Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (First Year)

Subject: Chemistry

Paper Code: CHC-152

Paper Title: General Industrial Chemistry

Unit: III

Module Name: Adsorption, Adsorption Isotherm and Applications

Module No: 5

Name of the Presenter: Ms. Nikita V. Naik

Notes

ADSORPTION

Definition:

- When a solid surface is exposed to a gas or a liquid, molecules from the gas or the solution phase accumulates or concentrates at the surface. The phenomenon of concentration of molecules of a gas or liquid at a solid surface is called Adsorption.
- The substrate that concentrates at the surface is called Adsorbate.
- The solid on whose surface the concentration occurs is called the Adsorbent.
- Examples:
- If finely divided charcoal is stirred into a dilute solution of methylene blue (organic dye), the depth of colour of the solution decreases appreciably. The dye molecules have been adsorbed by the charcoal particles.
- If a gas (SO_2, Cl_2,) is treated with powdered charcoal in a closed vessel, the gas pressure is found to decrease. The gas molecules concentrate on charcoal surface and are said to be adsorbed.

ADSORPTION VERSUS ABSORPTION

- Adsorption implies concentration at the surface only,
- Absorption implies penetration into the body of solid.

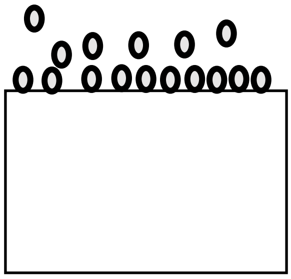


Fig.(a). Adsorption

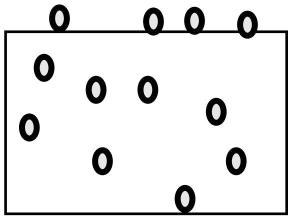
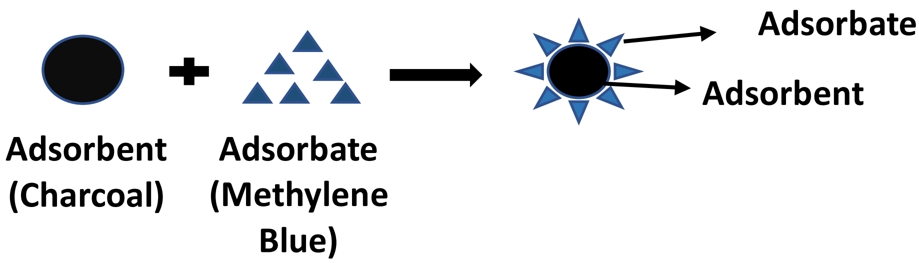


Fig.(b). Absorption

MECHANISM OF ADSORPTION

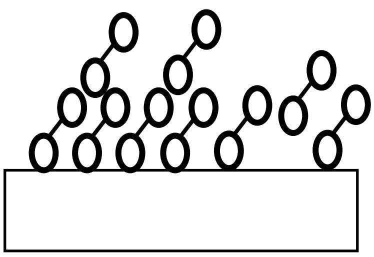
- Atoms or molecules of a solid surface behaves like the surface molecule of a liquid.
- These are not surrounded by the atoms or molecules of their kind on all sides. Therefore they possess unbalanced or residual attractive forces. These forces of the adsorbent are responsible for attracting and holding the adsorbate particles on its surface.



TYPES OF ADSORPTION

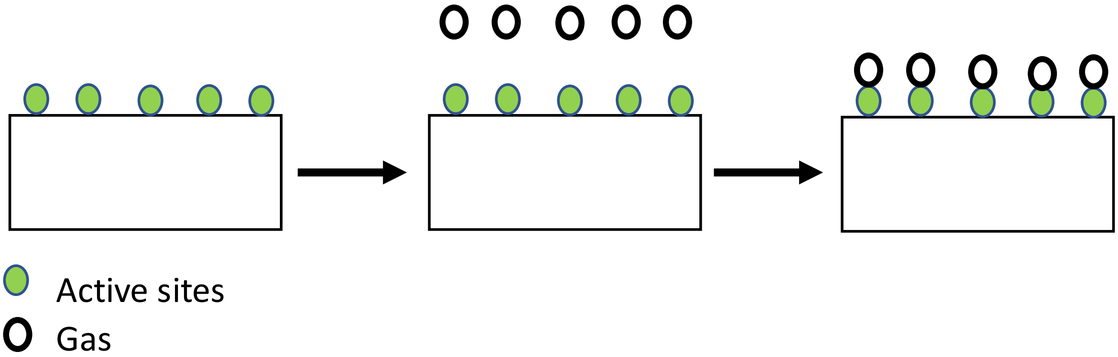
There are two types of Adsorption

a) ***Physical Adsorption:*** This is due to the gas molecules being held to the solid surface by van der Waal's attractive forces. It is also referred to as van der Waal's Adsorption.
Example: Adsorption of Hydrogen or Oxygen on Charcoal is Physical Adsorption.



b) ***Chemical Adsorption or Chemisorption:*** In this kind of adsorption, the gas molecules or atoms are held to the solid surface by chemical bonds. These bonds may be covalent or ionic in nature.

Example: Hydrogen molecule is first adsorbed and then dissociates.



ADSORPTION ISOTHERMS

- The adsorption of a gas on a solid adsorbent in a closed vessel is a reversible process.

  Gas $\longleftrightarrow$ Gas/adsorbent

- The amount of gas adsorbed depends on the equilibrium pressure and temperature.
- A mathematical expression or graphical curve which represents the relation between the amount of gas adsorbed by the adsorbent, and the equilibrium pressure is called the **Adsorption Isotherm**.

1. FREUNDLICH ADSORPTION ISOTHERM

Freundlich proposed an empirical relation in the form of a mathematical equation

$$\frac{w}{m} = k \times p^{1/n}$$

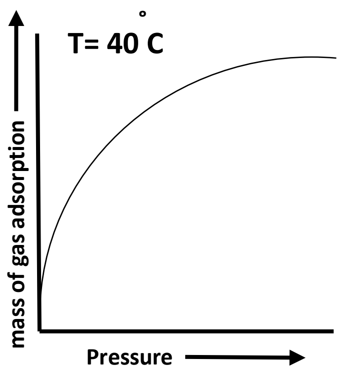
Where,

'w' is the mass of the gas adsorbed

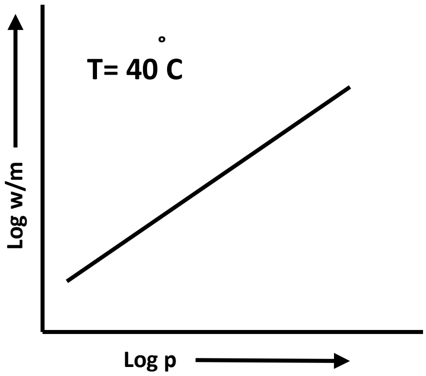
'm' mass of the adsorbent

'p' is the pressure

‘k’ and ‘n’ are constants depending on the nature of adsorbent and gas and on temperature.
The relation is generally represented in form of a curve when mass of gas adsorbed is plotted against pressure. The mathematical equation stated above and the mass/pressure curve are called Freundlich Adsorption Isotherms.



a) Freundlich Isotherm for the adsorption of ammonia by charcoal at 40 °C



b) Plot of log w/m against log p gives a straight line (adsorption of ammonia by charcoal) at 40 °C

- Freundlich adsorption isotherm stated above in the form of an equation may be tested as follows, $\frac{w}{m} = k \times p^{1/n}$
- Taking logarithms on both sides,

$$\log \frac{w}{m} = \log k + \frac{1}{n} \log p$$

- This equation is for a straight line. Hence if in actual practice, the plot of log (w/m) against log p comes out to be a straight line, the Freundlich Isotherm stands verified.
- However, Freundlich isotherm fails at high pressure.

2. LANGMUIR ADSORPTION ISOTHERM

- Langmuir derived an adsorption isotherm on theoretical consideration based on kinetic theory of gases. This was named as the Langmuir Adsorption isotherm.
- He assumed that the layer of the adsorbed gas was only one molecule thick. Therefore, Langmuir isotherm worked particularly well for chemisorption.

Langmuir considered that the gas molecules strike a solid surface and are thus adsorbed. Some of these molecules then evaporate or are 'desorbed' fairly rapidly.

- The rate of adsorption of the gas on the adsorbent surface will be proportional to the rate at which gas molecules strike the surface and the available surface.
- According to the kinetic theory, the rate of striking of gas molecules is proportional to the pressure of the gas (p) at constant temperature.
- If θ is the fraction of the surface covered by adsorbed molecules at any instance, the fraction of uncovered surface is (1- θ).

Therefore,

$$\textbf{Rate of Adsorption} \propto (1 - \theta)p$$

$$= K_1 (1 - \theta)p$$

Where 'K_1' is rate constant

$$\textbf{Rate of Adsorption} \propto \theta$$

$$\textbf{Rate of Desorption} = K_2\, \theta$$

Where 'K_2' is a rate constant

But at equilibrium,

Rate of Adsorption = Rate of Desorption

Therefore,

$$K_1 (1 - \theta)p = K_2\, \theta$$

$$\textbf{Hence } \theta = \frac{K_1 p}{K_1 p + K_2}$$

The mass (w) of gas adsorbed per unit mass of adsorbent is directly proportional to fraction of surface covered (θ).

That is,

$$w = K_3\theta$$

Where K_3 is constant of proportionality

Thus,

$$w = \frac{K_1 K_3 p}{K_1 p + K_2}$$

$$= \frac{\left(\frac{K_1 K_3}{K_2}\right) p}{\left(\frac{K_1}{K_2}\right) p + 1}$$

$$\text{or } w = \frac{Ap}{Bp + 1}$$

Where A and B are constants. This relation is known as **Langmuir Adsorption Isotherm.**

APPLICATIONS OF ADSORPTION IN INDUSTRIAL PROCESS

❖ **Froth Flotation Process:** The low grade sulphide ores (PbS, ZnS, Cu_2S) are freed from silica and other earthy matter by Froth Flotation Process.

- In this, the finely divided ore is mixed with oil (pine oil) and agitated with water containing a detergent (foaming agent). When air is bubbled through into this mixture, the air bubbles are stabilized by the detergent.
- These adsorb mineral particles wetted with oil and rise to the surface. The earthy matter wetted by water settles down at the bottom.

❖ **Chromatographic Analysis:** Mixture of small quantities of organic substances can be separated with the help of chromatography which involves the principle of selective adsorption.

- In this, the mixture is dissolved in a suitable solvent (hexane) and poured through tube containing the adsorbent (alumina).
- The material is separated into ‘bands’ in different parts of the tube.
- Each component dissolved in the solvent comes down by turn and is collected in a separate receiver.
- Mixture of gases can be separated by selective adsorption of gases by liquids (gas chromatography).

- **Ion-Exchange Adsorption:** It is a special form of adsorption in which the adsorbed ions can be exchanged for other like ions.

- The adsorbent if exchanges cations is termed a Cation Exchanger and if it exchanges anions an Anion Exchanger.
- Water Softening: Hard water is softened by passing through a column packed with sodium cation-exchanger resin (R^-……Na^+).
- The Ca^{+2} and Mg^{+2} ions in hard water are replaced by Na^+ ions.

$$\mathbf{2R^- \ldots\ldots Na^+ + Ca^{+2} \rightleftarrows R_2\,Ca^{+2} + Na^+}$$

Anion-exchanger resin	**Resin 'chloride'**