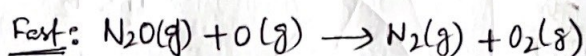
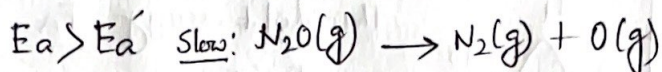
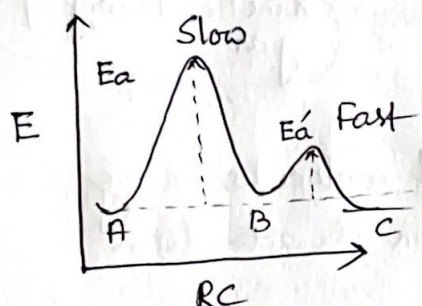


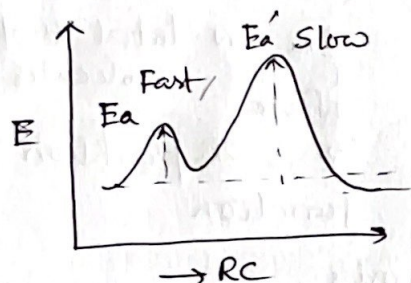
Set-6
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Multistep Reactions

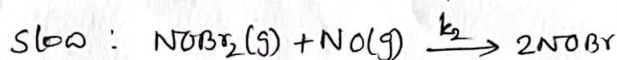
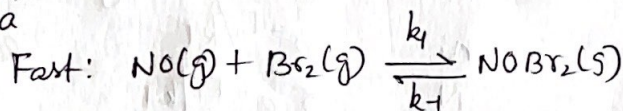
(15)



Find out the rate law of this reaction.
Which step is the rate determining step?



$E_a < E_a'$



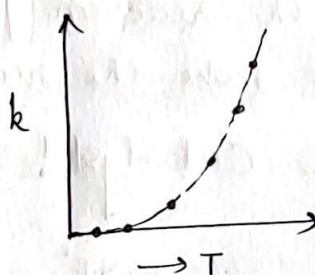
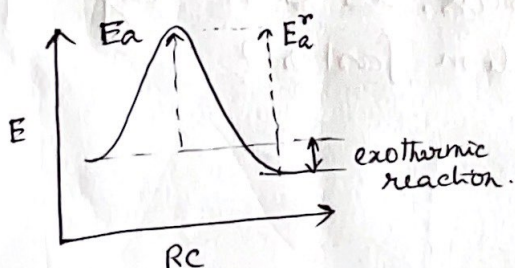
Show that the overall rate of this reaction follows the rate law

$\text{Rate} = k [\text{NO}]^2 [\text{Br}_2]$

⊗ Arrhenius equation

$k = A e^{-E_a/RT}$

Non-linear temperature-dependency!
(for most of the reactions)



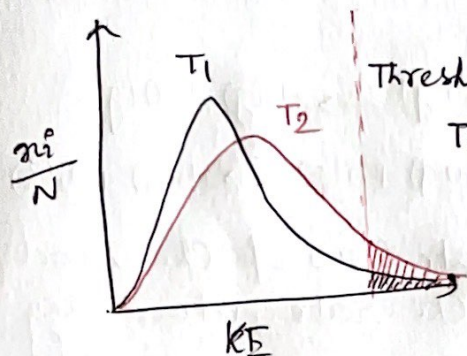
E_a : Activation energy for the forward reaction

E_a^r : Activation energy for the backward reaction

Exponential increase in the reaction rate constant as a function of temperature.

What happens when we increase the temperature?

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Threshold energy $\approx E_a$

$T_1 < T_2$

Larger fraction of molecules having energy more than the activation energy.

Kinetic Theory of gas

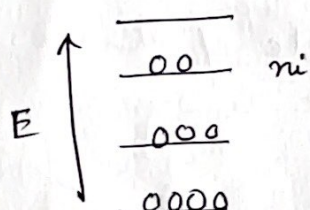
Boltzmann probability

$$\frac{n_i}{N} = \frac{e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} = \frac{e^{-E_i/kT}}{q}$$

$\sum_i n_i = N$ total # of molecules

where

q is the partition function

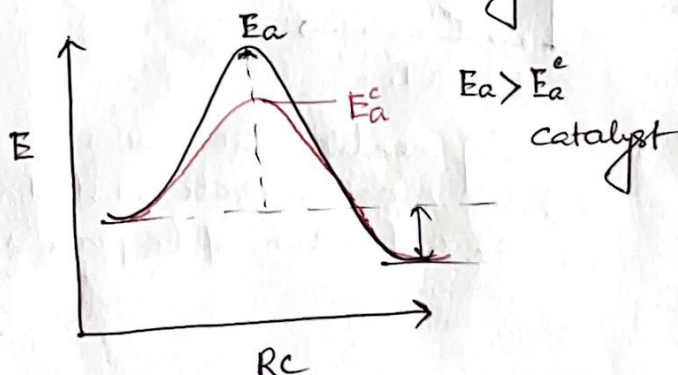


Statistical Thermodynamics

Increasing...

\Rightarrow Temperature or kinetic energy is a way to accelerate the reaction process. Is there any other way to make the reaction faster?

— Catalyst!



1. Reduce the activation energy
2. Alter the reaction mechanism — more favorable path!

Catalyst: A catalyst is a substance that can change ⁽¹⁷⁾ the speed of a transformation, in our context, chemical reaction without undergoing a permanent chemical change itself.

Examples?

- Homogeneous
- Heterogeneous

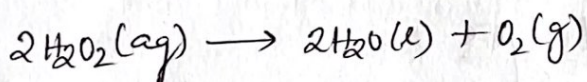
Industrial catalyst
'NH₃ synthesis'

Enzymatic catalyst

Human body - metabolism

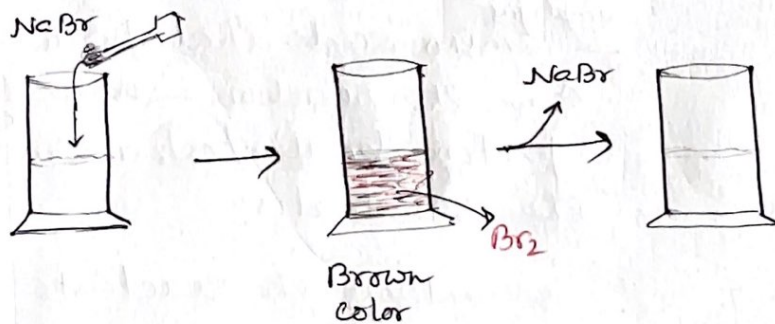
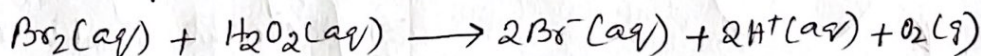
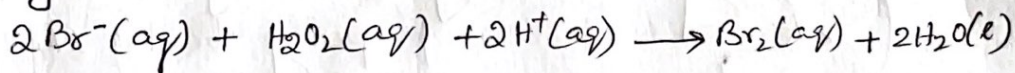
Homogeneous - the catalyst stays in the same phase as the reactants in a reaction mixture.

Decomposition of H₂O₂ in solution



Without a catalyst, the decomposition of H₂O₂ takes place very slowly - you hardly find bubbles of O₂ appearing from the H₂O₂!

However, if you add NaBr (white salt) into it, you'll start seeing O₂ bubbles. In acidic medium Br⁻ catalyses the decomposition of H₂O₂



Heterogeneous catalysis

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A heterogeneous catalyst exists in a different phase from the phase of the reactant molecules. Typical examples are reactions on solid surfaces. (metal or metal oxides) There are reactions that take place in porous solids, such as metal organic or covalent organic frameworks zeolites etc.

Hydrogenation reaction on Pt, Pd surfaces.
Electrochemical reactions on electrode surface.
Catalytic converters - convert toxic CO to CO₂ (less toxic).

Enzymatic catalysis

A class of proteins (amino acid chains) that perform chemical transformations in our body.

Decomposition of H₂O₂ in our body is catalysed by an enzyme, called, catalase.

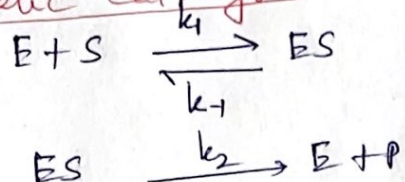


Enzymes catalyse a reaction by

- properly binding the substrates in favorable positions for reactions employing amino acids that participate in the reaction - usually proton donation/extraction to/from the substrates.
- sequestering the reactants from the bulk water increasing the reaction (collision) probability

Enzymatic catalysis

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$$\left\{ \begin{array}{l} k_2 = k_{cat} \\ k_{-1} = k_{off} \\ k_1 = k_{on} \end{array} \right\}$$

$$\frac{d[S]}{dt} = -k_1[E][S] + k_{-1}[ES] \quad \text{--- (1)}$$

$$\left\{ \begin{array}{l} \frac{d[E]}{dt} = -k_1[E][S] + k_{-1}[ES] + k_2[ES] \\ \quad = -k_1[E][S] + (k_{-1} + k_2)[ES] \end{array} \right. \quad \text{--- (2)}$$

$$\begin{aligned} \frac{d[ES]}{dt} &= k_1[E][S] - k_{-1}[ES] - k_2[ES] \\ \text{or } \frac{d[ES]}{dt} &= k_1[E][S] - (k_{-1} + k_2)[ES] \quad \text{--- (3)} \end{aligned}$$

↙
The rate of change of the activated complex.
Initial rate $t \rightarrow 0$ $\frac{d[ES]}{dt} = 0$ (SSA)

From eqⁿ (3)

$$0 = k_1[E][S] - (k_{-1} + k_2)[ES]$$

$$\text{or } k_1[E][S] = (k_{-1} + k_2)[ES] \quad \text{--- (4)}$$

$$\text{Mass balance } [E] = [E]_0 - [ES]$$

$$\text{or } k_1([E]_0 - [ES])[S] = (k_{-1} + k_2)[ES]$$

$$\text{or } [ES] = \frac{k_1[E]_0[S]}{k_1[S] + k_{-1} + k_2} \quad \text{--- (5)}$$

$$\begin{aligned} v_0 &= \left. \frac{d[P]}{dt} \right|_{t \rightarrow 0} = k_2[ES] \\ v_0 &= \frac{k_1 k_2 [E]_0 [S]}{k_1 [S] + k_{-1} + k_2} \end{aligned}$$

$$v_0 = \frac{k_2 [E]_0 [S]}{[S] + \left(\frac{k_{-1} + k_2}{k_1} \right)}$$

(20)

$$= \frac{k_2 [E]_0}{1 + \left(\frac{k_{-1} + k_2}{k_1} \right) / [S]} \quad \text{--- (5)}$$

When $[S] \rightarrow \infty$

$$v_{0, \text{max}} \approx k_2 [E]_0$$

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

Michaelis constant

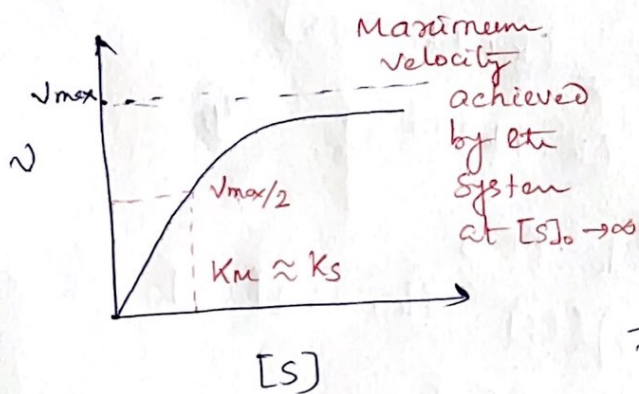
Reaction speed at saturating substrate concentration.

From (5)

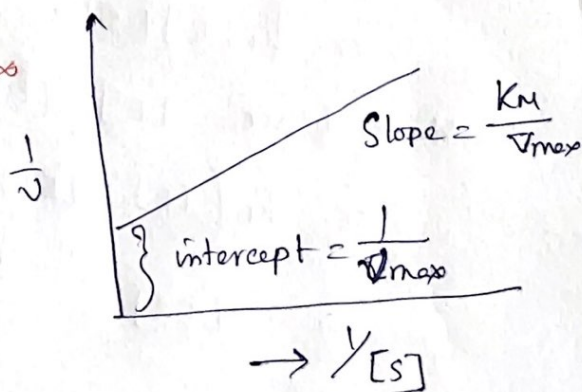
$$v_0 = \frac{v_{\text{max}}}{1 + \frac{K_M}{[S]}}$$

Michaelis-Menten equation.

$$\text{or } v = \frac{v_{\text{max}} [S]}{K_M + [S]}$$



$$\frac{1}{v} = \frac{1}{v_{\text{max}}} + \left(\frac{K_M}{v_{\text{max}}} \right) \cdot \frac{1}{[S]}$$



Free ligand approximation

$$[S] \approx [S]_0$$

at very high substrate concentration.

$$K_D = \frac{k_{\text{off}}}{k_{\text{on}}}$$

dissociation binding constant (binding affinity)