



The value of rate constant depends on how rate is defined

Usual definition for a reaction: $a\mathbf{A} \rightarrow b\mathbf{B}$

 $R = -\frac{1}{a}\frac{d[\mathbf{A}]}{dt} = \frac{1}{b}\frac{d[\mathbf{B}]}{dt} = k[\mathbf{A}]^{n}$









| | [NH ₄ +] _{ini} (<i>M</i>) | [NO ₂ -] _{ini} (<i>M</i>) | Rate _{ini} (<i>M</i> s ⁻¹) | | |
|---|---|--|--|--|--|
| Exp. 1 | 0.100 | 0.0050 | 1.35 × 10 ^{−7} | | |
| Exp. 2 | 0.100 | 0.010 | 2.70 × 10 ^{−7} | | |
| Exp. 3 | 0.200 | 0.010 | 5.40 × 10 ⁻⁷ | | |
| Rate $1 = 1.35 \times 10^{-7} = k[NH_4^+]_{ini1}^n [NO_2^-]_{ini1}^m$ | | | | | |
| Rate $2 = 2.70 \times 10^{-7} = k [NH_4^+]^n_{ini2} [NO_2^-]^m_{ini2}$ | | | | | |
| $\implies \frac{1}{2} = \left(\frac{0.0050}{0.010}\right)^{m} = (1/2)^{m} \implies m = 1$ | | | | | |
| Rate 2 2.70 1 $[NH_4^+]^n_{ini2} = (0.100)^n$ | | | | | |
| Rate 3 | 5.40 2 | [NH ₄ ⁺] ⁿ _{ini3} – | 0.200 | | |
| Overall Overall o | Rate = k[order = n + m = | $[NH_4^+][NO_2^-]$ = 1 + 1 = 2 | | | |
| | | S | Second order reaction | | |





* The integrated rate law
Consider
$$\mathbf{A} \rightarrow \text{products}$$

 $\mathbf{Rate} = -\frac{d[\mathbf{A}]}{dt} = k[\mathbf{A}]^n$
() First order reaction
 $\mathbf{n} = 1$
 $\mathbf{Rate} = -\frac{d[\mathbf{A}]}{dt} = k[\mathbf{A}]$
 $\frac{1}{[\mathbf{A}]}d[\mathbf{A}] = -kdt \Rightarrow d\ln[\mathbf{A}] = -kdt$
 $\int_0^t d\ln[\mathbf{A}] = -k\int_0^t dt \Rightarrow \ln[\mathbf{A}] - \ln[\mathbf{A}]_0 = -k(t-0)$
concentration at t
 $\therefore \ln[\mathbf{A}] = -kt + \ln[\mathbf{A}]_0$



This method is more accurate than getting the tangent line Ex. $2N_2O_5(aq) \Rightarrow 4NO_2(g) + O_2(g)$ first order in N_2O_5 $[N_2O_5]_{ini} = 0.100 M$ $k = 6.93 \times 10^{-3} \text{ s}^{-1}$ At t = 150 s, $[N_2O_5] = ?$ Soln. $\ln[N_2O_5] = -kt + \ln[N_2O_5]_0$ $= -(6.93 \times 10^{-3})(150) + \ln(0.100)$ = -3.343 $[N_2O_5] = 0.0353 M$

⊙ Half-life of a 1st order reaction
$$t_{1/2} \Rightarrow t \text{ at } [A] = \frac{[A]_o}{2}$$

$$\ln[A] = -kt + \ln[A]_o \implies \ln\frac{[A]}{[A]_o} = -kt$$

$$\ln\frac{1}{2} = -kt_{1/2} \implies t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$
Concentration independent A characteristic value

Ex. $t_{1/2} = 20.0 \text{ min for a } 1^{\text{st}} \text{ order reaction, } k = ?$ $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{20 \text{ min}} = 3.47 \times 10^{-2} \text{ min}^{-1}$ Time for 75% completion? $[\mathbf{A}] = 0.25 [\mathbf{A}]_0$ $\ln 0.25 = -(3.47 \times 10^{-2}) t$ t = 40. minTwo half-lives



At
$$t_{1/2}$$
 $[\mathbf{A}] = \frac{[\mathbf{A}]_0}{2}$
 $\frac{1}{[\mathbf{A}]_0/2} - \frac{1}{[\mathbf{A}]_0} = kt_{1/2} \Rightarrow \frac{2}{[\mathbf{A}]_0} - \frac{1}{[\mathbf{A}]_0} = kt_{1/2}$
 $t_{1/2} = \frac{1}{k[\mathbf{A}]_0} \leftarrow \text{Dependent on } [\mathbf{A}]_0$
 $[\mathbf{A}]_0 \downarrow \qquad t_{1/2} \uparrow$
Ex. The second half-life
 $t_{1/2}$ is doubled













| Molecularity The number of species that collide to produce the reaction | | | | |
|--|--|--|--|--|
| Elementary step | Molecularity | Rate law | | |
| A → products A + A → products A + B → products A + A + B → products A + B + C → products | unimolecular bimolecular bimolecular termolecular termolecular | Rate = k [A] Rate = k [A] ² Rate = k [A][B] Rate = k [A] ² [B] Rate = k [A][B][C] | | |
| | | | | |











Ex.
$$Cl_2(g) + CHCl_3(g) \rightarrow HCl(g) + CCl_4(g)$$

experiment \Rightarrow rate = $k[Cl_2]^{1/2}[CHCl_3]$
Proposed mechanism:
 $Cl_2 \xrightarrow{k_1} 2Cl$
 $Cl + CHCl_3 \xrightarrow{k_2} HCl + CCl_3$ slow
 $CCl_3 + Cl \xrightarrow{k_3} CCl_4$
From the mechanism \Rightarrow Rate = $k_2[Cl][CHCl_3]$
intermediate



☆ The steady-state approximation

When we are not sure about which one is the slowest step ⇒ Use steady-state approximation

 Assume the intermediate reaches a constant concentration i.e. Formation rate = Consumption rate

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*Intermediate is neither the starting material nor the product

Ex.
$$2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$

Proposed mechanism:

$$2NO \stackrel{k_1}{\longrightarrow} N_2O_2$$
$$N_2O_2 + H_2 \stackrel{k_2}{\longrightarrow} N_2O + H_2O$$

Assume N₂O₂ reaches a steady-state $2NO \frac{k_1}{k_{-1}} N_2O_2$ Formation rate of N₂O₂ $N_2O_2 + H_2 \stackrel{k_2}{\longrightarrow} N_2O + H_2O$ $2NO \stackrel{k_1}{\longrightarrow} N_2O_2$ Rate $= k_1[NO]^2$ Consumption rate of N₂O₂ $N_2O_2 \stackrel{k_{-1}}{\longrightarrow} 2NO$ $N_2O_2 + H_2 \stackrel{k_2}{\longrightarrow} N_2O + H_2O$ Rate $= k_{-1}[N_2O_2] + k_2[N_2O_2][H_2]$ At steady-state: $k_{-1}[N_2O_2] + k_2[N_2O_2][H_2] = k_1[NO]^2$ Derive the overall rate law

$$2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$
$$d[H_2]$$

Overall rate = $-\frac{d[H_2]}{dt}$

In the mechanism, step 2 involves the consumption of H_2

$$2NO \stackrel{k_{1}}{\longrightarrow} N_{2}O_{2}$$

$$N_{2}O_{2} + H_{2} \stackrel{k_{2}}{\longrightarrow} N_{2}O + H_{2}O - \frac{d[H_{2}]}{dt} = k_{2}[N_{2}O_{2}][H_{2}]$$
From steady-state approximation:
$$[N_{2}O_{2}] = \frac{k_{1}[NO]^{2}}{k_{-1} + k_{2}[H_{2}]} \implies -\frac{d[H_{2}]}{dt} = k_{2}\frac{k_{1}[NO]^{2}}{k_{-1} + k_{2}[H_{2}]}[H_{2}]$$

$$-\frac{d[H_2]}{dt} = \frac{k_1 k_2 [NO]^2 [H_2]}{k_{-1} + k_2 [H_2]} \iff \begin{array}{l} \text{Rate law from steady-state approximation is usually complicated} \\ \checkmark \text{ Test this rate law under some special condition} \\ \textcircled{O} \text{ When } [H_2] \text{ is very large} \\ k_2 [H_2] \gg k_{-1} \\ \Rightarrow \text{ Rate } = \frac{k_1 k_2 [NO]^2 [H_2]}{k_2 [H_2]} = k_1 [NO]^2 \\ \text{Reasonable!} \\ \begin{array}{l} 2NO \quad \frac{k_1}{k_{-1}} & N_2O_2 \\ N_2O_2 + H_2 \quad \frac{k_2}{2} & N_2O + H_2O \end{array} \\ \Rightarrow \text{ Rate depends on the forward reaction of step 1} \\ \end{array}$$

② At very low [H₂]
$$k_{-1} \gg k_{2}[H_{2}]$$

$$-\frac{d[H_{2}]}{dt} = \frac{k_{1}k_{2}[NO]^{2}[H_{2}]}{k_{-1} + k_{2}[H_{2}]}$$

$$\Rightarrow \text{Rate} = \frac{k_{1}k_{2}[NO]^{2}[H_{2}]}{k_{-1}} = k[NO]^{2}[H_{2}]$$

$$\left(k = \frac{k_{1}k_{2}}{k_{-1}}\right)$$

At low [H₂], step 2 is rate-determining (home work)

| 2NO | $\frac{k_1}{k_{-1}}$ | N_2O_2 |
|----------------|----------------------|---------------|
| $N_2O_2 + H_2$ | <u>k</u> 2 | $N_2O + H_2O$ |



© Substitute [I_n] into the rate law























Catalytic converter: A mixture of catalysts including Pd, Pt Catalyze oxidation of CO and NO but also $SO_2 \rightarrow SO_3$ Poisoned by tetraethyl lead

Desulfurization RSH → R-H + S A catalyst mixture of Mo, Co, and S

Homogeneous catalysis
 Occurs in the same phase

Ex. The role of NO toward ozone

Production of NO: $N_2(g) + O_2(g) \rightarrow 2NO(g)$

 $NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)$ $NO_2(g) \xrightarrow{h\nu} NO(g) + O(g)$ $O_2(g) + O(g) \rightarrow O_3(g)$ $\frac{3}{2}O_2(g) \rightarrow O_3(g)$





$$\frac{[E]}{[ES]} = \frac{k_2 + k_3}{k_1[S] + k_4[P]}$$
Consider only initial rate
[P] is very small $\Rightarrow k_4[P] \sim 0$
 $\Rightarrow \frac{[E]}{[ES]} = \frac{k_2 + k_3}{k_1[S]}$
Define $K_m = \frac{k_2 + k_3}{k_1}$ \leftarrow Michaelis-Menton constant
 $\Rightarrow \frac{[E]}{[ES]} = \frac{K_m}{[S]}$
Since $[E] = [E]_T - [ES] \Rightarrow \frac{[E]_T - [ES]}{[ES]} = \frac{K_m}{[S]}$

$$\frac{[E]_{T}}{[ES]} - 1 = \frac{K_{m}}{[S]} \Rightarrow \frac{[E]_{T}}{[ES]} = \frac{K_{m}}{[S]} + 1$$

$$E + S \xrightarrow{k_{1}}{k_{2}} ES$$

$$ES \xrightarrow{k_{3}}{k_{4}} E + P$$
At high [S] the active site of the enzyme is saturated
$$\Rightarrow [ES] = [E]_{T}$$

$$\Rightarrow A \text{ maximum rate is reached}$$

$$v_{max} = k_{3}[ES] = k_{3}[E]_{T}$$
Initial rate $V = k_{3}[ES]$ (ES \Rightarrow E + P is slow)
Therefore $\frac{V_{max}}{V} = \frac{[E]_{T}}{[ES]} = \frac{K_{m}}{[S]} + 1 = \frac{K_{m} + [S]}{[S]}$

$$\Rightarrow V = \frac{V_{max}[S]}{K_{m} + [S]} \leftarrow \text{Michaelis-Menton equation}$$



Recall: $E + S \xrightarrow{k_1} ES$ $ES \xrightarrow{k_2} ES$ $K_m = \frac{k_2 + k_3}{k_1}$ $K_m = \frac{k_2 + k_3}{k_1}$ $K_m = \frac{k_2 + k_3}{k_1}$ If $k_2 >> k_3 \Rightarrow K_m \approx \frac{k_2}{k_1}$ This is the equilibrium constant for $\Rightarrow ES \xrightarrow{k_2}{k_1} E + S$ K_m is equivalent to the dissociation constant of ES
Therefore, under this special condition K_m is a measurement of the affinity between E and S \Rightarrow Larger K_m : smaller affinity
Smaller K_m : higher affinity

If an enzyme has several substrates The smaller the K_m the higher the affinity of the enzyme for the substrate

