

# Rate of Reaction

$$\xi = \frac{n_i - n_i^0}{\nu_i}$$

For any species  $i$  (reactant or product):  $n_i = n_i^0 + \nu_i \xi$

$$\mathfrak{v} = \frac{1}{V} \frac{d\xi}{dt}$$

$$= \frac{1}{\nu_i V} \frac{d(n_i - n_i^0)}{dt}$$

$$= \frac{1}{\nu_i V} \frac{dn_i}{dt}$$

# Rate of Reaction

- If the volume does not change during the course of reaction,

$$\frac{dn_i}{V} = d(n_i/V) = dc_i \quad \text{where } c_i \text{ is the concentration of species } i$$

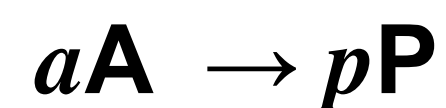
$$\Rightarrow v = \frac{1}{\nu_i} \frac{dc_i}{dt}$$

For the general reaction,  $aA + bB + \dots \rightarrow \dots yY + zZ$

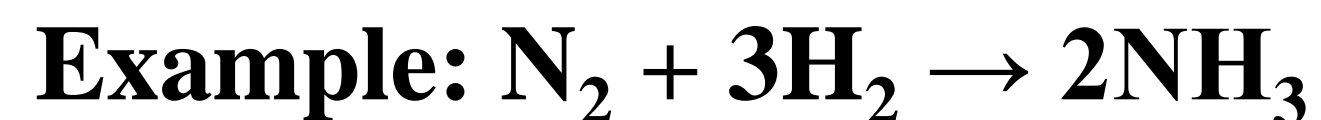
$$v = -\frac{1}{a} \frac{dc_A}{dt} = -\frac{1}{b} \frac{dc_B}{dt} = \frac{1}{y} \frac{dc_Y}{dt} = \frac{1}{z} \frac{dc_Z}{dt}$$

$$= -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{y} \frac{d[Y]}{dt} = \frac{1}{z} \frac{d[Z]}{dt}$$

## Mutual Relation Between Various Rates:



$$v = -\frac{v_A}{\nu_A} = \frac{v_P}{\nu_P}$$



$$v = v_{N_2} = \frac{v_{H_2}}{3} = \frac{v_{NH_3}}{2}$$

# Rate of Reaction

- When there is volume change during the course of reaction,

$$n_i = c_i V \Rightarrow dn_i = d(c_i V) = V dc_i + \underbrace{c_i dV}_{\text{Change in number of moles due to volume change}}$$

Change in number of moles  
due to volume change

- Rate of reaction when there is volume change

$$v = \frac{1}{v_i V} \frac{dn_i}{dt} = \frac{1}{v_i} \frac{dc_i}{dt} + \frac{c_i}{v_i V} \frac{dV}{dt}$$

Similarly,

- Rate of consumption of species  $i$  (reactant) when there is volume change

$$v_i = -\frac{1}{V} \frac{dn_i}{dt} = -\frac{dc_i}{dt} - \frac{c_i}{V} \frac{dV}{dt}$$

- Rate of formation of species  $j$  (product) when there is volume change

$$v_j = \frac{1}{V} \frac{dn_j}{dt} = \frac{dc_j}{dt} + \frac{c_j}{V} \frac{dV}{dt}$$

# Basics of rate laws

- Consider a reaction in which a single reactant decomposes into products:  $A \rightarrow P$

$$\text{Rate} \propto [A]^n$$

Law of mass action

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

Rate Law

Proportionality constant called as rate constant

Order of the reaction; it determines how rate depends on the concentration  
 $n$  is usually integer, but it can be fractional too.

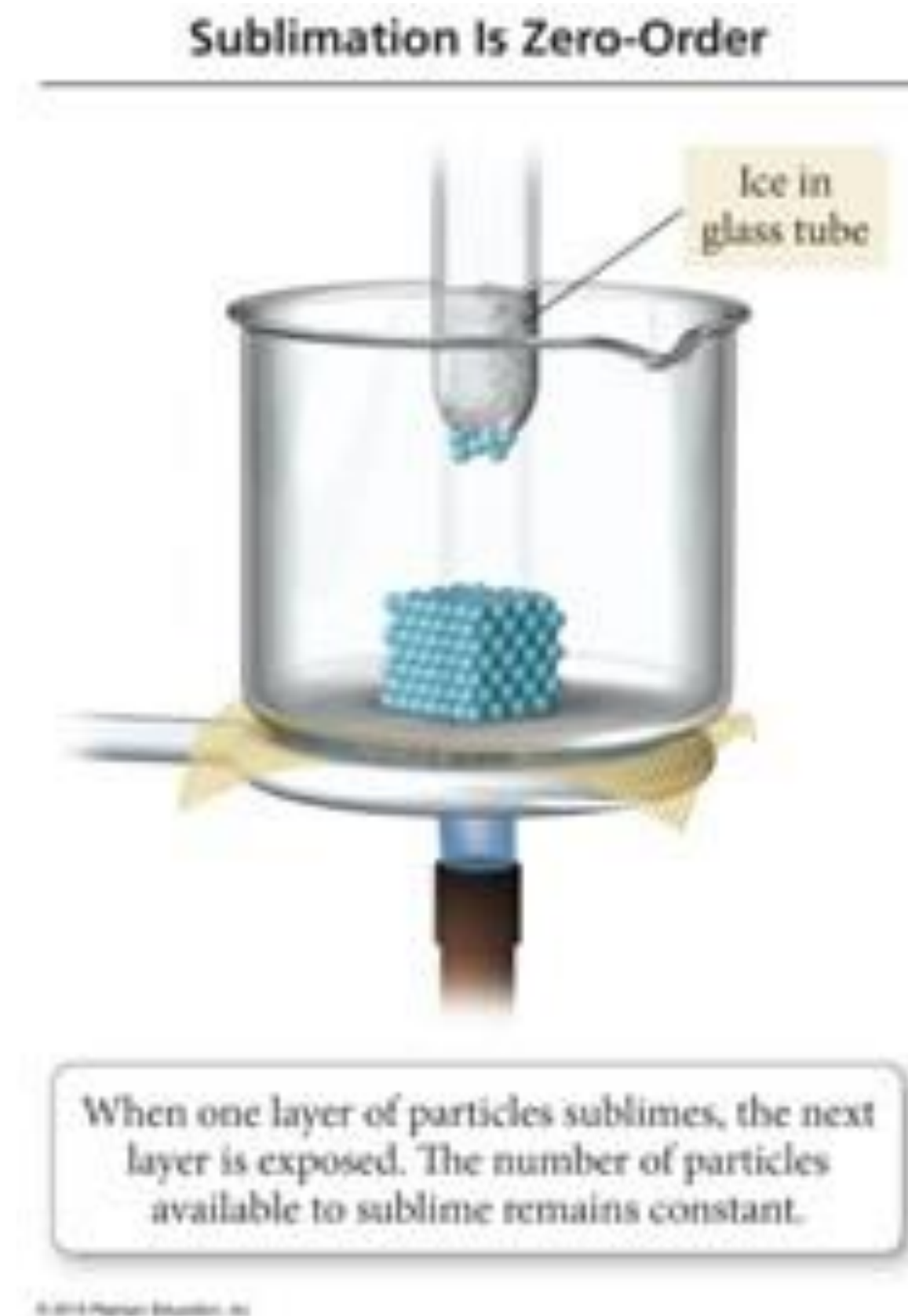
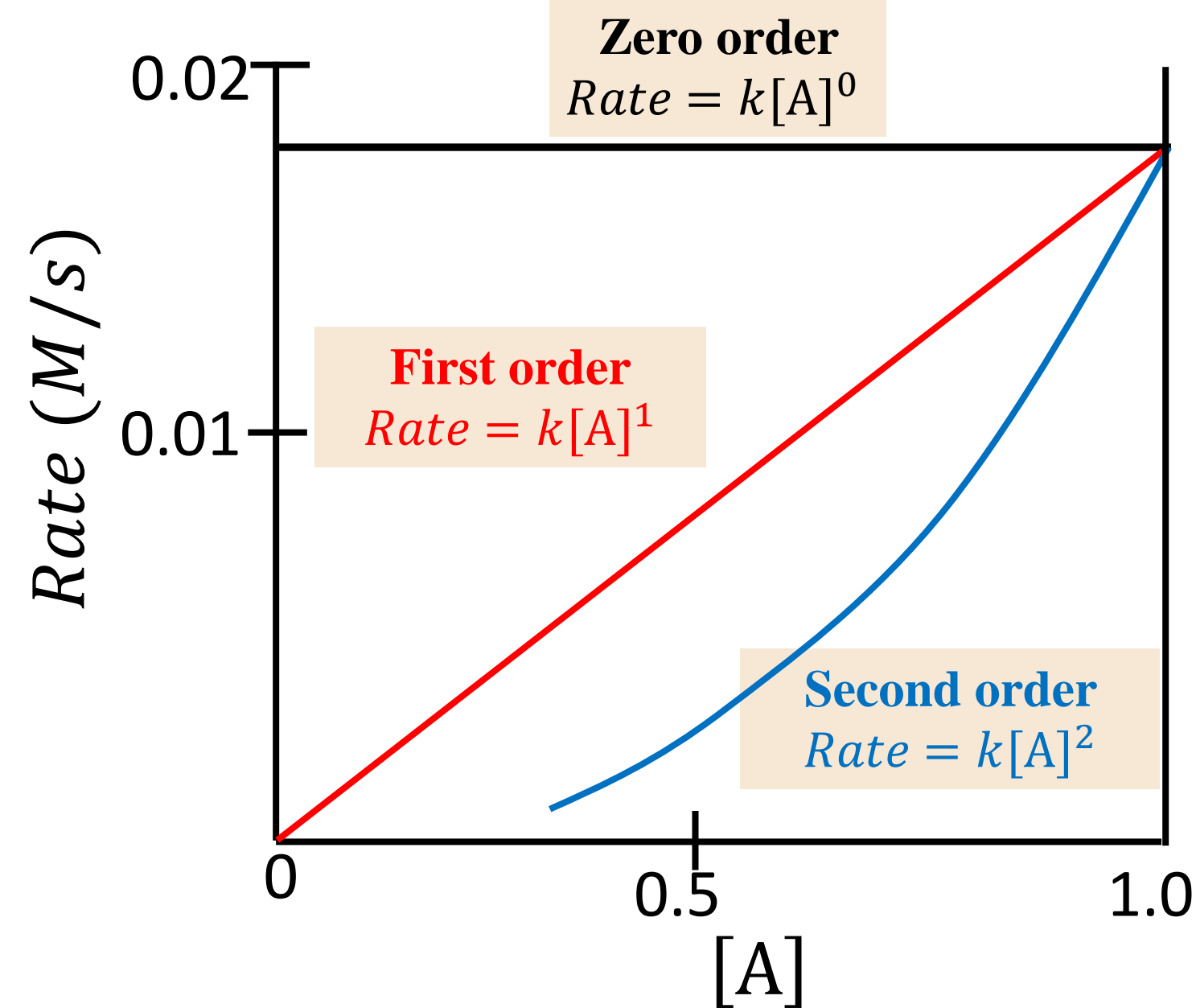
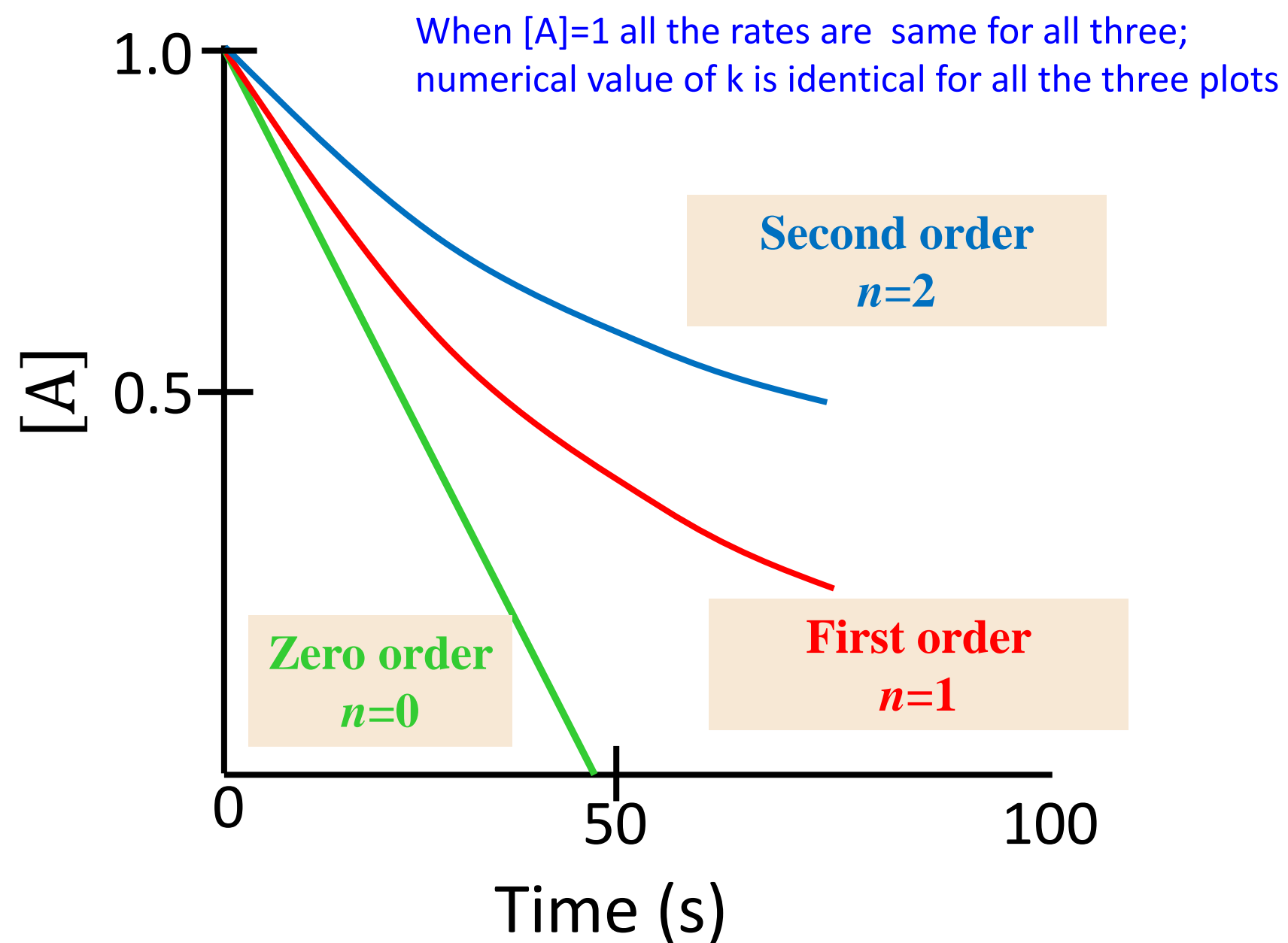
Most common cases:

- If  $n=0$ , the reaction is zero-order and the rate is independent of  $[A]$ ; Unit of  $k$  is  $M s^{-1}$

- If  $n=1$ , the reaction is first-order and the rate is directly proportional to  $[A]$ ; Unit of  $k$  is  $s^{-1}$

- If  $n=2$ , the reaction is second-order and the rate is proportional to square of  $[A]$ ; Unit of  $k$  is  $M^{-1}s^{-1}$

# Basics of rate laws



- **Zero order reactions occur under conditions where the amount of reactant actually available for the reaction is unaffected by the changes in the overall quantity of the reactant.**

**Example:** Sublimation is normally zero order because only surface molecules can sublime. The concentration of surface molecules does not change as amount of subliming substance decreases. When one layer sublimates, another layer is exposed.

- In first order reaction, the rate slows down as the reactions proceeds the concentration of the reactant decreases
- For second order reaction, the slowing down of the rate even more as the reactions proceeds

# Basics of rate laws

- Consider a reaction in which multiple reactants are involved:  $a\text{A} + b\text{B} \rightarrow y\text{Y} + z\text{Z}$

$$\text{Rate} \propto [\text{A}]^m [\text{B}]^n$$

Law of mass action

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

Rate Law

$m$  is reaction order with respect to A

$n$  is reaction order with respect to B

- The **overall order of reaction** is the sum of the exponents ( $m + n$ )
- Example 1:** For reaction,  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ ,  $\text{Rate} = [\text{H}_2]^1 [\text{I}_2]^1$  (Experimentally determined)
  - This means that the reaction is of first order w.r.t.  $\text{H}_2$  and first order w.r.t.  $\text{I}_2$ . The reaction is of second order overall.
- Example 2:** For reaction,  $2\text{H}_2(\text{g}) + 2\text{NO}(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ ,  $\text{Rate} = [\text{H}_2]^1 [\text{NO}]^2$  (Experimentally determined)
  - This means that the reaction is of first order w.r.t.  $\text{H}_2$  and second order w.r.t.  $\text{NO}$ . The reaction is of third order overall.

- Unimolecular Reactions:  $A \rightarrow P$

$$\text{Rate} = k[A]$$

- Bimolecular Reactions:  $2A \rightarrow P$ ,  $A + B \rightarrow P$

$$\text{Rate} = k[A]^2$$

$$\text{Rate} = k[A][B]$$

- Trimolecular Reactions:  $3A \rightarrow P$ ,  $2A + B \rightarrow P$ ,  $A + B + C \rightarrow P$

$$\text{Rate} = k[A]^3$$

$$\text{Rate} = k[A]^2[B]$$

$$\text{Rate} = k[A][B][C]$$



## Determination of the Order of a Reaction

### Zero Order ( $n = 0$ )

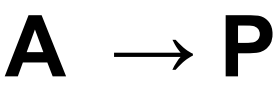
[A] (M)	Initial Rate (M/s)
0.10	0.020
0.20	0.020
0.40	0.020

### First Order ( $n = 1$ )

[A] (M)	Initial Rate (M/s)
0.10	0.020
0.20	0.040
0.40	0.080

### First Order ( $n = 2$ )

[A] (M)	Initial Rate (M/s)
0.10	0.020
0.20	0.080
0.40	0.320



- If the numbers are not that obvious. You can determine the rate as follows:

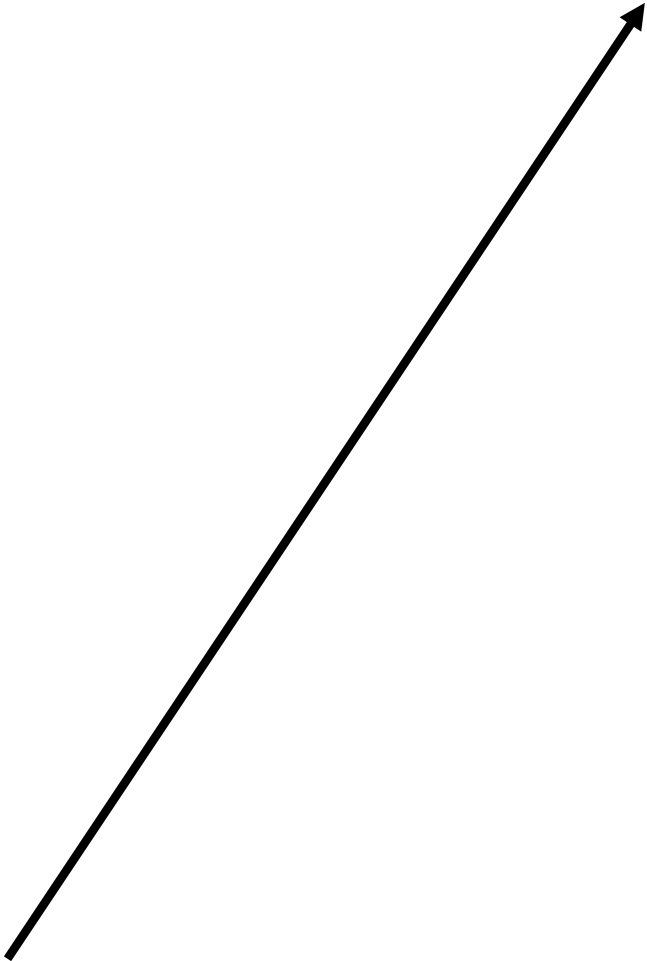
$$\frac{\text{rate } 2}{\text{rate } 1} = \frac{k[A]_2^n}{k[A]_1^n}$$

$$\frac{0.320 \text{ M/s}}{0.080 \text{ M/s}} = \frac{k(0.40\text{M})^n}{k(0.20)^2}$$

$$4.0 = 2^n$$

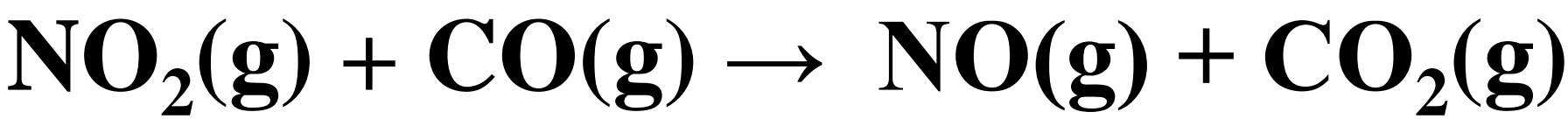
$$\log 4 = \log 2^n = n \log 2$$

$$n = \frac{\log 4}{\log 2} = 2$$





Determination of order of a Reaction



[NO <sub>2</sub> ] (M)	[CO] (M)	Initial Rate (M/s)
0.10	0.10	0.0021
0.20	0.10	0.0084
0.20	0.20	0.0084
0.40	0.10	0.0336

1.

- 1. To determine the rate law ?
- 2. To determine the rate constant (k) for the reaction ?

[NO <sub>2</sub> ] (M)	[CO] (M)	Initial Rate (M/s)
0.10	0.10	0.0021
↓ × 2	↓ constant	↓ × 4
0.20	0.10	0.0084
↓ constant	↓ × 2	↓ × 1
0.20	0.20	0.0084
↓ × 2	↓ × ½	↓ × 4
0.40	0.10	0.0336

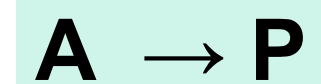
Write the overall rate expression:

Rate = k [NO<sub>2</sub>]<sup>2</sup> [CO]<sup>0</sup> = k [NO<sub>2</sub>]<sup>2</sup>

- 2. Write the rate law and substitute the concentration and initial rate from any one of the four measurements

Rate = k[NO<sub>2</sub>]<sup>2</sup>  
⇒ k = rate/[NO<sub>2</sub>]<sup>2</sup>  
⇒ k =  $\frac{0.0021 \text{ M/s}}{(0.10 \text{ M})^2} = 0.21 \text{ M}^{-1} \text{ s}^{-1}$

## Integrated Rate Law of Zero-Order Reaction (Dependence of Concentration with Time)



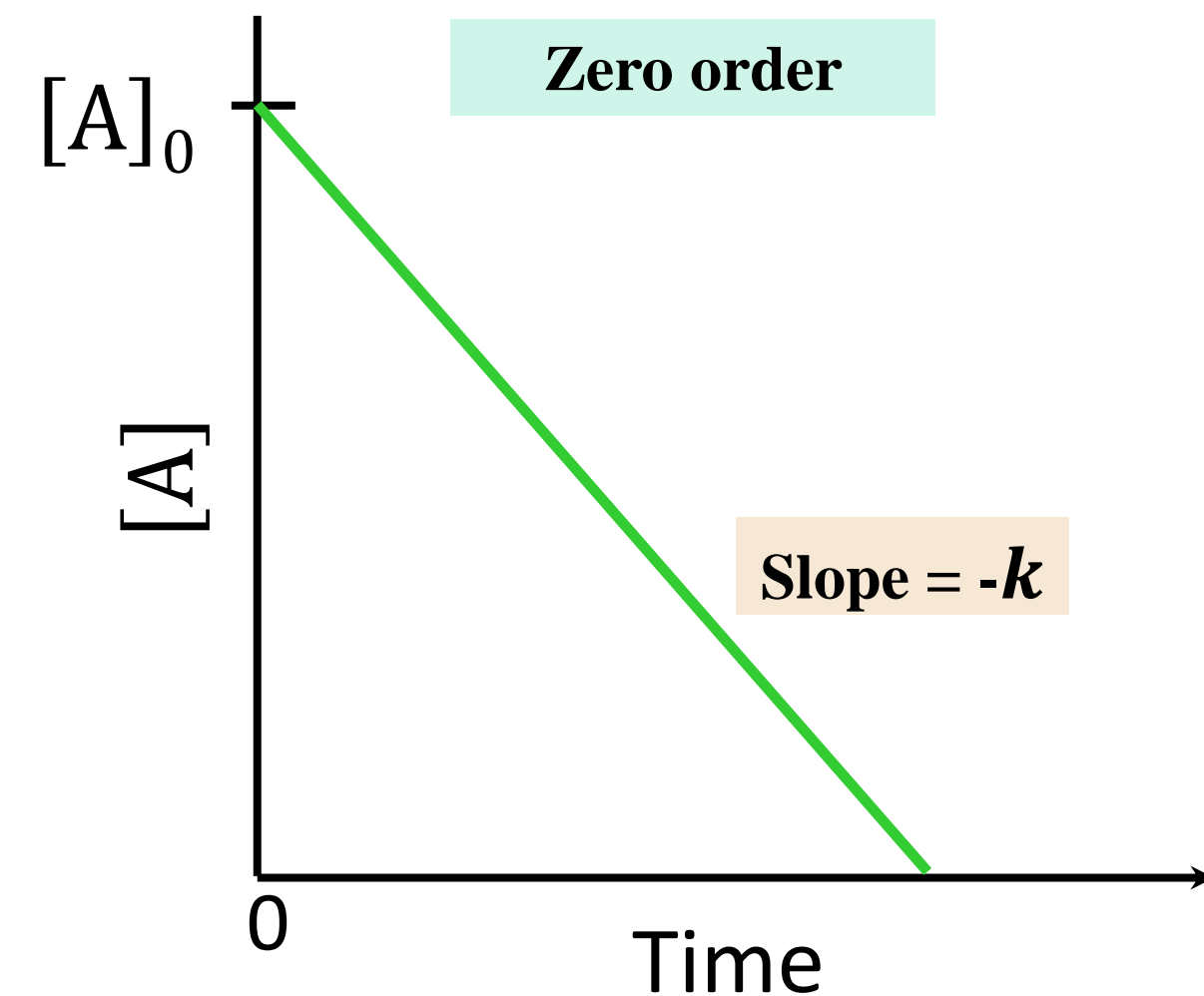
$$\text{Rate} = k[A]^0 = k$$

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

$$\int_{[A]_0}^{[A]} d[A] = -k \int_0^t dt$$

$$[[A]]_{[A]_0}^{[A]} = -k[t]_0^t$$

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

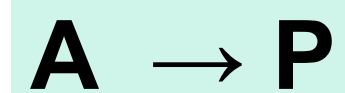


$$[A] = -kt + [A]_0$$

•  $y=mx + c$  form

**Interesting fact:** If the reaction is  $a\mathbf{A} \rightarrow \mathbf{P}$  instead of  $\mathbf{A} \rightarrow \mathbf{P}$ , then  $[A] = -akt + [A]_0$

## Integrated Rate Law of First-Order Reaction (Dependence of Concentration with Time)



$$\text{Rate} = k[A]^1 = k[A]$$

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

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt$$

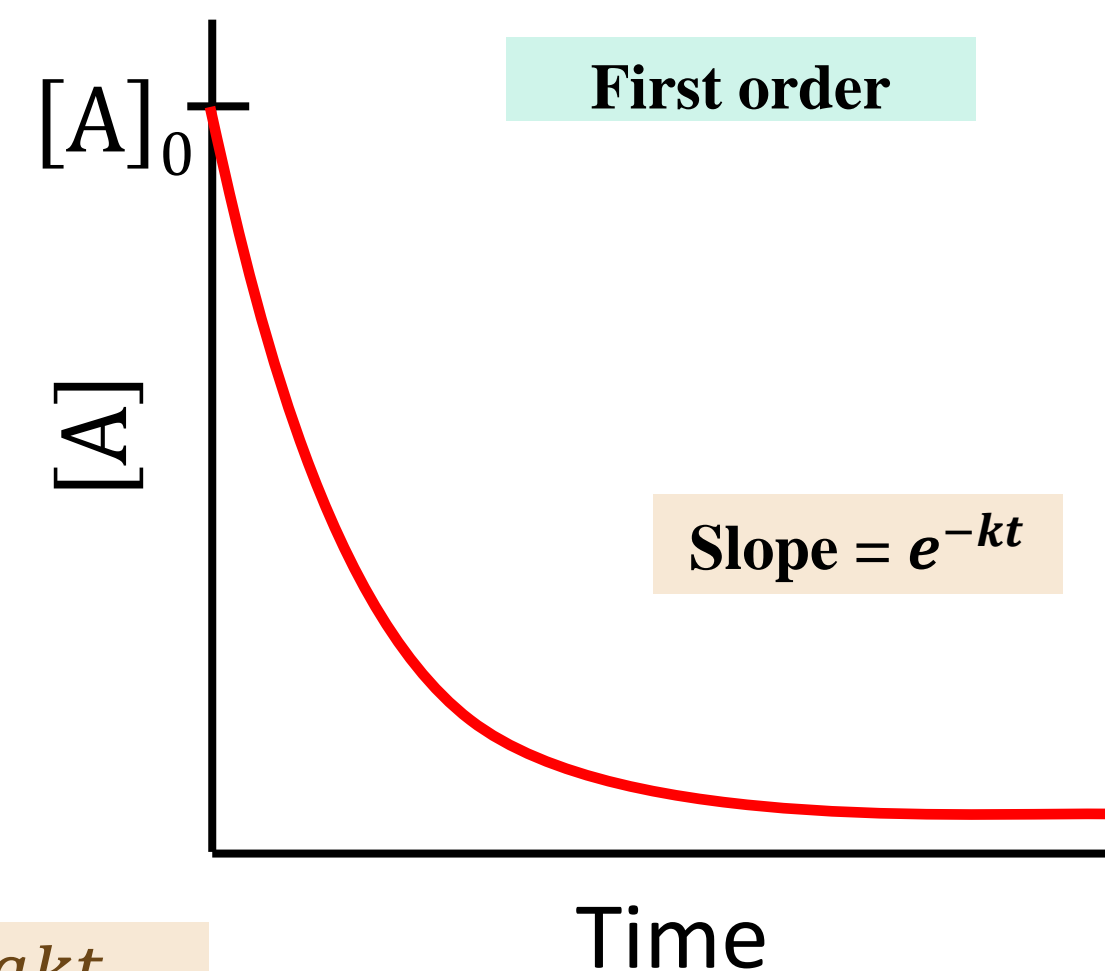
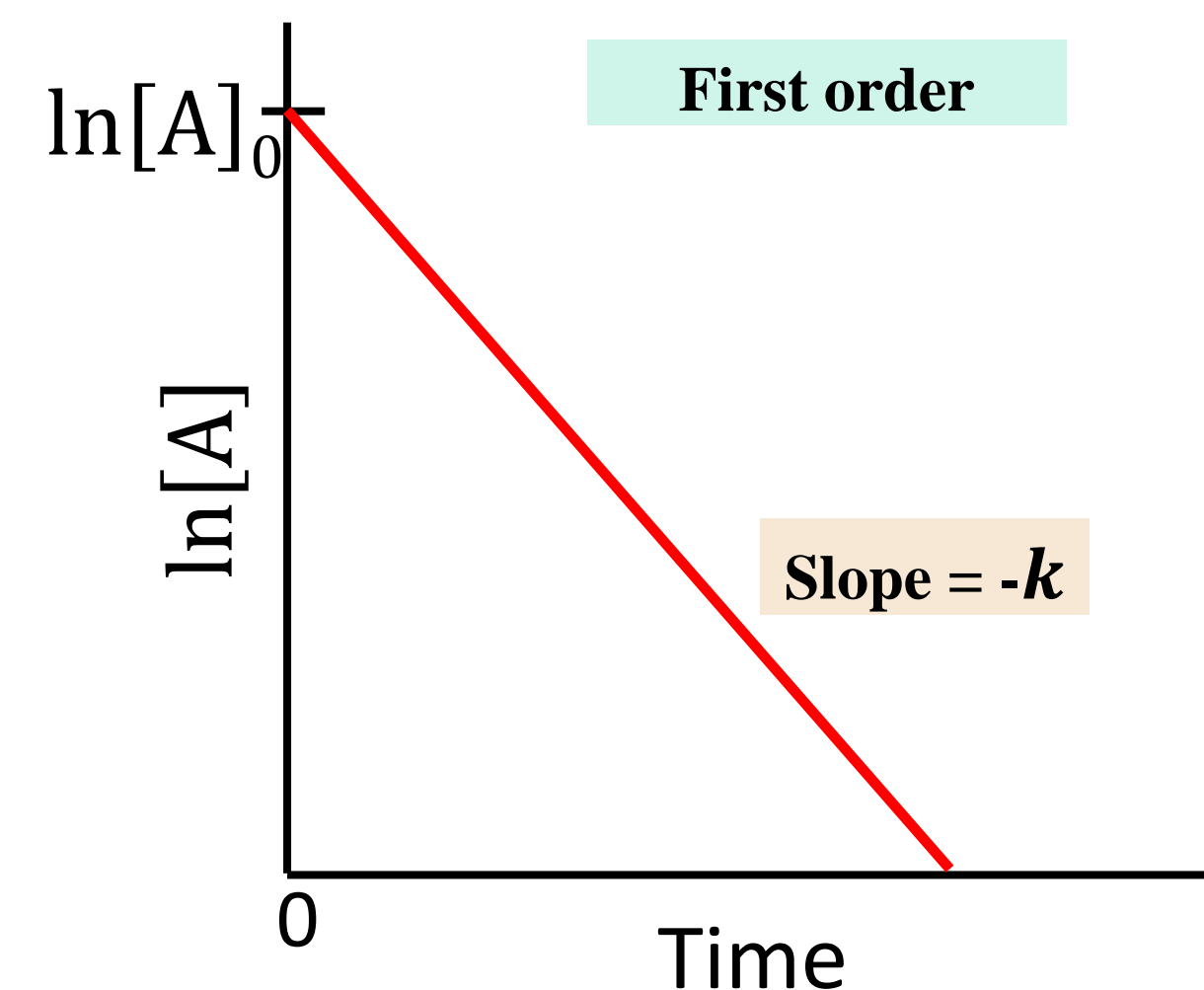
$$[\ln[A]]_{[A]_0}^{[A]} = -k[t]_0^t$$

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

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

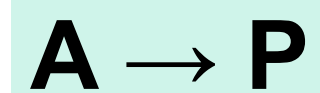
•  $y=mx + c$  form

$$[A] = [A]_0 e^{-kt}$$



**Interesting fact:** If the reaction is  $a\mathbf{A} \rightarrow \mathbf{P}$  instead of  $\mathbf{A} \rightarrow \mathbf{P}$ , then  $[A] = [A]_0 e^{-akt}$

# Integrated Rate Law of Second-Order Reaction (Dependence of Concentration with Time)



$$\text{Rate} = k[A]^2$$

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

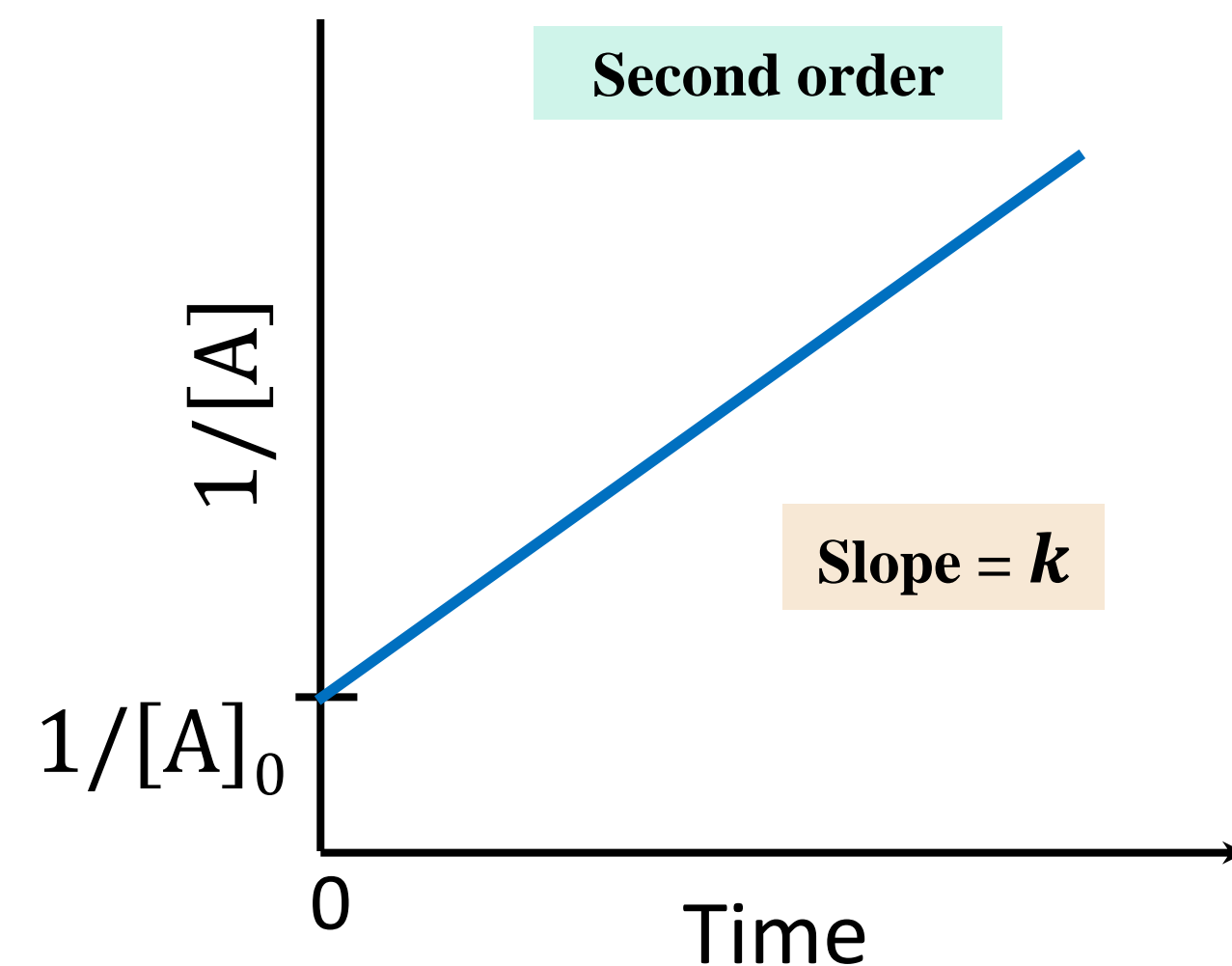
$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

$$\left[ -\frac{1}{[A]} \right]_{[A]_0}^{[A]} = -k[t]_0^t$$

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

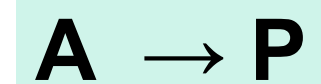
$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

•  $y=mx + c$  form



**Interesting fact:** If the reaction is  $a\mathbf{A} \rightarrow \mathbf{P}$  instead of  $\mathbf{A} \rightarrow \mathbf{P}$ , then  $\frac{1}{[A]} = akt + \frac{1}{[A]_0}$

# Integrated Rate Law of $n^{\text{th}}$ -Order Reaction



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

$$-\frac{d[A]}{dt} = k[A]^n$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^n} = -k \int_0^t dt$$

$$\left[ \frac{[A]^{-n+1}}{-n+1} \right]_{[A]_0}^{[A]} = -k[t]_0^t$$

$$-\frac{[A]^{-(n-1)}}{(n-1)} + \frac{[A]_0^{-(n-1)}}{(n-1)} = -kt$$

$$\frac{1}{[A]^{(n-1)}} - \frac{1}{[A]_0^{(n-1)}} = (n-1)kt$$

where  $n = \frac{1}{2}, \frac{3}{2}, 2, 3 \dots$  and  $n \neq 1$

## The Half-Life ( $t_{1/2}$ ) of a Reaction

The half-life ( $t_{1/2}$ ) of a reaction is the time after which the concentration of a reactant is decreased to one-half of its initial value.

**Example:** If  $t_{1/2}$  for a reaction is 100 seconds and if  $[A]_0$  is 1.0 M, then the  $[A] = 0.5$  M after 100 seconds

## The Half-Life ( $t_{1/2}$ ) of a Zero-Order Reaction

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

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

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

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

Solving for  $t_{1/2}$

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

- Half-life also depends on initial concentration; directly proportional
- Half-life becomes shorter as the concentration decreases

## The Half-Life ( $t_{1/2}$ ) of a First-Order Reaction

$$[A] = [A]_0 e^{-kt}$$

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

$$\frac{1}{2} [A]_0 = [A]_0 e^{-kt_{1/2}}$$

Solving for  $t_{1/2}$

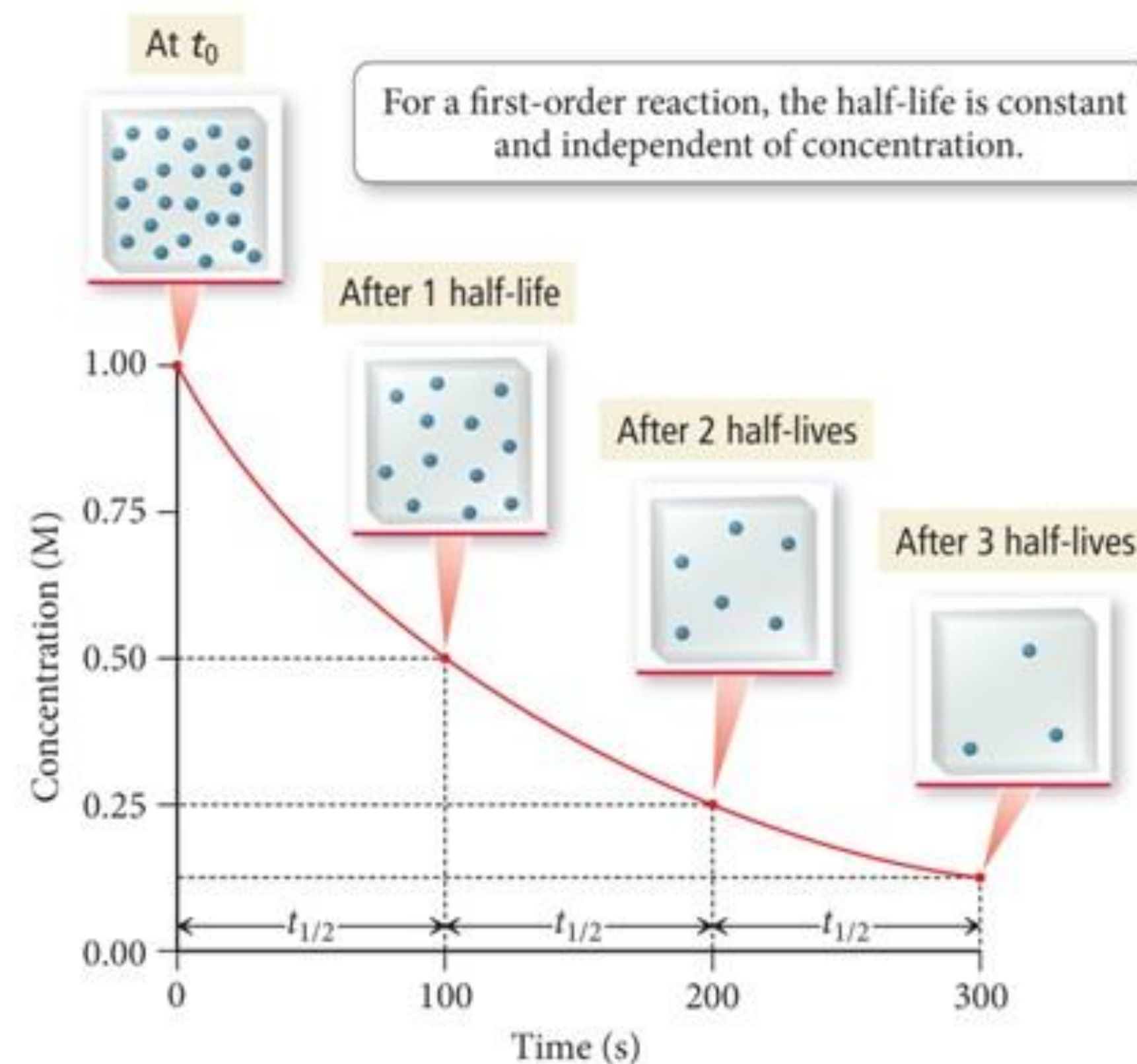
$$\frac{1}{2} = e^{-kt_{1/2}}$$

$$\ln \frac{1}{2} = -kt_{1/2}$$

$$kt_{1/2} = -\ln \frac{1}{2} = \ln 2$$

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

Half-Life for a First-Order Reaction



- Half-life is independent of the initial concentration

- Half-life is constant as the reaction proceeds



# The Half-Life ( $t_{1/2}$ ) of a Second-Order Reaction

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

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

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

Solving for  $t_{1/2}$

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

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

- Half-life depends on the initial concentration; inversely proportional

- Half-life becomes longer as the concentration decreases

# The Half-Life ( $t_{1/2}$ ) of $n^{\text{th}}$ -Order Reaction

**A  $\rightarrow$  P**

**Integrated rate law:**

$$\frac{1}{[A]^{(n-1)}} - \frac{1}{[A]_0^{(n-1)}} = (n-1)kt$$

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

$$\frac{1}{\frac{[A]_0^{(n-1)}}{2^{(n-1)}}} - \frac{1}{[A]_0^{(n-1)}} = (n-1)kt_{1/2}$$

$$\frac{2^{(n-1)}}{[A]_0^{(n-1)}} - \frac{1}{[A]_0^{(n-1)}} = (n-1)kt_{1/2}$$

**Solving for  $t_{1/2}$**

$$t_{1/2} = \frac{2^{(n-1)} - 1}{k(n-1)[A]_0^{(n-1)}}$$

**Where  $n = \frac{1}{2}, \frac{3}{2}, 2, 3 \dots$  and  $n \neq 1$**