaction rate by observing a chemiluminescence reaction (one that produces light). The characteristic glow of fireflies is another example of chemiluminescence. The characteristic glow of fireflies is a familiar example of chemiluminescence. Another is the light produced by Cyalume® light sticks, which contain chemicals that produce chemiluminescence when mixed.

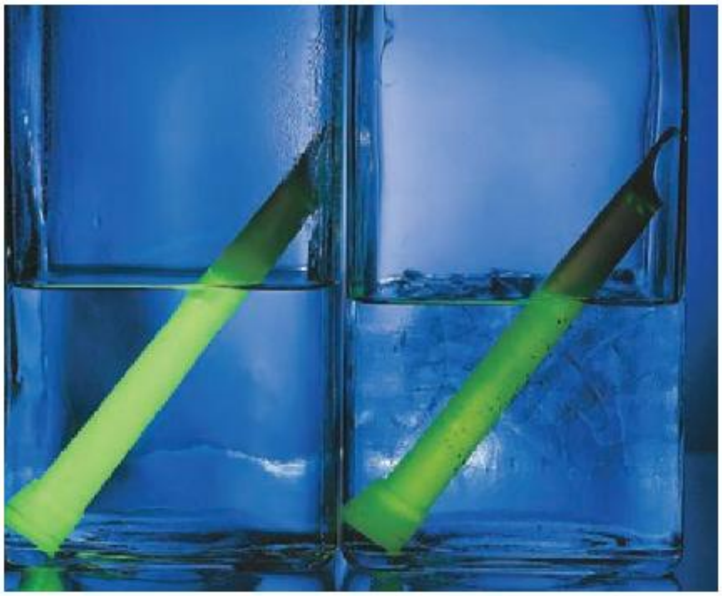


Figure 4

In Figure 4, these light sticks produce a brighter light at higher temperature. The amount of light produced is greater because the rate of the reaction is faster at the higher temperature. Although the light stick glows more brightly initially, its luminescence also dies out more rapidly.

How is this experimentally observed temperature effect reflected in the rate expression? The faster rate at higher temperature is due to an increase in the rate constant with increasing temperature. For example, let's **re**consider the first order reaction $CH_3NC \rightarrow CH_3CN$.

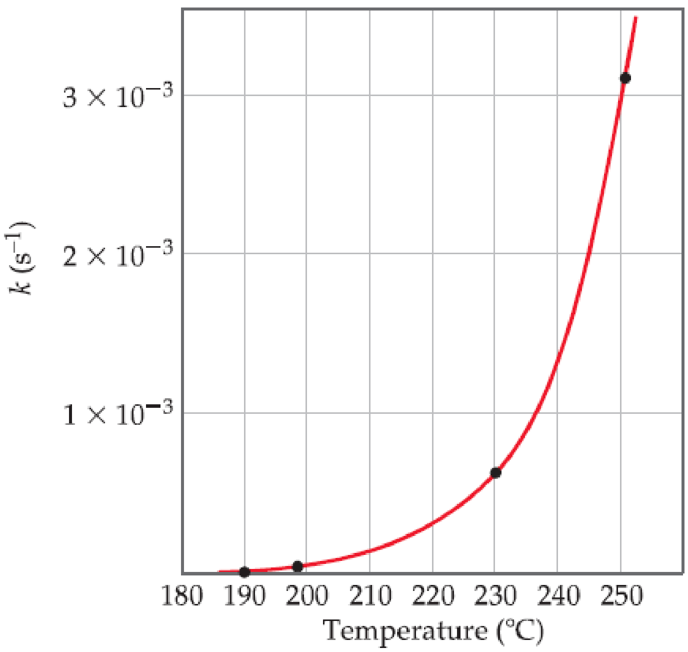


Figure 5 shows the rate constant for this reaction as a function of temperature. The rate constant, and hence the rate of the reaction, increases rapidly with temperature, approximately doubling for each 10 °C rise.

THE COLLISION MODEL

We have seen that reaction rates are affected both by the concentration of reactants and by temperature. The collision model, which is based on the kinetic molecular theory, accounts for both of these effects at the molecular level. The central idea of the collision model is that molecules must collide to react. The greater the number of collisions occurring per second, the greater is the reaction rate. As the concentration of reactant molecules increases, therefore, the number of collisions increases, leading to an increase in the reaction rate. According to the kinetic-molecular theory of gases, increasing the temperature increases the molecular speeds. As molecules move faster, they collide more forcefully (with more energy) and more frequently, increasing reaction rates.

For a reaction to occur, though, more is required than simply a collision. For most reactions, only a tiny fraction of the collisions leads to a reaction. For example, in a mixture of H_2 and I_2 at ordinary temperatures and pressures, each molecule undergoes about 10^{10} collisions per second. If every collision between H_2 and I_2 resulted in the formation of HI, the reaction would be over in much less than a second. Instead, at room temperature the reaction proceeds very slowly. Only about one in every 10^{13} collisions produces a reaction. What keeps the reaction from occurring more rapidly?

THE ORIENTATION FACTOR

In most reactions, molecules must be oriented in a certain way during collisions for a reaction to occur. The relative orientations of the molecules during their collisions determine whether the atoms are suitably positioned to form new bonds. For example, consider the reaction of Cl atoms with NOCl:

$$Cl + NOCl \rightarrow NO + Cl_2$$

The reaction will take place if the collision brings Cl atoms together to form Cl_2 as shown in Figure 6(a)! In contrast, the collision shown in Figure 6(b) will be ineffective and will not yield products. Indeed, a great many collisions do not lead to reaction, merely because the molecules are not suitably oriented. Another factor, however, is usually even more important in determining whether particular collisions result in reaction.

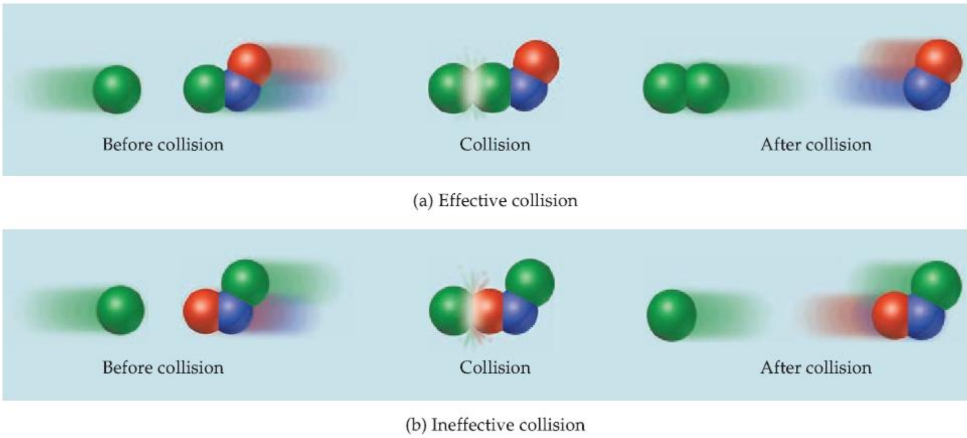
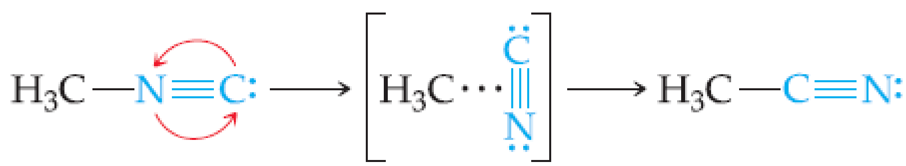


Figure 6

ACTIVATION ENERGY

In 1888, the Swedish chemist Svante Arrhenius suggested that molecules must possess a certain minimum amount of energy to react. According to the collision model, this energy comes from the kinetic energies of the colliding molecules. Upon collision, the kinetic energy of the molecules can be used to stretch, bend and ultimately break bonds, leading to chemical reactions. That is, the kinetic energy is used to change the potential energy of the molecule. If molecules are moving too slowly, with too little kinetic energy, they merely bounce off one another without changing. To react, colliding molecules must have a total kinetic energy equal to or greater than some minimum value. The minimum energy required to initiate a chemical reaction is called the activation energy, Ea. The value of Ea varies from reaction to reaction.

Molecules may require a certain minimum energy to break existing bonds during a chemical reaction. In the arrangement of methyl isonitrile to acetonitrile, for example, we might imagine the reaction passing through an intermediate state in which the $N \equiv C$ portion of the molecule is sitting sideways:



The change in the potential energy of the molecule during the reaction is shown in Figure 7. The diagram shows that the energy must be supplied to stretch the bond between the H_3C group and the N≡C group to allow the N≡C group to rotate. After the ≡NC group has twisted sufficiently, the C-C bond begins to form, and the energy of the molecule drops. Thus the barrier represents the energy necessary to force the molecule through the relatively unstable intermediate state to the final product. The energy difference between that of the starting molecule and the highest energy along the reaction pathway is the activation energy, E_a. The particular arrangement of atoms at the top of the barrier is called the activated complex, or the transition state.

The conversion of H_3C-N≡C to H_3C-C≡N is exothermic. Figure 7 therefore shows the product as having a lower energy than the reactant. The energy change for the reaction, ΔE, has no effect on the rate of the reaction. The rate depends on the magnitude of Ea; generally the lower Ea is the faster the reaction. Notice that the reverse reaction is endothermic. The activation barrier for the reverse reaction is equal to the sum of ΔE and Ea for the forward reaction.

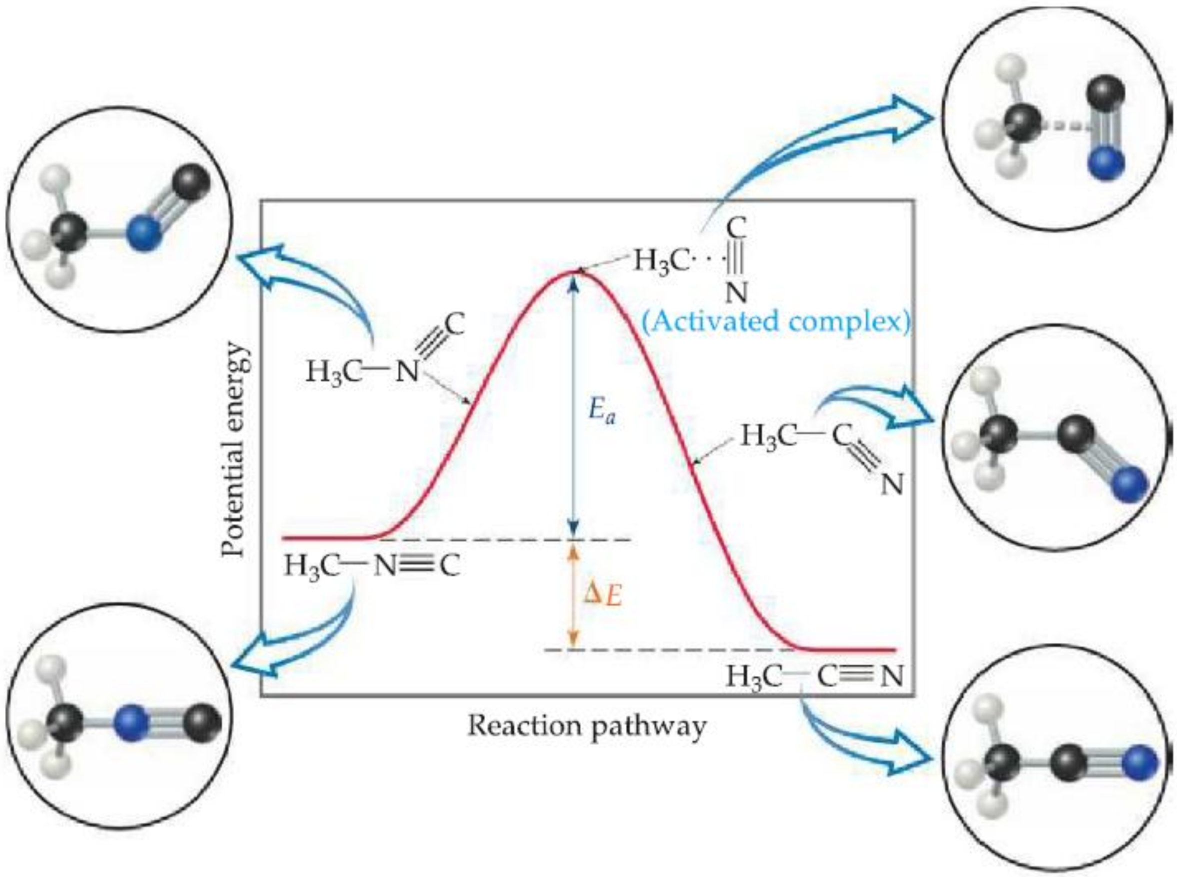

H3C—N≡C
H3C—N≡C
H3C· · C≡N
(Activated complex)
Ea
ΔE
H3C—C≡N
H3C—C≡N
Potential energy
Reaction pathway

Figure 7

1. CATALYSIS

A catalyst is a substance that changes the speed of a chemical reaction without undergoing a permanent chemical change itself in the process. Catalysts are very common; most reactions in the body, the atmosphere, and the oceans occur with the help of catalysts. Much industrial chemical research is devoted to the search for new and more effective catalysts for reactions of commercial importance. Extensive research efforts also are devoted to finding means of inhibiting or removing certain catalysts that promote undesirable reactions, such as those that corrode metals, age our bodies and cause tooth decay.

1.1. HOMOGENEOUS CATALYSIS

A catalyst that is present in the same phase as the reacting molecules is called a homogeneous catalyst. Examples abound both in solution and in the gas phase. Consider, for example, the decomposition of aqueous hydrogen peroxide, H_2O_2 (aq) into water and oxygen:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$ **Equation 1**

In the absence of a catalyst, this reaction occurs extremely slowly. Many different substances are capable of catalyzing the reaction above including the bromide ion, Br- (aq), shown in the figure below:

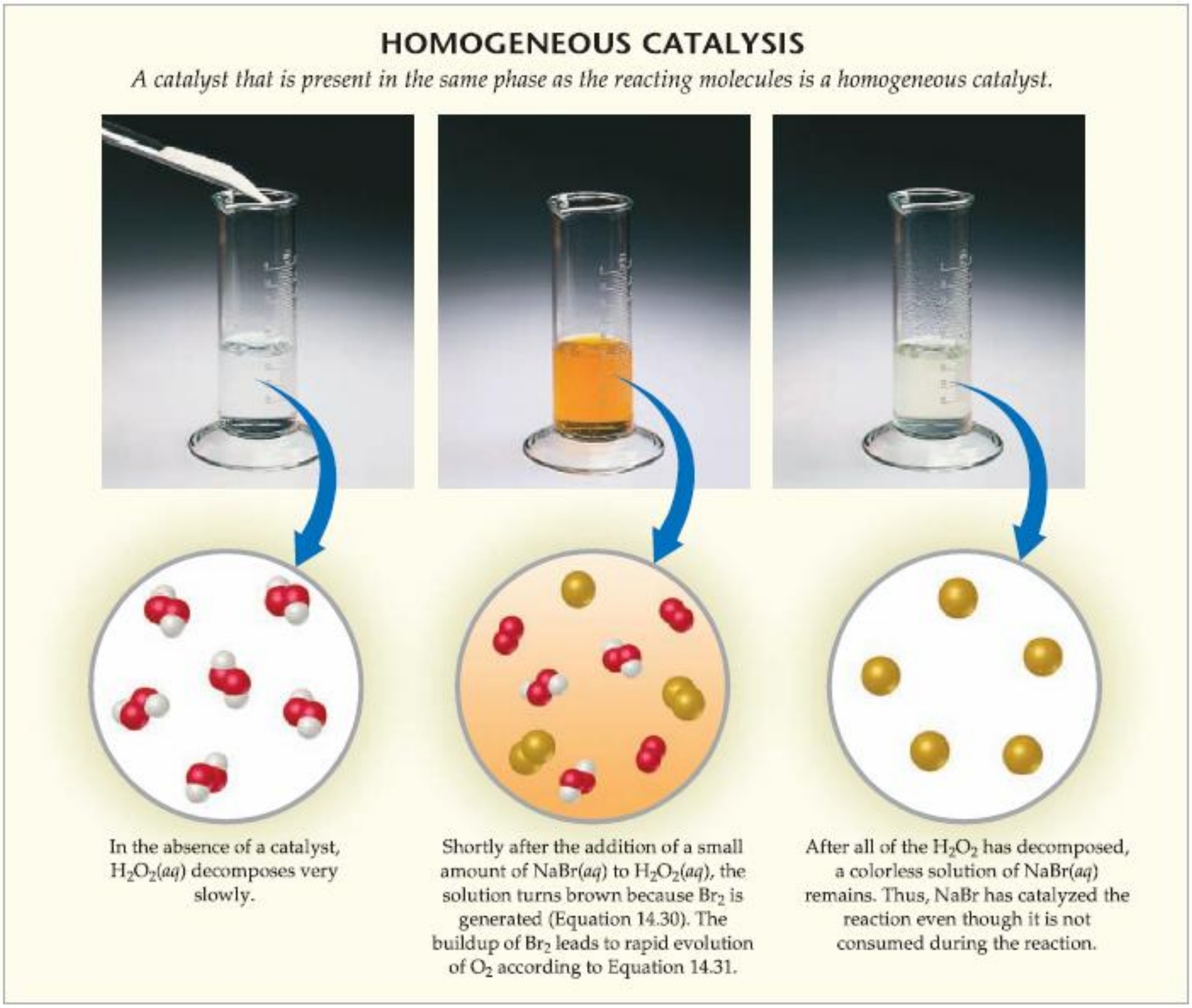


Figure 8

The bromide ion reacts with hydrogen peroxide in acidic solution, forming aqueous bromine and water:

$$\mathbf{2Br^{-}(aq) + H_2O_2(aq) + 2H^{+} \rightarrow Br_2(aq) + 2H_2O(l)}$$ **Equation 2**

The brown colour observed in the middle photograph of Figure 8 indicates the formation of Br_2(aq). If this were the complete reaction, bromide ion would not be a catalyst, because it undergoes chemical change during the reaction. However, hydrogen peroxide also reacts with Br_2(aq):

$$Br_2(aq) + H_2O_2(aq) \rightarrow 2Br^{-}(aq) + 2H^{+}(aq) + O_2(g)$$ **Equation 3**

The bubbling in Figure 8(b) is due to the formation of O_2 (g).The sum of the Equation 2 and Equation 3 is just Equation 1:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g) \qquad \textbf{Equation 4}$$

When H_2O_2 has been completely decomposed, we are left with a colourless solution of Br^- (aq), as seen in Figure 8. Bromide ion, therefore, is indeed a catalyst of the reaction because it speeds the overall reaction without itself undergoing any net change. It is added at the start of the reaction, reacts, and then reforms at the end. In contrast, Br_2 is an intermediate because it is first formed (Equation 2) and then consumed (Equation 3). Neither the catalyst nor the intermediate appears in the chemical equation for the overall reaction. Notice, however, that the catalyst is there at the start of the reaction, whereas the intermediate is formed during the course of the reaction.

A catalyst may affect the rate of reaction by altering the value of either Ea or A. The most dramatic catalytic effects come from lowering Ea. As a general rule, a catalyst lowers the overall activation energy for a chemical reaction. Usually it does this because it provides a different mechanism for the reaction. In the decomposition of hydrogen peroxide, for example, two successigve reactions of H2O2, with bromie and then with bromine, take place. Because these two reactions together serve as a catalytic pathway for hydrogen peroxide decomposition, both of them must have significantly lower activation energies than the un-catalyzed decomposition; as shown schematically in Figure 9.

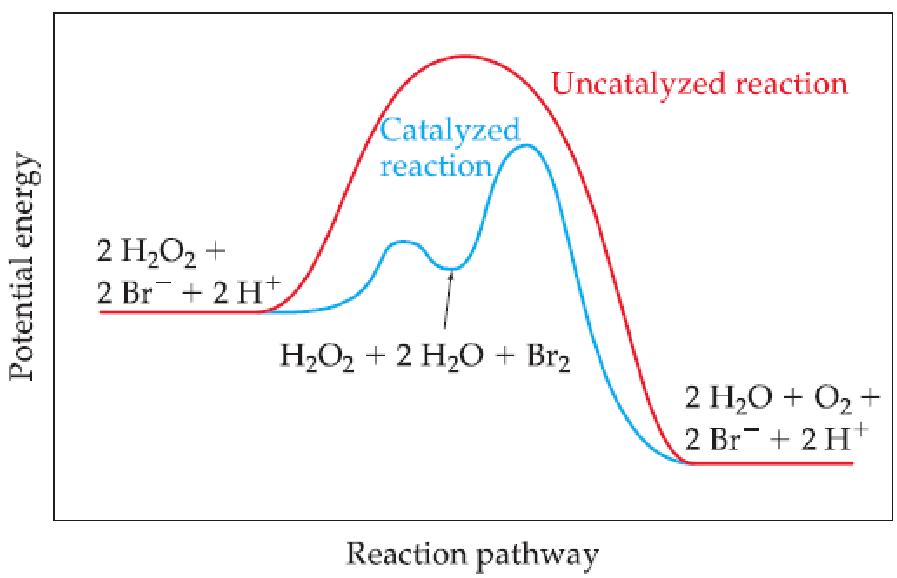


Figure 9

1.2. HETEROGENOUS CATALYSIS

A heterogeneous catalyst exists in a different phase from the reactant molecules, usually as a solid in contact with either gaseous reactants or with reactants in a liquid solution. Many industrially important reactions are catalyzed by the surfaces of solids. For example, hydrocarbon molecules are rearranged to form gasoline with the aid of what are called 'cracking' catalysts. Heterogeneous catalysts are often composed of metals or metal oxides. Because the catalyzed reaction occurs on the surface, special methods are often used to prepare catalysts so that they have very large surface areas. The initial step in heterogeneous catalysis is usually adsorption of reactants. Adsorption refers to the binding of molecules to a surface, where as absorption refers to the uptake of molecules into the interior of another substance. Adsorption occurs because the atoms or ions at the surface of a solid are extremely reactive. Unlike their counterparts in the interior of the substance, surface atoms and ions have unused bonding capacity. This unused bonding capability may be used to bond molecules from the gas or solution phase to the surface of the solid.

The reaction of hydrogen gas with ethylene gas to form ethane gas provides an example of heterogeneous catalysis:

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) \quad \Delta H^o = -137\frac{kJ}{mol}$$ **Equation 5**

Even though this reaction is exothermic, it occurs very slowly in the absence of a catalyst. In the presence of a finely powdered metal, however such as nickel, palladium or platinum, the reaction occurs rather easily at room temperature. The mechanism by which the reaction occurs is diagrammed in Figure 10

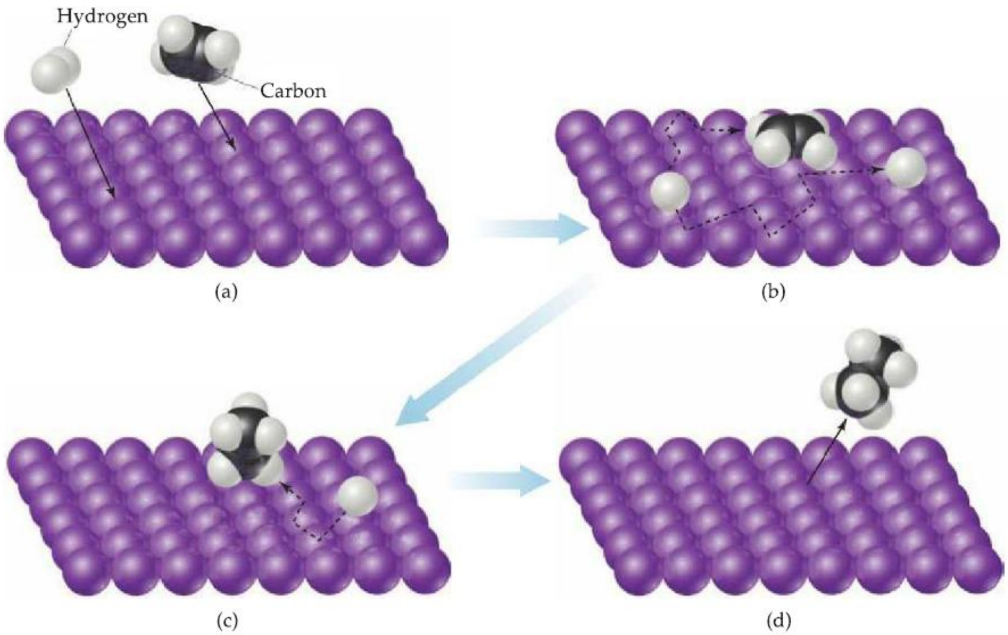


Figure 10

Both ethylene and hydrogen are adsorbed on the metal surface [Figure 10(a)]. Upon adsorption the H-H bond of H_2 breaks, leaving two H atoms that are bonded to the metal surface, as shown in [Figure 10(b)]. The hydrogen atoms are relatively free to move about the surface. When a hydrogen encounters an adsorbed ethylene molecule, it can form a σ bond to one of the carbon atoms, effectively destroying the C-C π bond and leaving and ethyl group (C_2H_5) bonded to the surface via a metal-to-carbon σ bond [Figure 10(c)]. This σ bond is relatively weak, so when the other carbon atom also encounters a hydrogen atom, a sixth C-H σ bond is readily formed and an ethane molecule is released from the metal surface [Figure 10(d)]. The site is ready to adsorb another ethylene molecule and thus begin the cycle again.

[The notes are taken from General Chemistry by Whitten, Davis and Peck]
Excuse my Plagiarism; Notes will be taken care of later on!