**Objectives**:

- Define half life
- Determine the order of reaction involving a single reactant
- Perform calculation by using the integrated rate equations

# Unit of Rate Constant

**Example:**

**First-order reaction**

$$r = k\,[A]^{1}$$

$$k = \frac{r}{[A]^{1}}$$

$$\text{Unit of } k = \frac{\cancel{M}\ s^{-1}}{\cancel{M}}$$

$$\text{Unit of } k = \mathbf{s^{-1}}$$

# Unit of Rate Constant

For Reaction: $A \longrightarrow$ Products

$$\text{Rate} = k\,[A]^x$$

**If x = 0**

The reaction is of zero-order with respect to *A*

Rate law: Unit of *k* =

**If x = 1**

The reaction is of first-order with respect to *A*

Rate Law: Unit of *k* =

**If x = 2**

The reaction is of second-order with respect to *A*

Rate = *k* Unit of *k* =

# Statement Method

# Statement Method

For Reaction: $A \longrightarrow$ Products

$$\text{Rate} = k\,[A]^x$$

**If x = 0** — The reaction is of zero-order with respect to *A*

**If x = 1** — The reaction is of first-order with respect to *A*

**If x = 2** — The reaction is of second-order with respect to *A*

The decay of a radioactive element is a first-order reaction !!

# Check Point

Write rate law for this equation,

$$A + B \longrightarrow C$$

i) When [A] is doubled, rate also doubles. But doubling the [B] has no effect on rate.

ii) When [A] is increased 3x, rate increases 3x, and increasing of [B] 3x causes the rate to increase 9x.

iii) Reducing [A] by half has no effect on the rate, but reducing [B] by half causes the rate to be half the value of the initial rate.

# Linear Graph Method

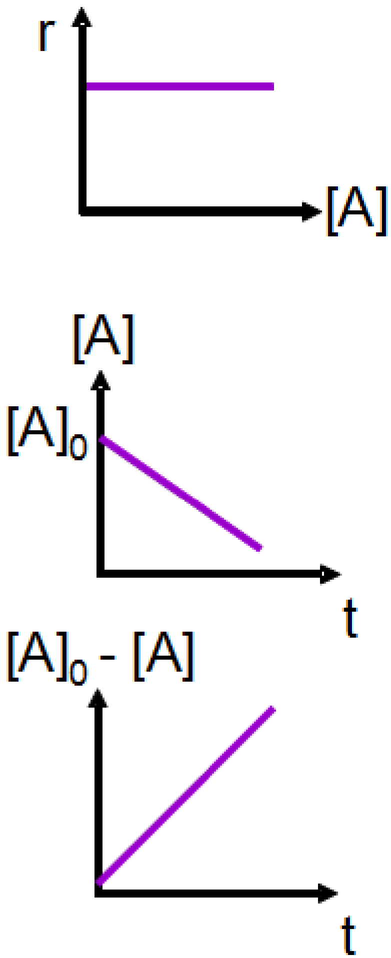
## Integrated Rate Equation / Integrated Rate Law

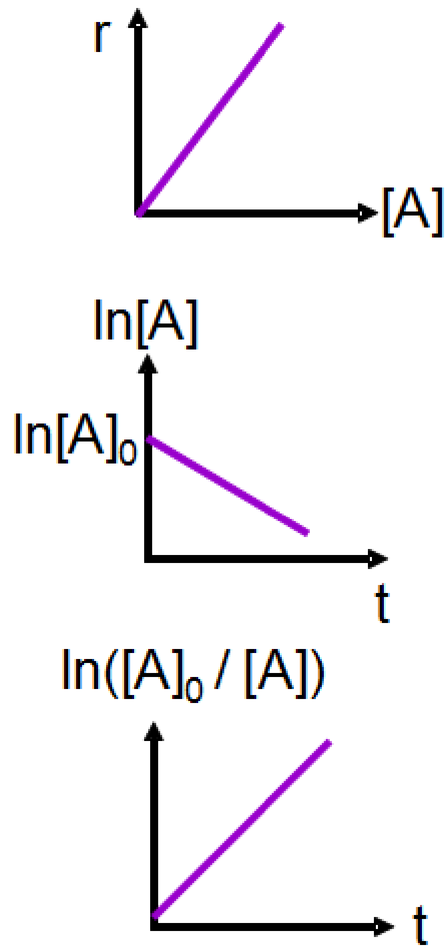
$$A \longrightarrow \text{product}$$

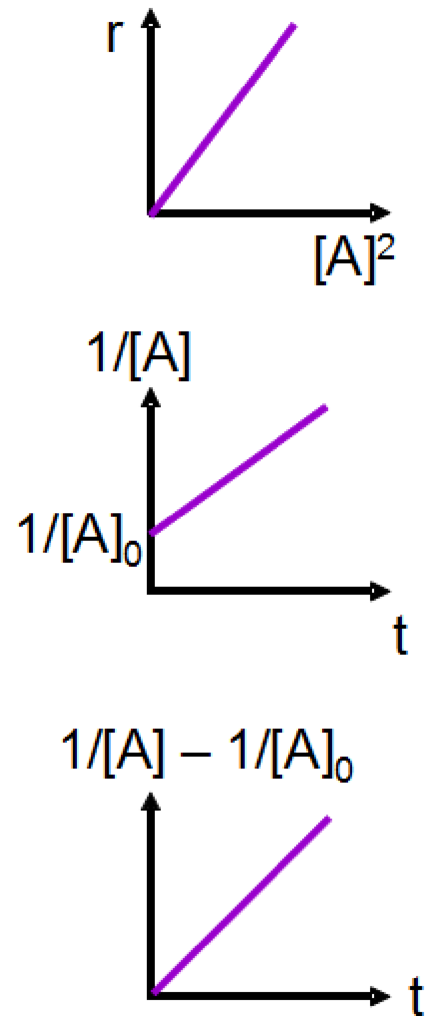
| Order | Rate Law | Integrated Rate equation | Half-Life |
|---|---|---|---|
| 0 | rate = $k$ | $[A]_o - [A]_t = kt$ | $t_{½} = \frac{[A]_0}{2k}$ |
| 1 | rate = $k\,[A]$ | $\ln [A]_o - \ln [A]_t = kt$ | $t_{½} = \frac{\ln 2}{k}$ |
| 2 | rate = $k\,[A]^2$ | $\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt$ | $t_{½} = \frac{1}{k\,[A]_0}$ |

# Linear Graph Method

| Zero order | 1st order | 2nd order |
|---|---|---|

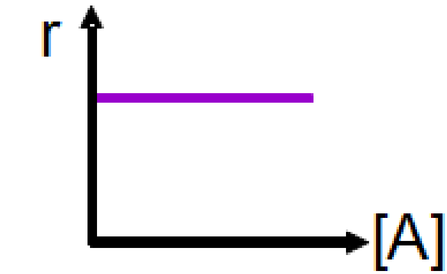


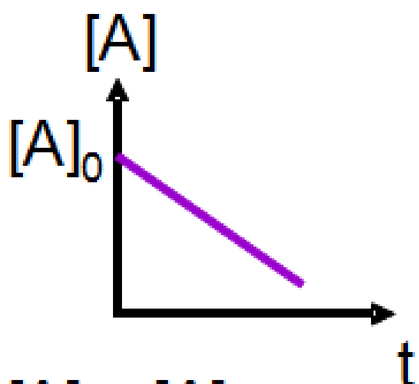



# Zero-Order Reaction

Graph of *rate* versus *[A]*

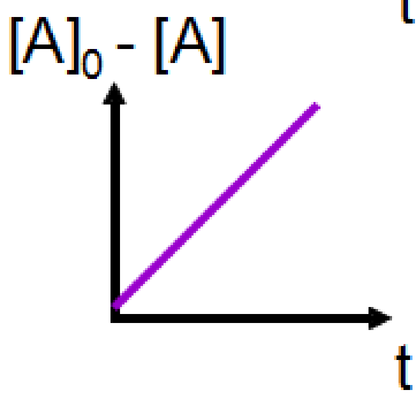



Graph of *[A]* versus *t*




$$[A] = -k\ t + [A]_o$$
$$y = m\ x + c$$

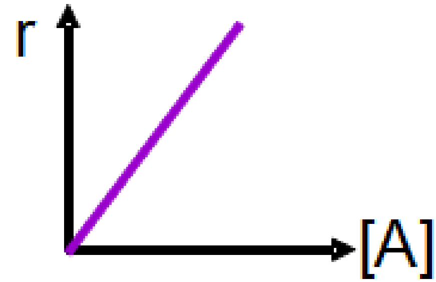
Graph of *[A]ₒ – [A]* versus *t*



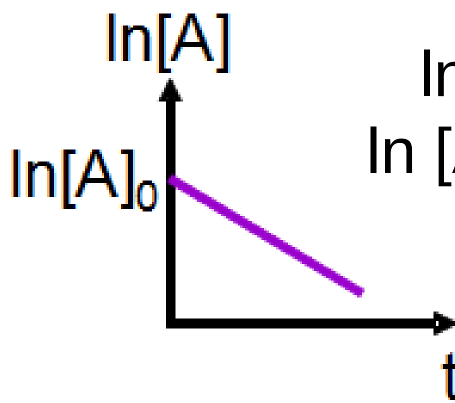

$$[A]_o – [A] = k\ t$$
$$y = mx + c$$

# First-Order

Graph of *rate* versus *[A]*

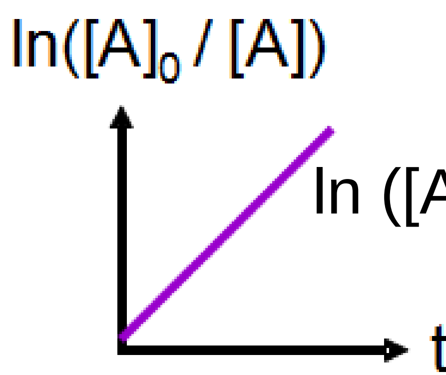



Graph of *[A]* versus *t*




$$\ln([A]_o/[A]) = kt$$
$$\ln[A]_o - \ln[A] = kt$$
$$\ln[A] = -kt + \ln[A]_o$$
$$y = mx + c$$

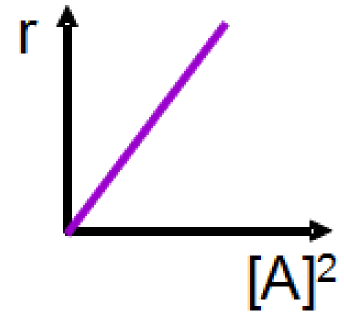
Graph of *ln [A]₀/[A]* versus *t*



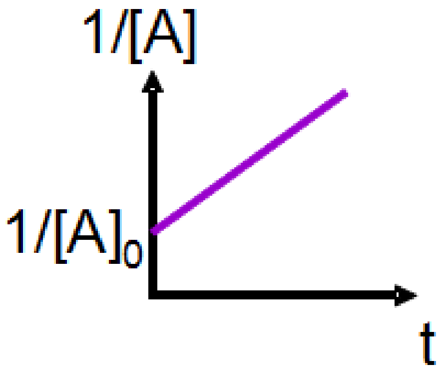

$$\ln([A]_o/[A]) = kt$$
$$y = mx$$

# Second-Order Reaction

Graph of *rate* versus *[A]²*



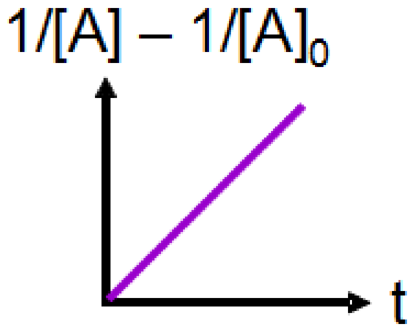

Graph of 1/*[A]* versus *t*




$$\frac{1}{[A]} = k\ t + \frac{1}{[A]_o}$$

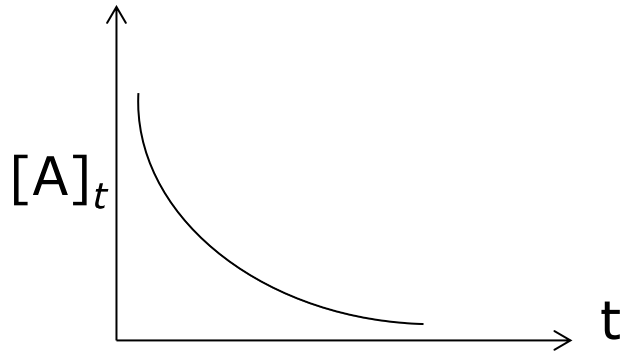
$$y = m\ x + c$$

Graph of *ln [A]₀/[A]* versus *t*

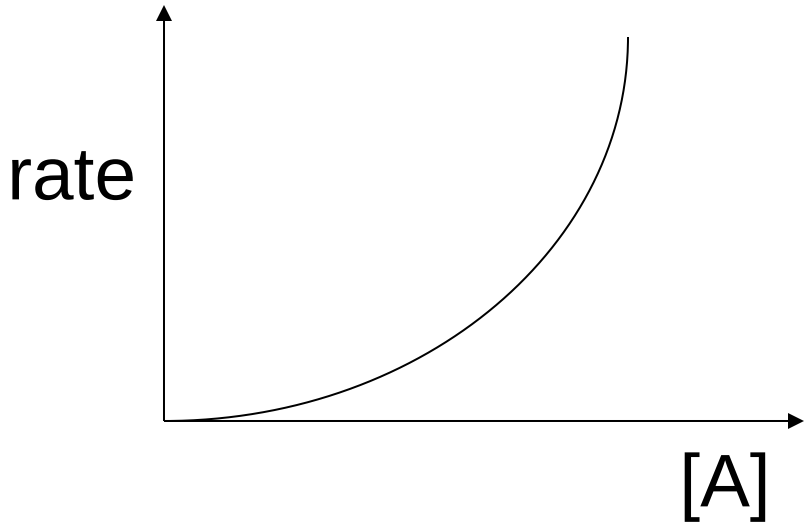


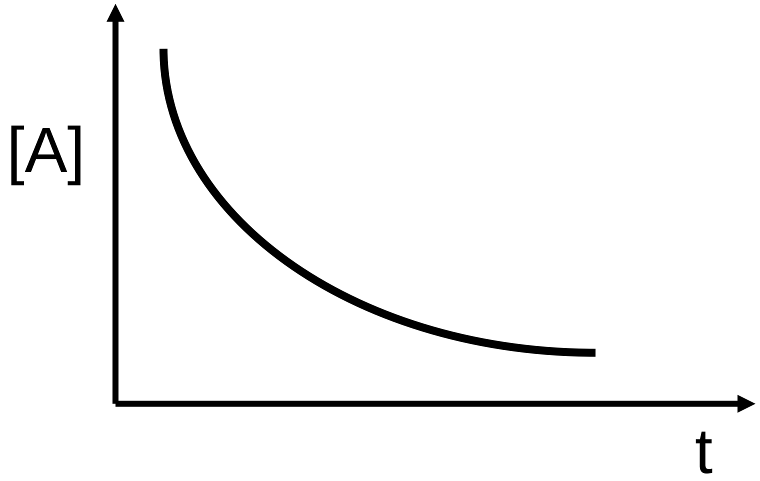
# Non-Linear Graph of First-Order

Graph of [A] versus t



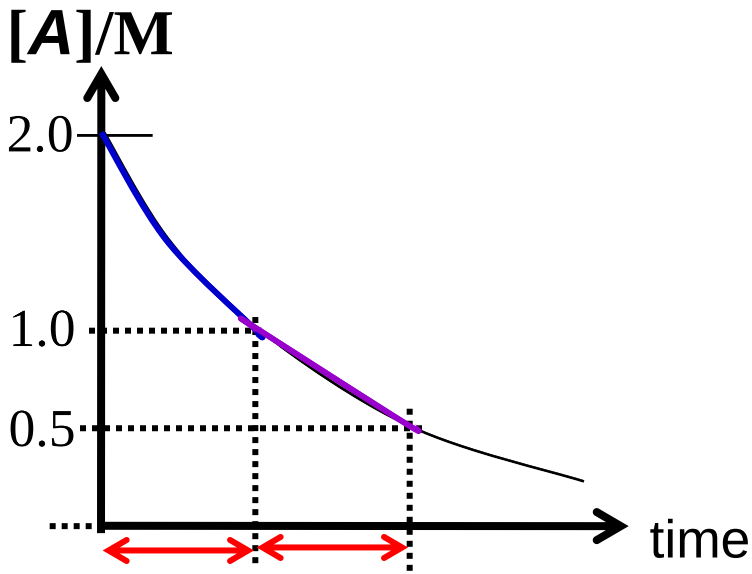
# Non-Linear Graph of Second-Order

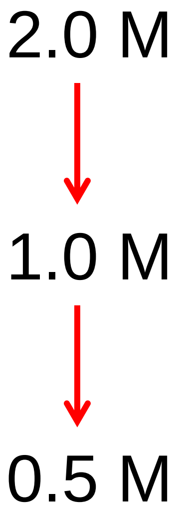


# Half-Life Method

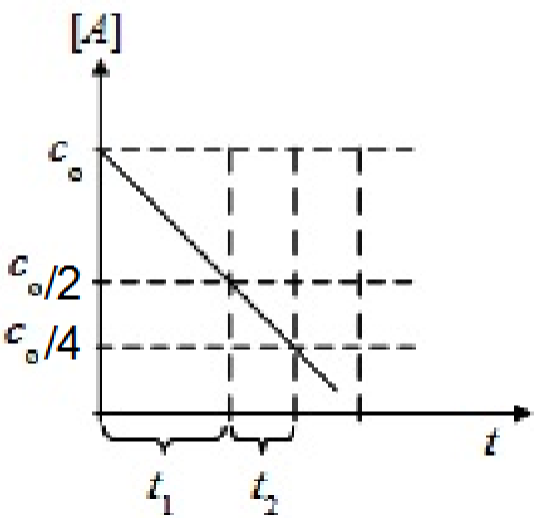
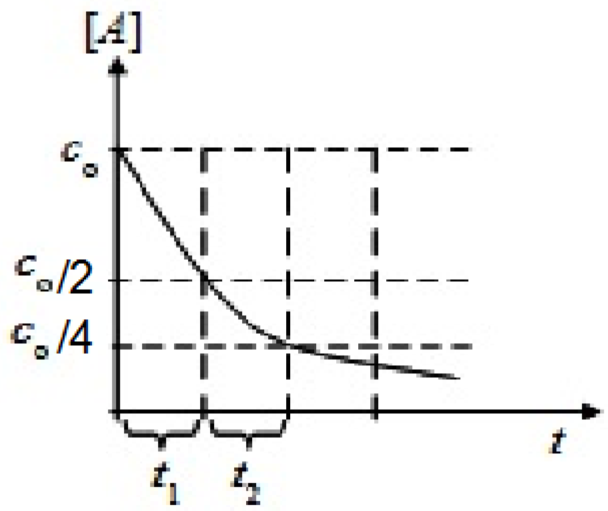
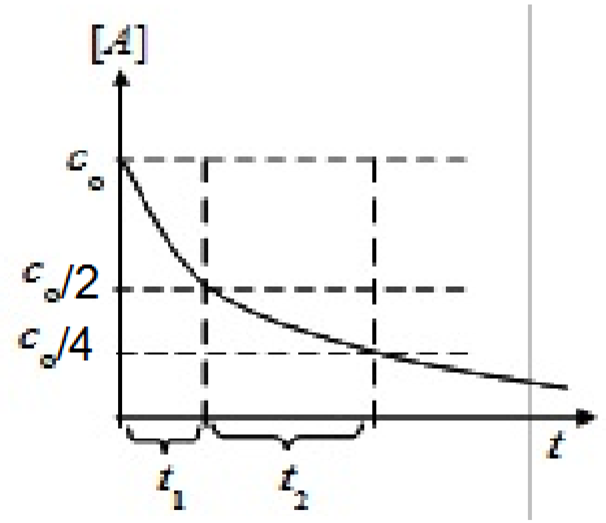
~ the **time required** for the amount (mole, percentage, mass, concentration) of a reactant to decrease to **half** of its initial/original value.



# Half-Life Method

## Comparing the first and the second half-life

| zero-order | $1^{st}$-order | $2^{nd}$-order |
|---|---|---|
|  |  |  |
| $t_1 = 2t_2$ | $t_1 = t_2$ | $2t_1 = t_2$ |

# Half-Life Method of Zero Order

Integrated rate law: $[A]_0 - [A] = kt$

Substituting $t = t_{1/2}$ , and $[A] = \frac{[A]_0}{2}$ into the zero order reaction, gives

$$[A]_0 – [A] = kt$$

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

Thus;

$$t_{1/2} = \frac{[A]_0}{2k}$$

# Half-Life Method of First Order

Integrated rate law: $\ln [A]_0 - \ln[A] = kt$

Substituting $t = t_{½}$ and $[A] = ½ [A]_o$

Thus,

$$\ln \frac{[A]_o}{½[A]_o} = kt_{½}$$

$$\ln 2 = kt_{½}$$

$$t_{½} = \frac{\ln 2}{k}$$

# Half-Life Method of Second Order

Integrated rate law: $\frac{1}{[A]} - \frac{1}{[A]_\circ} = kt$

Substituting t = **t½** and [A] = ½ **[A]**$_\circ$

Thus,

$$\frac{1}{\frac{[A]_\circ}{2}} - \frac{1}{[A]_\circ} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{k[A]_\circ}$$

# Example 1:

For each of the following reactions, determine the reaction order with respect to each reactant and the overall order from the given rate law.

**(a) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$; rate = $k[NO]^2[O_2]$**

**SOLUTION:**

# Example 2:

For each of the following reactions, determine the reaction order with respect to each reactant and the overall order from the given rate law.

**(a) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$; rate = $k[NO]^2[O_2]$**

**SOLUTION:**

# Example 3:

Iodine atoms combine to form molecular iodine in the gaseous phase

$$I_{(g)} + I_{(g)} \rightarrow I_{2(g)}$$

This reaction is a second order reaction , with the rate constant of 7.0 x $10^9$ $M^{-1}$ $s^{-1}$

If the initial concentration of iodine was 0.086 M,

i) calculate it's concentration after 2 min.

ii) calculate the half life of the reaction if the initial concentration of iodine is 0.06 M and 0.42 M respectively.

# SOLUTION:

# Example 4:

The following results were obtained from an experimental investigation on dissociation of dinitrogen pentoxide at 45°C

$$N_2O_5(g) \rightarrow 2\ NO_2(g) + \frac{1}{2}\ O_2(g)$$

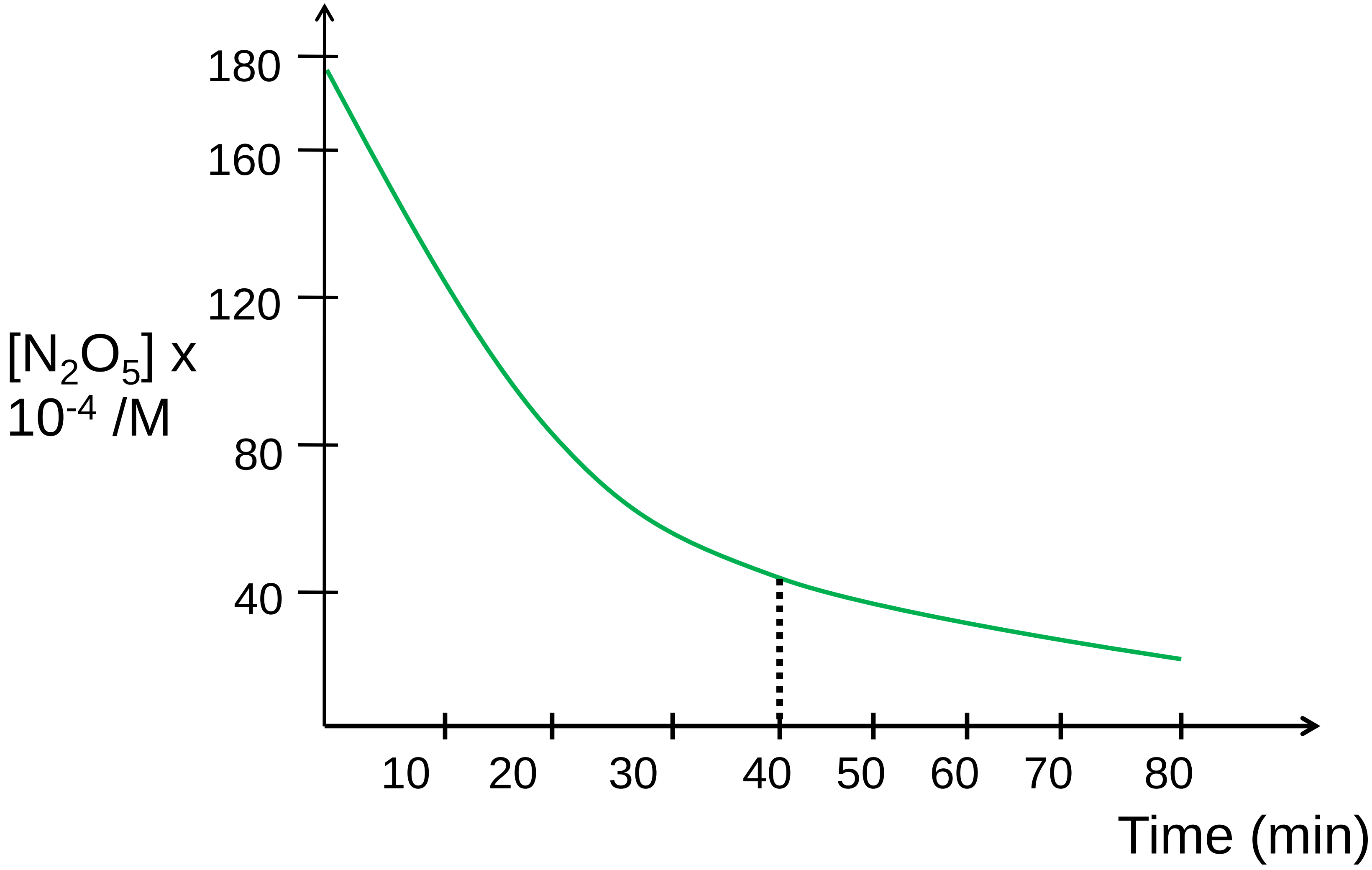
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| time, t/min | 0 | 10 | 20 | 30 | 40 | 50 | 60 |
| $[N_2O_5] \times 10^{-4}$ M | 176 | 124 | 93 | 71 | 53 | 39 | 29 |

Plot graph of $[N_2O_5]$ vs time, determine

i) The order of the reaction

ii) the rate constant k

**SOLUTION:**



i) Based on the above graph,

Time taken for concentration of $N_2O_5$ to change from $176 \times 10^{-4}$ M to $88 \times 10^{-4}$ M is _______

Time taken for concentration of $N_2O_5$ to change from $88 \times 10^{-4}$ M to $44 \times 10^{-4}$ M is also _______

The half life for the reaction is a _________ and ________ _______ on the initial concentration of $N_2O_5$

Thus, the above reaction is _____________.

ii)

# Example 5:

What is the half-life of $N_2O_5$ if it decomposes with a rate constant of $5.7 \times 10^{-4}\ s^{-1}$?

# SUMMARY

- Integrated rate equation
- Determination of the reaction order:

  -- from unit of rate constant

  -- from a linear graph

  -- from a statement in the question….