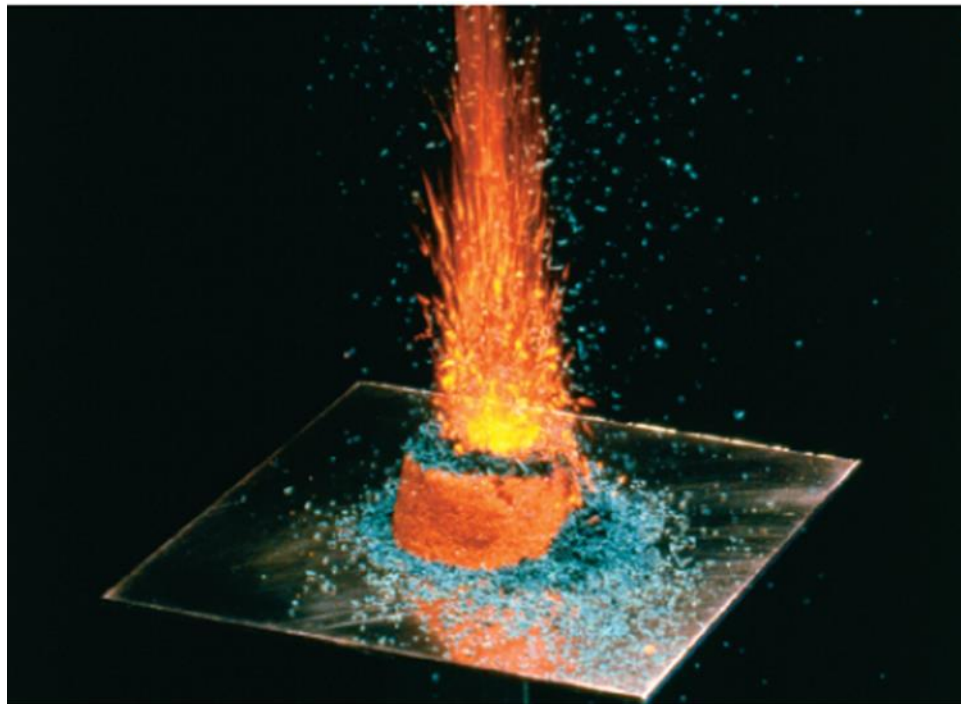


Chemical Kinetics



- References :
1. General Chemistry- principles and modern applications (Petrucci, Herring, Madura, Bissonnette)
 2. Chemistry-10th Edition (Raymond Chang)

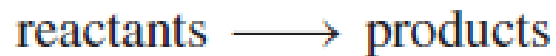
The Rate of a Reaction

Rate, or speed, refers to something that happens in a unit of time. A car traveling at 60 km/h, for example, covers a distance of 60 kilometers in one hour.

For chemical reactions, the rate of reaction describes how fast the concentration of a reactant or product changes with time.

There are many reasons for studying the rate of a reaction. To begin with, there is intrinsic curiosity about why reactions have such vastly different rates. Some processes, such as the initial steps in vision and photosynthesis and nuclear chain reactions, take place on a time scale as short as 10^{-12} s to 10^{-6} s. Others, like the curing of cement and the conversion of graphite to diamond, take years or millions of years to complete.

We know that any reaction can be represented by the general equation;



This equation tells us that during the course of a reaction, reactants are consumed while products are formed. As a result, we can follow the progress of a reaction by monitoring either the decrease in concentration of the reactants or the increase in concentration of the products.

Figure 13.1 shows the progress of a simple reaction in which A molecules are converted to B molecules:

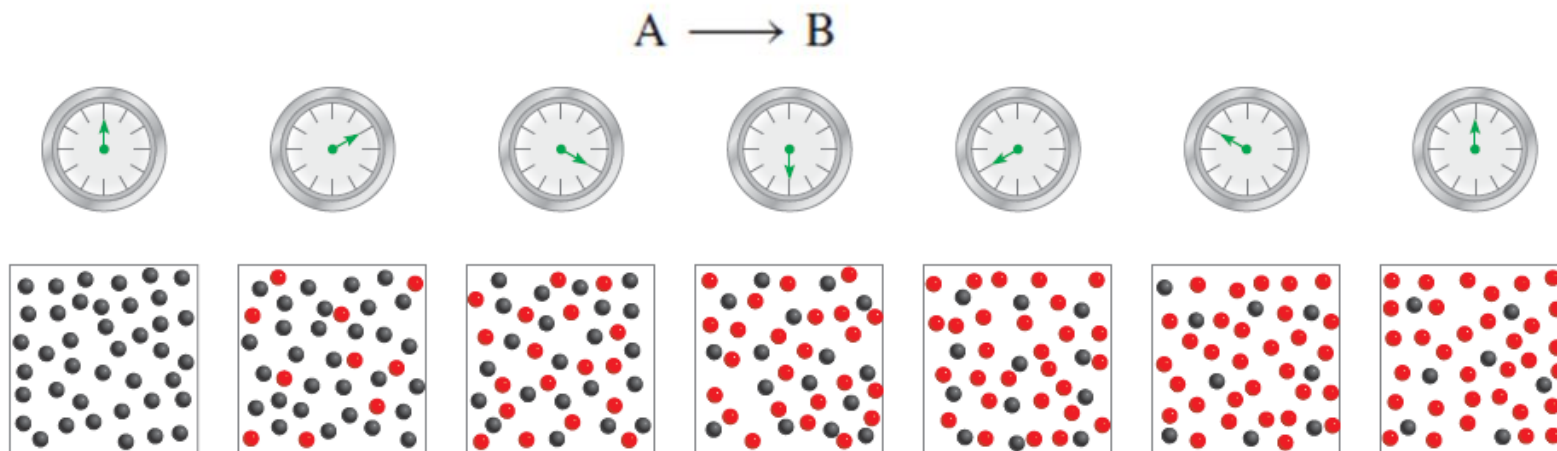


Figure 13.1 The progress of reaction $A \longrightarrow B$ at 10-s intervals over a period of 60 s. Initially, only A molecules (gray spheres) are present. As time progresses, B molecules (red spheres) are formed.

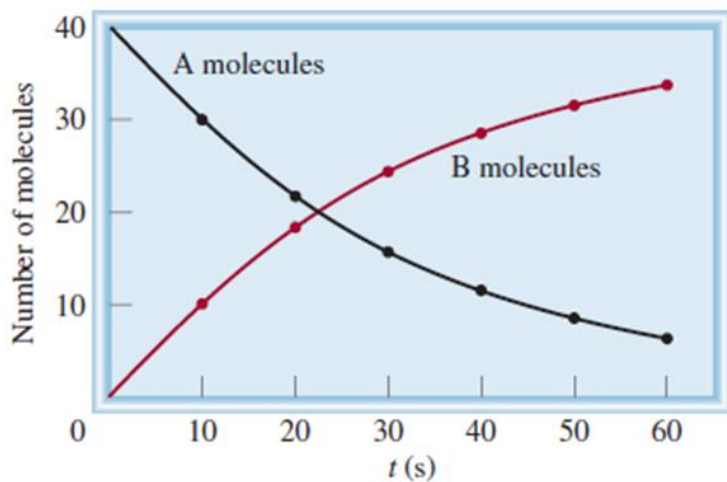


Figure 13.2 The rate of reaction $A \longrightarrow B$, represented as the decrease of A molecules with time and as the increase of B molecules with time.

In general, it is more convenient to express the reaction rate in terms of the change in concentration with time. Thus, for the reaction $A \rightarrow B$ we can express the rate as

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{or} \quad \text{rate} = \frac{\Delta[B]}{\Delta t}$$

In general, for the reaction

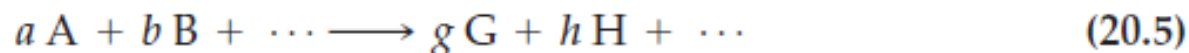


the rate is given by

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

The Rate Law

One of the goals in a chemical kinetics study is to derive an equation that can be used to predict the relationship between the rate of reaction and the concentrations of reactants. Such an experimentally determined equation is called a rate law, or rate equation

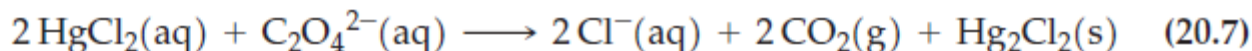


where a, b, \dots stand for coefficients in the balanced equation. The rate law for reaction (20.5) can often be expressed in the following general form.*

$$\text{rate of reaction} = k[A]^m[B]^n \dots \quad (20.6)$$

Method of Initial Rates

As its name implies, this method requires us to work with *initial* rates of reaction. As an example, let's look at a specific reaction: that between mercury(II) chloride and oxalate ion.



The tentative rate law that we can write for this reaction is

$$\text{rate of reaction} = k[\text{HgCl}_2]^m[\text{C}_2\text{O}_4^{2-}]^n \quad (20.8)$$

We can follow the reaction by measuring the quantity of $\text{Hg}_2\text{Cl}_2(\text{s})$ formed as a function of time. Some representative data are given in Table 20.3, which we can assume are based on either the rate of formation of Hg_2Cl_2 or the rate of disappearance of $\text{C}_2\text{O}_4^{2-}$. In Example 20-3, we will use some of these data to illustrate the method of initial rates.

TABLE 20.3 Kinetic Data for the Reaction:
 $2 \text{HgCl}_2 + \text{C}_2\text{O}_4^{2-} \longrightarrow 2 \text{Cl}^- + 2 \text{CO}_2 + \text{Hg}_2\text{Cl}_2$

Experiment	$[\text{HgCl}_2], \text{M}$	$[\text{C}_2\text{O}_4^{2-}], \text{M}$	Initial Rate, M min^{-1}
1	$[\text{HgCl}_2]_1 = 0.105$	$[\text{C}_2\text{O}_4^{2-}]_1 = 0.15$	$R_1 = 1.8 \times 10^{-5}$
2	$[\text{HgCl}_2]_2 = 0.105$	$[\text{C}_2\text{O}_4^{2-}]_2 = 0.30$	$R_2 = 7.1 \times 10^{-5}$
3	$[\text{HgCl}_2]_3 = 0.052$	$[\text{C}_2\text{O}_4^{2-}]_3 = 0.30$	$R_3 = 3.5 \times 10^{-5}$

Experiment	[HgCl ₂], M	[C ₂ O ₄ ²⁻], M	Initial Rate, M min ⁻¹
1	[HgCl ₂] ₁ = 0.105	[C ₂ O ₄ ²⁻] ₁ = 0.15	R ₁ = 1.8 × 10 ⁻⁵
2	[HgCl ₂] ₂ = 0.105	[C ₂ O ₄ ²⁻] ₂ = 0.30	R ₂ = 7.1 × 10 ⁻⁵
3	[HgCl ₂] ₃ = 0.052	[C ₂ O ₄ ²⁻] ₃ = 0.30	R ₃ = 3.5 × 10 ⁻⁵

We begin by writing

$$R_2 = k \times [\text{HgCl}_2]_2^m \times [\text{C}_2\text{O}_4^{2-}]_2^n = k \times (2 \times [\text{HgCl}_2]_3)^m \times [\text{C}_2\text{O}_4^{2-}]_3^n$$

$$R_3 = k \times [\text{HgCl}_2]_3^m \times [\text{C}_2\text{O}_4^{2-}]_3^n$$

$$\frac{R_2}{R_3} = \frac{2 \times R_3}{R_3} = 2 = \frac{k \times 2^m \times [\text{HgCl}_2]_3^m \times [\text{C}_2\text{O}_4^{2-}]_3^n}{k \times [\text{HgCl}_2]_3^m \times [\text{C}_2\text{O}_4^{2-}]_3^n} = 2^m$$

In order that $2^m = 2$, $m = 1$.

To determine the value of n , we can form the ratio R_2/R_1 . Now, [C₂O₄²⁻] is doubled and [HgCl₂] is held constant. This time, let's use actual concentrations instead of symbolic equivalents. Also, we now have the value $m = 1$.

$$R_2 = k \times [\text{HgCl}_2]_2^1 \times [\text{C}_2\text{O}_4^{2-}]_2^n = k \times (0.105)^1 \times (2 \times 0.15)^n$$

$$R_1 = k \times [\text{HgCl}_2]_1^1 \times [\text{C}_2\text{O}_4^{2-}]_1^n = k \times (0.105)^1 \times (0.15)^n$$

$$\frac{R_2}{R_1} = \frac{7.1 \times 10^{-5}}{1.8 \times 10^{-5}} \approx 4 = \frac{k \times (0.105)^1 \times 2^n \times (0.15)^n}{k \times (0.105)^1 \times (0.15)^n} = 2^n$$

In order that $2^n = 4$, $n = 2$.

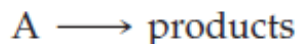
m+n = 3 (third order reaction)

The Relation Between Reactant Concentration and Time

Rate law expressions enable us to calculate the rate of a reaction from the rate constant and reactant concentrations. The rate laws can also be used to determine the concentrations of reactants at any time during the course of a reaction. We will illustrate this application by first considering two of the most common rate laws—those applying to reactions that are first order overall and those applying to reactions that are second order overall.

Zero-Order Reactions

An overall **zero-order reaction** has a rate law in which the sum of the exponents, $m + n \dots$, is equal to 0. As an example, let's take a reaction in which a single reactant A decomposes to products.

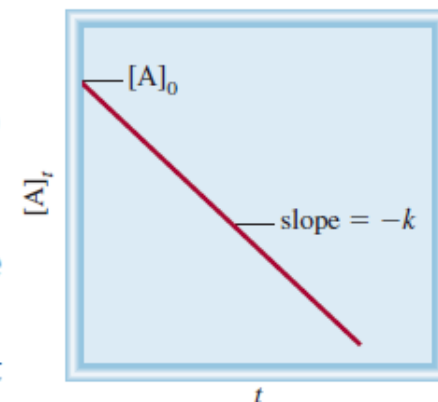


If the reaction is zero order, the rate law is

$$\text{rate of reaction} = k[A]^0 = k = \text{constant} \quad (20.9)$$

Other features of this zero-order reaction are:

- The concentration–time graph is a straight line with a *negative* slope (Fig. 20-3).
- The rate of reaction, which is equal to k and remains constant throughout the reaction, is the *negative* of the slope of this line.
- The units of k are the same as the units of the rate of a reaction: $\text{mol L}^{-1} (\text{time})^{-1}$, for example, $\text{mol L}^{-1} \text{s}^{-1}$ or M s^{-1} .

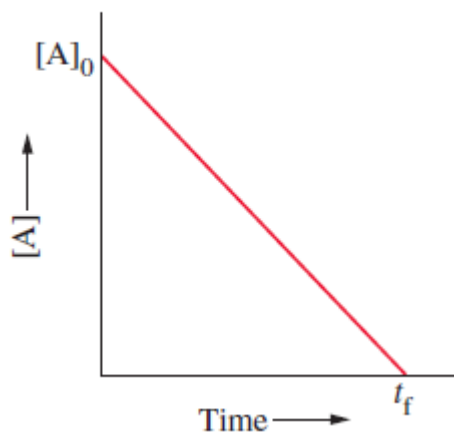


Equation (20.9) is the rate law for a zero-order reaction. Another useful equation, called an **integrated rate law**, expresses the concentration of a reactant as a function of time. This equation can be established rather easily from the graph in Figure 20-3. Let's start with the general equation for a straight line

$$y = mx + b$$

and substitute $y = [A]_t$ (the concentration of A at some time t); $x = t$ (time); $b = [A]_0$ (the initial concentration of A at time $t = 0$); and $m = -k$ (m , the slope of the straight line, is obtained as indicated in the caption to Figure 20-3).

$$[A]_t = -kt + [A]_0 \quad (20.10)$$

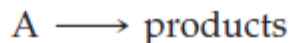


First-Order Reactions

An overall **first-order reaction** has a rate law in which the sum of the exponents, $m + n + \dots$, is equal to 1. A particularly common type of first-order reaction, and the only type we will consider, is one in which a single reactant decomposes into products.

An Integrated Rate Law for a First-Order Reaction

Let us begin our discussion of first-order reactions as we did zero-order reactions, by examining a hypothetical reaction



For a first-order reaction, the rate law is

$$\text{rate of reaction} = -\frac{\Delta[A]}{\Delta t} = k[A] \quad (20.12)$$

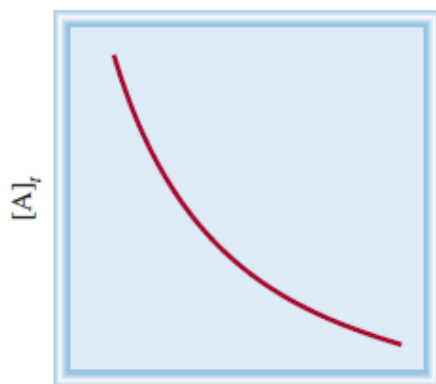
We can obtain the *integrated* rate law for this first-order reaction by applying the calculus technique of *integration* to equation (20.12). The result of this derivation (shown in Are You Wondering 20-4) is

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad \text{or} \quad \ln[A]_t = -kt + \ln[A]_0 \quad (20.13)$$

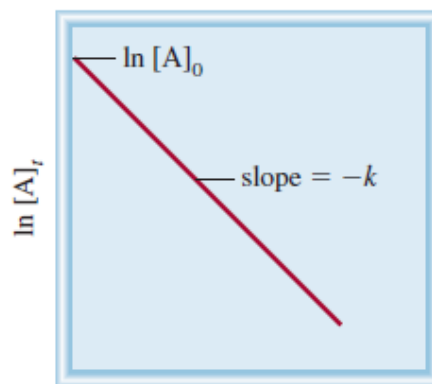
$[A]_t$ is the concentration of A at time t , $[A]_0$ is its concentration at $t = 0$, and k is the rate constant. Because the logarithms of numbers are dimensionless (have no units), the product $-k \times t$ must also be dimensionless. This means that the unit of k in a first-order reaction is $(\text{time})^{-1}$, such as s^{-1} or min^{-1} . Equation (20.13) is that of a straight line.

Equation of straight line

$$\underbrace{\ln[A]_t}_{y} = \underbrace{(-k)t}_{m \cdot x} + \underbrace{\ln[A]_0}_{b}$$



(a)



(b)

Figure 13.9 First-order reaction characteristics: (a) The exponential decrease of reactant concentration with time; (b) A plot of $\ln [A]_t$ versus t . The slope of the line is equal to $-k$.

$$\text{rate of reaction} = -\frac{\Delta[A]}{\Delta t} = k[A]$$

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



20-4 ARE YOU WONDERING?

How do we obtain the integrated rate law for a first-order reaction?

If the reaction $A \longrightarrow$ products is first order, then the rate law is, in differential form, $d[A]/dt = -k[A]$.

Separation of the differentials leads to the expression $d[A]/[A] = -k dt$.

Integration of this expression between the limits $[A]_0$ at time $t = 0$ and $[A]_t$ at time t is indicated through the expression

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_0^t dt$$

The result of the integration is equation (20.13), the integrated rate law.

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

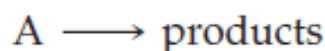
The **half-life** of a reaction is the time required for one-half of a reactant to be consumed. It is the time during which the amount of reactant or its concentration decreases to one-half of its initial value. That is, at $t = t_{1/2}$, $[A]_t = \frac{1}{2}[A]_0$. At this time, equation (20.13) takes the form

$$\ln \frac{[A]_t}{[A]_0} = \ln \frac{\frac{1}{2}[A]_0}{[A]_0} = \ln \frac{1}{2} = -\ln 2 = -k \times t_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \quad (20.14)$$

Second-Order Reactions

An overall second-order reaction has a rate law with the sum of the exponents, $m + n \dots$, equal to 2. As with zero- and first-order reactions, our discussion will be limited to reactions involving the decomposition of a single reactant



If the reaction is second order, then we can write

$$\text{rate of reaction} = k[A]^2 \quad (20.17)$$

Again, our primary interest will be in the integrated rate law that is derived from the rate law. For the reaction we are considering, the integrated rate law is

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \quad (20.18)$$

$$t_{1/2} = \frac{1}{k[A]_0} \quad (20.19b)$$

The Effect of Temperature on Reaction Rates

From practical experience, we expect chemical reactions to go faster at higher temperatures. To speed up the biochemical reactions involved in cooking, we raise the temperature, and to slow down other reactions, we lower the temperature—as in refrigerating milk to prevent it from souring.

In 1889, Svante Arrhenius demonstrated that the rate constants of many chemical reactions vary with temperature in accordance with the expression

$$k = Ae^{-E_a/RT} \quad (20.21)$$

By taking the natural logarithm of both sides of this equation, we obtain the following expression.

$$\ln k = -\frac{E_a}{RT} + \ln A$$

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

Subtracting $\ln k_2$ from $\ln k_1$ gives

$$\ln k_1 - \ln k_2 = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

Catalysis

A reaction can generally be made to go faster by increasing the temperature. Another way to speed up a reaction is to use a catalyst. A catalyst provides an alternative reaction pathway of lower activation energy. The catalyst participates in a chemical reaction but does not itself undergo a permanent change. As a result, the formula of a catalyst does not appear in the overall chemical equation (its formula is generally placed over the reaction arrow).

TABLE 20.5 Reaction Kinetics: A Summary for the Hypothetical Reaction $a A \longrightarrow \text{Products}$

Order	Rate Law ^a	Integrated Rate Equation ^b	Straight Line	$k =$	Units of k	Half-Life ^b
0	rate = k	$[A]_t = -akt + [A]_0$	$[A]$ v. time	$-\frac{1}{a} \times \text{slope}$	$\text{mol L}^{-1} \text{s}^{-1}$	$\frac{[A]_0}{2ak}$
1	rate = $k[A]$	$\ln[A]_t = -akt + \ln[A]_0$	$\ln[A]$ v. time	$-\frac{1}{a} \times \text{slope}$	s^{-1}	$\frac{0.693}{ak}$
2	rate = $k[A]^2$	$\frac{1}{[A]_t} = akt + \frac{1}{[A]_0}$	$\frac{1}{[A]}$ v. time	$\frac{1}{a} \times \text{slope}$	$\text{L mol}^{-1} \text{s}^{-1}$	$\frac{1}{ak[A]_0}$

$$^a \text{rate} = -\left(\frac{1}{a}\right) \frac{\Delta[A]}{\Delta t}$$

^bTo obtain the expressions for $a A \longrightarrow \text{products}$, we replace k with ak in the expressions given in the text for $A \longrightarrow \text{products}$.