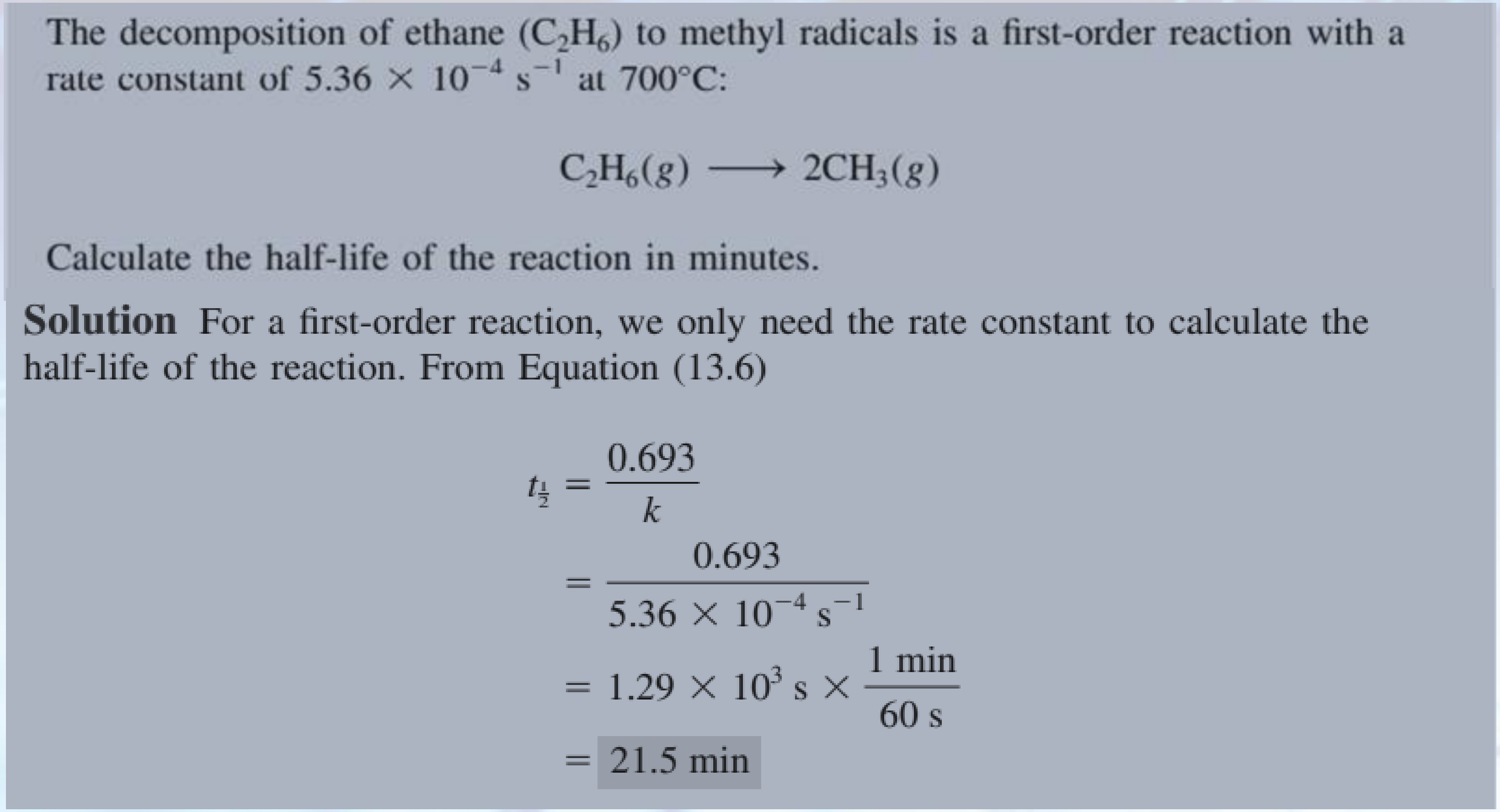
Biophysical chemistry

Part A
Chapter: 3
Chemical kinetics
Lecture - 4

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

Reaction Half-life



The decomposition of ethane (C_2H_6) to methyl radicals is a first-order reaction with a rate constant of $5.36 \times 10^{-4}\ s^{-1}$ at 700°C:

$$C_2H_6(g) \longrightarrow 2CH_3(g)$$

Calculate the half-life of the reaction in minutes.

Solution For a first-order reaction, we only need the rate constant to calculate the half-life of the reaction. From Equation (13.6)

$$\begin{aligned} t_{\frac{1}{2}} &= \frac{0.693}{k} \\ &= \frac{0.693}{5.36 \times 10^{-4}\ s^{-1}} \\ &= 1.29 \times 10^{3}\ s \times \frac{1\ min}{60\ s} \\ &= \boxed{21.5\ min} \end{aligned}$$

Second-Order Reactions

-is a reaction whose rate depends on the concentration of one reactant raised to the second power or on the concentrations of two different reactants, each raised to the first power.

The simpler type involves only one kind of reactant molecule:

$$A \rightarrow \text{product}$$

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

From the rate law,

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

As before, we can determine the units of k by writing

$$k = \frac{rate}{[A]^2} = \frac{M/S}{M^2} = 1/M.s$$

Another type of second-order reaction is

$$A + B \rightarrow \text{product}$$

and the rate law is given by

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

Second-Order Reactions

Using calculus, we can obtain the following expressions for “A → product” second-order reactions

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

Equation (13.7) is the result of

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

Equation (13.7) has the form of a linear equation. As Figure 13.13 shows, a plot of $1/[A]_t$ versus t gives a straight line with slope = k and y intercept = $1/[A]_0$.

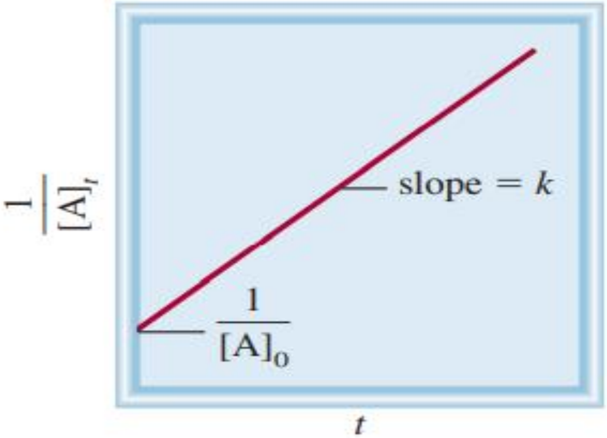
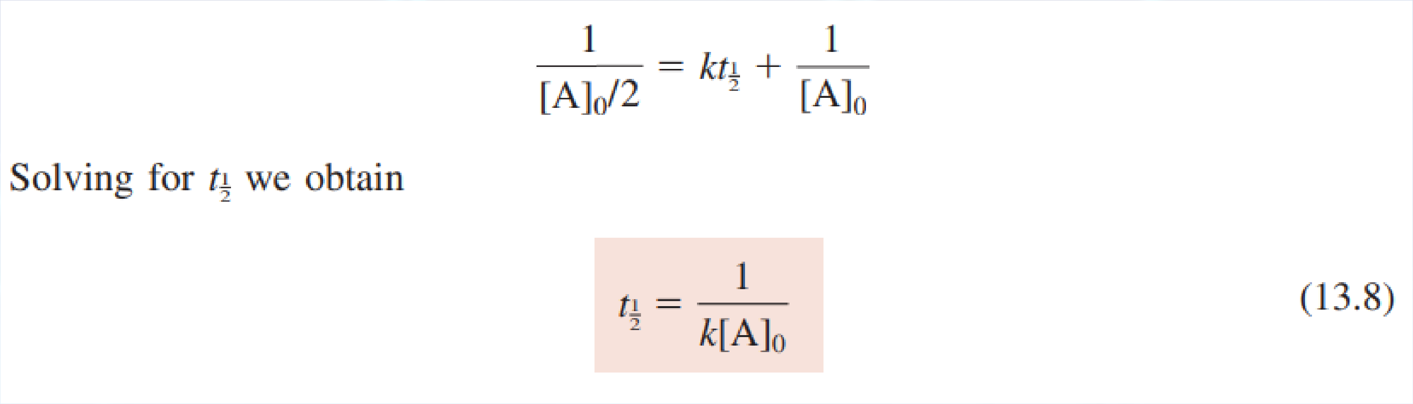


Figure 13.13 *A plot of $1/[A]_t$ versus t for a second-order reaction. The slope of the line is equal to k.*

Second-Order Reactions

We can obtain an equation for the half-life of a second-order reaction by setting $[A]_t = [A]_0/2$ in Equation (13.7).



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

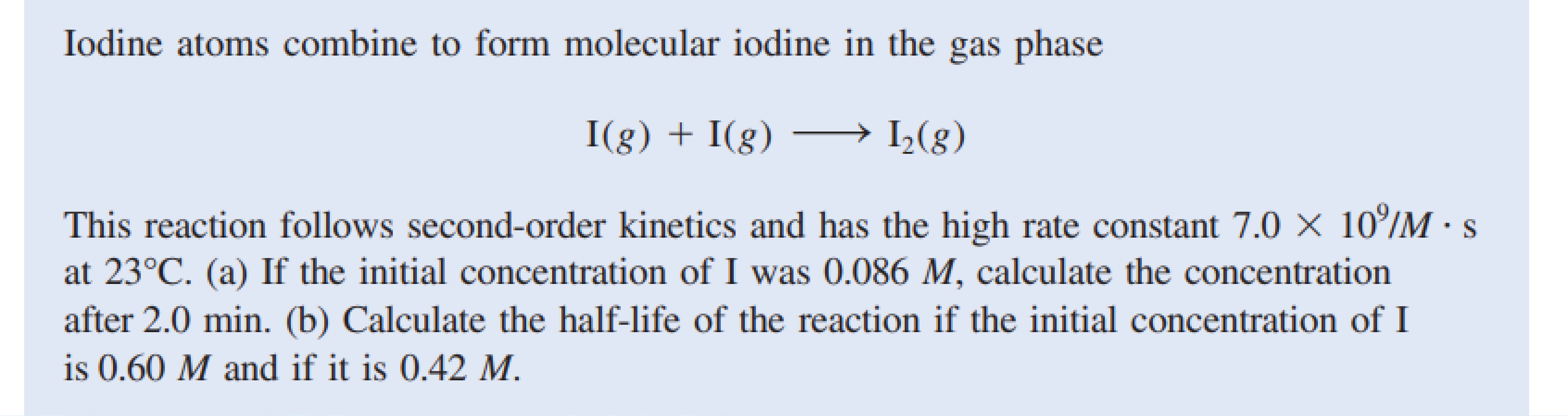
Solving for $t_{\frac{1}{2}}$ we obtain

$$\boxed{t_{\frac{1}{2}} = \frac{1}{k[\mathrm{A}]_0}} \qquad (13.8)$$

the half-life of a second-order reaction is inversely proportional to the initial reactant concentration.

Measuring the half-lives at different initial concentrations is one way to distinguish between a first-order and a second-order reaction.

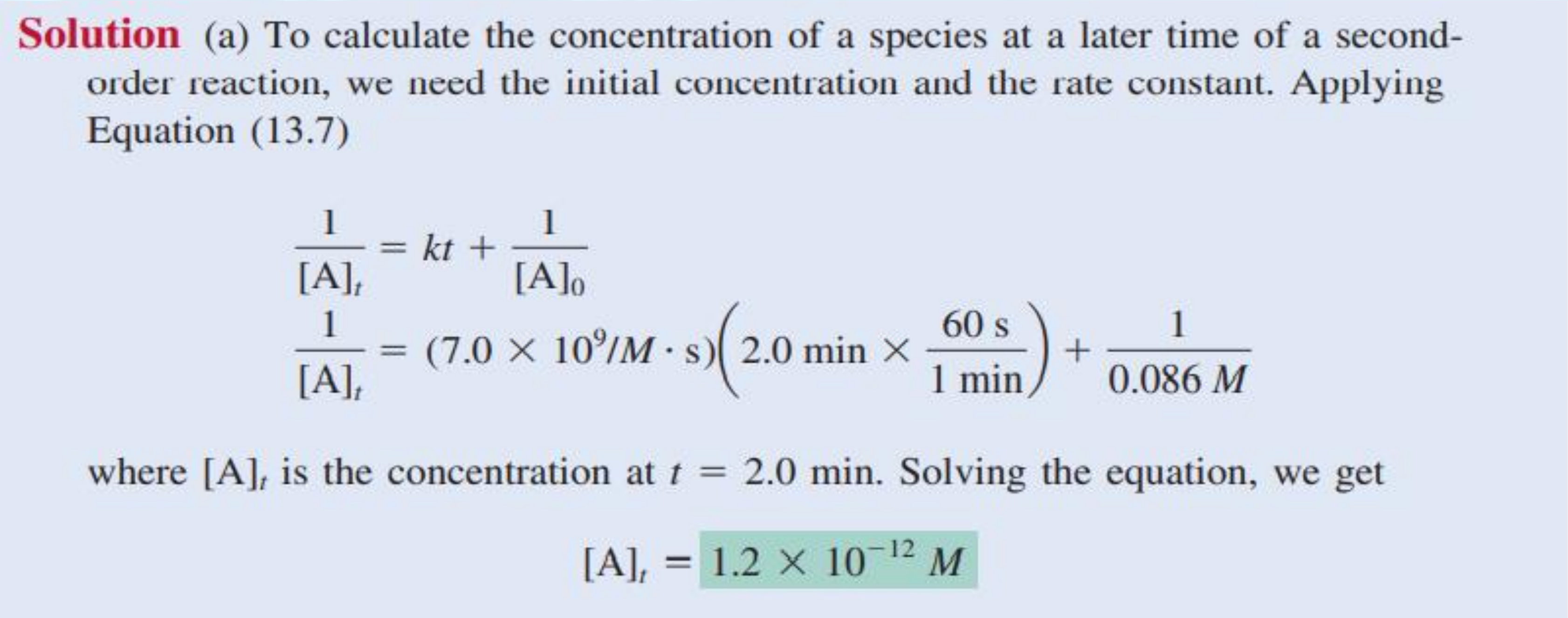
Second-Order Reactions



Iodine atoms combine to form molecular iodine in the gas phase

$$I(g) + I(g) \longrightarrow I_2(g)$$

This reaction follows second-order kinetics and has the high rate constant $7.0 \times 10^9/M \cdot s$ at 23°C. (a) If the initial concentration of I was 0.086 M, calculate the concentration after 2.0 min. (b) Calculate the half-life of the reaction if the initial concentration of I is 0.60 M and if it is 0.42 M.



Solution (a) To calculate the concentration of a species at a later time of a second-order reaction, we need the initial concentration and the rate constant. Applying Equation (13.7)

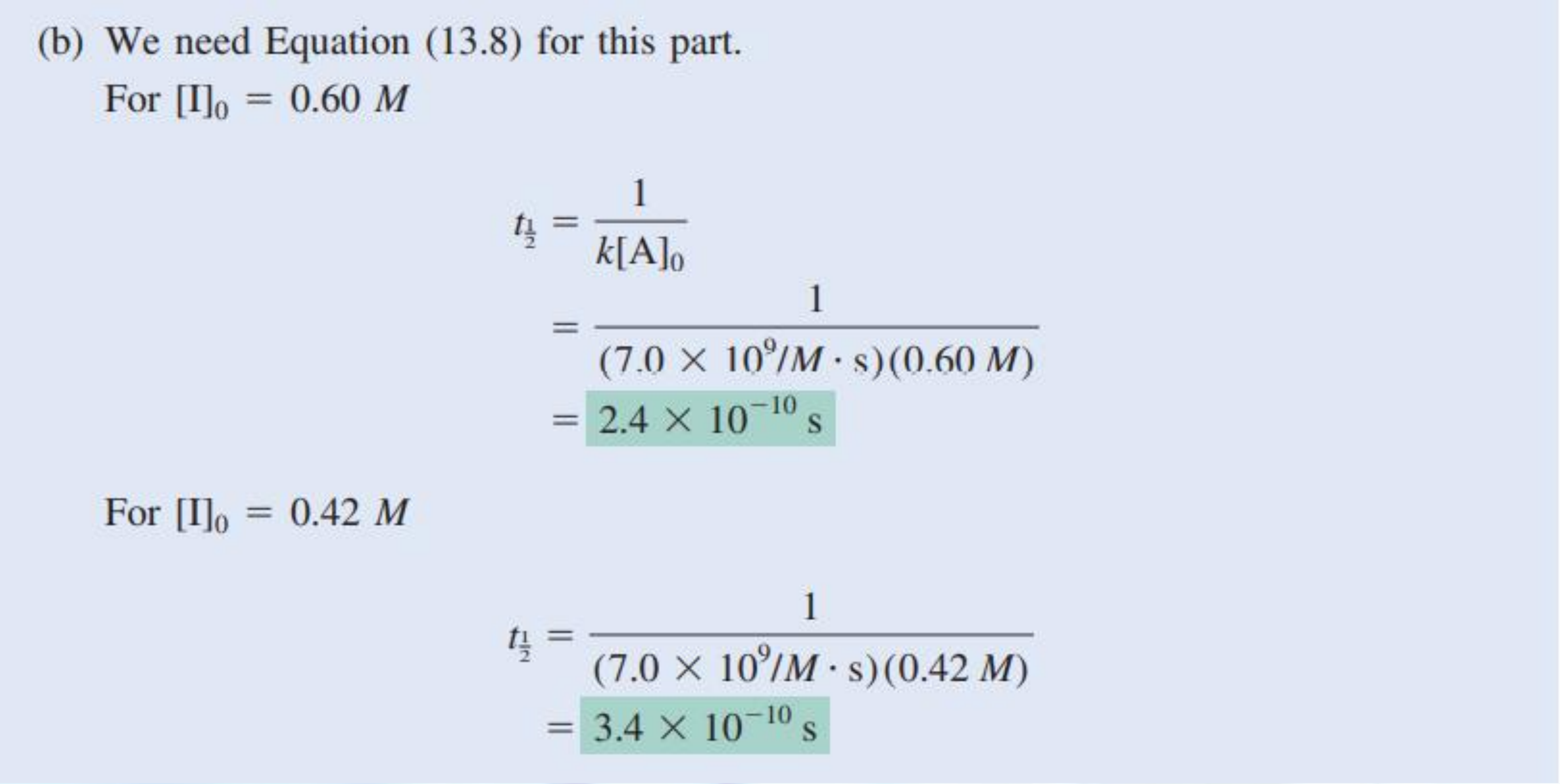
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$\frac{1}{[A]_t} = (7.0 \times 10^9/M \cdot s)\left(2.0\text{ min} \times \frac{60\text{ s}}{1\text{ min}}\right) + \frac{1}{0.086\ M}$$

where $[A]_t$ is the concentration at $t = 2.0$ min. Solving the equation, we get

$$[A]_t = 1.2 \times 10^{-12}\ M$$

Second-Order Reactions



(b) We need Equation (13.8) for this part.

For $[\mathrm{I}]_0 = 0.60\ M$

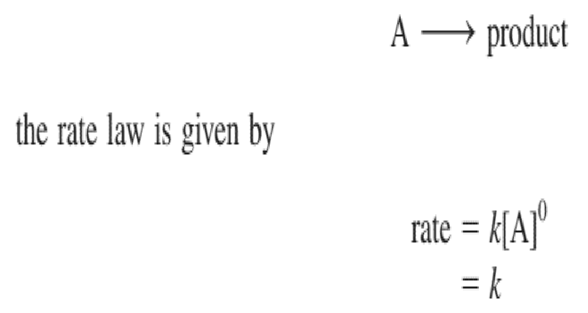
$$t_{\frac{1}{2}} = \frac{1}{k[\mathrm{A}]_0}$$
$$= \frac{1}{(7.0 \times 10^9/M \cdot \mathrm{s})(0.60\ M)}$$
$$= \boxed{2.4 \times 10^{-10}\ \mathrm{s}}$$

For $[\mathrm{I}]_0 = 0.42\ M$

$$t_{\frac{1}{2}} = \frac{1}{(7.0 \times 10^9/M \cdot \mathrm{s})(0.42\ M)}$$
$$= \boxed{3.4 \times 10^{-10}\ \mathrm{s}}$$

Zero-Order Reaction

For a zero-order reaction



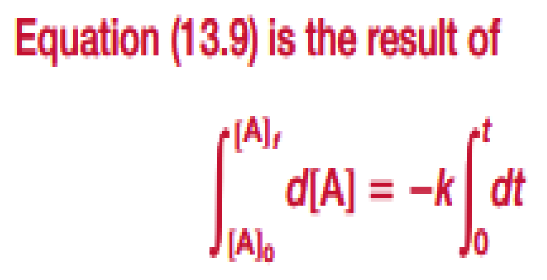
$$A \longrightarrow \text{product}$$

the rate law is given by

$$\begin{aligned}\text{rate} &= k[A]^0 \\ &= k\end{aligned}$$

Thus, the rate of a zero-order reaction is a constant, independent of reactant concentration. Using calculus, we can show

$$[A]_t = -kt + [A]_0 \qquad (13.9)$$



Equation (13.9) is the result of

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

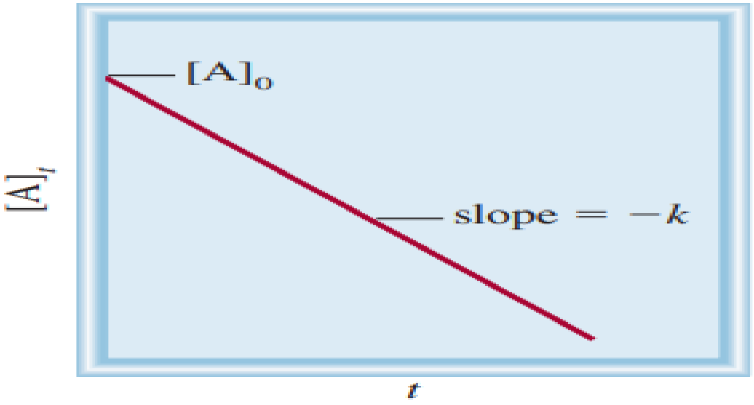


Figure 13.14 *A plot of $[A]_t$ versus t for a zero-order reaction. The slope of the line is equal to $-k$.*

Equation (13.9) has the form of a linear equation. As Figure 13.14 shows, a plot of [A]t versus t gives a straight line with slope = - k and y intercept = $[A]_0$.

Zero-Order Reaction

To calculate the half-life of a zero-order reaction, we set $[A]_t = [A]_0/2$ in Equation (13.9) and obtain

$$t_{\frac{1}{2}} = \frac{[A]_0}{2k} \qquad (13.10)$$

Many of the known zero-order reactions take place on a metal surface. An example is the decomposition of nitrous oxide (N2O) to nitrogen and oxygen in the presence of platinum (Pt):

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$$

When all the binding sites on Pt are occupied, the rate becomes constant regardless of the amount of N2O present in the gas phase.

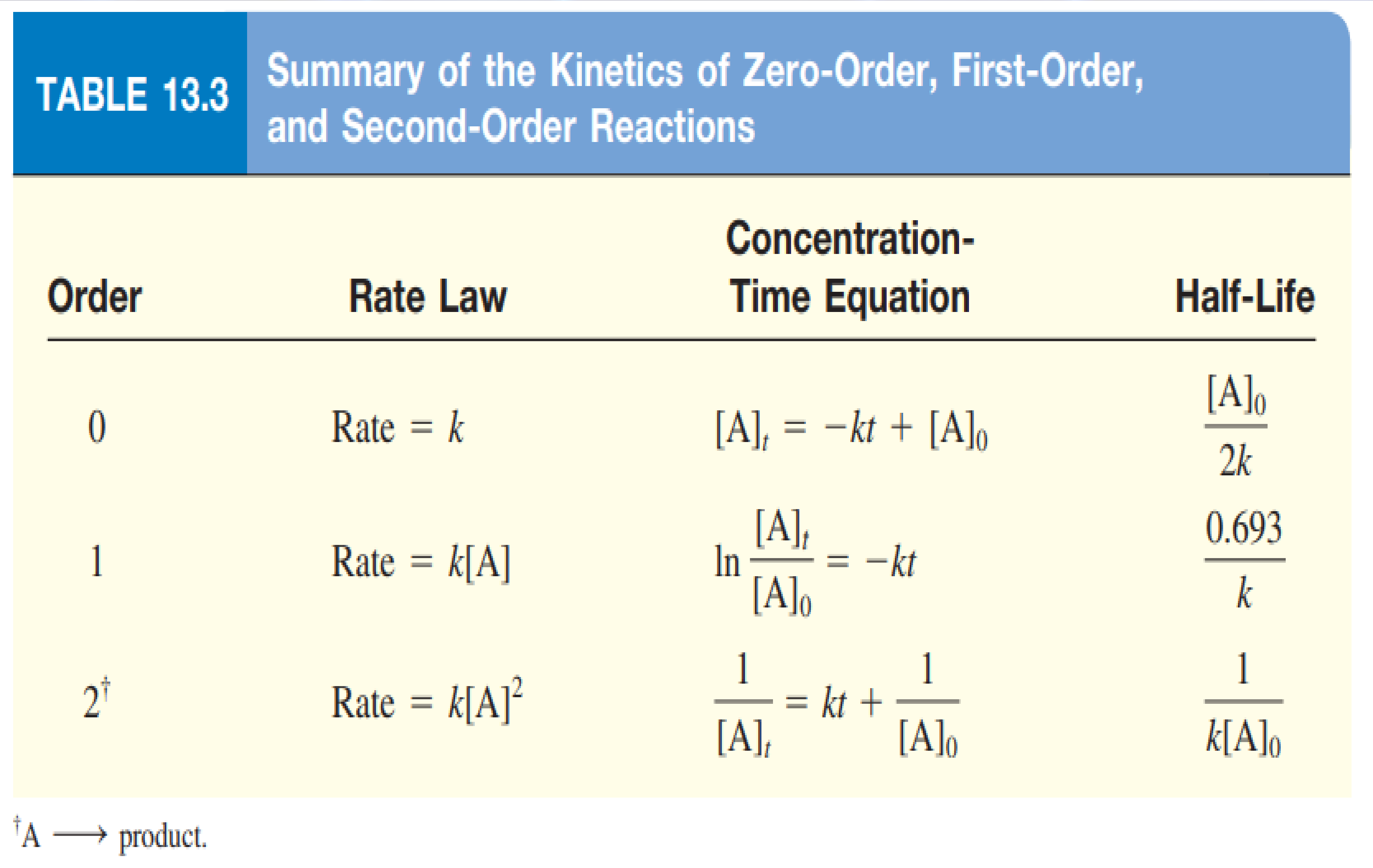


TABLE 13.3 Summary of the Kinetics of Zero-Order, First-Order, and Second-Order Reactions

Order	Rate Law	Concentration-Time Equation	Half-Life
0	Rate $= k$	$[\mathrm{A}]_t = -kt + [\mathrm{A}]_0$	$\dfrac{[\mathrm{A}]_0}{2k}$
1	Rate $= k[\mathrm{A}]$	$\ln \dfrac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -kt$	$\dfrac{0.693}{k}$
2[†]	Rate $= k[\mathrm{A}]^2$	$\dfrac{1}{[\mathrm{A}]_t} = kt + \dfrac{1}{[\mathrm{A}]_0}$	$\dfrac{1}{k[\mathrm{A}]_0}$

[†] $\mathrm{A} \longrightarrow$ product.

Chemistry in action

- How do scientists determine the ages of artifacts from archaeological excavations?
- If someone tried to sell you a manuscript supposedly dating from 1000 b.c., how could you be certain of its authenticity?
- Is a mummy found in an Egyptian pyramid really 3000 years old?
- Is the so-called Shroud of Turin truly the burial cloth of Jesus Christ?

The answers to these and other similar questions can usually be found by applying chemical kinetics and the radiocarbon dating technique.

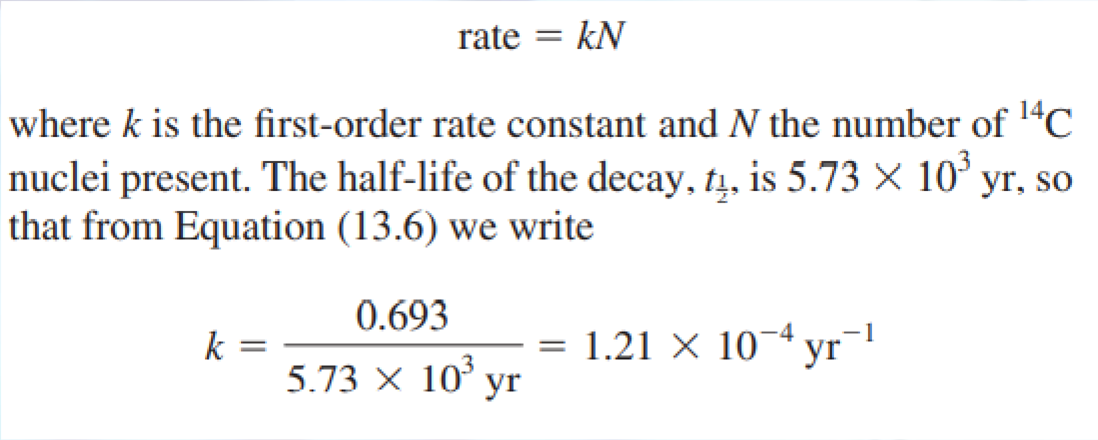
Determining the age of Shroud of turin

Earth’s atmosphere is constantly being bombarded by cosmic rays of extremely high penetrating power. These rays, which originate in outer space, consist of electrons, neutrons, and atomic nuclei.

One of the important reactions between the atmosphere and cosmic rays is the capture of neutrons by atmospheric nitrogen (nitrogen-14 isotope) to produce the radioactive carbon-14 isotope and hydrogen.

The unstable carbon atoms eventually form 14CO2, which mixes with the ordinary carbon dioxide (12CO2) in the air.

As the carbon-14 isotope decays, it emits beta particles (electrons). The rate of decay (as measured by the number of electrons emitted per second) obeys first-order kinetics. It is customary in the study of radioactive decay to write the rate law as



$$\text{rate} = kN$$

where k is the first-order rate constant and N the number of ^{14}C nuclei present. The half-life of the decay, $t_{\frac{1}{2}}$, is 5.73×10^3 yr, so that from Equation (13.6) we write

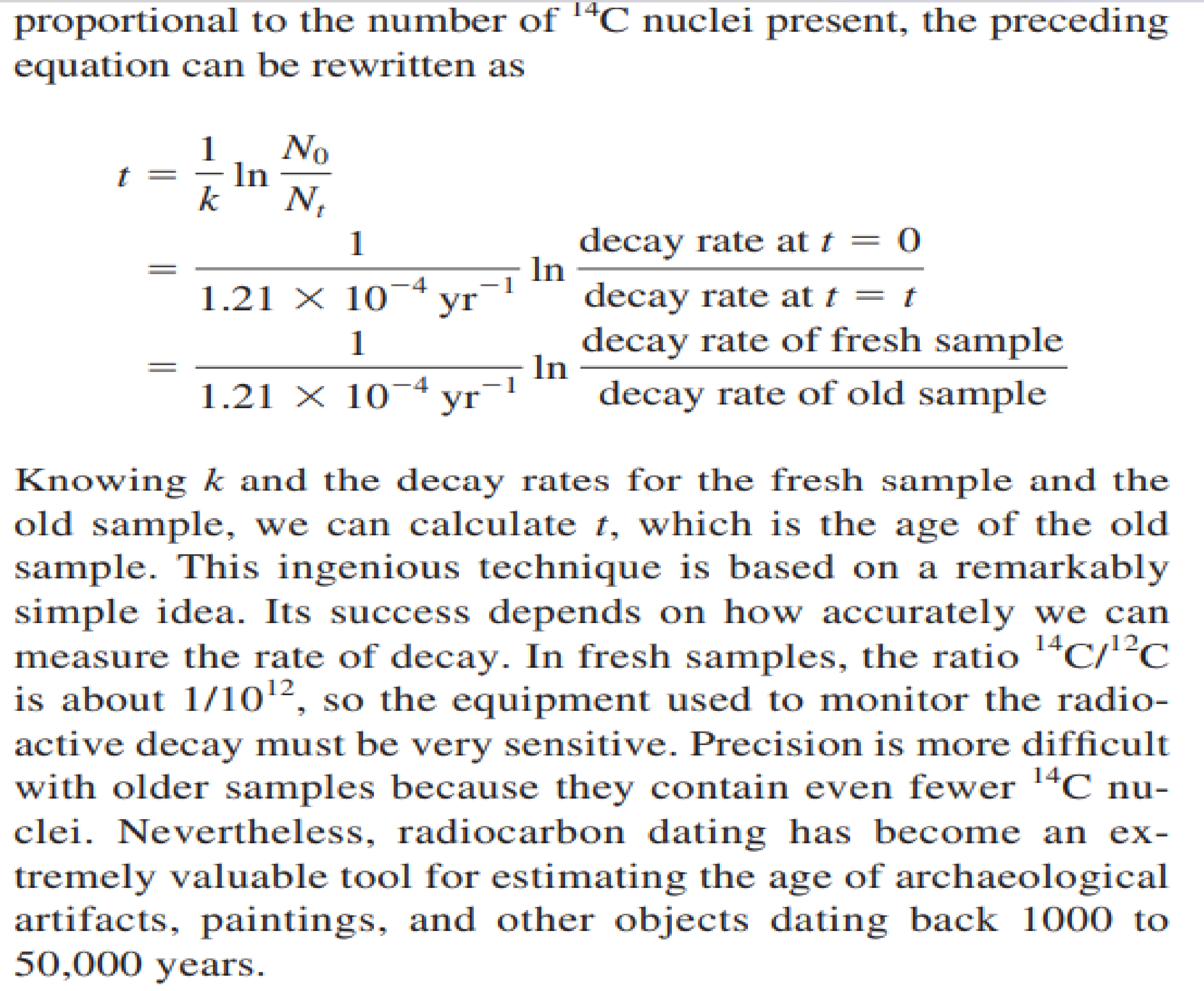
$$k = \frac{0.693}{5.73 \times 10^3\ \text{yr}} = 1.21 \times 10^{-4}\ \text{yr}^{-1}$$

The carbon-14 isotopes enter the biosphere when carbon dioxide is taken up in plant photosynthesis. Plants are eaten by animals, which exhale carbon-14 in CO_2. Eventually, carbon-14 participates in many aspects of the carbon cycle. The ^{14}C lost by radioactive decay is constantly replenished by the production of new isotopes in the atmosphere. In this decay-replenishment process, a dynamic equilibrium is established whereby the ratio of ^{14}C to ^{12}C remains constant in living matter. But when an individual plant or an animal dies, the carbon-14 isotope in it is no longer replenished, so the ratio decreases as ^{14}C decays. This same change occurs when carbon atoms are trapped in coal, petroleum, or wood preserved underground, and, of course, in Egyptian mummies. After a number of years, there are proportionately fewer ^{14}C nuclei in, say, a mummy than in a living person.

In 1955, Willard F. Libby[†] suggested that this fact could be used to estimate the length of time the carbon-14 isotope in a particular specimen has been decaying without replenishment. Rearranging Equation (13.3), we can write

$$\ln \frac{N_0}{N_t} = kt$$

where N_0 and N_t are the number of ^{14}C nuclei present at $t = 0$ and $t = t$, respectively. Because the rate of decay is directly



proportional to the number of ^{14}C nuclei present, the preceding equation can be rewritten as

$$\begin{aligned} t &= \frac{1}{k} \ln \frac{N_0}{N_t} \\ &= \frac{1}{1.21 \times 10^{-4}\ \mathrm{yr}^{-1}} \ln \frac{\text{decay rate at } t = 0}{\text{decay rate at } t = t} \\ &= \frac{1}{1.21 \times 10^{-4}\ \mathrm{yr}^{-1}} \ln \frac{\text{decay rate of fresh sample}}{\text{decay rate of old sample}} \end{aligned}$$

Knowing k and the decay rates for the fresh sample and the old sample, we can calculate t, which is the age of the old sample. This ingenious technique is based on a remarkably simple idea. Its success depends on how accurately we can measure the rate of decay. In fresh samples, the ratio $^{14}C/^{12}C$ is about $1/10^{12}$, so the equipment used to monitor the radioactive decay must be very sensitive. Precision is more difficult with older samples because they contain even fewer ^{14}C nuclei. Nevertheless, radiocarbon dating has become an extremely valuable tool for estimating the age of archaeological artifacts, paintings, and other objects dating back 1000 to 50,000 years.