Faculty of Engineering and Technology
Department of Chemical Engineering
University Of Jordan

Chemical Reaction Engineering

Reaction Mechanisms

Dr.-Eng. Zayed Al-Hamamre

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- ➢ **Finding the Reaction Mechanism**
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Active intermediates and nonelementary rate laws

power law models, $-r_A = kC_A^n$

where n was an integer of 0, 1, or 2 corresponding to a zero-, first-, and second-order reaction.

- For the reaction $CH_3CHO \rightarrow CH_4 + CO$ $\quad -r_{CH_3CHO} = kC_{CH_3CHO}^{3/2}$

  The order is noninteger

- For the reaction $H_2 + Br_2 \rightarrow 2HBr$

$$r_{HBr} = \frac{k_1 C_{H_2} C_{Br_2}^{3/2}}{C_{HBr} + k_2 C_{Br_2}}$$

- **Rate laws of this form usually involve a number of elementary reactions and at least one active intermediate**

Active intermediates and nonelementary rate laws

- An active intermediate is a high-energy molecule that reacts virtually as fast as it is formed.
- It is present in very small concentrations.
- The net rate of formation of an active intermediate (e.g. A*) is zero

$$r_{A^*} \equiv 0 \qquad \text{Pseudo-Steady-State Hypothesis}$$

If the active intermediate appears in n reactions, then

$$r_{A^*} = \sum_{i=1}^{n} r_{iA^*} = 0$$

Example

gas-phase decomposition of azomethane, AZO,

$$(CH_3)_2N_2 \longrightarrow C_2H_6 + N_2$$

at pressures greater than 1 atm $\qquad r_{C_2H_6} \propto C_{AZO}$

at pressures below 50 mmHg (low concentrations):

$$r_{C_2H_6} \propto C_{AZO}^2$$

propose the following mechanism

$$(CH_3)_2N_2 + (CH_3)_2N_2 \xrightarrow{k_1} (CH_3)_2N_2 + [(CH_3)_2N_2]^*$$ **R1**

An activated molecule,

Example Cont.

- The reaction is elementary, the rate of formation of the active intermediate

$$r_{1AZO^{\bullet}} = k_{1AZO^{\bullet}} C_{AZO}^2 \qquad AZO \equiv [(CH_3)_2N_2]$$

- The active intermediate (activated complex) may
  1. Become deactivated through collision with another molecule

$$[(CH_3)_2N_2]^* + (CH_3)_2N_2 \xrightarrow{k_2} (CH_3)_2N_2 + (CH_3)_2N_2$$ **R2**

$$r_{2AZO^{\bullet}} = -k_{2AZO^{\bullet}} C_{AZO^{\bullet}} C_{AZO}$$

  2. Decomposes spontaneously to form ethane and nitrogen:

$$[(CH_3)_2N_2]^* \xrightarrow{k_3} C_2H_6 + N_2 \qquad r_{3AZO^{\bullet}} = -k_{3AZO^{\bullet}} C_{AZO^{\bullet}}$$

Example Cont.

Nitrogen and ethane are only formed in the reaction

$$[(CH_3)_2N_2]^* \xrightarrow{k_3} C_2H_6 + N_2 \qquad \textbf{R3}$$

$$r_{N_2} = k_3 C_{AZO^*} \qquad r_{C_2H_6} = k_3 C_{AZO^*}$$

The concentration of the active intermediate, AZO*, is very difficult to measure, because it is highly reactive and very short-lived (~10^{-9} s).

the rate of formation of species *j* occurring in *n* different reactions as

$$r_j = \sum_{i=1}^{n} r_{ji}$$

Because the active intermediate, AZO*, is present in all three reactions in the decomposition mechanism, the net rate of formation of AZO* is the sum of the rates of each of the reaction equations,

Example Cont.

net rate of formation of AZO* = rate of formation of AZO” in **R1** + rate of formation of AZO” in **R2** + rate of formation of AZO” in **R3**

$$r_{AZO^*} = r_{1AZO^*} + r_{2AZO^*} + r_{3AZO^*}$$

$$r_{AZO^*} = k_1 C_{AZO}^2 - k_2 C_{AZO} C_{AZO^*} - k_3 C_{AZO^*}$$

Use the pseudosteady-state hypothesis (PSSH)

$$r_{AZO^*} \equiv 0.$$

$$r_{AZO^*} = k_1 C_{AZO}^2 - k_2 C_{AZO} C_{AZO^*} - k_3 C_{AZO^*} = 0$$

Example Cont.

Solving for C_{AZO^*} → $$C_{AZO^*} = \frac{k_1 C_{AZO}^2}{k_3 + k_2 C_{AZO}}$$

→ $$r_{N_2} = \frac{k_1 k_3 C_{AZO}^2}{k_3 + k_2 C_{AZO}}$$

At low concentrations $k_2 C_{AZO} \ll k_3$

for which case we obtain the following second-order rate law:

$$r_{N_2} = k_1 C_{AZO}^2$$

Example Cont.

At high concentrations $k_2 C_{AZO} \gg k_3$

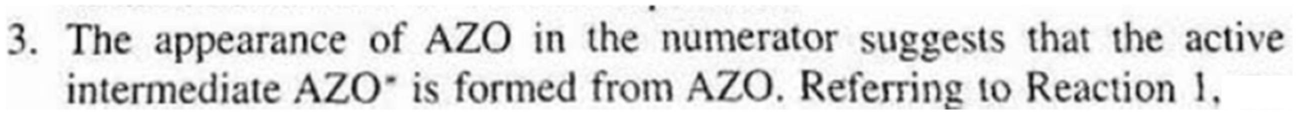
in which case the rate expression follows first-order kinetics,

$$r_{N_2} = \frac{k_1 k_3}{k_2} C_{AZO} = k C_{AZO}$$

General Considerations.

1. The active intermediate, AZO^*, collides with azomethane, AZO [Reaction 2], resulting in the concentration of AZO in the denominator.
2. AZO^* decomposes spontaneously [Reaction 3], resulting in a constant in the denominator of the rate expression.

Example Cont.

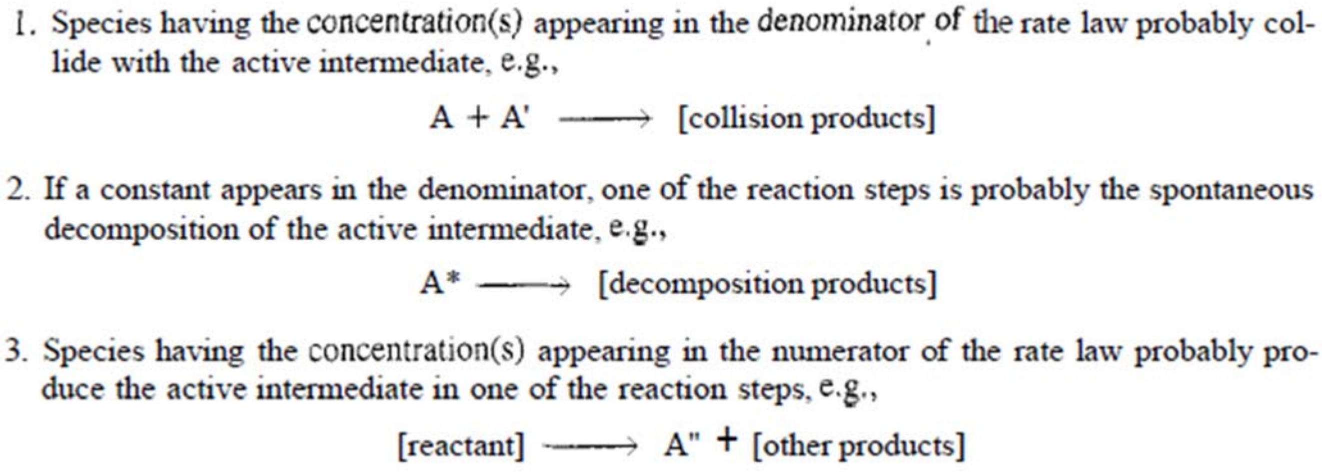


3. The appearance of AZO in the numerator suggests that the active intermediate AZO^* is formed from AZO. Referring to Reaction 1,

- In describing reaction orders for **this equation, one** would say **the** reaction is apparent ***first order*** **at** high **azomethane** concentrations and ***apparent second order*** at **low** azomethsne concentrations

Example Cont.

- **RULES OF THUMB** FOR **EVELOPMENT OF A MECHANISM**



1. Species having the concentration(s) appearing in the denominator of the rate law probably collide with the active intermediate, e.g.,

$$A + A' \longrightarrow [\text{collision products}]$$

2. If a constant appears in the denominator, one of the reaction steps is probably the spontaneous decomposition of the active intermediate, e.g.,

$$A^* \longrightarrow [\text{decomposition products}]$$

3. Species having the concentration(s) appearing in the numerator of the rate law probably produce the active intermediate in one of the reaction steps, e.g.,

$$[\text{reactant}] \longrightarrow A'' + [\text{other products}]$$

Example

$$A \rightarrow P \qquad -r_A = kC_A$$

- The reaction is first order but the reaction is not elementary.
- The reaction proceeds by first forming an active intermediate A^*, from the collision of the reactant molecule and 'an inert molecule of M

$$\text{Activation} \qquad (1) \quad A + M \xrightarrow{k_1} A^* + M$$

- This wildly oscillating active intermediate is deactivated by collision with inert **M**

$$\text{Deactivation} \qquad (2) \quad A^* + M \xrightarrow{k_2} A + M$$

- Or it decomposes to form product.

$$\text{Decomposition} \quad (3) \qquad A^* \xrightarrow{k_3} P \qquad r_P = k_3 C_{A^*}$$

Example Cont.

using the PSSH to find the concentrations of A*

$$r_P = -r_A = \frac{k_3 k_1 C_A C_M}{k_2 C_M + k_3}$$

Because the concentration of the inert M is constant,

$$k = \frac{k_1 k_3 C_M}{k_2 C_M + k_3}$$

$$\Rightarrow \qquad -r_A = kC_A$$

Finding the Reaction Mechanism

- To propose a mechanism that is consistent with the rate law which has been synthesized from the experimental data.

1. Assume an activated intermediate(s).
2. Postulate a mechanism, utilizing the rate law obtained from experimental data, if possible.
3. Model each reaction in the mechanism sequence as an elementary reaction.
4. After writing rate laws for the rate of formation of desired product, write the rate laws for each of the active intermediates.
5. Use the PSSH.
6. Eliminate the concentration of the intermediate species in the rate laws by solving the simultaneous equations developed in steps 4 and 5.
7. If the derived rate law does not agree with experimental observation, assume a new mechanism and/or intermediates and go to step 3. A strong background in organic and inorganic chemistry is helpful in predicting the activated intermediates for the reaction under consideration

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Example

Light is given off when a high-intensity ultrasonic wave is applied to water. This light results from micro-size bubbles (0.1 mm) being formed by the wave and then being compressed by it. During the compression stage of the wave, the contents of the bubble (e.g., water and whatever is dissolved in the water CS_2, O_2, N_2) are compressed adiabatically.

This compression gives rise to high temperatures, which generate active intermediates and cause chemical reactions to occur in the bubble.

$$M + H_2O \longrightarrow H_2\dot{O} + M$$

The intensity of the light given off, *I,* is proportional to the rate of deactivated and activated water molecule that has been formed in the micro-bubble

$$H_2O^* \xrightarrow{k_3} \text{H20} + h\nu$$

$$\text{intensity} \propto (-r_{H_2O^*}) = k_3 C_{H_2O^*}$$

An order-of-magnitude increase in the intensity of sonoluminescence is observed when either carbon disulfide or carbon tetrachloride is added to the water. The intensity of luminescence, *I,* for the reaction

Example Cont.

$$CS_2^* \xrightarrow{k_4} CS_2 + h\nu$$

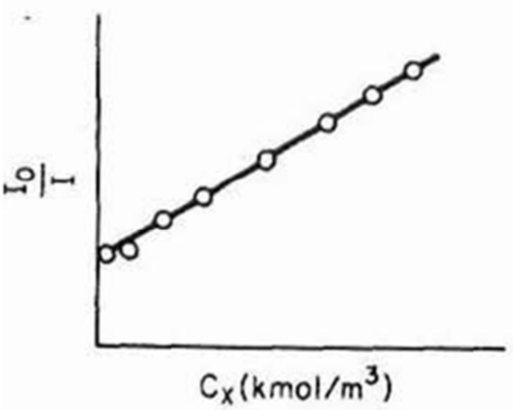
is

$$I \propto (-r_{CS_2^*}) = k_4 C_{CS_2^*}$$

A similar result exists for CCl_4.

However, when an aliphatic alcohol, X, is added to the solution, the intensity decreases with increasing concentration of alcohol. The data are usually reported in terms of a Stern–Volmer plot in which relative intensity is given as a function of alcohol concentration, C_X. (See Figure E7-1.1, where I_0 is the sonoluminescence intensity in the absence of alcohol and I is the sonoluminescence intensity in the presence of alcohol.) Suggest a mechanism consistent with experimental observation.

Example Cont.



Ratio of luminescence intensities as a function of Scavenger concentration.

Example Cont.

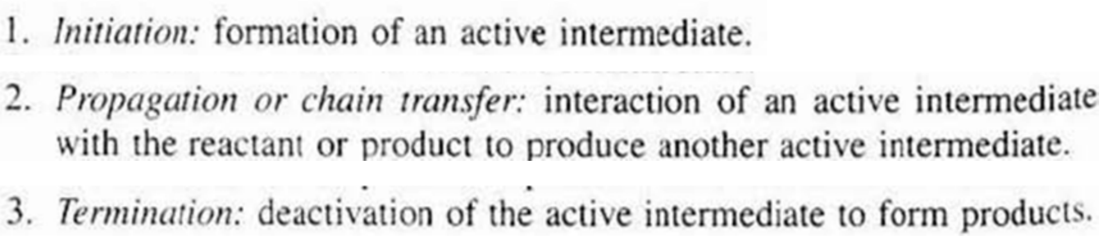
Example Cont.

Example Cont.

Example Cont.

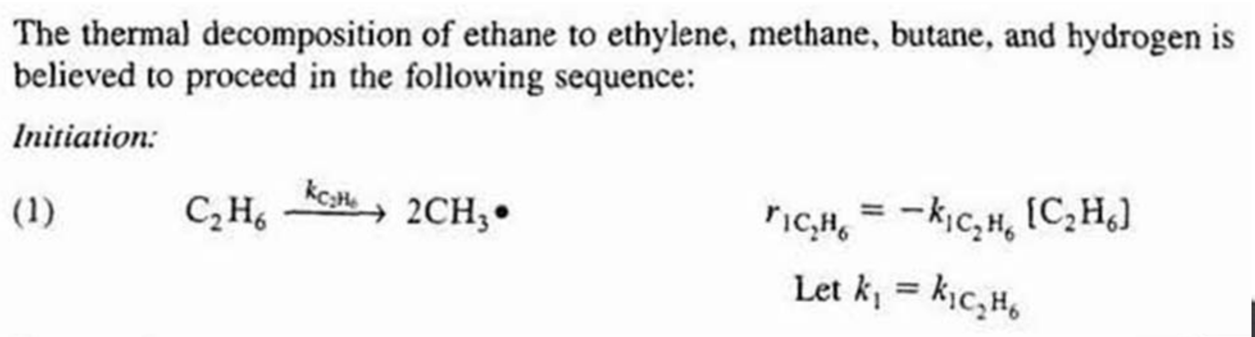
Chain Reactions

- A chain reaction consists of the following sequence



1. *Initiation:* formation of an active intermediate.
2. *Propagation or chain transfer:* interaction of an active intermediate with the reactant or product to produce another active intermediate.
3. *Termination:* deactivation of the active intermediate to form products.

Example



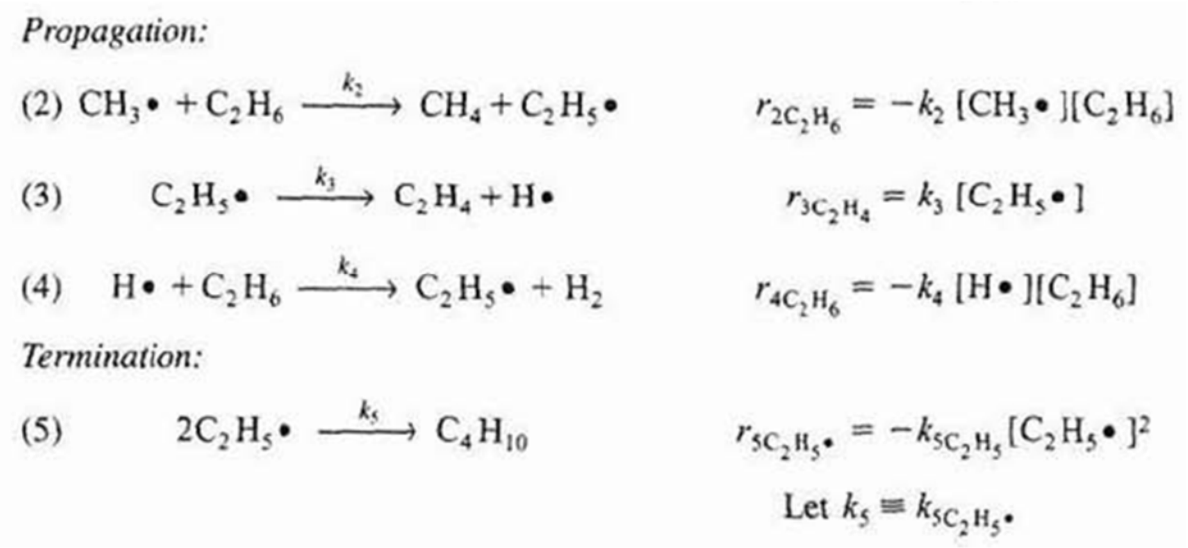
The thermal decomposition of ethane to ethylene, methane, butane, and hydrogen is believed to proceed in the following sequence:

Initiation:

(1) $C_2H_6 \xrightarrow{k_{C_2H_6}} 2CH_3\bullet$ $r_{1C_2H_6} = -k_{1C_2H_6}[C_2H_6]$

Let $k_1 = k_{1C_2H_6}$

Example Cont.



Propagation:

(2) $CH_3\bullet + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5\bullet$ $r_{2C_2H_6} = -k_2[CH_3\bullet][C_2H_6]$

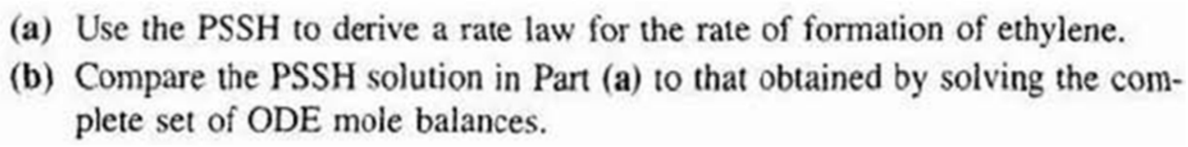
(3) $C_2H_5\bullet \xrightarrow{k_3} C_2H_4 + H\bullet$ $r_{3C_2H_4} = k_3[C_2H_5\bullet]$

(4) $H\bullet + C_2H_6 \xrightarrow{k_4} C_2H_5\bullet + H_2$ $r_{4C_2H_6} = -k_4[H\bullet][C_2H_6]$

Termination:

(5) $2C_2H_5\bullet \xrightarrow{k_5} C_4H_{10}$ $r_{5C_2H_5\bullet} = -k_{5C_2H_5}[C_2H_5\bullet]^2$

Let $k_5 \equiv k_{5C_2H_5\bullet}$



(a) Use the PSSH to derive a rate law for the rate of formation of ethylene.

(b) Compare the PSSH solution in Part (a) to that obtained by solving the complete set of ODE mole balances.

Example Cont.

Example Cont.

Example Cont.

Example Cont.

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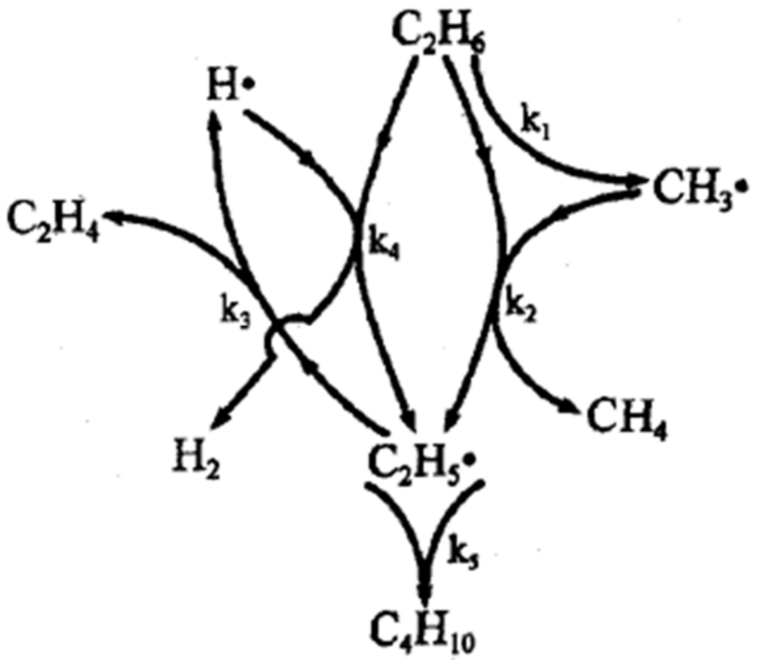
Example Cont.

Example Cont.

Pathway of ethane cracking.



Enzymatic Reaction Fundamentals

- An enzyme is a high-molecular-weight protein or protein-like substance that acts on a substrate (reactant molecule) to transform it chemically at a greatly accelerated rate, usually 10^3 to 10^{17} times faster than the uncatalyzed rate.
- Enzymes are usually present in small quantities and are not consumed during the course of the reaction nor do they affect the chemical reaction equilibrium.
- Enzymes provide an alternate pathway for the reaction to occur thereby requiring a lower activation energy,
- Enzymatic pathways have lower activation energies, enhancements in reaction rates can be enormous
- An important property of enzymes is that they are specific; that is. *One* enzyme can usually catalyze only one type of reaction

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Enzymatic Reaction Fundamentals

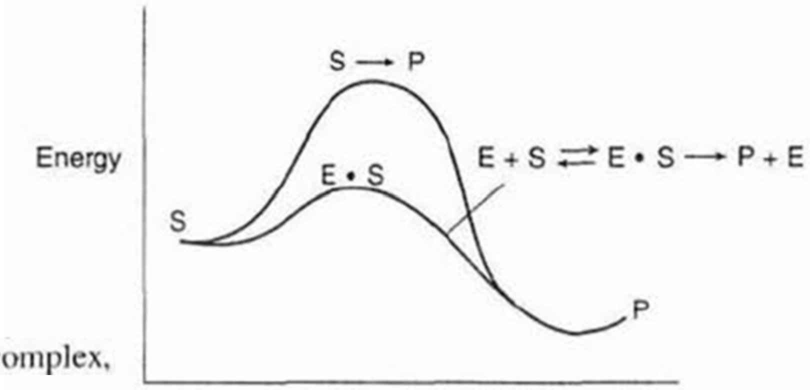
Uncatalyzed reaction

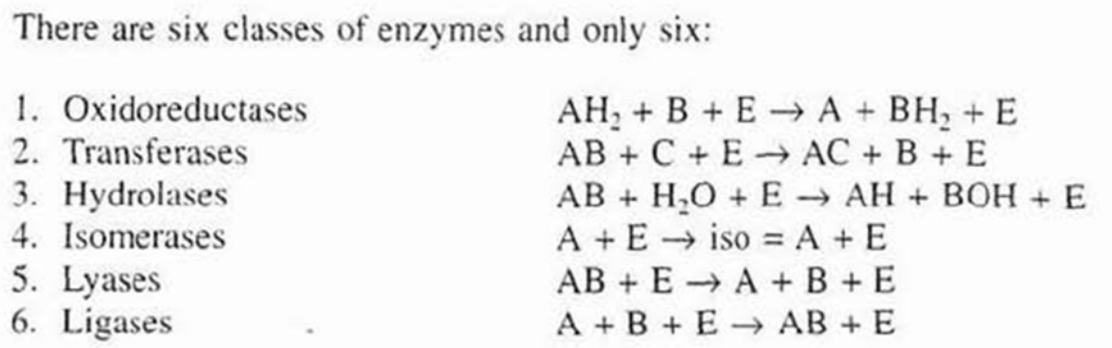
$$S \rightarrow P$$

Catalyzed reaction

$$S + E \rightleftarrows E{\cdot}S \rightarrow E + P$$

$(E \cdot S)$, *active intermediate*
the enzyme–substrate complex,





There are six classes of enzymes and only six:

1. Oxidoreductases $AH_2 + B + E \rightarrow A + BH_2 + E$
2. Transferases $AB + C + E \rightarrow AC + B + E$
3. Hydrolases $AB + H_2O + E \rightarrow AH + BOH + E$
4. Isomerases $A + E \rightarrow iso = A + E$
5. Lyases $AB + E \rightarrow A + B + E$
6. Ligases $A + B + E \rightarrow AB + E$

Enzymatic Reaction Fundamentals

Mechanisms

1. The enzyme urease (E) reacts with the substrate urea (S) to form an enzyme–substrate complex (E • S).

$$NH_2CONH_2 + \text{Urease} \xrightarrow{k_1} [NH_2CONH_2 \bullet \text{Urease}]^*$$

$$S + E \xrightarrow{k_1} E \bullet S \qquad r_{1S} = -k_1\,(E)(S)$$

2. This complex (E • S) can decompose back to urea (S) and urease (E):

$$[NH_2CONH_2 \bullet \text{Urease}]^* \xrightarrow{k_2} \text{Urease} + NH_2CONH_2$$

$$E \bullet S \xrightarrow{k_2} E + S \qquad r_{2S} = k_2\,(E \bullet S)$$

3. Or it can react with water (W) to give the products (P) ammonia and carbon dioxide, and recover the enzyme urease (E).

$$[NH_2CONH_2 \bullet \text{Urease}]^* + H_2O \xrightarrow{k_3} 2NH_3 + CO_2 + \text{Urease}$$

$$E \bullet S + W \xrightarrow{k_3} P + E \qquad r_{3P} = k_3\,(E \bullet S)\,(W)$$

Where $P = 2NH_3 + CO_2$.

Enzymatic Reaction Fundamentals

The net rate of disappearance of the substrate, $-r_S$, is

$$-r_S = k_1(E)(S) - k_2(E \bullet S)$$

The net rate of formation of the enzyme–substrate complex is

$$r_{E \bullet S} = k_1(E)(S) - k_2(E \bullet S) - k_3(W)(E \bullet S)$$

Using the PSSH, $r_{E \bullet S} = 0$,

$$(E \bullet S) = \frac{k_1(E)(S)}{k_2 + k_3(W)}$$

➡ $$-r_S = k_1(E)(S) - k_2\frac{k_1(E)(S)}{k_2 + k_3(W)}$$

Simplifying

$$-r_S = \frac{k_1 k_3(E)(S)(W)}{k_2 + k_3(W)}$$

Enzymatic Reaction Fundamentals

In the absence of enzyme denaturization,

$$(E_t) = (E) + (E \bullet S) \qquad (\text{kmol/m}^3 \text{ or g/dm}^3).$$

(E), Concentrations of the free or unbonded enzyme

(E_t): total concentration of the enzyme *in* the *system*

$(E \bullet S)$: the enzyme–substrate complex.

$$\rightarrow \quad (E_t) = (E) + \frac{k_1(E)(S)}{k_2 + k_3(W)}$$

$$\rightarrow \quad (E) = \frac{(E_t)(k_2 + k_3(W))}{k_2 + k_3(W) + k_1(S)}$$

$$\rightarrow \quad -r_S = \frac{k_1 k_3(W)(E_t)(S)}{k_1(S) + k_2 + k_3(W)}$$

Enzymatic Reaction Fundamentals

Assuming the concentration of water is constant and dividing the numerator and denominator by k

$$-r_S = \frac{k_{cat}(E_t)(S)}{(S) + K_M} \qquad \text{Where} \quad k_{cat} = k_3(W) \text{ and } K_M = \frac{k_{cat} + k_2}{k_1}$$

Michaelis–Menten equation

K_M (mol/dm³) is the Michaelis constant *affinity* constant

a measure of the attraction of the enzyme for its substrate.

k_{cat} is also referred to as the *turnover number*.

It is the number of substrate molecules converted to product in a given time on a single-enzyme molecule when the enzyme is saturated with substrate (i.e., all the active sites on the enzyme are occupied, S>>K_M).

Enzymatic Reaction Fundamentals

let $V_{\max}$ represent the maximum rate of reaction for a given total enzyme concentration,

$$V_{\max} = k_{cat}(\mathrm{E}_t)$$

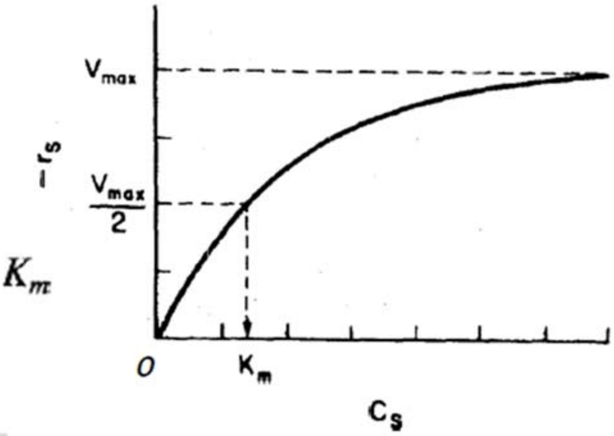
$$\rightarrow \quad -r_s = \frac{V_{\max}(\mathrm{S})}{K_m + (\mathrm{S})}$$

At low substrate concentration,

$$-r_s \cong \frac{V_{\max}(\mathrm{S})}{K_m}$$

At high substrate concentration, $(\mathrm{S}) \gg K_m$

$$-r_s \cong V_{\max}$$



Enzymatic Reaction Fundamentals

Consider the case when the substrate concentration is such that the reaction rate is equal to one-half the maximum rate,

$$-r_s = \frac{V_{\max}}{2} \quad \rightarrow \quad \frac{V_{\max}}{2} = \frac{V_{\max}(\mathrm{S}_{1/2})}{K_m + (\mathrm{S}_{1/2})}$$

the Michaelis constant $K_m = (\mathrm{S}_{1/2})$

For Evaluation of Michaelis-Menten Parameters

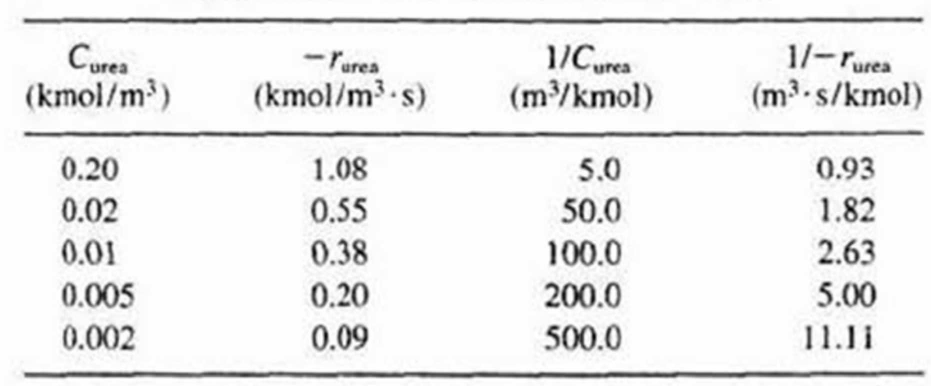
$$\frac{1}{-r_s} = \frac{(\mathrm{S}) + K_M}{V_{\max}(\mathrm{S})} = \frac{1}{V_{\max}} + \frac{K_M}{V_{\max}}\frac{1}{(\mathrm{S})}$$

Lineweaver–Burk

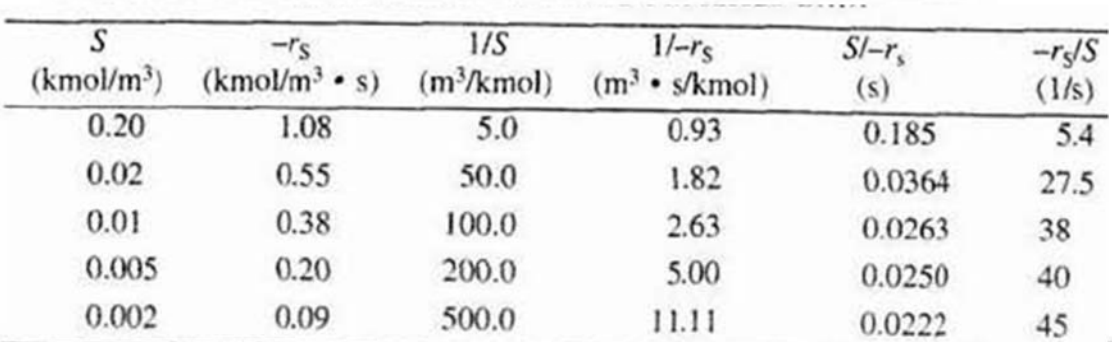
$$\frac{(S)}{-r_S} = \frac{K_M}{V_{\max}} + \frac{1}{V_{\max}}(S)$$

Eadie–Hofstee form,

Enzymatic Reaction Fundamentals



C_{urea} (kmol/m^3)	$-r_{urea}$ (kmol/m$^3\cdot$s)	$1/C_{urea}$ (m^3/kmol)	$1/-r_{urea}$ (m$^3\cdot$s/kmol)
0.20	1.08	5.0	0.93
0.02	0.55	50.0	1.82
0.01	0.38	100.0	2.63
0.005	0.20	200.0	5.00
0.002	0.09	500.0	11.11



S (kmol/m^3)	$-r_S$ (kmol/m^3 • s)	$1/S$ (m^3/kmol)	$1/-r_S$ (m^3 • s/kmol)	$S/-r_s$ (s)	$-r_S/S$ (1/s)
0.20	1.08	5.0	0.93	0.185	5.4
0.02	0.55	50.0	1.82	0.0364	27.5
0.01	0.38	100.0	2.63	0.0263	38
0.005	0.20	200.0	5.00	0.0250	40
0.002	0.09	500.0	11.11	0.0222	45

Enzymatic Reaction Fundamentals

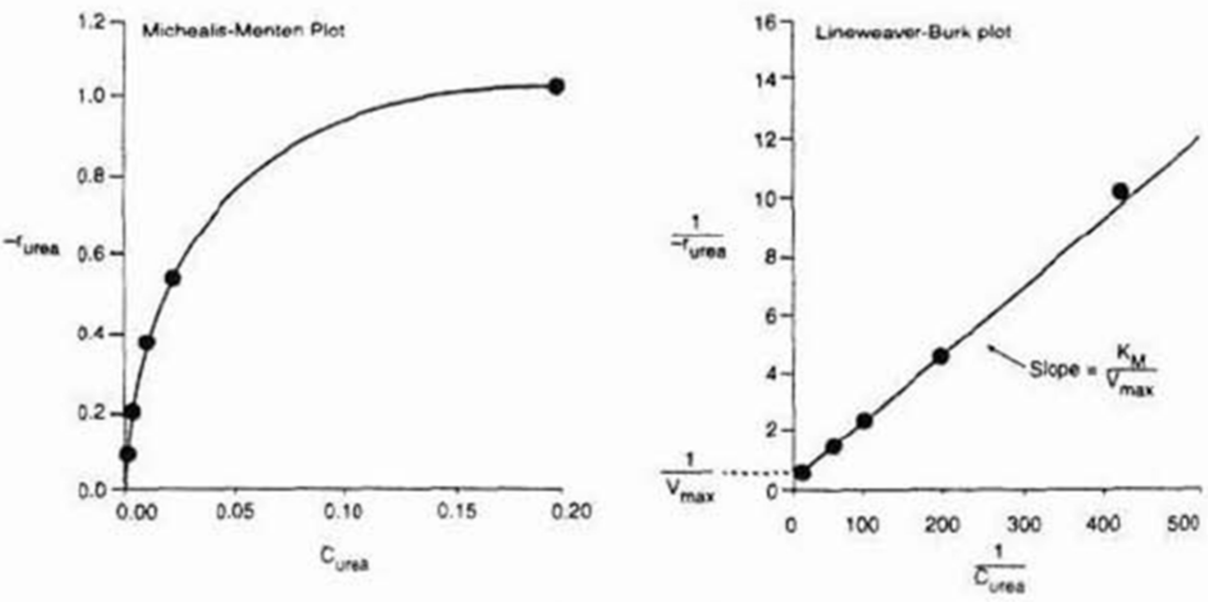


Figure E7-3.1 (a)Michaelis–Menten plot; (b) Lineweaver–Burk plot.

Enzymatic Reaction Fundamentals

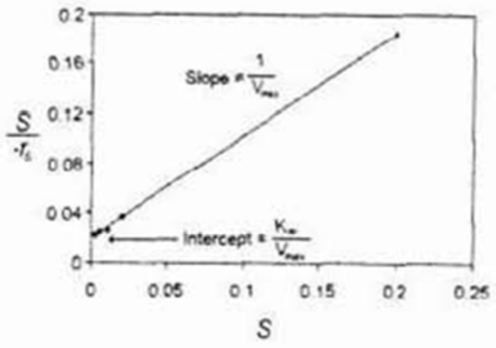


Figure E7-3.2 Hanes–Woolf plot.

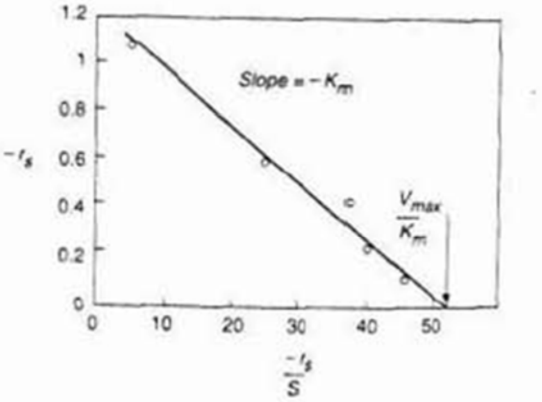


Figure E7-3.3 Eadie-Hofstee plot.

Batch Reactor Calculations for Enzyme Reactions

Batch Reactor Calculations for Enzyme Reactions

$$-\frac{dN_{\text{urea}}}{dt} = -r_{\text{urea}}V \quad \Rightarrow \quad -\frac{dC_{\text{urea}}}{dt} = -r_{\text{urea}}$$

The rate law for urea decomposition is

$$-r_{\text{urea}} = \frac{V_{\max}C_{\text{urea}}}{K_M + C_{\text{urea}}}$$

$$\Rightarrow \quad t = \int_{C_{\text{urea}}}^{C_{\text{urea0}}} \frac{dC_{\text{urea}}}{-r_{\text{urea}}} = \int_{C_{\text{urea}}}^{C_{\text{urea0}}} \frac{K_M + C_{\text{urea}}}{V_{\max}C_{\text{urea}}}\, dC_{\text{urea}}$$

$$t = \frac{K_M}{V_{\max}} \ln \frac{C_{\text{urea0}}}{C_{\text{urea}}} + \frac{C_{\text{urea0}} - C_{\text{urea}}}{V_{\max}}$$

Batch Reactor Calculations for Enzyme Reactions

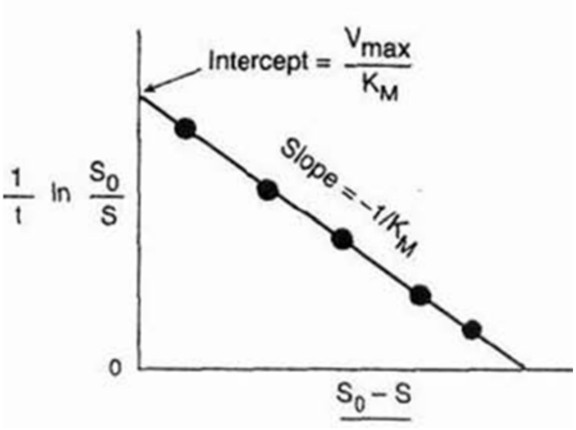
$$C_{\text{urea}} = C_{\text{urea}0}(1 - X)$$

$$t = \frac{K_M}{V_{\max}} \ln \frac{1}{1-X} + \frac{C_{\text{urea}0} X}{V_{\max}}$$

$$\frac{1}{t} \ln \frac{1}{1-X} = \frac{V_{\max}}{K_M} - \frac{C_{\text{urea}0} X}{K_M t}$$

in terms of the substrate concentration S:

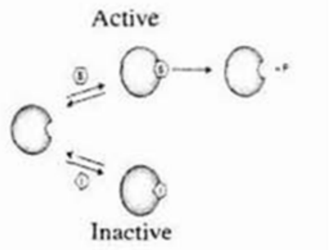
$$\frac{1}{t} \ln \frac{S_0}{S} = \frac{V_{\max}}{K_M} - \frac{S_0 - S}{K_M t}$$



Inhibition of Enzyme Reactions

Competitive Inhibition

- In competitive inhibition another substance, I, competes with the substrate for the enzyme molecules to form an inhibitor-enzyme complex



(1) $E + S \xrightarrow{k_1} E \bullet S$

(2) $E \bullet S \xrightarrow{k_2} E + S$

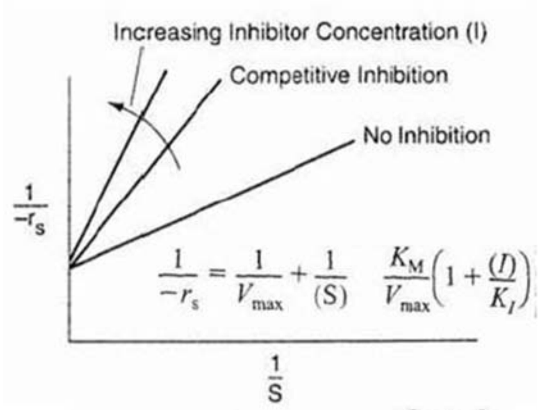
(3) $E \bullet S \xrightarrow{k_3} P + E$ $\qquad r_P = k_3 (E \bullet S)$

(4) $I + E \xrightarrow{k_4} E \bullet I$ (inactive)

(5) $E \bullet I \xrightarrow{k_5} E + I$

$$r_P = -r_S = \frac{V_{\max}(S)}{S + K_M\left(1 + \frac{I}{K_I}\right)}$$

the inhibition constant K_I (mol/dm³) is $K_I = \frac{k_5}{k_4}$



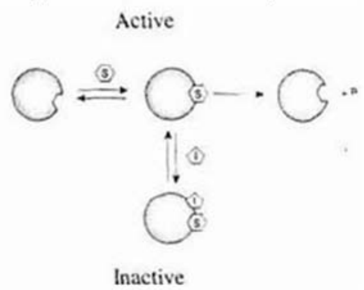
$$\frac{1}{-r_s} = \frac{1}{V_{\max}} + \frac{1}{(S)} \frac{K_M}{V_{\max}}\left(1 + \frac{(I)}{K_I}\right)$$

$$V_{\max} = k_3 E_t \text{ and } K_M = \frac{k_2 + k_3}{k_1}$$

Inhibition of Enzyme Reactions

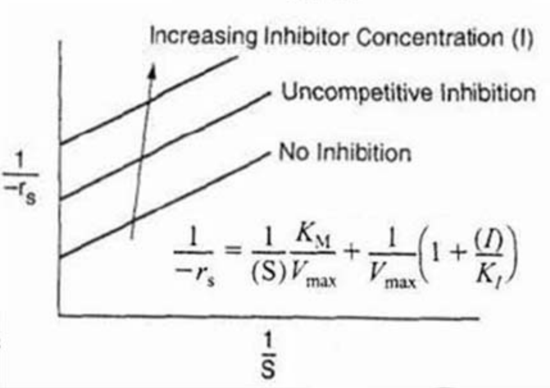
Uncompetitive Inhibition

- The inhibitor has no affinity for the enzyme itself and thus does not compete with the substrate for the enzyme; instead it ties up the enzyme-subs complex by forming an inhibitor-enzyme-substrate complex. (I .E.S) which is inactive.



$$
\begin{array}{ll}
(1) & E + S \xrightarrow{k_1} E \bullet S \\
(2) & E \bullet S \xrightarrow{k_2} E + S \\
(3) & E \bullet S \xrightarrow{k_3} P + E \\
(4) & I + E \bullet S \xrightarrow{k_4} I \bullet E \bullet S \ \text{(inactive)} \\
(5) & I \bullet E \bullet S \xrightarrow{k_5} I \bullet E \bullet S
\end{array}
$$

$$-r_s = r_p = \frac{V_{max}(S)}{K_M + (S)\left(1 + \frac{(I)}{K_I}\right)} \quad \text{where } K_I = \frac{k_5}{k_4}$$

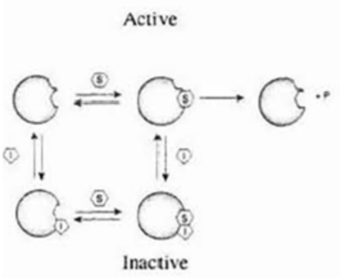


$$\frac{1}{-r_s} = \frac{1}{(S)}\frac{K_M}{V_{max}} + \frac{1}{V_{max}}\left(1 + \frac{(I)}{K_I}\right)$$

Inhibition of Enzyme Reactions

Noncompetitive Inhibition (Mixed Inhibition)

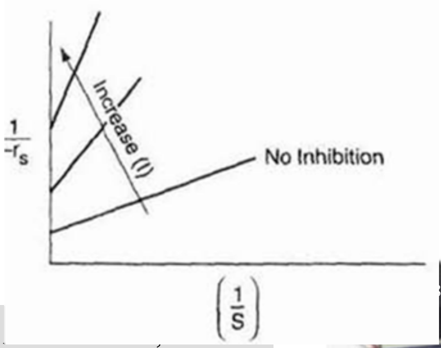
- In noncompetitive inhibition, also called mixed inhibition, the substrate and inhibitor molecules react with different types of sites on the enzyme molecule. Whenever the inhibitor is attached to the enzyme it is inactive and cannot form products



$$
\begin{array}{ll}
(1) & E + S \rightleftarrows E \bullet S \\
(2) & E + I \rightleftarrows I \bullet E \ \text{(inactive)} \\
(3) & I + E \bullet S \rightleftarrows I \bullet E \bullet S \ \text{(inactive)} \\
(4) & S + I \bullet E \rightleftarrows I \bullet E \bullet S \ \text{(inactive)} \\
(5) & E \bullet S \longrightarrow P
\end{array}
$$

$$-r_s = \frac{V_{max}(S)}{((S) + K_M)\left(1 + \frac{(I)}{K_I}\right)}$$

$$\frac{1}{-r_s} = \frac{1}{V_{max}}\left(1 + \frac{(I)}{K_I}\right) + \frac{1}{(S)}\frac{K_M}{V_{max}}\left(1 + \frac{(I)}{K_I}\right)$$



Inhibition of Enzyme Reactions

Substrate Inhibition

the substrate itself can act as a inhibitor.

$$S + E \cdot S \longrightarrow S \cdot E \cdot S \quad \text{(inactive)}$$

$$-r_s = \frac{V_{\max} S}{K_M + S + \dfrac{S^2}{K_I}}$$