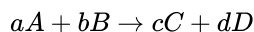


Rate Law

For any general reaction occurring at a fixed temperature



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

- experimental concept
- k is the rate constant (units dependent on exponents), which is specific for a given reaction at a given temperature
- m, n is the order of reaction with respect to reactants A and B
- k, m, n are all independent of concentration
- $m + n =$ overall reaction order.
- the order number can be negative or fractions, but they are mostly whole numbers.

Rate Constant

- the larger k , the faster the reaction
- the units of k depend on the order of the reaction (exponent)

Reaction Orders

- **the value of n is not necessarily related to the coefficient a**

$n = 0 \Rightarrow$ zero order reaction

- no change in rate, constant

$n = 1 \Rightarrow$ first order

Method of Initial Rates

Reactions with one reactant

- conduct experiments with different initial reactant concentrations and measure initial rates to determine the order of the reactant.
- by adjusting the concentration of a reactant, we can see how the initial rate changes and can determine the order of reaction from

$$\frac{\text{Rate1}}{\text{Rate2}} = \left(\frac{[A_1]}{[A_2]} \right)^n$$

$$k = \frac{\text{rate}}{[A]}$$

Reactions with multiple reactants

- keep the concentration of one of the reactants constant

Integrated Rate Laws

- integrated rate laws are different forms of the rate law that express concentration as a function of time
- they are more practical than differential rate laws as they can help us determine how much product was formed or how much reactant disappeared at any given time.

Differential rate law:

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

Integrated rate law:

$$\ln([A]_t) = -kt + \ln([A]_0)$$

- the form of the integrated rate law is dependant on the order of the reaction

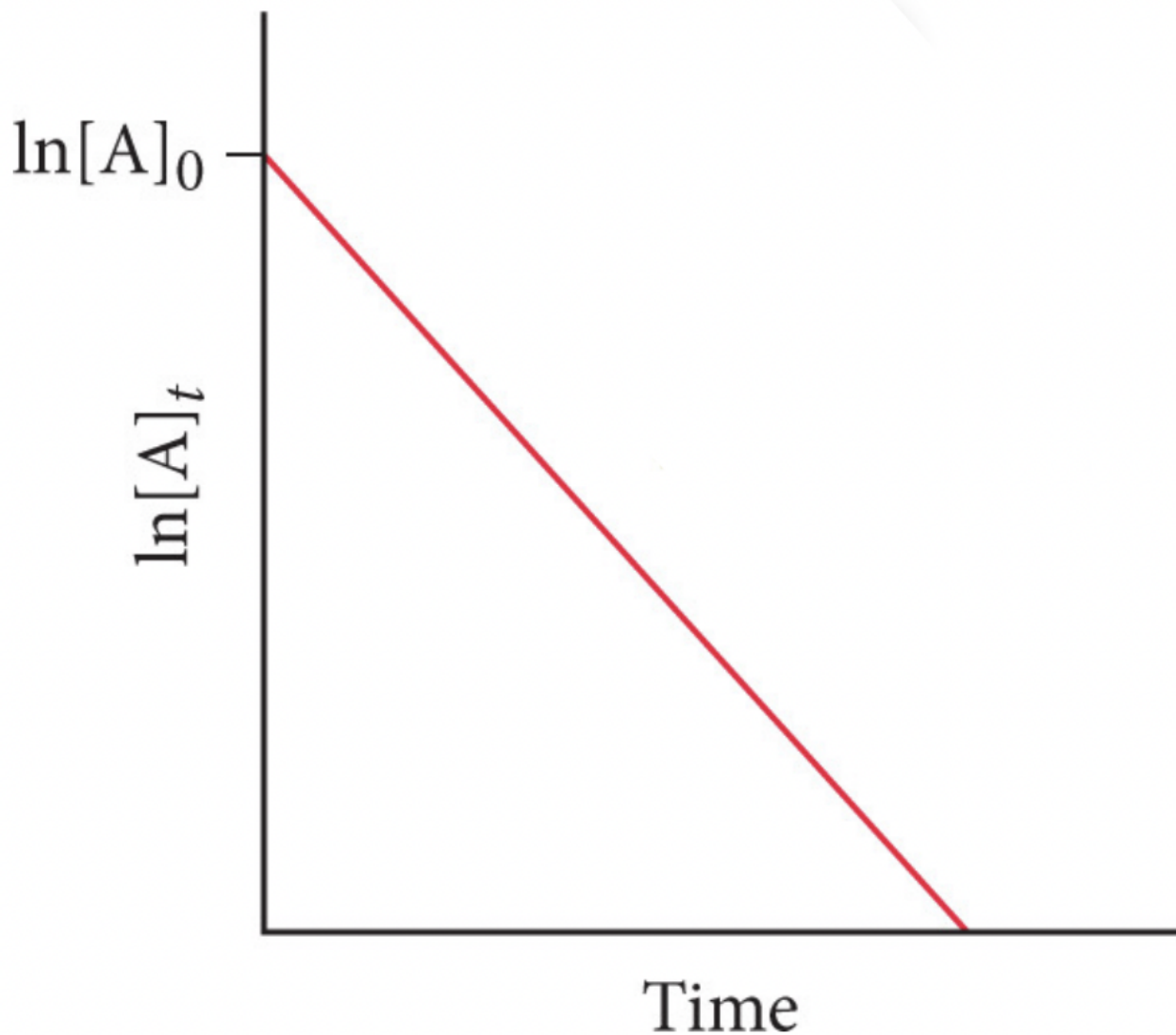
First-Order IRL

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

Linearized:

$$\ln([A]_t) = -kt + \ln([A]_0)$$

- the slope of the linearized graph is $-k$, with units of s^{-1}
- initial concentration can be found by looking at the y-intercept
- if the graph of $\ln[A]_t$ vs t is a straight line, it is a first order IRL



Half-Life

- the time taken for one half of a reactant to be consumed

First Order Half Life:

$$\ln \frac{[A]_0}{[A]_t} = kt \implies t_{1/2}, [A] = \frac{[A]_0}{2} \implies t_{1/2} = \frac{\ln 2}{k}$$

- $t_{1/2}$ is constant at any given temperature and is independent of $[A]_0$

Radioactive Decay

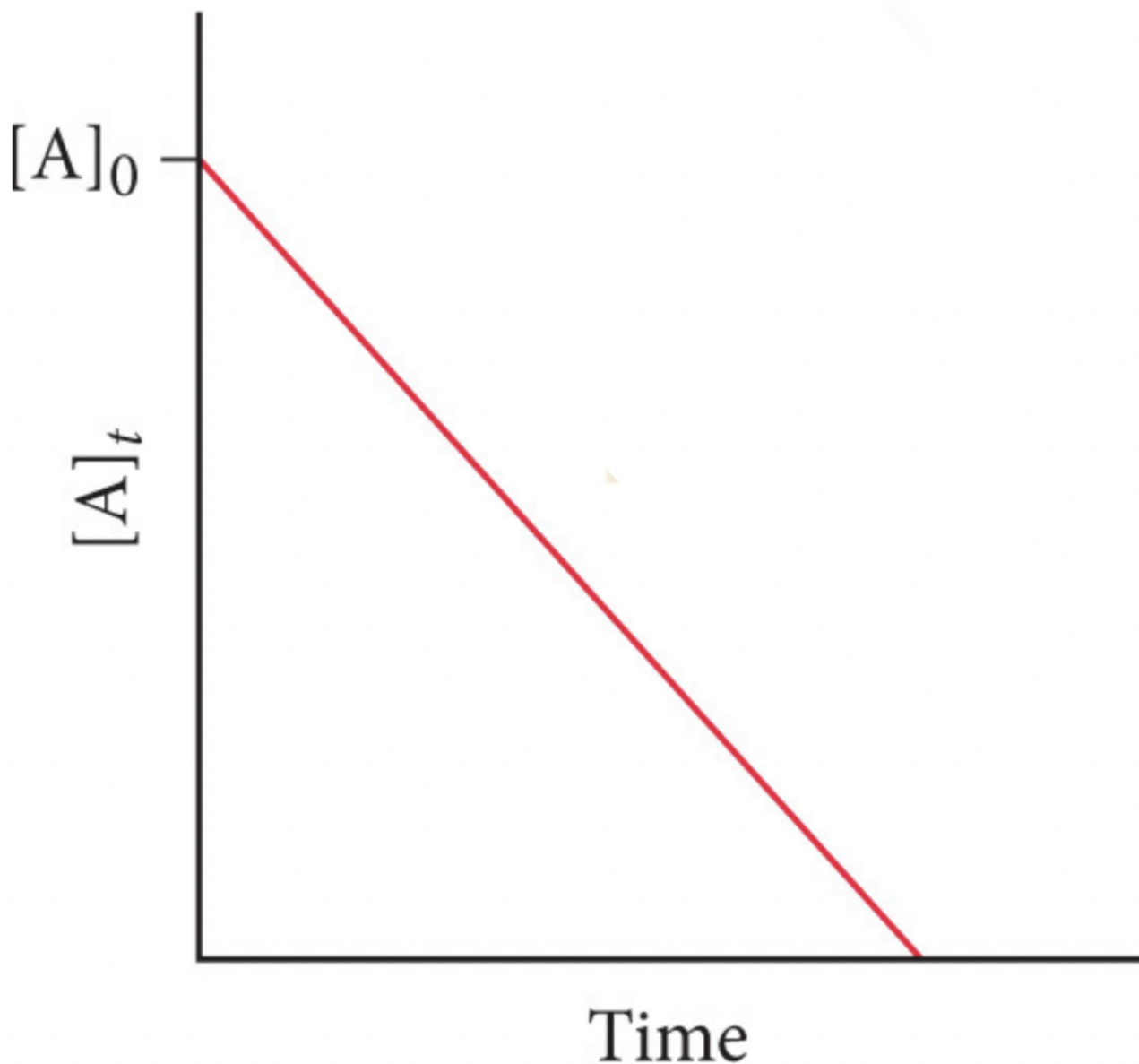
- radioactive decay is always a first-order reaction
- as long as volume stays constant, you can use ratios of mass in the first order IRL equations

Zero-Order IRL

Linearized:

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

- the slope of the linearized graph is $-k$, with units of $M s^{-1}$



Zero-Order Half-Life

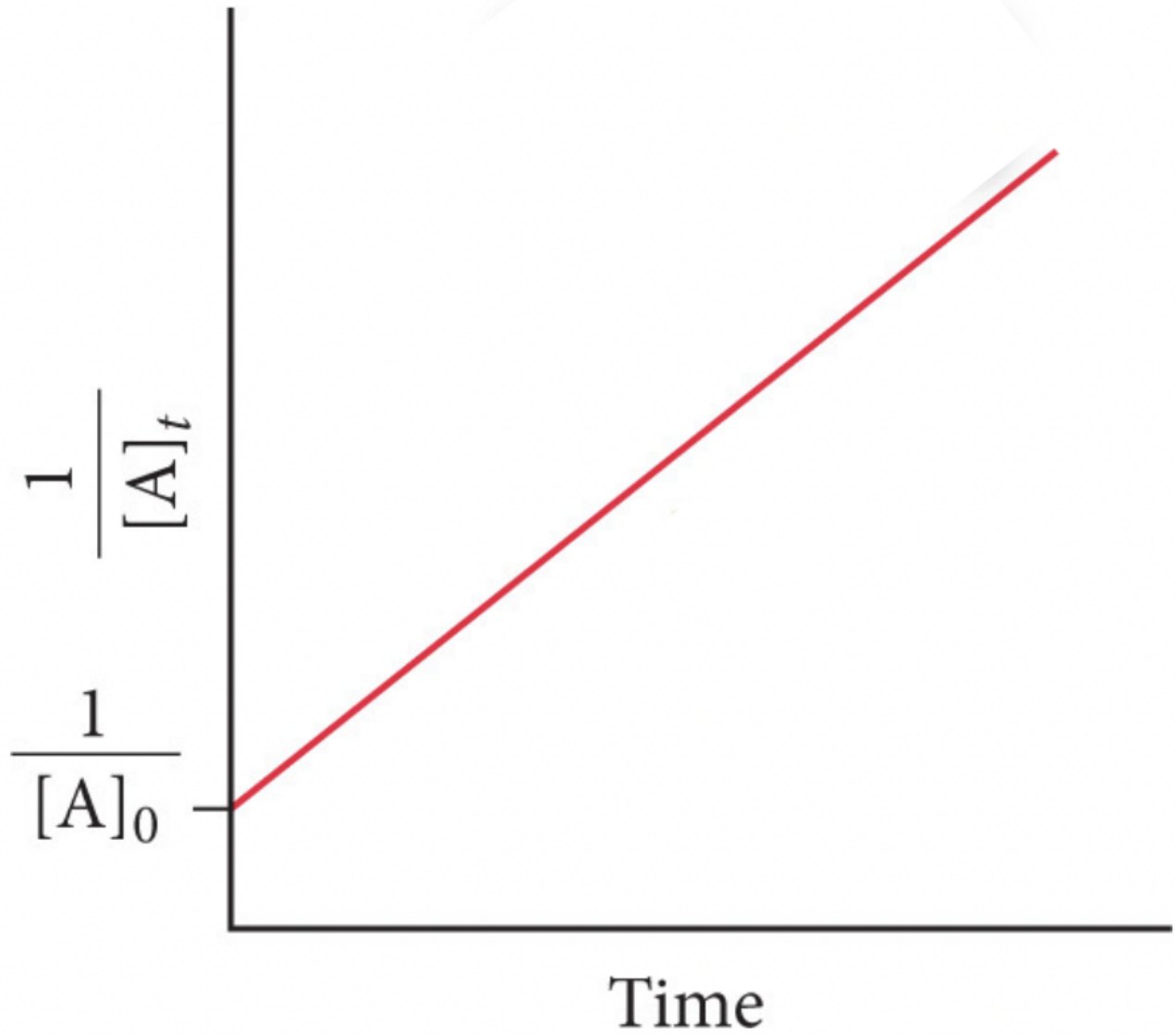
$$[A]_t = -kt + [A]_0 \implies t_{1/2}, [A] = \frac{[A]_0}{2} \implies t_{1/2} = \frac{[A]_0}{2k}$$

- unlike first-order half life, the zero-order half life is dependent on concentration
- as the reaction progresses, the half-life will decrease

Second-Order IRL

Linearized:

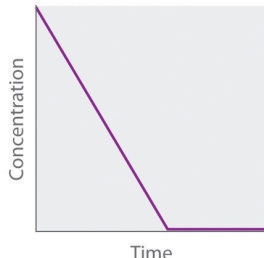
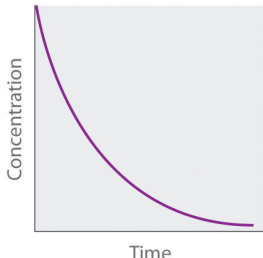
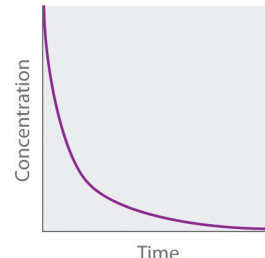
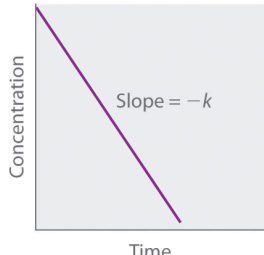

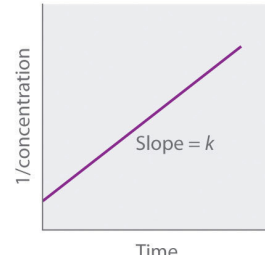
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$



Second-Order Half-Life

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \Rightarrow t_{1/2}, [A] = \frac{[A]_0}{2} \Rightarrow t_{1/2} = \frac{1}{k[A]_0}$$

Recap

	Zeroth Order	First Order	Second Order																								
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$																								
Concentration vs. time																											
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$																								
Straight-line plot to determine rate constant																											
Relative rate vs. concentration	<table><tr><th>[A], M</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>1</td></tr><tr><td>3</td><td>1</td></tr></table>	[A], M	Rate, M/s	1	1	2	1	3	1	<table><tr><th>[A], M</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>2</td></tr><tr><td>3</td><td>3</td></tr></table>	[A], M	Rate, M/s	1	1	2	2	3	3	<table><tr><th>[A], M</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>4</td></tr><tr><td>3</td><td>9</td></tr></table>	[A], M	Rate, M/s	1	1	2	4	3	9
[A], M	Rate, M/s																										
1	1																										
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Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$																								
Units of k, rate constant	M/s	1/s	M ⁻¹ ·s ⁻¹																								