

BT209

Bioreaction Engineering

16/01/2023

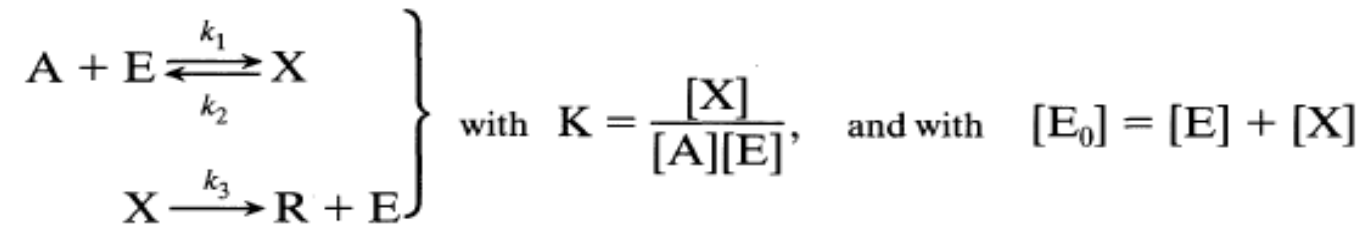
Problem 1

Ex-1: A reaction has the stoichiometric equation $A+2B=3T$.

What is the order of reaction?

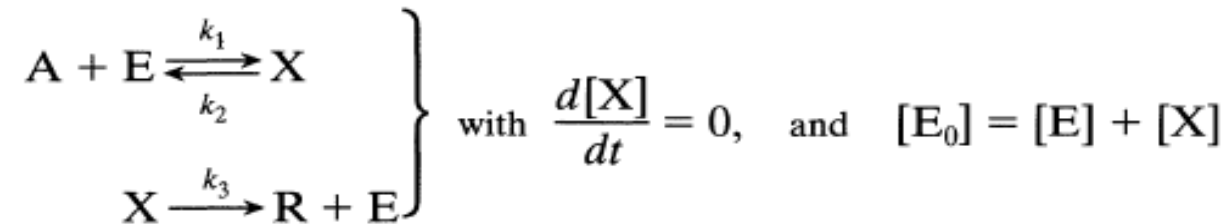
Problem 2

Mechanism for enzyme catalyzed reactions. To explain the kinetics of enzyme-substrate reactions, Michaelis and Menten (1913) came up with the following mechanism, which uses an equilibrium assumption



and where $[E_0]$ represents the total enzyme and $[E]$ represents the free unattached enzyme.

G. E. Briggs and J. B. S. Haldane, *Biochem J.*, **19**, 338 (1925), on the other hand, employed a steady-state assumption in place of the equilibrium assumption

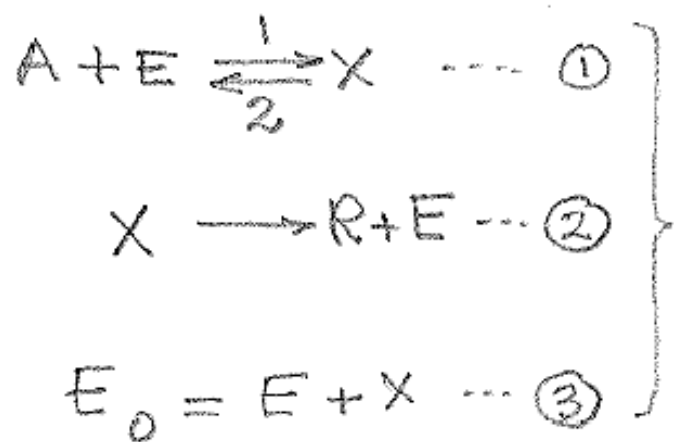


What final rate form $-r_A$ in terms of $[A]$, $[E_0]$, k_1 , k_2 , and k_3 does

(a) the Michaelis-Menten mechanism give?

(b) the Briggs-Haldane mechanism give?

with



M-M assume that the reverse reactions of $\textcircled{1}$ approach equilibrium quickly, or

$$K = \frac{X}{AE} = \frac{k_1}{k_2} \quad \dots \textcircled{4}$$

B-H assume that quickly

$$dX/dt = 0 \quad \dots \textcircled{5}$$

For M-M

From (2)

$$r_R = k_3 X \dots (6)$$

From (5)

$$X = \frac{k_1}{k_2} AE$$

Eliminate E with (3)

$$X = \frac{k_1}{k_2} A(E_0 - X)$$

or

$$X = \frac{\frac{k_1}{k_2} AE_0}{1 + \frac{k_1}{k_2} A} \dots (7)$$

Eq (7) in (6) gives

$$r_R = \frac{k_3 AE_0}{\frac{k_2}{k_1} + A}$$

These equations give essentially the same result

For B-H

From (2)

$$r_R = k_3 X \dots (8)$$

From (5)

$$\frac{dX}{dt} = 0 = k_1 AE - (k_2 + k_3) X$$

Eliminate E with (3)

$$k_1 A(E_0 - X) - (k_2 + k_3) X = 0$$

or

$$X = \frac{k_1 AE_0}{k_1 A + k_2 + k_3} \dots (9)$$

Eq (9) in (8) gives

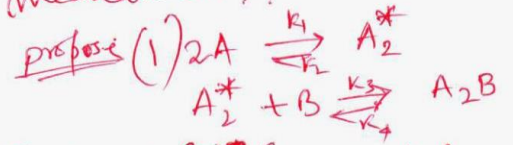
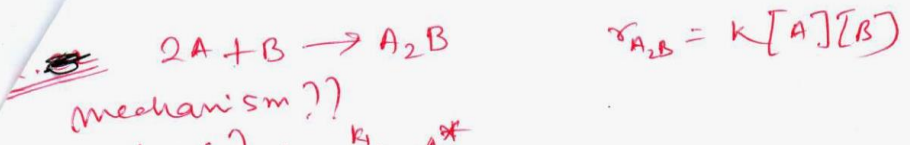
$$r_R = \frac{k_3 AE_0}{\frac{k_2 + k_3}{k_1} + A}$$

This is called the Michaelis constant, C_M

Problem 3

Come up with (guess and then verify) a mechanism that is consistent with the experimentally found rate equation for the following reaction





$$r_{A_2B} = k_3 C_{A_2^*} C_B - k_4 C_{A_2B}$$

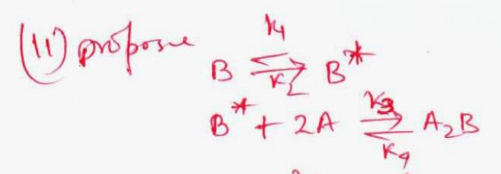
$$r_{A_2^*} = k_1 C_A^2 - k_2 C_{A_2^*} - k_3 C_{A_2^*} C_B + k_4 C_{A_2B} = 0$$

$$C_{A_2^*} = \frac{k_1 C_A^2 + k_4 C_{A_2B}}{k_2 + k_3 C_B}$$

$$r_{A_2B} = k_3 \left[\frac{k_1 C_A^2 + k_4 C_{A_2B}}{k_2 + k_3 C_B} \right] C_B - k_4 C_{A_2B}$$

$$k_4 \rightarrow 0 \quad r_{A_2B} = \frac{k_1 k_3 C_A^2 C_B}{k_2 + k_3 C_B}$$

i) $k_2 \gg k_3 C_B$
 $r_{A_2B} = k C_A^2 C_B$
 ii) $k_2 \leq k_3 C_B$
 $r_{A_2B} = k_1 C_A^2$



$$r_{A_2B} = k_3 C_{B^*} C_A^2 - k_4 C_{A_2B}$$

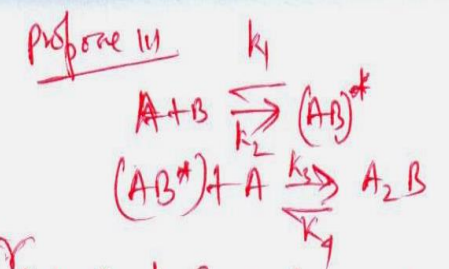
$$r_{B^*} = k_1 C_B - k_2 C_{B^*} - k_3 C_{B^*} C_A^2 + k_4 C_{A_2B} = 0$$

$$C_{B^*} = \frac{k_1 C_B + k_4 C_{A_2B}}{k_2 + k_3 C_A^2}$$

$$r_{A_2B} = k_3 C_A^2 \left[\frac{k_1 C_B + k_4 C_{A_2B}}{k_2 + k_3 C_A^2} \right] - k_4 C_{A_2B}$$

$$k_4 \rightarrow 0 \quad r_{A_2B} = \frac{k_1 k_3 C_A^2 C_B}{k_2 + k_3 C_A^2}$$

$k_2 \gg k_3 C_A^2$
 $k_2 \leq k_3 C_A^2$



$$r_{A_2B} = k_3 C_{AB^*} C_A - k_4 C_{A_2B}$$

$$r_{AB^*} = k_1 C_A C_B - k_2 C_{AB^*} - k_3 C_{AB^*} C_A + k_4 C_{A_2B} = 0$$

$$C_{AB^*} = \frac{k_1 C_A C_B + k_4 C_{A_2B}}{k_2 + k_3 C_A}$$

$$r_{A_2B} = k_3 \left[\frac{k_1 C_A C_B + k_4 C_{A_2B}}{k_2 + k_3 C_A} \right] - k_4 C_{A_2B}$$

$$k_4 \rightarrow 0 \Rightarrow r_{A_2B} = \frac{k_1 k_3 C_A C_B}{k_2 + k_3 C_A}$$

(i) $k_2 \gg k_3 C_A$
 $r_{A_2B} = k C_A C_B \checkmark$

Problem 2

For a gas reaction at 400 K the rate is reported as

$$-\frac{dp_A}{dt} = 3.66p_A^2, \quad \text{atm/hr}$$

- (a) What are the units of the rate constant?
- (b) What is the value of the rate constant for this reaction if the rate equation is expressed as

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = kC_A^2, \quad \text{mol/m}^3 \cdot \text{s}$$

a) We are given $-\frac{dp_A}{dt} = k_p p_A^2$

\nearrow atm/hr \nearrow 3.66 \nearrow (atm)²

Balancing dimensions we find $k_p = 3.66 (\text{atm})^{-1} (\text{hr})^{-1}$ ————— a)

b) For an ideal gas $p_A V = n_A RT$ or $p_A = C_A RT$

Thus $-\frac{dp_A}{dt} = 3.66 p_A^2$... becomes ... $-\frac{d(C_A RT)}{dt} = 3.66 (C_A RT)^2$

or $-\frac{dC_A}{dt} = \underbrace{[3.66 (\text{atm})^{-1} \text{hr}^{-1}] RT}_{\text{new rate constant} = k'} C_A^2$

where $k' = 3.66 \frac{1}{\text{atm} \cdot \text{hr}} \cdot \frac{(1 \text{ atm})(22.4 \text{ l})}{(1 \text{ mol})(273^\circ \text{K})} \cdot (400^\circ \text{K}) = 120 (\text{hr})^{-1} (\text{mol/l})^{-1}$ ————— b)

Problem 3

On doubling the concentration of reactant, the rate of reaction triples for the reaction $A \rightarrow B$.

Find the reaction order

$$-r_A = k C_A^n \quad \dots \quad \frac{-r_2}{-r_1} = \frac{k (2C_A)^n}{k C_A^n} = 2^n \quad \therefore n = 1.585$$

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