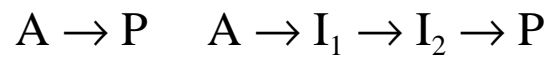
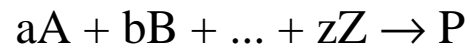


## Elementary Reactions



Rate equation



$$\text{rate} = k[A]^a[B]^b \dots [Z]^z$$

k is rate constant

Order is the sum of the exponents

For elementary reactions, order is the molecularity

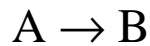
## Rates of reaction

$$v = -\frac{d[A]}{dt} = \frac{d[P]}{dt}$$

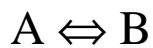
### Zero order

$$-\frac{d[A]}{dt} = k_0 \quad [A] = [A]_0 - k_0 t$$
$$k_0 = \text{M s}^{-1} \quad t_{1/2} = \frac{[A]_0}{2k_0}$$

### First order



$$-\frac{d[A]}{dt} = k_1[A] \quad [A] = [A]_0 e^{-k_1 t}$$
$$k_1 = \text{s}^{-1} \quad t_{1/2} = \frac{\ln 2}{k_1}$$

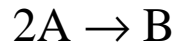


$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]$$

at equilibrium, rate = 0

$$\frac{[B]_{eq}}{[A]_{eq}} = \frac{k_1}{k_{-1}} = K_{eq}$$

## Second order



$$-\frac{1}{2} \frac{d[A]}{dt} = k_2[A]^2 \quad \frac{1}{[A]} = \frac{1}{[A]_0} + 2k_2t$$

$$k_2 = \text{M}^{-1} \text{s}^{-1} \quad t_{1/2} = \frac{1}{k_2[A]_0}$$



$$-\frac{d[A]}{dt} = k_2[A][B] \quad [B] = [A] \frac{[B]_0}{[A]_0} e^{-k_2t([B]_0 - [A]_0)}$$

## Graph methods

### First order reactions

$\ln[A]$  vs  $t$

initial rate vs  $[A]_0$

slope =  $-k_1$  or  $k_1$

### Second order reactions

$[A]^{-1}$  vs  $t$

initial rate vs  $[A]_0^2$

slope =  $2k_2$

## Michaelis-Menten Equation

Sucrose + H<sub>2</sub>O → glucose + fructose



$$v = \frac{d[\mathbf{P}]}{dt} = k_2[\mathbf{ES}]$$

$$\frac{d[\mathbf{ES}]}{dt} = k_1[\mathbf{E}][\mathbf{S}] - k_{-1}[\mathbf{ES}] - k_2[\mathbf{ES}]$$

Need to make assumptions to solve this:

1. Assume equilibrium

$$K_s = \frac{k_{-1}}{k_1} = \frac{[\mathbf{E}][\mathbf{S}]}{[\mathbf{ES}]}$$

2. Assume steady state

$$\frac{d[\mathbf{ES}]}{dt} = 0$$

$$[\mathbf{E}]_T = [\mathbf{E}] + [\mathbf{ES}]$$

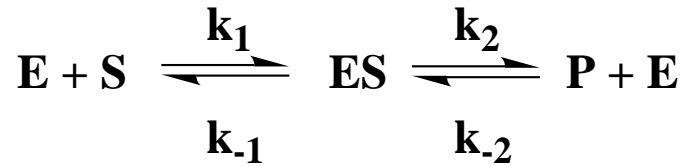
$$v_0 = k_2[\mathbf{ES}] = \frac{k_2[\mathbf{E}]_T[\mathbf{S}]}{K_m + [\mathbf{S}]}$$

$$\text{where } K_m = \frac{k_{-1} + k_2}{k_1}$$

$$\text{define } V_{\max} = k_2[\mathbf{E}]_T$$

$$v_0 = \frac{V_{\max}[\mathbf{S}]}{K_m + [\mathbf{S}]}$$

## Reversible Reactions



$$v = \frac{\frac{V_{\max}^f [S]}{K_m^S} - \frac{V_{\max}^r [P]}{K_m^P}}{1 + \frac{[S]}{K_m^S} + \frac{[P]}{K_m^P}}$$

$$\text{where } V_{\max}^f = k_2[E]_T \quad V_{\max}^r = k_{-1}[E]_T$$

$$K_m^S = \frac{k_{-1} + k_2}{k_1} \quad K_m^P = \frac{k_{-1} + k_2}{k_{-2}}$$

$$[E]_T = [E] + [ES]$$

## Haldane Relationship

Kinetic parameters of a reversible enzymatically catalyzed reaction are related by the equilibrium constant

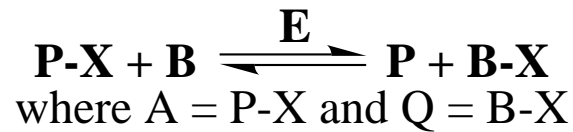
set  $v = 0$  and solve:

$$K_{\text{eq}} = \frac{[P]}{[S]} = \frac{V_{\max}^f K_m^P}{V_{\max}^r K_m^S}$$

## Bisubstrate Reactions



Almost all are transferase (transfer of functional group)



or oxidation-reduction (transfer of reducing equivalents)  
reactions

Terminology:

substrates - A, B, C in order they add to enzyme

products - P, Q, R in order they leave enzyme

stable enzyme forms - E, F, G

Uni - one

Bi - two

Ter - three

Quad - four

Applies to naming reactions type - i.e., one S and two P

Uni Bi reaction

Cleland Notation

## **Sequential - Single Displacement reaction**

transfer of functional group directly from

A (=P-X) to B yielding P and Q (=B-X)

Ordered

NAD<sup>+</sup>- and NADP<sup>+</sup>-requiring dehydrogenases

Random

dehydrogenases and kinases

## **Ping Pong - Double Displacement reaction**

transfer of functional group to enzyme  
and release of first product

then transfer of bound functional group  
from enzyme to second substrate  
to release second product

chymotrypsin, transaminases, some flavoenzymes

## Isotope Exchange

May be used to distinguish between single- (Sequential) and double-displacement (Ping Pong) reactions

Sequential reactions do not exchange isotope labels

Ping Pong reactions are capable of exchanging an isotope from the first product P back to the first substrate A in the absence of the second substrate



where A = P-X, Q = B-X and X is the transferred group





Compare sucrose phosphorylase with maltose phosphorylase:

