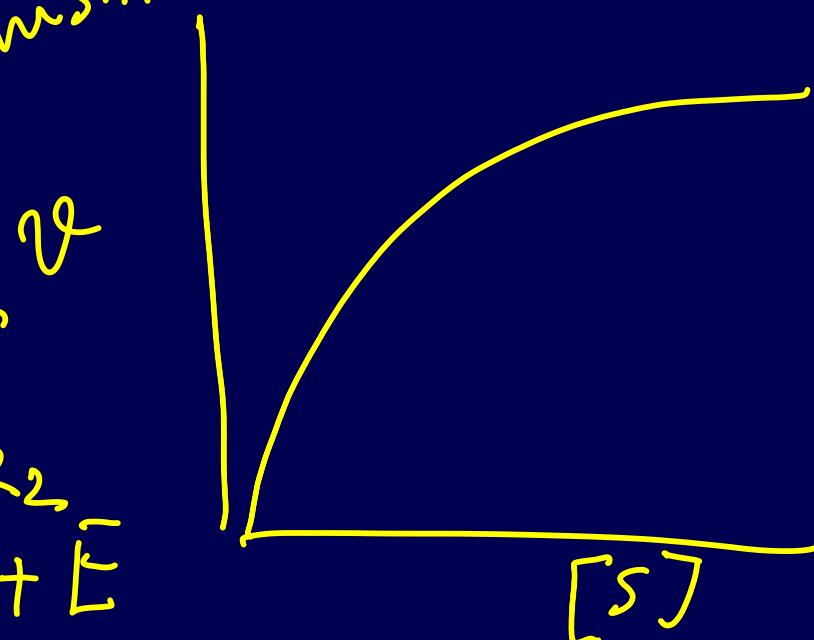
Class 5: Enzyme kinetics continued and surface reactions

$$E + S \longrightarrow P$$

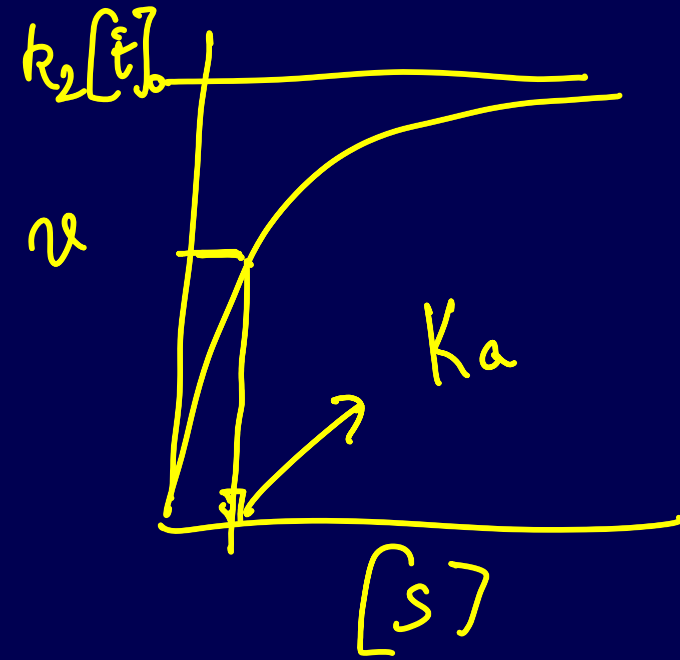
Michaelis-Menten mechanism

$$E + S \rightleftharpoons ES \xrightarrow{k_2} P + E$$



$k_2 \rightarrow$ first order rate constant

"turnover number"



$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \longrightarrow P$$

ES → pre-equilibrium

Briggs-Haldane

JBS

$[E]_0$

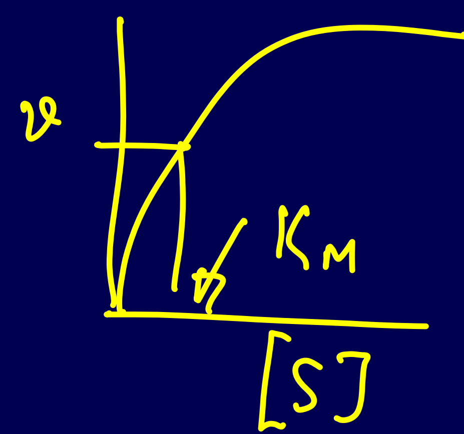
$$ES \overset{K_a}{\rightleftharpoons} E + S$$

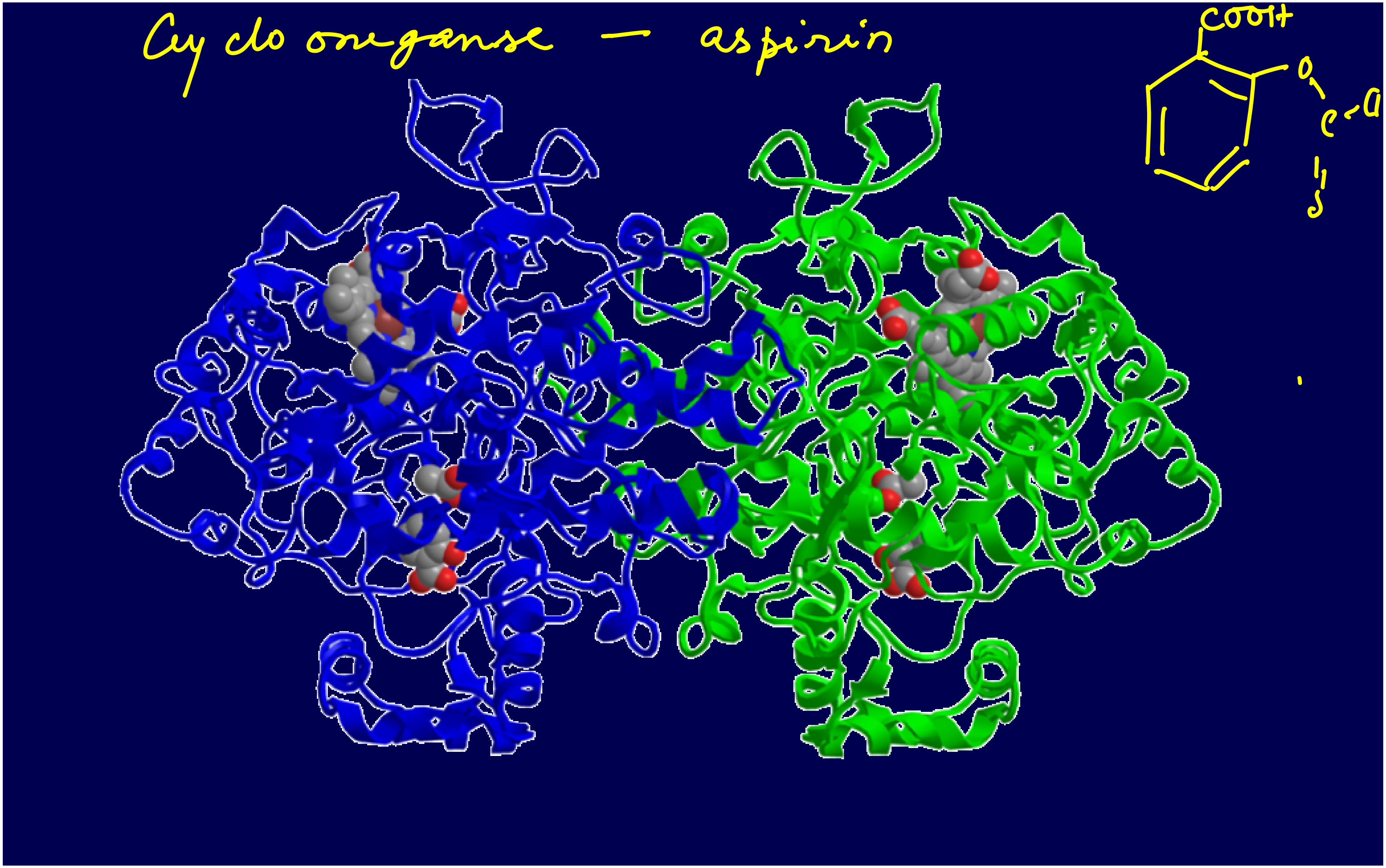
$$\frac{d[ES]}{dt} = 0$$

$$K_M = \frac{k_{-1} + k_2}{k_1}$$

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

$K_M \leftarrow K_a$




Cyclo oxygenase — aspirin

$$E + S \underset{}{\overset{K_a}{\rightleftharpoons}} ES \overset{k_2}{\not\rightarrow} P$$

cyclooxygenase-2

$I \downarrow\uparrow K_I$

EI

Competitive inhibition

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

$$K_I = \frac{[E][I]}{[EI]}$$

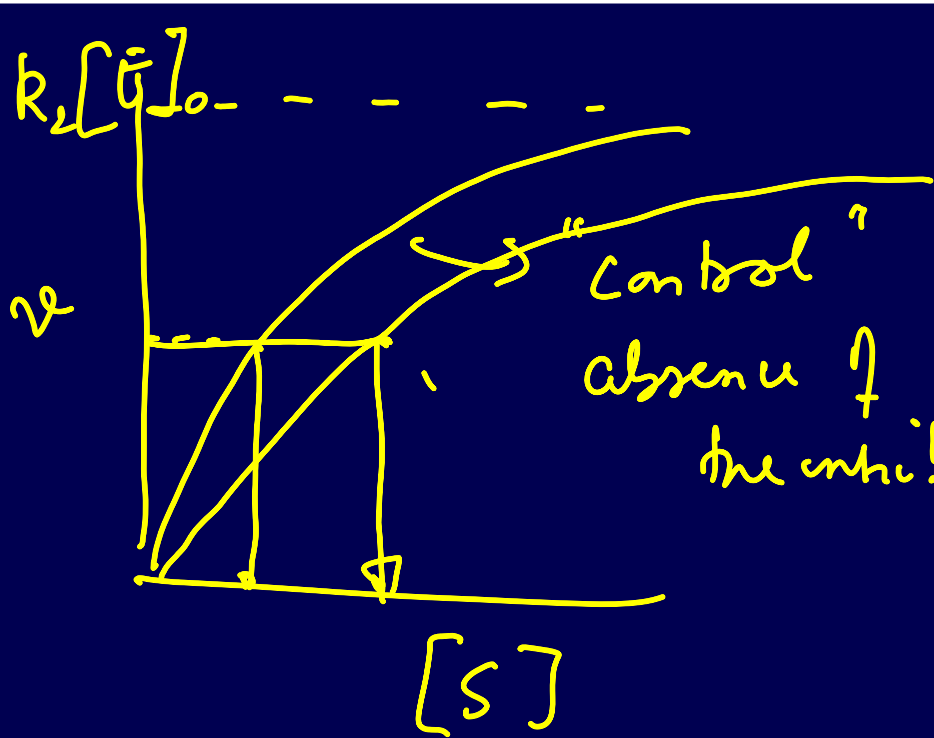
$$v = k_2 [ES]$$

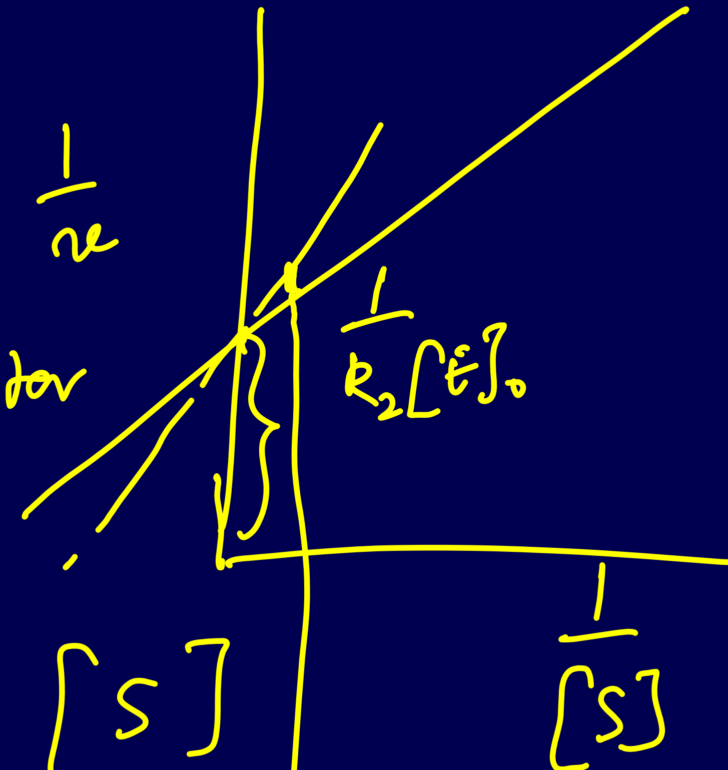
$$[E]_0 = [E] + [ES] + [EI]$$

$$v_{max} \leftarrow \frac{v}{k_2 [E]_0} = \frac{[ES]}{[E] + [ES] + [EI]}$$

$$\frac{v}{v_{max}} = \frac{\frac{[E][S]}{K_a}}{[E] + \frac{[E][S]}{K_a} + \frac{[E][I]}{K_I}}$$

$$\frac{v}{v_{max}} = \frac{[S]}{K_a + [S]} = \frac{\frac{[S]}{K_a}}{1 + \frac{[S]}{K_a} + \frac{[I]}{K_I}}$$





Competitive inhibition

$$\frac{v}{v_{max}} = \frac{[S]}{K_a\left(1 + \frac{[I]}{K_I}\right) + S}$$

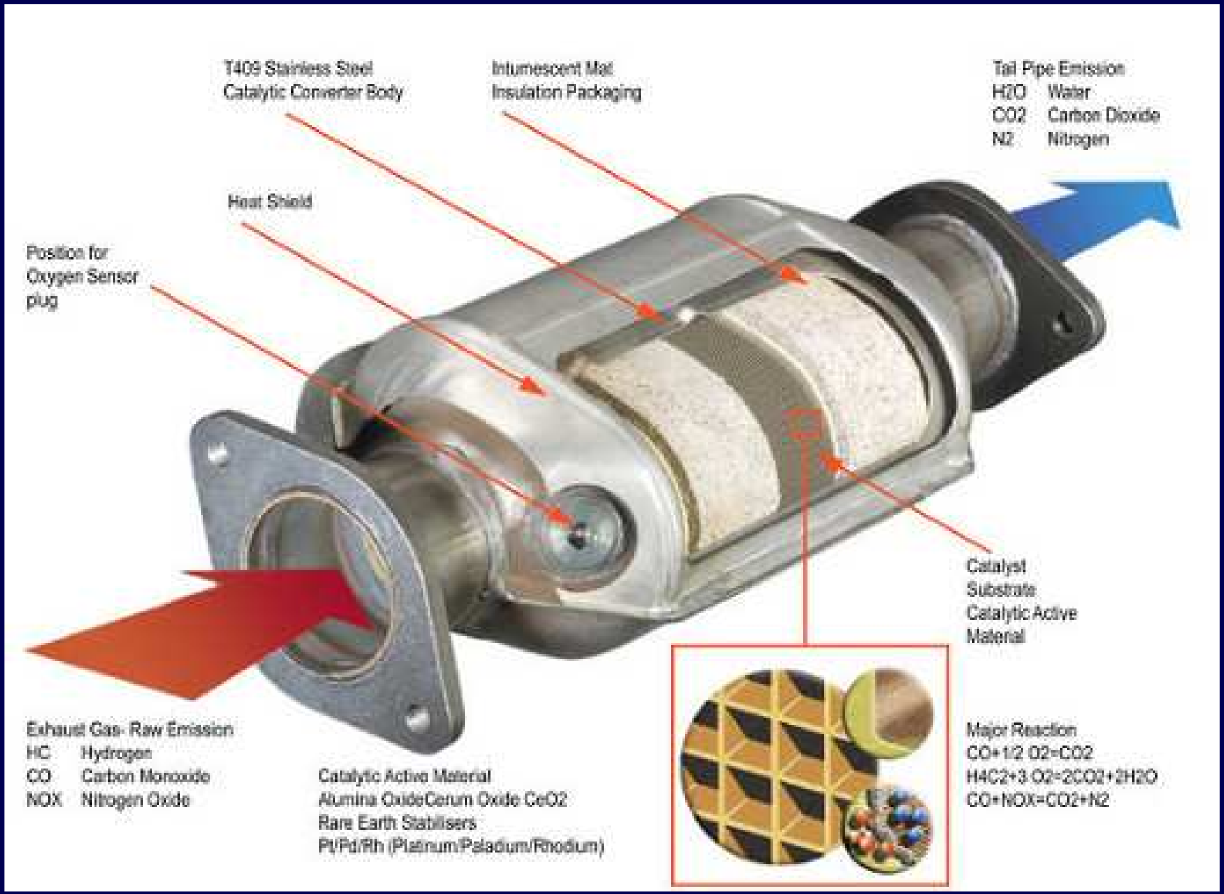
$$E + S \rightleftharpoons ES \rightarrow \text{Product}$$

$$E + I \rightleftharpoons EI \qquad ES + I \rightleftharpoons [ESI]$$

$$EI + S \rightleftharpoons [ESI]$$

"Non-competitive inhibition"

Heterogeneous catalysis & surface reactions



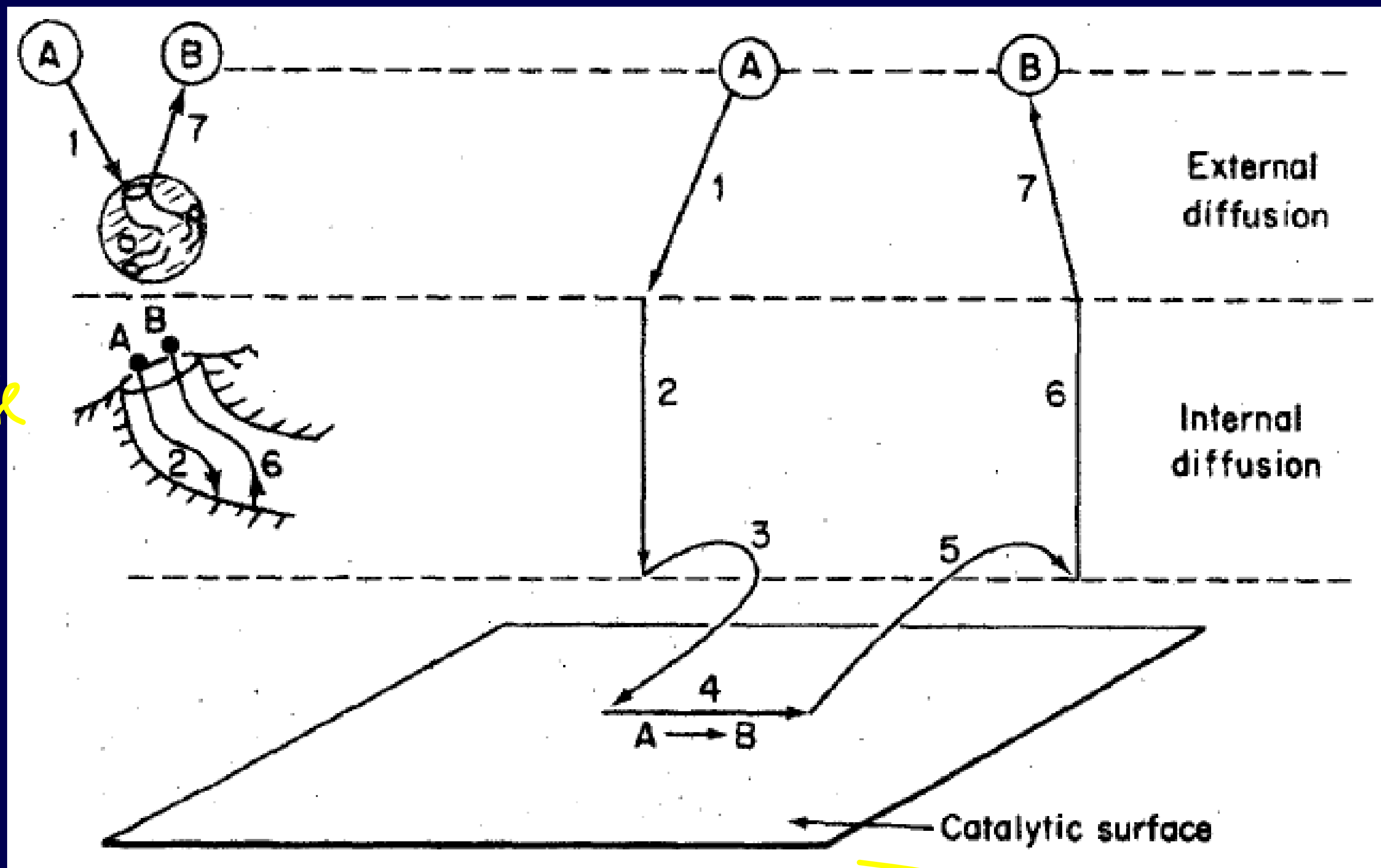
CeO_2

Pt/Pd

NOx

Oxidation	$2CO + O_2 \rightarrow 2CO_2$
	$HC + O_2 \rightarrow CO_2 + H_2O$ [a]
Reduction/three-way	$2CO + 2NO \rightarrow 2CO_2 + N_2$
	$HC + NO \rightarrow CO_2 + H_2O + N_2$ [a]
	$2H_2 + 2NO \rightarrow 2H_2O + N_2$
WGS	$CO + H_2O \rightarrow CO_2 + H_2$
Steam reforming	$HC + H_2O \rightarrow CO_2 + H_2$ [a]

"three-way catalysts"

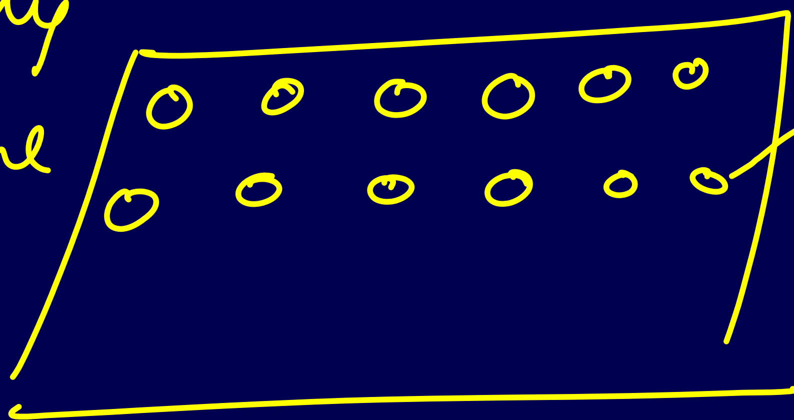


A (ad) ↓ B (ad) } rate

A(g) → B(g)

$$A(g) \underset{k_d \text{ desorption}}{\overset{k_a \text{ adsorption}}{\rightleftharpoons}} A(ad)$$

1) Each site may be occupied by at most one atom



Imagine a surface having σ_0 sites for adsorption

2) energetics of adsorption independent of occupancy of neighboring site

3) Monolayer adsorption