

# **SURFACE CHEMISTRY**

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# INTRODUCTION

Surface chemistry is the study of processes that occur at the interface of two bulk phases.

The bulk phases can be of the type :

**Solid - gas**

**Liquid - liquid**

**SOLID - LIQUID**

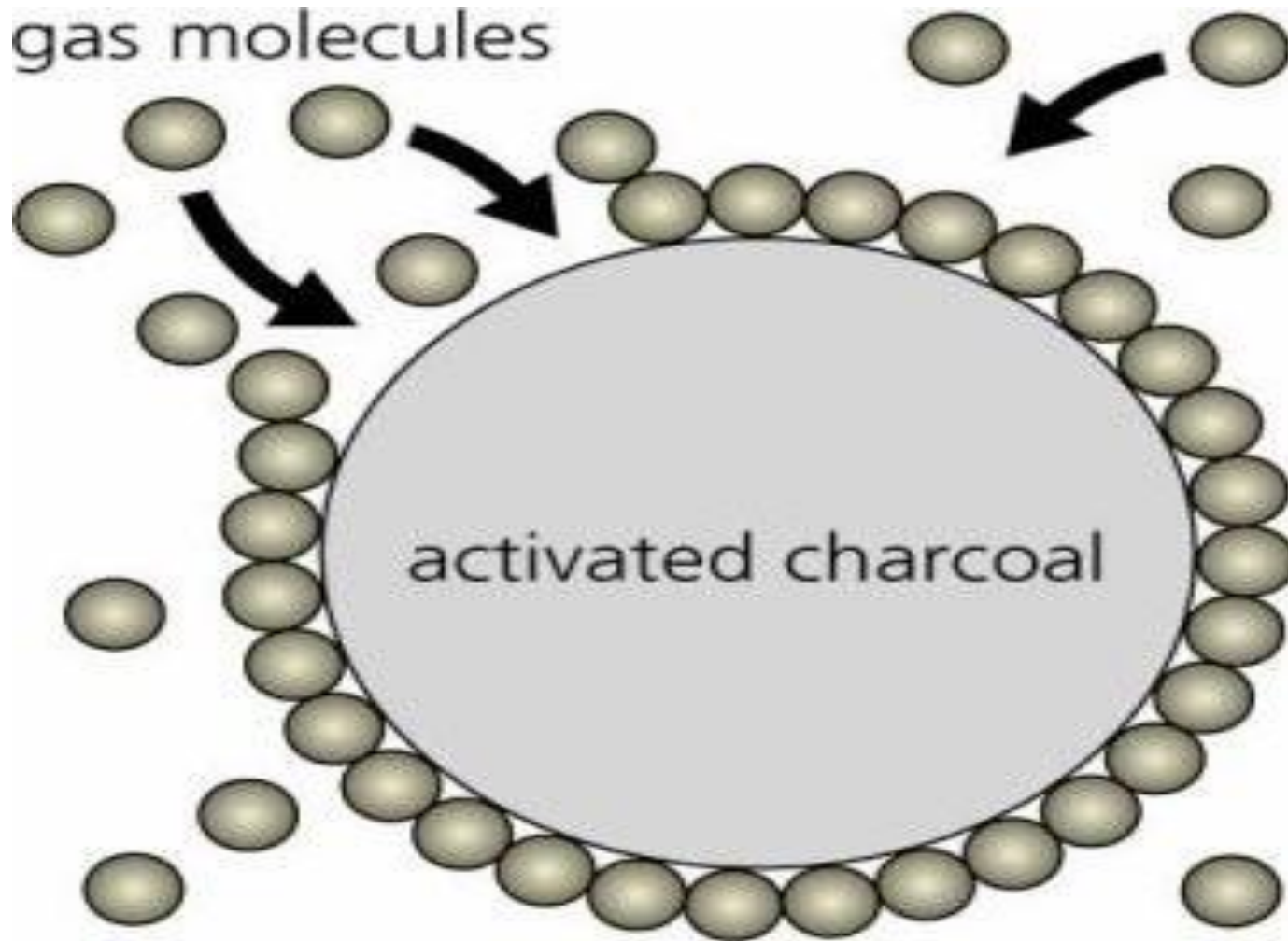
**LIQUID - GAS**

# TYPES

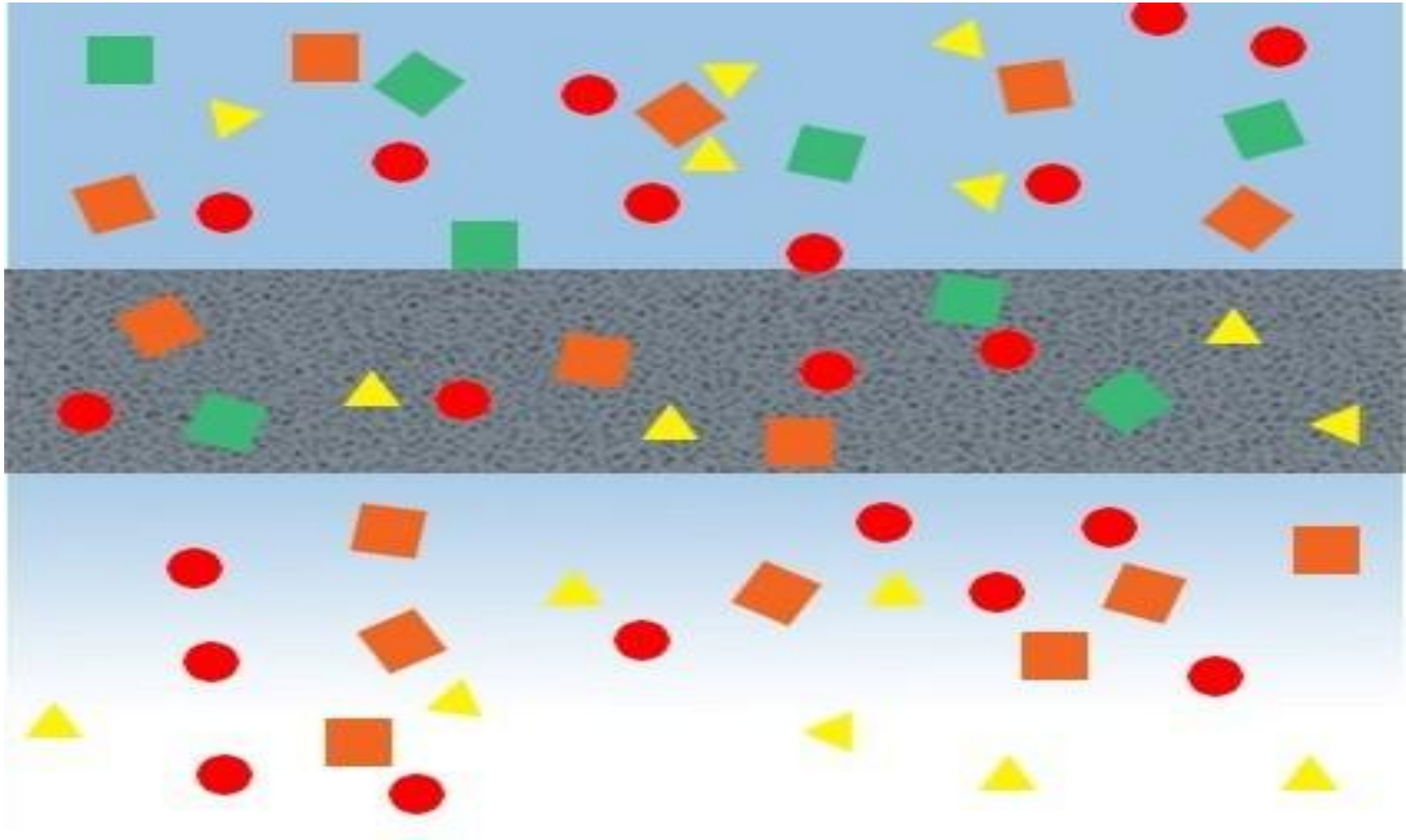


- **ADSORPTION:** is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface.
- **ABSORPTION:** is a physical or chemical phenomenon or a process in which atoms, molecules, or ions enter some bulk phase - gas, liquid, or solid material.

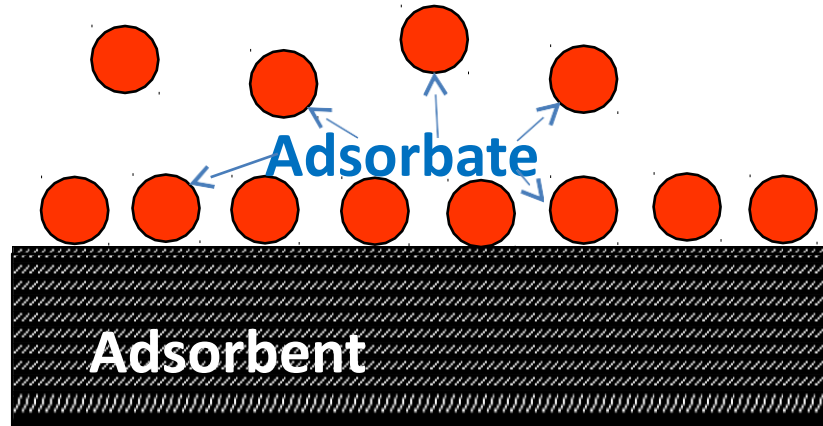
# Adsorption on activated charcoal



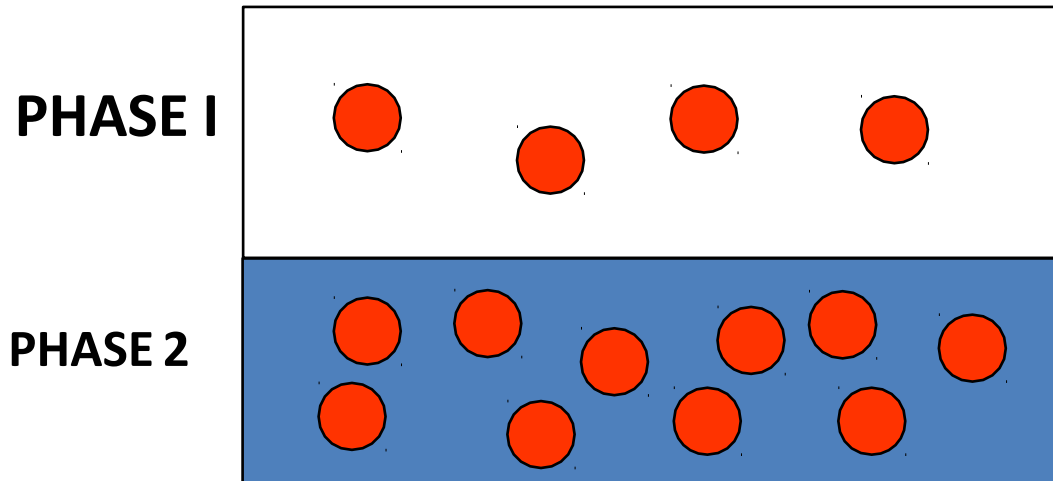
# Absorption through a membrane



# Adsorption



# Absorption ("partitioning")



# Adsorption

**Physical adsorption:** Van der Waals attraction between adsorbate and adsorbent. The attraction is not fixed to a specific site and the adsorbate is relatively free to move on the surface. This is relatively weak, reversible, adsorption capable of multilayer

**Chemical adsorption:** Some degree of chemical bonding between adsorbate and adsorbent characterized by strong attractiveness. Adsorbed molecules are not free to move on the surface. There is a high degree of specificity and typically a monolayer is formed. The process is seldom reversible.

## **ADSORPTION EQUILIBRIA:**

If the adsorbent and adsorbate are contacted long enough an equilibrium will be established between the amount of adsorbate adsorbed and the amount of adsorbate in solution. The equilibrium relationship is described by ISOTHERMS

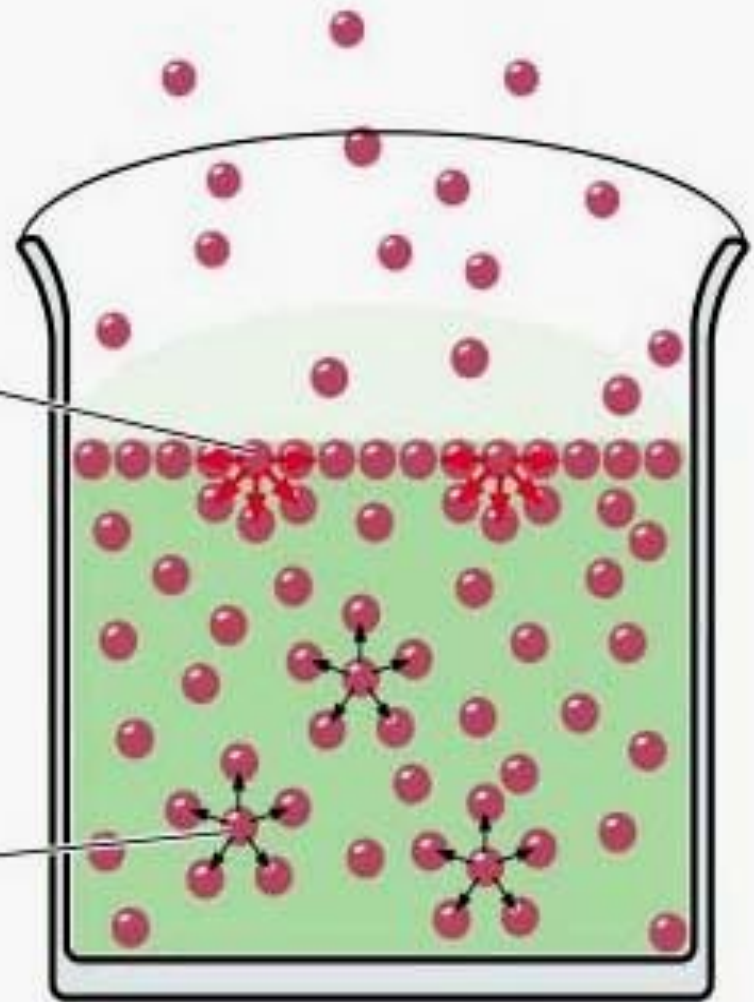


# Causes of Adsorption

- **Dislike of Water Phase** – ‘Hydrophobicity’
- **Attraction to the Sorbent Surface**
  - **van der Waals forces**: physical attraction
  - **electrostatic forces** (surface charge interaction)
  - **chemical forces** (e.g.,  $\pi$ - and hydrogen bonding)

Surface molecules exert particularly strong attractive forces to their sides, front and back, and below.

Interior molecules exert weaker forces in all directions.



# Types of Adsorption



Depending on the nature of attractive forces existing between the adsorbate and adsorbent, **adsorption can be classified as:**

**Physical  
Adsorption**

**Chemical  
Adsorption**

# Difference between

## Physisorption

- Forces of attraction are vander Waals' forces
- **Low enthalpy of adsorption (20 - 40 k.J/mole)**
- **This process is observed under conditions of low temperature**
- It is not specific
- Multi-molecular layers may be formed
- **This process is reversible**

## Chemisorption

- Forces of attraction are chemical bond forces
- High enthalpy of adsorption (200 - 400 k.J/mole)**
- This process takes place at high temperatures**
- It is highly specific
- Generally, monomolecular layer is formed
- This process is irreversible**

• **Physisorption** is a general phenomenon and occurs in any solid/fluid or solid/gas system.

• In physisorption, perturbation of the electronic states of adsorbent and adsorbate is minimal

• **Typical binding energy of Physisorption is about 10–100 meV.**

• The elementary step in Physisorption from a gas phase does not involve an activation energy.

• For Physisorption, under appropriate conditions, gas phase molecules can form multilayer adsorption.

• **Chemisorptions** is characterized by chemical specificity.

• For chemisorption, changes in the electronic states may be detectable by suitable physical means.

• **Chemisorption usually forms bonding with energy of 1–10 eV.**

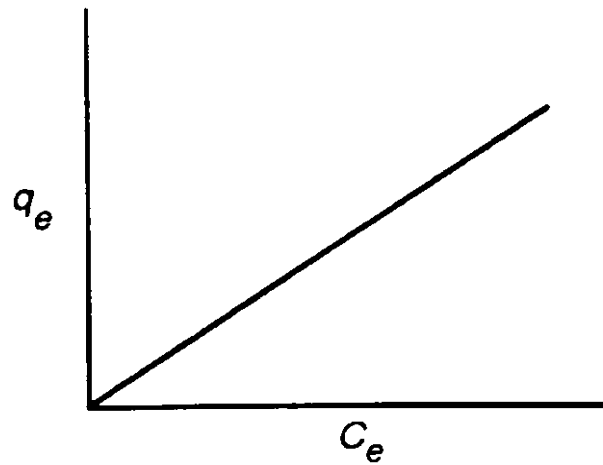
• Chemisorption often involves an activation energy.

• In chemisorption, molecules are adsorbed on the surface by valence bonds and only form monolayer adsorption.

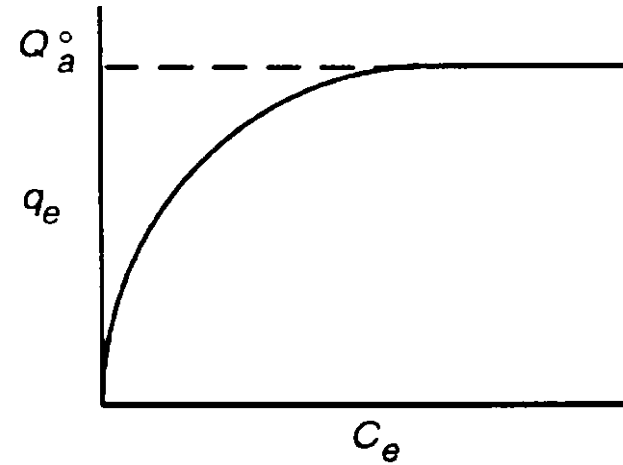
# ADSORPTION ISOTHERMS

- **Adsorption isotherm describes the equilibrium of the sorption of a material at a surface at constant temperature.**
- **It represents the amount of material bound at the surface as a function of the material present in the gas phase and/or in the solution.**
- **Sorption isotherms are often used as empirical models, which do not make statements about the underlying mechanisms and measured variables.**
- **They are obtained from measured data by means of regression analysis. The most frequently used isotherms are the linear isotherm, Freundlich isotherm, the Langmuir isotherm, and the BET model.**

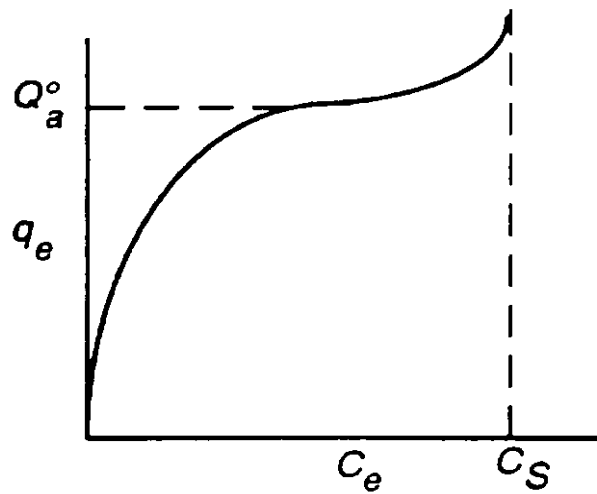
# Commonly Reported Adsorption Isotherms



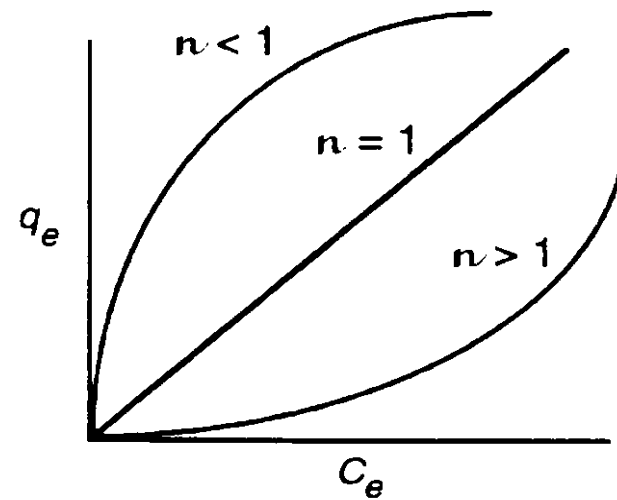
(a) Linear



(b) Langmuir



(c) BET



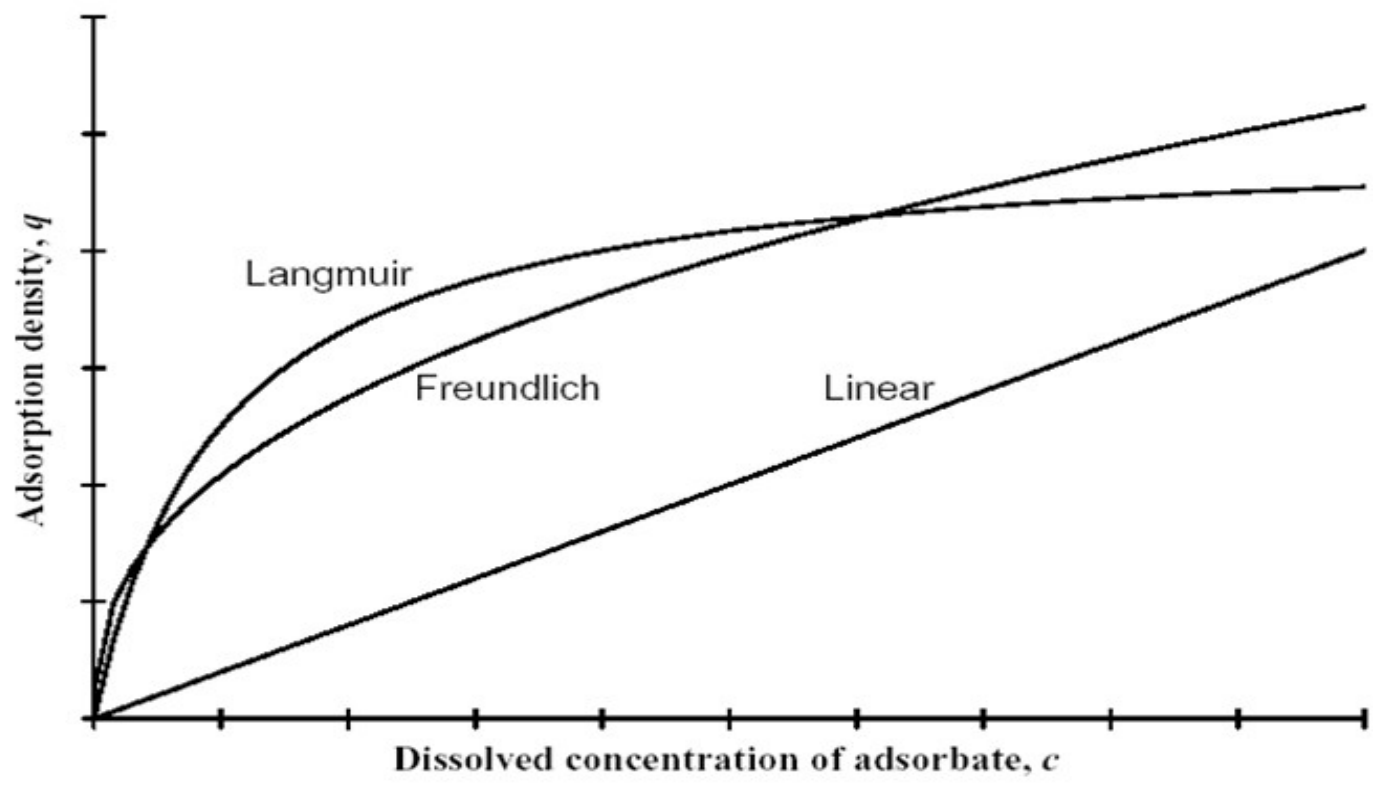
(d) Freundlich

Linear:  $q = k_{lin}c$  (7-2)

Langmuir:  $q = \frac{q_{max}K_{Lang}c}{1 + K_{Lang}c}$  (7-3)

Freundlich:  $q = k_f c^n$  (7-4)

where  $k_{lin}$ ,  $K_{Lang}$ ,  $q_{max}$ ,  $k_f$ , and  $n$  are all empirical constants.<sup>2</sup>





## Langmuir Isotherm:

This model assumes monolayer coverage and constant binding energy between surface and adsorbate. The model is:

$$q_e = \frac{K_a \cdot Q_e^0 \cdot C_e}{1 + K \cdot C_e}$$

$Q_a^0$  represents the maximum adsorption capacity (monolayer coverage) (g solute/g adsorbent).

$C_e$  has units of mg/L.

$K$  has units of L/mg

For the Langmuir model linearization gives:

$$\frac{C_e}{q_e} = \frac{1}{K \cdot Q_a^0} + \frac{C_e}{Q_a^0}$$

A plot of  $C_e/q_e$  versus  $C_e$  should give a straight line with intercept :

$$\frac{1}{K \cdot Q_a^0} \quad \text{and slope:} \quad \frac{1}{Q_a^0}$$

$$\frac{1}{q_e} = \frac{1}{Q_a^0} + \frac{1}{K \cdot Q_a^0} \cdot \frac{1}{C_e}$$

Here a plot of  $1/q_e$  versus  $1/C_e$  should give a straight line with intercept  $1/Q$  and slope

$$\frac{1}{K \cdot Q_a^0}$$

For the Freundlich isotherm use the log- log version :

$$\log q_e = \log K_F + \frac{1}{n} \log C$$

A log-log plot should yield an intercept of  $\log K_F$  and a slope of  $1/n$ .

# Freundlich Isotherm:

For the special case of heterogeneous surface energies in which the energy term, “ $K_F$ ”, varies as a function of surface coverage we use the Freundlich model.

$$q_e = K_F C_e^{\frac{1}{n}}$$

$n$  and  $K_F$  are system specific constants.

# Factors which affect adsorption extent

## Solubility:

- In general, as solubility of solute increases the extent of adsorption decreases. This is known as the “Lundelius’ Rule”.
- Factors which affect solubility include molecular size (high MW- low solubility), ionization (solubility is minimum when compounds are uncharged), polarity (as polarity increases get higher solubility because water is a polar solvent).

## pH:

pH often affects the surface charge on the adsorbent as well as the charge on the solute. Generally, for organic material as pH goes down adsorption goes up.

## Temperature

Adsorption reactions are typically exothermic i.e.,  $\Delta H_{\text{rxn}}$  is generally negative. Here heat is given off by the reaction therefore as Temp. increases extent of adsorption decreases.

## **Presence of other solutes:**

In general, get competition for a limited number of sites therefore get reduced extent of adsorption or a specific material.

# Applications of Adsorption

**Adsorption finds extensive applications both in research laboratory and in industry. A few applications are discussed below/;**

In preserving vacuum: In Dewar flasks activated charcoal is placed between the walls of the flask so that any gas which enters into the annular space either due to glass imperfection or diffusion though glass is adsorbed.





## In gas masks:

All gas masks are devices containing suitable adsorbent so that the poisonous gases present in the atmosphere are preferentially adsorbed and the air for breathing is purified.



## In clarification of sugar:

Sugar is decolorized by treating sugar solution with charcoal powder. The latter adsorbs the undesirable colors present.



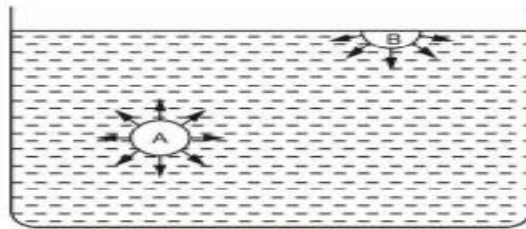
## In paint industry:



The paint should not contain dissolved gases as otherwise the paint does not adhere well to the surface to be painted and thus will have a poor covering power. The dissolved gases are therefore, removed by suitable adsorbents during manufacture. Further, all surfaces are covered with layers of gaseous, liquid or solid films. These have to be removed before the paint is applied. This is done by suitable liquids which adsorb these films. Such liquids are called wetting agents. The use of spirit as wetting agent in furniture painting is well known.

# Surface tension

consider a molecule, A in the interior of a liquid. It is being attracted by neighboring molecules equally in all direction and thus the resultant force on it is zero. Now consider another molecule, B at the surface. It is experiencing a resultant force downward because of greater attraction for molecules in the liquid than molecules in the vapors above the liquid. This is the case with the molecules at the surface. The surface of the liquid tends to contract to have the minimum surface area possible. This force in the surface called surface tension.



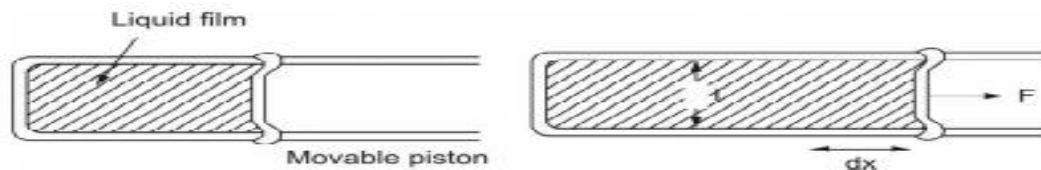
**Fig. 2.1** Force acting on a molecule in a liquid

$$W = Fdx \quad \dots(1)$$

This causes an increase in the surface area of the film given by

$$\Delta A = 2(l \times dx) \quad \dots(2)$$

where  $l$  is length of the film. The factor 2 is introduced because there are two sides of the film.



**Fig. 2.2** Calculation of force on a liquid surface

Since the force  $F$  is applied against the force of surface of tension acting on the film, therefore, if  $\gamma$  is the force per centimeter along the movable wire, then

$$F = \gamma \times 2l \quad \dots(3)$$

$$\gamma = \left( \frac{F}{2l} \right) = \frac{\text{Force}}{\text{Unit length}}$$

Therefore, 
$$W = g \cdot 2ldx$$

$$= \gamma \times \Delta A$$

or 
$$\gamma = \frac{W}{\Delta A} = \frac{\text{Work}}{\text{Area}} \quad \dots(4)$$

From equation (3), surface tension is defined as the force in dynes acting per unit length and from equation (4), it can be defined as the work in ergs required to generate a unit increase in surface area. The units of surface tension are dynes/cm or ergs/cm<sup>2</sup>. SI units of surface tension is newton/m.