# UNIT 2

## Part 1

# CHEMICAL KINETICS

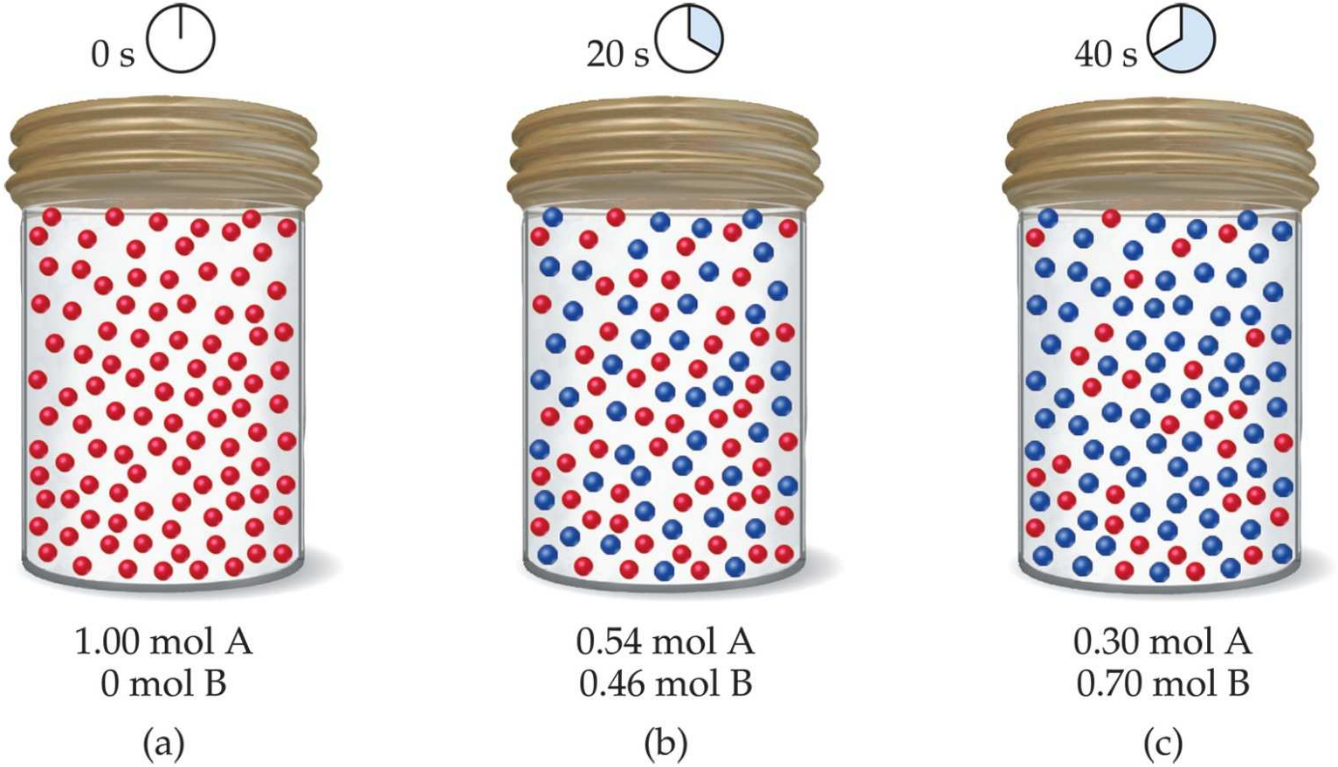
# Chemical Kinetics

When we mix chemicals together several questions arise:

- Will a reaction take place under the given conditions?
- What heat change will accompany the reaction?
- How much product will be formed?
- ***How fast will the reaction occur?*** REACTION RATE
- ***What exactly takes place at the molecular level?*** REACTION MECHANISM

The objective of chemical kinetics is to answer the last two questions.

# Rate of Reaction



1.00 mol A
0 mol B
(a)

0.54 mol A
0.46 mol B
(b)

0.30 mol A
0.70 mol B
(c)

$$A \longrightarrow B$$

# Factors That Affect the Rates of Chemical Reactions

- The nature of the reactants
- The reaction medium
- The concentration of the reactants
- The temperature
- The surface area of solid reactants
- The presence of a catalyst

# Reaction Rate

***Reaction rate*** is defined as the increase in molar concentration of a product or the decrease in molar concentration of a reactant in unit time.

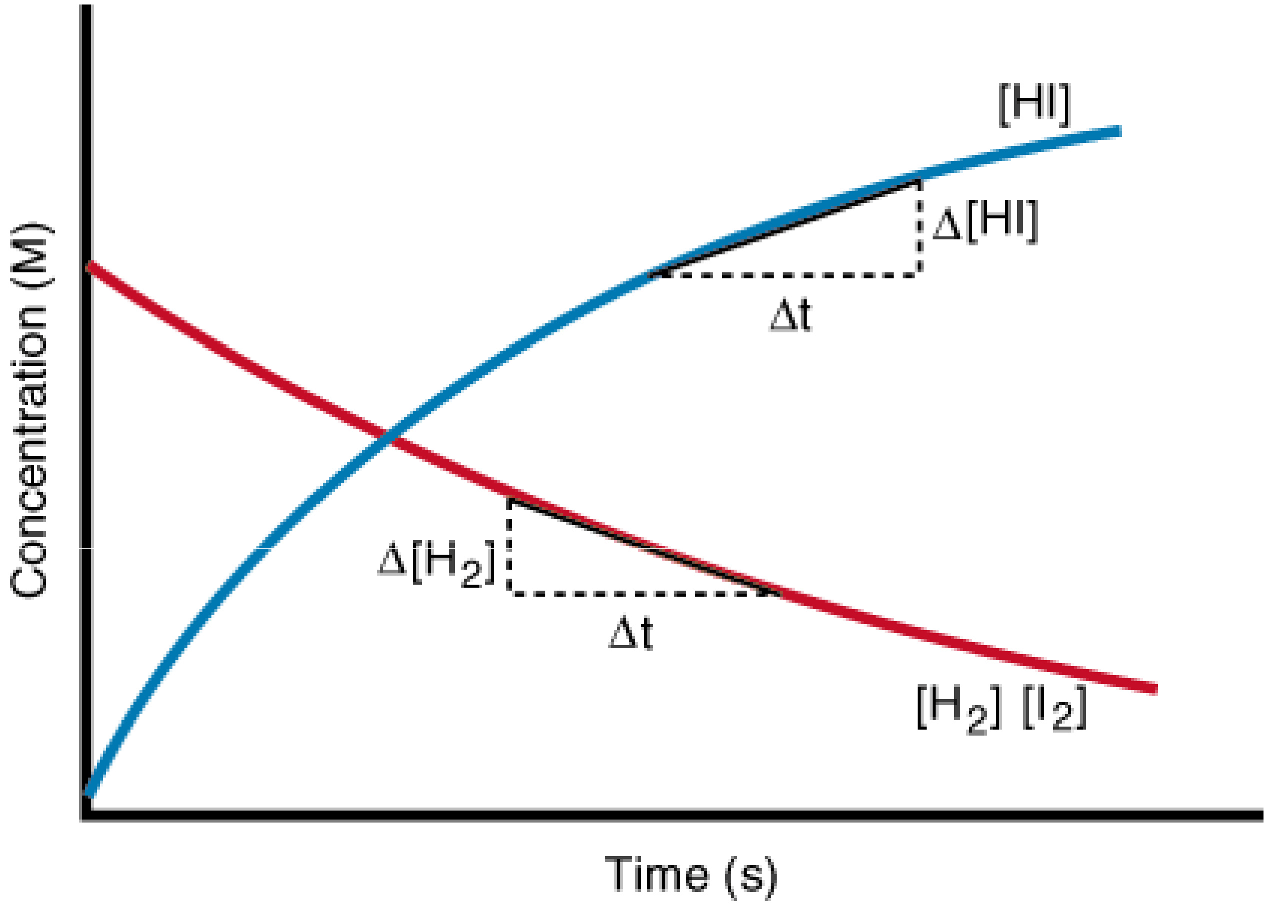
$$\frac{\Delta[\mathrm{P}]}{\Delta t} = \frac{[\mathrm{P}]_2 - [\mathrm{P}]_1}{t_2 - t_1}$$

$$-\frac{\Delta[\mathrm{R}]}{\Delta t} = -\frac{[\mathrm{R}]_2 - [\mathrm{R}]_1}{t_2 - t_1}$$

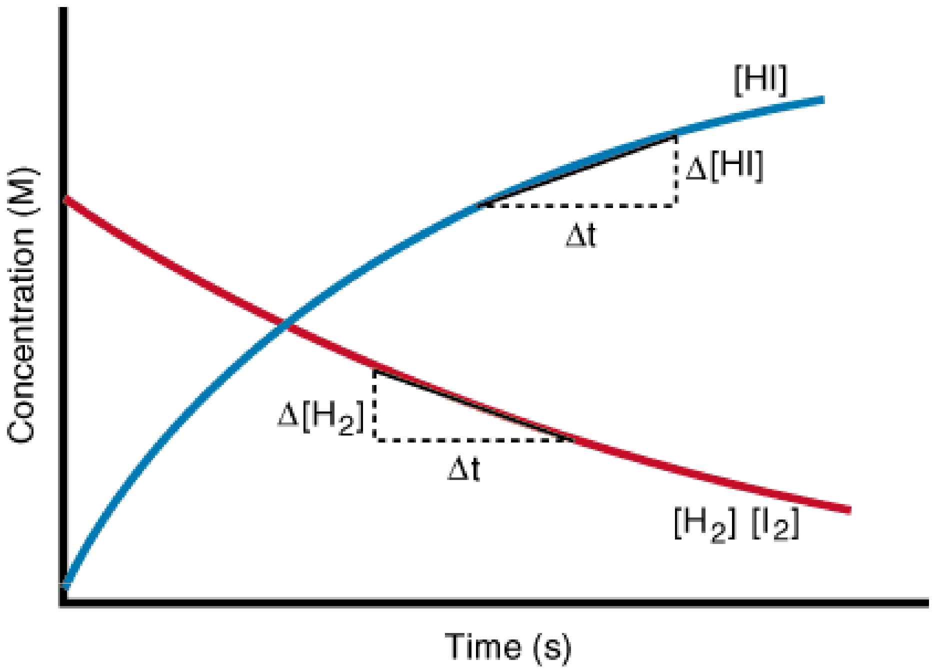
**Average** reaction rates

Units

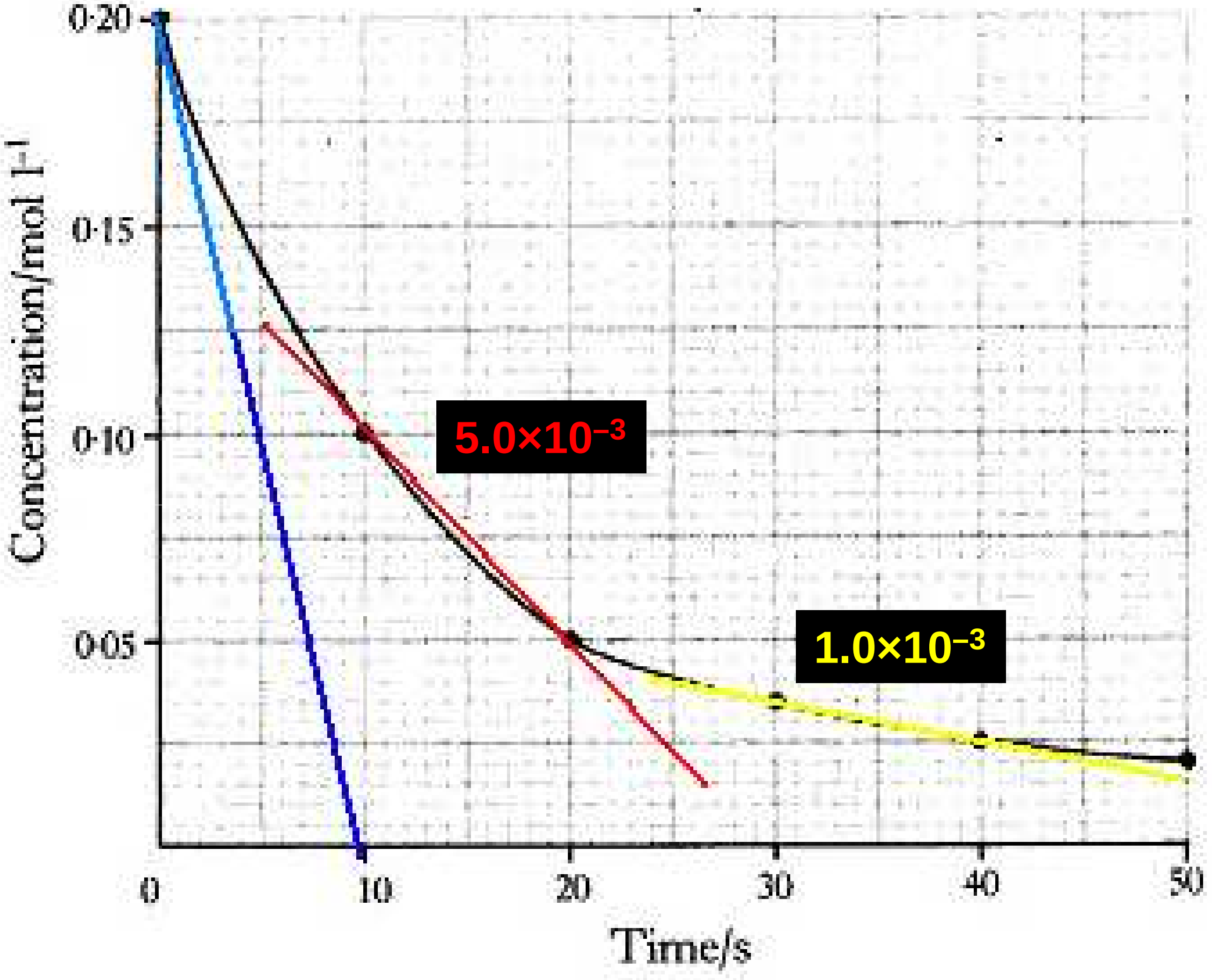
Mol/dm$^3$·s or mol/L·s



$$H_2 + I_2 \longrightarrow 2HI$$



Note that the rate changes and, in the above example, gets smaller with time, until the reactants are used up or an equilibrium is established.



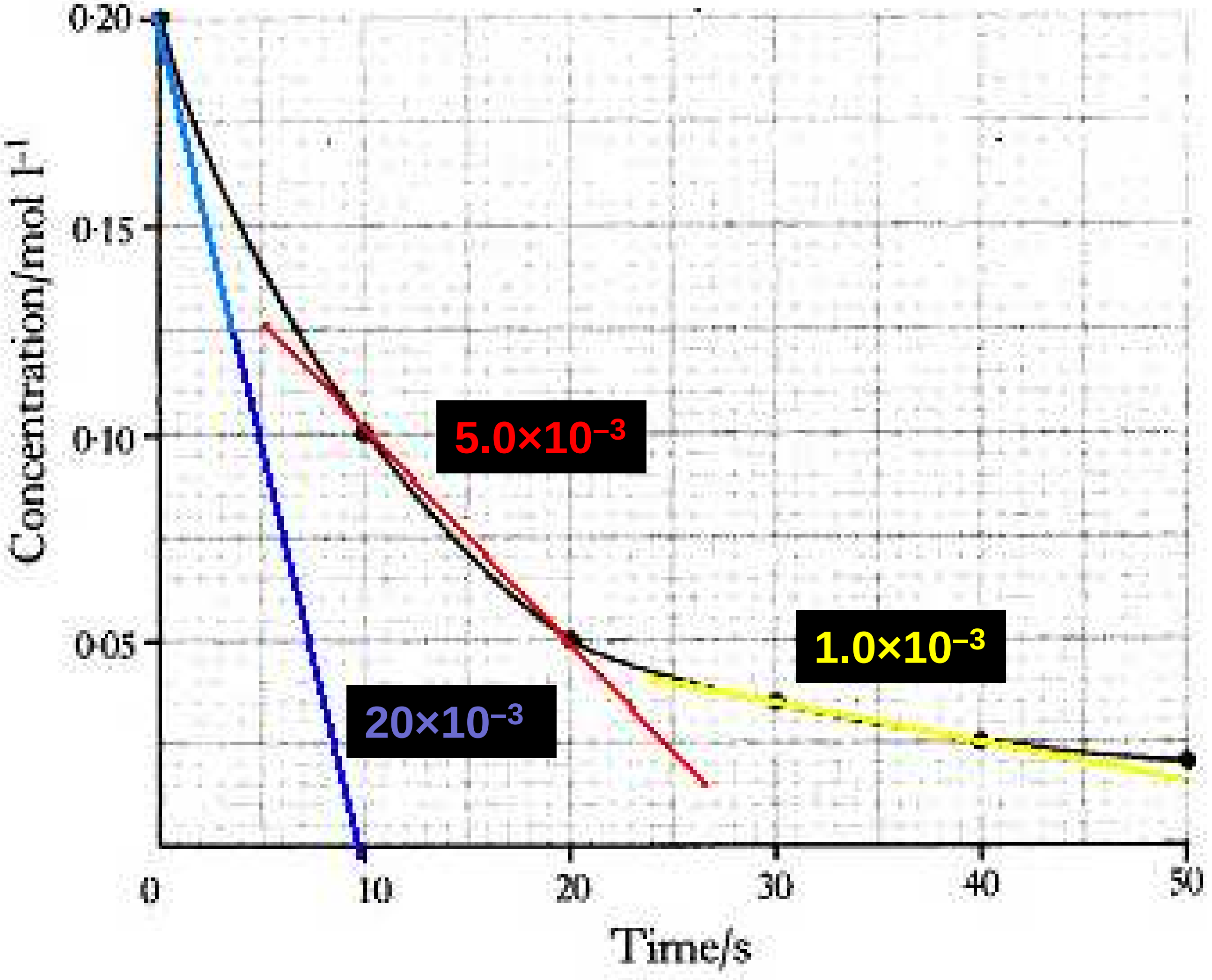
0·20
0·15
0·10
0·05
Concentration/mol l⁻¹
0
10
20
30
40
50
Time/s
5.0×10⁻³
1.0×10⁻³

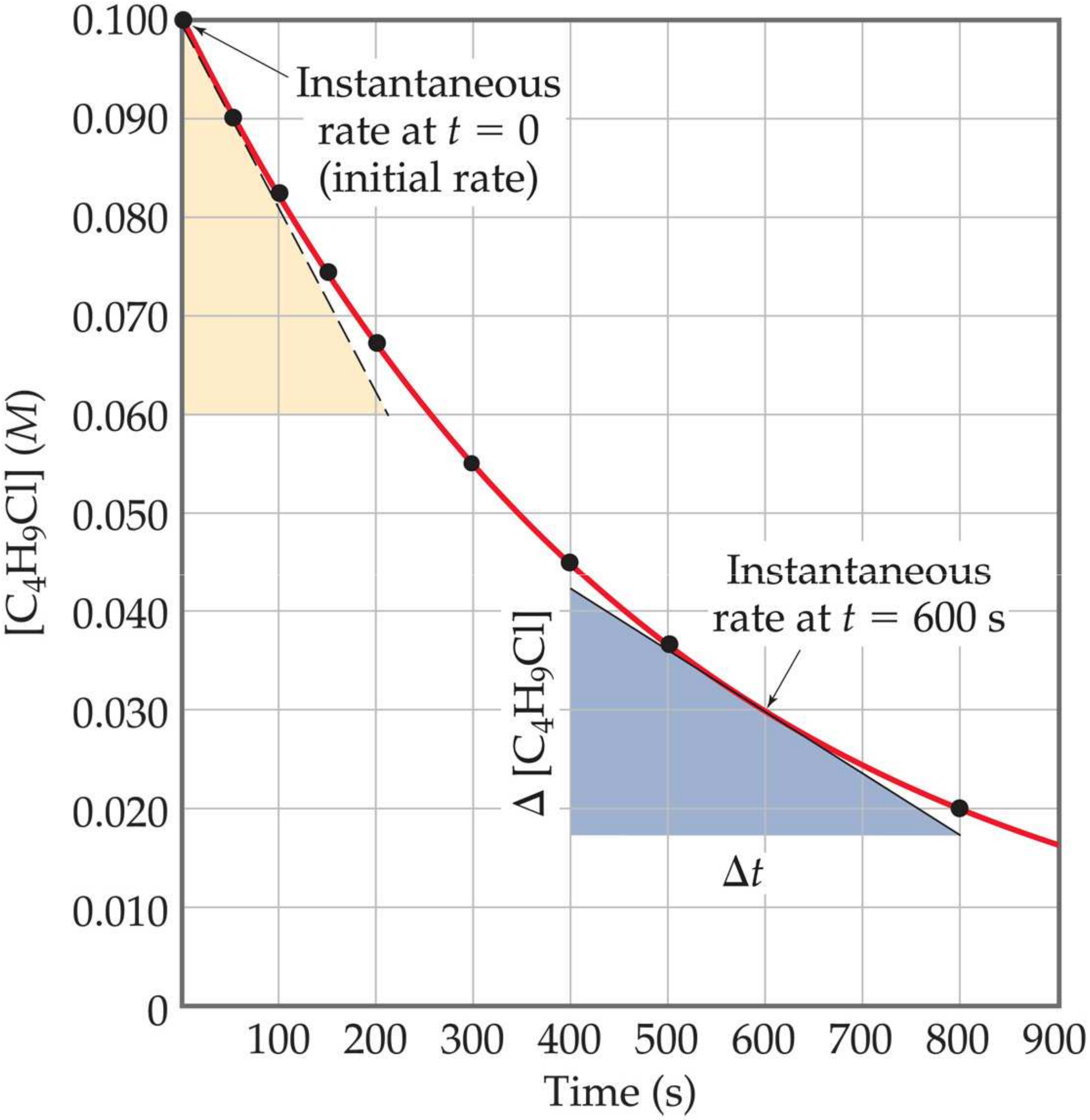
# Reaction Rate

The instantaneous rate at a given time , $t_1$, is given by the slope of the tangent at the point ($t_1$, $C_1$) of the concentration vs. time graph.

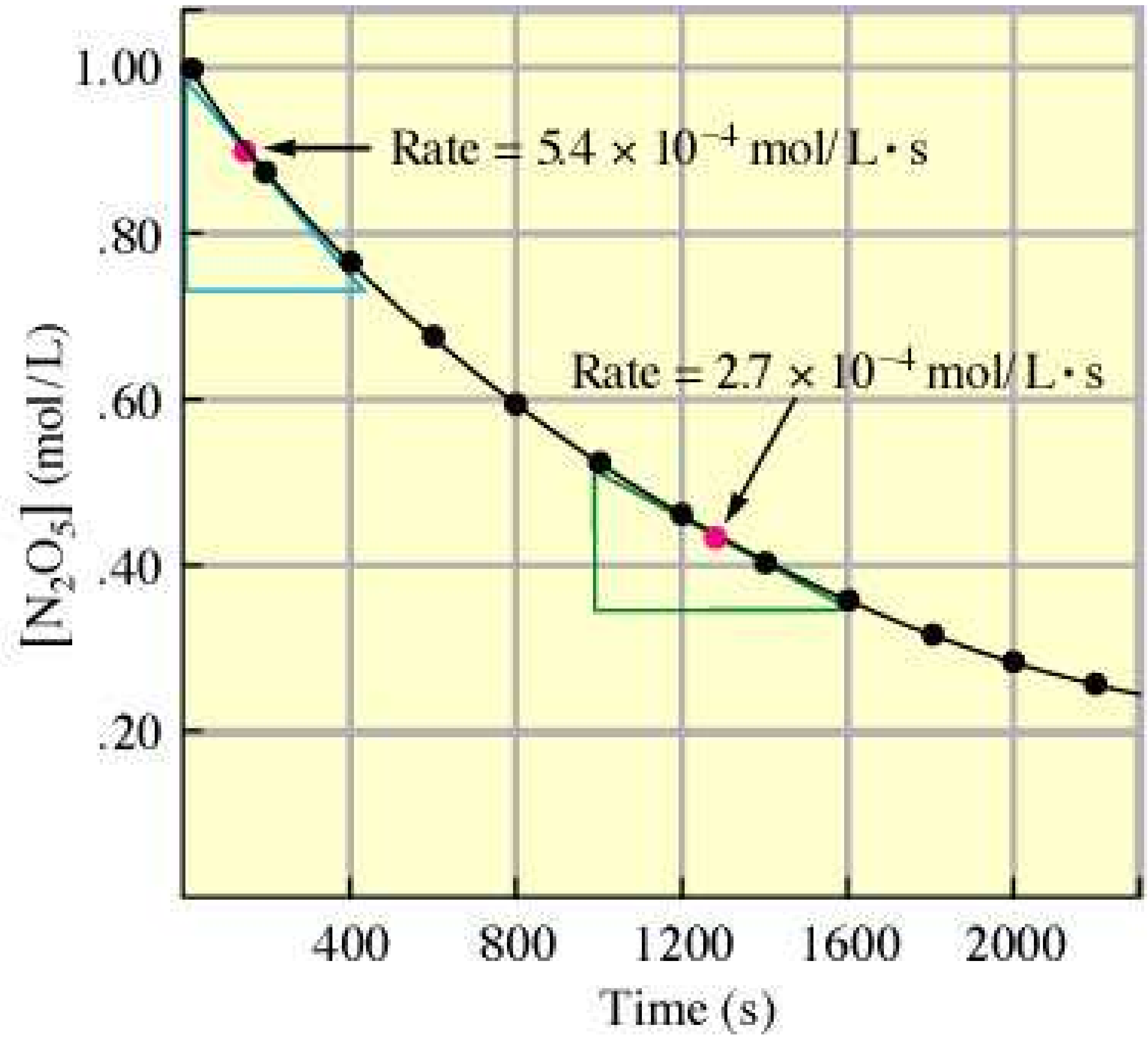
$$\text{Rate} = -\frac{\mathrm{d}[\mathrm{R}]}{\mathrm{d}t}$$

**Instantaneous** reaction rate

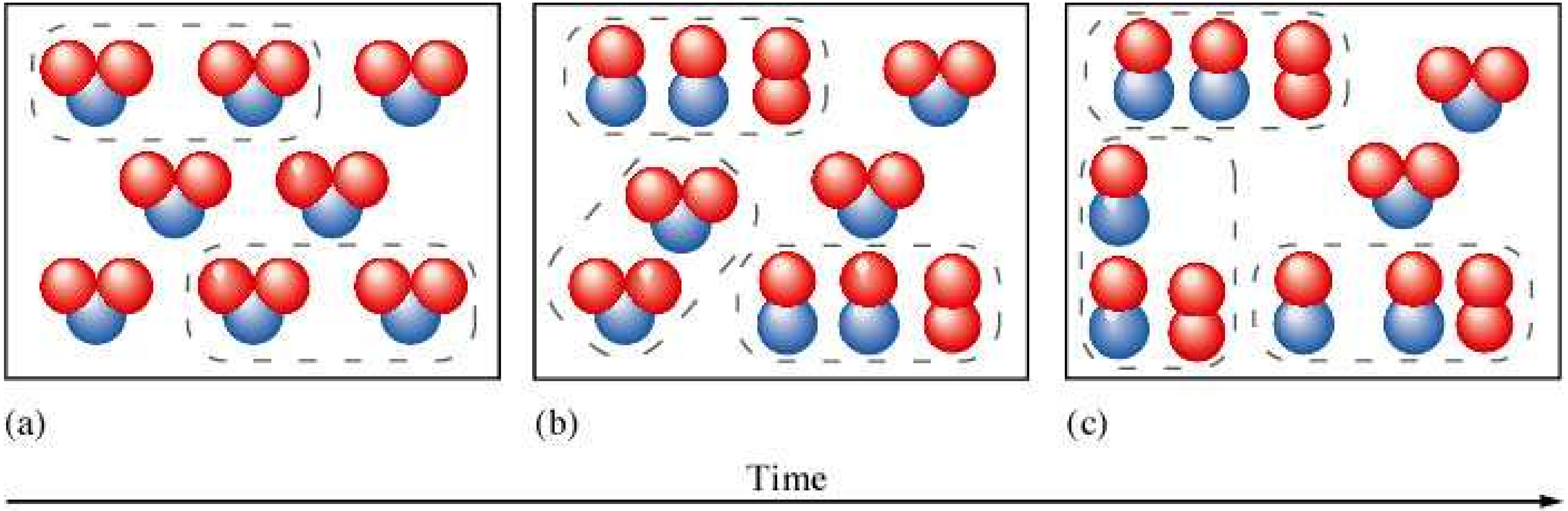

0·20
0·15
0·10
0·05
Concentration/mol l$^{-1}$
0
10
20
30
40
50
Time/s
5.0×10$^{-3}$
1.0×10$^{-3}$
20×10$^{-3}$


0.100
0.090
0.080
0.070
0.060
0.050
0.040
0.030
0.020
0.010
0
100
200
300
400
500
600
700
800
900
Time (s)
$[C_4H_9Cl]$ (*M*)
Instantaneous rate at *t* = 0 (initial rate)
Instantaneous rate at *t* = 600 s
$\Delta[C_4H_9Cl]$
$\Delta t$

$2N_2O_5 \leftrightharpoons 4NO_2 + O_2$



$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$



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

The rate of the above reaction can be expressed variously as:

$$-\frac{\Delta[NO_2]}{\Delta t},\ \frac{\Delta[NO]}{\Delta t},\ \frac{\Delta[O_2]}{\Delta t}$$

These rates are related as follows:

$$-\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[NO]}{\Delta t} = 2\frac{\Delta[O_2]}{\Delta t}$$

# Relative Rate of Reaction

The ***relative average rate of reaction*** for the chemical change $aA + bB \rightarrow cC + dD$ is given by:

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

# Differential Rate Laws

# Differential Rate Laws

All chemical reactions are ***reversible.***

$$2\ NO_2(g) \underset{R_f}{\overset{R_r}{\leftrightharpoons}} 2\ NO(g) + O_2(g)$$

$\Delta[NO_2]$ is unambiguously related to $R_f$ only when $[NO]$ and $[O_2]$ are zero or very low.  Under these conditions we can write the following expression:

# Differential Rate Laws

***Order*** of reaction with respect to $NO_2$

$$R_f = R_i = -\frac{d[NO_2]}{dt} = k[NO_2]^n$$

***Initial rate***

***Rate constant*** or ***specific rate***

# Differential Rate Laws

Generally, for the reaction

$$a\mathrm{A} + b\mathrm{B} \leftrightharpoons \text{products}$$

the rate is given by

Order of reaction with respect to A

Rate constant or specific rate

Order of reaction with respect to B

$$R = k\,[\mathrm{A}]^m[\mathrm{B}]^n$$

Overall order of reaction is ***m+n***

# Determination of the Rate Law

## Method of Initial Rates

The initial rate of a reaction is the instantaneous rate, $-d[A]/dt$, at $t = 0$.

Initial rates are measured for several different initial concentrations.

For a reaction $a\mathrm{A} + b\mathrm{B} + c\mathrm{C} \rightleftharpoons$ products,

a reasonably simple rate law, of the form $R = k\,[\mathrm{A}]^{m}[\mathrm{B}]^{n}\,[\mathrm{C}]^{p}$, is assumed at first.

The concentration of only one reactant is varied from one run to the other.

If only the concentration of A is varied in the second run, by a factor $x$ , then

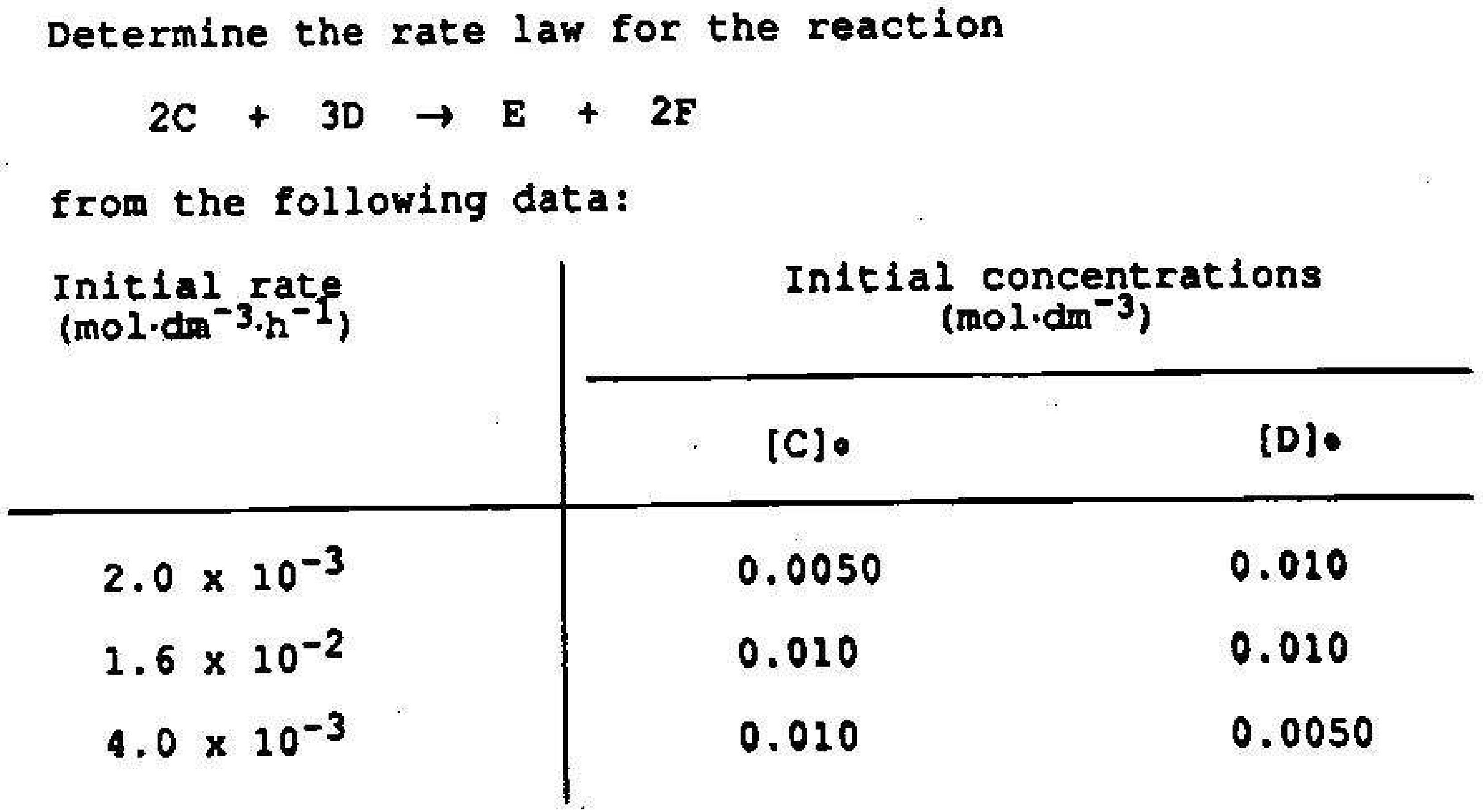
$$R_1 = k[\mathrm{A}]_0^m[\mathrm{B}]_0^n[\mathrm{C}]_0^p \qquad R_2 = k(x[\mathrm{A}]_0)^m[\mathrm{B}]_0^n[\mathrm{C}]_0^p$$

and

$$\frac{R_2}{R_1} = x^m$$

Thus, the exponents ***m, n***, and ***p*** and the rate constant, ***k*** , can be determined.

# Exercise 1



Determine the rate law for the reaction

$$2C + 3D \rightarrow E + 2F$$

from the following data:

| Initial rate ($mol \cdot dm^{-3} \cdot h^{-1}$) | Initial concentrations ($mol \cdot dm^{-3}$) | |
|---|---|---|
| | $[C]_0$ | $[D]_0$ |
| $2.0 \times 10^{-3}$ | 0.0050 | 0.010 |
| $1.6 \times 10^{-2}$ | 0.010 | 0.010 |
| $4.0 \times 10^{-3}$ | 0.010 | 0.0050 |

# Integrated Rate Laws

# Integration of Simple Rate Laws

Consider the reaction $a\mathrm{A} \rightleftharpoons$ products.

$$R = -\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}]^n$$

DIFFERENTIAL RATE LAW

Rate = f(concentration)

Integrating the above equation gives the corresponding ***integrated rate law***.

# First Order Rate Law (*n* =1)

Integrating,

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} -\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]} = \int_{t=0}^{t} k_1 \mathrm{d}t$$

$$\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - k_1 t$$

$$\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]} = k_1 t$$

↔

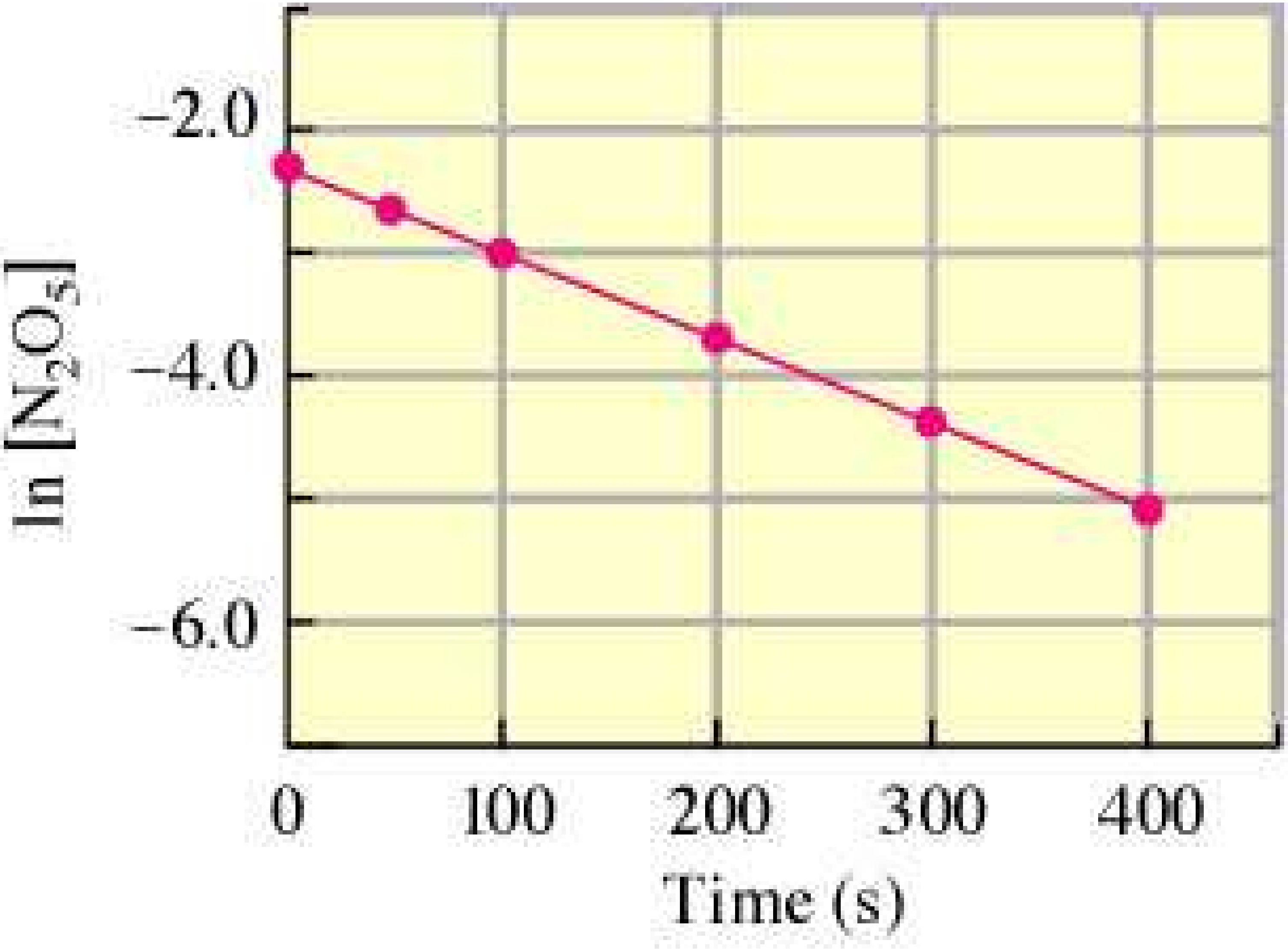
$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t}$$

Concentration = f(time)

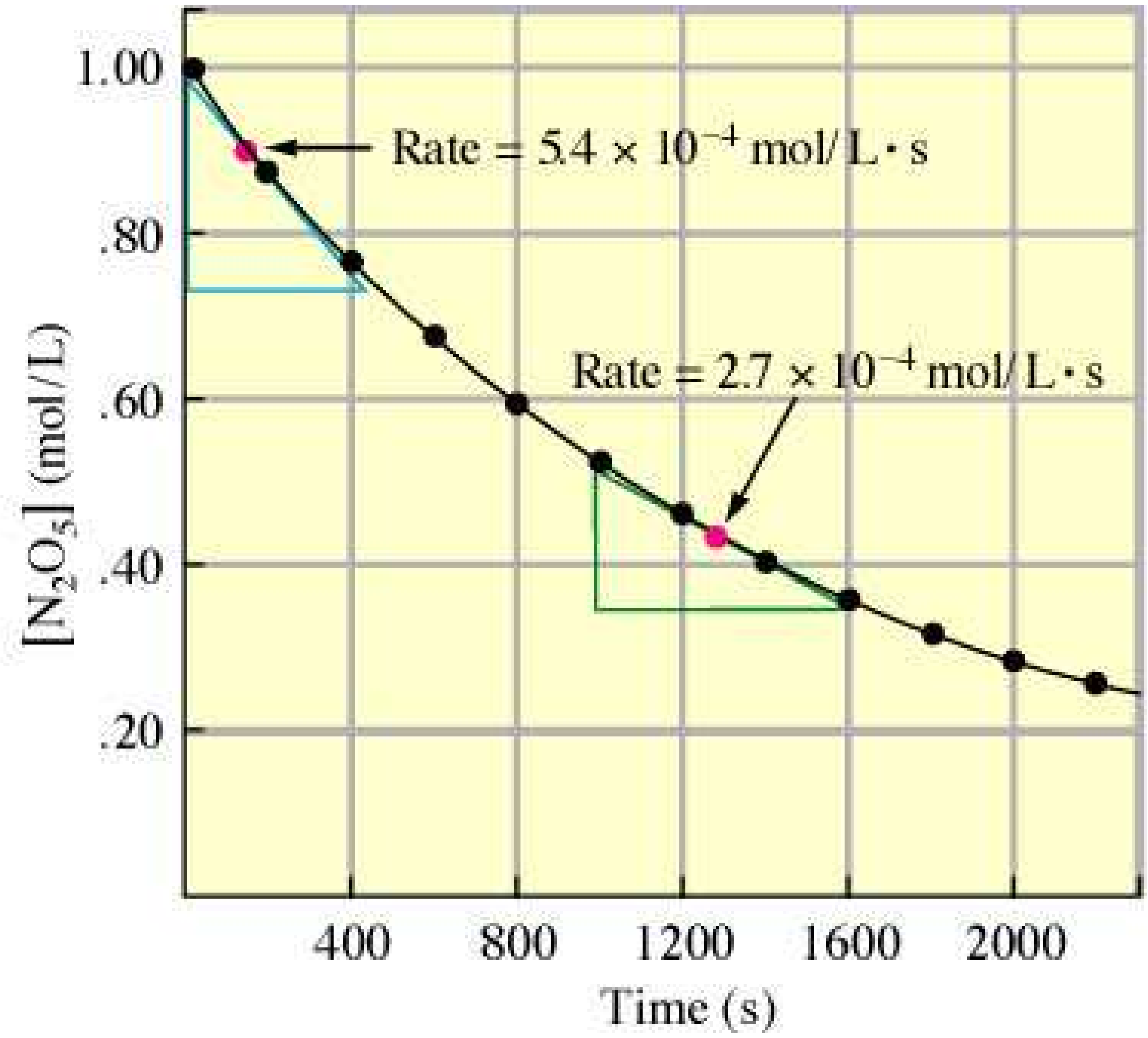
A plot of ln[A] vs. *t* yields a straight line.

First-Order Reaction

$2N_2O_5 \leftrightharpoons 4NO_2 + O_2$



$2N_2O_5 \leftrightharpoons 4NO_2 + O_2$



# Exercise 2

The rate constant for the first-order decomposition of cyclobutane is 0.0078 $s^{-1}$. What is the **concentration, in mol/L**, of a sample whose initial concentration was 0.500 mol/L after an elapsed time of 5 min.

# Second Order Rate Law (*n* =2)

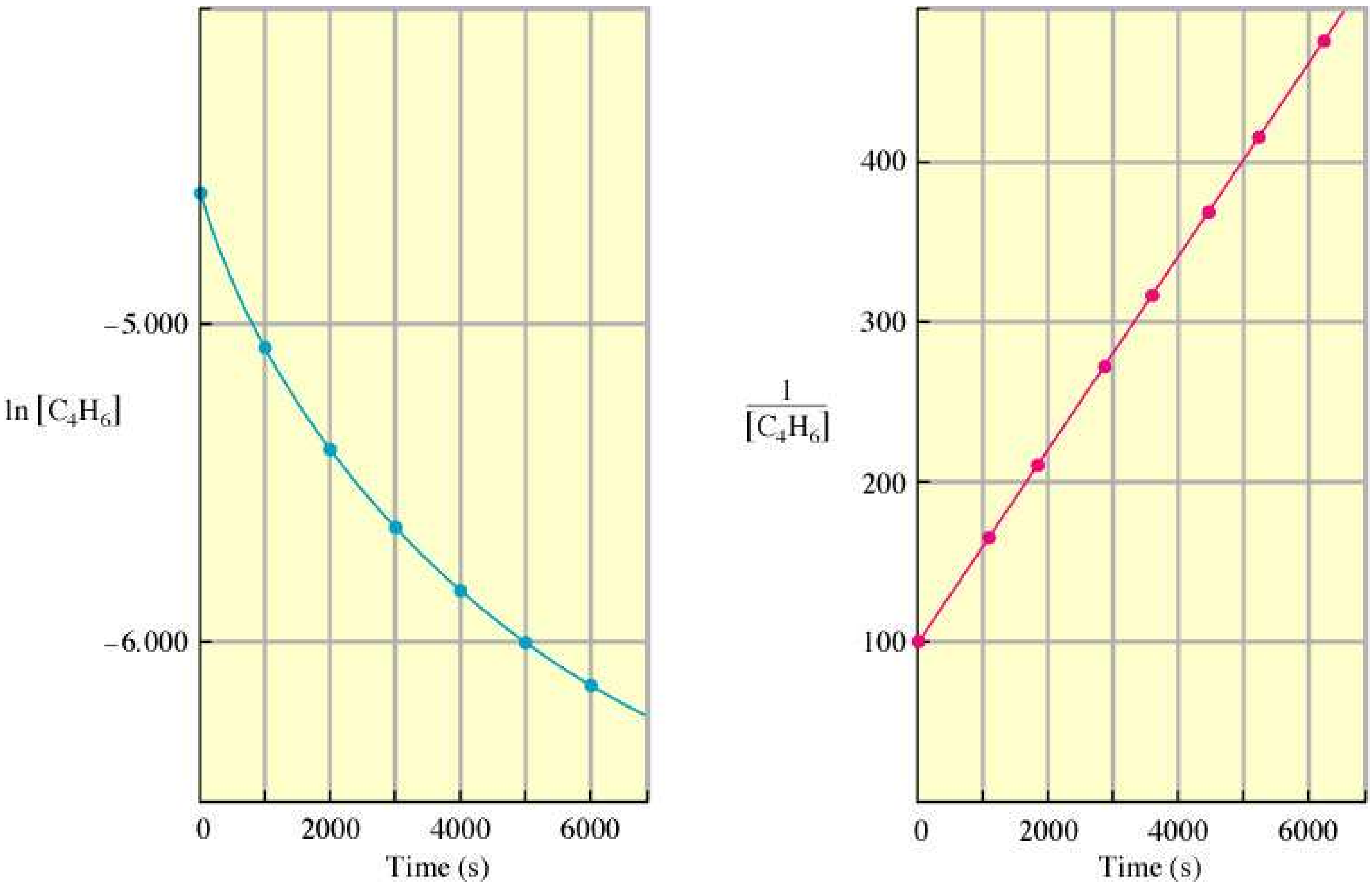
$$R = -\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_2[\mathrm{A}]^2$$

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} -\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]^2} = \int_{t=0}^{t} k_2 \mathrm{d}t$$

$$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + k_2 t$$

A plot of 1/[A] vs. *t* yields a straight line.

# Second-Order Reaction



(a)

(b)

# Exercise 3

A certain substance in solution, initially at a concentration of 0.10 mol/L, decomposes by second order kinetics with a rate constant, k = 0.40 L/mol·min. How much **time, in minutes**, is required for the concentration to reach 0.050 mol/L.

# Zero Order Rate Law (*n* =0)

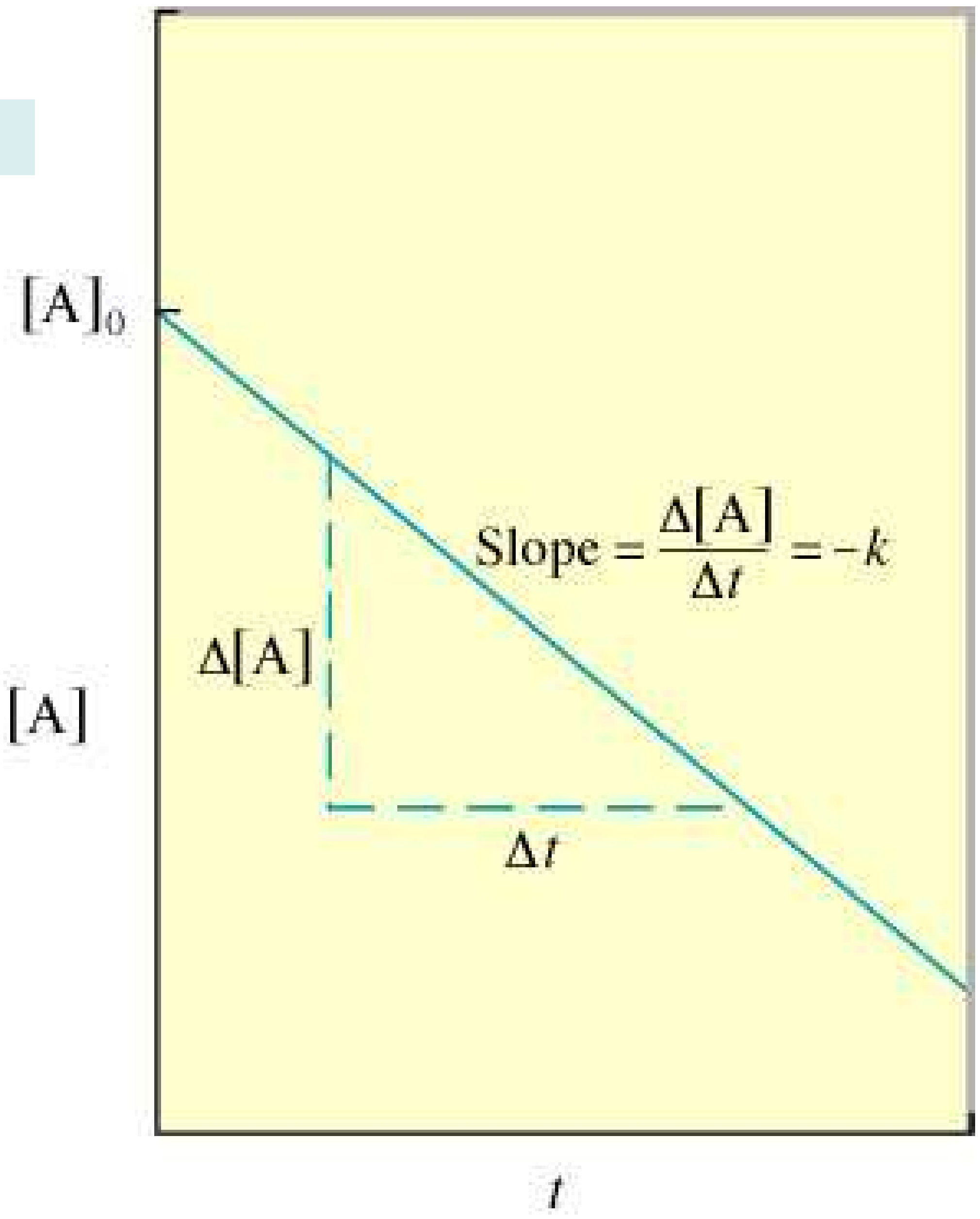
$$R = -\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_0$$

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} -\mathrm{d}[\mathrm{A}] = \int_{t=0}^{t} k_0 \mathrm{d}t$$

$$[\mathrm{A}] = [\mathrm{A}]_0 - k_0 t$$

A plot of [A] vs. *t* yields a straight line.

Zero-Order Reaction



# Reactions With Two or More Reactants

Consider, $a\mathrm{A} + b\mathrm{B} + c\mathrm{C} \rightleftharpoons$ products.

$$R = -\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{B}][\mathrm{C}]^2$$

EXPERIMENTAL

Under special conditions, where

$$[\mathrm{B}]_0 = [\mathrm{C}]_0 >> [\mathrm{A}]_0$$

ISOLATED REACTANT

it can be assumed that throughout the course of the reaction $[\mathrm{B}] = [\mathrm{B}]_0$ and $[\mathrm{C}] = [\mathrm{C}]_0$

and $R = k_1'[\mathrm{A}]$

PSEUDO-FIRST ORDER RATE LAW

where $k_1' = k[\mathrm{B}]_0[\mathrm{C}]_0^2$

OBTAINED FROM ln[A] vs. *t*

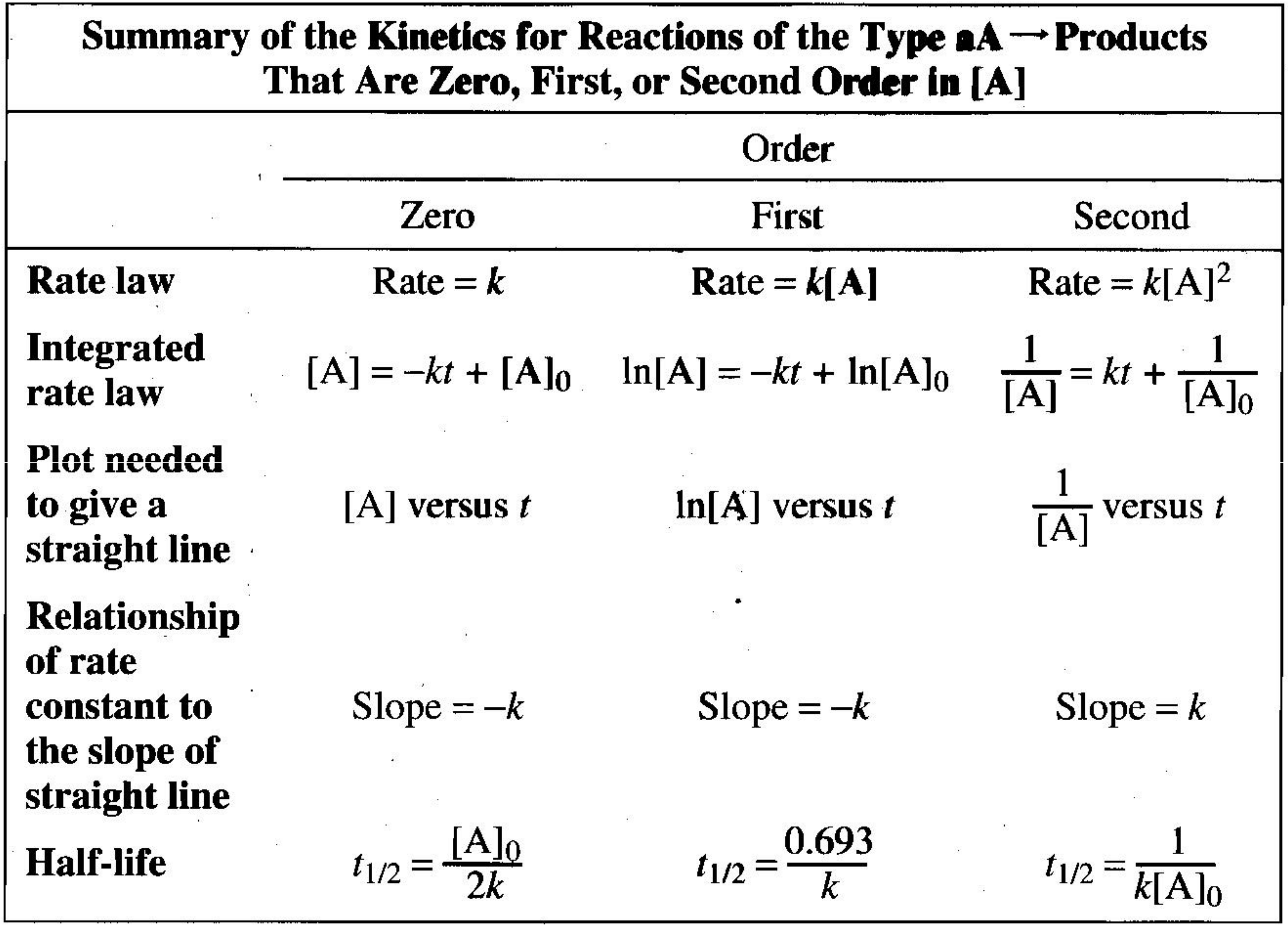
$$k = \frac{k_1'}{[\mathrm{B}]_0[\mathrm{C}]_0^2}$$

KNOWN

# Half-Life ($t_{\frac{1}{2}}$)

The time required for a reactant to reach half its initial concentration is called the ***half-life*** of the reaction.

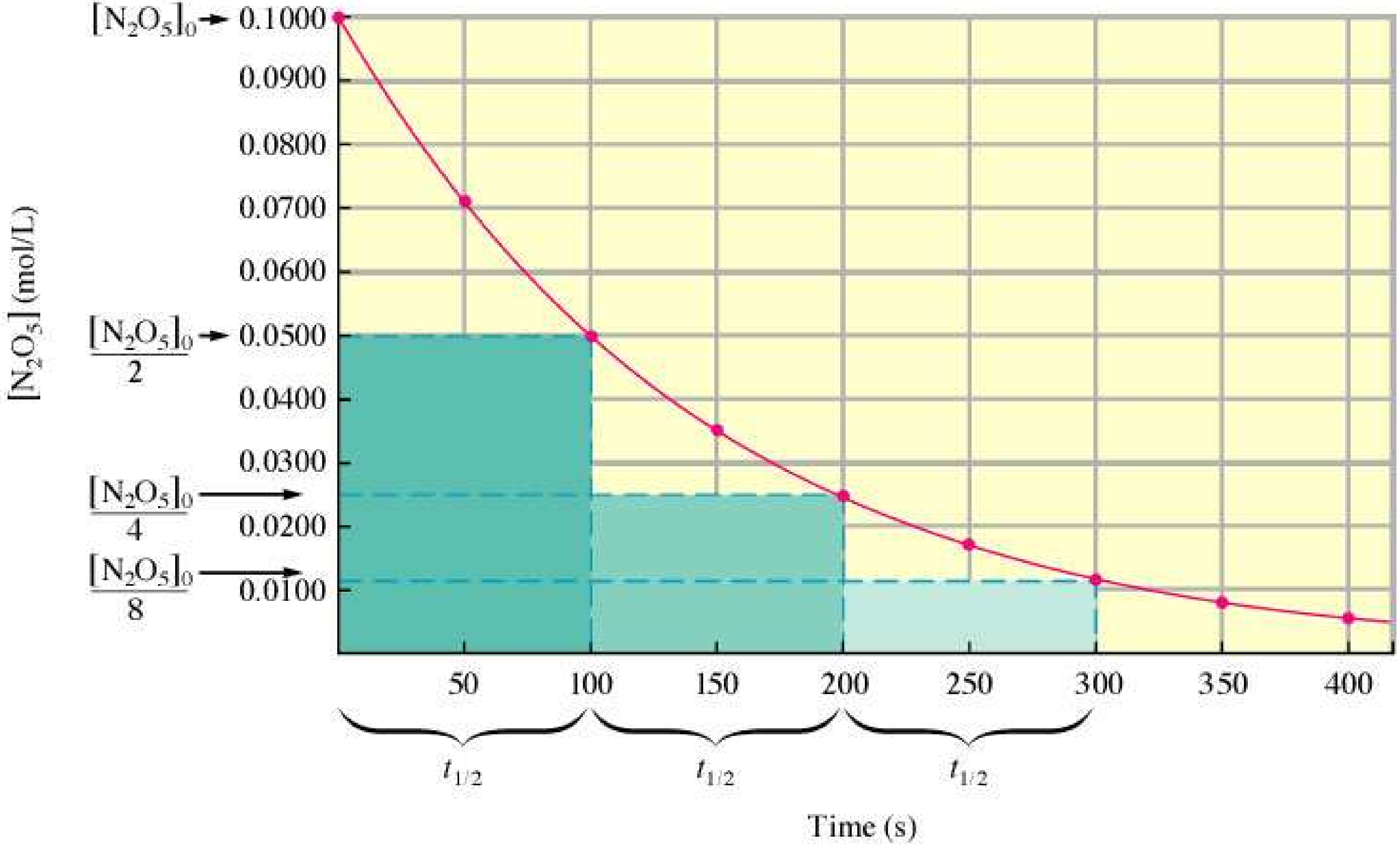
$$t = t_{\frac{1}{2}} \quad \text{when} \quad [A] = \tfrac{1}{2}\,[A]_0$$



**Summary of the Kinetics for Reactions of the Type $aA \rightarrow \text{Products}$ That Are Zero, First, or Second Order in [A]**

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

$2N_2O_5 \leftrightharpoons 4NO_2 + O_2$



# Exercise 4

The rate constant for the first-order decomposition of chloroethane is $k$ = 0.13 $s^{-1}$ at 100 $^{o}$C.  What is the **half-life, in seconds,** of the reaction at this temperature?

# End of Part 1