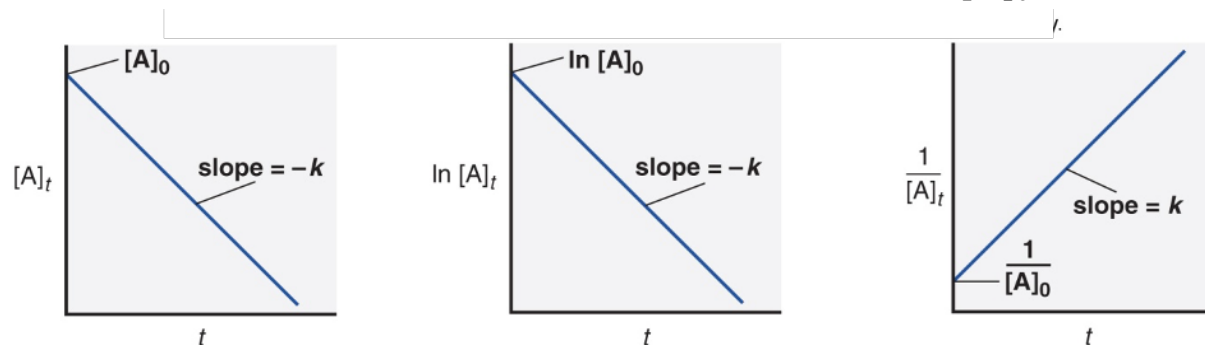


An Overview of Zero-Order, First-Order, and Simple Second-Order Reactions

| | Zero Order | First Order | Second Order |
|--|-----------------------------|-----------------------------|--|
| Rate law | $\text{rate} = k$ | $\text{rate} = k[A]$ | $\text{rate} = k[A]^2$ |
| Units for k | $\text{mol/L}\cdot\text{s}$ | $1/\text{s}$ | $\text{L/mol}\cdot\text{s}$ |
| Half-life | $\frac{[A]_0}{2k}$ | $\frac{\ln 2}{k}$ | $\frac{1}{k[A]_0}$ |
| Integrated rate law in straight-line form | $[A]_t = -kt + [A]_0$ | $\ln[A]_t = -kt + \ln[A]_0$ | $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ |
| Plot for straight line | $[A]_t$ vs. t | $\ln[A]_t$ vs. t | $\frac{1}{[A]_t}$ vs. t |
| Slope, y intercept | $-k, [A]_0$ | $-k, \ln[A]_0$ | $k, \frac{1}{[A]_0}$ |



Half-life Equations

For a **first-order** reaction, $t_{1/2}$ does not depend on the initial concentration.

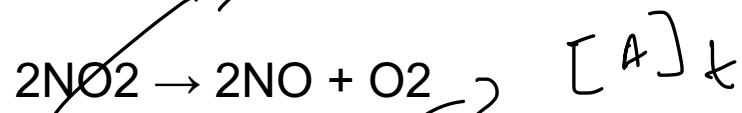
For a **second-order** reaction, $t_{1/2}$ is **inversely** proportional to the initial concentration:

$$t_{1/2} = \frac{1}{k[A]^0} \quad (\text{second order process; rate} = k[A]^2)$$

For a **zero-order** reaction, $t_{1/2}$ is **directly** proportional to the initial concentration:

$$t_{1/2} = \frac{[A]_0}{2k} \quad (\text{zero order process; rate} = k)$$

The reaction $\rightarrow [A]_0$



follows second-order kinetics. At 300 °C, $[\text{NO}_2]$ drops from 0.0100 M to 0.00650 M in 100.0 s. The rate constant for the reaction is _____ M⁻¹s⁻¹.

- A) 0.096
- B) 0.65
- C) 0.81
- D) 1.2
- ☒ E) 0.54

$$\frac{1}{[A]_t} = k \cdot t + \frac{1}{[A]_0}$$

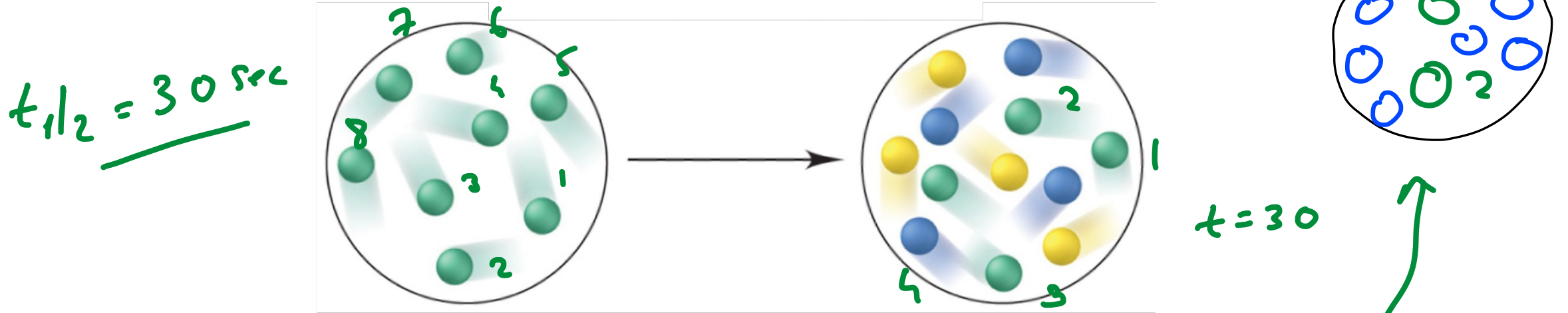
$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = k \cdot t$$

$$\frac{1}{0.00650} - \frac{1}{0.0100} = k \cdot 100$$

$$53.846 = k \cdot 100$$

$$k = 0.538 \rightarrow 0.54$$

PROBLEM: Substance A (green) decomposes to two other substances, B (blue) and C (yellow), in a first-order gaseous reaction. The molecular scenes below show a portion of the reaction mixture at two different times:



(a) Draw a similar molecular scene of the reaction mixture at $t = 60.0 \text{ s}$.

(b) Find the rate constant of the reaction.

$$t_{1/2} = \frac{0.693}{k} \quad \text{so} \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30.0} = 2.31 \times 10^{-2} \text{ s}^{-1}$$

(c) If the total pressure (P_{total}) of the mixture is 5.00 atm at 90.0 s, what is the partial pressure of substance B (P_B)?

At $t = 90 \text{ sec}$: $7 \text{ B}, 7 \text{ C}, 1 \text{ A}$

$$x_B = \frac{7}{1+7+7} = 0.467$$

$$P_B = x_B \cdot P_{\text{total}} = 0.467 \times 5.00 = \underline{2.33 \text{ atm}}$$

Consider the following reaction: $\underset{=}{4} \underset{=}{\text{NH}_3} + \underset{=}{5} \underset{=}{\text{O}_2} \rightarrow \underset{=}{4} \underset{=}{\text{NO}} + \underset{=}{6} \underset{=}{\text{H}_2\text{O}}$

Which compound(s) has/have the fastest reaction rate (i.e. which reactant or product is consumed/formed the fastest)?

A. NH_3

B. O_2

C. NO

☒ D. H_2O

$$3 \text{ hours} \times \frac{60 \text{ min}}{1 \text{ hour}} \times \frac{60 \text{ sec}}{1 \text{ min}} = 10,800$$

Butadiene, C_4H_6 (used to make synthetic rubber and latex paints) reacts to C_8H_{12} with a rate law of **rate = $0.014 \text{ L}/(\text{mol}\cdot\text{s}) [\text{C}_4\text{H}_6]^2$** . What will be the concentration of C_4H_6 after 3.0 hours if the initial concentration is 0.025 M ?

☒ A. 0.0052 M

B. 0.024 M

C. 43 M

D. 190 M

E. 0.000

2nd order:

$$\frac{1}{[A]_t} = k \cdot t + \frac{1}{[A]_0}$$

$$\frac{1}{[A]_t} = (10,800)(0.014) + \left(\frac{1}{0.025}\right)$$

$$\frac{1}{[A]_t} = 191.2 \Rightarrow [A]_t = 0.005230$$

The rate law for the reaction $3A \rightarrow C$ is

$$\text{Rate} = 4.36 \times 10^{-2} \text{ L mol}^{-1} \text{ hr}^{-1} [A]^2$$

What is the half-life for the reaction if the initial concentration of A is 0.250 M?

$$k = 4.36 \times 10^{-2} \text{ L mol}^{-1} \text{ hr}^{-1}$$

$$[A]_0 = 0.250 \text{ M}$$

A. 0.0109 hr

B. 0.0629 hr

C. 15.9 hr

D. 23.9 hr

E. 91.7 hr

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

$$t_{1/2} = \frac{1}{(4.36 \times 10^{-2})(0.250)} = 91.7 \text{ hour}$$

Which one of the following sets of units is appropriate for a third-order rate constant?

A. s^{-1}

B. $\text{mol L}^{-1} \text{s}^{-1}$

C. $\text{L mol}^{-1} \text{s}^{-1}$

D. $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$

E. $\text{L}^3 \text{mol}^{-3} \text{s}^{-1}$

$$\begin{aligned} \text{Rate} &= k [A]^3 \\ \frac{\text{M}}{\text{s}} &= k \text{ M}^3 \\ k &= \frac{\text{M/s}}{\text{M}^3} = \text{M}^{-2} \text{s}^{-1} \\ &= (\text{L} \cdot \text{mol})^{-2} \cdot \text{s}^{-1} \end{aligned}$$

The rate constant for a reaction is $4.65 \text{ L mol}^{-1}\text{s}^{-1}$. What is the overall order of the reaction?

- A. zero
- ☒ B. second
- C. third
- D. First
- E. Not enough information to decide.

\Rightarrow second order

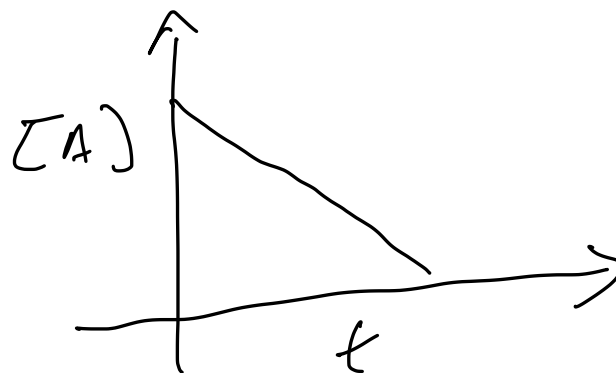
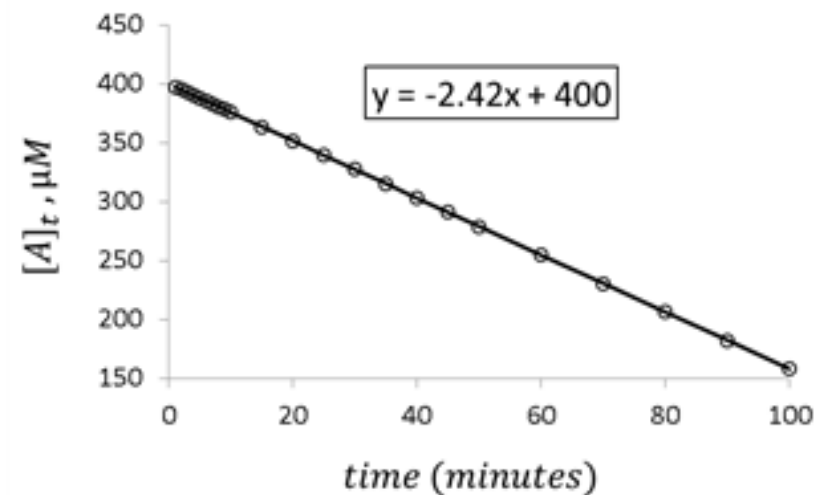
$$\frac{\text{M}}{\text{s}} = k [\text{A}]^x$$

$$4.65 \frac{\text{L}}{\text{mol} \cdot \text{s}} = 4.65$$

$$\frac{\text{M}}{\text{s}} = (4.65) \cdot \frac{1}{\text{M} \cdot \text{s}} \cdot \text{M}^2$$

$$\boxed{\frac{\text{M}}{\text{s}} = \frac{\text{M}}{\text{s}}}$$

For the hypothetical reaction **aA** \rightarrow **products**, the concentration of A was monitored with time. Given the following graph of the experimental data, what is the rate constant for the loss of reactant A?



$$[A]_t = -k \cdot t + [A]_0$$
$$k = -(-2.42) = +2.42$$

- A. $2.42 \mu\text{M}^{-1} \cdot \text{min}^{-1}$
- B. $400.00 \mu\text{M}^{-1} \cdot \text{min}^{-1}$
- C. $-2.42 \mu\text{M}^{-1} \cdot \text{min}^{-1}$
- D. $-400 \mu\text{M}^{-1} \cdot \text{min}^{-1}$
- E. $24.2 \mu\text{M}^{-1} \cdot \text{min}^{-1}$