

General Chemistry - Extra Session

Chemical Kinetics

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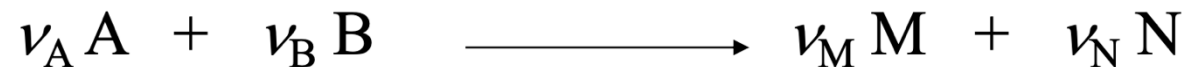
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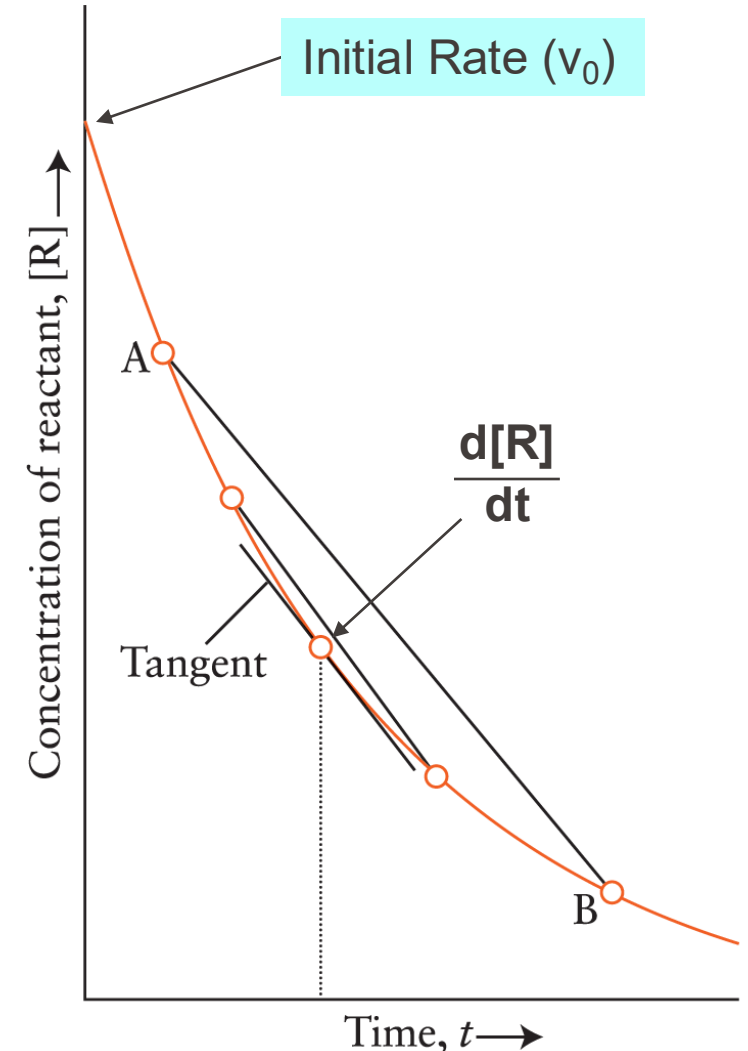
9th of December 2025

Reaction rate

- A reaction rate is a measure of how fast the concentration (or pressure) of a reactant or product changes with time.
- **Reaction rate** can be calculated at any time point by determining the value of the first derivative in the Concentration vs Time plot (slope of the tangent)
- For a general reaction at a constant volume and T:



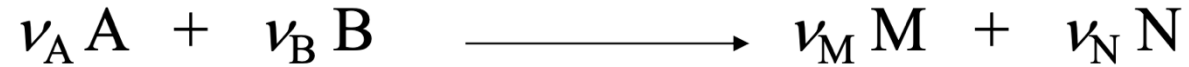
$$\text{Reaction rate } (v) = -\frac{1}{\nu_A} \frac{d[A]}{dt} = -\frac{1}{\nu_B} \frac{d[B]}{dt} = +\frac{1}{\nu_M} \frac{d[M]}{dt} = +\frac{1}{\nu_N} \frac{d[N]}{dt} \quad (\text{mol L}^{-1}\text{s}^{-1})$$



Note that here we use the stoichiometric coefficients for normalization

Empirical rate law and concentration

- For a general reaction:



- The reaction rate can be presented as:

v - Reaction rate

$$v = k [A]^\alpha [B]^\beta$$

Units: concentration or pressure / time

v - Reaction rate

k - Rate constant (depends on T)

$[A]$, $[B]$ - Concentrations of reactants

α - Reaction order of reactant A

β - Reaction order of reactant B

k - Reaction rate constant

Units: Units vary depending on the rate value itself

- The reaction rate constant quantifies the probability per unit time that reactant molecules will successfully transform into products when they collide.

Rate constant

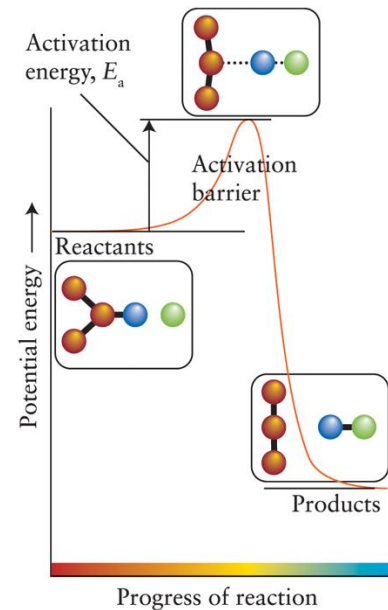
- Rate constant originates from the Collision and Transition-state theories and describes the probability of successful molecule collision leading to product generation

Arrhenius equation:

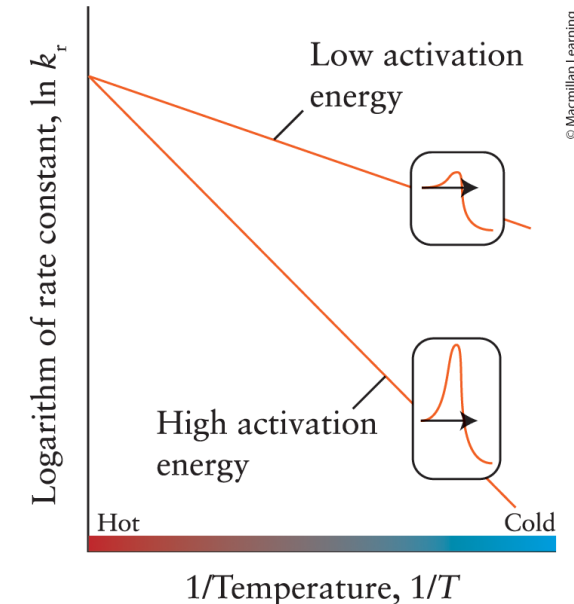
$$k_r = Ae^{-\frac{E_a}{RT}}$$

k_r - Reaction rate constant
A - Collision frequency factor
 E_a - Activation energy
 T - Temperature
 R - Universal gas constant

Activation energy



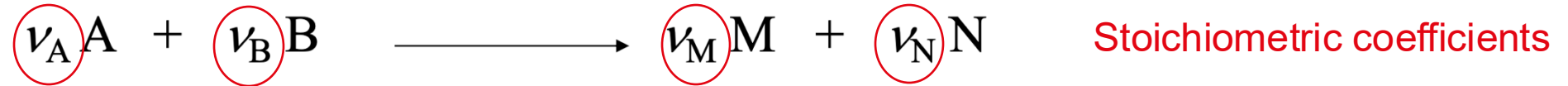
$$\ln(k) = \ln(A) - E_a/R \cdot 1/T$$



$$k = \underbrace{\{\text{frequency of collision per unit of concentration} \times \text{orientation probability}\}}_A \times \underbrace{\{\text{fraction with sufficient energy}\}}_{e^{-\frac{E_a}{RT}}}$$

Concentration dependence

- For a general reaction:



- The reaction rate can be presented as:

v - Reaction rate

$$v = k [A]^\alpha [B]^\beta$$

α - Reaction order of reactant A
 β - Reaction order of reactant B

Units: concentration or pressure / time

- Intuitively this makes sense as the concentration will impact collisions and increasing the concentration of any reagent (or both simultaneously) will have an effect on v

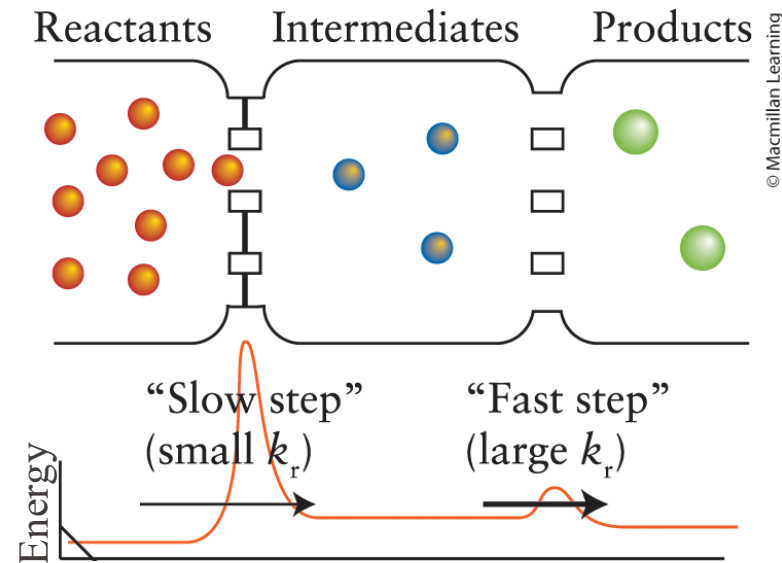
$$v = k [A]^{\nu_A} [B]^{\nu_B}$$

Why not use stoichiometric coefficients?

Elementary reactions

- A reaction can be considered **elementary** only when it corresponds to a single, indivisible molecular event, one collision step or one activated-complex-forming step.
- Typically, these reactions involve a small number of molecules and are kinetically simple

Substitution reactions are often elementary:



- For elementary reactions the partial reaction orders match the stoichiometric coefficients

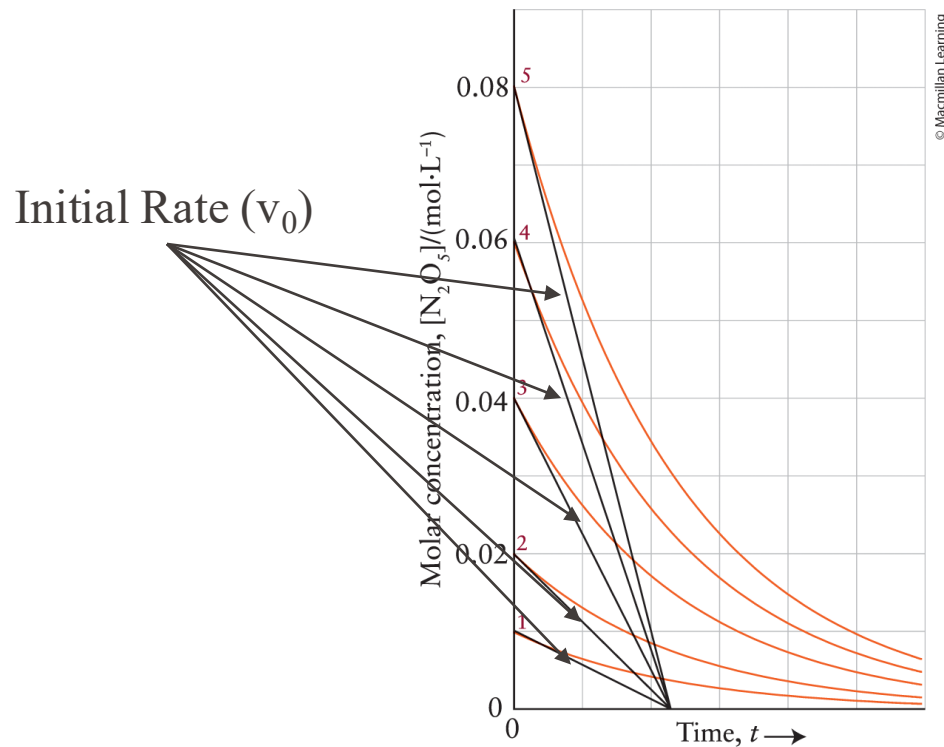
Reaction order can be equal to molecularity

- **Molecularity** refers to the number of reactant molecules that participate in a single elementary step of a reaction mechanism.
- The reaction mechanism can explain the rate law as a series of **elementary reactions**
- If the reaction steps are elementary, then **the order is equal to molecularity**

Molecularity	Reaction	Reaction speed	Reaction order
Unimolecular	$A \rightarrow \text{Products}$	$v = k \cdot [A]$	1
Bimolecular	$A + A \rightarrow \text{Products}$	$v = k \cdot [A]^2$	2
Bimolecular	$A + B \rightarrow \text{Products}$	$v = k \cdot [A] \cdot [B]$	2
Termolecular	$A + A + A \rightarrow \text{Products}$	$v = k \cdot [A]^3$	3
Termolecular	$A + A + B \rightarrow \text{Products}$	$v = k \cdot [A]^2 \cdot [B]$	3
Termolecular	$A + B + C \rightarrow \text{Products}$	$v = k \cdot [A] \cdot [B] \cdot [C]$	3

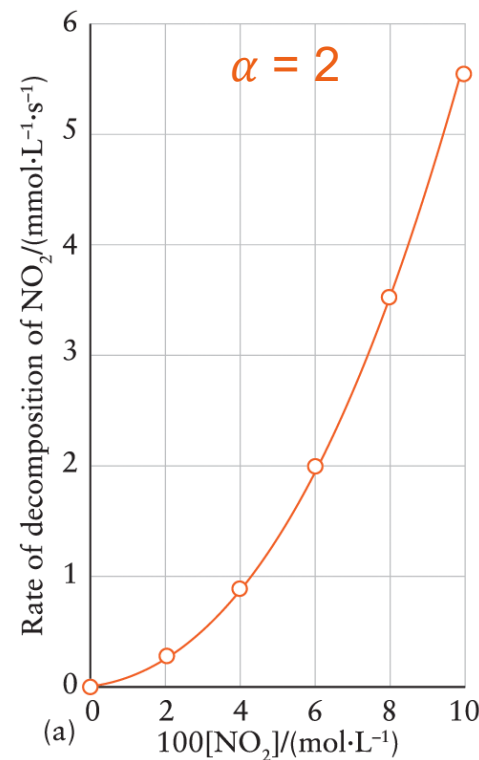
Determining partial reaction orders (1 reactant)

- Initial reaction rates (v_0) are measured across different starting concentrations $[R]_0$ of a given reactant. The v_0 vs $[R]_0$ plot is used to determine the partial reaction order for R

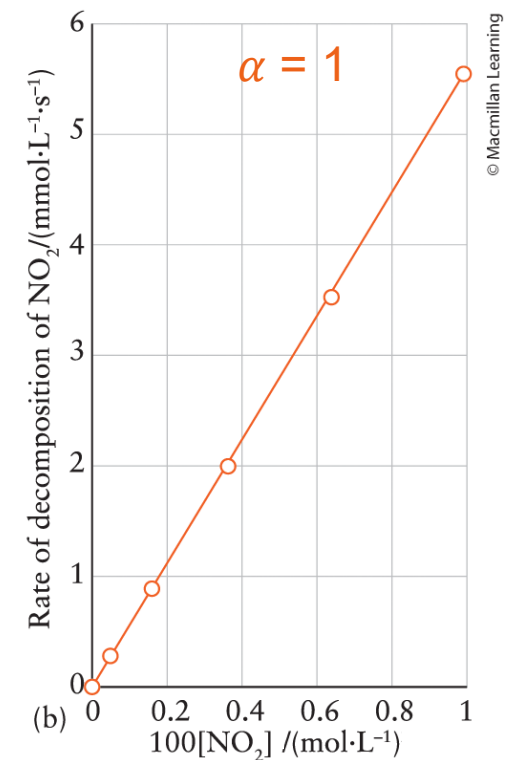


5 reaction curves

$$v_0 = k \cdot [\text{N}_2\text{O}_5]^2$$



$$v_0 = k \cdot [\text{N}_2\text{O}_5]^1$$



Plot of initial rates (v_0) vs Initial concentrations

Determining partial reaction orders (>1 reactants)

- Higher number of reactants increases the complexity of these experiments, as there are more species that simultaneously contribute to product formation:



- The way to approach these experiments is to vary the concentration of one reactant and measure reaction rate, while keeping all the other reactants at a constant concentration.

$$v_0 = k[A]_0^\alpha [B]_0^\beta [C]_0^\gamma$$

$$v_0' = k[nA]_0^\alpha [B]_0^\beta [C]_0^\gamma$$

$$\frac{v_0'}{v_0} = \frac{k[nA]_0^\alpha [B]_0^\beta [C]_0^\gamma}{k[A]_0^\alpha [B]_0^\beta [C]_0^\gamma} = n^\alpha$$

- Example: You doubled the initial concentration of A (n=2) and the result was:

$$v_0' / v_0 = 1 \quad \rightarrow \quad \alpha = 0$$

$$v_0' / v_0 = 2 \quad \rightarrow \quad \alpha = 1$$

$$v_0' / v_0 = 4 \quad \rightarrow \quad \alpha = 2$$

$$v_0' / v_0 = 8 \quad \rightarrow \quad \alpha = 3$$

Determining partial reaction orders (>1 reactants)

- Let's evaluate the following reaction involving 2 reactants (NO and Cl₂):



- The following initial rates were recorded for the corresponding starting conditions:

Condition	[NO] ₀ (mol · L ⁻¹)	[Cl ₂] ₀ (mol · L ⁻¹)	V ₀ (mol · L ⁻¹ · s ⁻¹)
1	0.0125	0.0255	2.27 · 10 ⁻⁵
2	0.0125	0.0510	4.55 · 10 ⁻⁵
3	0.0250	0.0255	9.08 · 10 ⁻⁵

- If [Cl₂]₀ increases by 2-fold the V₀ increases by 2-fold → 1st order dependence
- If [NO]₀ increases by 2-fold the V₀ increases by 4-fold → 2nd order dependence



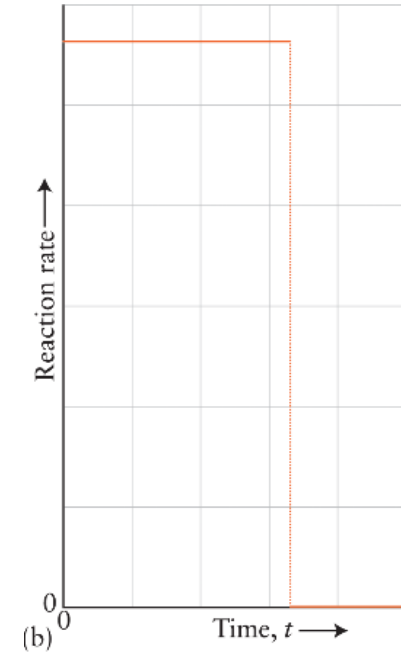
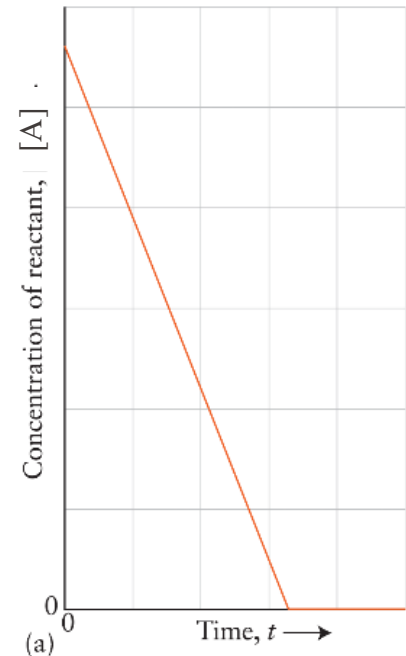
- A zero-order reaction is a reaction whose rate is independent of the concentration of the reactant(s).
- Changing the reactant concentration does not change the reaction rate.

Example: Decomposition of ammonia



Reaction rate: $v = - \frac{d[A]}{dt} = k$

After integration: $[A] = [A]_0 - kt$



- Typically occurring in photochemical or surface-catalyzed reactions (e.g., NH₃ decomp.)

- A first-order reaction is a reaction whose rate depends linearly on the concentration of one reactant. These typically involve unimolecular rearrangements or decomposition

Example: Hydrogen peroxide decomposition

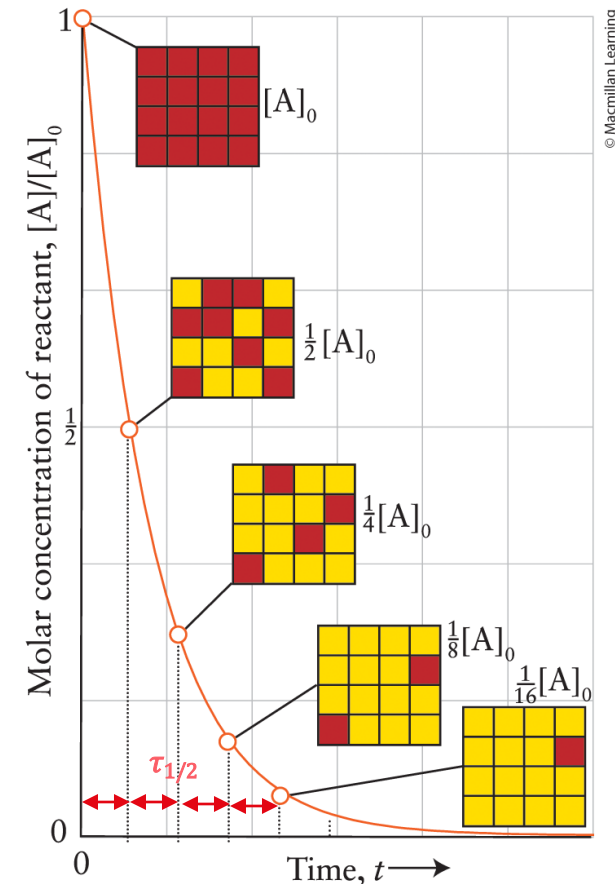


Reaction rate: $v = -\frac{d[A]}{dt} = k[A]$

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

Constant

$$[A]\tau_{1/2} = \frac{1}{2} [A]_0 \longrightarrow \tau_{1/2} = \frac{\ln(2)}{k}$$

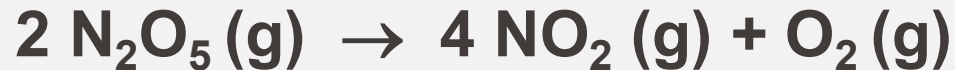


- A time of half-life ($\tau_{1/2}$) determines how quickly the concentration decreases by 50%.

Second order chemical reactions

- A second-order reaction is a reaction whose rate depends on the square of one reactant concentration or on the product of two reactant concentrations.

Example: Dinitrogen pentoxide decomposition

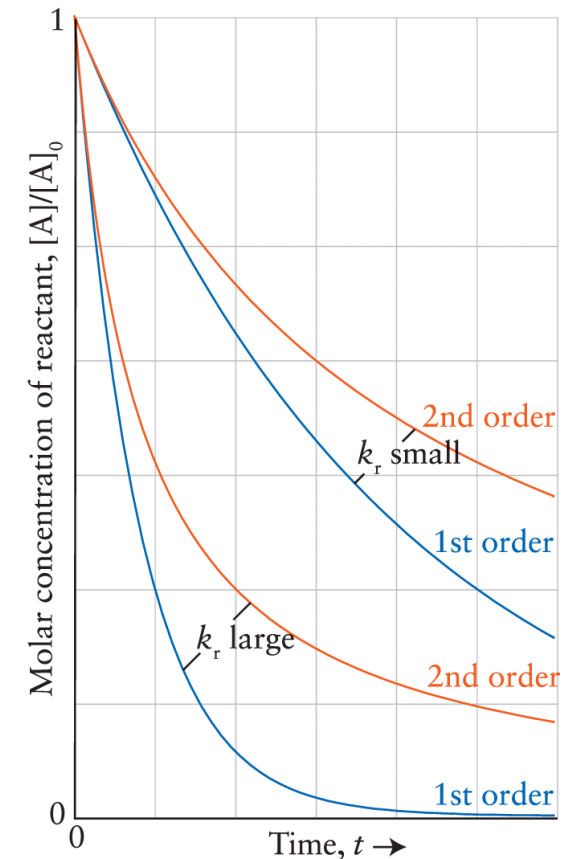


Reaction rate: $v = -\frac{d[A]}{dt} = k[A]^2$

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

Depends on $[A]_0$

$$\frac{1}{[A]_{\tau_{1/2}}} = \frac{1}{[A]_0} + k \tau_{1/2} \longrightarrow \tau_{1/2} = \frac{1}{k[A]_0}$$



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- At concentrations <1 mol/L, 2nd order reactions are slower than 1st order of equal k