CHEMICAL KINETICS

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Reaction Rates

- Reaction Rates
- Factors affecting rate
- Quantitative rate expressions
- Determination
- Factors
- Models for rates
- Reaction mechanisms
- Effects of catalysts

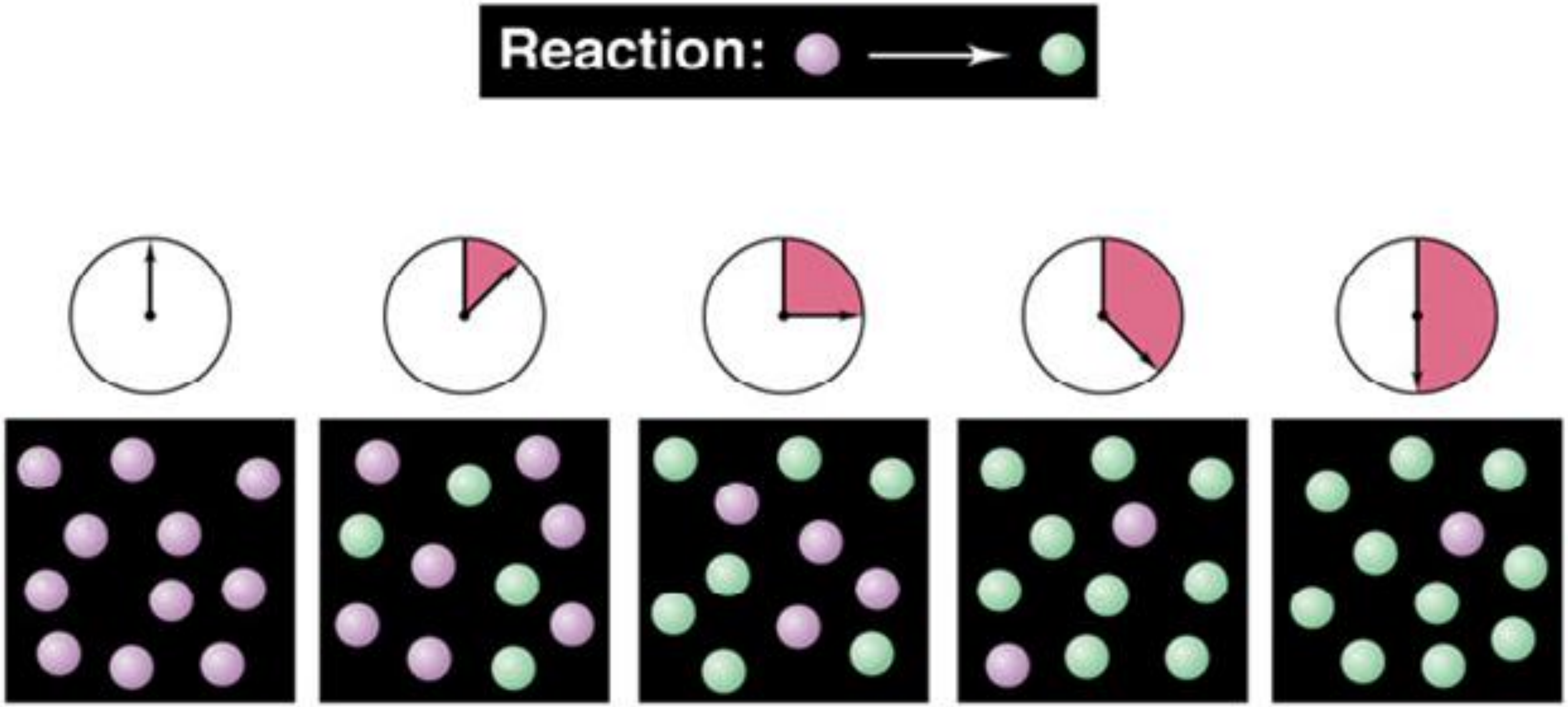
Rates

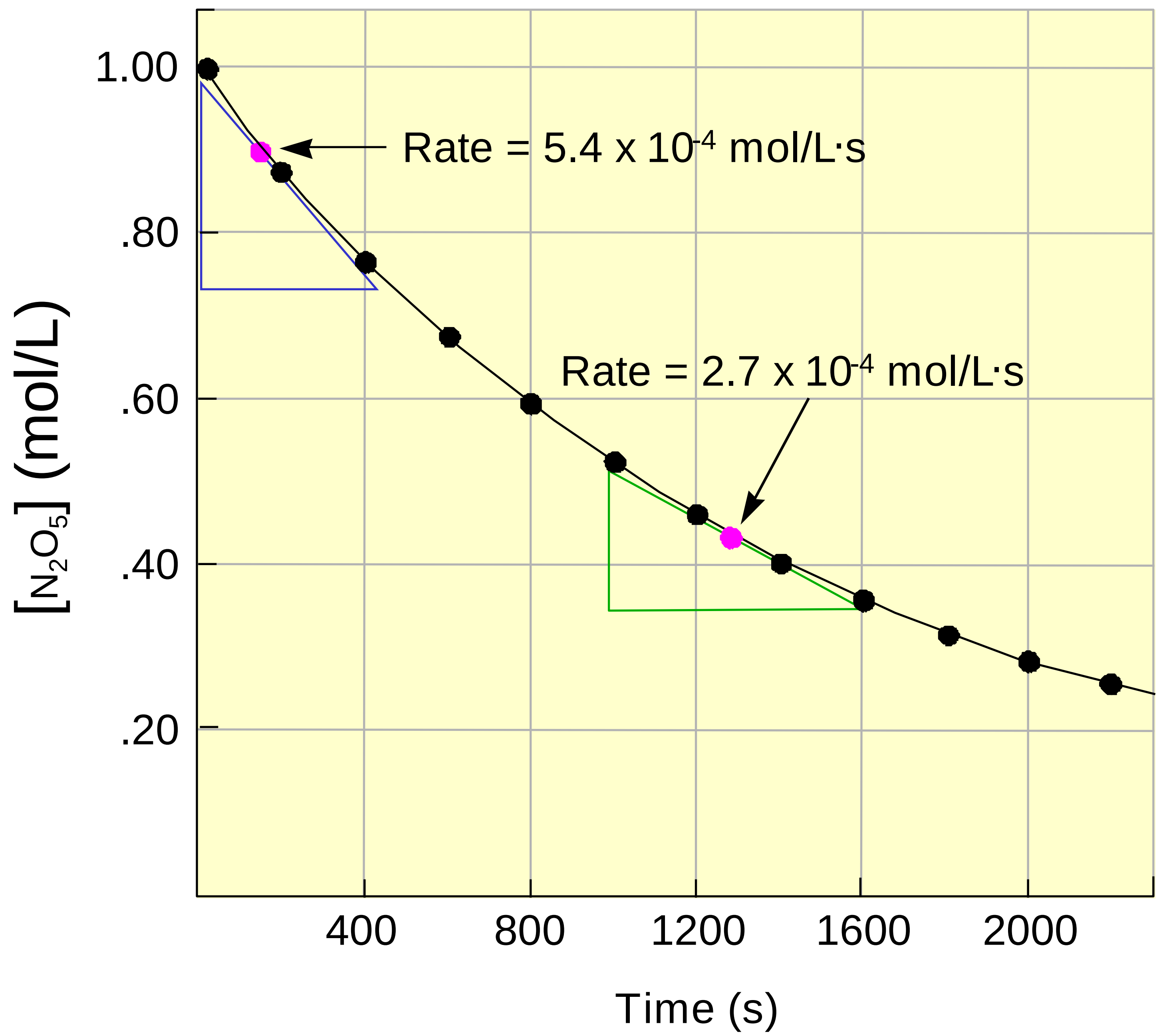
- Change in concentration of a reactant or product per unit time

$$A \rightarrow B$$

$$\frac{\text{Change in conc, A}}{\text{Change in time, t}} = \frac{[A]_t - [A]_0}{t_t - t_0} = \frac{\Delta[A]}{\Delta t}$$

Reaction Rate





Rate = 5.4 x 10-4 mol/L·s
Rate = 2.7 x 10-4 mol/L·s
1.00
.80
.60
.40
.20
[N2O5] (mol/L)
400
800
1200
1600
2000
Time (s)

Factors affecting rates

- Nature of the reactants
- State of subdivision / surface area
- Concentration
- Temperature
- Catalysts

$$C_2H_4 + O_3 \rightarrow C_2H_4O + O_2$$

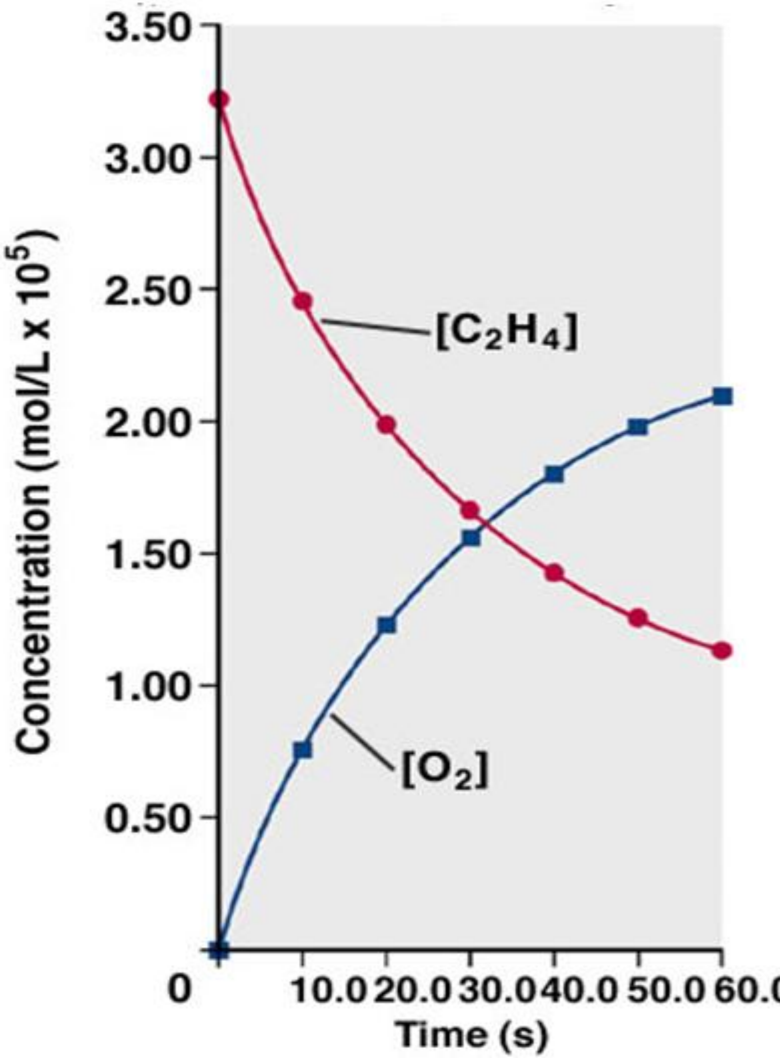
Concentration of O_3 vs. Time

Table 16.1 O_3 Concentration at Various Times in Its Reaction with C_2H_4 at 303 K

Time (s)	Concentration of O_3 (mol/L)
0.0	3.20×10^{-5}
10.0	2.42×10^{-5}
20.0	1.95×10^{-5}
30.0	1.63×10^{-5}
40.0	1.40×10^{-5}
50.0	1.23×10^{-5}
60.0	1.10×10^{-5}

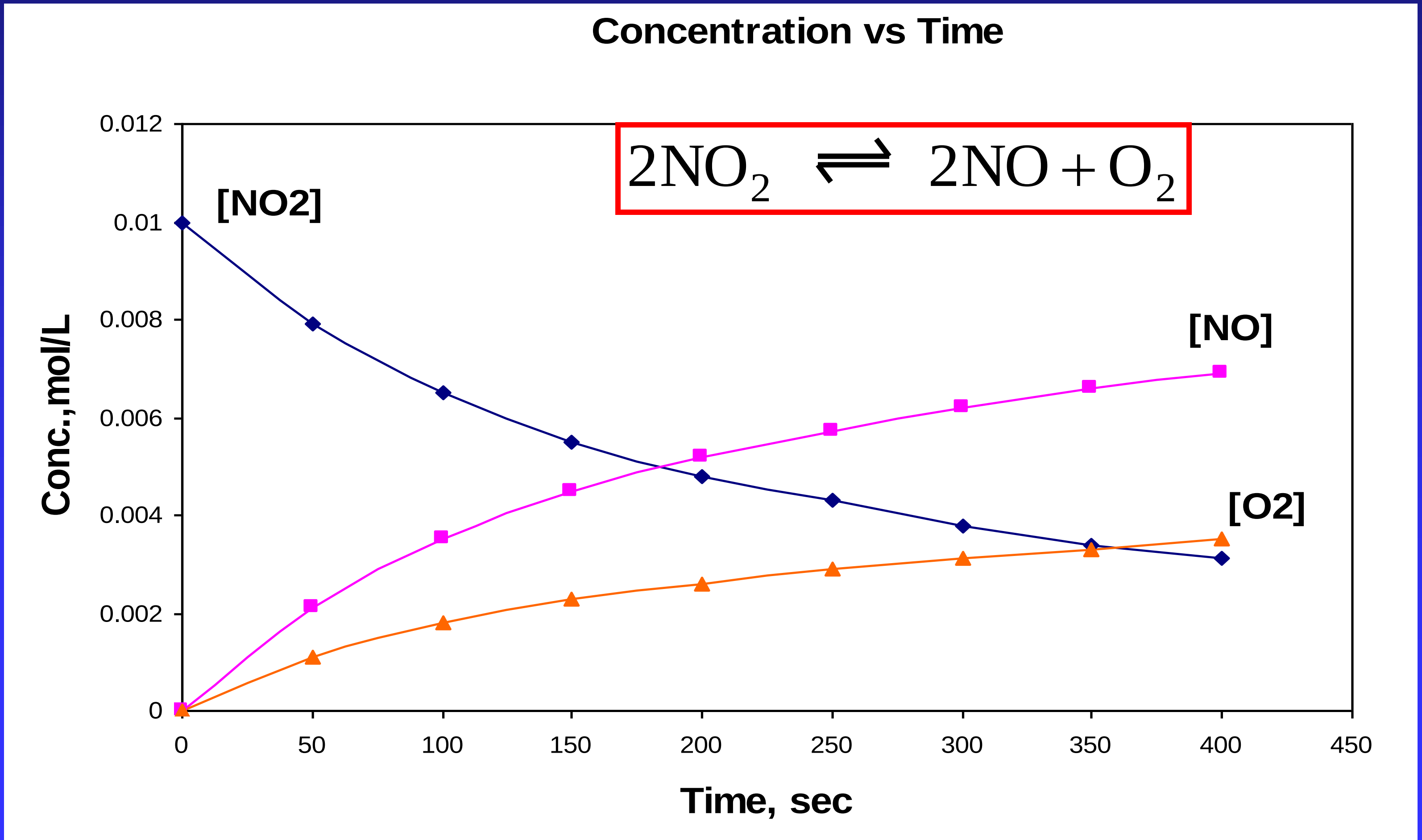
$$C_2H_4 + O_3 \rightarrow C_2H_4O + O_2$$

Plots of $[C_2H_4]$ and $[O_2]$ vs. Time



Graph: Concentration vs. time

$$\frac{\Delta[NO_2]}{\Delta t} = \frac{[NO_2]_{400} - [NO_2]_0}{t_{400} - t_0} = \frac{[0.0031] - [0.0100]}{400 - 0} = -1.725 \times 10^{-5}\,M$$



Rate Laws

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

k = rate constant

m, n = order

$$2NO_2 \rightleftharpoons 2NO + O_2$$

rate = $k[NO_2]^n$

First Order Reactions

For a A $\rightarrow$ products

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

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

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

Half-life, first order reactions

Integrated law :

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

Half-life :

Half of initial reacted

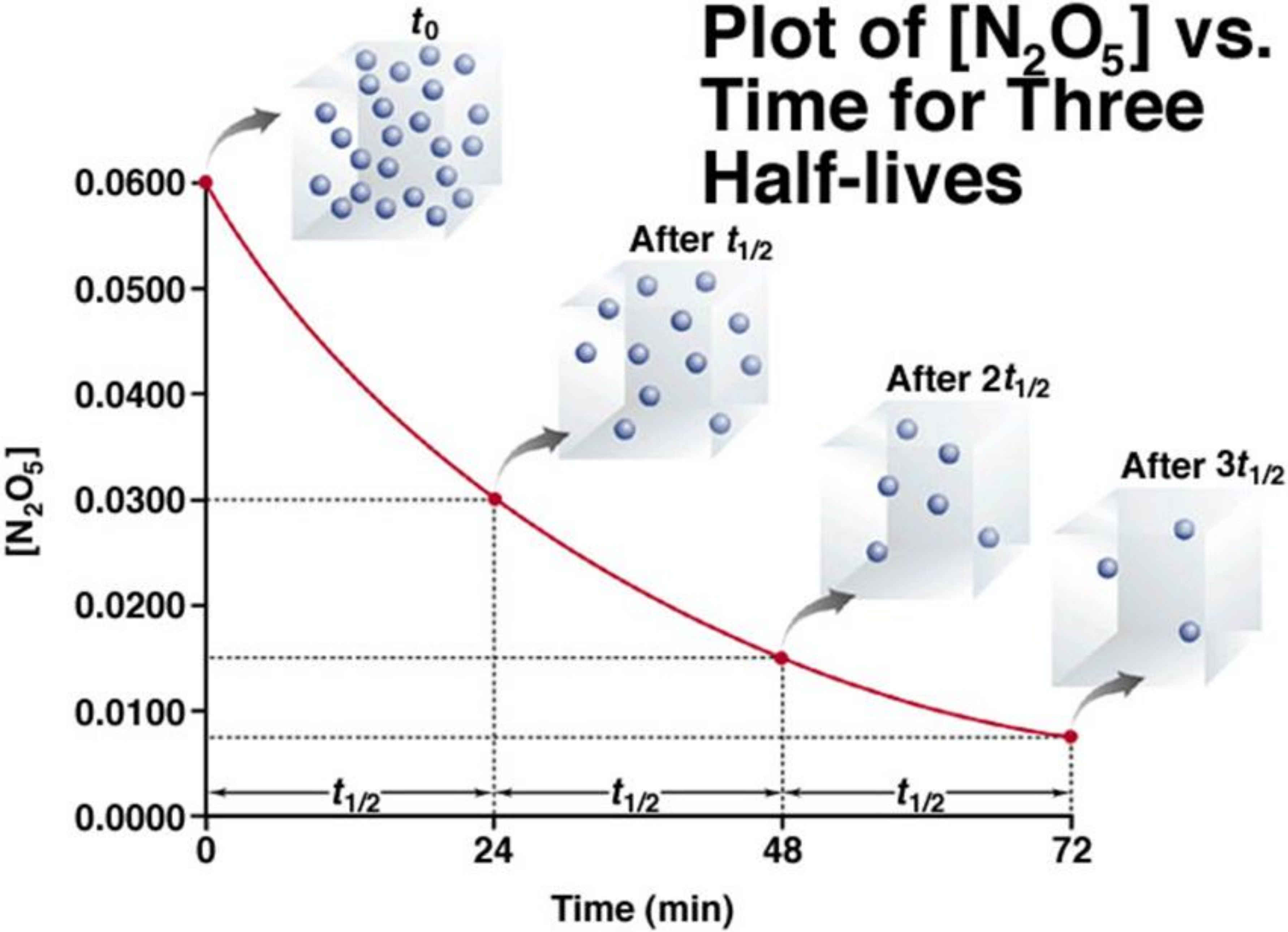
$[A]_t = \frac{1}{2}[A]_0$

$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

Independent of $[A]_0$

Plot of $[N_2O_5]$ vs. Time for Three Half-lives



Zero Order Reactions

For a A → products

Differential:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^0 = k$$

Integrated:

$$[\text{A}]_t = -kt + [\text{A}]_0$$

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

Elementary Reactions and Molecularity

Table 16. Rate Laws for General Elemetary Steps

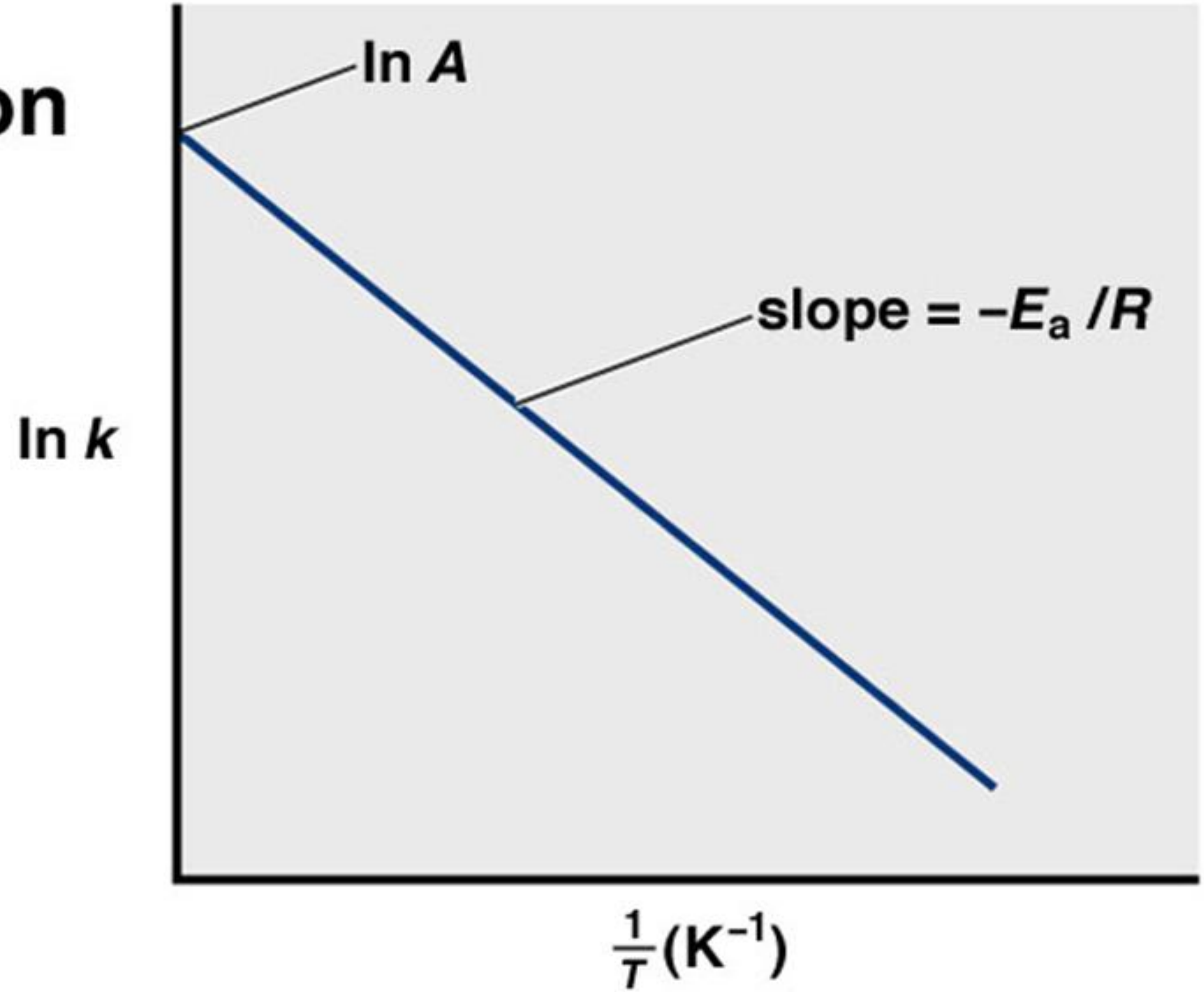
Elementary Step	Molecularity	Rate Law
$A \longrightarrow$ product	Unimolecular	Rate = $k[A]$
$2A \longrightarrow$ product	Bimolecular	Rate = $k[A]^2$
$A + B \longrightarrow$ product	Bimolecular	Rate = $k[A][B]$
$2A + B \longrightarrow$ product	Termolecular	Rate = $k[A]^2[B]$

Arrhenius Equation

$$k = Ae^{-\frac{E_a}{RT}}$$

- k : rate constant
- E_a: activation energy (minimum required)
- T: absolute temperature
- R: universal gas constant
- A: orientation factor

Determination of the Activation Energy.




Thank you!