

Lecture 1

Introduction to catalysis

The science and technology of catalysis is of great significance as it affects our daily life. Four major sectors of the world economy; petroleum and energy production, chemicals and polymer production, food industry and pollution control, involve catalytic processes.

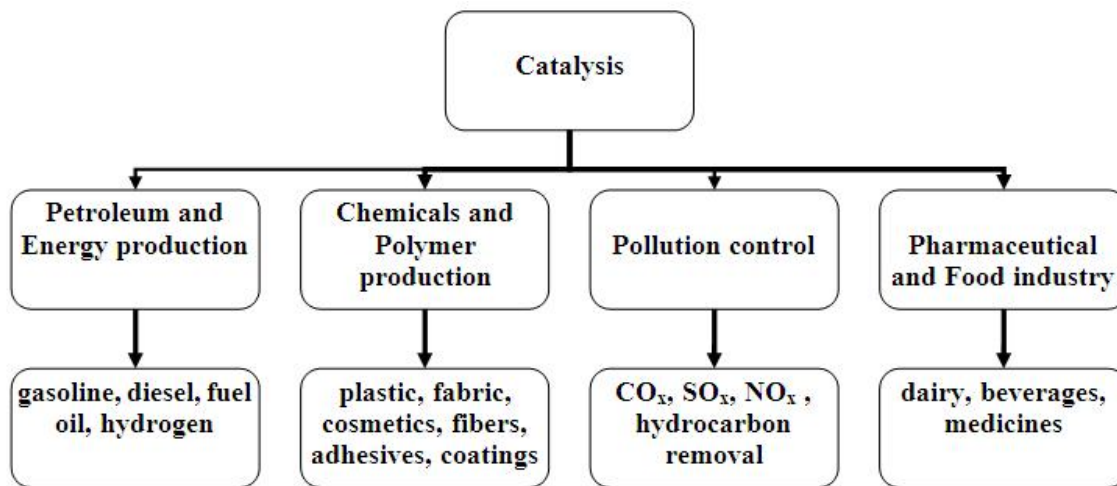


Fig. 1. Four major sectors of world economy that involve catalytic processes

Catalysts are used to produce fuels such as gasoline, diesel, heating oil, fuel oil etc. Production of plastics, synthetic rubbers, fabrics, cosmetics etc. involve catalytic processes. The production of clean energy from renewable energy sources, such as hydrogen for fuel cells and transportation fuels from non-edible biomass are also catalyst dependent processes. Automobile emission catalysts are used to reduce emissions of CO, NO_x and hydrocarbons from mobile vehicles. Catalysts are also used in the production of the polymers including adhesives, coatings, foams, textile and industrial fibers. The pharmaceutical industry uses catalysts for production of drugs that are used to save lives and improve the health of people. Catalysts are also widely used in food processing. More than 90 % of industrial processes actually use catalysts in one form or the other. Owing to expanding need of mankind, production in all sectors is increasing at a fast rate and catalysis science and technology has a major contribution in this. Thrusts are being given in the areas of catalyst upgrading to new and more efficient catalysts. Increasing catalyst life is another area of importance to maximize catalyst efficiency.

History : Catalyst technology has been used for many centuries. It ranged from inorganic catalyst to make soaps to enzyme catalysts for producing wines, cheese and other food and beverages. The industrial catalyst technology started with the large-scale production of sulfuric acid on platinum catalyst in 1875. In subsequent years, various major catalytic processes were invented. In 1903, ammonia oxidation on Pt gauze was developed by Ostwald for nitric acid production. Another major breakthrough was ammonia synthesis with promoted iron in 1908-1914 by Mittasch, Bosch and Haber.

Conversion of synthesis gas to liquid hydrocarbons by hydrogenation of CO, which was developed in 1920-1940, was a major development in the energy sector. In petroleum industry, the development of catalytic cracking process during 1935- 1940 changed the energy scenario. This process used a solid catalyst in the petroleum industry for the first time. Subsequent decades saw the development of various catalytic hydrocarbon processes such as catalytic naphtha reforming (1950) and hydrotreating for removal of sulphur, nitrogen, metals from petroleum feed stock (1960). With the discovery of Ziegler-Natta catalyst in 1955, the polymer industry grew significantly. The first large scale industrial homogeneous catalytic process came up in 1960 in the form of Walker process for making acetaldehyde from ethylene. The development of shape selective catalysts such as molecular sieves or zeolites for cracking (1964) resulted in the production of exclusively shape selective products. The other major development in catalysis was in 1970-1980 for environmental pollution control. Noble metal catalysts were developed for emission control of CO, NO_x and hydrocarbons from automobiles. Vanadia-titania and zeolite catalysts were developed for selective reduction of NO_x. Catalysis is a continuously growing area and discovery of new catalysts and their applications has led to major development in the chemical industry.

The economic significance of the catalyst industry is enormous. The catalytic processes contribute greater than 35% of global GDP. The world catalyst industry amounts to US \$ 12 billion. It is expected to grow annually by 6 % to US \$16 billion ~~US\$~~ in 2012. Polymerization catalysts are expected to grow most rapidly due to significant expansion in polymer industry. Enzyme and organometallic catalysts will also grow. Reduction of sulphur levels in fuels and ongoing shifts towards heavy grade crude oil with high sulphur content is expected to contribute to the growth of catalytic hydrocarbon industry.

Catalysis involves understanding of the thermodynamics, kinetics, electronic interaction, crystal structure, reactor design and process development for a catalytic process. It is an interdisciplinary area involving contribution from chemical engineers, chemists and material scientists for successful implementation of the entire process starting from preparation of catalysts to final utilization in a chemical reactor.

Catalytic reactions

In a thermodynamically feasible chemical reaction, when addition of a small amount a chemical substance increases the rate of attainment of chemical equilibrium but the substance itself does not undergo any chemical change, then the reaction is called a catalytic reaction. The substance that enhances the reaction rate is called a catalyst. Catalysts work by providing alternative mechanism involving a different transition state of lower energy. Thereby, the activation energy of the catalytic reaction is lowered compared to the uncatalyzed reaction as shown in Fig 2.

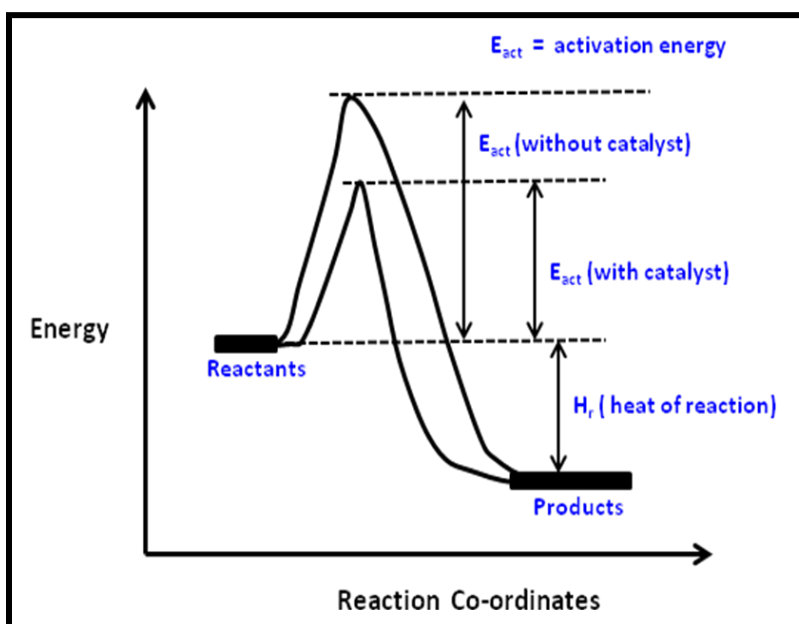
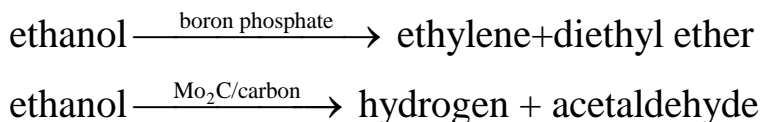


Fig. 2 . Comparison of activation energies of exothermic catalytic and non-catalytic reactions

A catalyst accelerates both the rates of the forward and reverse reaction. Equilibrium of a reversible reaction is not altered by the presence of the catalyst. For example, when oxidation of SO_2 is carried out in the presence of three different catalysts, namely Pt, Fe_2O_3 and V_2O_5 , the equilibrium composition is the same in all three cases. Another important characteristic of catalyst is its effect on selectivity. The presence of different catalysts can result in different product distribution from the same starting material. For example, decomposition of ethanol in the presence of different catalysts results in different products as shown below.



Types of catalytic reactions

Catalytic reactions can be divided into two main types –

1. Heterogeneous
2. Homogeneous

Heterogeneous catalysis

In heterogeneous catalytic reaction, the catalyst and the reactants are in different phases. Reactions of liquid or gases in the presence of solid catalysts are the typical examples.

An example is the Contact Process for manufacturing sulphuric acid, in which the sulphur dioxide and oxygen are passed over a solid vanadium oxide catalyst producing sulphur trioxide. Several hydrocarbon transformation reactions such as cracking, reforming, dehydrogenation, isomerization also fall in this category.

Homogeneous catalysis

In a homogeneous catalytic reaction, the catalyst is in the same phase as the reactants. Typically, all the reactants and catalysts are either in one single liquid phase or gas phase. Most industrial homogeneous catalytic processes are carried out in liquid phase. Ester hydrolysis involving general acid-base catalysts, polyethylene production with

organometallic catalysts and enzyme catalyzed processes are some of the important examples of industrial homogeneous catalytic processes.

Relative significance

Catalytic processes have great significance and about 90 % of all chemical industry involves catalytic processes. Of all the industrial catalytic processes, approximately 80 % involve the use of solid catalysts, 17 % homogeneous catalysts and rest 3 % biocatalysts. Thus, heterogeneous catalysts, particularly solid catalysts, dominate the industrial catalytic processes. Though the contributions of homogeneous catalytic processes in chemical industry are significantly smaller than that of heterogeneous catalytic processes, but because of high selectivities, homogeneous process are finding increasing importance for production of many important value added products such as manufacturing of tailor made plastics, fine chemicals, pharmaceutical intermediates etc.

Heterogeneous catalytic theory

In general, it is believed that the entire surface of the solid catalyst is not responsible for catalyzing any reaction. Only certain sites on the catalyst surface actually participate in the reaction and these sites are called active sites on the catalysts. These sites may be the unsaturated atoms resulting from surface irregularities or atoms with chemical properties that enable the interaction with the adsorbed reactant atoms or molecules. Activity of the catalyst is directly proportional to the number of these active sites available on the surface and is often expressed in terms of turnover frequency. Turnover frequency is defined as the number of molecules reacting per active site per second at the condition of experiments.

A solid catalytic reaction $A \rightarrow B$ goes through the following steps. The steps are illustrated in Fig 3.

1. Transportation of reactant (A) from bulk fluid to pore mouth on the external surface of catalysts pellets
2. Diffusion of the reactant (A) from the pore mouth through the catalyst pores to the immediate vicinity of internal catalytic surface
3. Adsorption of reactant (A) onto the catalyst surface
4. Reaction of (A) on the catalyst surface producing product (B)
5. Desorption of the product (B) from the surface

6. Diffusion of the product (B) from interior part of the pores to the pore mouth on the external surface
7. Transfer of the product (B) from pore mouth on the external surface to the bulk fluid

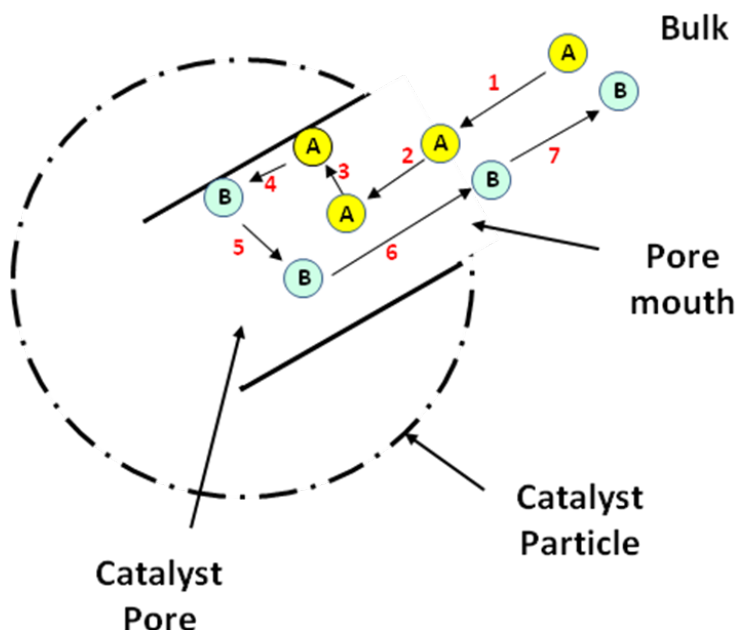


Fig. 3. Steps in solid catalytic reactions.

The overall rate of reaction is equal to the rate of slowest step in the mechanism. When the mass transfer and diffusion steps [1,2,6,7] are very fast compared to adsorption and reaction steps [3,4,5], concentration in the immediate vicinity of the active sites is the same or indistinguishable from that in the bulk fluid. Consequently, the transport or diffusion steps do not affect the overall rate of the reaction. Alternatively, if reaction and diffusion steps are fast compared to the mass transfer steps, then mass transfer does affect the rate of reaction. When mass transfer from the bulk phase to the pore mouth is slow and affects the reaction rate, then changing the flow conditions past the catalyst should change the overall reaction rate. In case of porous catalysts, diffusion within the catalyst pores may limit the reaction rate. Under this condition external flow does not affect the reaction rate but internal diffusion does affect.

Book References

- R. J. Farrauto & C. H. Bartholomew, Fundamentals of Industrial catalytic Processes, Blackie Academic & Professional, 1997
- H. S. Fogler, Elements of Chemical reaction engineering, Prentice – Hall of India, 2002, Third edition.
- J.J. Carberry , Chemical and catalytic reaction Engineering, Dover Publications, 2001
- J. M. Thomas & W. J. Thomas, Principles and Practice of Heterogeneous Catalysis, VCH, 1997
- J. M. Smith , Chemical Engineering Kinetics, McGraw-Hill Book Company, 1981

Lecture 2

Adsorption on solid surfaces

Importance of adsorption in solid catalysis

As discussed in the previous section, heterogeneous solid catalysis is strongly associated with adsorption phenomenon. In solid catalysis, at least one of the reactant needs to be adsorbed on the surface of the catalyst. Adsorption of a component 'A' on surface of material 'B' is defined as preferential accumulation of the component 'A' on the surface of the material 'B'. The component 'A' is called adsorbate and surface 'B' is called adsorbent. The surfaces include both external surface and internal surface due to the pores. For highly porous material, the internal surface area due to the pores is much higher than the external surface area. The pores in a solid material can be of different dimensions. Pores with diameter less than 2nm (20 \AA) are called micropores, pores in the range of 2- 50 nm ($20 - 500 \text{ \AA}$) are called mesopores, whereas pores greater than 50 nm are called macropores. The pore size distribution of a catalyst is affected by preparation condition and amount of loading of active component. Usually a wide pore size distribution exists in a catalyst. However, catalyst can also be designed to have a very narrow pore size distribution. Fig 1 shows the schematic representation of a typical porous solid catalyst particle having both the mesopores and micropores. The active sites are dispersed throughout the porous matrix. Under suitable conditions of temperature and pressure, a gas can gradually adsorb on the solid surface and finally lead to its complete coverage.

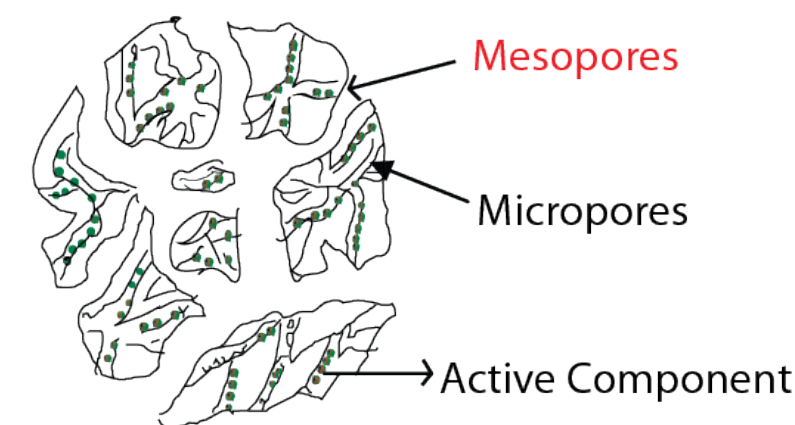


Fig. 1. Schematic representation of typical porous support impregnated with active component

Why adsorption takes place on solid surface

In the bulk of the adsorbent, the molecules are associated with their neighbours equally in all direction and the molecular forces are therefore balanced. However on the adsorbent surface, the molecules are bounded to the inner molecules at one side leaving unbalanced molecular forces on the other side. These unbalanced molecular forces on adsorbent surfaces create the attractive force for the adsorbate molecules approaching the surface. These molecular forces are weak in nature and called van der Waals attraction forces.

Types of adsorption

Depending on the nature of interaction, the adsorption can be of two types:

1. Physisorption
2. Chemisorption

The phenomenon of adsorbate molecules attaching themselves to adsorbent surface under the influence of van der Waals forces is called physisorption or physical adsorption. The van der Waals forces mainly consist of dipole –dipole interactions. This is an exothermic process with a low enthalpy change known as heat of adsorption. This process resembles liquefaction and heat of adsorption for physisorption is also known as heat of liquefaction.

At higher temperature, the adsorbed molecules can undergo electronic rearrangement with the surface molecules. This phenomenon is called chemisorption. The electronic rearrangement may include formation and breaking of chemical bonds. The electronic rearrangement occurs only when there is significant interaction between adsorbate and the adsorbent molecules. Hence all adsorbate will not be chemisorbed on all adsorbent surfaces. Chemisorption process is selective and an adsorbate molecule will chemisorbed only on selected adsorbent. The adsorption processes are shown in Fig 2. The Fig. 2(a) depicts the situation when the adsorbate molecule approach any adsorbent surface under the influence of attractive forces created by the unbalanced molecular forces on adsorbent surfaces. The Fig. 2(b) represents the phenomenon, when any molecule is physisorbed on surface by van der Waals forces. No bond formation occurs in this situation. A chemisorption situation is represented in Fig. 2(c) when there is a weak bond formation between adsorbate and adsorbent molecule. As discussed above, the adsorbate molecule will be chemisorbed only on selected adsorbent surface with which it can interact significantly.

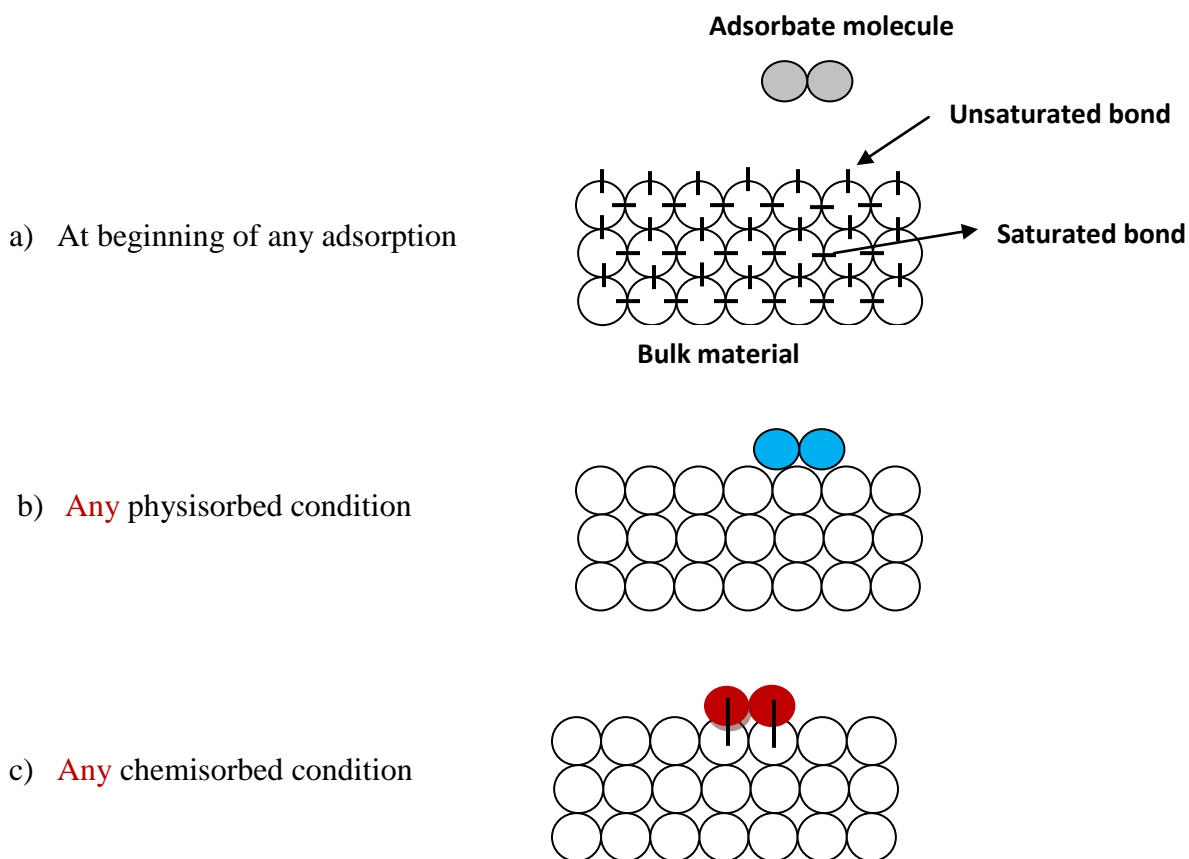


Fig. 2. Schematic representation of different adsorption processes

Physisorption versus Chemisorption

1. Since physisorption involves only weak molecular interaction, the associated enthalpy changes are small (in the range of 10 to 40 kJ /mol) . On the other hand, in case of chemisorption, enthalpy change is quite large and can range from 80-400 kJ /mol.
2. The Fig. 3 compares the volume of gas adsorbed as a function of temperature under physisorbed and chemisorbed conditions. In physisorption, the molecules are adsorbed on surface by weak interaction. With increase in temperature, adsorbed molecules gain excess energy and their tendency to escape from the surface increases. Hence volume of gas adsorbed on the surface decreases with temperature as shown in Fig. 3. However, the chemisorption involves higher interaction energy between adsorbate and adsorbent molecules and hence is favored by temperature rise. Hence at low temperature range volume of adsorbed gas increases with temperature. However, at higher temperature range as the adsorbed molecules gains excess energy, rate of desorption becomes higher resulting in decrease in adsorbed gas volume as shown in Fig. 3.

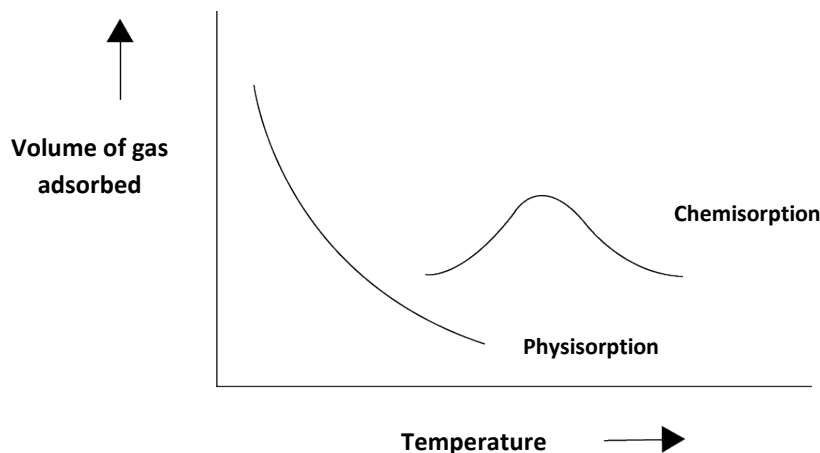


Fig. 3. Volume of gas adsorbed as a function of temperature for physisorption and chemisorption processes

3. In case of chemisorption, since there is electronic interaction between adsorbate and adsorbent molecules, only a monolayer of adsorbate can be formed on the adsorbent surface. In case of physisorption, the first monolayer formed on the surface of the adsorbent can act as adsorbing surface for formation of next layer of adsorbate and so on. This phenomenon is called multilayer adsorption. The formation of monolayer and multilayers of the adsorbed molecules on a surface is shown in Fig. 4. For the physisorption, volume of gas adsorbed increases with pressure due to increase in concentration of adsorbate and formation of multilayers. However for chemisorption process which corresponds to monolayer formation, the effect of pressure is not significant.

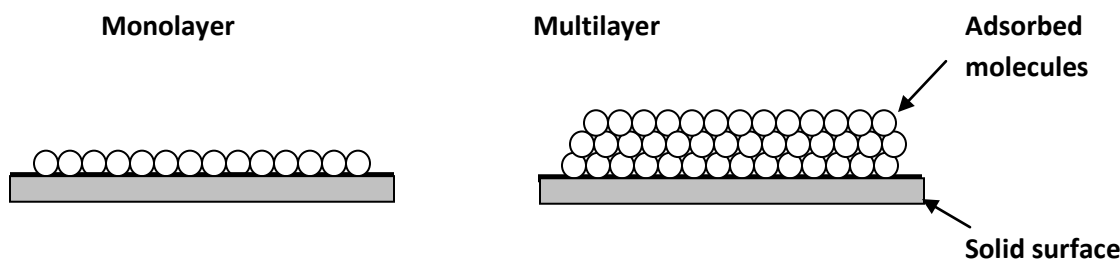


Fig. 4 . Monolayer and multilayer formation of the adsorbed molecules on a surface

4. Chemisorption is specific for adsorbate and adsorbent pair. Specific solid adsorbent can undergo electronic interaction only with specific adsorbate gas molecule.
5. Physisorption is highly reversible while chemisorption can be irreversible.
6. Physisorption is important for estimating the total surface area. It also provides a basis for estimating the pore volume and pore size distributions. On the other hand, chemisorption is important in estimation of area of catalytic active sites as well as its dispersion.

Examples :

Physisorption : Adsorption of nitrogen on carbon or alumina.

Chemisorption : Adsorption of hydrogen on active platinum sites on any support.

Potential energy diagram of approaching molecule towards a solid surface

The potential energy variation of a molecular system as it approaches a solid surface can be depicted by the potential energy diagram, where the potential energy is plotted as a function of distance of the approaching molecule from adsorbent surface. When the molecule approaches the surface, at first it becomes attracted by a weak attractive force resulting in relatively flat potential minimum corresponding to non – dissociative physical adsorption. Then depending on extent of interaction it can be carried to non-dissociative chemisorbed state and finally to stable dissociated state. When the extent of interaction is less, the adsorbate molecules are only physically adsorb on the adsorbent surface or may occur in non-dissociative chemisorbed state. If the interaction is only van der Waals type then the adsorbates will be in physisorbed state. In case of stronger electronic interaction the process may be directly carried on to dissociative chemisorption. If the crossing points are below the line of zero potential energy as shown in Fig. 5, then the overall process is non-activated. If they are above, the overall process requires activation.

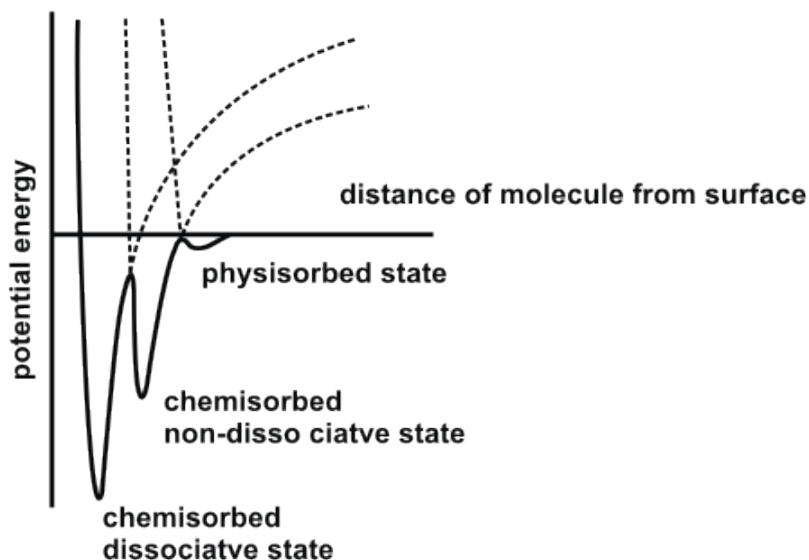


Fig. 5. Potential energy diagram for non activated dissociative chemisorption

Book References :

- J.J. Carberry , Chemical and catalytic reaction Engineering, Dover Publications, 2001
- J. M. Thomas & W. J. Thomas, Principles and Practice of Heterogeneous Catalysis, VCH, 1997
- J. M. Smith , Chemical Engineering Kinetics, McGraw-Hill Book Company, 1981
- R. J. Farrauto & C. H. Bartholomew, Fundamentals of Industrial catalytic Processes, Blackie Academic & Professional, 1997
- D.M. Ruthven, Principle of adsorption & adsorption processes, John Wiley & sons, 1984.

Lecture 3

Adsorption kinetics

Rate of adsorption : From kinetic theory the rate of collision, r_c , is the rate at which molecules of a gas **strike** a bare surface per cm^2 per sec at pressure p . The r_c is given as $r_c = \frac{p}{(2\pi mk_B T)^{1/2}}$ molecules / cm^2 .sec, where ' k_B ' is Boltzmanns constant, ' m ' is mass and ' T ' is temperature.

Then the rate of adsorption is $r_a = r_c s = \frac{sp}{(2\pi mk_B T)^{1/2}}$ -----[1]

The ' s ' is known as the sticking coefficient and defined as fraction of molecules bombarding or impinging on the catalyst surface that stick to the surface on impact. The ' s ' is also called the sticking probability.

Now whether a molecule will be adsorbed (chemisorbed) depends on two main parameters: activation energy and configuration. Only those molecules possessing the required activation energy can be chemisorbed. Even if the molecules possess the necessary energy they may not be chemisorbed if the configuration of the molecule and surface site do not allow the activated complex to be traversed. The fraction of molecules possessing the required energy is $\exp\left(\frac{-E_a}{RT}\right)$, where E_a is the activation energy for chemisorption.

The configuration probability that a molecule will occupy a single site is proportional to the fraction of unoccupied surface, $1-\theta$, where θ is the fraction of surface covered.

Therefore, $s = \alpha(1-\theta)\exp\left(\frac{-E_a}{RT}\right)$ -----[2]

α is the proportionality constant often known as 'condensation coefficient'. It is the fraction of those molecules with energy greater than E_a that is adsorbed.

Combining equation [1] and [2] gives

$$r_a = \frac{p}{(2\pi mk_B T)^{1/2}} \alpha (1-\theta) \exp\left(\frac{-E_a}{RT}\right)$$

$$\text{or } r_a = \frac{p}{(2\pi mk_B T)^{1/2}} \alpha \exp\left(\frac{-E_a}{RT}\right) f(\theta) \text{ -----[3]}$$

For non- dissociative adsorption, $f(\theta)$ = fraction of surface uncovered = $(1-\theta)$. For dissociative adsorption into two fragments, $f(\theta) = (1-\theta)^2$ and $f(\theta) = (1-\theta)^3$ for three fragments. The type of adsorption depends on extent on interaction between adsorbate and adsorbent surface molecules.

In actual adsorption, the observed rate decreases rapidly with increasing surface coverage which implies that the activation energy increases with the surface coverage, θ . The condensation coefficient α also varies with θ . These variations are caused by surface heterogeneity, that is the activity of the adsorbent sites varies and different sites possess different values of α and E_a . The most active sites are associated with lowest activation energy. Hence probability of occupation of these sites by adsorbate molecules is higher. Further, the interaction between occupied and unoccupied site also affects the rate of adsorption. Hence α and E_a should be represented as function of θ .

$$r_a = \frac{p}{(2\pi mk_B T)^{1/2}} \alpha(\theta) \exp\left(\frac{-E_a(\theta)}{RT}\right) (1-\theta)$$

Rates of desorption

The rate of desorption is given by Polanyi –Wigner equation as

$$r_d = -\frac{dN_a}{dt} = \nu N_a^m \exp\left[\frac{-E_d}{RT}\right] \text{ -----[4]}$$

where, E_d is activation energy for desorption, ν is the pre-exponential factor of the desorption rate coefficient, N_a is the number of binding sites for the adsorbed molecules and m is kinetic order for desorption process. Kinetic order suggests the nature of elementary steps that governs

the desorption. A zero-order kinetics indicates that desorption occurs from multilayer where desorption is independent of coverage. A first order kinetics indicates the presence of single surface species whereas second order kinetics indicates recombination of adsorbate atoms leading to production of a diatomic molecule that is then desorbed.

Adsorption Isotherms and Isobars

When an adsorbate molecule in the gas phase comes in contact with the surface of the adsorbent, an equilibrium distribution of the adsorbate molecules takes place between the adsorbent surface and the gas phase. This equilibrium distribution depends upon various factors including partial pressure of adsorbate, temperature, nature of adsorbate, and the surface area and nature of adsorbent. Adsorption isotherm shows the amount of molecules adsorbed on the solid surface as a function of the equilibrium partial pressure at constant temperature.

Adsorption isobar shows the variation of adsorbed species with temperature at constant pressure.

The adsorption-desorption isotherm characterizes the adsorbent. It depicts the nature of adsorption-desorption process occurring on the surface and also reveals the pore structure of the adsorbent. Often the isotherm is expressed as standard volume adsorbed as a function of relative pressure. Relative pressure is defined as the ratio of actual gas partial pressure over the saturated vapor pressure of adsorbate (P_0) under constant temperature. By Brunauer empirical classification, five types of isotherms are observed for solid adsorbents as shown in Fig 1.

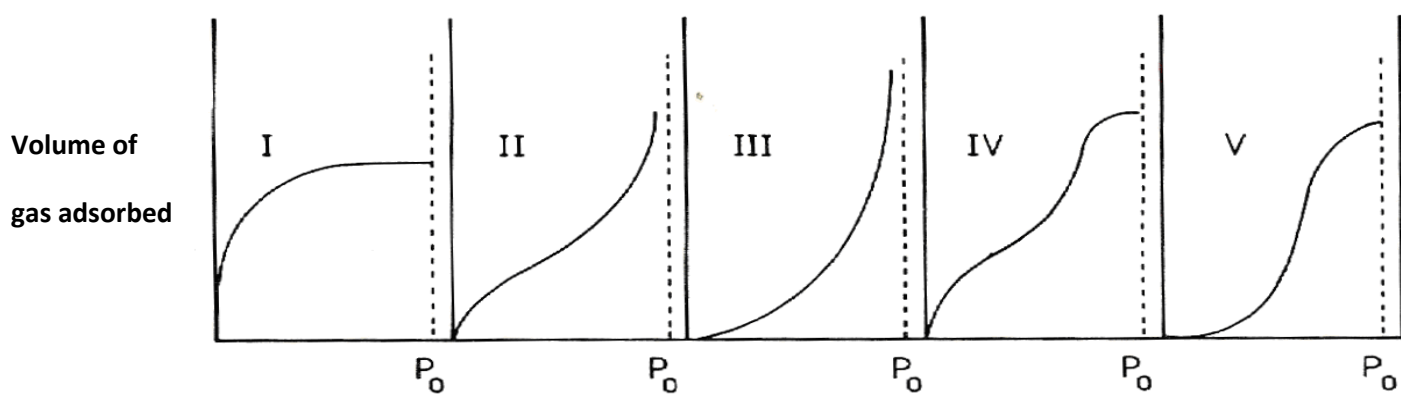


Fig. 1. Types of adsorption isotherm according to Brunauer classification

Type I isotherm is for very small pores or microporous adsorbents. Adsorption occurs by filling of the micropores. The adsorbate uptake rate depends on the accessible micropore volume rather than total internal surface area. **Type II** and **Type IV** isotherms are observed for non-porous or macroporous adsorbents with unrestricted monolayer-multilayer adsorption. At first the adsorption volume rapidly increases at low relative pressures of less than 0.01 due to interaction of the adsorbate molecules with the higher energetic region followed by the interaction with less energetic region. When the monolayer formation of the adsorbed molecules is complete, multilayer formation starts to take place corresponding to the ‘sharp knee’ of the isotherms. As the relative pressure approaches unity an abrupt rise indicates the bulk condensation of adsorbate gas to liquid. **Type III** and **Type V** isotherms do not have the ‘sharp knee’ shape implying stronger adsorbate – adsorbate interactions than adsorbate-adsorbent interaction.

Hysteresis Loop

In case of isotherms for nonporous material, the desorption curve traces the adsorption curve.

However, for the mesoporous and macroporous materials, desorption curve do not retrace the adsorption curve resulting in a wide loop. This is known as hysteresis loop and corresponds to the capillary condensation of adsorbate in the multilayer region, pore filling and emptying mechanism. The nature of the hysteresis loop is associated with different pore shapes and is shown in Fig 2.

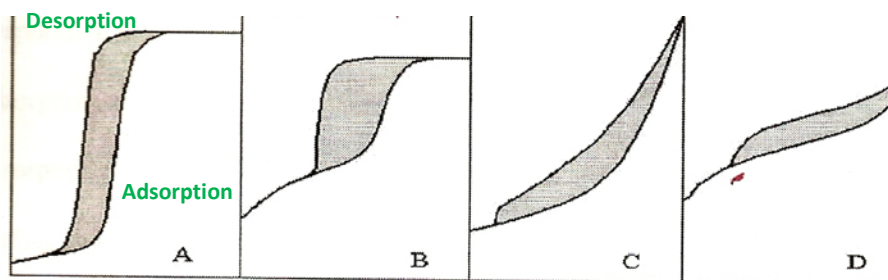


Fig. 2. Different hysteresis loops as represented by IUPAC

Type A hysteresis is attributed to cylindrical or tubular type pores of adsorbent with a narrow distribution of uniform pores. It is characterized by steep and narrow parallel adsorption and desorption curves. Type B has a long flat plateau adsorption with a steep desorption curve. This is a complex structure of pores with interconnected networks or ink bottle shaped pores. Type C represents aggregates of adsorbent that contain parallel plates, slit- shape pores or wide capillaries ($> 500 \text{ \AA}$). Type D is associated with slit- shape pores that are mainly in the micropore region.

Langmuir treatment of adsorption

Langmuir isotherm is derived based on the following assumptions:

1. Surface is energetically uniform, that is all the surface sites have the same activity for adsorption.
2. Adsorbed molecules do not interact with the other adsorbed molecules on the surface.
3. Heat of adsorption is therefore constant throughout the fractional surface coverage of 0 to 1.
4. Adsorption of all molecules occurs by the same mechanism and results in the same adsorbed structure.
5. Extent of adsorption is less than one complete monolayer coverage.

When a gas is in contact with a solid surface, the gas molecules continuously strike the surface and a fraction of these adhere. However, the more energetic molecules also continuously leave the surface. Eventually, the equilibrium is established so that the rate of adsorption equals the rate at which the molecules leave the surface.

Now, the rate of adsorption is equal to the rate of collision of molecules with the surface multiplied by a factor 's' representing the fraction of the colliding molecules that adhere to the surface. At a given temperature, the rate of collision will be proportional to the partial pressure 'p' of the gas (its concentration) and the fraction 's' will be constant. Hence, the rate of adsorption per unit of bare surface will be $r_a = r_c s = k' p s = k p$, where **k** is the constant involving 's' and proportionality constant 'k'.

Now, since the adsorption is limited to a monolayer coverage, the surface can be divided in two parts :

1. fraction θ covered by adsorbed molecule
2. fraction $(1-\theta)$ which is bare

Since only those molecules that strike the uncovered part of the surface can adsorb, the rate of adsorption per unit of total surface will also be proportional to $(1-\theta)$. Therefore, the rate of adsorption is $r_a = k p (1-\theta)$. Rate of desorption on the other hand is proportional to fraction of covered surface that is $r_d = k' \theta$

At equilibrium, $r_a = r_d$

$$\text{or } kp(1-\theta) = k' \theta$$

$$\text{or } \theta = \frac{Kp}{1 + Kp}$$

where $K = \frac{k}{k'}$ = adsorption equilibrium constant, (pressure^{-1}) .

Further θ can be written as $\theta = \frac{v}{v_m}$

where v = volume of gas adsorbed and v_m = volume of gas adsorbed at monolayer coverage.

$$\therefore \frac{v}{v_m} = \frac{Kp}{1 + Kp} \text{ ----- [5]}$$

This is known as the Langmuir isotherm. Among the empirical isotherms, only Type I isotherm (Fig.1) agrees with the Langmuir equation. The Langmuir equation is valid for less than monolayer coverage and therefore more suited for chemisorption as chemisorption is limited to monolayer coverage. Deviations for other isotherms are mainly due to certain assumptions such as

1. sites are of equal activity
2. no interaction between adsorbed molecules

These assumptions correspond to constant heat of adsorption. However, for real systems, the heat of adsorption changes with surface coverage. The adsorption of H_2 on metal films of Fe, Ni, W, drops with the increase in surface coverage. Two other well known isotherms, Temkin isotherm and Freundlich isotherm, are derived in terms of dependency of heat of adsorption on fraction of surface coverage. The Temkin isotherm may be derived from the Langmuir isotherm by assuming that the heat of adsorption decreases linearly with increasing surface coverage θ . The result is $\theta = k_1 \ln k_2 p$, where k_1 and k_2 are constants at a given temperature. The Freundlich isotherm can be derived assuming a logarithmic decrease in heat of adsorption with surface coverage, i.e. $\Delta H_a = -\Delta H_o \ln \theta$. The isotherm is in the form of $\theta = c(p)^{1/n}$. The value of 'n' is generally greater than unity. The adsorption of H_2 gas on tungsten follows this isotherm.

Derivation of adsorption isotherm from kinetics

An equation for adsorption isotherm can also be derived by equating the rates of adsorption and desorption at equilibrium. From equations [3] and [4], at equilibrium, $r_a = r_d$. For the simplest case of non dissociative adsorption where $f(\theta) = (1 - \theta)$ and $N_a^m = \theta$, we obtain

$$\frac{p}{(2\pi m k_B T)^{1/2}} \alpha \exp\left(\frac{-E_a}{RT}\right) (1 - \theta) = \nu \theta \exp\left[\frac{-E_d}{RT}\right]$$

Noting that $E_d - E_a = -\Delta H$ = heat of adsorption,

$$p = (2\pi m k_B T)^{1/2} \frac{\nu}{\alpha} \frac{\theta}{(1 - \theta)} \frac{\exp\left[\frac{-E_d}{RT}\right]}{\exp\left(\frac{-E_a}{RT}\right)}$$

$$\text{or } p = (2\pi m k_B T)^{1/2} \frac{\nu}{\alpha} \frac{\theta}{(1 - \theta)} \exp\left(\frac{\Delta H}{RT}\right)$$

$$\text{Or } p = \frac{\theta}{b(1 - \theta)} \quad \text{where } \frac{1}{b} = (2\pi m k_B T)^{1/2} \frac{\nu}{\alpha} \exp\left(\frac{\Delta H}{RT}\right)$$

If heat of adsorption remains constant with coverage, b is a function only of temperature and

$$p = \frac{\theta}{b(1-\theta)}$$

$$\text{or } \theta = \frac{bp}{1+bp} \text{-----[6].}$$

This equation [6] is the well-known Langmuir isotherm.

Extended Langmuir model for adsorption in a multi-adsorbate system

The Langmuir model is also used to evaluate adsorption equilibrium data in a multi-adsorbate system and is known as extended Langmuir model. The extended Langmuir model mostly has been used to evaluate adsorption equilibrium data in binary system. The extended Langmuir model was first proposed by Butler and Ockrent [1]. Their model was based on the same assumptions as that of Langmuir model for single adsorbates. That is the model assumed (i) a homogeneous surface with respect to the energy of adsorption, (ii) no interaction between adsorbed species, and (iii) that all adsorption sites are equally available to all adsorbed species. Assuming the rate of adsorption of a species at equilibrium is equal to its rate of desorption, the following equations were derived.

$$X_1 = \frac{X_{m1}b_1C_1}{1+b_1C_1+b_2C_2} \text{-----[7]}$$

$$X_2 = \frac{X_{m2}b_2C_2}{1+b_1C_1+b_2C_2} \text{-----[8]}$$

Where, the X_1 and X_2 are the amount of solute 1 and solute 2 respectively, which are absorbed per unit weight or per unit surface area of absorbent at equilibrium concentrations C_1 and C_2 , respectively. The X_{m1} and X_{m2} are the maximum values of X_1 and X_2 , respectively, that can be obtained in single solute system and correspond to monolayer coverage of the adsorbent. The b_1 and b_2 are constants and function of the energy of adsorption of solutes 1 and 2, respectively, in a single solute system.

When some of the adsorption sites are inaccessible or unavailable to one type of solute in a bisolute system then, a fraction of the adsorption occurs without competition that is $X_{m1} \neq X_{m2}$. Jain and Snoeyink [2] proposed the following equations taking into account adsorptions with and without competition.

$$X_1 = \frac{(X_{m1} - X_{m2})b_1C_1}{1 + b_1C_1} + \frac{X_{m2}b_1C_1}{1 + b_1C_1 + b_2C_2} \quad \because (X_{m1} > X_{m2}) \text{-----}[9]$$

$$X_2 = \frac{X_{m2}b_2C_2}{1 + b_1C_1 + b_2C_2} \text{-----}[10]$$

The first term on the right hand side of Eq. 9 is the number of molecules of solute 1 that adsorb without competition on the surface area proportional to $(X_{m1} - X_{m2})$. The second term represents the number of solute 1 adsorbed on the surface area proportional to X_{m2} under competition with solute 2 and is based on the Langmuir model for competitive adsorption. The number of molecules of solute 2 adsorbed on surface area proportional to X_{m2} under competition with solute 1 can be calculated from Eq.10.

Book References :

- J.J. Carberry , Chemical and catalytic reaction Engineering, Dover Publications, 2001
- J. M. Thomas & W. J. Thomas, Principles and Practice of Heterogeneous Catalysis, VCH, 1997
- J. M. Smith , Chemical Engineering Kinetics, McGraw-Hill Book Company, 1981
- R. J. Farrauto & C. H. Bartholomew, Fundamentals of Industrial catalytic Processes, Blackie Academic & Professional, 1997
- D.M. Ruthven, Principle of adsorption & adsorption processes, John Wiley & sons, 1984.

Publication reference

1. J. A. V Butler, C Ockrent, J. Phys. Chem. 34(1930) 2841-2845.
2. J. S Jain, V. L. Snoeyink, J. Water Pollut. Control Fed. 45(1973) 2463-2479.

Lecture 4

Multilayer adsorption theory

Langmuir equation is valid for adsorption less than monolayer coverage and therefore more suited for chemisorption studies as it involves only monolayer coverage. Physical adsorption is not limited to monolayer formation and multilayer adsorption can occur on subsequent layers. Hence Langmuir isotherm is not applicable to multilayer adsorption. Brunauer, Emmette and Teller derived an relationship between the volume of gas physically adsorbed and the partial pressure of the adsorbate which is valid for multilayer adsorption. This relationship is utilized for measuring the total surface area of an adsorbent.

Multilayer adsorption: BET equation derivation

Let $s_0, s_1, s_2, s_3, \dots, s_i$ be the surface area covered by 0, 1, 2, 3, ..., i layers of adsorbed molecules as shown in the Fig. 1. The total area of the adsorbent therefore, can be obtained by the summation of all the individual surface areas.

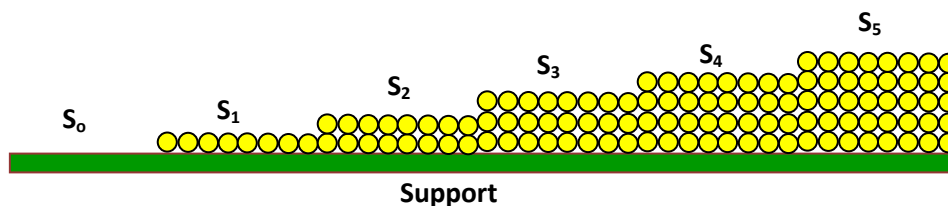


Fig.1. The representation of s_0, s_1, s_2, s_3, s_4 and s_5 surface areas covered by 0, 1, 2, 3, 4 and 5 layers of adsorbed molecules respectively.

$$\text{Rate of adsorption on bare surface } s_0 \text{ is } = a_1 p s_0 \exp \left[\frac{-E_a}{RT} \right]$$

$$\text{Rate of desorption from surface area } s_1 \text{ having the first layer} = b_1 s_1 \exp \left[\frac{-E_d}{RT} \right]$$

Since at equilibrium s_0 must remain constant, the rate of adsorption (or condensation) on bare surface is equal to the rate of desorption (evaporation) from first layer. Therefore,

$$a_1 p s_0 \exp \frac{-E_a}{RT} = b_1 s_1 \exp \left[\frac{-E_d}{RT} \right]$$

or $a_1 p s_0 = b_1 s_1 \exp \left[\frac{-H_1}{RT} \right]$, where $E_d - E_a = -H_1$ heat of adsorption of first layer.

This is Langmuir equation for unimolecular adsorption. It is assumed that a, b and H are independent of the number of adsorbed molecules already present in the first layer.

Similarly, the rate of adsorption on s_1 = rate of desorption from s_2 .

Therefore, $a_2 p s_1 = b_2 s_2 \exp \left[\frac{-H_2}{RT} \right]$

Extending to layer s_i with ‘i’ no of layers, $a_i p s_{i-1} = b_i s_i \exp \left[\frac{-H_i}{RT} \right]$

Total surface area = $A = \sum_{i=0}^{\infty} s_i$, s_i = surface area with ‘i’ no of layers

Total volume adsorbed = $v = v_0 \sum_{i=0}^{\infty} i s_i$

or, $\frac{v}{A v_0} = \frac{\sum_{i=0}^{\infty} i s_i}{A}$

$$\frac{v}{v_m} = \frac{\sum_{i=0}^{\infty} i s_i}{\sum_{i=0}^{\infty} s_i} \quad \text{----- [1]}$$

v_0 is volume of gas adsorbed per unit area of adsorbent surface and v_m is the volume of gas adsorbed when the entire adsorbent surface is covered with a complete unimolecular layer.

For simplification, it is assumed that the heat of adsorption of the 2nd, 3rd.....upto i^{th} layer are equal to each other and equal to heat of liquefaction of the adsorbate.

$$\text{Or } H_2 = H_3 = \dots\dots\dots = H_i = H_L$$

$$\text{and } \frac{b_2}{a_2} = \frac{b_3}{a_3} = \dots\dots\dots = \frac{b_i}{a_i} = g, \text{ } g \text{ being an appropriate constant.}$$

Now $s_1, s_2, \dots\dots\dots s_i$ can be expressed in term of s_0

$$a_1 p s_0 = b_1 s_1 \exp \frac{-H_1}{RT}$$

$$s_1 = \left(\frac{a_1}{b_1} \right) p \exp \left(\frac{H_1}{RT} \right) s_0 = y s_0 \qquad \because y = \left(\frac{a_1}{b_1} \right) p \exp \left(\frac{H_1}{RT} \right)$$

$$a_2 p s_1 = b_2 s_2 \exp \left(\frac{-H_2}{RT} \right)$$

$$s_2 = \left(\frac{a_2}{b_2} \right) p \exp \left(\frac{H_2}{RT} \right) s_1 = x s_1 \qquad \because x = \left(\frac{a_2}{b_2} \right) p \exp \left(\frac{H_2}{RT} \right) = \left(\frac{p}{g} \right) \exp \left(\frac{H_L}{RT} \right)$$

$$s_3 = x s_2 = x^2 s_1$$

$$s_i = x^{i-1} s_1 = x^{i-1} y s_0 = \frac{y}{x} x^i s_0 = c x^i s_0 \qquad \because c = \frac{y}{x}$$

$$c = \frac{y}{x} = \frac{\left(\frac{a_1}{b_1} \right) p \exp \left(\frac{H_1}{RT} \right)}{\left(\frac{p}{g} \right) \exp \left(\frac{H_L}{RT} \right)} = \left(\frac{a_1}{b_1} \right) g \exp \left(\frac{H_1 - H_L}{RT} \right)$$

Substituting $s_i = cx^i s_0$ in $\frac{v}{v_m} = \frac{\sum_{i=0}^{\infty} is_i}{\sum_{i=0}^{\infty} s_i}$ we get

$$\frac{v}{v_m} = \frac{cs_0 \sum_{i=1}^{\infty} ix^i}{s_0 + cs_0 \sum_{i=1}^{\infty} x^i} = \frac{cs_0 \sum_{i=1}^{\infty} ix^i}{s_0 \left[1 + c \sum_{i=1}^{\infty} x^i \right]}$$

Sum of the infinite geometric progression

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1-x}$$

$$\sum_{i=1}^{\infty} ix^i = \frac{x}{(1-x)^2}$$

Substituting ,

$$\frac{v}{v_m} = \frac{c \frac{x}{(1-x)^2}}{1 + \frac{cx}{1-x}} = \frac{cx}{[(1-x) + cx](1-x)} \text{-----[2]}$$

For adsorption on free surface, at saturation pressure of gas p_0 , infinite no of layers can build up on the surface. Further to make $v \rightarrow \infty$ at $p = p_0$, x must be equal to unity in equation [2].

Now,

$$x = \frac{p}{p_0} \exp \frac{H_L}{RT}$$

$$\therefore 1 = \frac{p_0}{p} \exp \frac{H_L}{RT}$$

$$x = \frac{p}{p_0} \exp \frac{H_L}{RT}$$

$$x = \frac{p}{p_0}$$

Substituting this in equation [2]

$$\frac{v}{v_m} = \frac{c \left(\frac{p}{p_0} \right)}{\left(1 - \frac{p}{p_0} + \frac{cp}{p_0} \right) \left(1 - \frac{p}{p_0} \right)}$$

$$\text{Or } \frac{v}{v_m} = \frac{cp}{\left(1 + (c-1) \frac{p}{p_0} \right) (p_0 - p)}$$

$$\text{Or } \frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \frac{p}{p_0} \text{----- [3]}$$

The Eq. 3 is known as the BET equation for multilayer adsorption. This equation can explain type II isotherm.

Table 1. Isotherms most commonly used in catalysis

Type	Isotherm equations	Type of adsorption
Langmuir	$\frac{v}{v_m} = \theta = \frac{bp}{1 + bp}$	Chemisorption Physisorption
Freundlich	$v = c p^{1/n} \quad (n > 1)$	Chemisorption and physisorption at low coverage
Temkin	$\frac{v}{v_m} = \theta = k_1 \ln k_2 p$	Chemisorption
Brunauer-Emmet-Teller	$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \frac{p}{p_0}$	Multilayer physical adsorption

Capillary (pore) condensation and evaporation: Kelvin equation

As discussed in the previous section for porous solids, the desorption curve lies above the adsorption curve from $\frac{P}{P_0} = 1$ to some intermediate value resulting in a hysteresis loop. This phenomenon occurs due to capillary condensation – evaporation process. It was recognized by Kelvin that the vapor pressure of a liquid contained in a small diameter capillary is less than the normal value for a free surface.

Consider a capillary filled with a liquid of surface tension σ . The change in free energy due to evaporation of a differential volume of liquid ‘dv’ is $n \Delta G$, where $n = \frac{dv}{v_{mol}}$. Here v_{mol} is the molar volume. Now ,

$$n\Delta G = \text{change in surface} \times \text{surface tension}$$

$$n\Delta G = (2\pi r dl) \sigma \cos \theta \text{ -----[4]}$$

$$\text{Again , } n\Delta G = -nRT \left(\ln \frac{P}{P_0} \right) \text{ -----[5]}$$

Equating [4] and [5]

$$(2\pi r dl) \sigma \cos \theta = -nRT \left(\ln \frac{P}{P_0} \right) = -\frac{\pi r^2 dl}{v_{mol}} RT \left(\ln \frac{P}{P_0} \right) \quad \because n = \frac{dv}{v_{mol}} = \frac{\pi r^2 dl}{v_{mol}}$$

$$\text{Or , } \ln \frac{P}{P_0} = -\frac{2v_{mol}\sigma}{rRT} \quad \cos \theta = 1$$

$$\frac{P}{P_0} = \exp \left[-\frac{2v_{mol}\sigma}{rRT} \right]$$

This is the general form of the Kelvin equation assuming wetting angle to be zero. This equation states that the pressure at which condensation or evaporation will occur is always less than the free surface vapor pressure if the capillary radius is small enough for the given liquid. When a nonporous solid or solid containing large pores is subjected to physical adsorption – desorption

equilibrium experiments, actual condensation of adsorbate will occur when the gas pressure equals the vapor pressure at the prevailing temperature; that is at $\frac{p}{p_0} = 1$. On other hand, if pores

of appropriate radius exists, condensation will occur before $\frac{p}{p_0} = 1$. Thus, liquid N_2 will form

within the pores at $\frac{p}{p_0} < 1$. On adsorption, this would account for the rapid increase in the

volume of gas adsorbed with $\frac{p}{p_0}$, typical of adsorption isotherms of porous solids.

However, this mechanism does not account for the occurrence of hysteresis loop, if filling of pores on adsorption and their emptying on desorption follow the same mechanism. In this physisorption mechanism, pores are assumed to undergo vertical filling and emptying. Therefore, occurrence of hysteresis suggests that filling mechanism of pores is different than the desorption mechanism. Later a different mechanism was forwarded for pore filling by Cohan [1]. It was suggested that during adsorption, the pores may be filling radially instead of vertically. As gas molecules are condensing radially on the surface of pores, the effective radius 'r' is decreased on condensation of first layers. This causes further condensation at a fixed p/p_0 . In other words, pores of a radius 'r' corresponding to a given p/p_0 , fill instantaneously. In this condition, the change in volume $dv = 2\pi r l dr$ and that of surface is $2\pi l dr$. Kelvin equation can be modified

$$\text{as } \frac{p}{p_0} = \exp \frac{-\sigma v_{mol}}{rRT}$$

For a given pore radius r , adsorption with radial capillary condensation occurs at

$$p_{ads} = p_0 \exp \frac{-\sigma v_{mol}}{rRT}$$

While vertical emptying of the pores occurs during desorption at about

$$p_{des} = p_0 \exp \frac{-2\sigma v_{mol}}{rRT}$$

Wetting angle is taken as zero. The adsorption pressure is related to the desorption pressure by $p_{ads}^2 = p_0 p_{des}$. This implies that the pressure required to empty the capillary is proportional to the square of that necessary to fill it and hence hysteresis.

Book References :

- J.J. Carberry , Chemical and catalytic reaction Engineering, Dover Publications, 2001
- J. M. Thomas & W. J. Thomas, Principles and Practice of Heterogeneous Catalysis, VCH, 1997
- J. M. Smith , Chemical Engineering Kinetics, McGraw-Hill Book Company, 1981
- R. J. Farrauto & C. H. Bartholomew, Fundamentals of Industrial catalytic Processes, Blackie Academic & Professional, 1997
- D.M. Ruthven, Principle of adsorption & adsorption processes, John Wiley & sons, 1984.

Journal reference

1. L.H. Cohan, J. Am. Chem. Soc. 60(1938) 433