Focus 17: Chemical Kinetics

The rates of chemical reactions

Integrated rate laws

- Reactions approaching equilibrium
- The Arrhenius equation

Reaction mechanisms

Photochemistry

Elementary reactions are the simplest types of chemical reactions.

They occur in a single step and involve a direct transformation of reactants into products at the molecular level.

Has only one transition state.

$H + Br_2 \rightarrow HBr + Br$

bimolecular reaction

$H + Br_2 \rightarrow HBr + Br$

Molecularity = 2 number of molecules coming together to react

bimolecular reaction

$H + Br_2 \rightarrow HBr + Br$

Molecularity = overall order = 2

bimolecular reaction

The rate law of a unimolecular elementary reaction is firstorder in the reactant:

$$A \rightarrow P \qquad \frac{d[A]}{dt} = -k_r[A]$$

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An elementary bimolecular reaction has a second-order rate law:

$$A+B \rightarrow P \qquad \frac{d[A]}{dt} = -k_r[A][B]$$



 $A \xrightarrow{k_a} I \xrightarrow{k_b} P$



Reaction Coordinate



- it's neither the reactant nor it is a product
- it resembles both to some extent, and
- it's not something that can be isolated (exists only a vibration-long)



Reaction Coordinate





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- it's not something that can be isolated (exists only a vibration-long)

Comparatively long-lived, can be experimentally detected and isolated



Reaction Coordinate



rate of unimolecular decomposition of A

 $\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{a}}[\mathrm{A}]$



rate of unimolecular decomposition of A

The net rate of formation of I

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{a}}[\mathrm{A}]$$

 $\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} = k_{\mathrm{a}}[\mathrm{A}] - k_{\mathrm{b}}[\mathrm{I}]$



rate of unimolecular decomposition of A

The net rate of formation of I

product P

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{a}}[\mathrm{A}]$$

 $\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} = k_{\mathrm{a}}[\mathrm{A}] - k_{\mathrm{b}}[\mathrm{I}]$

 $\frac{d[P]}{dt} = k_{b}[I]$

$$A \xrightarrow{k_a} I \xrightarrow{k_b} P$$

initial $[A]_0$; 0; 0;

rate of unimolecular decomposition of A

The net rate of formation of I

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rate of unimolecular decomposition of A

The net rate of formation of I

product P

$$\frac{d[A]}{dt} = -k_a[A]$$
$$\frac{d[I]}{dt} = k_a[A] - k_b[I]$$

 $\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k_{\mathrm{b}}[\mathrm{I}]$

$$[\mathbf{A}] = [\mathbf{A}]_0 \mathbf{e}^{-k_{\mathbf{a}}t}$$

$$A \xrightarrow{k_a} I \xrightarrow{k_b} P$$

initial $[A]_0$; 0; 0;

rate of unimolecular decomposition of A

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1 . . .

$$A \xrightarrow{k_a} I \xrightarrow{k_b} P$$

initial $[A]_0$; 0; 0;

rate of unimolecular decomposition of A

The net rate of formation of I

product P

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

$$\frac{d[I]}{dt} = k_{a}[A] - k_{b}[I]$$

$$\frac{d[P]}{dt} = k_{b}[I]$$

$$[I] = \frac{k_{a}}{k_{b} - k_{a}}(e^{-k_{a}t} - e^{-k_{b}t})[A]_{0}$$

$$\mathbf{A} \xrightarrow{k_{\mathrm{a}}} \mathbf{I} \xrightarrow{k_{\mathrm{b}}} \mathbf{P}$$

 $[A]_0: 0: 0$ initial

rate of unimolecular decomposition of A

The net rate of formation of I

product P

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

$$\frac{d[I]}{dt} = k_{a}[A] - k_{b}[I]$$

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At all tim

$$A \xrightarrow{k_a} I \xrightarrow{k_b} P$$

initial $[A]_0$; 0; 0;

$$[\mathbf{A}] = [\mathbf{A}]_0 \mathbf{e}^{-k_{\mathbf{a}}t}$$

$$[I] = \frac{k_{a}}{k_{b} - k_{a}} (e^{-k_{a}t} - e^{-k_{b}t}) [A]_{0}$$

$$[P] = \left\{ 1 + \frac{k_{a}e^{-k_{b}t} - k_{b}e^{-k_{a}t}}{k_{b} - k_{a}} \right\} [A]_{0}$$

$$A \xrightarrow{k_a} I \xrightarrow{k_b} P$$

initial $[A]_0$

$$[A]_{0} = 0$$



At what time will I be present in greatest concentration?





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 $\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}$

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$$[I] = \frac{k_{a}}{k_{b} - k_{a}} (e^{-k_{a}t} - e^{-k_{b}t}) [A]_{0}$$

 $\frac{d[I]}{dt}$

Steady-state approximation

Concentrations of intermediates remain small and hardly change during most of the course of the reaction

Products Reactants Intermediates

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$$\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} \approx 0$$

Tlme, t





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Tlme, t

Products Products Intermediates

 $A \xrightarrow{k_a} I \xrightarrow{k_b} P$

Tlme, t

Concentrations of intermediates remain small and hardly change during most of the course of the reaction

$$\frac{d[I]}{dt} \approx 0$$

$$\frac{d[I]}{dt} = k_a[A] - k_b[I] \qquad [I] = \frac{k_a}{k_b}[A]$$

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$$\frac{d[P]}{dt} = k_b[I]$$

 $A \xrightarrow{k_a} I \xrightarrow{k_b} P$

Products Reactants Concentrationi, [J] Intermediates



Concentrations of intermediates remain small and hardly change during most of the course of the reaction

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Steady-state approximation



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$$[A] = [A]_{0}e^{-k_{a}t}$$

 $[P] = [A]_0 (1 - e^{-k_a t})$



 $A \xrightarrow{k_a} I \xrightarrow{k_b} P$



Products Reactants Concentrationi, [J] Intermediates

Tlme, t

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 $A \xrightarrow{k_a} I \xrightarrow{k_b} P$

Steady-state approximation



Exact results (solid lines)

VS

Steady-state approximation (dotted lines)

Rate determining step (RDS)

The slowest step in a reaction mechanism, which determines the overall rate of the reaction

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Progress of reaction

Rate determining step (RDS)

The slowest step in a reaction mechanism, which determines the overall rate of the reaction



Smallest rate constant

Highest activation energy
A reaction between NO and H_2 occurs in the following three-step process:



a. What is the rate determining step?

b. Write the balanced equation for the overall reaction.

c. Are there any intermediates? If so, state what they are.

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 $2NO + 2H_2 \rightarrow N_2 + 2H_2O.$

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 $egin{aligned} NO+NO &
ightarrow N_2O_2 & ext{(fast)} \ N_2O_2+H_2 &
ightarrow N_2O+H_2O & ext{(slow)} \ N_2O+H_2 &
ightarrow N_2+H_2O & ext{(fast)} \end{aligned}$

a. What is the rate determining step?

b. Write the balanced equation for the overall reaction.

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 $N_2O_2 + H_2
ightarrow N_2O + H_2O$

 $2NO+2H_2 \rightarrow N_2+2H_2O.$

 N_2O_2 and N_2O_1

Pre-equilibria
$$A+B \xrightarrow[k_a]{k_a} I \xrightarrow{k_b} P \quad k'_a >> k_b$$

Pre-equilibria
$$A+B \xrightarrow[]{k_a}{k_a} I \xrightarrow[]{k_b}{} P \qquad k'_a >> k_b$$

$$K = \frac{[I]c^{\ominus}}{[A][B]}$$

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$$A+B \xrightarrow[k_a]{k_a} I \xrightarrow{k_b} P \quad k'_a >> k_b$$

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$$\frac{d[P]}{dt} = k_r[A][B] \text{ with } k_r = \frac{k_b k_a}{k'_a}$$

composite rate constant

Pre-equilibria

$$A+B \xleftarrow{k_{a}}{K_{a}} I \xrightarrow{k_{b}} P \qquad k'_{a} \gg k_{b}$$
Arrhenius equation

$$K = \frac{[I]c^{\ominus}}{[A][B]} \qquad k_{r} = \frac{k_{b}k_{a}}{k'_{a}} \qquad k_{r} = \frac{(A_{a}e^{-E_{aa}/RT})(A_{a'}e^{-E_{aa'}})}{A_{a'}e^{-E_{aa'}}}$$

$$[I] = \frac{K}{c^{\ominus}} [A][B] = \frac{k_{a}}{k'_{a}} [A][B]$$

$$k_{\rm r} = \frac{(A_{\rm a} e^{-E_{\rm a,a}/RT})(A_{\rm b} e^{-E_{\rm a,b}/RT})}{A_{\rm a'} e^{-E_{\rm a,a'}/RT}}$$

 $\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k_{\mathrm{b}}[\mathrm{I}] = k_{\mathrm{b}}\frac{k_{\mathrm{a}}}{k_{\mathrm{a}}'}[\mathrm{A}][\mathrm{B}]$

$$\frac{d[P]}{dt} = k_r[A][B] \text{ with } k_r = \frac{k_b k_a}{k'_a}$$

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$$Pre-equilibria \qquad A+B \xleftarrow{k_a} I \xrightarrow{k_b} P \qquad k'_a >> k_b$$

Arrhenius equation

 $k_{\rm r} = \frac{(A_{\rm a} e^{-E_{\rm a,a}/RT})(A_{\rm b} e^{-E_{\rm a,b}/RT})}{A_{\rm a'} e^{-E_{\rm a,a'}/RT}}$

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$$\frac{d[P]}{dt} = k_r[A][B] \text{ with } k_r = \frac{k_b k_a}{k'_a}$$

composite rate constant

The effective activation energy

 $E_{a} = E_{a,a} + E_{a,b} - E_{a,a'}$

 $k_{\rm r} = \frac{k_{\rm b}k_{\rm a}}{k'}$



becomes energetically excited

$$A + A \rightarrow A^* + A$$

$$\frac{\mathrm{d}[\mathrm{A}^*]}{\mathrm{d}t} = k_{\mathrm{a}}[\mathrm{A}]^2$$





becomes energetically excited

$$A+A \rightarrow A^*+A$$

lose its excess energy

$$A+A^* \rightarrow A+A$$

$$\frac{\mathrm{d}[\mathrm{A}^*]}{\mathrm{d}t} = k_{\mathrm{a}}[\mathrm{A}]^2$$

$$\frac{\mathrm{d}[\mathrm{A}^*]}{\mathrm{d}t} = -k'_{\mathrm{a}}[\mathrm{A}][\mathrm{A}^*]$$



becomes energetically excited

$$A+A \rightarrow A^*+A$$

lose its excess energy

$$\mathrm{A}{+}\mathrm{A}^{\star}\rightarrow\mathrm{A}{+}\mathrm{A}$$

$$\frac{\mathrm{d}[\mathrm{A}^*]}{\mathrm{d}t} = k_{\mathrm{a}}[\mathrm{A}]^2$$

 $\frac{\mathrm{d}[\mathrm{A}^*]}{\mathrm{d}t} = -k_{\mathrm{a}}'[\mathrm{A}][\mathrm{A}^*]$

Second step,

$$\mathbf{A}^{\star} \to \mathbf{P}$$

$$\frac{\mathrm{d}[\mathrm{A}^*]}{\mathrm{d}t} = -k_{\mathrm{b}}[\mathrm{A}^*]$$



becomes energetically excited

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 $\frac{d[A^*]}{dt} = k_a[A]^2 - k'_a[A][A^*] - k_b[A^*]$



becomes energetically excited

$$A + A \rightarrow A^* + A$$

lose its excess energy

$$A+A^* \rightarrow A+A$$

 $\frac{\mathrm{d}[\mathrm{A}^{\star}]}{\mathrm{d}t} = k_{\mathrm{a}}[\mathrm{A}]^{2}$

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Second step,

$$\mathbf{A}^{\star} \to \mathbf{P}$$

$$\frac{\mathrm{d}[\mathrm{A}^*]}{\mathrm{d}t} = -k_{\mathrm{b}}[\mathrm{A}^*]$$

 $\frac{d[A^*]}{dt} = k_a[A]^2 - k'_a[A][A^*] - k_b[A^*] \approx 0 \quad ; SSA$



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$$\frac{\mathrm{d}[\mathrm{A}^*]}{\mathrm{d}t} = -k'_{\mathrm{a}}[\mathrm{A}][\mathrm{A}^*]$$

Second step,

$$\mathbf{A}^{\star} \to \mathbf{P}$$

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 $\frac{d[A^*]}{dt} = k_a[A]^2 - k'_a[A][A^*] - k_b[A^*] \approx 0 \quad ; SSA$

$$[\mathbf{A}^*] = \frac{k_{\mathbf{a}}[\mathbf{A}]^2}{k_{\mathbf{b}} + k_{\mathbf{a}}'[\mathbf{A}]}$$



becomes energetically excited

$$A+A \rightarrow A^*+A$$

lose its excess energy

$$A+A^* \rightarrow A+A$$

 $\frac{\mathrm{d}[\mathrm{A}^{\star}]}{\mathrm{d}t} = k_{\mathrm{a}}[\mathrm{A}]^{2}$

$$\frac{\mathrm{d}[\mathrm{A}^*]}{\mathrm{d}t} = -k_{\mathrm{a}}'[\mathrm{A}][\mathrm{A}^*]$$

Second step,

$$\mathbf{A}^{\star} \to \mathbf{P}$$

$$\frac{\mathrm{d}[\mathrm{A}^*]}{\mathrm{d}t} = -k_{\mathrm{b}}[\mathrm{A}^*]$$

 $\frac{d[A^*]}{dt} = k_a[A]^2 - k'_a[A][A^*] - k_b[A^*] \approx 0 \quad ; SSA$

$$[A^*] = \frac{k_a[A]^2}{k_b + k'_a[A]} \qquad \frac{d[P]}{dt} = k_b[A^*] = \frac{k_a k_b[A]^2}{k_b + k'_a[A]}$$







Greater deactivation

High Pressure!

 $k'_{a}[A][A^{*}] \gg k_{b}[A^{*}],$





Greater deactivation

High Pressure!

 $k'_{a}[A][A^{*}] >> k_{b}[A^{*}],$

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becomes energetically excited

$$A+A \rightarrow A^* + A \qquad \frac{d[A^*]}{dt} = k_a[A]^2$$
lose its excess energy

$$A+A^* \rightarrow A+A \qquad \frac{d[A^*]}{dt} = -k'_a[A][A^*]$$
Second step,

$$A^* \rightarrow P \qquad \frac{d[A^*]}{dt} = -k_b[A^*]$$

 $\frac{d[P]}{dt} = k_{b}[A^{*}] = \frac{k_{a}k_{b}[A]^{2}}{k_{b}+k_{a}'[A]}$

Greater deactivation

High Pressure!

 $k'_{a}[A][A^{*}] \gg k_{b}[A^{*}],$

 $k'_{a}[A] >> k_{b},$

$$\frac{d[P]}{dt} = k_r[A] \text{ with } k_r = \frac{k_a k_b}{k'_a}$$

Greater decay to form products

Low Pressure!

 $k'_{a}[A][A^*] \ll k_{b}[A^*]$

becomes energetically excited $A+A \rightarrow A^* + A \qquad \frac{d[A^*]}{dt} = k_a[A]^2$ lose its excess energy $A+A^* \rightarrow A+A \qquad \frac{d[A^*]}{dt} = -k'_a[A][A^*]$ Second step, $A^* \rightarrow P \qquad \frac{d[A^*]}{dt} = -k_b[A^*]$



Greater deactivation

High Pressure!

 $k_{\mathrm{a}}'[\mathrm{A}][\mathrm{A}^*] \gg k_{\mathrm{b}}[\mathrm{A}^*],$

 $k'_{a}[A] >> k_{b},$

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k_{\mathrm{r}}[\mathrm{A}] \quad \text{with} \quad k_{\mathrm{r}} = \frac{k_{\mathrm{a}}k_{\mathrm{b}}}{k_{\mathrm{a}}'}$$

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 $k'_{a}[A][A^*] \ll k_{b}[A^*]$

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 $k'_{a}[A][A^*] \ll k_{b}[A^*]$

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$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k_{\mathrm{a}}[\mathrm{A}]^2$$



ES -

 $\xrightarrow{k_{\rm b}} P+E$

Michaelis–Menten mechanism



The substrate binds (non-covalent interactions) to the active site of the enzyme (biological catalysts), and the enzyme facilitates the conversion of the substrate into one or more products



Michaelis–Menten mechanism

rate of product formation

$$ES \xrightarrow{k_b} P+E$$

$$v = k_{\rm b}[{\rm ES}]$$

$$E + S \xrightarrow[k_a]{k_a} ES$$

 $ES \xrightarrow{k_b} P + E$

Michaelis–Menten mechanism

rate of product formation

 $v = k_{\rm b}[{\rm ES}]$

steady-state approximation

 $\frac{d[ES]}{dt} = k_a[E][S] - k'_a[ES] - k_b[ES] \approx 0$

$$E + S \xrightarrow[k_a]{k_a} ES$$

 $ES \xrightarrow{k_b} P + E$

Michaelis–Menten mechanism

rate of product formation

 $v = k_{\rm b}[{\rm ES}]$

steady-state approximation

 $\frac{\mathrm{d}[\mathrm{ES}]}{\mathrm{d}t} = k_{\mathrm{a}}[\mathrm{E}][\mathrm{S}] - k_{\mathrm{a}}'[\mathrm{ES}] - k_{\mathrm{b}}[\mathrm{ES}] \approx 0$

 $[\text{ES}] = \frac{k_{\text{a}}[\text{E}][\text{S}]}{k_{\text{a}}' + k_{\text{b}}}$

$$E + S \xrightarrow[k_a]{k_a} ES$$

Michaelis–Menten mechanism

rate of product formation

 $v = k_{\rm b}[{\rm ES}]$

steady-state approximation

 $\frac{d[ES]}{dt} = k_a[E][S] - k'_a[ES] - k_b[ES] \approx 0$

 $[\text{ES}] = \frac{k_{\text{a}}[\text{E}][\text{S}]}{k_{\text{a}}' + k_{\text{b}}}$

Michaelis constant $K_{\rm M} = \frac{k_{\rm a}' + k_{\rm b}}{k_{\rm a}}$





 $ES \xrightarrow{k_b} P + E$

Michaelis–Menten mechanism

rate of product formation

 $v = k_{\rm b}[{\rm ES}]$

steady-state approximation

$$\frac{d[ES]}{dt} = k_a[E][S] - k'_a[ES] - k_b[ES] \approx 0$$

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Michaelis constant
$$K_{\rm M} = \frac{k_{\rm a}' + k_{\rm b}}{k_{\rm a}}$$

$$[E]_0 = [E] + [ES].$$

 $[E] = [E]_0 - [ES]$



 $ES \xrightarrow{k_b} P + E$

Michaelis–Menten mechanism

rate of product formation

 $v = k_{\rm b}[{\rm ES}]$

steady-state approximation

$$\frac{d[ES]}{dt} = k_a[E][S] - k'_a[ES] - k_b[ES] \approx 0$$

 $[\text{ES}] = \frac{k_{\text{a}}[\text{E}][\text{S}]}{k_{\text{a}}' + k_{\text{b}}}$

Michaelis constant $K_{\rm M} = \frac{k_{\rm a}' + k_{\rm b}}{k_{\rm a}}$

$$[E]_0 = [E] + [ES]$$

$$[E] = [E]_0 - [ES]$$

$$[ES] = \frac{([E]_0 - [ES])[S]}{K_M}$$



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 $[E]_0 = [E] + [ES].$ $[E] = [E]_0 - [ES]$

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The substrate is typically in large excess relative to the enzyme

 $[S] \approx [S]_0$



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Michaelis constant $K_{\rm M} = \frac{k_{\rm a}' + k_{\rm b}}{k_{\rm a}}$

 $[E]_0 = [E] + [ES].$ $[E] = [E]_0 - [ES]$

$$[\mathrm{ES}] = \frac{([\mathrm{ES}]_0 - [\mathrm{ES}])[\mathrm{S}]}{K_{\mathrm{M}}}$$

The substrate is typically in large excess relative to the enzyme

 $[S] \approx [S]_0$

$$[ES] = \frac{[S]_0[E]_0}{K_M + [S]_0} = \frac{[E]_0}{1 + K_M / [S]_0}$$
$$E+S \xrightarrow[k_a]{k_a} ES$$

Michaelis–Menten mechanism

$$ES \xrightarrow{k_b} P+E$$

$$v = k_{b}[ES]$$

 $[ES] = \frac{[S]_{0}[E]_{0}}{K_{M} + [S]_{0}} = \frac{[E]_{0}}{1 + K_{M} / [S]_{0}}$

$$E+S \xrightarrow[k_a]{k_a} ES$$

 $ES \xrightarrow{k_b} P + E$

Michaelis–Menten mechanism

$$v = k_{\rm b}[{\rm ES}]$$

[ES] = $\frac{[S]_0[E]_0}{K_{\rm M} + [S]_0} = \frac{[E]_0}{1 + K_{\rm M} / [S]_0}$

Michaelis-Menten equation

$$v = \frac{k_{\rm b}[{\rm E}]_{\rm 0}}{1 + K_{\rm M}/[{\rm S}]_{\rm 0}}$$

$$E + S \xrightarrow[k_a]{k_a} ES$$

 $ES \xrightarrow{k_b} P + E$

Michaelis–Menten mechanism

$$v = k_{b}[ES]$$

[ES] = $\frac{[S]_{0}[E]_{0}}{K_{M} + [S]_{0}} = \frac{[E]_{0}}{1 + K_{M} / [S]_{0}}$

Michaelis-Menten equation

$$v = \frac{k_{\rm b}[{\rm E}]_0}{1 + K_{\rm M}/[{\rm S}]_0}$$

When $[S]_0 \ll K_M$,

$$\nu = \frac{k_{\rm b}}{K_{\rm M}} [\rm S]_0 [\rm E]_0$$

When
$$[S]_0 \gg K_M$$
,

$$v_{\rm max} = k_{\rm b} [\rm E]_0$$





Michaelis–Menten mechanism



Lineweaver–Burk plot

