Topic 7B - Integrated Rate Laws

Reaction Orders

Cannot, in general, be determined from the reaction stoichiometry

Must be experimentally determined

Types of Reaction Orders

Zero-Order
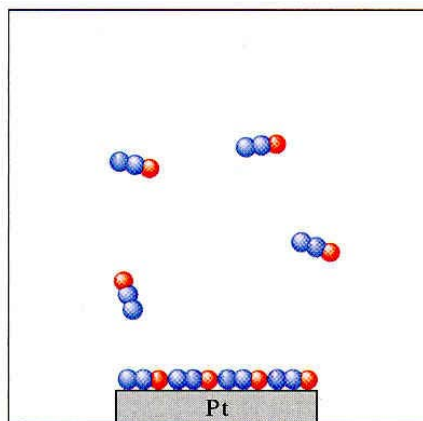
Rate not dependent on [A]

Differential expression:

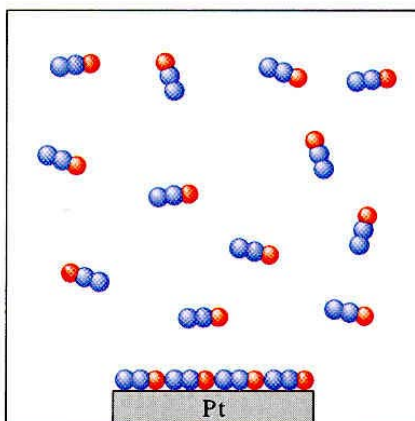$$\text{Rate} = k_0[A]^0 = k_0 = -\frac{1}{a}\frac{d[A]}{dt}$$

Integrated expression:

$$[A] = -ak_0t + [A]_i$$

Thus, a plot of [A] vs. t yields a straight line, with Slope = -ak$_0$ and Intercept = [A]$_i$

Example:

$$2\,N_2O \rightarrow 2\,N_2 + O_2 \qquad \text{(over Pt catalyst)}$$

$\text{\textcircled{N N O}} = N_2O$

(a)   (b)

The decomposition reaction
$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$ takes place on a platinum surface. Although $[N_2O]$ is twice as great in (b) as in (a), the rate of decomposition of N_2O is the same in both cases since the platinum surface can accommodate only a certain number of molecules. As a result, this reaction is zero order.

First-Order

Rate dependent on $[A]^1$

Differential expression:

$$Rate = \frac{1}{a}\frac{d[A]}{dt} = -k_1[A]$$

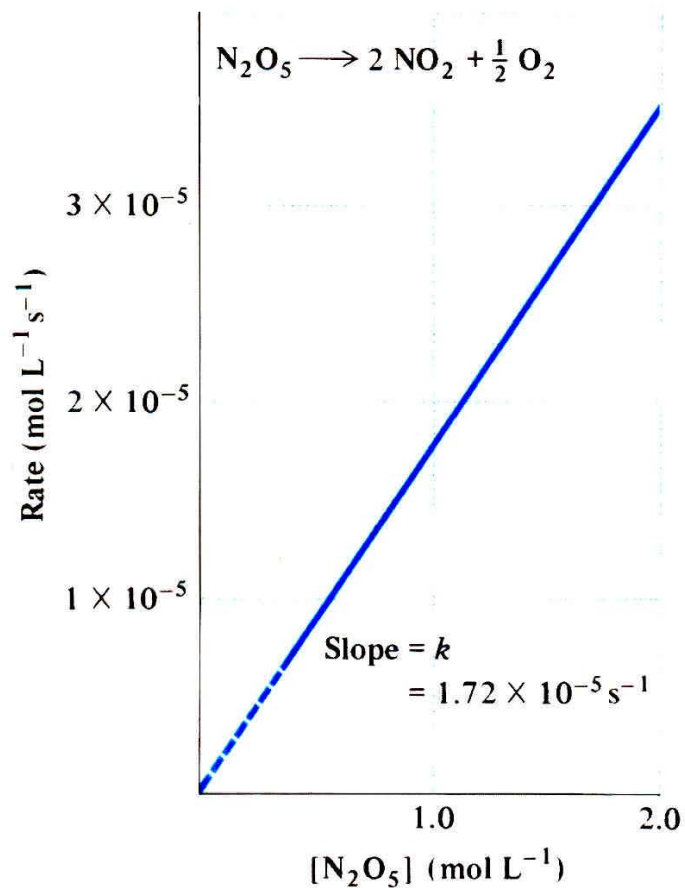### Integrated expression:

$$\ln[A] = -ak_1t + \ln[A]_i$$

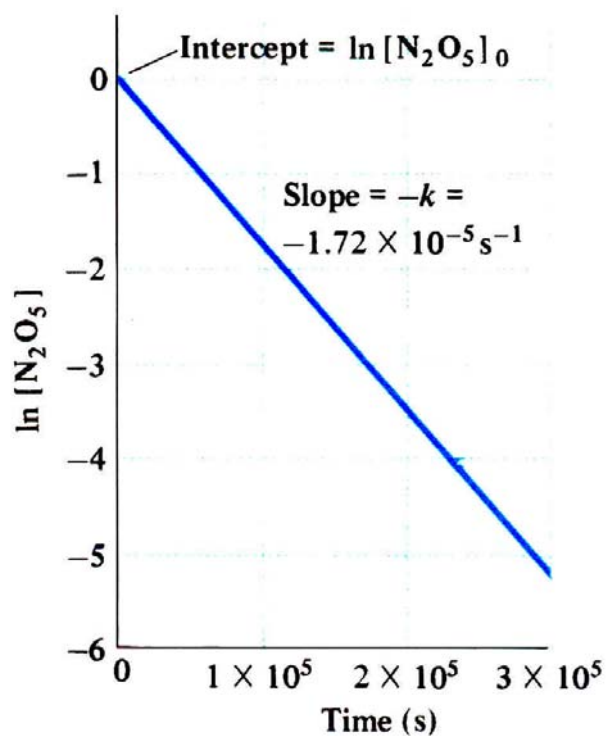Thus, a plot of $\ln[A]$ vs. t yields a straight line, with Slope = $-ak_1$ and Intercept = $\ln[A]_i$

Example:
$$N_2O_5 \rightarrow 2\ NO_2 + \tfrac{1}{2}\ O_2$$

Figure 11-4
The rate of decomposition of $N_2O_5(g)$ at 25°C is proportional to its concentration. The slope of this line is equal to the rate constant k for the reaction.

$$\text{Rate} = \frac{d[N_2O_5]}{dt} = -k[N_2O_5]$$

$$\ln \frac{[N_2O_5]}{[N_2O_5]_0} = -kt$$

$$\ln[N_2O_5] = -kt + \ln[N_2O_5]_0$$

Figure 11-5

In a first-order reaction such as the decomposition of N_2O_5, a graph of the natural logarithm of the concentration against time is a straight line, the negative of whose slope gives the rate constant for the reaction.

Second-Order

Rate dependent on $[A]^2$

Differential expression:

$$\text{Rate} = \frac{1}{a}\frac{d[A]}{dt} = -k_2[A]^2$$

Integrated expression:

$$\frac{1}{[A]} = ak_2t + \frac{1}{[A]_1}$$

Thus, a plot of $[A]^{-1}$ vs. t yields a straight line, with Slope = ak_2 and Intercept = $[A]_i^{-1}$

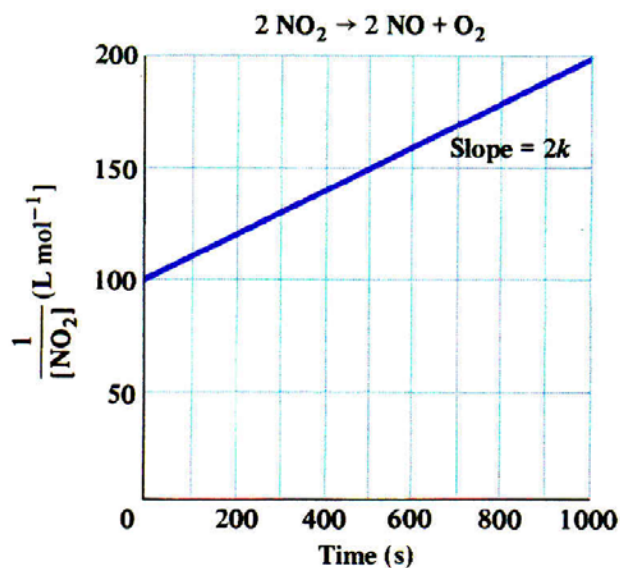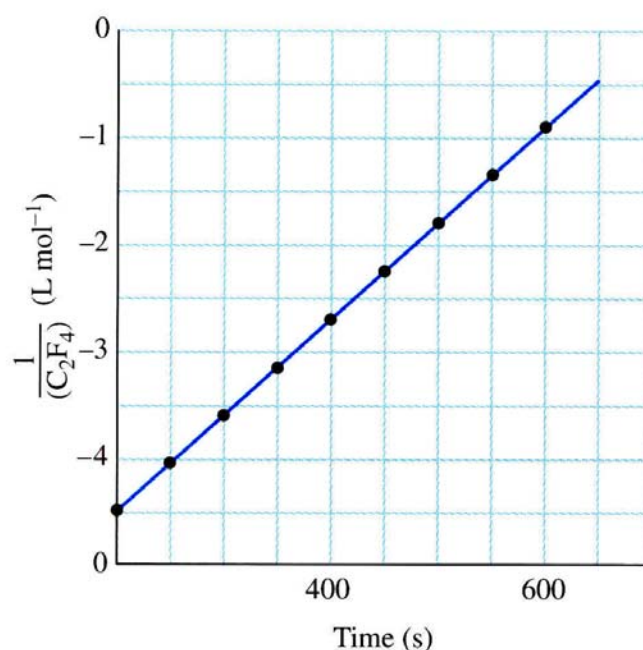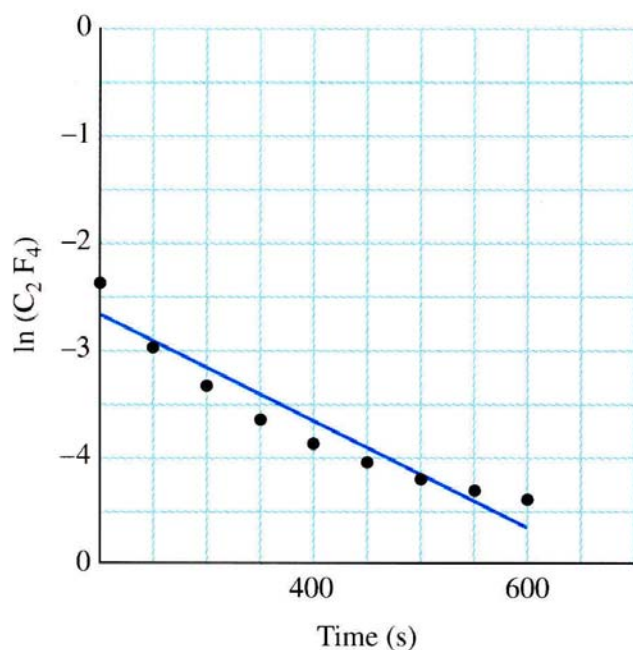### Example:

$$2\ NO_2 \rightarrow 2\ NO + O_2$$

Figure 11-7
For a second-order reaction such as $2\ NO_2 \rightarrow 2\ NO + O_2$, a graph of the reciprocal of the concentration against time is a straight line with slope $2k$.

$$2\,C_2F_4 \longrightarrow C_4F_8 \quad (AT\ 450\ K)$$

		Order	
	Zero	**First**	**Second**
Rate law	Rate $= k$	Rate $= k[A]$	Rate $= k[A]^2$
Integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\dfrac{1}{[A]} = kt + \dfrac{1}{[A]_0}$
Plot needed to give a straight line	$[A]$ versus t $k = \dfrac{[A]}{t}$	$\ln[A]$ versus t $k = \dfrac{1}{t}$	$\dfrac{1}{[A]}$ versus t $k = \dfrac{1}{[A]\,t}$
Relationship of rate constant to the slope of straight line	Slope $= -k$	Slope $= -k$	Slope $= k$
Half-life	$t_{1/2} = \dfrac{[A]_0}{2k}$	$t_{1/2} = \dfrac{0.693}{k}$	$t_{1/2} = \dfrac{1}{k[A]_0}$

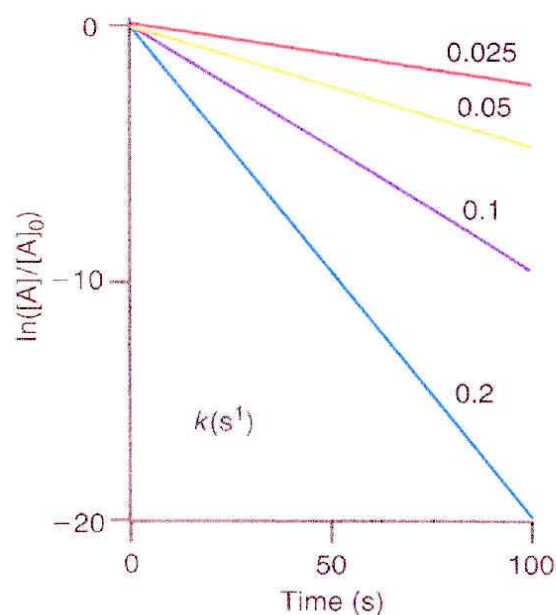**Summary of the Kinetics for Reactions of the Type aA → Products That Are Zero, First, or Second Order in [A]**

Summary of the kinetics for reactions of the type aA → Products that are zero, first, or second order in [A]

# Figure 15.3: Time Profiles for Different Orders in the Rate Law
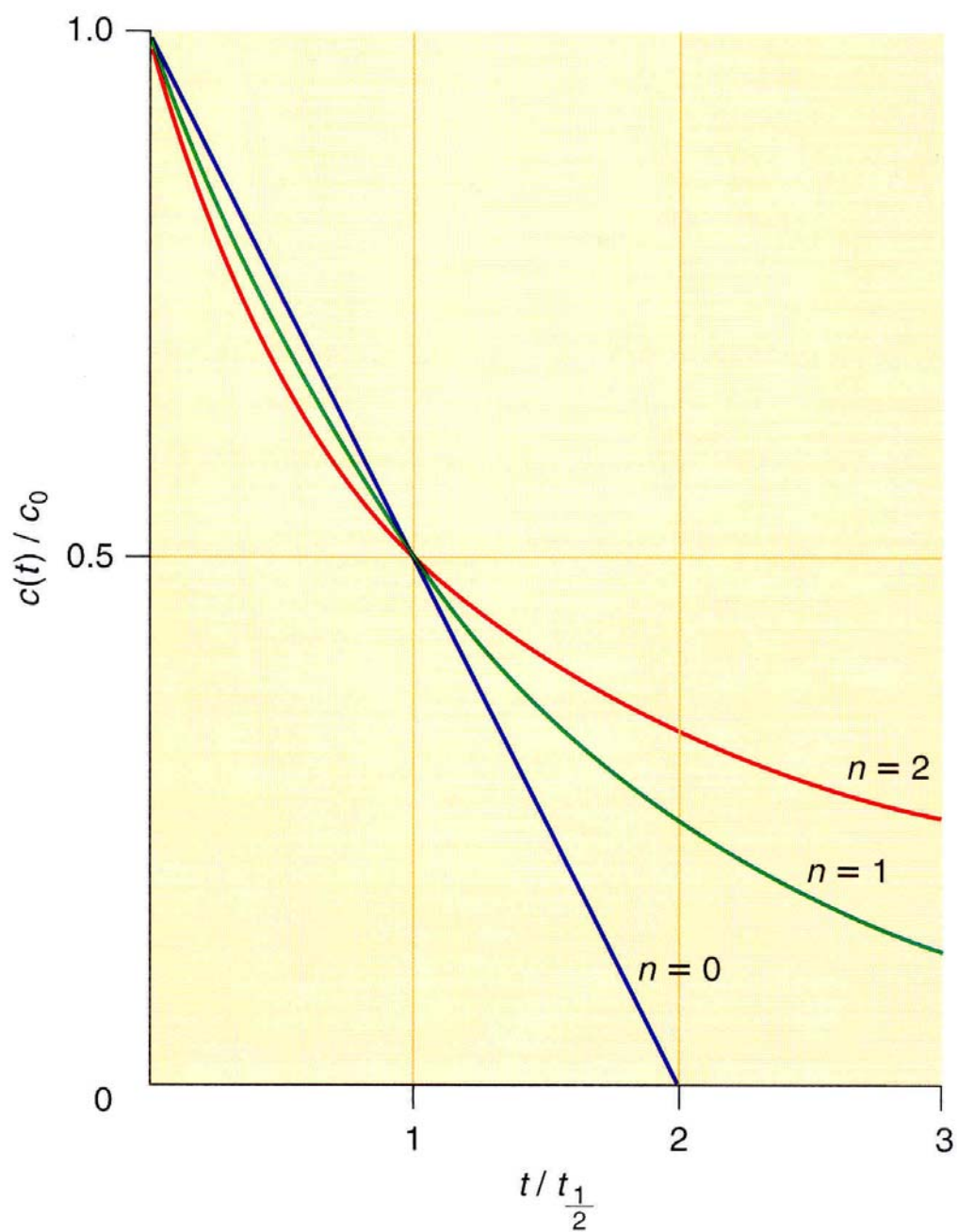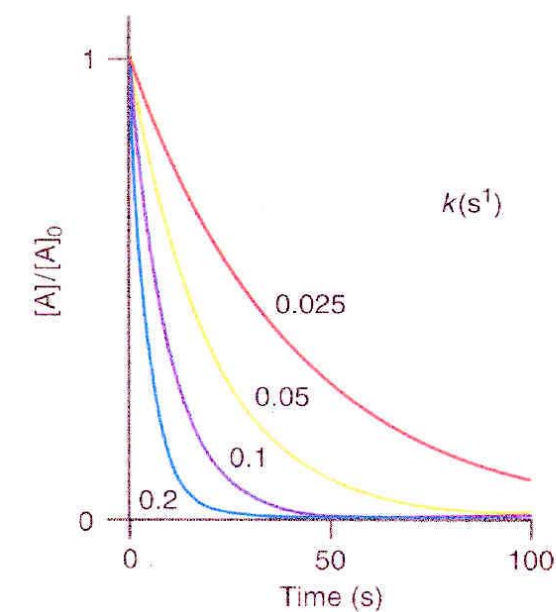
(a)

(b)

FIGURE 18.4

Reactant concentration as a function of time for a first-order chemical reaction as given by Equation (18.27). **(a)** Plots of [A] as a function of time for various rate constants k. The rate constant of a given curve is provided in the figure. **(b)** The natural log of reactant concentration as a function of time for a first-order chemical reaction as given by Equation (18.28).
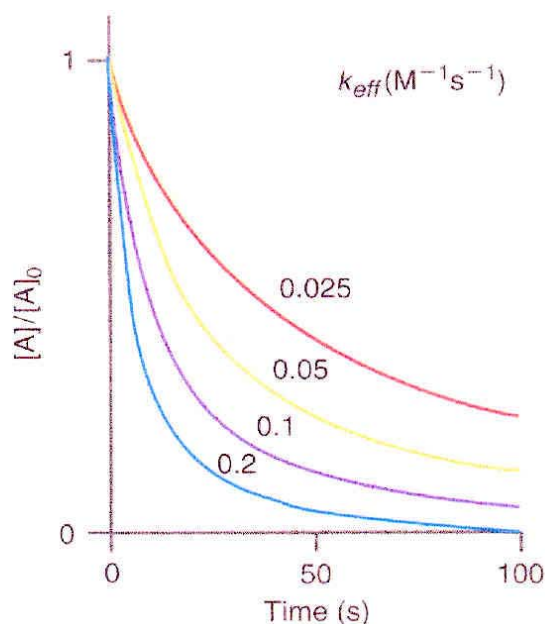
(a)
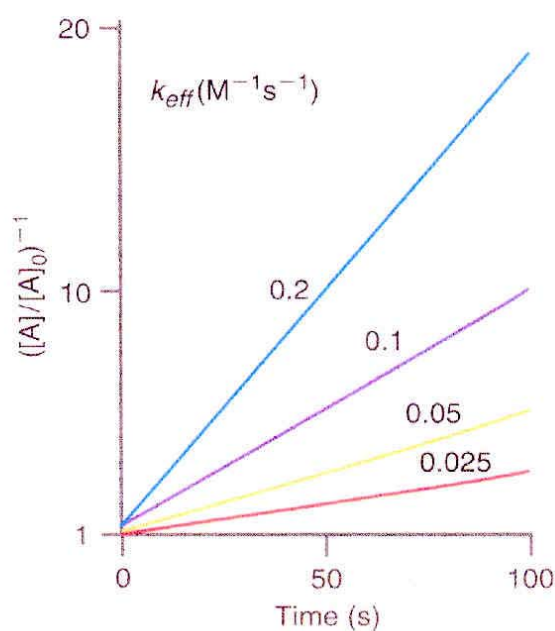
(b)

FIGURE 18.5

Reactant concentration as a function of time for a type I second-order chemical reaction. **(a)** Plots of [A] as a function of time for various rate constants. The rate constant of a given curve is provided in the figure. **(b)** The inverse of reactant concentration as a function of time as given by Equation (18.34).

Half-Lives

Zero-Order:

$$[A] = -ak_0t + [A]_i$$

$$\text{At } t_{1/2}, \ [A] = \frac{[A]_i}{2}$$

$$\text{Thus,} \frac{[A]_i}{2} - [A]_i = -ak_0t_{1/2} \text{ and}$$

$$t_{1/2,0} = \frac{[A]_i}{2ak_0}$$

First-Order:

$$\ln[A] = -ak_1t + \ln[A]_i$$

$$\text{At } t_{1/2}, \ [A] = \frac{[A]_i}{2}$$

$$\text{Thus, } \ln\frac{[A]_i}{2[A]_i} = -ak_1t_{1/2,1} \text{ and}$$

$$t_{1/2,1} = \frac{\ln2}{ak_1} = \frac{0.693}{ak_1}$$

Second-Order:

$$\frac{1}{[A]} = ak_2t + \frac{1}{[A]_i}$$

$$\text{At } t_{1/2}, \ [A] = \frac{[A]_i}{2}$$

$$\text{Thus, } \frac{2}{[A]_i} + \frac{1}{[A]_i} = -ak_2t_{1/2} \text{ and}$$

$$t_{1/2,2} = \frac{1}{ak_2[A]_i}$$

The figure shows a plot of $[N_2O_5]$ (mol/L) on the vertical axis versus Time (s) on the horizontal axis, with a red decay curve. Labeled on the vertical axis: $[N_2O_5]_0 \rightarrow 0.1000$, $\dfrac{[N_2O_5]_0}{2} \rightarrow 0.0500$, $\dfrac{[N_2O_5]_0}{4} \rightarrow 0.0250$, $\dfrac{[N_2O_5]_0}{8} \rightarrow 0.0100$.

Handwritten annotations:

$$t_{1/2} = \frac{\ln 2}{k} = 100\ s$$

$$k = \frac{\ln 2}{100} = 6.9 \times 10^{-3}\ s^{-1}$$

Three successive intervals along the time axis are each marked $t_{1/2}$.
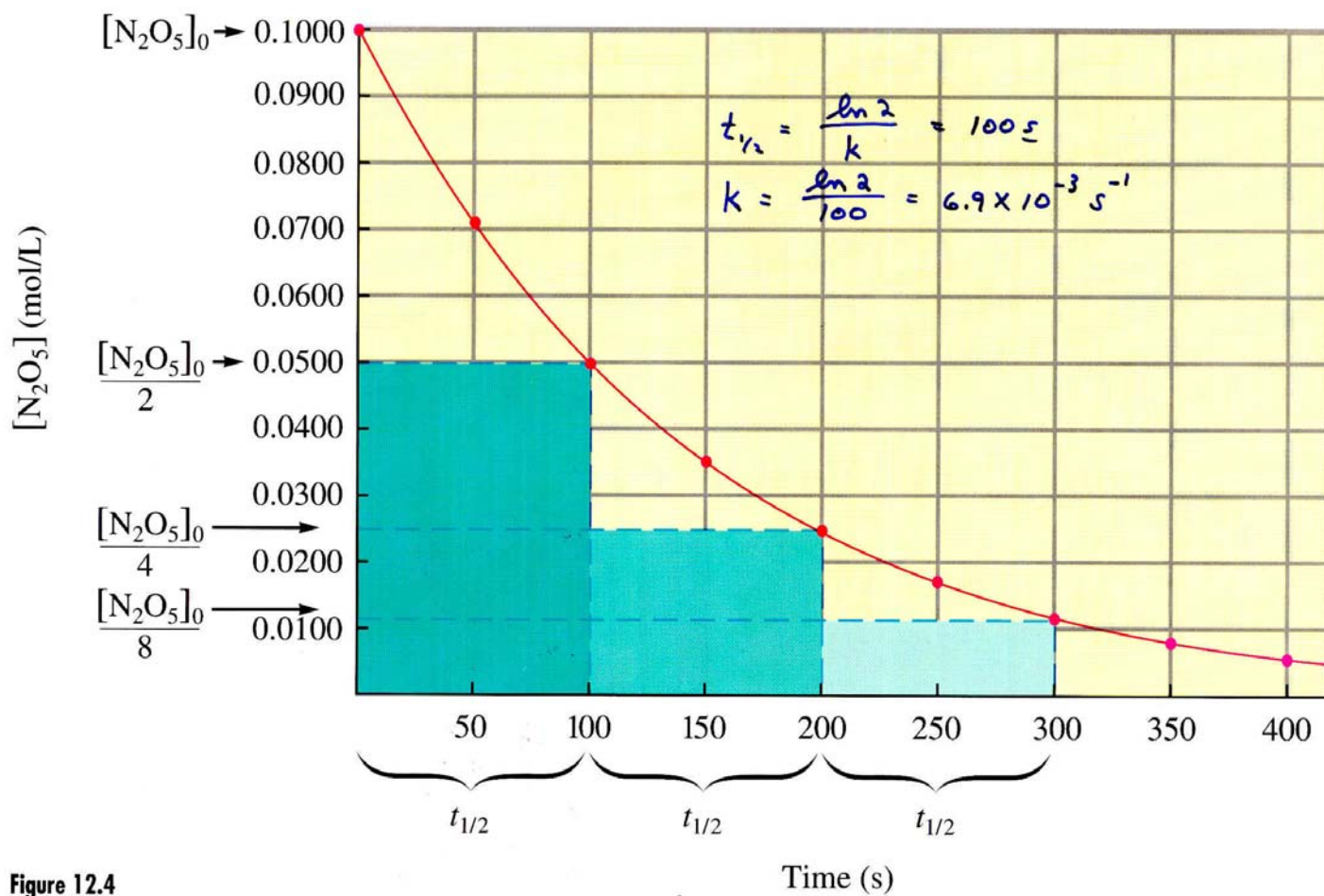
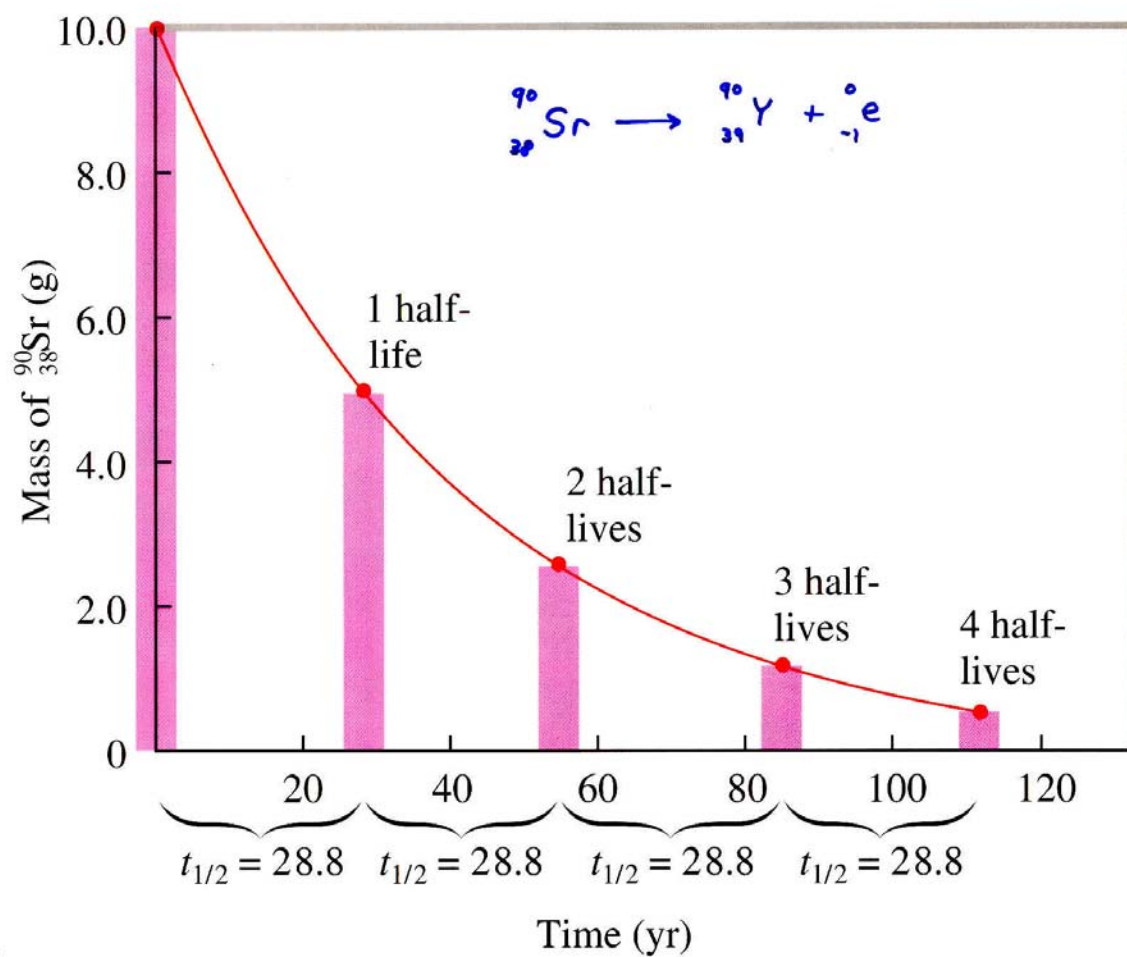**Figure 12.4**
Constant half life for first-order process

Figure 21.3
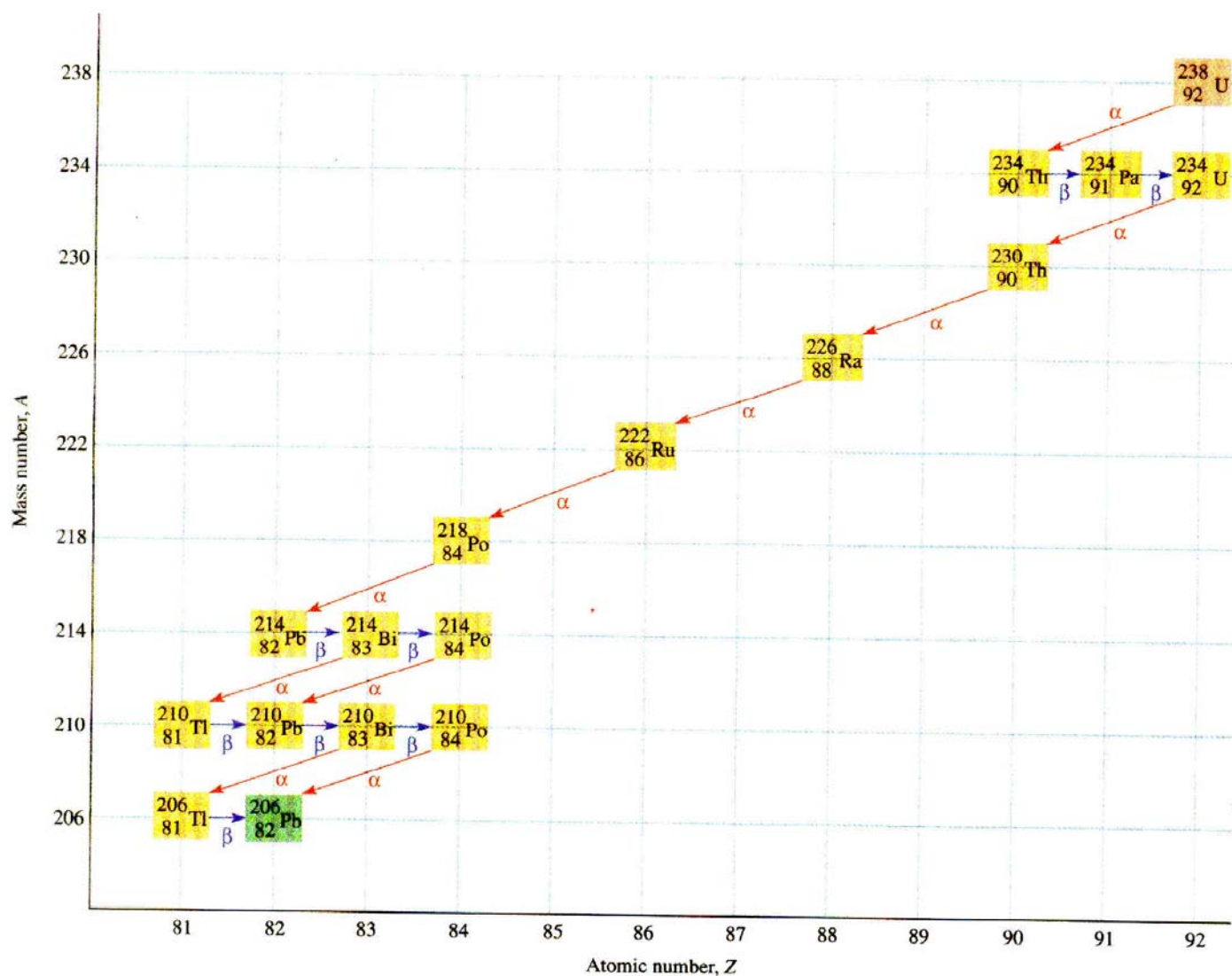**A schematic showing the half life for ⁹⁰Sr**

Figure 12-6

The radioactive nuclide ^{238}U decays via a series of alpha and beta emissions to the stable nuclide ^{206}Pb.

Table 12-2 Decay Characteristics of Some Radioactive Nuclei

Nuclide	$t_{1/2}$	Decay Mode†	Daughter
$^{3}_{1}H$ (tritium)	12.26 years	e^-	$^{3}_{2}He$
$^{8}_{4}Be$	$\sim 1 \times 10^{-16}$ s	α	$^{4}_{2}He$
$^{14}_{6}C$	5730 years	e^-	$^{14}_{7}N$
$^{22}_{9}Na$	2.601 years	e^+	$^{22}_{10}Ne$
$^{24}_{9}Na$	15.02 hours	e^-	$^{24}_{12}Mg$
$^{32}_{15}P$	14.28 days	e^-	$^{32}_{16}S$
$^{35}_{16}S$	87.2 days	e^-	$^{35}_{17}Cl$
$^{36}_{17}Cl$	3.01×10^5 years	e^-	$^{36}_{18}Ar$
$^{40}_{19}K$	1.28×10^9 years	$\begin{cases} e^- (89.3\%) \\ \text{E.C. } (10.7\%) \end{cases}$	$^{40}_{20}Ca$ $^{40}_{18}Ar$
$^{59}_{26}Fe$	44.6 days	e^-	$^{59}_{27}Co$
$^{60}_{27}Co$	5.27 years	e^-	$^{60}_{28}Ni$
$^{90}_{38}Sr$	29 years	e^-	$^{90}_{39}Y$
$^{109}_{48}Cd$	453 days	E.C.	$^{109}_{47}Ag$
$^{125}_{53}I$	59.7 days	E.C.	$^{125}_{52}Te$
$^{131}_{53}I$	8.041 days	e^-	$^{131}_{54}Xe$
$^{127}_{54}Xe$	36.41 days	E.C.	$^{127}_{53}I$
$^{137}_{57}La$	$\sim 6 \times 10^4$ years	E.C.	$^{137}_{56}Ba$
$^{222}_{86}Rn$	3.824 days	α	$^{218}_{84}Po$
$^{226}_{88}Ra$	1600 years	α	$^{222}_{86}Rn$
$^{232}_{90}Th$	1.40×10^{10} years	α	$^{228}_{88}Ra$
$^{235}_{92}U$	7.04×10^8 years	α	$^{231}_{90}Th$
$^{238}_{92}U$	4.468×10^9 years	α	$^{234}_{90}Th$
$^{239}_{93}Np$	2.350 days	e^-	$^{239}_{94}Pu$
$^{239}_{94}Pu$	2.411×10^4 years	α	$^{235}_{92}U$

† E.C. stands for electron capture; e^+, for positron emission; e^-, for beta emission; α, for alpha emission.

Multi-Reactant Reactions

Reactions having more than one reactant will exhibit a separate reaction order in each reactant:

$$aA + bB + cC + \ldots \rightarrow \text{Products}$$

for which

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = -\frac{1}{c}\frac{d[C]}{dt} = k[A]^x[B]^y[C]^z$$

in which x, y, and z are the reaction orders in reactants A, B, and C, respectively. The <u>overall</u> reaction order is x + y + z.

For the following reaction, for example, the experimental data below were collected:

$$BrO_3^- \ (aq) + 5\ Br^- \ (aq) + 6\ H_3O^+ \ (aq) \rightarrow 3\ Br_2 \ (aq) + 9\ H_2O \ (l)$$

Experiment	Initial concentration (mol·L^{-1})			Initial rate ((mmol BrO$_3^-$)·L^{-1}·s^{-1})
	BrO_3^-	Br^-	H_3O^+	
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.5
4	0.20	0.10	0.15	5.5

The kinetic rate law that is consistent with these data is:

$$\text{Rate} = k\,[BrO_3^-]^1\,[Br^-]^1\,[H_3O]^2$$

Thus, the reaction is first-order in both BrO_3^- and Br^- and second-order in H_3O^+, and fourth-order overall.

The overall fourth-order rate constant can be calculated from the experimental data as follows:

$$k = \frac{\text{Rate}}{[BrO_3^-]\,[Br^-]\,[H_3O^+]^2}$$

$$= \frac{5.5 \times 10^{-3}\ \text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}}{(0.20\ \text{mol}\cdot\text{L}^{-1}) \times (0.10\ \text{mol}\cdot\text{L}^{-1}) \times (0.15\ \text{mol}\cdot\text{L}^{-1})^2}$$

$$= 12\ \text{L}^3\cdot\text{mol}^{-3}\cdot\text{s}^{-1}$$