

Catalyst and catalysis

Definition:

Generally, the process by which a catalyst affects a reaction, speeds up or slows down, is called catalysis.

A catalyst is defined as any substance “organic, synthetic, or metal” that works to accelerate a chemical reaction by reducing its activation energy (E_a) without affecting in any way the possibilities for this reaction within a chemical system.

Scientifically, catalyst within the catalysis lowers the value of activation energy and therefore increases the rate of reaction, without being consumed in the reaction and without it is changing the original energies (i.e. enthalpy “ ΔH ” or free energy “ ΔG ” states) of neither the reactants nor the products. Therefore, the required energy to allow the reactants to enter the transition state to react and thereby to initiate the reaction is seen to be extensively reduced by applying the more stable and active catalyst to the reaction.

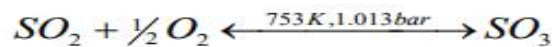
E_a is the activation energy in $\text{kJ}\cdot\text{mol}^{-1}$, which is defined as the energy that must be overcome in order for a chemical reaction to occur, it may otherwise be denoted as the minimum energy necessary for a specific reaction to occur. The classical exponential law of Arrhenius can be applied to estimate the kinetic parameters for the reaction:

$$\left[k = A \cdot \exp\left(-\frac{E_a}{RT}\right) \right]$$

Where k is the rate constant (i.e. reaction rate coefficient), A is the attempt frequency of the reaction (i.e. an empirical relationship between the temperature and the rate coefficient), which denotes the total number of collisions between reactant molecules having the correct orientation so as to lead to products, T is the absolute reaction temperature in degree Kelvin (i.e. the reactor bed temperature), and R is symbolized as the molar gas constant with the value of $8.314 \times 10^{-3} \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The Boltzmann constant ($K_B = 1.38066 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$) is usually used instead of the gas law constant, when E_a is given in molecular units (i.e. Joules per molecule).

Adding the catalyst diminishes decomposition temperature and promotes decomposition speed, hence makes a chemical process more efficient and reduces pollution by saving energy while minimising unnecessary products and by-products.

For example; the following chemical reaction reaches the equilibrium at 50% of the conversion of SO_2 into SO_3 as shown in Figure 1:



Using the catalyst leads to reduce both the reaction time and the cost by means of increasing the speed of the reaction.

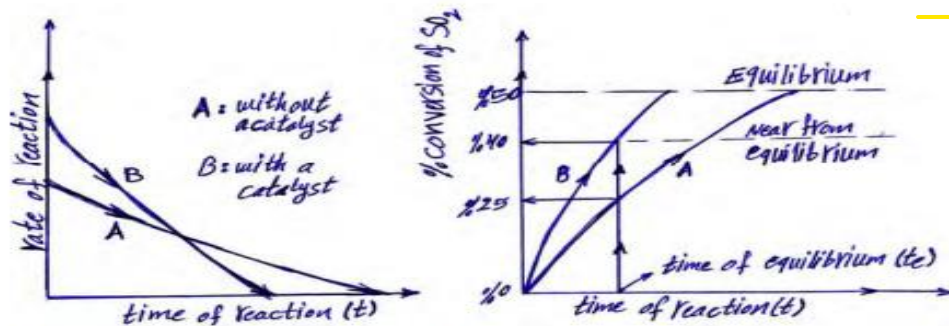


Figure 1: The effects of the catalyst on both the time and the rate of chemical reaction.

In fact, the possibilities for the reaction described in terms of thermodynamics by means of the Gibbs free energy of the materials involved in the reaction – the reaction proceeds spontaneously if $\Delta G < 0$ and vice versa, as shown in Figure 2.

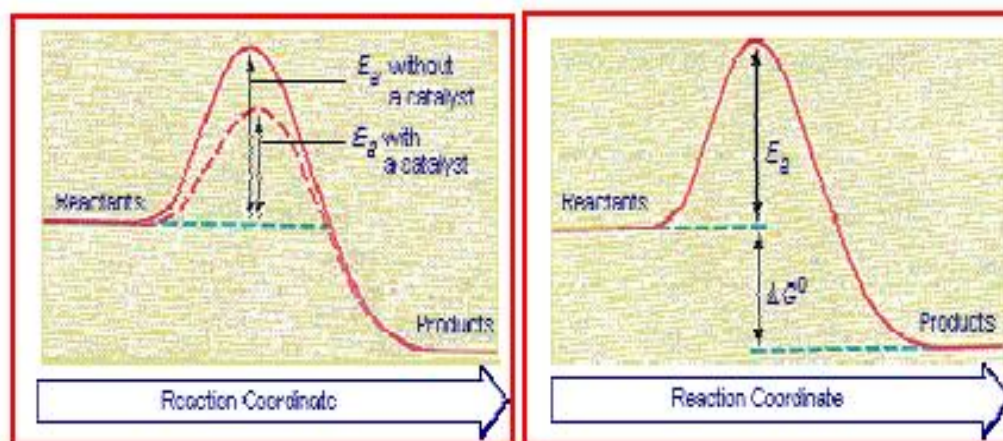


Figure 2 The left diagram shows that reactants can be converted into products, when the free energy of the system overcome the activation energy for the reaction, while the right diagram shows that catalysts provide a new mechanism by supplying acidic sites for the adsorption and dissociation of the reactants in order to increase the rates of reactions.

The change in free energy (ΔG), which is related to the reaction enthalpy (ΔH) and reaction entropy (ΔS) by the equation:

$$\Delta G = \Delta H - T.\Delta S$$

is equal to the difference between the respective energies of formation of products and reactants from their elements at the reaction temperature (T):

$$\Delta G = G (\text{products}) - G (\text{reactants})$$

In terms of partial pressures (P), the equilibrium constants ($K_p = [P (\text{products}) / P (\text{reactants})]$), is given by the expression:

$$\Delta G = -R.T. \ln K_p$$

$$K_p = \exp \left(\frac{\Delta S - \frac{\Delta H}{T}}{R} \right)$$

Where ΔH is the enthalpy of transition (KJ.mol^{-1}), which measures the heat content. Changes of state or phase of matter are also accompanied by enthalpy changes, and if ΔH is positive, the reaction is endothermic such as in a melting process – heat is absorbed by the system. In contrast, if ΔH is negative, the reaction is exothermic such as in a freezing process – heat is desorbed from the system.

According to the transition state theory the activated complex can be formed by either the left or the right diagram as shown in Figure 3.

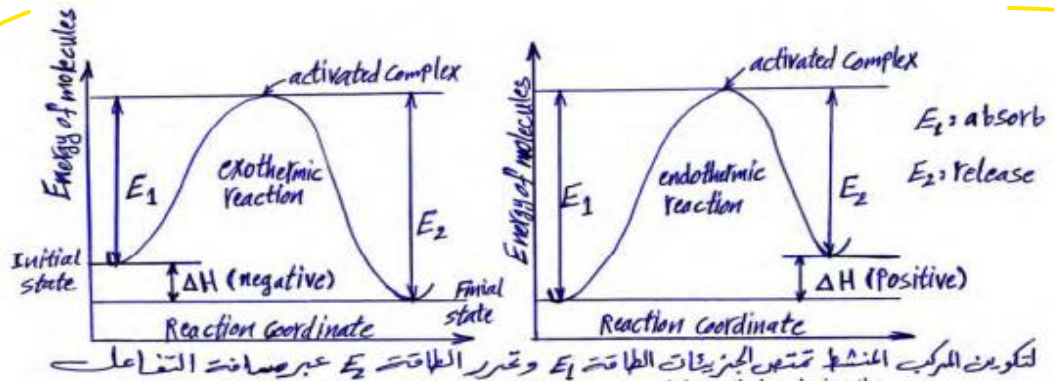


Figure 3: The relationship between the activation energy and the enthalpy during the reaction.

Classification of catalyst:

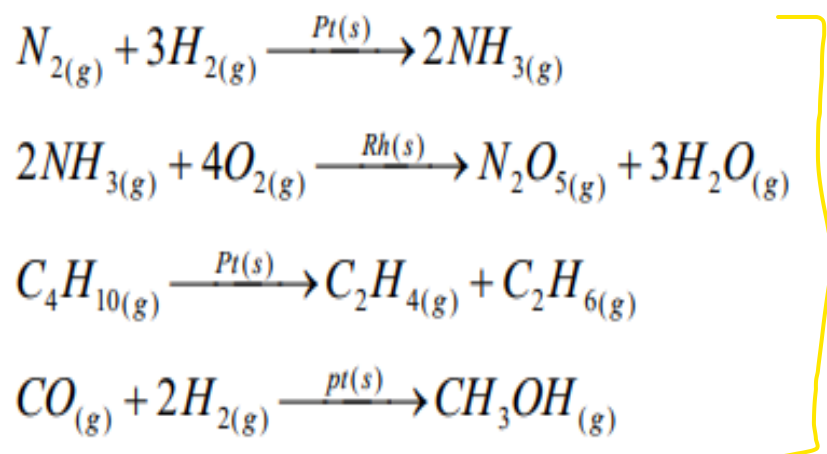
A catalyst can be either hetero-geneous or homo-geneous with bio-catalysts (enzymatic) are often seen as a separate group. Accordingly, there are two types of reactions:

1- Homogenous Reaction

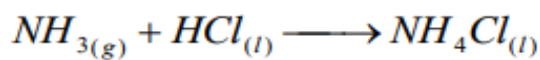
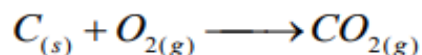
In this type of reaction both the catalyst and the reactants are existing in the same phase (e.g. either the catalytic reactions in most of the liquid phase or the noncatalytic reactions in most of the gaseous phase).

2- Heterogeneous Reaction

In this type of reaction the catalyst and the reactants are existing in the different phase, as in the case of the following catalytic reactions:



Or in the case of the following noncatalytic reactions:



Mechanisms of heterogeneous catalysis:

Theoretically, the overall reaction that takes place throughout the active sites on the catalyst's surface follow a five-step mechanism, as shown in the schematic diagram in Figure 4. These stages are: –

- 1- Thermal decomposition, generally after the transport of reactants from the homogeneous phase (i.e gaseous or liquid) to the solid surface.
- 2- Primary catalytic reaction following absorption of reactants on specific sites of the surface so as to produce the intermediate chemisorbed species.
- 3- Secondary reactions between primary products in the sorbed phase.
- 4- Desorption of the products from the sorbed phase to release the sites.
- 5- Removal of the products from the catalyst surface into the homogeneous phase, and accumulation of polymerizable products from further reaction by their adsorption on the surface of the catalyst as coke.

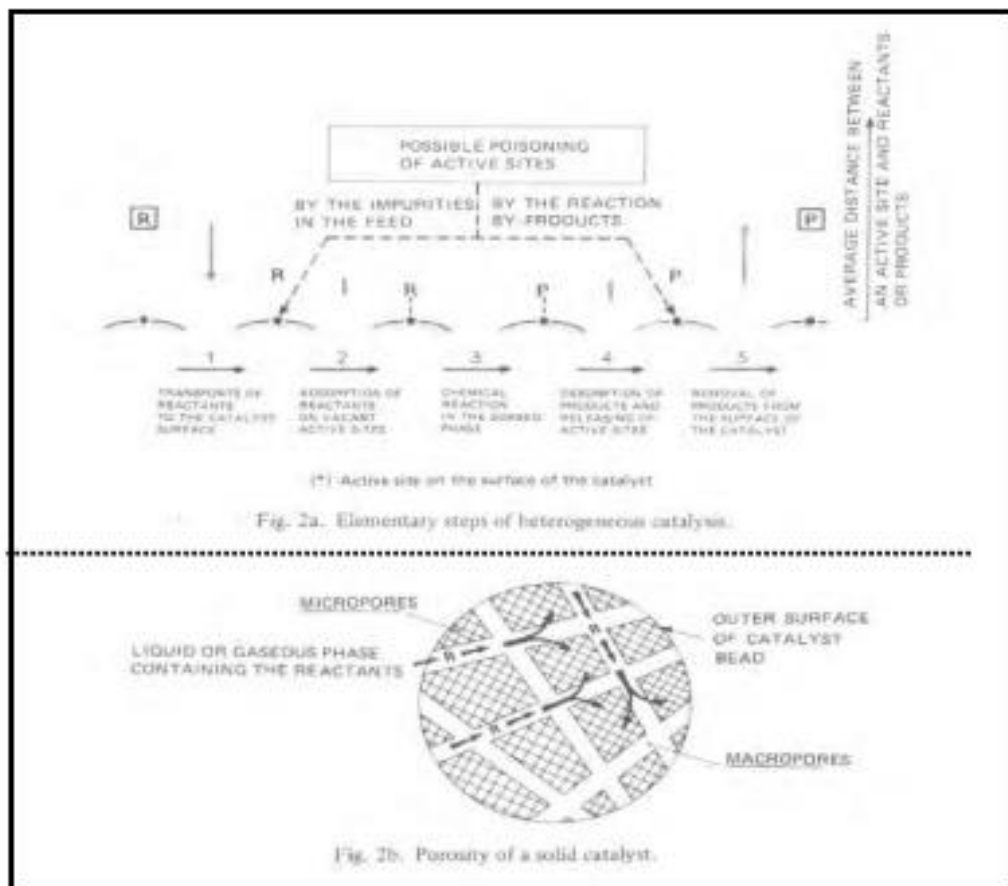


Figure 4 (a) Reaction occurs on the catalyst surface “heterogeneous catalysis”, (b) Porosity