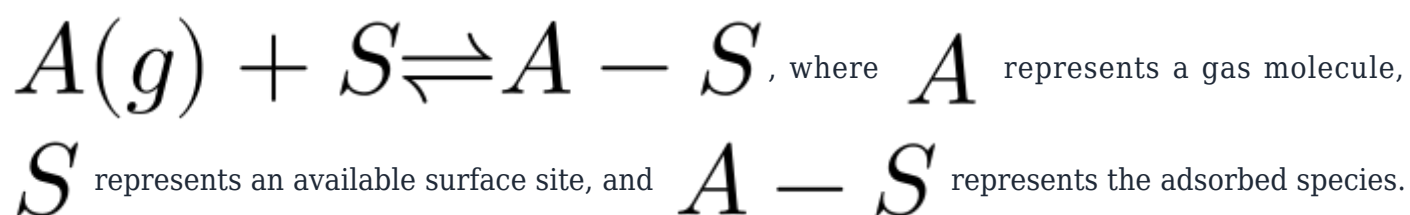


Adsorption

Adsorption is a surface phenomenon in which atoms, ions, or molecules of one substance become concentrated at the surface of another substance. The substance that provides the surface is called the **adsorbent**, while the substance that becomes accumulated at the surface is called the **adsorbate**. Since adsorption occurs at the interface, the nature and extent of the surface play a major role in determining the amount of substance that can be adsorbed.

The origin of adsorption can be understood from the structure of a solid surface. A particle situated inside a solid is surrounded by neighbouring particles and experiences attractive forces in different directions. These forces are approximately balanced. A particle situated at the surface, however, has fewer neighbouring particles because one side is exposed to the surrounding phase. Consequently, the attractive forces acting on surface particles are not completely satisfied. The surface therefore possesses excess free energy. When molecules from the surrounding phase approach the surface, they can interact with these unsatisfied forces and become attached to the surface. The resulting decrease in surface free energy provides the thermodynamic basis for adsorption.

For a gas-solid system, adsorption may be represented schematically as



The process is reversible in many systems. Initially, when a clean surface is exposed to the gas, adsorption occurs rapidly because a large number of surface sites are vacant. As the surface becomes occupied, the rate of adsorption decreases. At equilibrium, adsorption and desorption occur simultaneously at equal rates and the amount adsorbed remains constant.

Adsorption is fundamentally different from absorption. In adsorption, the substance is concentrated mainly at the surface of the adsorbent, whereas in absorption the substance penetrates into the bulk of the absorbing material. Thus, adsorption is a surface phenomenon while absorption is a bulk phenomenon. When both processes occur together, the general term **sorption** is used.

The extent of adsorption depends strongly upon the surface area of the adsorbent. A finely divided or porous solid provides a much larger surface area than a compact solid of the same mass and consequently provides a greater number of sites for adsorption. Activated charcoal, silica gel, alumina, and finely divided metals are therefore commonly used as adsorbents. The effectiveness of an adsorbent depends not only on its total surface area but also on the nature, accessibility, and distribution of its surface sites.

The nature of the adsorbate also affects adsorption. Molecules differ in size, shape, polarity, polarizability, and chemical reactivity, and these properties determine their interaction with a particular surface. A substance having a stronger attraction for the surface will generally be adsorbed

more readily than one having a weaker interaction. The chemical nature of the adsorbent is equally important because different surfaces have different affinities for the same adsorbate.

Temperature has an important effect on adsorption. Adsorption is generally accompanied by the evolution of heat because the adsorbed state is usually at a lower energy than the separated adsorbate and adsorbent. Consequently, physical adsorption generally decreases with increase in temperature. At higher temperature, adsorbed molecules possess greater thermal energy and can leave the surface more readily. Chemisorption may show a different temperature dependence because the formation of the chemical bond between the adsorbate and surface may require an activation energy.

Pressure is particularly important in the adsorption of gases. At relatively low pressure, increasing the pressure increases the number of gas molecules striking the surface per unit time and therefore increases the amount adsorbed. As the pressure is increased further, the available surface sites gradually become occupied. Once the surface approaches saturation, a further increase in pressure produces a much smaller increase in the amount adsorbed.

Adsorption is commonly classified into **physical adsorption** and **chemical adsorption**. In physical adsorption, the adsorbate is held at the surface mainly by relatively weak intermolecular forces. In chemical adsorption, the interaction between the adsorbate and the surface is much stronger and may involve the formation of a chemical bond. The two types differ in the strength of interaction, heat of adsorption, reversibility, specificity, and dependence on temperature and pressure.

Adsorption is important in heterogeneous reactions because it brings reactant molecules from the bulk phase onto the solid surface. Once adsorbed, the molecules may become suitably oriented or activated for a surface reaction. A second reactant may also become adsorbed and react with the first adsorbed species. The products can subsequently leave the surface by desorption, allowing the surface sites to participate in another reaction cycle. Thus, adsorption can be an essential initial step in many gas-solid heterogeneous reactions.

The study of adsorption therefore provides the foundation for understanding the subsequent topics in this unit. The nature of the interaction between the adsorbate and the surface determines whether the process is physical adsorption or chemisorption, while the subsequent removal of adsorbed species is described by desorption. In gas-solid systems, the relationship between the amount adsorbed and pressure at a fixed temperature is described by adsorption isotherms, which will be considered when gas-solid adsorption is discussed.