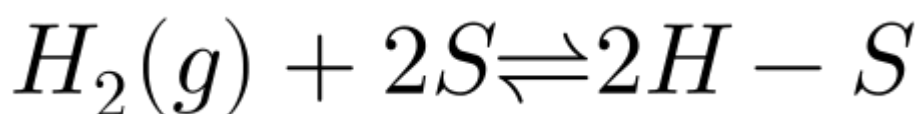


Chemisorption

Chemisorption is the adsorption of a substance on a solid surface in which the adsorbed species is held by a chemical interaction with the surface. The interaction is much stronger than the forces responsible for physical adsorption and, in many cases, involves the formation of a chemical bond between the adsorbate and surface atoms. Chemisorption is therefore closely related to the chemical nature of the surface and is usually much more specific than physical adsorption.

The possibility of chemisorption arises because the atoms present at a surface have unsatisfied valencies or unbalanced forces. When a molecule approaches such a surface, its electrons can interact with the electronic states of the surface atoms. Depending upon the nature of the two substances, this interaction may involve sharing of electrons, transfer of electrons, or formation of a surface bond. The adsorbed molecule may consequently have an electronic structure different from that of the molecule in the gas phase.

For example, hydrogen can be chemisorbed on a metal surface. The hydrogen molecule approaches the surface and interacts with suitable active sites. On some metal surfaces the H-H bond is weakened and may break, producing hydrogen atoms attached to the surface. The process can be represented as



where S represents an available surface site and $H - S$ represents hydrogen chemically bonded to the surface. The dissociation of a molecule during adsorption is particularly important in heterogeneous catalysis because the adsorbed atoms can participate in subsequent surface reactions.

Chemisorption is generally restricted to particular sites on the surface. These sites may be associated with surface atoms having unusual coordination, defects, edges, corners, or other regions of relatively high surface energy. Once the available sites have been occupied, further adsorption cannot normally occur by simply building successive layers of the same chemically bonded species. For this reason, chemisorption is generally described as a monolayer phenomenon.

The strength of the surface-adsorbate interaction is reflected in the heat evolved during adsorption. The heat of chemisorption is considerably larger than that of physisorption and is of the same general order as the energy involved in chemical bonding. Consequently, removal of a chemisorbed species may require considerable energy. Chemisorption is therefore often less readily reversible than physisorption.

An important feature of chemisorption is its dependence on temperature. Formation of the chemical bond may require an activation energy, particularly when an existing bond in the adsorbate has to be

weakened or broken. Thus, unlike ordinary physical adsorption, the amount of chemisorption may initially increase with temperature. At sufficiently high temperature, however, desorption becomes increasingly important and the amount of adsorbed material may decrease.

The distinction between physical adsorption and chemisorption is consequently not merely one of the strength of attraction. In physical adsorption, the adsorbate is held mainly by weak intermolecular forces and retains its chemical identity to a large extent. In chemisorption, the interaction with the surface is strong enough to alter the electronic structure of the adsorbate and, in many cases, to produce a new surface chemical species.

Physical adsorption	Chemisorption
Weak intermolecular forces are involved.	Strong chemical interaction with the surface is involved.
Usually non-specific.	Usually specific to the adsorbent and adsorbate.
Generally small heat of adsorption.	Generally large heat of adsorption.
Usually readily reversible.	Often less readily reversible.
Multilayer adsorption may occur.	Generally limited to a monolayer.
Usually no appreciable activation energy is required.	An activation energy may be required.

The importance of chemisorption becomes particularly clear in heterogeneous catalysis. A catalyst surface can adsorb a reactant strongly enough to weaken one or more of its bonds, while still allowing the resulting surface species to react with another adsorbed species. The catalyst therefore provides a surface on which the reaction can proceed through a different pathway from that available in the gas or liquid phase.