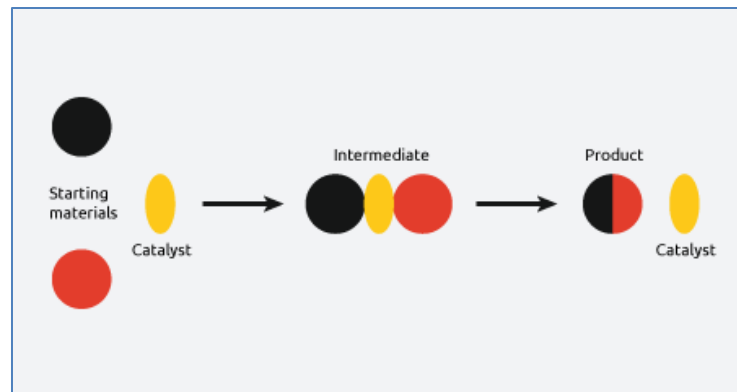
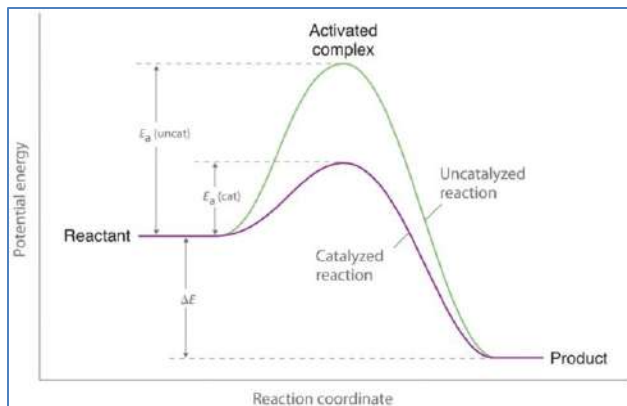


Catalysis

C.U Syllabus - General principles and properties of catalysts, homogenous catalysis (catalytic steps and examples) and heterogenous catalysis (catalytic steps and examples) and their industrial applications, Deactivation or regeneration of catalysts. Phase transfer catalysts, application of zeolites as catalysts



Catalyst and Catalysis

- Catalysis is a term describing a process in which the rate and/or the outcome of the reaction is influenced by the presence of a substance (the catalyst) that is not consumed during the reaction and that is subsequently removed if it is not to constitute as an impurity in the final product.
- It is a process that provides a new way to a chemical reaction with the lowest activation energy.
- The substance that plays the key role in this route without being consumed is called a catalyst.
- In catalyzed mechanisms, the catalyst usually reacts to form an intermediate, which then regenerates the original catalyst in a process.
- Enzymes are natural catalysts, which catalyze the synthesis of a vast number of biomolecular structures, and are well-known models of energy-efficient, environmentally benign chemical agents.

The productivity of a catalyst can be described by the **turnover number** (or TON) and the catalytic activity by the **turn over frequency** (TOF), which is the TON per time unit.

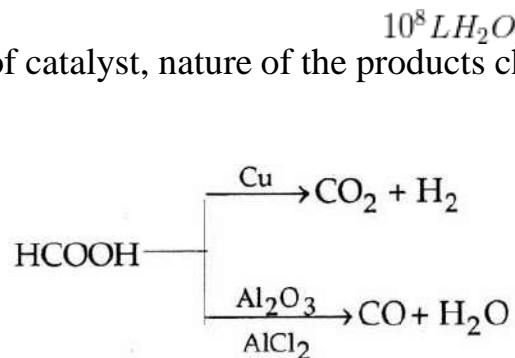
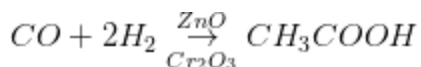
Catalytic processes and their catalysts

process	catalyst
ammonia synthesis	iron
sulfuric acid manufacture	nitrogen(II) oxide, platinum
cracking of petroleum	zeolites
hydrogenation of unsaturated hydrocarbons	nickel, platinum, or palladium
oxidation of hydrocarbons in automobile exhausts	copper(II) oxide, vanadium(V) oxide, platinum, palladium
isomerization of n-butane to isobutane	aluminum chloride, hydrogen chloride

Characteristics of Catalysts:

1. The catalyst remains unchanged (in mass and chemical composition) in the reaction (Activity of catalyst.)
2. A small quantity of the catalyst is required. e.g. One mole of colloid Pt catalyses
3. The catalyst does not change the equilibrium constant. But the equilibrium approaches earlier.
4. **Specificity of Catalyst:**

The catalyst is specific in nature. It means by the change of catalyst, nature of the products changes or specific catalyst for a specific reaction.

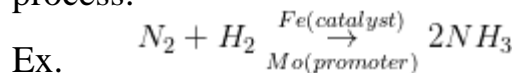


The catalyst stabilizes the transition state more than it stabilizes the starting material. It decreases the kinetic barrier by decreasing the difference in energy between starting material and transition state. It does not change the energy difference between starting materials and products (thermodynamic barrier), or the available energy (this is provided by the environment as heat or light).

5. The catalyst can not make impossible reaction to occur and does not initiate a reaction.

Catalyst Poison: There are certain substances which decrease or destroy the activity of the catalyst. Such substances are known as catalytic poisons. E.g. arsenic destroys the catalytic activity of the platinum catalyst in the manufacture of sulphuric acid.

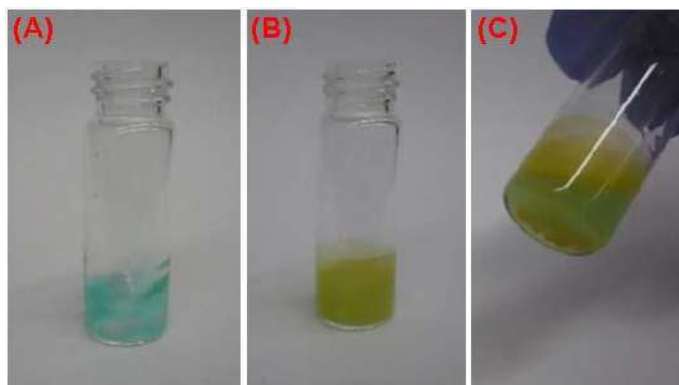
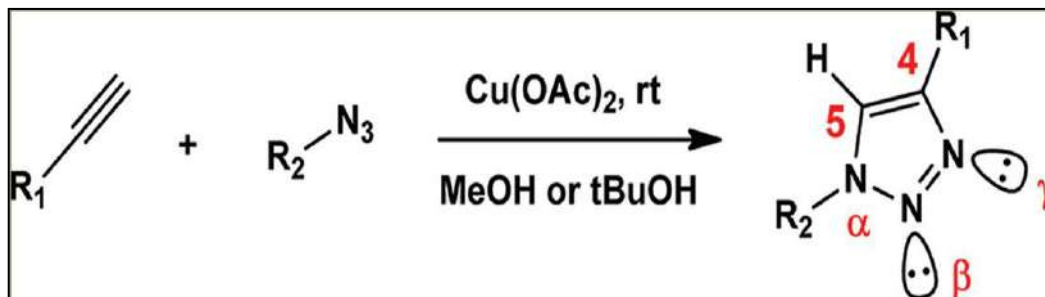
Catalyst Promoter: There are certain substances which increase the activity of the catalyst. Such substances are known as catalyst promoters e.g. Mo acts as a promoter in the manufacture of ammonia by Haber's process.



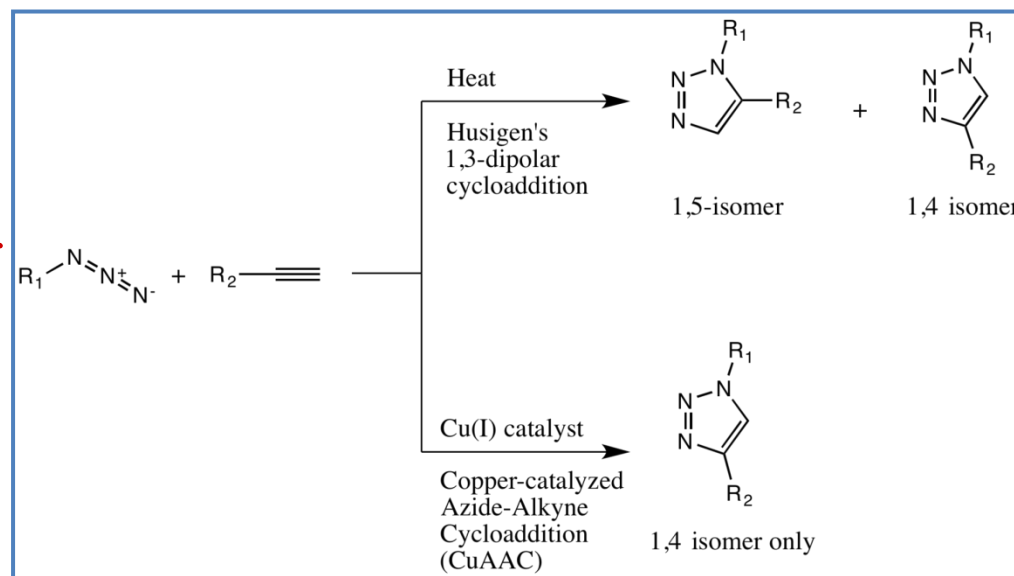
Ex. 2. In Bosch process of preparation of H_2 , Cr_2O_3 acts as a promoter for catalyst Fe_2O_3 . Catalyst Poison or Promoter does not act like a catalyst.

6. The catalyst exhibits maximum activity at a particular temperature which is known as **optimum temperature**.

Copper(II) acetate acts as a catalyst and accelerates azide alkyne cycloaddition



1, 4 vs 1, 5 Triazole Product



- The copper(I)-catalysis of the Huisgen 1,3-dipolar cycloaddition was discovered concurrently and independently by the groups of **Valery V Fokin and K. Barry Sharpless**.
- The copper-catalyzed version of this reaction gives only the 1,4-isomer, whereas Huisgen's non-catalyzed 1,3-dipolar cycloaddition gives both the 1,4- and 1,5-isomers, is slow, and requires a temperature of 100°C.
- An analogous RuAAC reaction catalyzed by ruthenium, instead of copper, was reported by the Sharpless group in 2005, and allows for the selective production of 1,5-isomers

Catalyst : properties-

1. Unchangeability of the Catalyst :

A Catalyst remains unchanged in mass & chemical composition at the end of the reaction. But there may be little change in its physical state.

Ex.

MnO_2 is used as a catalyst in the preparation of O_2 from KClO_3 . MnO_2 is solid, but during the reaction particle size of MnO_2 is decreased.

2. Small quantity of the catalyst-

Usually small quantity of the catalyst is sufficient to carry out the reaction because catalyst is not used up during the reaction.

Ex. Only one gram of colloidal Pt is sufficient to increase the rate of decomposition of 106 litre of H_2O_2 .

Exceptions : In many homogeneous catalytic reactions, the rate of reaction is proportional to the concentration of catalyst.

In some heterogeneous reactions, the rate of reaction is proportional to the surface area of solid catalyst.

3. Initiation of reaction-

A catalyst doesn't start a reaction. A catalyst only increases or decreases the rate of reaction. It doesn't start the reaction.

4. Catalyst & the nature of product:

Generally catalyst don't change the nature of product. Some exceptions are :

5. Catalysts are specific in their action-

A substance acts as a catalyst for a particular reaction. It is not necessary that it will act as a catalyst for any other reaction. Hence catalysts are specific in their action.

6. Effect of Temperature-

Activity of a catalyst is maximum at a definite temperature which is known as optimum temperature.

7. A Catalyst doesn't Change the state of equilibrium of a reaction-

A catalyst increases the rate of both the forward & backward reaction equally. Hence catalyst doesn't influence the state of equilibrium of a reversible reaction but equilibrium is attained earlier.

8. Activity of Finely divided Catalyst is Greater –

It is because surface area of finely divided catalyst is greater

9. A catalyst lowers the activation energy-

According to arrhenious collision theory , reaction occurs on account of effective collisions between the reacting molecules. For effective collision it is necessary that the molecule must possess a minimum amountof energy known as activation energy. The catalyst provides a new path way involving lower amount of activation energy. Hence large number of effective collisions occur in presence of catalyst in comparison to the effective collisions at the same temperature in absence of catalyst. Therefore the presence of a catalyst makes the reaction to go faster.

Classification Of Catalysts

- Catalysts may be classified generally according to their physical state, their chemical nature, or the nature of the reactions that they catalyze.
- They are generally classified
 - a) heterogeneous
 - b) homogeneousdepending on the form in which they are employed in the process.
- Contribution of homogeneous catalytic process in chemical industry is significantly smaller compared to heterogeneous catalytic process, it is only about 17-20 %.

Homogeneous catalysis

- In homogeneous catalysis, all the reactants and catalysts are present in a single fluid phase and usually in the liquid phase.
- The homogeneous catalysts employed in practice cover the following types:
 - i) soluble nonmetallic acids and bases,
 - ii) metal salts,
 - iii) organometallic complexes with monodentate or bidentate ligands,
 - iv) nonaqueous ionic liquids (NAILs),
 - v) metal clusters,
 - vi) enzymes.

Advantages -

Advantages of homogeneous processes can be summarized as follows:

- (a) feasibility at milder operating conditions facilitating wider applicability to reactants, including some thermally sensitive and nonvolatile reactants involved in specialty products.
- (b) higher activity and selectivity as a result of low temperature and ease of access to catalytic sites
- (c) can be tailored to give high regio- and stereoselectivity useful in synthesis of optically active products
- (d) can be synthesized and characterized in a well-defined and reproducible way
- (e) heat and mass transfer resistances can be easily eliminated, leading to better control of temperature at catalytic sites due to higher heat capacity and efficient heat transfer in the liquid phase unlike heterogeneous catalysis in which hot spot formation is a major problem
- (f) The ability to activate substrates such as hydrogen, carbon monoxide (CO), oxygen, and olefins at milder operating conditions.
- (g) better understanding of the nature of active species, catalytic reaction pathways, and reaction mechanism

Disadvantages

Homogeneous processes are also associated with some major disadvantages which result in limited use of these processes. These disadvantages are –

(a) Since the catalysts are molecularly dispersed in the phase as the reactant, products and solvents, the separation at end of the process is difficult and expensive. In many cases, it is not possible to recover the catalyst.

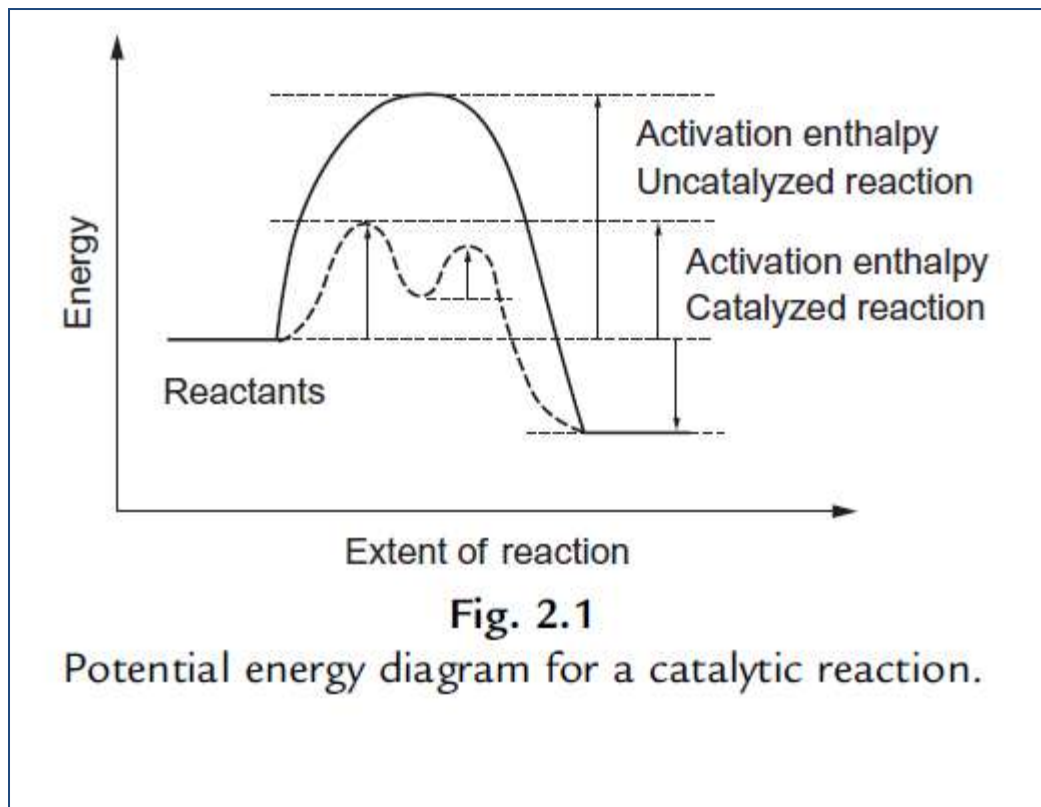
(b) most promising reactions employ expensive catalysts consisting of noble metal complexes, the recovery, recycle, and reuse processes for which are also highly expensive

(c) sensitivity of the catalysts to trace impurities and thermal stability, leading to catalyst deactivation and posing difficulties in handling.

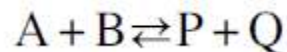
Most of the successful homogeneous catalytic processes are those in which the products are volatile and separable by distillation without affecting the catalyst.

Basic Concepts -

- It is generally understood that a catalyst “accelerates” a chemical reaction, and the fundamental understanding of the role of catalysis depends on the elementary interactions among the reactants and catalyst precursors or the active species formed during the reactions.
- In most homogeneous catalysts, co-catalysts, ligands, and promoters are involved which also participate in stoichiometric interactions in such a way that the catalyst/co-catalyst/promoters are regenerated during a catalytic cycle while transforming the reactants to the products.
- The presence of a catalyst does not change the reaction equilibrium but accelerates the rate at which equilibrium is attained. The catalyst alters the reaction pathway in such a way that the free energy of activation is reduced significantly compared to the uncatalyzed reaction, whereas the overall change in the free energy of the reaction equals that of an uncatalyzed reaction.
- The role of catalysts and reaction pathways would also depend on the type of catalyst used, which can be illustrated for homogeneous transition metal complex catalysts.



Let us consider a reaction of components A and B to give products P and Q in the presence of a catalyst C:



The elementary steps in a catalytic cycle -

- (a) conversion of a catalyst precursor complex to an active form either by ligand dissociation or interaction with a co-catalyst or promoter
- (b) activation of reactant A by the active complex,
- (c) activation of reactant B by the product of step b, and
- (d) intramolecular reaction in coordination sphere followed by reductive elimination to form a product and regenerate the catalyst in original active form.

- Homogeneous transition metal complex catalysts generally involve a metal and a ligand with or without a promoter.
- The feasibility of these steps would depend on some concepts established in coordination chemistry of transition metals, thermodynamics, and kinetics of elementary steps.

Some examples –

$\text{RhCl}(\text{PPh}_3)_3$, Wilkinson catalyst for hydrogenation of olefins

$\text{HRh}(\text{CO})(\text{PPh}_3)_3$, for hydroformylation of olefins

$[\text{Rh}(\text{CO})_2\text{I}_2]/\text{HI}$, for carbonylation of methanol

$\text{Co}(\text{OAc})_2/\text{Co}(\text{OAc})_2/\text{HBr}$, for oxidation of p-xylene

$\text{Pd}(\text{pyca})(\text{PPh}_3)(\text{OTs})/\text{TsOH}/\text{LiCl}$, for carbonylation of aryl alcohols/olefins

Why transition metals?



- (a) transition metal elements distinguish from the main group elements in which their d-shells are only partially filled with electrons, which facilitates coordination with ligands and activation of reactants through formation of σ or π bonds.
- (b) the accessibility of different oxidation states and coordination numbers
- (c) the ability to stabilize a variety of unstable intermediates such as metal hydrides, carbonyls, and metal alkyls in relatively stable but kinetically reactive forms
- (d) the ability to promote rearrangements via ligand migration (reactions within the coordination sphere)
- (e) the ability to assemble and orient several reaction components within the coordination sphere (template effect)
- (f) the ability to accommodate both participative and non-participative ligands.

Types of reactions

1. Acid base catalysis –

These type of catalysts are used in different reactions e.g Condensation, Dehydration, Hydrolysis , Halogenations etc.

2. Catalysis by metal ions

3. Catalysis by organometallic complexes

4. Catalysis by Lewis acids

5. Catalysis by porphyrin complexes

6. Catalysis by enzymes

Activity of a catalyst –

The homogeneous catalyst precursors are added in the reaction system in different forms and are transformed into the active form insitu. During one catalytic cycle, the catalyst may pass through several intermediate forms and finally produce the products. After end of each catalytic cycle, the catalyst itself should be regenerated without any change.

A catalyst should be able to pass through the catalytic cycle multiple times. Higher the number of times the catalyst passes through this cycle, higher is the activity of the catalyst. The number of times that a catalyst can go through this cycle converting substrate molecule to product molecules is defined as the turnover number. In other words, the turnover number, TON, is the total number of substrate molecules that a catalyst can convert into product molecules. In homogeneous systems, the turnover frequency is defined as the number of molecules of substrate converted per second which is the turnover number in a certain period of time.

$$\text{TON} = \frac{\text{Amount of substrate reacted}}{\text{Amount of catalyst}}, \text{ (mole/mole)}$$

$$\text{TOF} = \frac{\text{Amount of substrate reacted}}{\text{Amount of catalyst} \times \text{time}}, \left(\frac{\text{mole}}{\text{mole time}} \right) \text{ or } \frac{1}{\text{time}}$$

TOF is a measure of intrinsic catalytic activity and is determined at low conversion levels (<10%). It requires a precise knowledge of the catalytic species on a molecular level, which is often possible in homogeneous catalysis.

Heterogeneous Catalyst

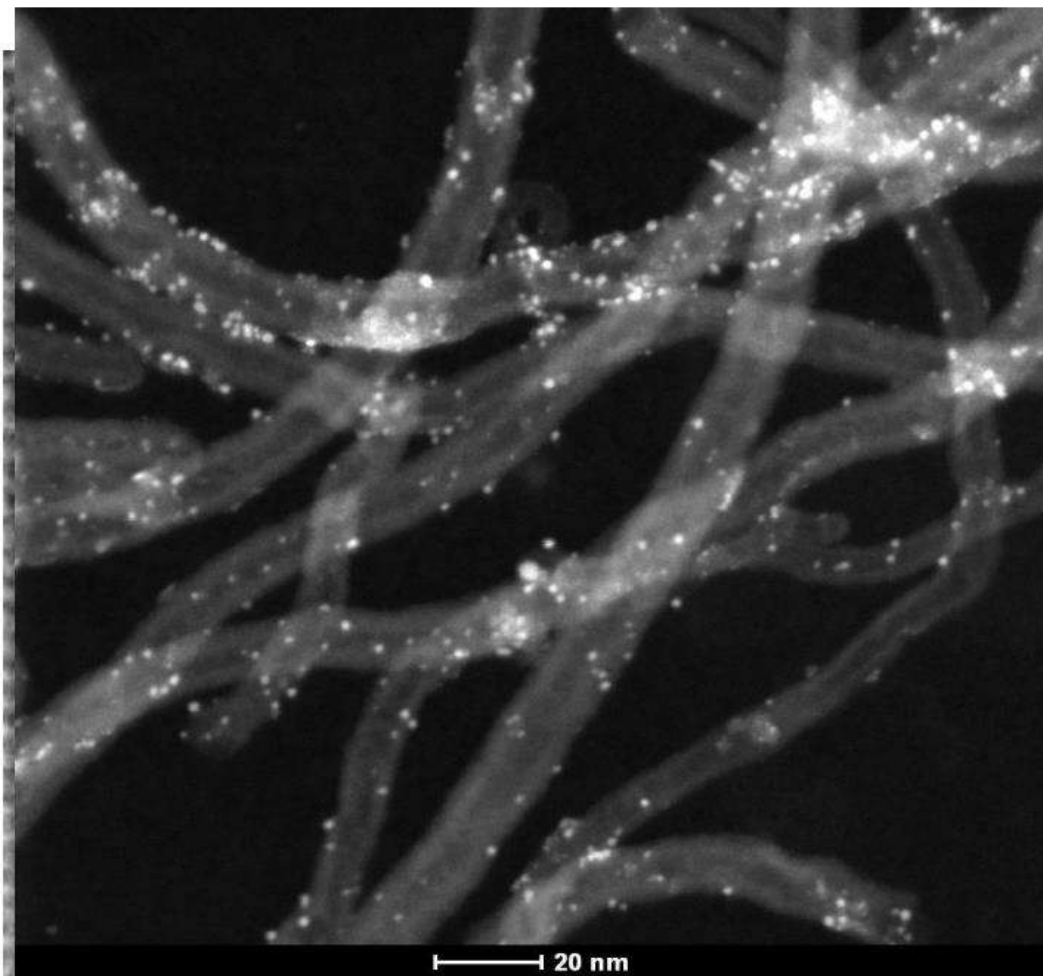
- Many catalytic processes are known in which the catalyst and the reactants are not present in the same phase. These are known as heterogeneous catalytic reactions. They include reactions between gases or liquids or both at the surface of a solid catalyst also also immiscible mixtures (e.g. oil and water), or anywhere an interface is present
- A heterogeneous catalytic reaction involves adsorption of reactants from a fluid phase onto a solid surface, surface reaction of adsorbed species, and desorption of products into the fluid phase.
- Clearly, the presence of a catalyst provides an alternative sequence of elementary steps to accomplish the desired chemical reaction from that in its absence. If the energy barriers of the catalytic path are much lower than the barrier(s) of the noncatalytic path, significant enhancements in the reaction rate can be realized by use of a catalyst.

Heterogeneous catalysis has a number of benefits. For one, heterogeneous catalysts can be separated from a reaction mixture in a straightforward manner, such as by filtration. In this way, expensive catalysts can be easily and effectively recovered, which is an important consideration for industrial manufacturing processes.

However, one limitation of heterogeneous catalysis has to do with the available surface area of the catalyst. Once the surface of the catalyst is completely saturated with reactant molecules, the reaction cannot proceed until products leave the surface, and some space opens up again for a new reactant molecule to adsorb, or attach. It is for this reason that the adsorption step in a heterogeneously catalyzed reaction is oftentimes the rate-limiting step. Despite this, the overall benefits of heterogeneous catalysis often outweigh its disadvantages, in that the catalyzed reaction is still much faster than the uncatalyzed reaction.

Catalytic Steps in Heterogeneous Catalysis

- Heterogeneous catalysis is a surface phenomenon.
- The surface area of the catalyst should be large, and the surface must be accessible to reactants.
- The necessary first step in a heterogeneous catalytic reaction involves activation of a reactant molecule by adsorption onto a catalyst surface. The activation step implies that a fairly strong chemical bond is formed with the catalyst surface. This mode of adsorption is called chemisorption, and it is characterized by an enthalpy change typically greater than 80 kJ mol^{-1} and sometimes greater than 400 kJ mol^{-1} .
- Chemisorption implies that only a single layer, or monolayer, of adsorbed molecules is possible since every adsorbed atom or molecule forms a strong bond with the surface. Once the available surface sites are occupied, no additional molecules can be chemisorbed.
- Since a chemical bond is formed with the catalyst surface, chemisorption is specific in nature, meaning only certain adsorbate-adsorbent combinations are possible



In heterogeneous catalysis the catalyst is assumed to contain stable active sites that are regenerated into their active form after each reaction cycle.

The reaction is dynamical. Reactants can diffuse after chemisorption to “high energy sites” and desorb through dynamics.

The catalyst material is static and pre-determined by synthesis: during operation no structural modification but participation of charge carrier reservoirs are assumed.

- A catalyst is chosen that releases the products formed as readily as possible; otherwise the products remain on the catalyst surface and act as poisons to the process.
- Chemisorption can occur over a wide temperature range, the most effective temperature for adsorption depending on the nature of the catalyst.

Examples - Hydrogen is chemisorbed readily by many metals even at liquid air temperatures (below $-180\text{ }^{\circ}\text{C}$ [$-290\text{ }^{\circ}\text{F}$]). With a series of hydrogenation-dehydrogenation catalysts—e.g., zinc oxide–chromic oxide ($\text{ZnO-Cr}_2\text{O}_3$)—chemisorption of hydrogen often occurs above room temperature.

Nitrogen is rapidly chemisorbed on synthetic ammonia-iron catalyst in the region above $400\text{ }^{\circ}\text{C}$ ($750\text{ }^{\circ}\text{F}$). It has been shown that iron films chemisorb nitrogen even at liquid air temperatures, with additional chemisorption found above room temperatures.

➤ For supported metal catalysts, no simple calculation is possible. A direct measurement of the metal crystallite size or a titration of surface metal atoms is required

➤ Two common methods to estimate the size of supported crystallites are transmission electron microscopy and X-ray diffraction line broadening analysis.

➤ Transmission electron microscopy is excellent for imaging the crystallites. However, depending on the contrast difference with the support, very small crystallites may not be detected. X-ray diffraction is usually ineffective for estimating the size of very small particles, smaller than about 2 nm.

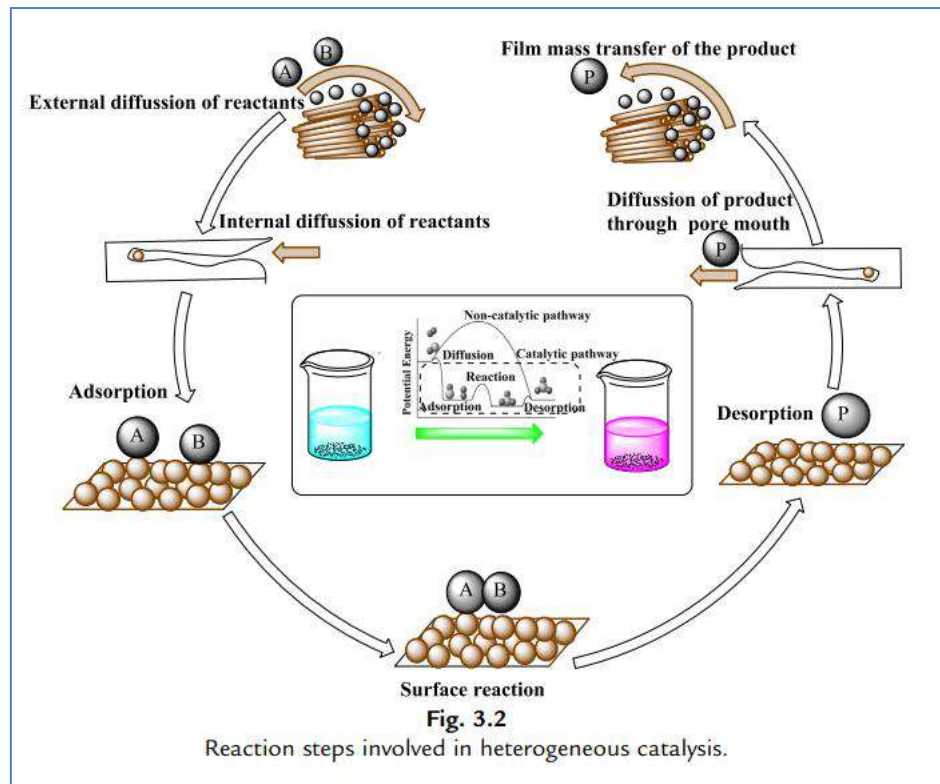
➤ The most common method for measuring the number density of exposed metal atoms is selective *chemisorption* of a probe molecule like H₂, CO, or O₂.

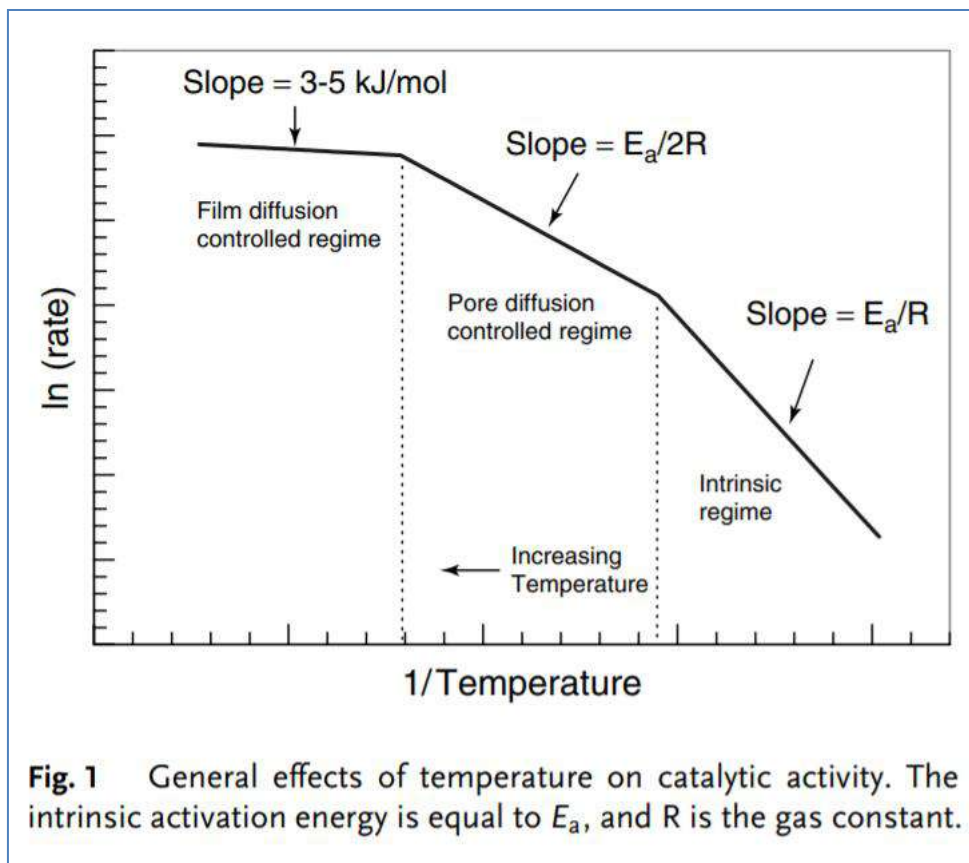
Catalytic Steps in Heterogeneous Catalysis

The elementary steps involved in heterogeneous catalytic reaction are as follows:

- 1) external diffusion of reactants from bulk phase to catalyst surface followed by its internal diffusion to approach active sites,
- 2) adsorption of reactants on active sites,
- 3) surface reaction, and
- 4) desorption of products from the active sites followed by their diffusion out of the catalyst.

All these steps are important in determining the overall rate of the catalytic reaction.





Desired Characteristics of a Catalyst -

The following list provides several of the key attributes of a good catalyst:

- The catalyst should exhibit good selectivity for production of the desired products and minimal production of undesirable by products.
- The catalyst should achieve adequate rates of reaction at the desired reaction conditions of the process (remembering that achieving good selectivity is usually more important than achieving high catalytic activity).
- The catalyst should show stable performance at reaction conditions for long periods of time, or it should be possible to regenerate good catalyst performance by appropriate treatment of the deactivated catalyst after short periods.
- The catalyst should have good accessibility of reactants and products to the active sites such that high rates can be achieved per reactor volume

phase to the reactants and products, and is often favoured in industry, being easily separated from the products, although it is often less specific and allows side reactions to occur.

Heterogeneous catalysis

The most common examples of heterogeneous catalysis in industry involve the reactions of gases being passed over the surface of a solid, often a metal, a metal oxide or a zeolite (Table 1).

Process	Catalyst	Equation
Making ammonia	Iron	$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
Making synthesis gas (carbon monoxide and hydrogen)	Nickel	$\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$
Catalytic cracking of gas oil	Zeolite	Produces: a gas (e.g. ethene, propene) a liquid (e.g. petrol) a residue (e.g. fuel oil)
Reforming of naphtha	Platinum and rhenium on alumina	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3(\text{g}) \rightarrow \text{C}_6\text{H}_{12}(\text{g}) + \text{H}_2(\text{g})$
Making epoxyethane	Silver on alumina	$\text{C}_2\text{H}_4(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{C}-\text{O}-\text{CH}_2(\text{g})$
Making sulfuric acid	Vanadium(V) oxide on silica	$\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$
Making nitric acid	Platinum and rhodium	$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$

Table 1 Examples of industrial processes using heterogeneous catalysis.

The gas molecules interact with atoms or ions on the surface of the solid. The first process usually involves the formation of very weak intermolecular bonds process known as physisorption, followed by chemical bonds being formed, a process known as chemisorption.

An example of the stepwise processes that occur in heterogeneous catalysis is the oxidation of carbon monoxide to carbon dioxide over palladium. This is a very important process in everyday life. Motor vehicles are fitted with catalytic converters. These consist of a metal casing in which there are two metals, palladium and rhodium, dispersed very finely on the surface of a ceramic support that resembles a honeycomb of holes. The converter is placed between the engine and the outlet of the exhaust pipe.

The exhaust gases contain carbon monoxide and unburned hydrocarbons that react with the excess oxygen to form carbon dioxide and water vapour, the reaction being catalysed principally by the palladium:

The exhaust gases also contain nitrogen(II) oxide (nitric oxide, NO), and this is removed by reactions catalysed principally by the rhodium:

The accepted mechanism for the oxidation of carbon monoxide to carbon dioxide involves the chemisorption of both carbon monoxide molecules and oxygen molecules on the surface of the metals. The adsorbed oxygen molecules dissociate into separate atoms of oxygen. Each of these oxygen atoms can combine with a chemisorbed carbon monoxide molecule to form a carbon dioxide molecule. The carbon dioxide molecules are then desorbed from the surface of the catalyst. A representation of these steps is shown in Figure 1.

Figure 1 A mechanism for the oxidation of carbon monoxide.

Each of these steps has a much lower activation energy than the homogeneous reaction between the carbon monoxide and oxygen.

The removal of carbon monoxide, unburned hydrocarbons and nitrogen(II) oxide from car and lorry exhausts is very important for this mixture leads to photochemical smogs which aggravate respiratory diseases such as asthma.

The enthalpy of chemisorption has to be sufficiently exothermic for chemisorption to take place, but not so high that it does not allow further reaction to proceed. **For example**, in the oxidation of carbon monoxide, molybdenum might at first sight be favoured as a choice, as oxygen is readily chemisorbed by the metal. However, the resulting oxygen atoms do not react further as they are too strongly adsorbed on the surface. Platinum and palladium, on the other hand, have lower enthalpies of chemisorption with oxygen, and the oxygen atoms can then react further with adsorbed carbon monoxide.

General requirements for a heterogeneous catalyst

To be successful the catalyst must allow the reaction to proceed at a suitable rate under conditions that are economically desirable, at as low a temperature and pressure as possible. It must also be long lasting. Some reactions lead to undesirable side products. For example in the cracking of gas oil, carbon is formed which is deposited on the surface of the catalyst, a zeolite, and leads to a rapid deterioration of its effectiveness. Many catalysts are prone to poisoning which occurs when an impurity attaches itself to the surface of the catalyst and prevents adsorption of the reactants. Minute traces of such a substance can ruin the process, One example is sulfur dioxide, which poisons the surface of platinum and palladium. Thus all traces of sulfur compounds must be removed from the petrol used in cars fitted with catalytic converters.

Further, solid catalysts are much more effective if they are finely divided as this increases the surface area.

Phase-Transfer Catalyst

A phase-transfer catalyst or PTC is a catalyst that facilitates the migration of a reactant from one phase into another phase where reaction occurs

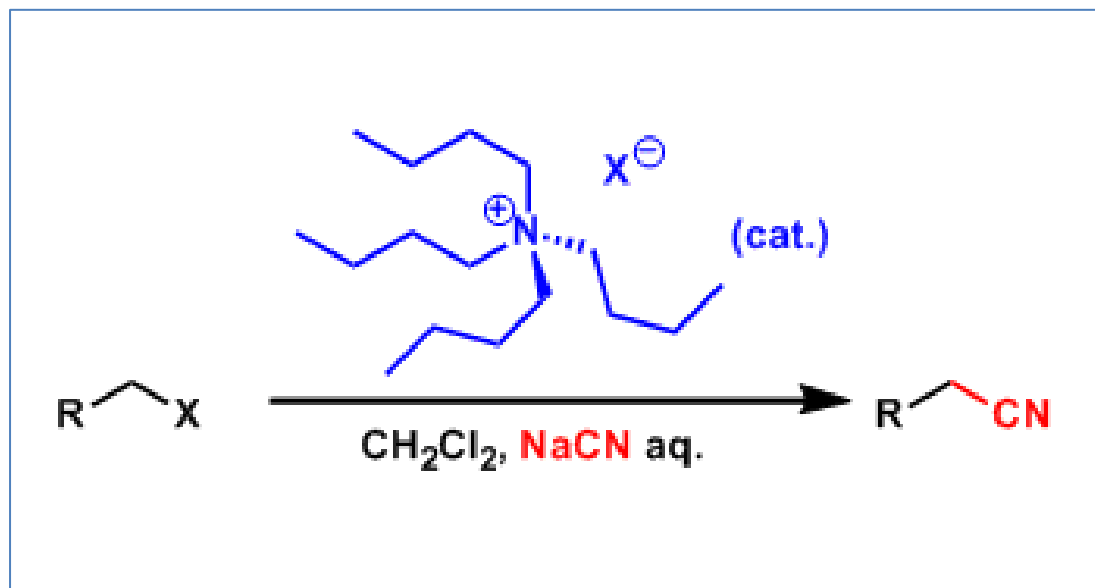
Phase-transfer catalysis is a special form of heterogeneous catalysis

Ionic reactants are insoluble in an organic phase in the absence of the phase-transfer catalyst but they are soluble in aq. phase

Phase-transfer catalysts are especially useful in green chemistry—by allowing the use of water, the need for organic solvents is reduced

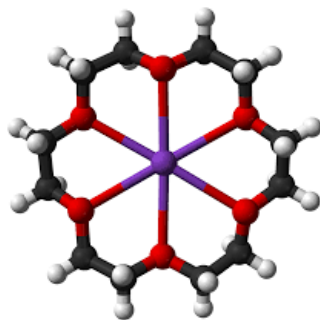
Examples of PTC -

1. Quaternary ammonium halide -

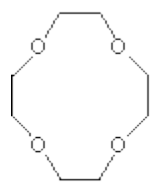
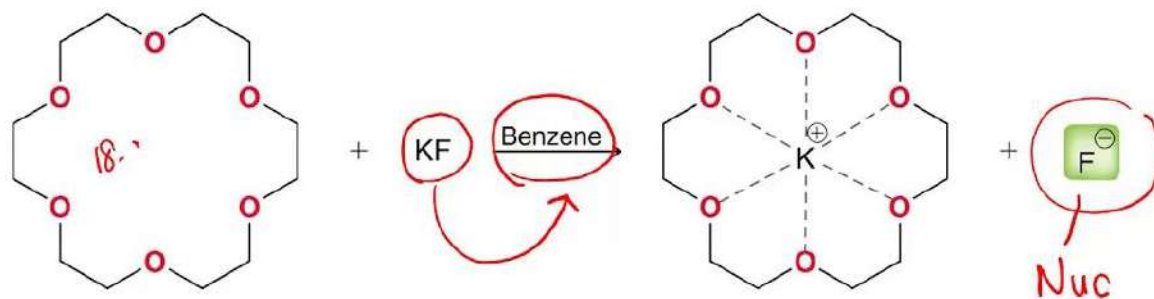


Examples of PTC -

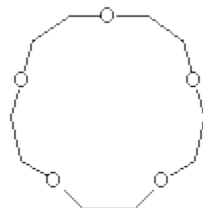
2. Crown ethers -



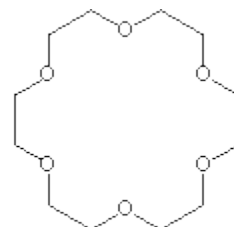
- The F^- ion below is ready to react because the K^+ ion is “hosted” by 18-crown-6
- Without the crown ether, the solubility of KF in benzene is miniscule



12-crown-4



15-crown-5



18-crown-6

TYPES OF PHASE-TRANSFER CATALYSTS

There are many types of phase transfer catalysts, such as quaternary ammonium and phosphonium salts, crown ethers, cryptands, etc.

Among these, the quaternary ammonium salts are the cheapest and hence the most widely used in the industry.

PRINCIPLE

The principle of PTC is based on the ability of certain phase-transfer agents (the PT catalysts) to facilitate the transport of one reagent from one phase into another (immiscible) phase wherein the other reagent exists

reaction is made possible by bringing together the reagents which are originally in different phases

it is also necessary that the transferred species is in an active state for effective PT catalytic action, and that it is regenerated during the organic reaction

MECHANISMS OF PTC

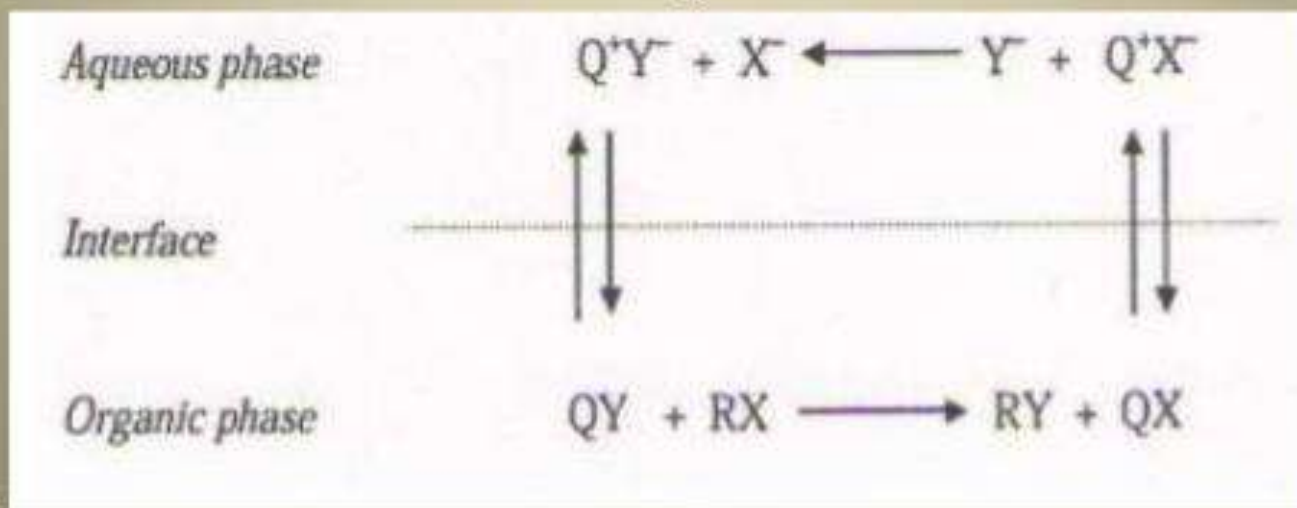
A quaternary ammonium halide dissolved in the aqueous phase (Q^+X^-) undergoes anion exchange with the anion of the reactant dissolved in the aqueous solution

The ion-pair formed (Q^+Y^-) can cross the liquid-liquid interface due to its lipophilic nature and diffuses from the interface into the organic phase, this step being the phase-transfer

In the organic phase, the anion of the ion-pair being quite nucleophilic undergoes a nucleophilic substitution reaction with the organic reagent forming the desired product (RY)

The catalyst subsequently returns to the aqueous phase and the cycle continues.

An overview of PTC reactions is given in the scheme bellow:



APPLICATIONS OF PTC

PTC finds applications in a variety of reactions

- PTC is widely exploited industrially
- Applications involving the use of a co-catalyst include co-catalysis by surfactants, alcohols and other weak acids in hydroxide transfer reactions, use of iodide, or reactions carried out with dual PI catalysts have been also reported
- In nucleophilic substitution reactions and in reactions in the presence of bases involving the deprotonation of moderately and weakly acidic organic compounds
- PTC has made possible the use of cheaper and easily available alternative raw materials like potassium carbonate and aqueous NaOH solution, thereby obviating the need of severe anhydrous conditions, expensive solvents, and dangerous bases such as metal hydrides and organometallic reagents
- When any kind of chemical reactions are carried out in the presence of a PT catalyst in biphasic systems, simple, cheap and mild bases like NaOH and K₂CO₃ can be used instead of toxic alkali metal alkoxides, amides, and hydrides
- Perfumery and Fragrance Industry like Synthesis of phenylacetic acid, an intermediate in the perfumery industry

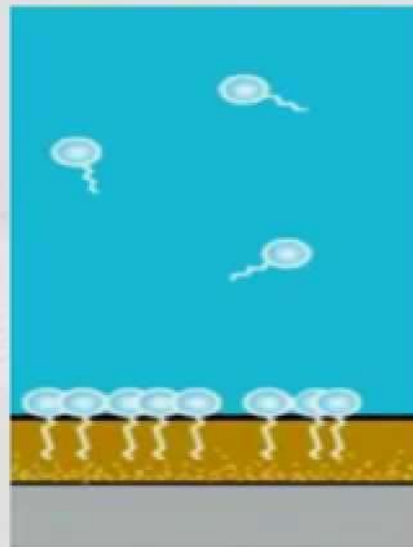
- In the field of Pharmaceuticals like Synthesis of various drugs like dicyclonine, phenoperidine, oxaladine, ritaline, etc.
- Polymeric bonded PTC for the determination of cyanide, iodide, nitrite, sulphide and thiocyanate, led to easy layer separation and PTC-free injection of the sample into the chromatograph
- However, the main disadvantages of PTC, especially in commercial applications, are the need to separate the catalyst from the product organic phase
- PTC can also be used for the synthesis process for fine chemicals manufacture industries
- Polyester polymers
for example are prepared from acid chlorides and bisphenol-A
- Phosphothioate -based pesticides are generated by PTC-catalyzed alkylation of phosphothioates
- One of the more complex applications of PTC involves asymmetric alkylations, which are catalyzed by chiral quaternary ammonium salts derived from cinchona alkaloids

Similar to PTC

Cleansing Action Of Detergent



Detergent molecule dissociates to form sodium ion (or potassium ion) and detergent ion



Hydrophilic region dissolves in water. Hydrophobic region dissolves in grease



Detergent ion will remove the grease when the water is shaken.

PURPLE BENZENE



The term "**purple benzene**" refers to benzene with permanganate in it.

Salts which are normally insoluble in organic solvents are made soluble by crown ether. For example, potassium permanganate dissolves in **benzene** in the presence of 18-crown-6, giving the so-called "**purple benzene**", which can be used to oxidize diverse organic compounds.