Biophysical chemistry

Part A
Chapter: 3
Chemical kinetics
Lecture - 1

Fahmida Akter Lia
Department of Biochemistry
National Institute of Science and Technology(NIST)

The Relation Between Reactant Concentration and Time

The rate laws can be used to determine the concentrations of reactants at any time during the course of a reaction

First-Order Reactions

A ***first-order reaction*** is *a reaction whose rate depends on the reactant concentration raised to the first power*. In a first-order reaction of the type

$$\text{A} \longrightarrow \text{product}$$

the rate is

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

From the rate law we also know that

$$\text{rate} = k[\text{A}]$$

To obtain the units of k for this rate law, we write

$$k = \frac{\text{rate}}{[\text{A}]} = \frac{M/\text{s}}{M} = 1/\text{s or } \text{s}^{-1}$$

First-Order Reactions

Combining the first two equations for the rate we get

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

Using calculus, we can show from Equation (1) that

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

t = 0 need not correspond to the beginning of the experiment; it can be any time when we choose to start monitoring the change in the concentration of A.

Equation (1) can be rearranged as follows:

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

In differential form, Equation (1) becomes

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

Rearranging, we get

$$-\frac{d[A]}{[A]} = -kdt$$

Integrating between $t = 0$ and $t = t$ gives

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

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

or

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

First-Order Reactions

Equation (1) has the form of the linear equation $y = mx + b$, in which m is the slope of the line that is the graph of the equation:

$$\begin{array}{ccccccc} \ln [A]_t & = & (-k)(t) & + & \ln [A]_0 \\ \updownarrow & & \updownarrow \ \updownarrow & & \updownarrow \\ y & = & m \ \ x & + & b \end{array}$$

For a first-order reaction, if we plot ln $[A]_t$ versus time (y versus x), we obtain a straight line with a slope equal to -k and a y intercept equal to ln $[A]_0$
we can calculate the rate constant from the slope of this plot.

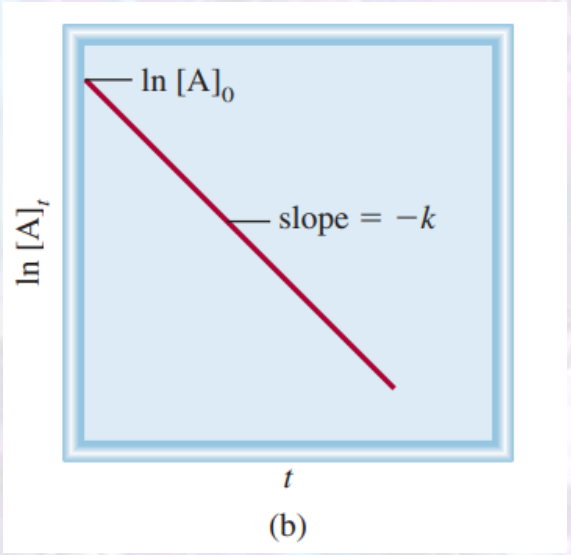
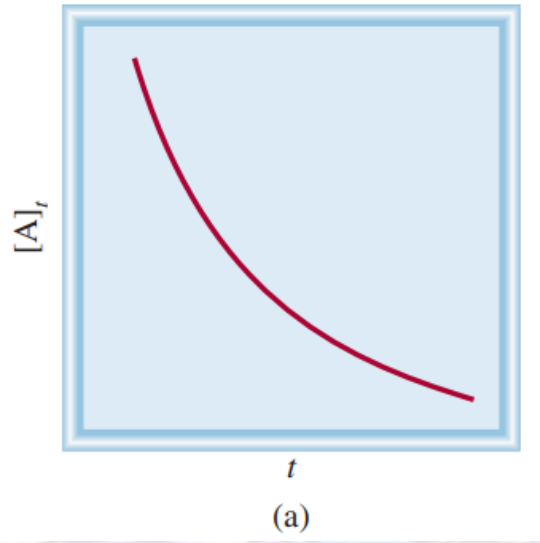


Figure 13.9 *First-order reaction characteristics: (a) The exponential decrease of reactant concentration with time; (b) A plot of ln $[A]_t$ versus t. The slope of the line is equal to −k.*



First-Order Reactions

There are many first-order reactions. An example is the decomposition of ethane (C_2H_6) into highly reactive fragments called methyl radicals (CH_3):

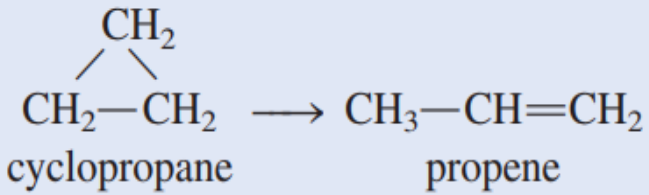
$$C_2H_6 \longrightarrow 2CH_3$$

The decomposition of N_2O_5 is also a first-order reaction

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

First-Order Reactions

The conversion of cyclopropane to propene in the gas phase is a first-order reaction with a rate constant of $6.7 \times 10^{-4}\ s^{-1}$ at 500°C.



(a) If the initial concentration of cyclopropane was 0.25 *M*, what is the concentration after 8.8 min? (b) How long (in minutes) will it take for the concentration of cyclopropane to decrease from 0.25 *M* to 0.15 *M*? (c) How long (in minutes) will it take to convert 74 percent of the starting material?

Solution (a) In applying Equation (1), we note that because k is given in units of s^{-1}, we must first convert 8.8 min to seconds:

$$8.8 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} = 528 \text{ s}$$

We write

$$\begin{aligned} \ln [A]_t &= -kt + \ln [A]_0 \\ &= -(6.7 \times 10^{-4}\ s^{-1})(528 \text{ s}) + \ln (0.25) \\ &= -1.74 \end{aligned}$$

Hence, $[A]_t = e^{-1.74} = 0.18\ M$

First-Order Reactions

(b) Using Equation (1)

$$\ln \frac{0.15\ M}{0.25\ M} = -(6.7 \times 10^{-4}\ \text{s}^{-1})t$$

$$t = 7.6 \times 10^{2}\ \text{s} \times \frac{1\ \text{min}}{60\ \text{s}}$$

$$= 13\ \text{min}$$

(c) From Equation (1)

$$\ln \frac{0.26}{1.00} = -(6.7 \times 10^{-4}\ \text{s}^{-1})t$$

$$t = 2.0 \times 10^{3}\ \text{s} \times \frac{1\ \text{min}}{60\ \text{s}} = 33\ \text{min}$$

First-Order Reactions

For gas-phase reactions we can replace the concentration terms in Equation (1) with the pressures of the gaseous reactant. Consider the first-order reaction

$$A(g) \longrightarrow \text{product}$$

Using the ideal gas equation we write

$$PV = n_A RT$$

or

$$\frac{n_A}{V} = [A] = \frac{P}{RT}$$

Substituting $[A] = P/RT$ in Equation (1), we get

$$\ln \frac{[A]_t}{[A]_0} = \ln \frac{P_t/RT}{P_0/RT} = \ln \frac{P_t}{P_0} = -kt$$

The equation corresponding to Equation (13.4) now becomes

$$\ln P_t = -kt + \ln P_0$$

First-Order Reactions

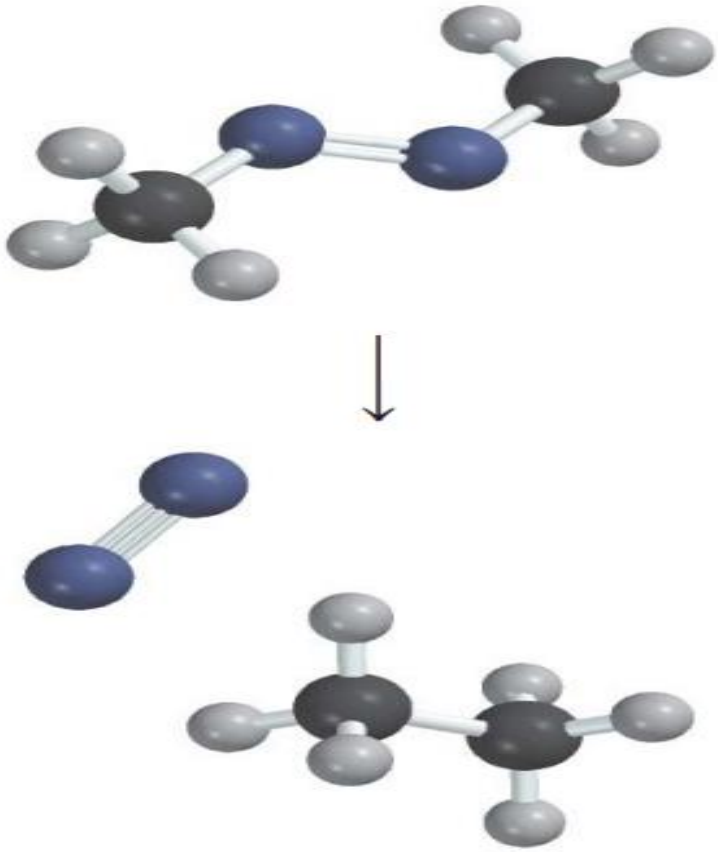
The rate of decomposition of azomethane ($C_2H_6N_2$) is studied by monitoring the partial pressure of the reactant as a function of time:

$$CH_3—N{=}N—CH_3(g) \longrightarrow N_2(g) + C_2H_6(g)$$

The data obtained at 300°C are shown in the following table:

Time (s)	Partial Pressure of Azomethane (mmHg)
0	284
100	220
150	193
200	170
250	150
300	132

Are these values consistent with first-order kinetics? If so, determine the rate constant.



$C_2H_6N_2 \longrightarrow N_2 + C_2H_6$

First-Order Reactions

Strategy To test for first-order kinetics, we consider the integrated first-order rate law that has a linear form, which is Equation (13.4)

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

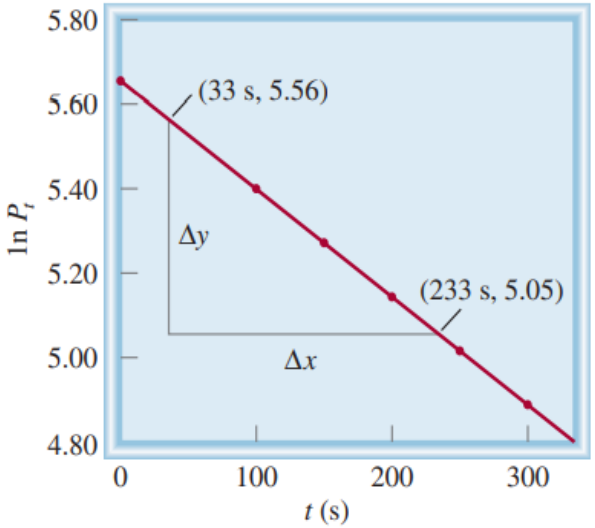
If the reaction is first order, then a plot of $\ln [A]_t$ versus t (y versus x) will produce a straight line with a slope equal to $-k$. Note that the partial pressure of azomethane at any time is directly proportional to its concentration in moles per liter ($PV = nRT$, so $P \propto n/V$). Therefore, we substitute partial pressure for concentration [Equation (13.5)]:

$$\ln P_t = -kt + \ln P_0$$

where P_0 and P_t are the partial pressures of azomethane at $t = 0$ and $t = t$, respectively.

Solution First we construct the following table of t versus $\ln P_t$.

t (s)	$\ln P_t$
0	5.649
100	5.394
150	5.263
200	5.136
250	5.011
300	4.883



First-Order Reactions

Figure 13.11, which is based on the data given in the table, shows that a plot of ln P_t versus t yields a straight line, so the reaction is indeed first order. The slope of the line is given by

$$\text{slope} = \frac{5.05 - 5.56}{(233 - 33)\ \text{s}} = -2.55 \times 10^{-3}\ \text{s}^{-1}$$

According to Equation (13.4), the slope is equal to $-k$, so $k = 2.55 \times 10^{-3}\ \text{s}^{-1}$.

First-Order Reactions

Reaction Half-life

Another measure of the rate of a reaction, relating concentration to time, is the half-life,

-is the time required for the concentration of a reactant to decrease to half of its initial concentration.

Equation (13.3) can be rearranged to give

$$t = \frac{1}{k} \ln \frac{[A]_0}{[A]_t}$$

By the definition of half-life, when $t = t_{\frac{1}{2}}$, $[A]_t = [A]_0/2$, so

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

or

$$t_{\frac{1}{2}} = \frac{1}{k} \ln 2 = \frac{0.693}{k} \qquad (13.6)$$

Measuring the half-life of a reaction is one way to determine the rate constant of a first-order reaction.

Reaction Half-life

Equation (13.6) tells us that the half-life of a first-order reaction is independent of the initial concentration of the reactant.

`Thus, it takes the same time for the concentration of the reactant to decrease from 1.0 M to 0.50 M, say, as it does for a decrease in concentration from 0.10 M to 0.050 M

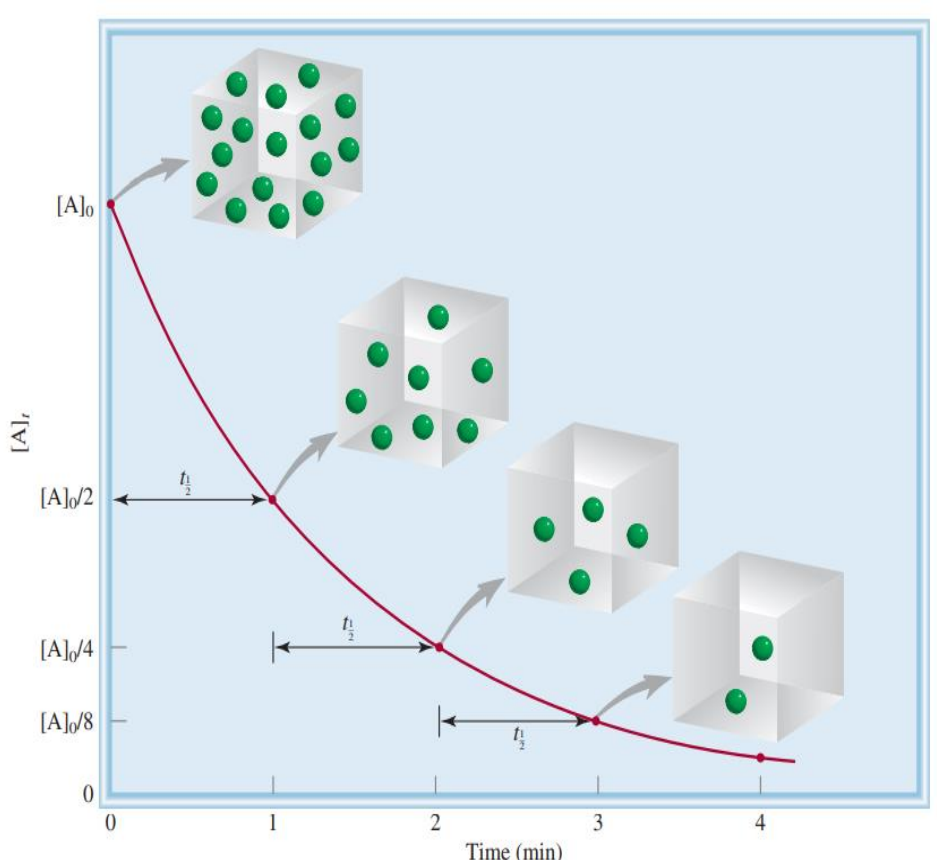


Figure 13.12 *A plot of $[A]_t$ versus time for the first-order reaction A ⟶ products. The half-life of the reaction is 1 min. After the elapse of each half-life, the concentration of A is halved.*