Class 4: Unimolecular reactions and enzyme kinetics

$$k \propto T^{1/2} e^{-E_a/RT}$$

cis-2-butene $\rightleftharpoons$ trans-2-butene

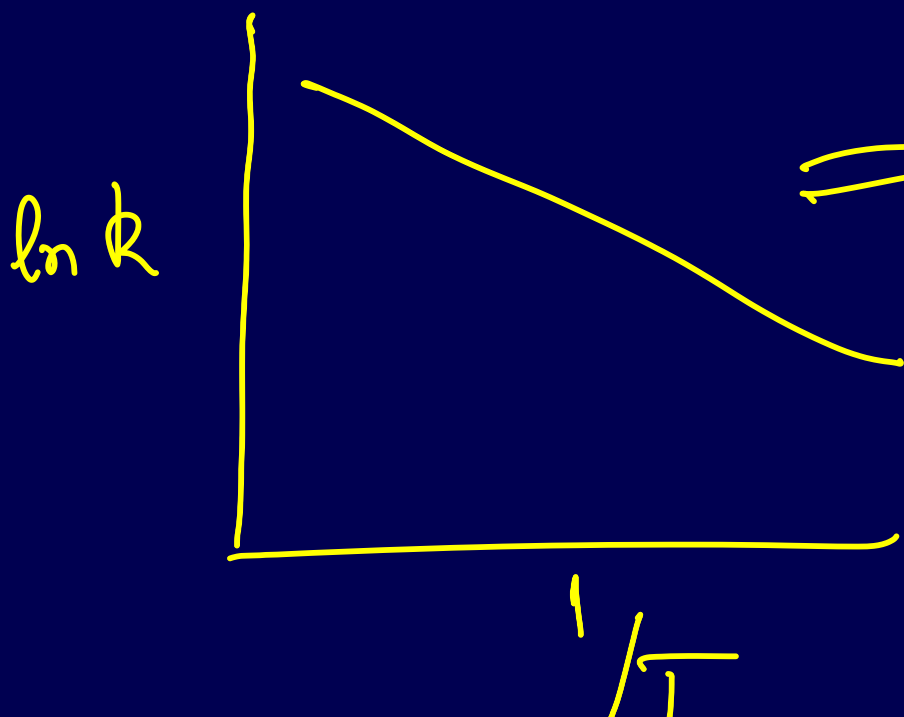
$CH_3NC \rightleftharpoons CH_3CN$

cyclopropane $\rightleftharpoons$ propene

For the 3 reactions given above and for a host of other reactions we find that

(a) Rate = k [reactant]

(b)



⇒ Thermal reaction

↓

collisions

Qn: How can you have unimolecular collision reactions?

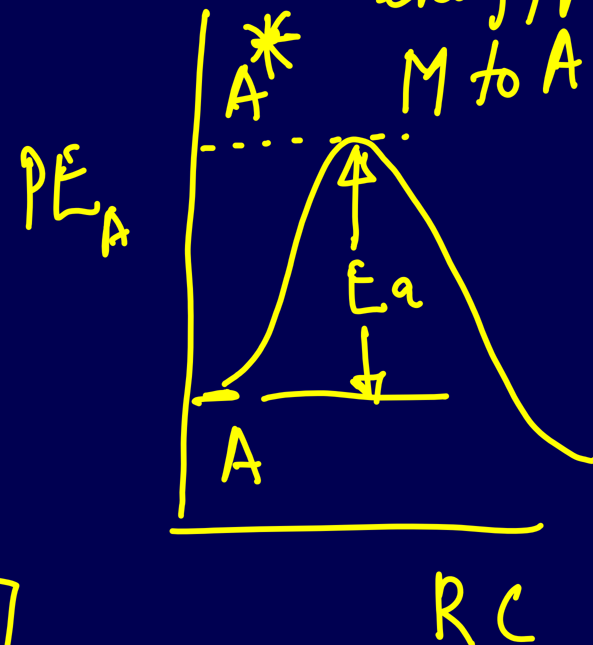
Lindemann mechanism

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

(transfer of energy from M to A

M: any species with excess energy

A^* has more energy than E_a



$$A^* \xrightarrow{k_2} P$$

$$\frac{d[P]}{dt} = k_2 [A^*]$$

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*]$$

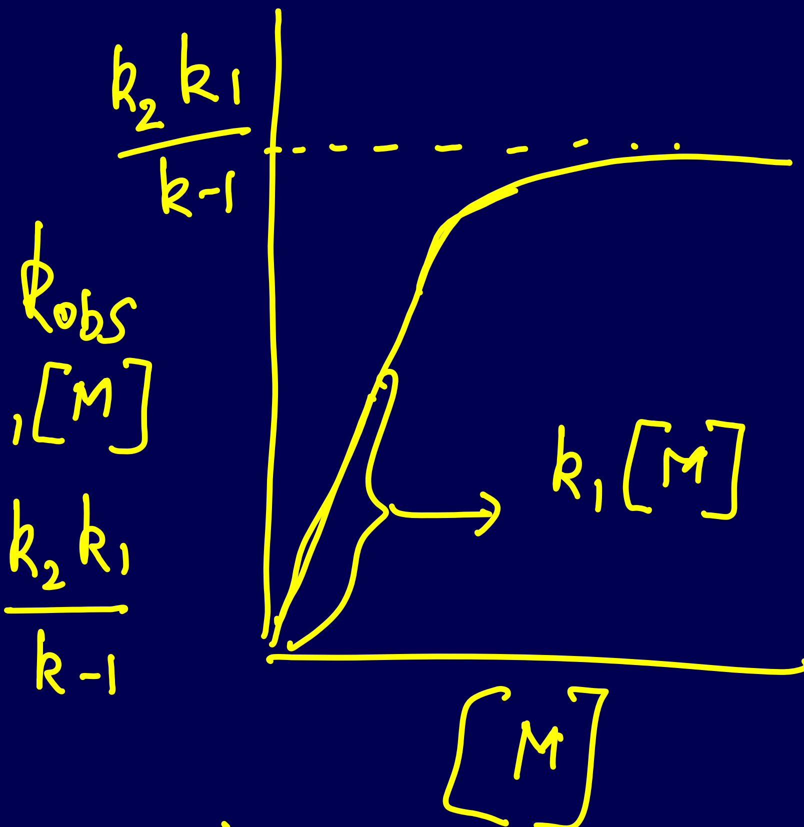
$$[A^*]_{ss} = \frac{k_1[A][M]}{k_2 + k_{-1}[M]}$$

$$\text{Rate} = \frac{k_2 k_1 [A][M]}{k_2 + k_{-1}[M]} = k_{obs}[A]$$

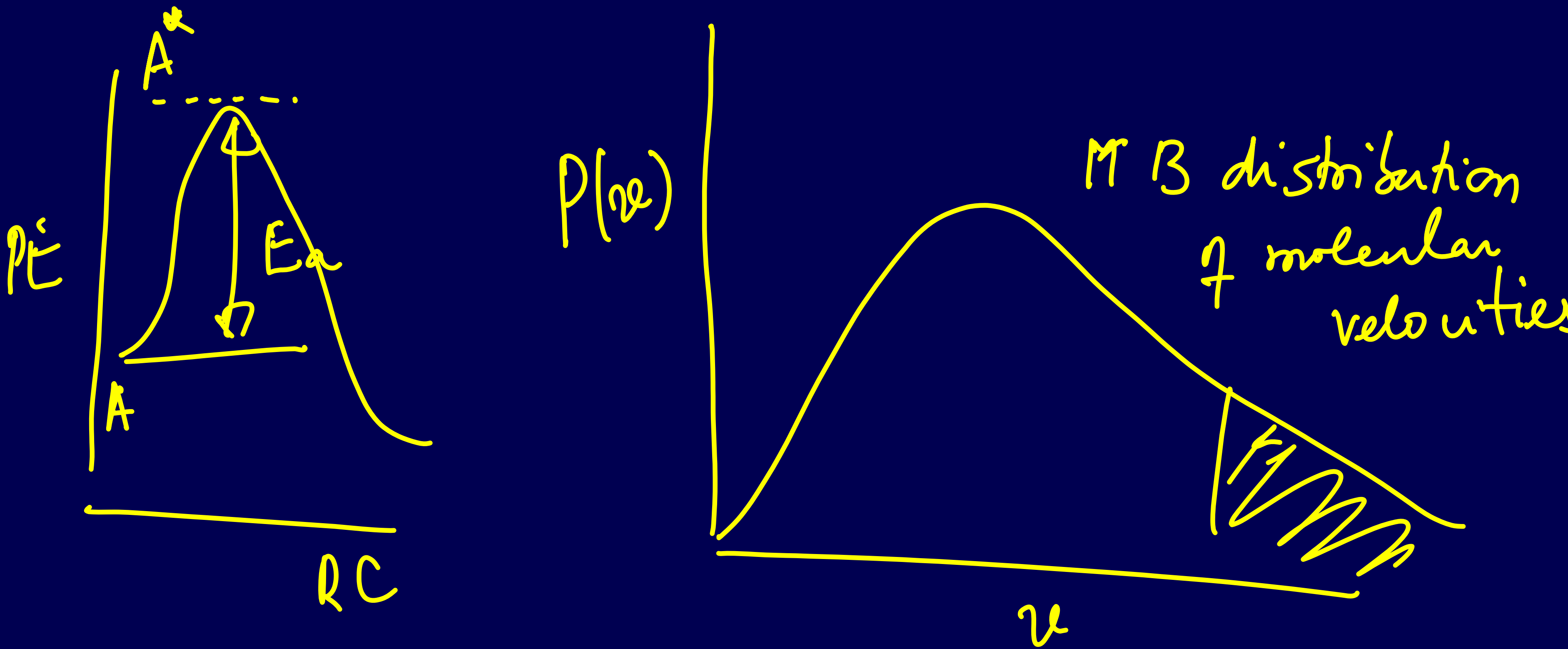
$$k_{obs} = \frac{k_2 k_1 [M]}{k_{-1}[M] + k_2}$$

If $k_{-1}[M] \ll k_2$, $k_{obs} = k_1[M]$

If $k_{-1}[M] \gg k_2$, $k_{obs} = \frac{k_2 k_1}{k_{-1}}$



and $-\frac{d[A]}{dt} = k_{obs}[A] \rightarrow$ unimolecular


A*
PE
Ea
A
RC
P(v)
v
M B distribution of molecular velocities

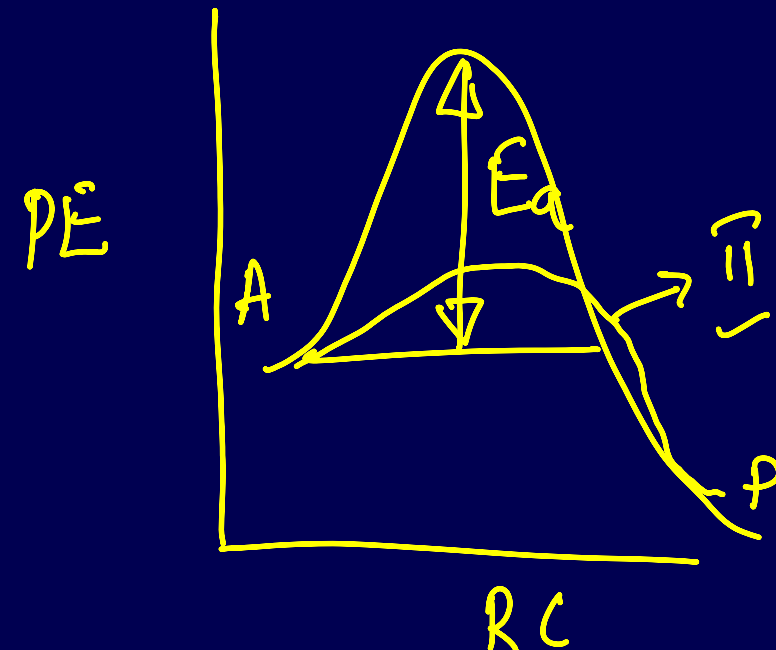
Enzyme catalysis

$A \longrightarrow P$

k_{uncat}

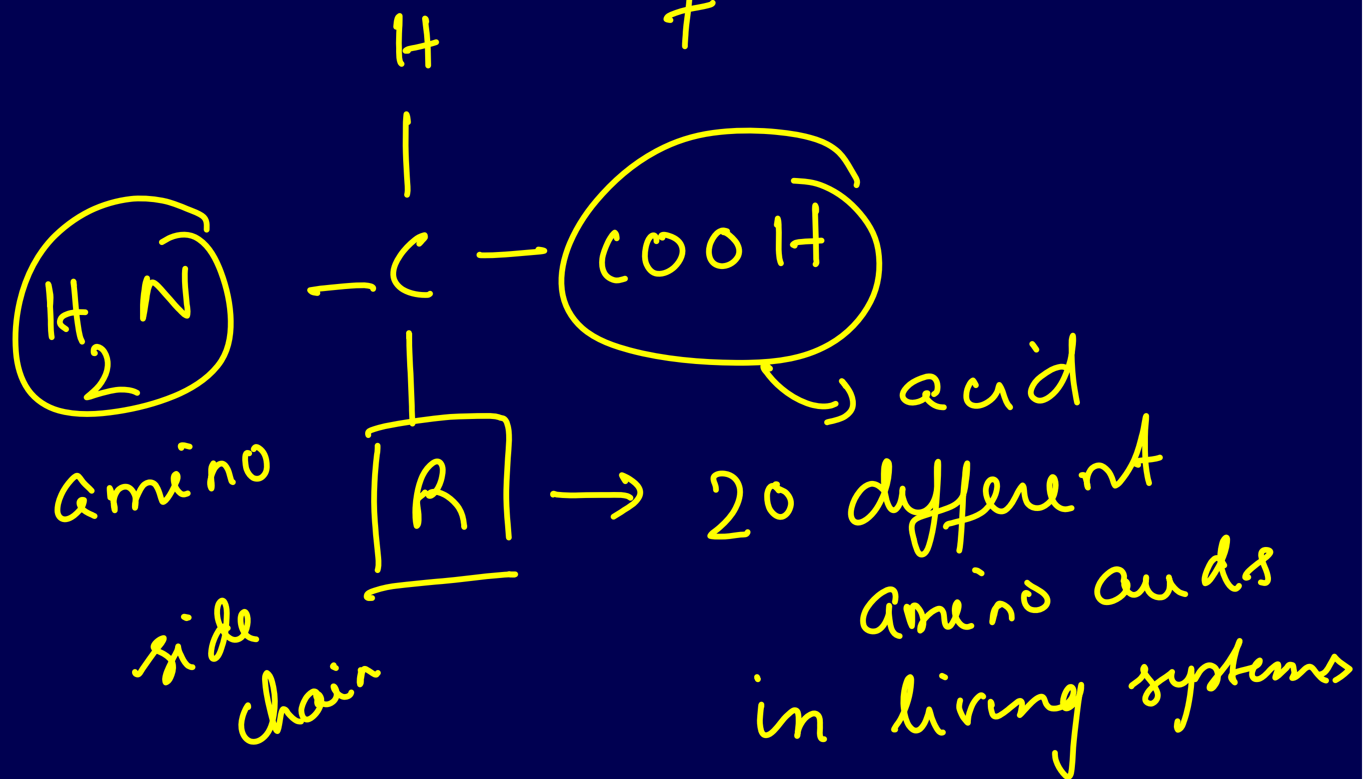
$A \longrightarrow P$

$k_{catalyzed}$

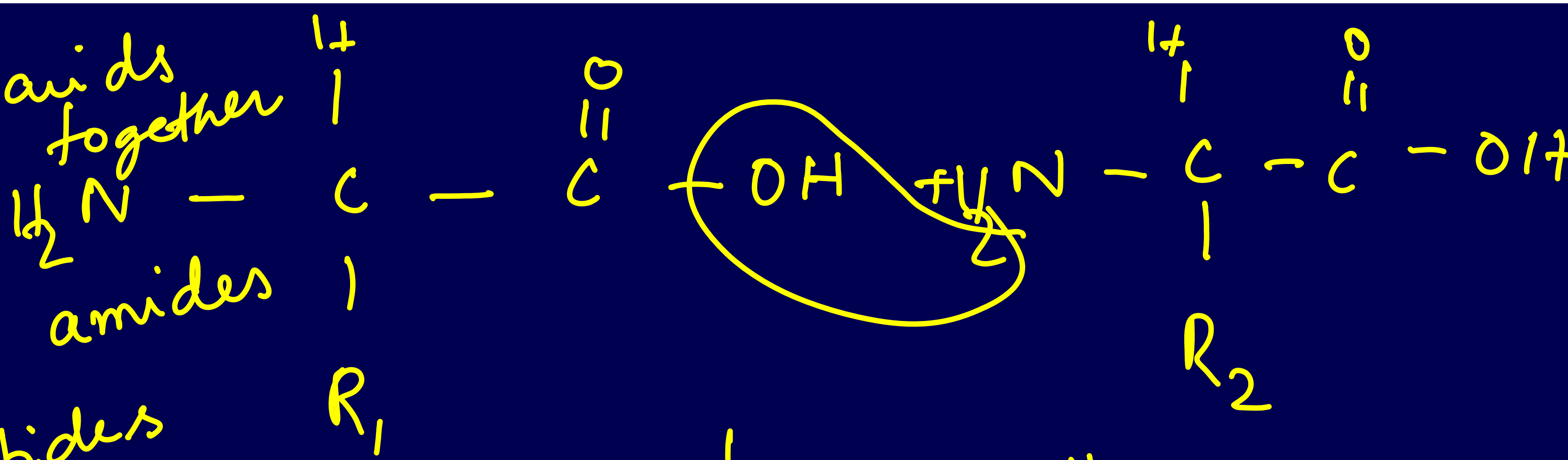


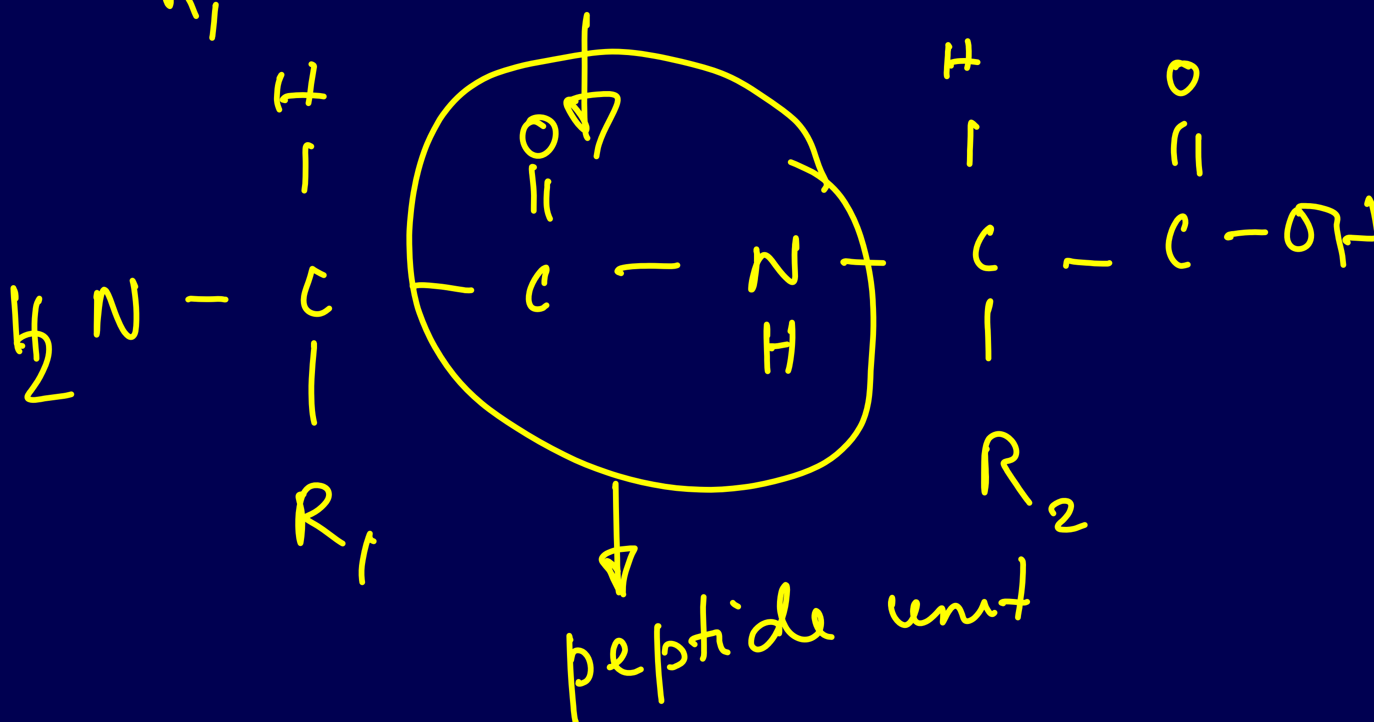
Enzymes $\longrightarrow \dfrac{k_{catalyzed}}{k_{uncat}} \approx 10^{7} \quad (10^{20})$

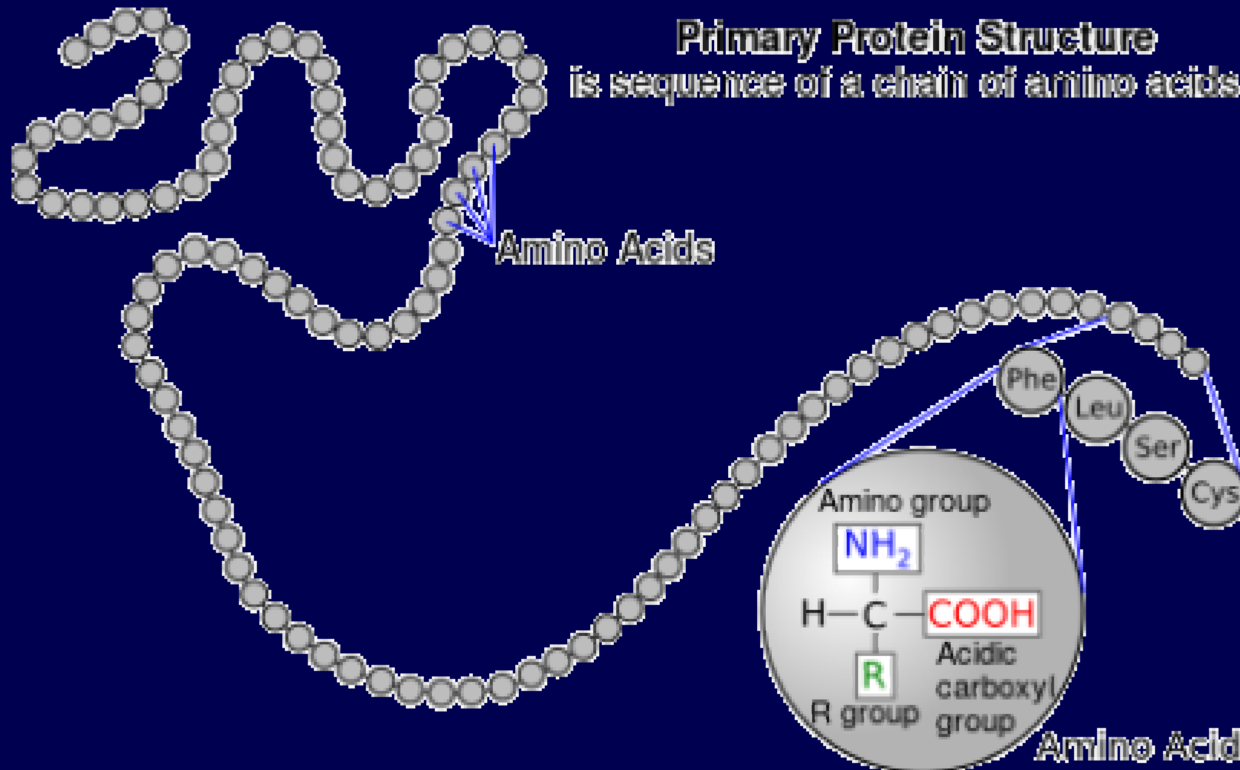
Most enzymes are proteins. Proteins are made up of amino acids



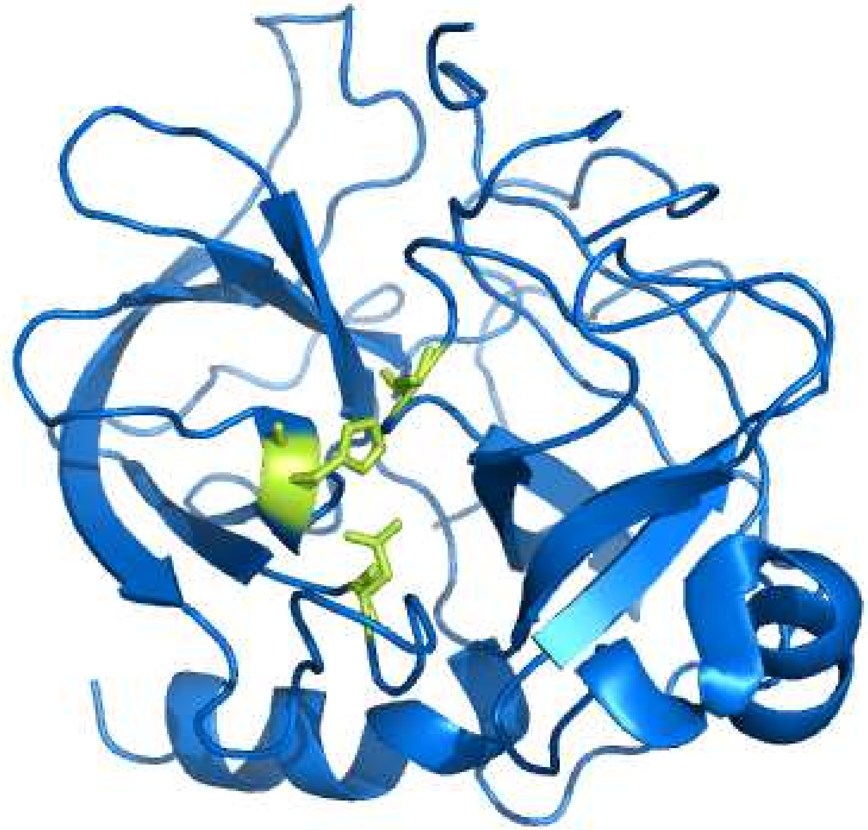
Amino acids combine together to form amides – peptides






Primary Protein Structure
is sequence of a chain of amino acids
Amino Acids
Phe
Leu
Ser
Cys
Amino group
NH2
H
C
COOH
R
Acidic carboxyl group
R group
Amino Acid

Active form of enzymes have unique "folded" structure



Chymotrypsin

$$\text{Proteins} \xrightarrow{\text{Chymotrypsin}} \text{Hydrolyzed products}$$

$$-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}- \;\rightarrow\; -\overset{O}{\overset{\|}{C}}-OH + H_2N-\cdots$$

enzyme + substrate → product

↓ enzyme → Lock

↓ substrate → key

Michaelis-Menton mechanism

$$E + S \rightleftharpoons [ES]$$

fast preequilb

enzyme-substrate complex

$$[ES] \rightarrow \text{product} + E$$

$$\frac{[ES]}{[E][S]} = \frac{1}{K_a}$$

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

$$= \frac{k_2 [E][S]}{K_a}$$

$$\frac{[ES]}{[E][S]} = \frac{1}{K_a}$$

$$\boxed{[E]_0 = [E] + [ES]}$$

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

$$\text{Rate} = \frac{k_2 [E]_0 [S]}{K_a + [S]}$$

When $[S] << K_a$

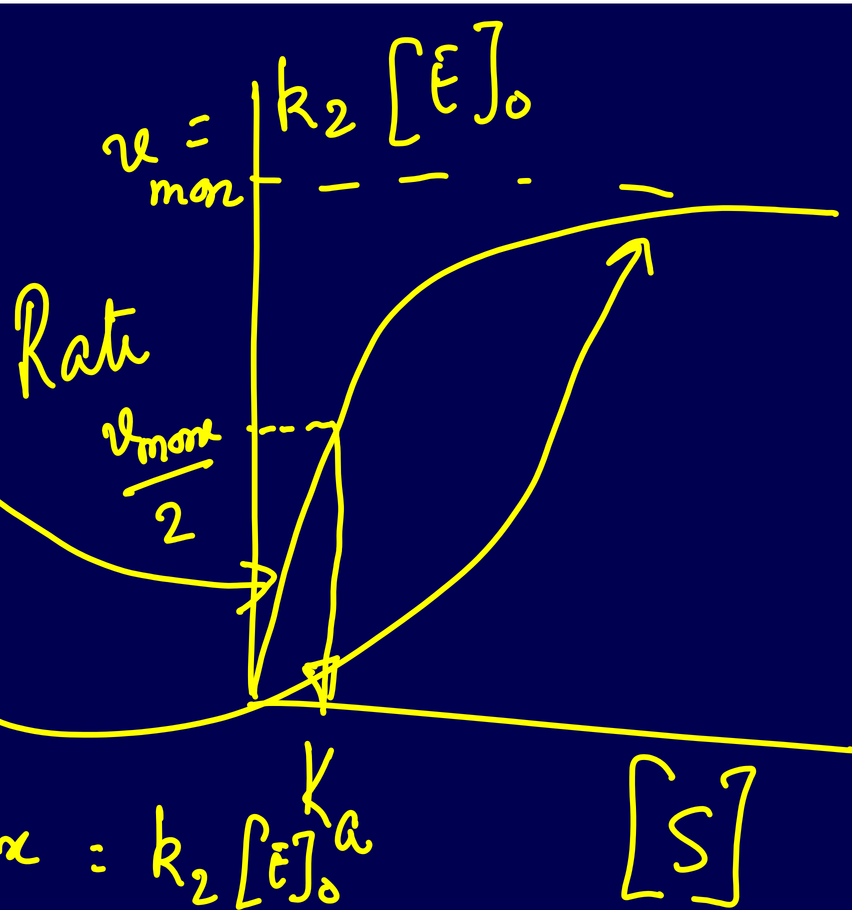
$$v = \frac{k_2[E]_0[S]}{K_a}$$

When $[S] >> K_a$

$$v = k_2[E]_0$$

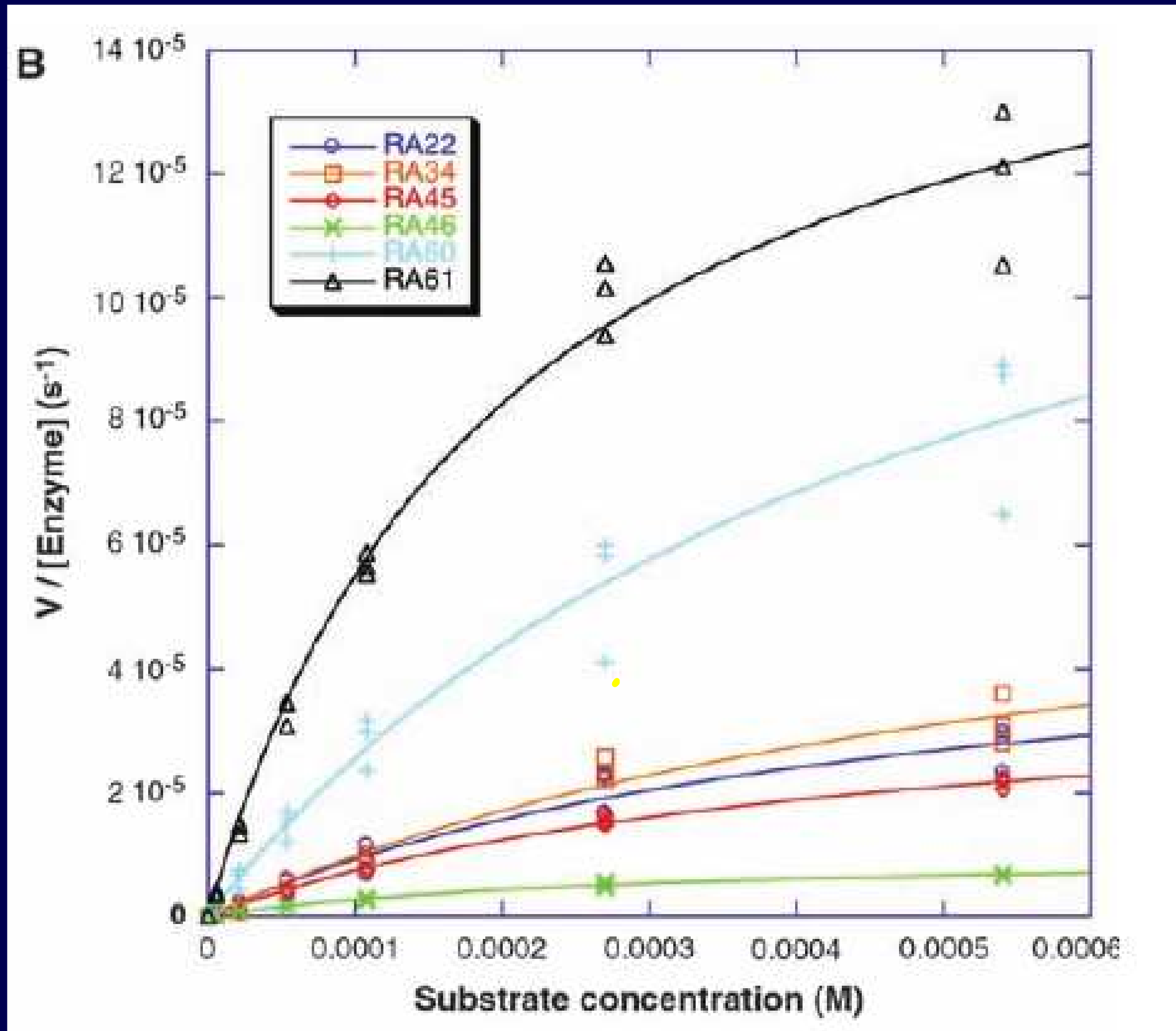
When $v = \frac{v_{max}}{2} = \frac{k_2[E]_0}{2}$

$$[S] = K_a$$



"synthetic enzymes"

retro Diels-Alder reaction



"State of the art"

Analysis of Michaelis-Menten kinetics

$$v = \frac{k_2 [E]_0 [S]}{K_a + [S]}$$

rate

$$\frac{1}{v} = \frac{K_a + [S]}{k_2 [E]_0 [S]}$$

$$= \frac{1}{k_2 [E]_0} + \frac{K_a}{k_2 [E]_0} \frac{1}{[S]}$$

"Intercept" "slope"