The Rate Laws

First-Order Reactions

the only significant concentration is that of the single reactant

$$aA \longrightarrow \text{products}$$

if determined experimentally to be first order:

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

First-order rate plot

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

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

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

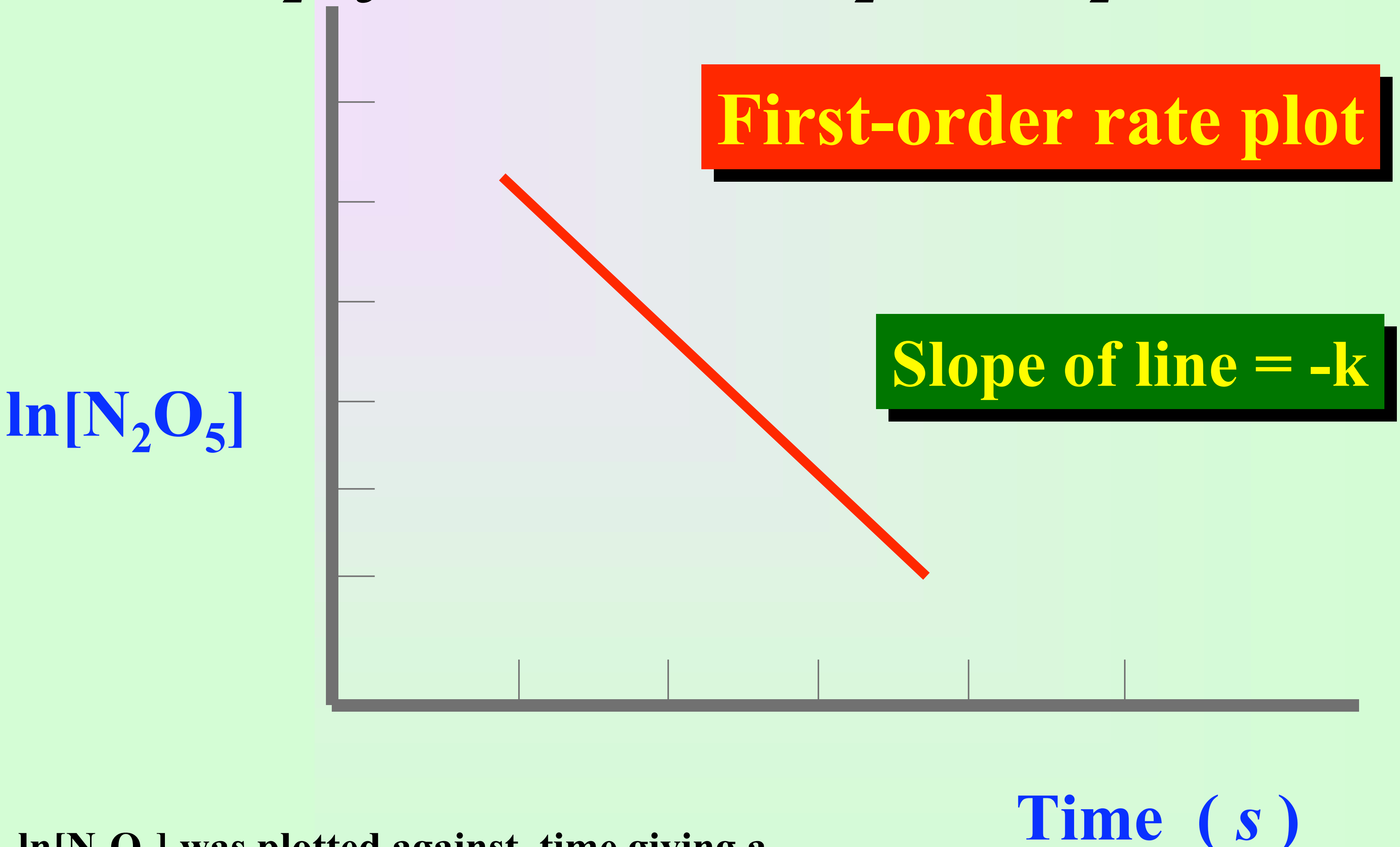
y intercept is $\ln[A]_0$

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

$$\text{rate} = k\,[N_2O_5]$$

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

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$



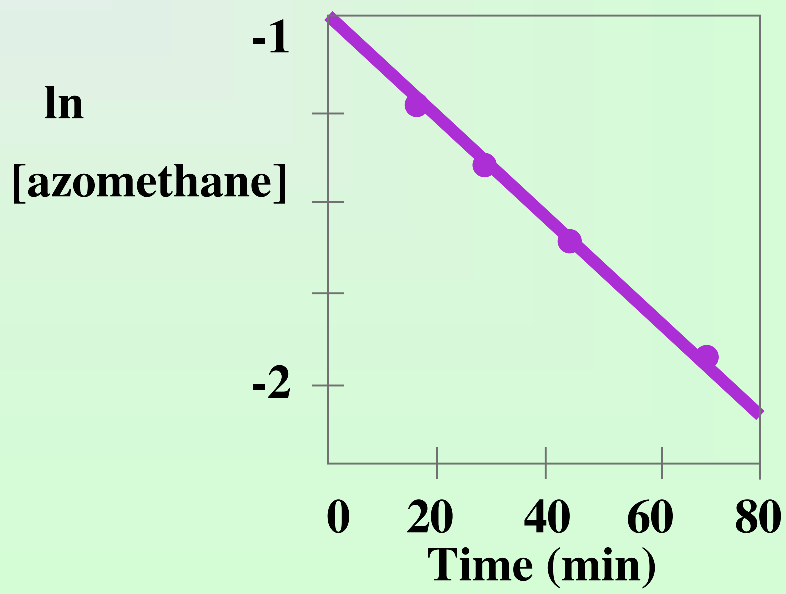
ln[N_2O_5] was plotted against time giving a straight line

Example

$$CH_3N = NCH_3 \longrightarrow CH_3CH_3 + N_2$$

is this reaction shown first order in azomethane?

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

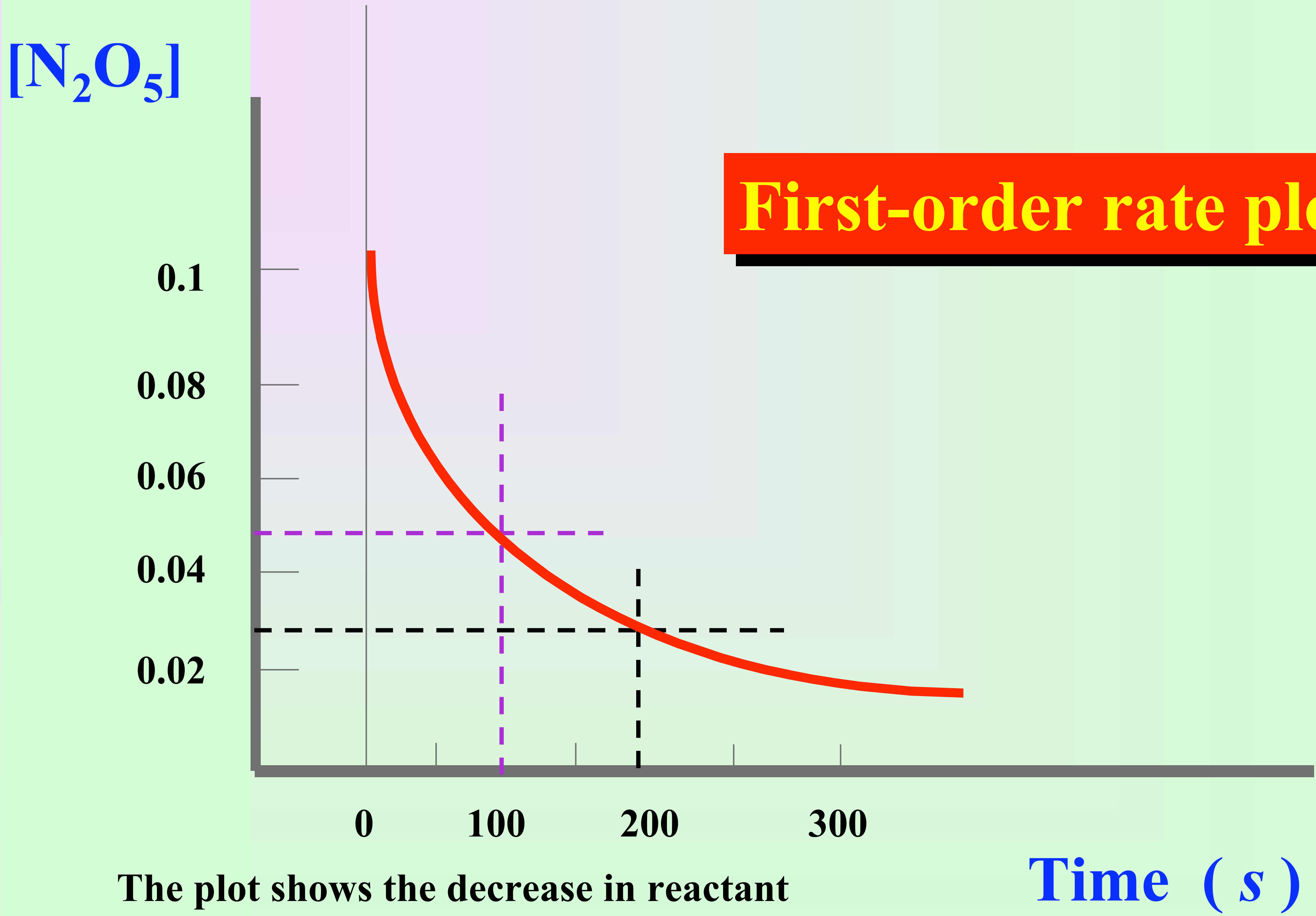


Half-life

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

First-order rate plot



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

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

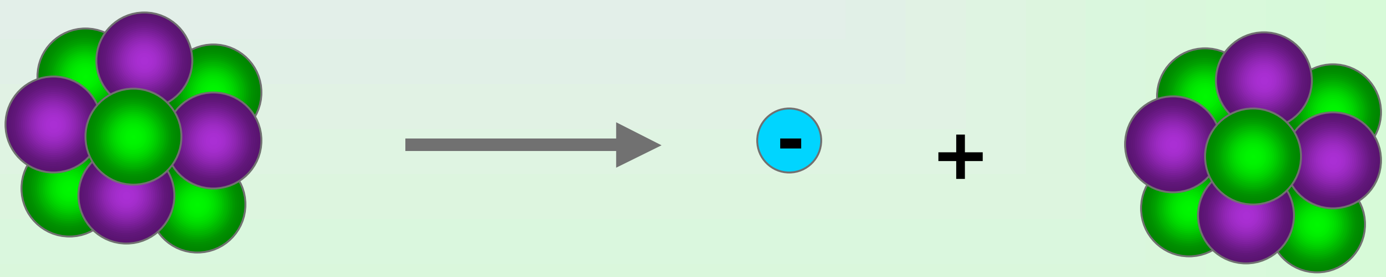
Natural abundance: 1 part in 10^{12}

□ □ emitter

Half-life = 5730 years

used to date archeological artifacts younger than 30,000 years

$$^{14}_{6}C \longrightarrow {}^{0}_{-1}e + {}^{14}_{7}N$$



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 14C is known to be 5730 years

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

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

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

t =2770 years

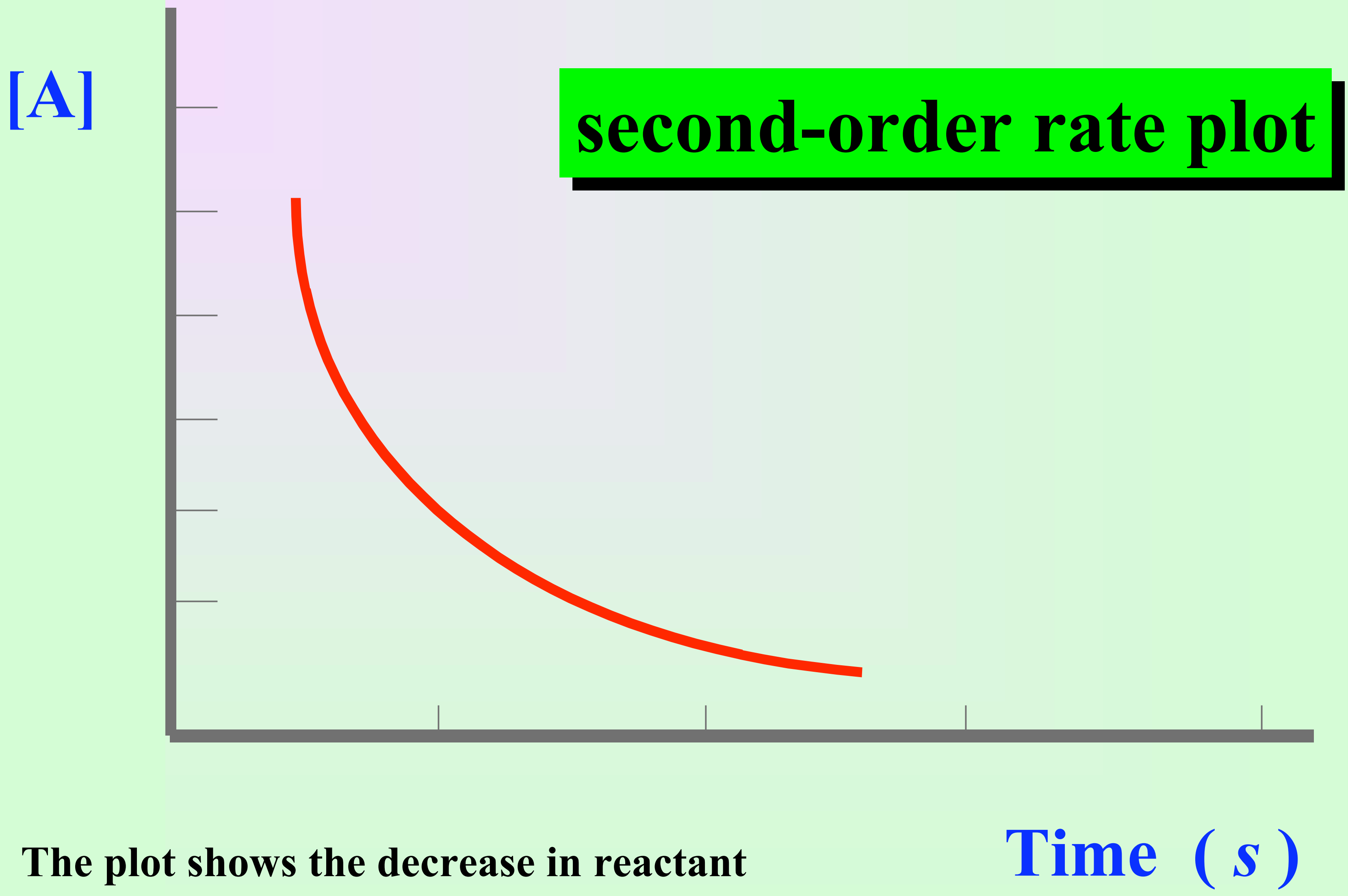
Some representative half-lives

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.

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



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

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

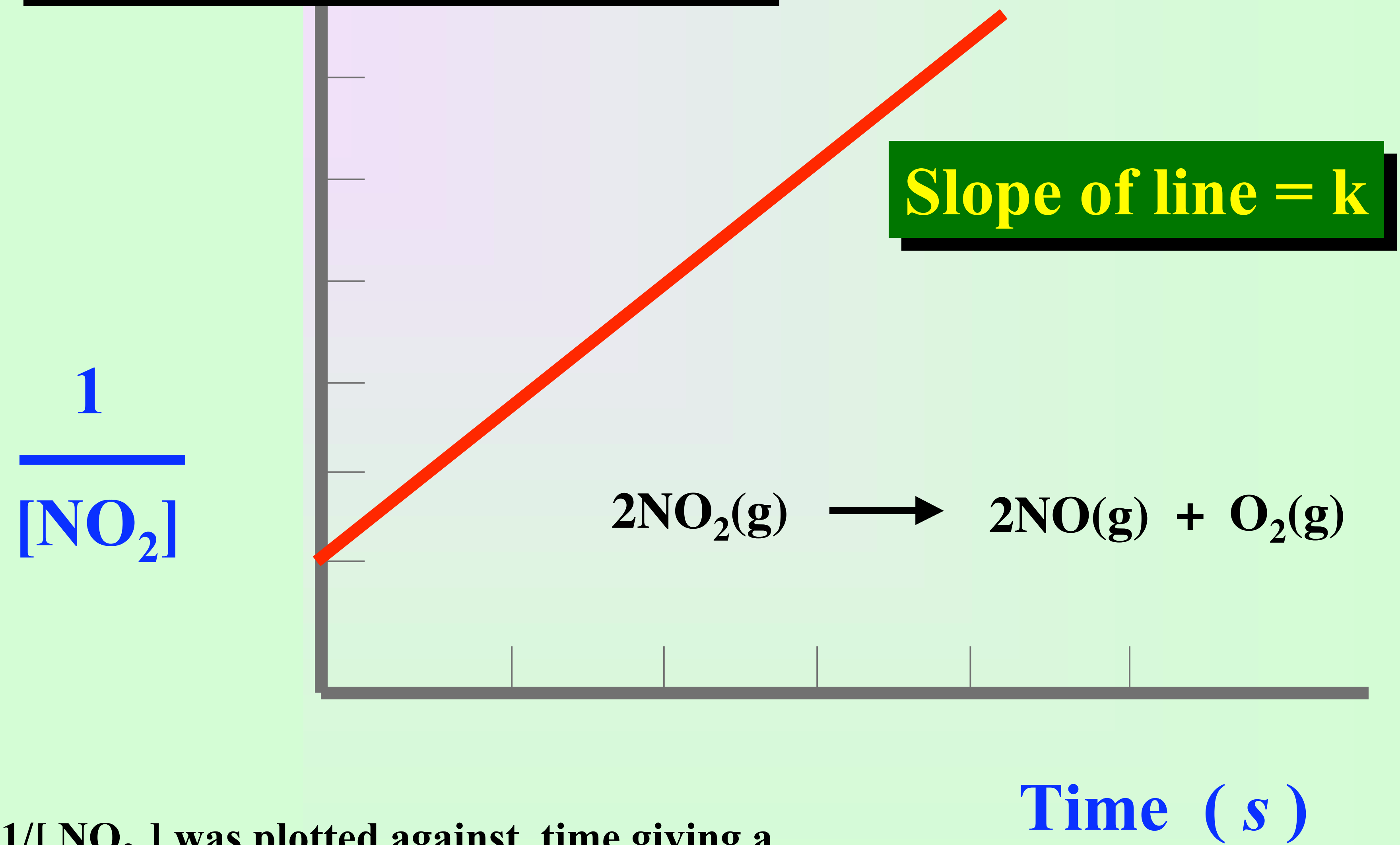
$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$$

The reaction for the decomposition of pure nitrogen dioxide

The following concentration data were collected at 592 K:

Time (s)	$[NO_2]$ mol/L	$1/[NO_2]$
0.0	0.0015	6.67×10^2
100.0	0.00139	7.19×10^2
200.0	0.00130	7.69×10^2
400.0	0.00114	8.77×10^2
800.0	0.00092	1.08×10^2
1200.0	0.00077	1.29×10^3
1600.0	0.00066	1.50×10^3

second-order rate plot



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

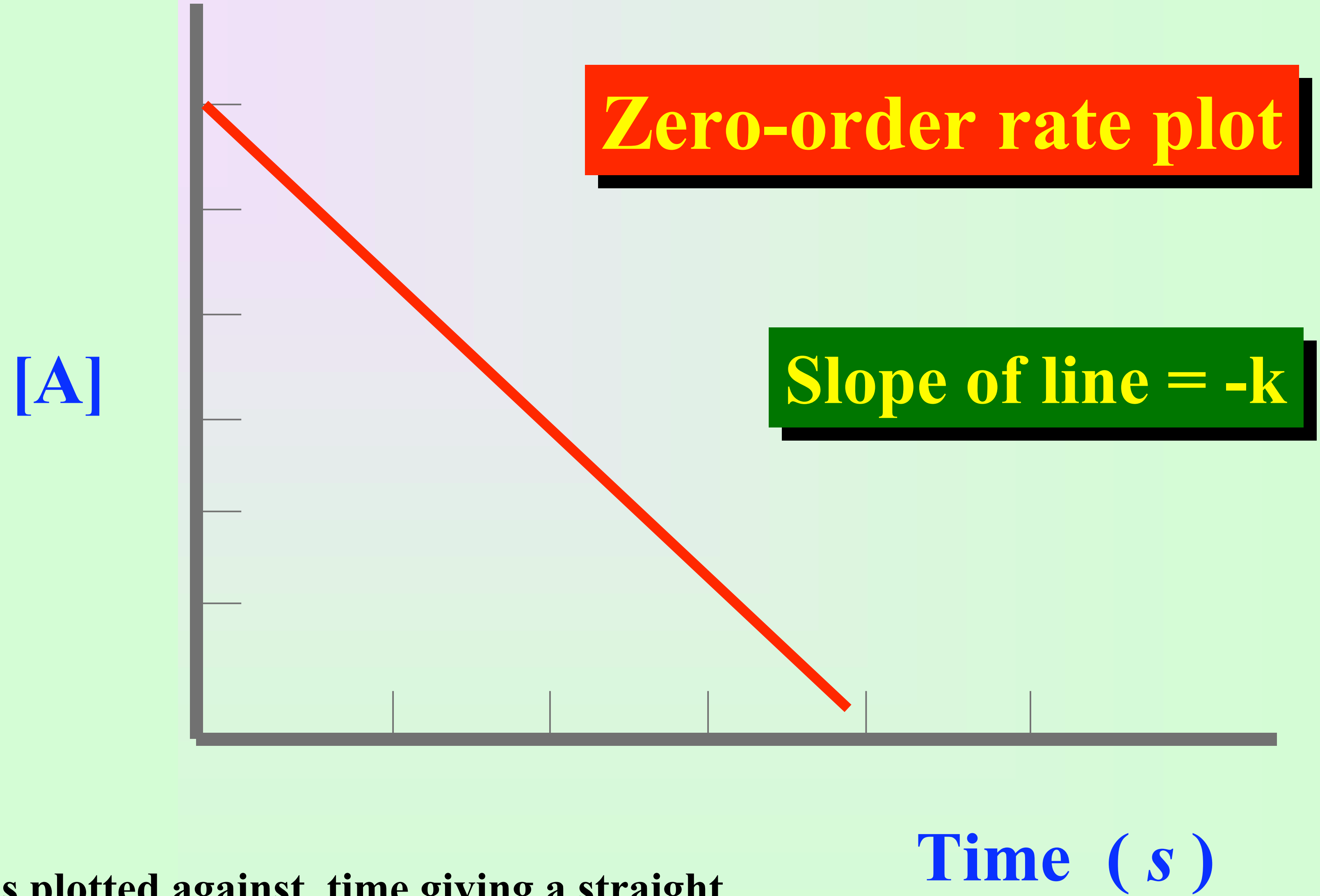
1/[NO_2] was plotted against time giving a straight line

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] was plotted against time giving a straight line

Integrated rate law

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

$$[A]_{0} \; \square \; [A] = kt$$

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