

Catalysis

It is defined as a substance, a small amount of which alters (increases or decreases) the velocity of a chemical reaction, without itself undergoing any change in mass and composition at the end of the reaction.

This phenomenon of altering the velocity of a chemical reaction by the presence of a catalyst is called catalysis.

(*) When a catalyst accelerates the speed of the reaction it is called positive catalyst.
 ⇒ e.g. MnO_2 in decomposition of $KClO_3$ into KCl and O_2 .

(*) Platinum black in the oxidation of SO_2 by the atmospheric oxygen.

(*) If the catalytic substance retards the chemical reaction it is called negative catalyst.
 e.g. alcohol retards the oxidation of chloroform to poisonous phosgene gas.

Bucine retards the atmospheric oxidation of alkaline sodium bisulphite.

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Auto catalysis

When the Pdt. formed in the course of rxn enhances the velocity of the rxn. (or acts as catalyst)

e.g. Hydrolysis of an ester by water is an auto-catalytic process. The acid liberated as a result of hydrolysis catalyses the rxn.



* Oxidn of Oxalic Acid by acidified solⁿ of potassium manganate (VII) pot. permanganate



The Reaction is very slow at room temp.

The rxn is catalysed by Mn(II) ions.

More & more catalyst is produced as the rxn proceeds so the rxn speeds up.

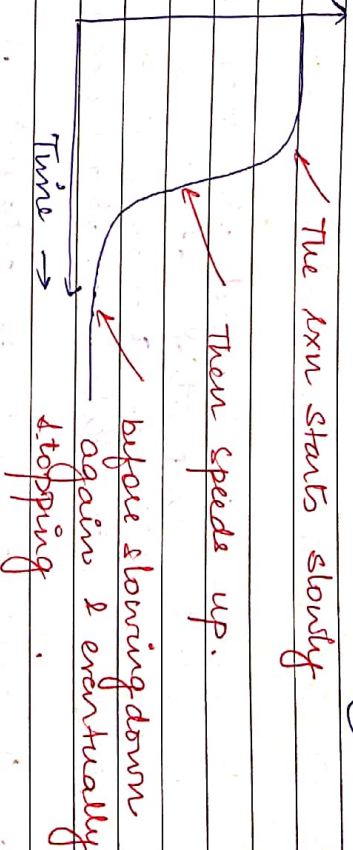
Can be plotted as a fn of concⁿ of one of reactants.

Eventually the rate falls again as the things get used up.

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concⁿ of [R]

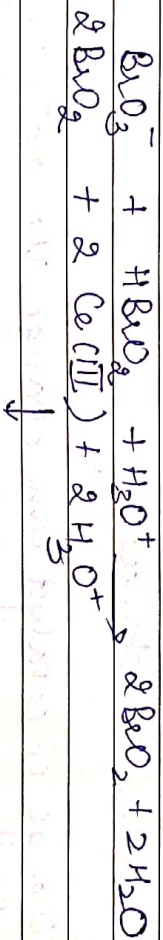


* Another Example is:-

Belousov-Zhabotinski rxn (BZ rxn, oscillating rxn).

Mix. of Pot. Bromate, malonic acid, cerium (IV) salt in acidic solⁿ.

Here HBrO_2 as an autocatalyst.



HBrO_2 is a reactant in the first step and provides a feedback mech. that enhances the rate of formation of HBrO_2 .

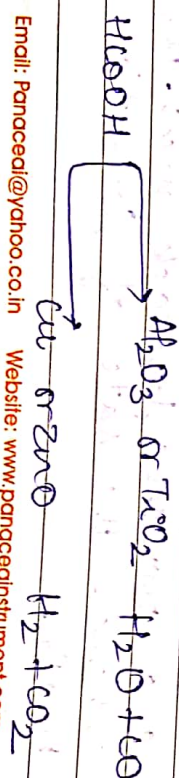
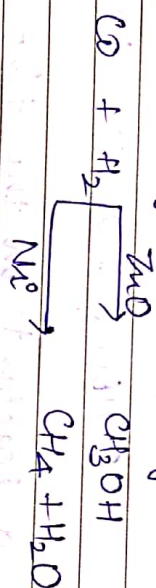
Characteristics of catalyst:

⇒ It remains unchanged in mass & chemical composition at the end of the rxn. (though a change in the physical state, colour etc. may occur).

⇒ A small amount of catalyst is sufficient to bring about the appreciable change in the velocity of the rxn.
e.g. 1 mg Pt enough for 2.5 g of a mix. of H_2 & O_2 to form H_2O .

⇒ A catalyst can exert a selective action, like a key can open a particular lock.
e.g. MnO_2 can catalyse the decomp. of pot. chlorate but not KNO_3 or other substances.

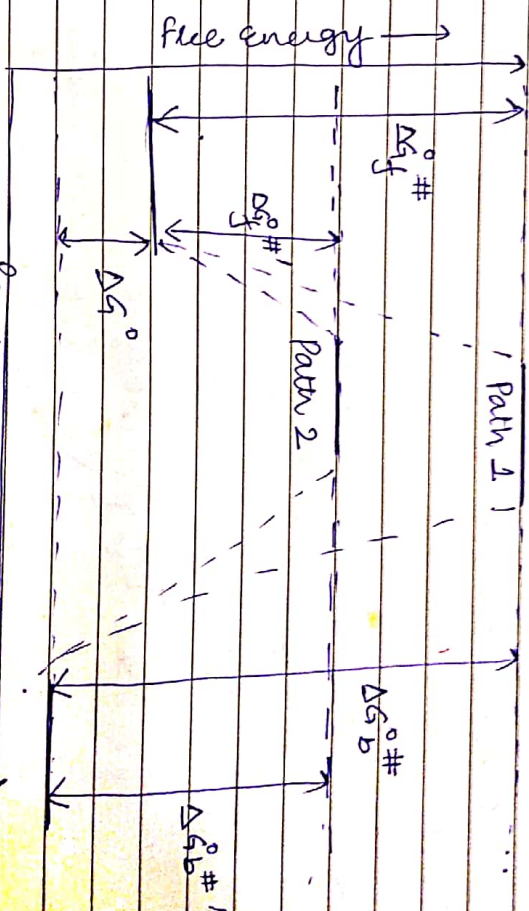
Change of catalyst can change the nature of rxn.



⇒ A catalyst can only alter the speed of the rxn, but doesn't affect the final state of the system.
(It changes the rate of forward & backward rxn to the same extent).

⇒ Acc. to Ostwald, catalyst cannot start a rxn. but can only alter the rate (but there are some reactions like perfectly dry H_2 and O_2 don't combine to form water even left in contact for years but in presence of a little water (catalyst) the rxn proceeds rapidly).

⇒ A catalyst is most active at a particular temperature called opti



$$k_f = (k_B T/h) \exp(-\Delta G^\ddagger / RT)$$

The Arrhenius eqⁿ states that rate constant 'k' of a rxn is directly proportional to the frequency factor (A)

Inversely proportional to the activation energy E_a

Directly to Temperature

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

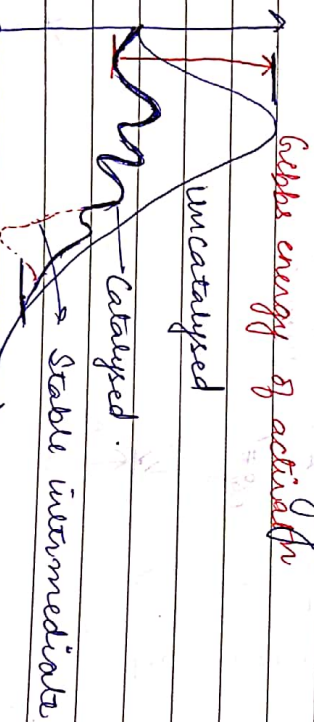
so k is large when $T \uparrow$ or $E_a \downarrow$.

so if the catalyst has to $\uparrow$ its rate of rxn it has to :-

1. $\uparrow$ the frequency factor A (ie $\uparrow$ the rate of successful molecular collisions)

2. decrease the activation energy

Gibbs energy



so a catalyst typically $\uparrow$ the reaction rate by lowering the ~~activation~~ activation energy by opening up pathways with lower Gibbs free energy

A catalyst does not affect the Gibbs free energy of overall reaction because 'G' is a state fn.

* In the profile :- The stable catalytic intermediate should not occur in the cycle and the product must be released in a thermodynamically favourable step. If a stable pdt is formed with the catalyst it would turn out to be the final pdt of the reaction and the catalytic cycle will not continue.

Classification of catalysts

1. Homogeneous
2. Heterogeneous

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Comparison of Homo & Hetero Catalysts

<u>Parameter</u>	<u>Homogeneous</u>	<u>Heterogeneous</u>
1. Phase	liquid / solid soluble in the reactants	Gas / Solid
2. Reqd. Temp	Low ($< 250^{\circ}\text{C}$)	High
3. Activity	High	Low
4. Diffusion	Facile	Very Imp.
5. Heat transfer	Facile	Problematic
6. Product selectivity	More	Less
7. Recycling	Expensive & complex	Simple / cost effec.
8. Mechanism	Well Understood	Poorly Understood
9. Pdt separat ⁿ from catalyst	elaborate & sometimes problematic	Easy
10. fine tuning	Easy	Difficult
11. Deactivat ⁿ	More sensitive	Less sensitive