

The Rate Laws

First-Order Reactions

the only significant concentration is that of the single reactant



if determined experimentally to be first order:

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

$[\text{N}_2\text{O}_5]$



First-order rate plot

The plot shows the decrease in reactant concentration with time for a first-order process

Time (s)

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

we can also use the rate equation to calculate the concentrations of reactants at any **time during the reaction**

First-Order Reactions Integrated

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

the integrated form of the rate law is:

$$\ln([A]_0 / [A]) = kt$$

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

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

concentration
at time t

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

initial
concentration

Integrated rate law

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

alternatively,

$$\log[A] = -\frac{kt}{2.303} + \log [A]_0$$

Integrated rate law

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

The integrated form of the rate law allows us to calculate concentrations at any time after the reaction has started

Integrated rate law

is an equation for a straight line

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

$$y = mx + b$$

Plot $\ln[A]$ versus t

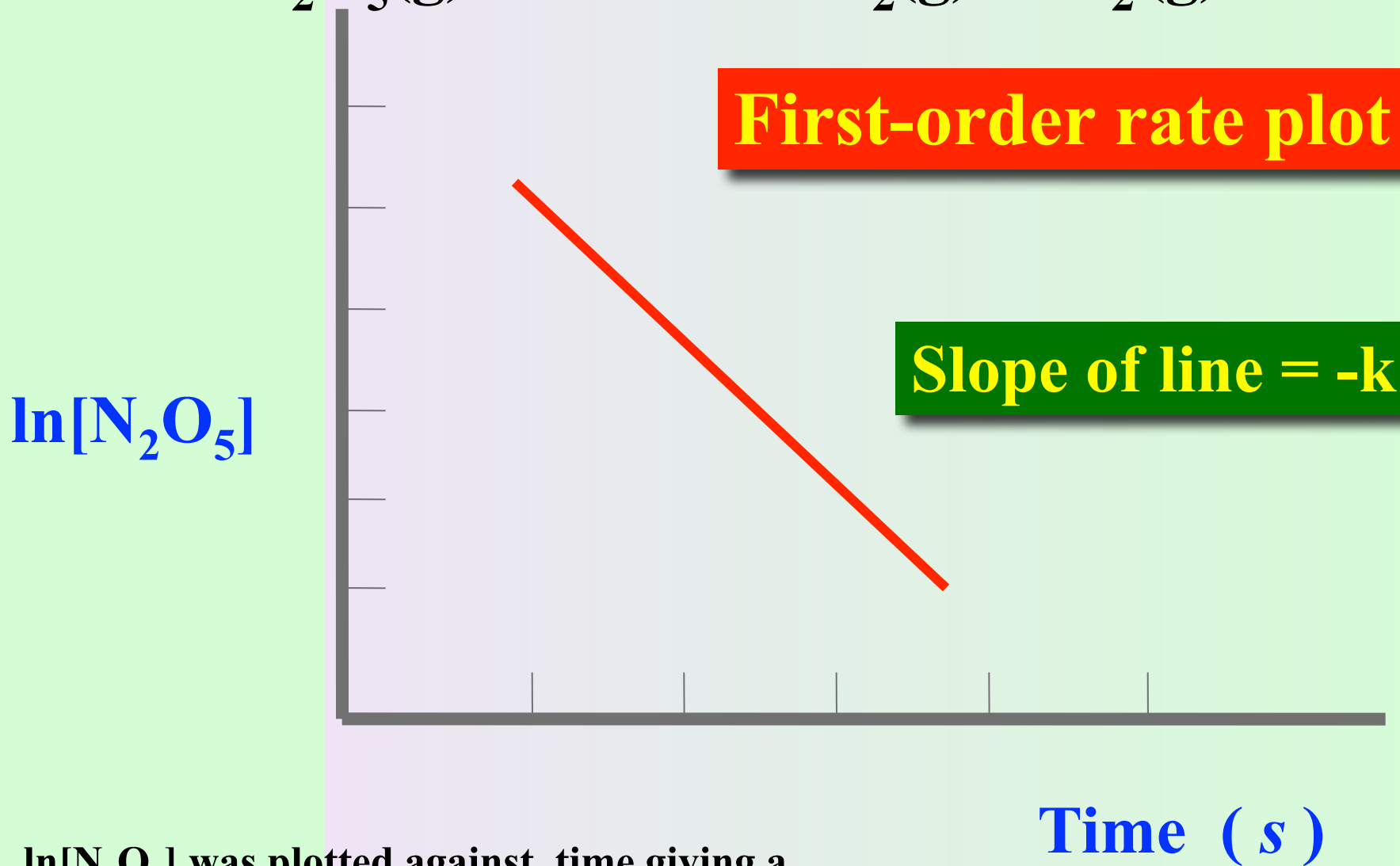
Slope = $-k$

y intercept is $\ln[A]_0$



$$\text{rate} = k [\text{N}_2\text{O}_5]$$

Concentration effect on reaction rate established by experiment is determined to be first order in N_2O_5



ln[N₂O₅] was plotted against time giving a straight line

Example



is this reaction shown first order in azomethane?

Time (min)	[azomethane]
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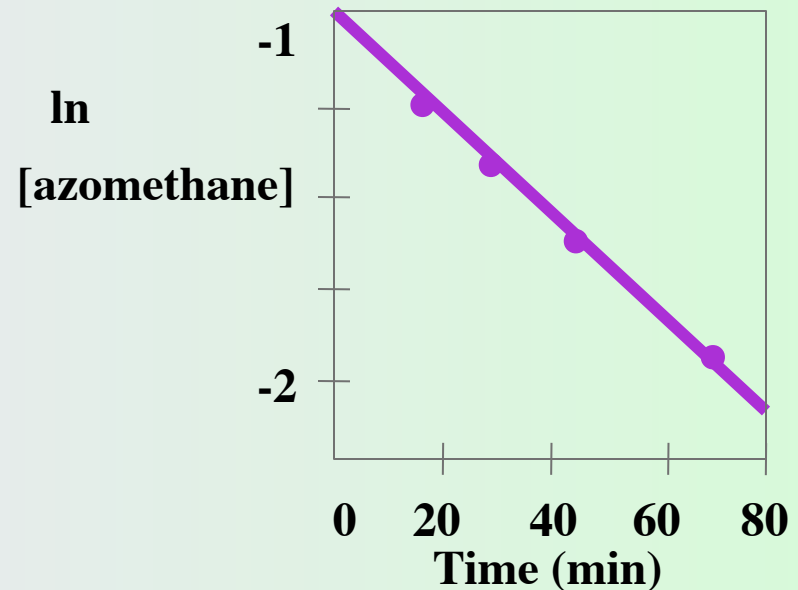
0	0.36
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15	0.30
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30	0.25
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48	0.19
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75	0.13
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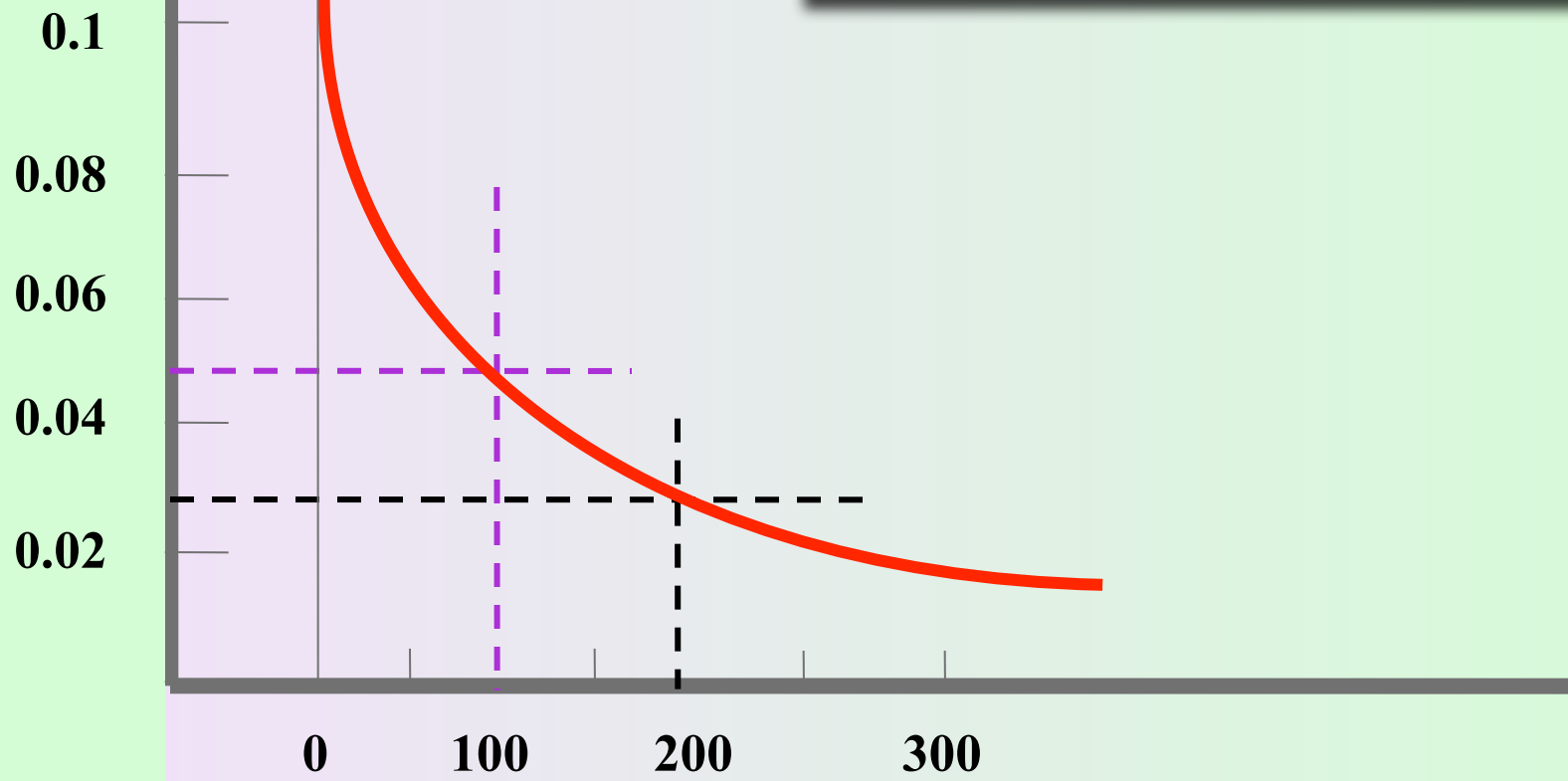
Half-life

the time for the concentration of a reactant to decrease to one-half of its initial concentration

the half-life of a first order reaction is the same regardless of the concentration

$[N_2O_5]$

First-order rate plot



The plot shows the decrease in reactant concentration with time for a first-order process

Time (s)

Half-life for a First-Order Reaction

$$\ln([A]_0 / [A]) = kt$$

when $t = t_{1/2}$

then $[A] = [A]_0 / 2$

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

$$\ln(2) = kt_{1/2}$$

$$t_{1/2} = \frac{\ln(2)}{k}$$

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

Radiocarbon Dating

Willard Libby (Nobel Prize, 1960)

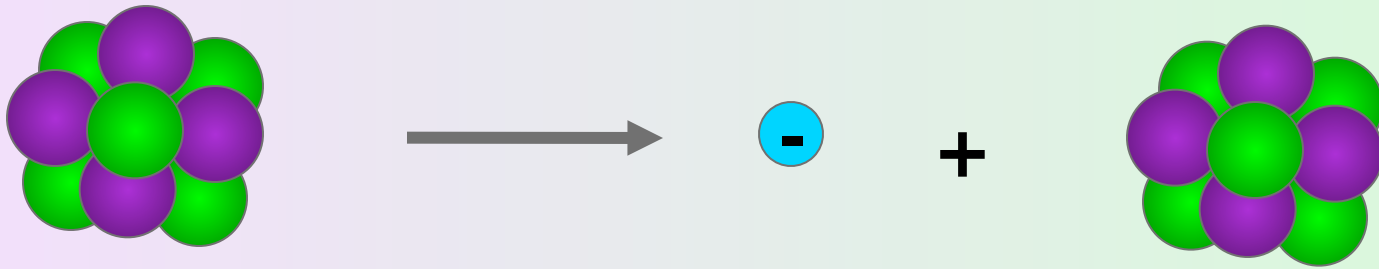
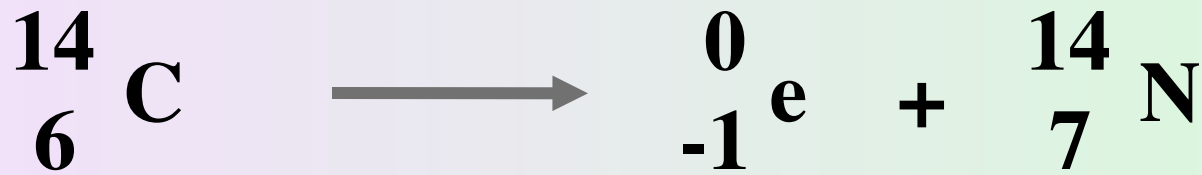
Carbon-14

Natural abundance: 1 part in 10^{12}

β – emitter

Half-life = 5730 years

used to date archeological artifacts younger than 30,000 years



Example

The C-14 decay rate of wood obtained from a live tree is 0.260 disintegration per second per gram of sample. A sample of wood from an archaeological site has C-14 decay rate of 0.186 disintegration per second per gram. How old is the sample?

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$t_{1/2}$ for ^{14}C is known to be 5730 years

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

Therefore, $k = (0.693/5730 \text{ yr}) = 1.21 \times 10^{-4} \text{ yr}^{-1}$

$$\ln \frac{[A]_0}{[A]} = kt \quad \ln \frac{260}{186} = (1.21 \times 10^{-4} \text{ yr}^{-1}) t$$

$$t = 2770 \text{ years}$$

Some representative half-lives

Tc-99	6 hours
Mo-99	67 hours
Sr-90	28.8 years
C-14	5730 years
K-40	1,300,000 years
U-238	45, 000,000 years

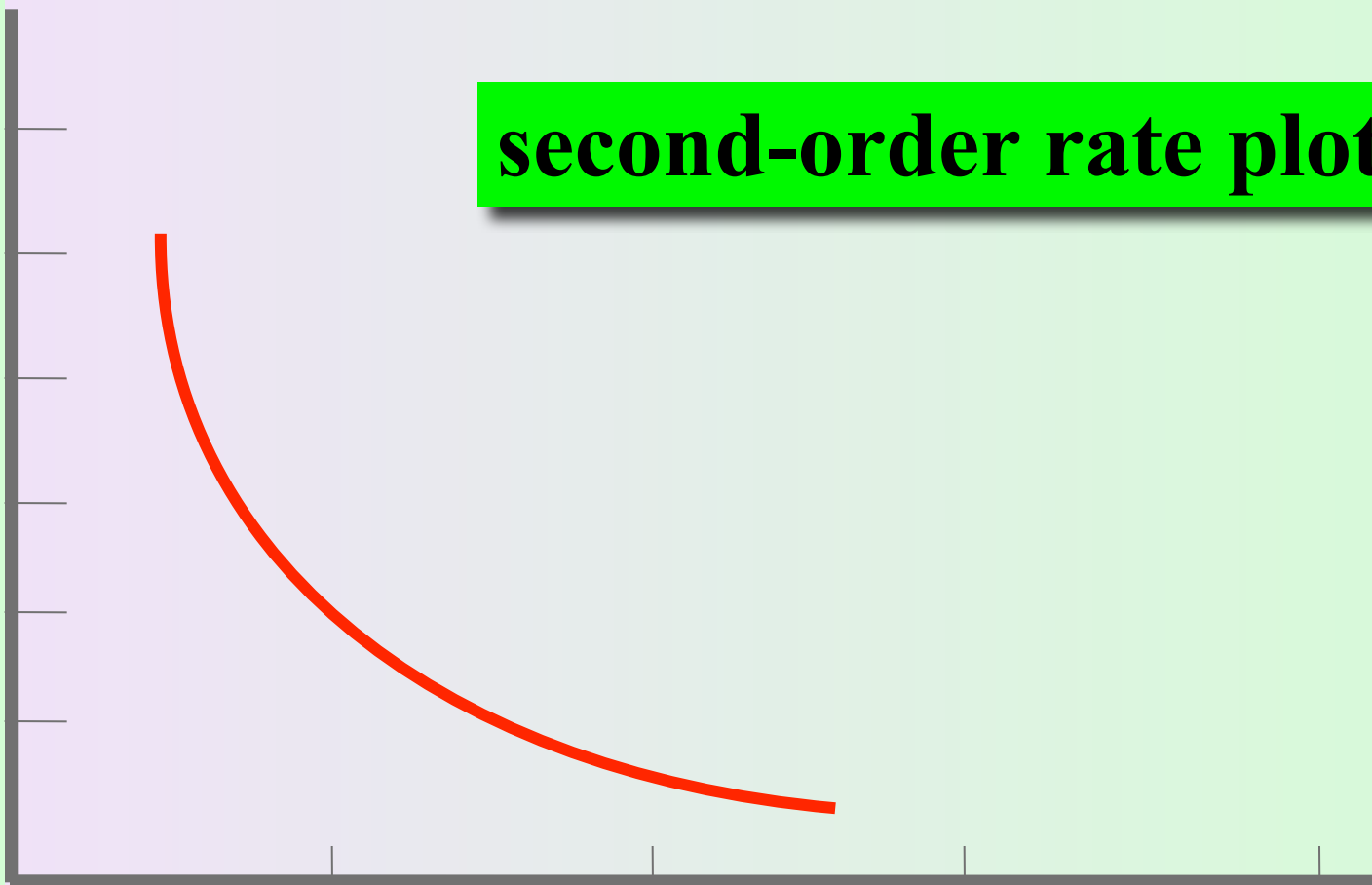
second-Order Reactions

The rate of a second order reaction depends on reactant concentration rate to the second power or on the concentrations of two different reactants, each raised to the first power.

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

[A]

second-order rate plot



The plot shows the decrease in reactant concentration with time for a second-order process

Time (s)

Integrated rate law

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

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

Plot of $1/[A]$ vs t gives straight line with slope equal to k

Example



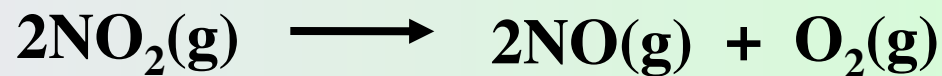
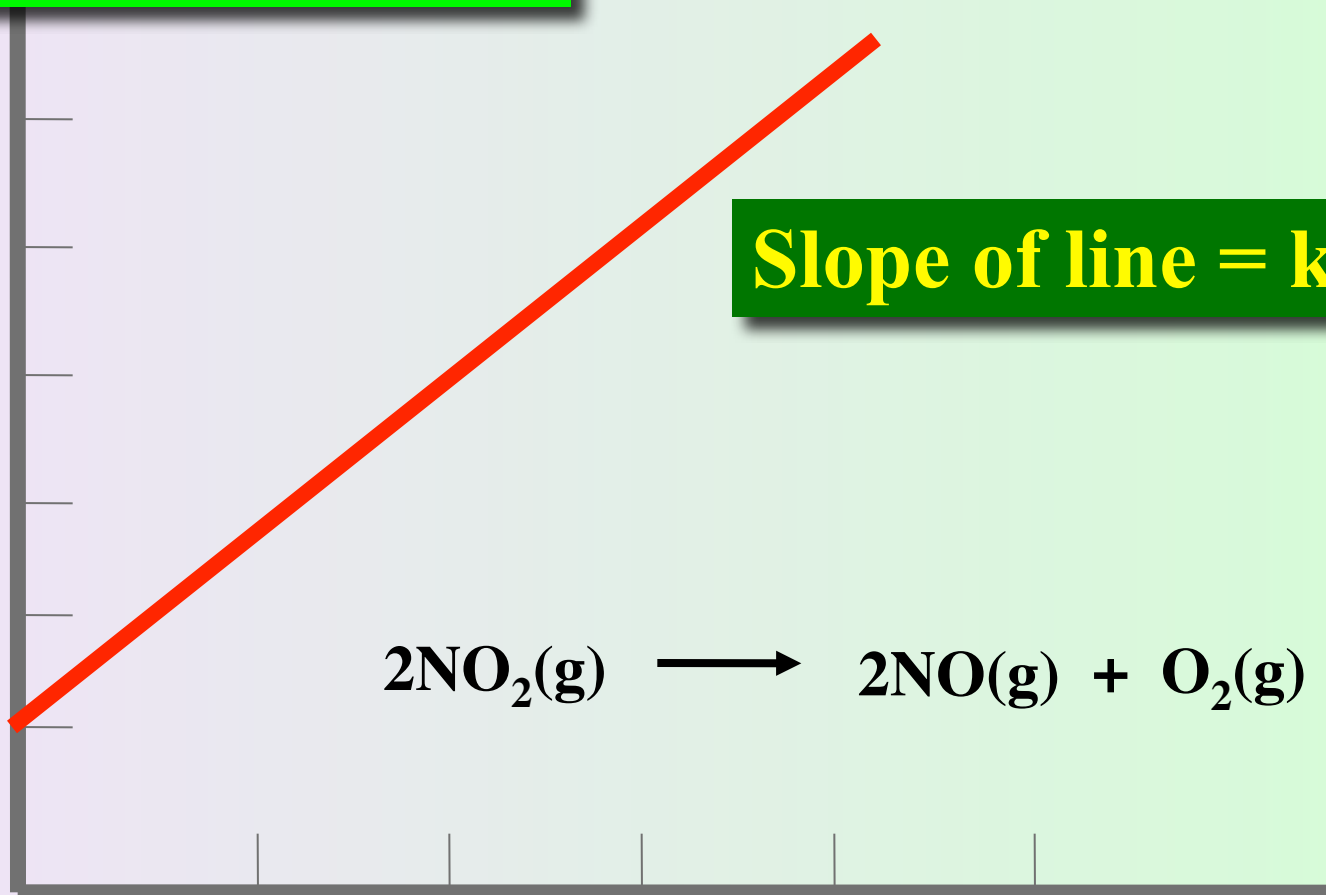
The reaction for the decomposition of pure nitrogen dioxide

The following concentration data were collected at 592 K:

Time (s)	[NO₂] mol/L	1/ [NO₂]
0.0	0.0015	6.67 x 10²
100.0	0.00139	7.19 x 10²
200.0	0.00130	7.69 x 10²
400.0	0.00114	8.77 x 10²
800.0	0.00092	1.08 x 10²
1200.0	0.00077	1.29 x 10³
1600.0	0.00066	1.50 x 10³

second-order rate plot

$$\frac{1}{[\text{NO}_2]}$$



Time (s)

$1/[\text{NO}_2]$ was plotted against time giving a straight line

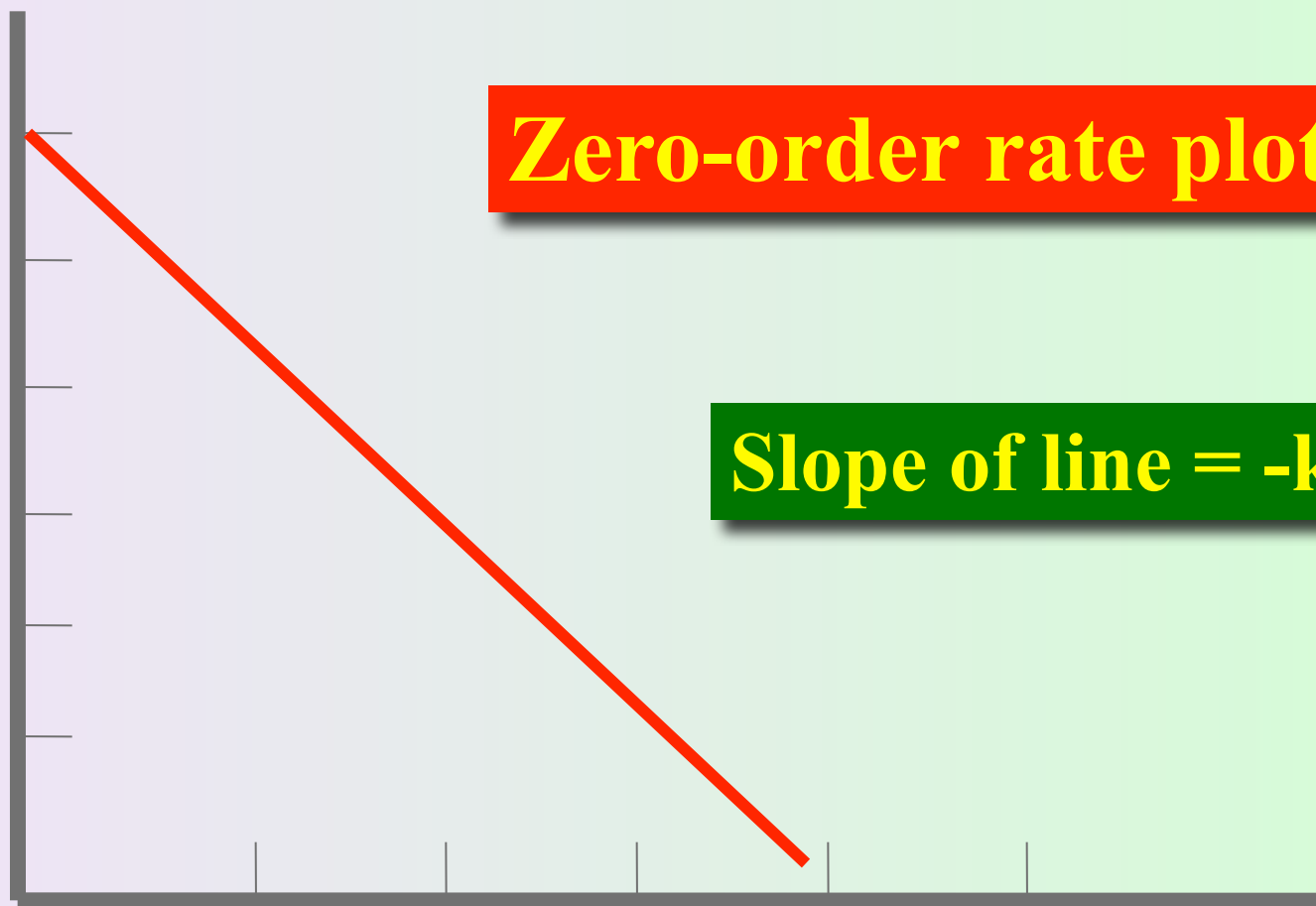
Zero-Order Reactions

Reaction rate does not change with a change in reactant concentrations

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

Zero order reactions are most often encountered when an enzyme or metal surface is required for the reaction to occur

[A]



Slope of line = -k

[A] was plotted against time giving a straight line

Time (s)

Integrated rate law

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

$$[A]_0 - [A] = kt$$

Plot of $[A]$ vs t gives straight line with slope equal to *zero*