Adsorption

Adsorption – the first step in a catalytic process

- Heterogeneously catalyzed reactions are strongly associated with the adsorption phenomenon

- For such reactions on solid surfaces, at least one or all the reactants must be adsorbed on the surface of the solid

Adsorption is a process in which molecules of the gas (or liquid) phase land on, interact with and attach to the solid surface

- The species getting adsorbed is called the *adsorbate* and the solid surface is the *adsorbent*

- Adsorption occurs on the active sites present on both the external surface and the internal surface (pores) of the catalyst

- The molecular forces associated with adsorbent molecules in the bulk of the adsorbent are balanced

- On the surface, these molecules are bounded to the inner adsorbent molecules only and there are unbalanced molecular forces on the surface

- These unbalanced molecular forces on adsorbent surfaces create the attractive force for the adsorbate molecules approaching the surface
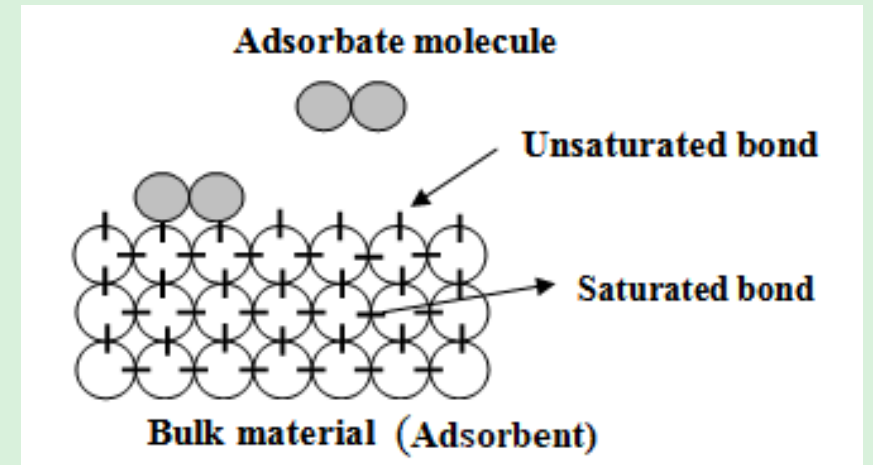
Types of adsorption

Molecules can attach to the surface in two different ways depending on the nature of interaction and the forces involved

- Physical adsorption (Physisorption)
- Chemical adsorption (Chemisorption)

Physisorption

The phenomenon of adsorbate molecules attaching themselves to adsorbent surface under the influence of van der Waals forces is called physisorption
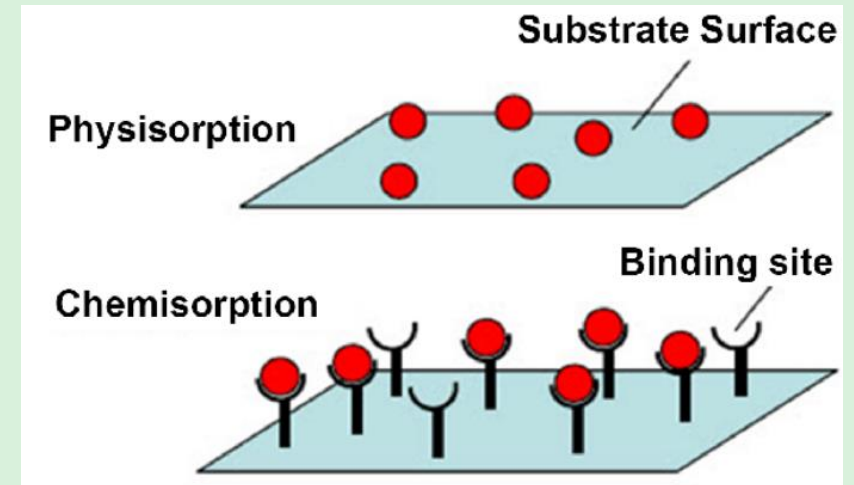
- The **van der Waals forces** (mainly dipole-dipole interactions) of attraction between the fluid molecules and solid are **relatively weak**
- This process is **non-specific** and similar to the process of condensation
- This is an **exothermic process** with a low heat of adsorption. Heat of adsorption is around 1-15 kcal/mol (4.2-63 kJ/mol)
- The amount of gas physically **adsorbed decreases rapidly** with increasing **temperature**
- Physisorption is **not responsible for catalysis**
- It is **proportional to the amount of surface** and is not limited to monolayer on the surface
- Mainly used for determining the physical properties of solid catalysts such as **surface area and pore size distribution**

Chemisorption

The process of adsorption where the gas molecules or atoms are held to the solid surface by chemical bonds is known as chemisorption

- The **valence forces** involved are of the **same** kind as those involved in the **formation of chemical compounds**
- The **valence forces** are **much stronger** than those involved in physical adsorption
- For chemisorption there is a **rearrangement of electron density** – electron structure of a gas molecule has a certain binding with the electron structure of the adsorbent
- Chemisorption is **specific** and an adsorbate molecule will chemisorbed only on selected adsorbent
- It is mostly an **exothermic process** and the heat of adsorption is of the same magnitude as the heat of a chemical reaction (40 - 400 kJ/mol)
- It is **irreversible** in nature due to formation of surface compound
- Chemisorption **does not exceed monolayer**, valence forces holding the molecules on the surface diminish rapidly with distance

Difference between physisorption and chemisorption

Process	Physisorption	Chemisorption
Forces of attraction	van der Waals	Valence forces (similar to chemical bond)
Heat of adsorption	Low (< 15 kcal)	High (>15 kcal) exception: endothermic adsorption
Activation energy	Very low (close to zero)	High (similar to a chemical reaction)
Temp range	Low	High
Specificity of adsorbate-adsorbent interactions	Non-specific (All gases adsorbed on all solids)	Specific (Some gases chemisorbed on some solids)
Coverage	multilayer	≤ monolayer
Reversibility	Fully reversible	Irreversible
Use	For determination of surface area and pore size	For determination of metal area or active area of catalyst or surface reaction kinetics

Adsorption processes are usually exothermic

- Physisorption processes are always exothermic
$$\Delta G = \Delta H - T\Delta S$$

  - For a **spontaneous** process, $\Delta \boldsymbol{G}$ **must be negative**
  - Physisorption process is always accompanied by a **decrease in entropy** (ΔS<0)
  - Since the term $[-T\Delta S]$ becomes positive, $\Delta \boldsymbol{H}$ **must be negative** for ΔG to be negative
  - Hence, physisorption is always exothermic (ΔH <0)

- Most chemisorption processes are exothermic, only in some cases it is endothermic
  - For chemisorption processes that are exothermic, ΔS<0 and ΔH also needs to be <0 for ΔG to be <0
  - In certain cases of **dissociative chemisorption** (H_2 is dissociatively chemisorbed on Fe surface), the adsorbed molecules have two-dimensional mobility (increase in degree of freedom). This results in $\Delta \boldsymbol{S}$> **0**
$$\text{Now,} \quad \Delta H = \Delta G + T\Delta S$$
  - As ΔG is negative, if the value $\boldsymbol{T\Delta S} > \boldsymbol{\Delta G}$, ΔH becomes positive ($\Delta \boldsymbol{H}$ > **0**) : **endothermic adsorption process**

Adsorption Isotherms

- Quantitative expressions for adsorption are necessary to develop the rate expressions for catalytic reactions

- The adsorption and desorption steps in the reaction process may be fast and be near equilibrium

- **A relation between the amount of adsorbate adsorbed on a given surface at constant temperature and the equilibrium concentration of the substrate in contact with the adsorbent is known as Adsorption Isotherm**

- Such isotherms portray the amount of gas adsorbed on a solid at different pressures but one temperature

Now let us look at some adsorption isotherms

Langmuir adsorption isotherm

Assumptions:
(i)   The entire surface is energetically uniform – all the surface has the same activity for adsorption
(ii) There is no interaction between the adsorbed molecule
(iii) All adsorption occurs by the same mechanism and each adsorbed complex has the same structure
(iv) The extent of adsorption is less than one complete monolayer on the surface
(v) Heat of adsorption (ΔH_a) remains constant with surface coverage(θ)
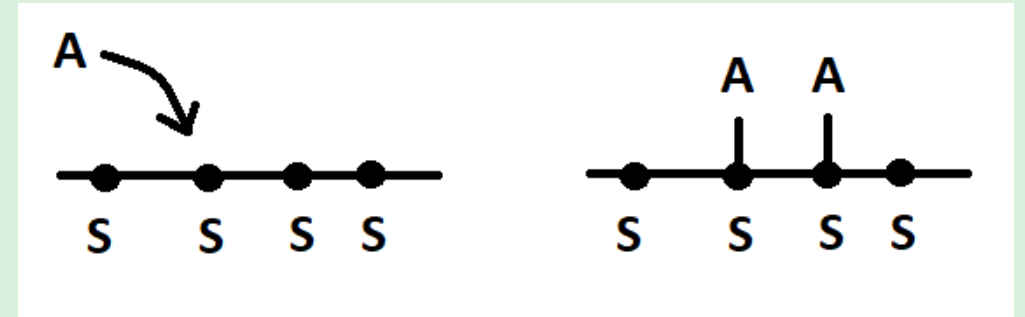
Langmuir adsorption isotherm

A: reactant adsorbed on site S

C_t : total molar concentration of active sites per unit mass
   of catalyst = active sites per unit mass/ Avogadro number

C_v : molar concentration of vacant sites
   = vacant sites per unit mass/ Avogadro number

$C_{i.S}$: surface concentration of sites occupied by species i,
   gmol/g cat

Site balance, $C_t = C_v + \sum C_{i.S}$

For reactant A $C_t = C_v + C_{A.S}$

- **Rate of attachment of A** to the surface is $\propto$ **number of collisions** that is made on the surface per second (collision rate)
  The **collision rate** is $\propto$ **partial pressure of A** and the **concentration of vacant sites** (as reactant A can adsorb only on the vacant site)
- **Rate of detachment** is $\propto$ **concentration of sites occupied** by the adsorbed molecule A

Rate of attachment = $k_A p_A C_v$

Rate of detachment = $k_{-A} C_{A.S}$

Net rate of adsorption, $r_A = k_A p_A C_v - k_{-A} C_{A.S}$

At equilibrium, $r_A = 0$ and $\mathbf{k_A p_A C_v = k_{-A} C_{A.S}}$
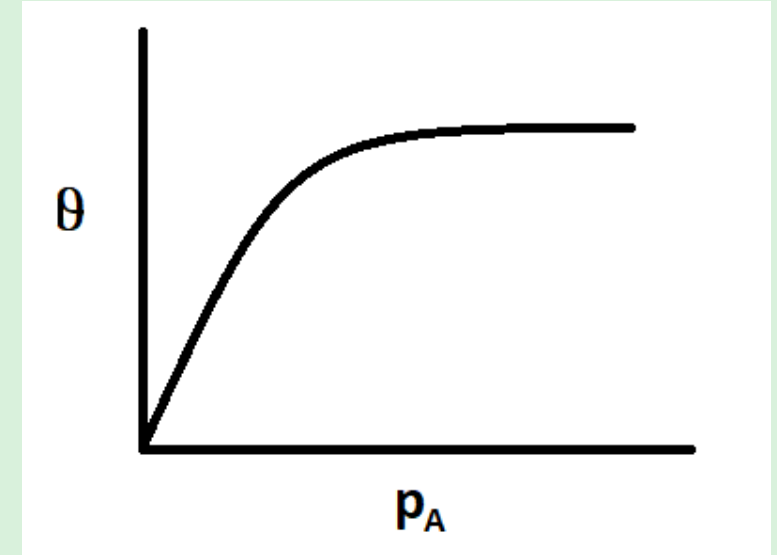
Site balance - $C_t = C_v + C_{A.S}$,

$$k_A p_A (C_t - C_{A.S}) = k_{-A} C_{A.S}$$

or, $\quad k_A p_A C_t - k_A p_A C_{A.S} = k_{-A} C_{A.S}$

or, $\quad K_A p_A C_t - K_A p_A C_{A.S} = C_{A.S} \quad \left(\because K_A = \dfrac{k_A}{k_{-A}} \right)$

or, $\quad \boxed{\dfrac{C_{A.S}}{C_t} = \dfrac{K_A p_A}{1 + K_A p_A}}$

K_A : Adsorption equilibrium constant

Now, $\quad \theta = \dfrac{volume\ of\ gas\ adsorbed}{volume\ of\ gas\ adsorbed\ at\ monolayer\ coverage} = \dfrac{v}{v_m} = \dfrac{C_{A.S}}{C_t} = \dfrac{no.of\ adsorption\ sites\ occupied}{total\ conc.of\ adsorption\ sites}$

$\therefore \quad \boxed{\theta = \dfrac{K_A p_A}{1 + K_A p_A}}$

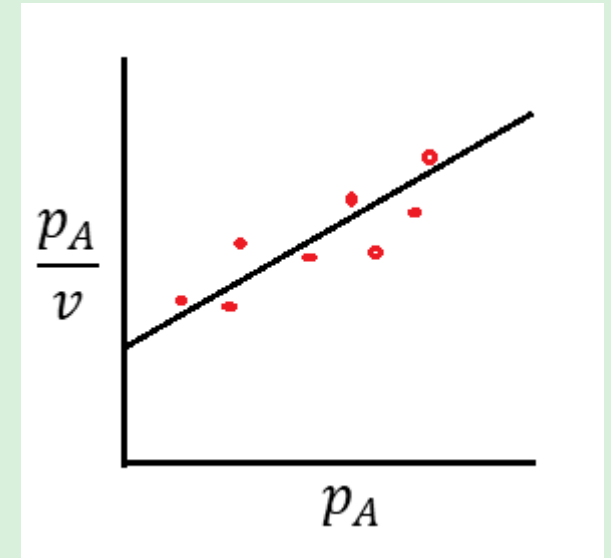This is called the **Langmuir isotherm**

During the conduction of an **adsorption experiment**, the values of **volume of gas adsorbed (v)** and **partial pressure of gas A (p$_A$)** are usually measured

$$\frac{v}{v_m} = \frac{K_A p_A}{1 + K_A p_A}$$

$$\frac{K_A p_A}{v} = \frac{1 + K_A p_A}{v_m}$$

$$\boxed{\frac{p_A}{v} = \frac{1}{K_A v_m} + \frac{1}{v_m} p_A}$$

If a plot of $\frac{p_A}{v}$ versus p_A is a straight line, the data fits the Langmuir isotherm

The **Langmuir equation in the form of concentration** can be written as

Rate of adsorption (mol/s.gcat), $r_a = k_c C_g (\overline{C_m} - \bar{C})$
Rate of desorption, $r_d = k_c' \bar{C}$
At equilibrium, the two rates are equal, $k_c C_g (\overline{C_m} - \bar{C}) = k_c' \bar{C}$

$\bar{C}$: concentration of adsorbed species
$\overline{C_m}$: concentration corresponding to complete monolayer of molecules
C_g : concentration of adsorbate(gas conc)

$$\boxed{\bar{C} = \frac{K_c C_g \overline{C_m}}{1 + K_c C_g}} \qquad (\because \ K_c = \frac{k_c}{k_c'})$$

$$\boxed{\theta = \frac{K_c C_g}{1 + K_c C_g}}$$

Linearizing we get, $\boxed{\frac{C_g}{\bar{C}} = \frac{1}{K_c \overline{C_m}} + \frac{1}{\overline{C_m}} C_g}$

Limitations of Langmuir Isotherm

(i)   The catalyst surface **in reality is non-homogeneous** (unlike assumption). Atoms at the crystal edges and crystal corners are the most unsaturated and adsorption energies are greater at these sites than at the middle of the surface

(ii)   There are **interactions between the molecules** which are close to one another on the surface (unlike assumption)

Assignment

Show that the Langmuir isotherm has the following form when more than one species is adsorbed.

$$\sum \theta_i = \frac{\sum K_i p_i}{1 + \sum K_i p_i}$$

Hint: Start with adsorption of three species A, B, C

Site balance, $C_t = C_v + C_{A.S} + C_{B.S} + C_{C.S}$

For A, $k_A p_A (C_t - C_{A.S} - C_{B.S} - C_{C.S}) = k_{-A} \, C_{A.S}$