Chapter 5

Surface Chemistry

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ADSORPTION

Adsorption refers to the intriguing process whereby atoms, ions, or molecules exhibit a tendency to adhere to a surface, regardless of whether it originates from a gas, liquid, or dissolving solid. This adherence culminates in the formation of a distinct layer of adsorbate atop the surface of the adsorbent. Essentially, adsorption underscores the innate ability of diverse substances to allure and securely hold onto molecules found within the liquids or gases they encounter on their surfaces.

This discourse delves into the intricate facets of adsorption, exploring its nuanced manifestations which encompass chemical, physical, and isothermal variations. Furthermore, we embark on an exploration of the diverse categories of adsorbates and adsorbents to deepen ours.

Introduction of Colonial Cities

Surface chemistry is a specialized field within chemistry devoted to investigating the phenomena that occur at the boundary between two bulk phases, known as the interface. This interface can manifest between various combinations of phases, such as solid and gas, liquid and gas, or solid and liquid. Examples of phenomena that occur at these interfaces include dissolution, crystallization, corrosion, heterogeneous catalysis, and electrode processes.

The representation of the interface typically involves separating the two bulk phases with a hyphen or a slash, for instance, solid-gas or solid/gas. In cases where gases are completely miscible, there is no distinct interface. The thickness of the interface is usually only a few molecules, although its area can vary depending on the size of the particles present in the bulk phases.

Surface chemistry has widespread applications across different domains, including industry, analytical work, and everyday life situations. Its principles are utilized in various industrial processes, analytical techniques, and even in understanding natural phenomena encountered in daily life.

Define Adsorption

Adsorption entails the accumulation of molecules on the internal or external surfaces of a solid or even on the surface of a liquid. The

- Catalyst and Catalysis and Some Other Terms

gathering of molecules by the internal or external covering, such as the walls of capillaries or fissures, of solids or even on the surfaces of liquids is designated as adsorption. The process of penetrating the substance of amorphous liquids or solids, or even the actual inner crystals, is identified as absorption. In instances where a solid assimilates a liquid or gas without specifying a distinct absorption or adsorption process, the term used is sorption.

Absorption

The process wherein a substance disperses evenly throughout the entirety of a solid or liquid is termed absorption. This phenomenon contrasts with adsorption, which specifically involves the accumulation of molecules on the surface of a material. For instance, water vapors are uniformly absorbed into anhydrous calcium chloride, whereas they are accumulated on the surface of silica gel, thus undergoing adsorption. Similarly, ammonia molecules adhere to the surface of charcoal, demonstrating adsorption behavior.

Difference between Adsorption & Absorption

Many individuals find these two terms confusing due to their similar sound, yet their processes are distinct. The surface phenomenon of adsorption is characterized by an exothermic nature. This process is temperature-dependent, and the methods initially undergo slow expansion and reduction. On the other hand, absorption is an endothermic reaction. Temperature has minimal impact on absorption, allowing it to occur consistently. Substances permeate the material's surface in absorption. Unlike adsorption, absorption takes place spontaneously. Adsorption is not limited solely to the surface area but is distinctive across the entire surface. Absorption exhibits a relatively higher level of molecule interaction compared to adsorption.

Types of Adsorptions

There are two main types of adsorptions: physical adsorption and chemical adsorption. Adsorption, in general, is an exothermic process where heat is generated due to an attractive force between the adsorbent and the adsorbate. The nature of the forces between the adsorbent and adsorbate plays a crucial role in distinguishing between physical and chemical adsorption. Physical adsorption, influenced by Van der Waals forces or interactions among adsorbates with solid absorbents, leads to the condensation of gases into liquids.

Solids can adsorb any gas, irrespective of its chemical characteristics, when the temperature decreases and the gas pressure increases. In contrast, chemical adsorption relies on chemical forces acting on solid surfaces and gas adsorbates. Compared to physical adsorption, chemical adsorption requires a higher temperature. The process of chemical adsorption involves energy activation, making it a prolonged but slow procedure.

Adsorption Isotherm

In environmental studies and adsorption methods, the adsorption isotherm proves valuable as it aids in determining the adsorption capacity of solid materials. Additionally, an adsorption isotherm serves as a graphical representation illustrating the quantity of adsorbed adsorbate solely on the surface of an adsorbent under constant pressure and temperature conditions.

Application of Adsorption

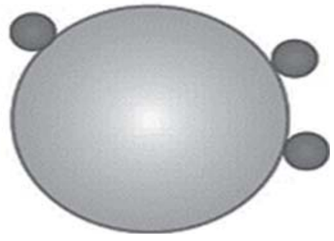
Charcoal achieves decolorization of colored sugar solutions by adsorbing the coloring molecules. Silica gel is employed in desiccators to absorb moisture, serving as an adsorbent that effectively manages humidity in workplaces or rooms. Activated charcoal is a component in gas masks, leveraging its ability to adsorb vapors and harmful fumes, thereby purifying the air. The technique of adsorption is utilized in heterogeneous catalysis. Charcoal can function as an absorbent for the separation of noble gases. The phenomenon of adsorption finds application in chromatographic analysis. Stable emulsions are produced through adsorption for syrups or cosmetics. The adsorption of drugs contributes to the destruction of bacteria.

Conclusion

The processes of absorption and adsorption are fundamentally distinct and should not be mistaken for one another. Adsorption involves the collection of a liquid or gas on a liquid or solid surface, forming an atomic or molecular film. In contrast, the absorption process entails the diffusion of a material into a liquid or solid, resulting in the creation of a solution. Here, molecules undergoing resorption are taken up by the volume, not just the surface.

Mechanism of Adsorption

1. Adsorption refers to the surface phenomenon where molecules accumulate on a surface.
2. The surface where this phenomenon occurs is termed the adsorbate, and the molecular species are referred to as adsorbents.
3. This process is exothermic, leading to the release of energy.
4. The enthalpy of adsorption is defined as the energy released when one mole of adsorbate is adsorbed on the adsorbent.
5. The enthalpy of adsorption is negative due to a decrease in entropy.
6. The negativity of the enthalpy of adsorption results from the restriction of molecular randomness.
7. Adsorption is a spontaneous process that occurs at a constant temperature and pressure.
8. Common examples of adsorbents include clay, silica gel, and colloids.
9. The image below illustrates the process of adsorption:



Adsorption

Mechanism

- Adsorption takes place when the particle on the surface and the particle within the bulk of the adsorbent exist in different environments.
- Residual attractive forces, also referred to as unbalanced forces, act upon the surface particle.
- These forces cause the particles on the surface of the adsorbent to attract the particles of the adsorbate.
- Adsorption consistently leads to a reduction in the residual attractive forces on the surface.
- In other words, the energy of the surface decreases, and this reduction is expressed as heat, known as the heat of adsorption.

- The negative enthalpy change is indicative of the fact that when adsorbate molecules are adsorbed on the surface, their freedom of movement is constrained, resulting in a decrease in entropy.

Types of Adsorption and Factors Affecting Extent of Adsorption

Types of Adsorptions

On the basis of interaction forces between adsorbate and adsorbent, adsorption is of two types.

1. **Physical Adsorption**

   This form of adsorption is alternatively referred to as physisorption, arising from the weak Van der Waals forces between the adsorbate and adsorbent. An illustration of this is the adsorption of H_2 and N_2 gases on coconut charcoal.

2. **Chemical Adsorption**

   This form of adsorption is alternatively referred to as chemisorption, stemming from robust chemical bonding forces between the adsorbate and adsorbent. An example involves the formation of iron nitride on the surface when iron is heated in N_2 gas at 623 K.

   Adsorption of gas on a solid represents a spontaneous exothermic reaction. The quantity of heat released when a unit mass of gas is adsorbed on the surface is termed the heat of adsorption.

Factors Affecting the Extent of Adsorption

The occurrence of adsorption on a solid surface is influenced by several factors:

Nature of adsorbent: The adsorption of gas is contingent upon the nature of the adsorbent. Different adsorbent surfaces may result in varying amounts of gas adsorption.

For instance, hydrogen exhibits weak adsorption on alumina surfaces, while it strongly adsorbs on nickel surfaces under specific conditions.

Surface area: Increasing the surface area of the adsorbent leads to enhanced gas adsorption. This is attributed to the greater number of adsorbing sites available when the surface area is increased. Therefore, finely divided solids and certain porous substances make effective adsorbents.

Nature of the gas: Generally, gases that are more liquefiable tend to be more easily absorbed.

For example, easily liquefiable gases like NH_3, HCl, Cl_2, CO_2 are readily adsorbed on solid surfaces compared to permanent gases like O_2, H_2, etc.

Exothermic nature: The heat of adsorption, defined as the energy released when 1 g mol of a gas is adsorbed on a solid surface, plays a crucial role. Increasing the temperature boosts the kinetic energy of gas molecules, leading to more collisions between molecules and the surface.

Pressure: The solid surface possesses a fixed number of adsorption sites where gas molecules can be adsorbed. Initially, as pressure increases, the rate of adsorption rises due to more gas molecules striking the surface. However, there comes a point where pressure no longer affects the rate of adsorption. At this juncture, the number of adsorption sites is fixed, and further pressure increase does not result in additional adsorption. Consequently, the extent of adsorption becomes independent of pressure.

Types of Adsorption Isotherm

Various Adsorption Isotherms

The various types of adsorption isotherms are:

I **Classical Freundlich Adsorption Isotherm**

in 1909, Freundlich proposed an empirical equation and was known as Freundlich adsorption isotherm. This equation is as follows:

$$x/m = kp^{1/n} \quad \text{... (i)}$$

where x is amount of adsorbate, m is the amount of adsorbent, p is the pressure, k and n are two constants depending upon the nature of the adsorbent and adsorbate, and n being less than unity.

Equation (i) is applicable to the adsorption of gases on solids.

In case of solution, equation (i) takes the form

$$x/m = kc^{1/n} \quad \text{...(ii)}$$

where c is the concentration of the solute in gm moles per liter.

Equations (i) and (ii) predict the effect of pressure (or concentration) on the adsorption of gases (or solution) at constant temperature in a quantitative manner.

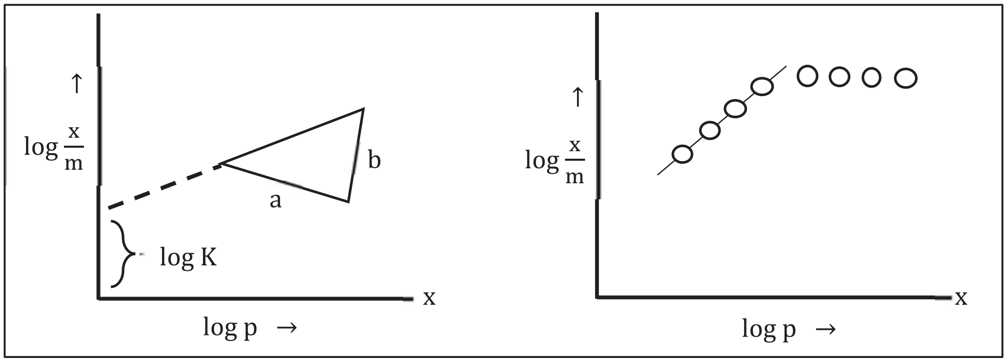
Test of Freundlich's Adsorption Isotherm

Taking logarithms of equations (i) and (ii), we get

$$\text{Log}\frac{x}{m} = \log k + \frac{1}{n}\log p \quad \text{... (iii)}$$

$$\text{and } \log\frac{x}{m} = \log k + \frac{1}{n}\log c \quad \text{... (iv)}$$

f log $\frac{x}{m}$ is plotted against log p or log c, a straight line should be obtained as shown in fig. The slope of the line will give the value of and the $\frac{1}{n}$ intercept on the Y-axis gives the value of log k, i.e.



Intercept = log k

and slope $= \frac{b}{a} = \frac{l}{n}$

Therefore, utilizing equations (iii) and (iv), the values for k and n can be determined based on the graph (fig). Examination of the graph reveals that with an increase in pressure (p), the ratio $\frac{x}{m}$ also increases. Consequently, Freundlich's equation suggests an unlimited rise in $\frac{x}{m}$ with increasing pressure. However, experimental values, when graphed, exhibit deviations from linearity, particularly at low pressures, as depicted in the figure. Comparing the theoretical and experimental curves (fig), it is evident that they align only within a specific pressure range. Thus, Freundlich's equation is constrained by its validity over a limited pressure range.

Limitations of Freundlich's Equation

1. It is valid over a certain range of pressure only.
2. The constant k and n vary with the temperature.
3. Freundlich adsorption equation is a purely empirical formula without theoretical foundation.

II Langmuir Adsorption Isotherm

It has been mentioned that the Freundlich adsorption isotherm is applicable only within a specific pressure range. To address this limitation, Langmuir (1916) developed an alternative adsorption isotherm known as Langmuir's adsorption isotherm.

The key assumptions are:

a. The adsorbed layer on the solid adsorbent is assumed to be unimolecular in thickness. This perspective is widely accepted for adsorption at low pressure or moderately high temperatures. However, at relatively low temperatures and pressures approaching saturation, the adsorbed molecules may hold other gas molecules through van der Waals forces, allowing for multimolecular layers. Langmuir, however, considered only the formation of a unimolecular layer when deriving this relation.

b. Adsorption occurs at fixed sites, and there is no interaction between the adsorbed molecules on the surface. Each site adsorbs one molecule. When the entire surface is covered by a unimolecular layer of gas, further adsorption becomes impossible, indicating the maximum saturation of adsorption.

c. The adsorption process is dynamic, involving two opposing processes:

   (i) Condensation Process:

   This process entails the condensation of gas molecules onto the surface of a solid material. During adsorption, gas molecules transition from the gaseous phase to a condensed state as they adhere to the solid surface. The interaction between the gas molecules and the solid's surface leads to the accumulation of a layer of gas molecules on the exterior of the solid material. This phenomenon occurs at the molecular level, with individual gas molecules adhering to specific sites on the solid surface. The adsorption process is characterized by the establishment of a dynamic equilibrium between the adsorbed gas molecules and those remaining in the gaseous phase. The condensed layer on the solid surface is crucial in understanding various aspects of adsorption, including factors influencing its extent and the specific characteristics of the adsorbate-adsorbent interaction.

   (ii) Evaporation Process:

   This process entails the evaporation of adsorbate molecules from the surface of the adsorbent. At the initiation of adsorption, the entire surface of the adsorbent remains uncovered, resulting in the maximum initial rate of condensation. As the surface gradually becomes covered with adsorbed molecules, the rate of condensation diminishes. In contrast, the initial rate of evaporation (desorption) of the condensed molecules is minimal at the onset of adsorption but increases as the surface becomes progressively covered. Ultimately, when equilibrium is established, the rate of condensation equals the rate of evaporation. This equilibrium signifies that the number of gas molecules condensing on the given surface is equivalent to the number of molecules evaporating from the same surface per unit time, indicating a unidirectional arrangement of the adsorbed molecules on the surface.

d. Gas behaves ideally.

e. Surface is uniform energetically.

Uses and Application of Adsorption

1. Air pollution masks: These masks incorporate silica gel or activated charcoal powder. When dust or smoke is passed through them, these particles are adsorbed on the surface of these materials.
2. Separation of noble gases by Dewar's flask process: A mixture of noble gases, including Ne, Ar, and Kr, is directed through Dewar's flask in the presence of heated coconut charcoal. Argon and Krypton become adsorbed, leaving Neon.
3. Purification of water: The addition of alum stone to water causes impurities to be adsorbed on the alum, purifying the water.
4. Removal of moisture and humidity: Moisture in the air is eliminated by placing silica gel, on which water molecules get adsorbed.
5. Adsorption chromatography: This method is employed to separate pigments and hormones.
6. Ion exchange method: In this approach to water hardness removal, calcium and magnesium ions become adsorbed on the surface of ion exchange resin.
7. In metallurgy: During the froth floatation process for ore concentration, particles get adsorbed on the froth.