

Module 5: "Adsoption"

Lecture 25:

The Lecture Contains:

- ☰ Definition
- ☰ Applications
- ☰ How does Adsorption occur?
 - Physisorption
 - Chemisorption
- ☰ Energetics
- ☰ Adsorption Isotherms
- ☰ Different Adsorption Isotherms
- ☰ Langmuir Adsorption Isotherm

◀◀ Previous Next ▶▶

Module 5: "Adsorption"

Lecture 25:

Adsorption is one of the most important surface processes and its knowledge is essential for a chemical engineer due to its wide range of applications in almost all fields of science and technology.

Definition:

Adsorption is defined in many ways, some of the standard definitions of adsorptions are:

- Adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface
- The process by which molecules of a substance, such as a gas or a liquid, collect on the surface of another substance
- Adsorption is the process through which a substance, originally present in one phase, is removed from that phase by accumulation at the interface between that phase and a separate (solid) phase.

Applications:

Some of the standard applications of adsorption are:

- Heterogeneous Catalysis- This is probably the most important application relevant to chemical engineering. The reaction mechanism of how a reactant reacts on a catalyst surface revolves around adsorption. Therefore designing catalyst, reactors and studying them requires knowledge of adsorption
- Separation- Adsorption is used as a separation process in many chemical as well as bio chemical industries to separate gaseous or liquid mixtures. Designing adsorption equipment like fixed bed adsorbers, gas drying, pressure swing adsorption etc. , chromatography requires knowledge of adsorption.
- Many experiments in the lab use adsorption as a process to calculate various parameters like surface concentration, porosity, change in surface energies, pore surface area etc.

NOTE: Adsorption must not be confused with absorption which is a bulk process in which a substance diffuses into the bulk of another substance unlike adsorption which is only a surface process.

Module 5: "Adsorption"

Lecture 25:

How Does Adsorption occur?

As mentioned above adsorption is a surface phenomenon. It occurs due to the imbalance of forces at the surface of a material. This lead to formation of bonds (Covalent, ionic, Van der Waals, Hydrogen bonds etc.) between the surface molecules (adsorbents) and the molecules in the fluid phase (adsorbate).

Physisorption

Adsorption in which the forces involved are intermolecular (i.e., van der Waals, hydrogen bonding) of the same kind as those responsible for the non-ideality of real gases and the condensation of vapours etc. , and which do not involve a significant change in the electronic orbital patterns of the species involved is called physisorption.

Chemisorption

A chemical process in which a reacting molecule forms a definite chemical bond with an unsaturated atom, or a group of atoms (an active centre) on a catalyst surface, and electron transfer is involved is known as chemisorption.

Note: In practice no absolutely sharp distinction can be made between chemisorption and physisorption, although generalities apply.

Energetics

The potential energy diagram of a general adsorption process can be modeled on the basis of summation of attractive and repulsive forces between the adsorbate and adsorbent and thus gives rise to a *Lennard-Jones* like Potential Energy Diagram as follows. On the horizontal axis, r is the distance between the two molecules. As the adsorbate molecule is brought close to the surface the corresponding potential energy is plotted in vertical axis. First the interaction is attractive and the particle falls in an energy well, afterwards the interaction is highly repulsive.

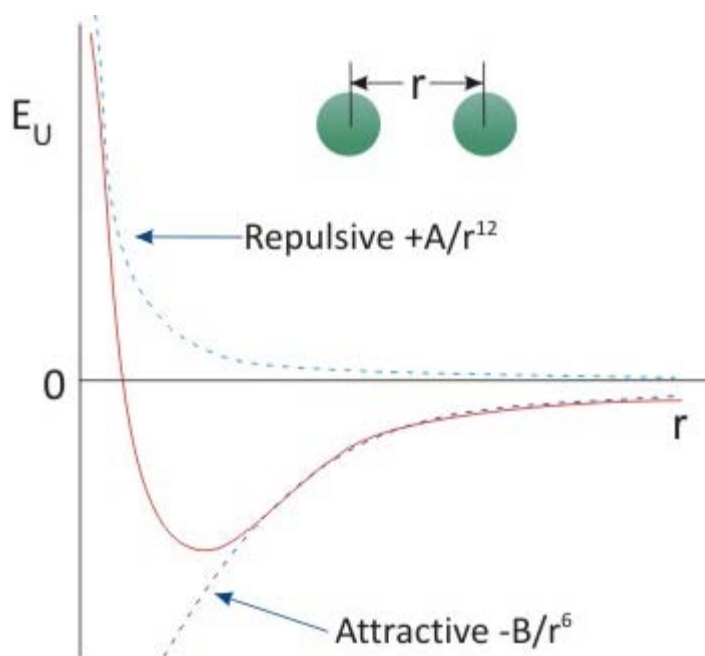


Fig. 7.1: Potential energy diagram for adsorption

◀◀ Previous Next ▶▶

Adsorption Isotherms

Now let us study a bit more of the physics of adsorption. Adsorption is usually described through adsorption isotherms that is *the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature*. The adsorption isotherm is the equilibrium relationship between the concentration in the fluid phase and the concentration in the adsorbent particles at a given temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. Some typical adsorptions are shown in the figure below

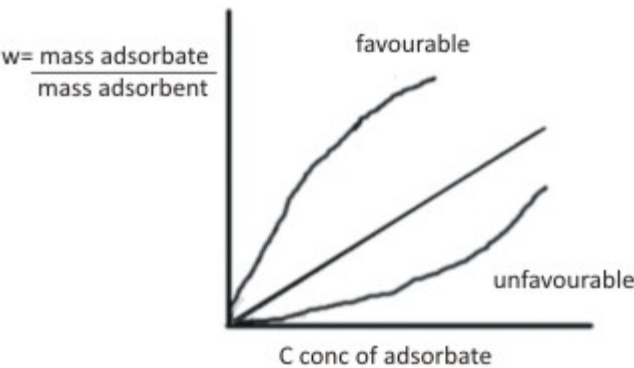


Fig. 7.2: Favourable and unfavourable adsorption

Module 5: "Adsoption"

Lecture 25:

Different adsorption isotherms

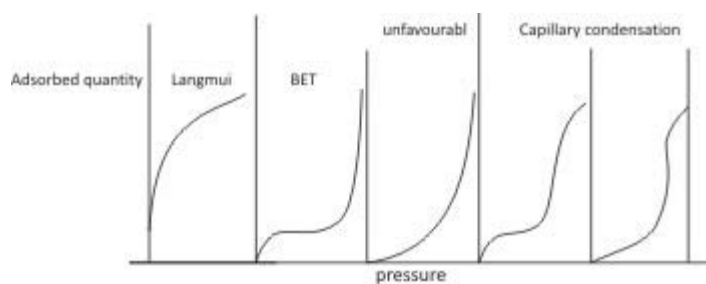


Fig. 7.3: Different adsorption isotherms

Module 5: "Adsorption"

Lecture 25:

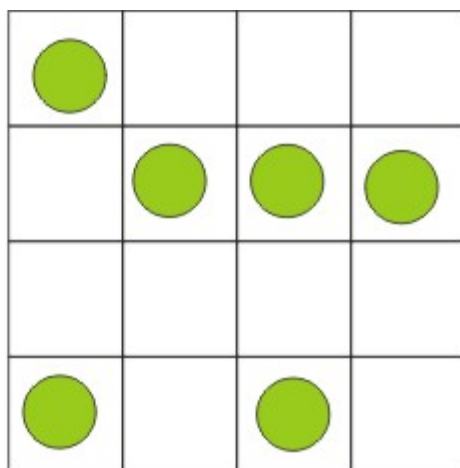
Langmuir Adsorption Isotherm

The simplest equation for adsorption under dynamic equilibrium condition was derived by **Irving Langmuir** in 1916. He got the **Nobel Prize in 1932** in chemistry for his contributions to surface chemistry. It can be used to predict monolayer physisorption as well as chemisorption. Let us derive its equation in terms of partial pressure of the gas (at constant temperature) and the amount of adsorbate adsorbed.

Assumptions

Langmuir made several assumptions in order to simplify his analysis. The main assumptions in Langmuir adsorption isotherm are

- The surface is like a checkerboard and made up of many active (adsorbing) sites (see figure below).
- Each active site can adsorb only one molecule of the adsorbate.
- There cannot be multilayer adsorption. (In other words the process is adsorption limited)
- All surface sites have constant heat of adsorption (there is no difference between any two active sites)
- Adsorbed molecules don't interact with each other on the surface. (there is no motion of adsorbed molecules on the surface)
- The surface containing the active sites is perfectly like a flat plane with no corrugations.



□ = catalyst adsorption site

● = gas atom/molecule

Fig. 7.4: Surface of adsorbent

Module 5: "Adsoption"

Lecture 25:

According to Langmuir, the rate of adsorption depends on the following 4 factors

- The rate of collision of the adsorbate molecule of mass '**m**' which is at pressure '**p**' is proportional to $\frac{p}{\sqrt{2\pi mkT}}$ per unit surface area at the constant temperature.
- The activation energy **E^{act}** of adsorption ,since this determines the fraction of the colliding molecules possessing the necessary energy to be adsorbed (see figure 7.5)

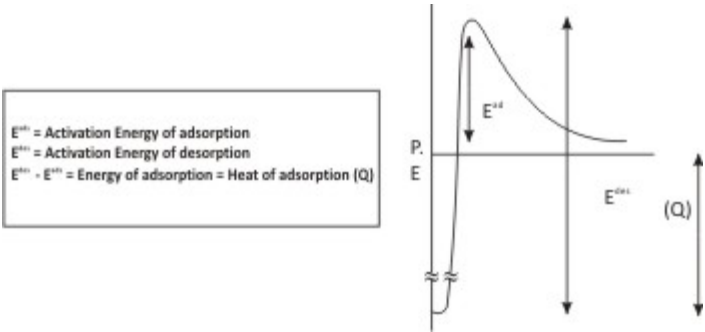


Fig. 7.5: Activation energy diagram for adsorption

- The fractional coverage of the surface **f(θ)** which is the amount of surface that is exposed/available for a single site adsorption = **(1 - θ)**, where

$\theta = \text{fraction of sites covered} = \frac{\text{number of sites which have absorbed molecules}}{\text{total number of sites}} \tag{7.1}$

- **σ** which is the 'fraction of the total number of colliding molecules which results in adsorption'.

Module 5: "Adsoption"

Lecture 25:

Based on the previous assumptions and the factors, the rate of adsorption can be written as

$$r_{ads} = \frac{\sigma p}{\sqrt{2\pi m k T}} f(\theta) \exp\left(\frac{-E^{ads}}{RT}\right) \quad (7.2)$$

Similarly the rate of desorption depends on

- Fractional sites available for desorption $\Phi(\theta) = \theta$
- The activation energy of desorption E^{des}
- A rate constant

Hence the rate of desorption can be written as

$$r_{des} = k_{-1} \varphi(\theta) \exp\left(\frac{-E^{des}}{RT}\right) \quad (7.3)$$

NOTE: Like any other case, it is assumed that the dependence of rate on Activation Energy follows Arrhenius type of equation.

Module 5: "Adsorption"

Lecture 25:

At equilibrium,

Rate of adsorption = rate of desorption

Thus, equating the above two equations we get

$$\frac{\sigma p}{\sqrt{2\pi mkT}} f(\theta) \exp\left(\frac{-E^{ads}}{RT}\right) = k_{-1} \phi(\theta) \exp\left(\frac{-E^{des}}{RT}\right) \quad (7.4)$$

As given above,

$$\phi(\theta) = \theta$$

$$f(\theta) = 1 - \theta$$

$$E^{des} - E^{ads} = Q$$

Therefore the above equation can be rewritten as

$$p = \frac{k_{-1}}{\sigma} \sqrt{2\pi mkT} \exp\left(\frac{-Q}{RT}\right) \quad (7.5)$$

$$\text{Put } \frac{1}{b} = \frac{k_{-1}}{\sigma} \sqrt{2\pi mkT} \exp\left(\frac{-Q}{RT}\right)$$

since all the terms are constant at constant equation. Hence,

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

$$\theta = \frac{bp}{1 + bp} \quad (7.6)$$

This is the standard form of Langmuir adsorption isotherm.

Module 5: "Adsoption"

Lecture 25:

Shortcomings of the Langmuir adsorption isotherm

- Langmuir assumed that the heat of adsorption is independent of the coverage θ which is not what is observed.
- Multilayer adsorption is not taken into account
- Lateral interactions on the surface were ignored

Non Langmuirian Adsorption Isotherms

Many corrections to the Langmuir adsorption isotherm were suggested that accounted for its shortcoming. Two of the more famous ones are

- **Freundlich isotherm:** $\theta = k \cdot p^n$.

It can be theoretically derived from Langmuir isotherm by assuming that heat of adsorption falls exponentially as the coverage is increased.

1. **Temkin isotherm:** $\theta = \frac{RT}{\Delta H\alpha} \ln(A_0 p)$.

It can be derived from Langmuir isotherm assuming the heat of adsorption decreases linearly with coverage.

NOTE: Langmuir adsorption isotherm can also be derived using basic statistical mechanics principles by considering the grand canonical ensemble and the corresponding Helmholtz free energy.

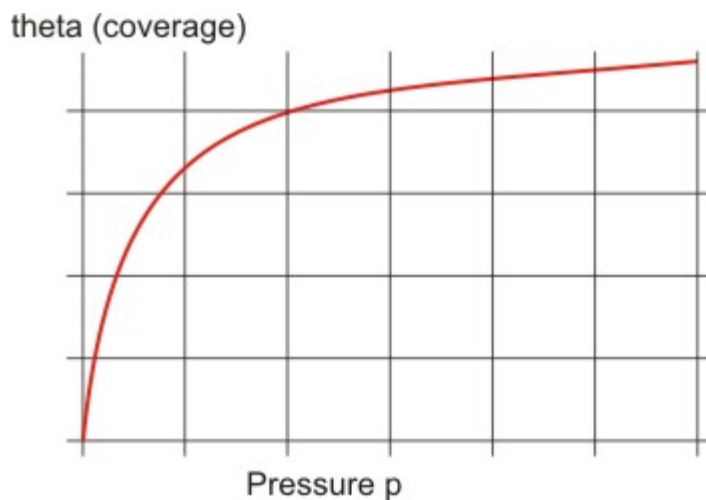


Fig. 7.6: Langmuir Adsorption Isotherm