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Sorbents for Air and Gas Purification

Sorbents are materials that can attract and hold gases or liquids. They can be split into four basic classes: adsorbents, catalysts, chemisorbents, and absorbents. Some sorbents can actually fit within more than one class. For example, activated alumina is often used as a high surface adsorbent. But it can also be employed as a sub-base for chemical impregnates, and is also used as a catalyst in oil fields to crack petroleum products. Depending on the application, different types of sorbents have varying capabilities – and each type is optimal for certain types of applications. In some cases, two or more sorbents are used synergistically to provide the highest level of purification. The first step in any of the sorbent purification processes is to attract and sequester the contaminant molecules by adsorption.

Adsorption is a surface phenomenon whereby fluid molecules are attracted to and temporarily retained on a surface by physical forces. Adsorption occurs at the interface between the adsorbate molecules and the surface of the adsorbent. The fluid molecules, either liquid or gas, are attracted and restrained by weak physical forces called van der Waals forces. The process of adsorption is totally reversible, normally without physical or chemical changes to either the adsorbate or the adsorbent.

The weak adhesive physical forces involved in the unit operation of adsorption are understood to a limited extent. Van der Waals forces is a collective term and encompasses numerous molecular forces, both attracting and repulsing. They are electromagnetic and include polar-polar, ion-ion, polar-ion, London forces, induced polar forces and even gravity. Not all of the forces are thoroughly understood, or even known. Nevertheless, they have been quantified sufficiently to be able to predict the affects of adsorption and the degree of fractionation produced by adsorption.

Adsorption is a universal process that occurs spontaneously at all temperatures and pressures, even at temperatures above the critical temperature of the adsorbed gas though it is most effective at low temperatures. It occurs on all surfaces, without energy of activation, and without chemical bonding with the probable exception of hydrogen bonding. When gases or vapors are adsorbed, their molecules lose a degree of freedom and energy is liberated as predicted by Gibbs's law. The energy released is in the order of the heat of condensation. The heat of adsorption is greater than the heat of condensation when the adhesive forces between the surface and the gas molecules are greater than the cohesive forces between the gas molecules, and less than the heat of condensation when the cohesive forces are greater. The theories of adsorption are embedded in thermodynamics.

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Adsorption is a continuing, reversible process. Fluid molecules are constantly being adsorbed and others desorbed from an adsorbent surface. When the rate of molecule adsorption onto the surface is equal to the rate of molecule desorption, the system is said to be in adsorption equilibrium. The concentration of fluid molecules on the surface at the equilibrium condition is dependent on the activity of the surface, the adsorbability of the fluid molecules, the system temperature and the partial pressure or concentration of the fluid molecules in the continuum beyond the adsorbent surface. The concentration at equilibrium is greater at lower temperatures and higher partial pressures, and lower at elevated temperatures and lower partial pressures. Adsorption is a preferential process and the more adsorbable fluid molecules will displace and cause to desorb the less adsorbable molecules. At equilibrium, the total adsorbed concentration is constant and the energy liberated during the continuing adsorption process is identical to the energy consumed in desorption.

The affinity of a surface for specific adsorbates can be determined by analyzing the adsorbability of the vapor or gas and the activity of the adsorbent surface. The affinity for adsorption is determined from the molecular electronic polarization which is a function of the refractive index of the contaminant fluid.

Physical adsorption can be characterized by several general observations:

1. Adsorption is a **surface** phenomenon.
2. Adsorption is a **physical** phenomenon.
3. Adsorption is a **reversible** process.
4. Adsorption is a **universal** process.
5. Adsorption is a **continuing** process.
6. Adsorption is a **selective** process.
7. Adsorption is a **concentrating** process.
8. Adsorption is a **fractionating or partitioning** process.
9. Adsorption is a **spontaneous** process.
10. Adsorption is an **exothermic** process.

Physical adsorption differs in several important aspects from other molecular fractionating processes: chemisorption, absorption, and condensation. In chemisorption, chemical bonds are formed resulting in total restraint of the chemisorbed molecules, and the energy released is an order of magnitude greater than the heat of adsorption. Chemisorption is not universal; it can only occur between molecules which can form covalent or electrovalent bonds. Chemical bonding is more effective at elevated temperatures and often requires heat of activation to initiate the process.

Absorption is not a surface phenomenon. The absorbed fluid penetrates the substance of the absorbent forming a common substance, a solution, either a solid solution as in absorption by cellulosic fabrics, or by the formation of liquid solutions. The absorption process includes capillary filling where the absorbate fills the voids between fibrous media and is retained by the surface tension at the capillary openings. Deliquescence is another form of absorption in which salt solutions are formed between the absorbed water vapor and the deliquescent, absorbent, salt. Liquid absorbents include acid solutions and glycol solutions. In absorption, heat of solution is liberated and the temperature of the system is elevated.

Condensation closely approximates the process of adsorption. It involves cohesive forces between fluid molecules rather than adhesive forces between unlike molecules as in the adsorption process. Condensation requires the cooling of gases and vapors below their condensation temperatures, dew points, and it can not occur under any condition above the critical temperature of the gas.

Adsorbents used to dry gases and liquids are called desiccants. Other drying agents include deliquescent salts such as calcium chloride, absorbing solutions such as glycol, and chemisorbents such as calcium carbonate.

Media used to accomplish the adsorption separation of fluids can be devised to achieve high efficiencies. The ideal adsorbent is characterized by the following properties:

1. A highly active surface, either polar or ion filled.
2. A large surface area provided by a plethora of micropores.
3. Granular form to provide sufficient interstitial void space for external flow and high fluid phase mass transfer rate
4. A large macropore network within the media to permit rapid solid phase mass transfer by diffusion into the intrastitial spaces.
5. Chemically inert and stable to prevent chemical reaction with fluids in contact with the surface.
6. Non-toxic and insoluble.
7. Hard, abrasion resistant physical structure.
8. Dense media to provide high volumetric capacity for adsorption and resistance to attrition forces.

Adsorbents cause molecules to adhere to their surface. They are typically activated by chemical and/or thermal processing, and provide a porous intrastitial structure and very active interfacial surfaces. Activation also provides for a significant macroporous structure to permit rapid internal diffusion. Adsorbents can be categorized as organic or inorganic. Inorganic adsorbents include activated aluminas, silica gels, adsorbent clays, molecular sieves and natural zeolites.¹ Organic adsorbents are composed of activated carbons, polymeric adsorbents and carbonaceous media. Desiccants are adsorbents that have a particular affinity for water.²

All solid materials exhibit adsorption properties to varying degrees. On the surface, there are unsatisfied ions and polar molecules with adsorptive capabilities. Even if the molecules are fully bonded within the solid media, there is a discontinuity at the interfacial surfaces, and the molecules are not fully satisfied on the exposed surfaces. Some solids such as plastic, glass and graphite are composed of very well bonded crystalline molecules, and will therefore have very little adsorption activity. But even these demonstrate adsorptive activity to some extent.

Catalysts exhibit such strong adsorptive activity that adsorption is followed by catalytic reaction – often in a multi-stepped process rather than a singular event. The physical forces are so great that not only does the solid surface attract fluid molecules, but also the bonds within the molecule itself can be broken. Oxides of platinum, palladium, copper, manganese, iron, and silver are examples of very effective catalysts. A catalyst such as platinum oxide is often impregnated onto the surface of an adsorbent to obtain a large surface area internal to the adsorbent.

Because metal oxides are often quite expensive, impregnants are typically spotted on the internal surface (at typically less than 5% surface coverage), rather than actually coating the entire surface with the impregnant. Alumina, silica gel and activated carbon are frequently used as the base substrate media to support the metal catalyst.

¹ Sorbents and Desiccants, 1989 ASHRAE Handbook, Fundamentals, p. 19.5.

² Ibid., p. 19.1

Chemisorbents are produced by impregnating a high surface area substrate material with a chemical reactant such as potassium permanganate, an amine such as pyridine, or hexavalent chromium. This class of sorbent is used to chemically react with the contaminant fluid, resulting in a chemical change in both the contaminant and impregnant reactant.

Absorbents “suck up” or “take in” fluid molecules.³ Where gases or liquids stick to the surface of an adsorbent, they fill in or occupy the voids of an adsorbent. Examples of solid absorbents are salt crystals (e.g., sodium chloride), hydroxides, and urea. Certain absorbents react with water vapor to form a salt solution in liquid form. And some absorbents react with other gases such as carbon dioxide to form a liquid or solid carbonate. Absorbents are often used as impregnates on adsorbents (e.g., KINA activated carbons impregnated with potassium iodide (a salt) and sodium hydroxide).

Adsorbents share a chemical commonality with other better known minerals. Aluminum oxide, the basic material in activated alumina, is also the basic material in rubies and sapphires, only the molecular structure or morphology is different. Opals and silica gel are both composed of amorphous, non-crystalline, silicon dioxide. Molecular sieves and natural zeolites are composed of alumina silicates as are emeralds. Carbon is the common substance in both activated carbons and diamonds. The porosity and surface activity separate the adsorbents from their related gemstones.

³ Merriam Webster Online Dictionary: <http://www.m-w.com/cgi-bin/dictionary?book=Dictionary&va=absorb>