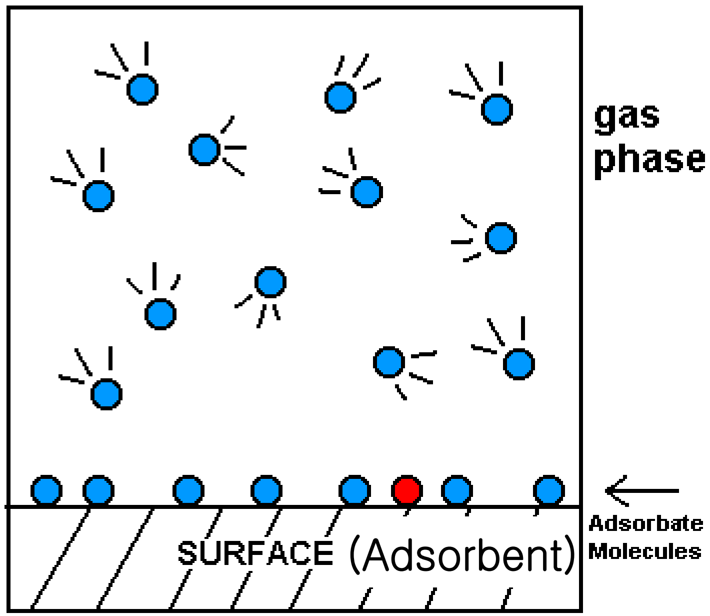
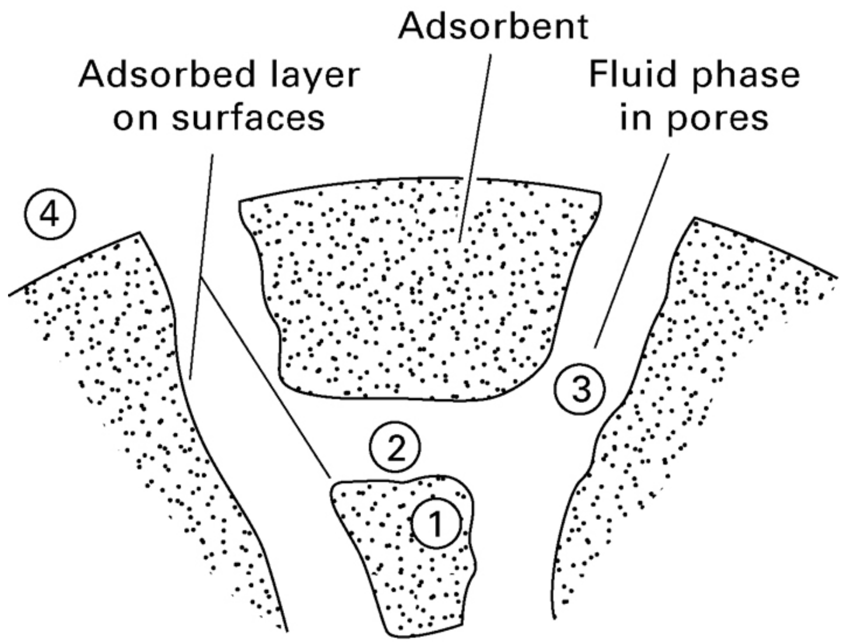
Lecture 18.
Adsorption, Ion Exchange, and Chromatography
[Ch. 15]

- Adsorption
- Ion-Exchange
- Chromatography
- Regeneration
- Sorbents
  - Adsorbents
  - Physisorption *vs.* chemisorption
  - Porosity

Adsorption

- The binding (attachment) of molecules or particles (from the gas or liquid phase) to a surface of a solid phase
- Molecules, atoms, or ions in a gas or liquid diffuse to the surface of a solid → bond with the solid surface or are held there by weak intermolecular forces

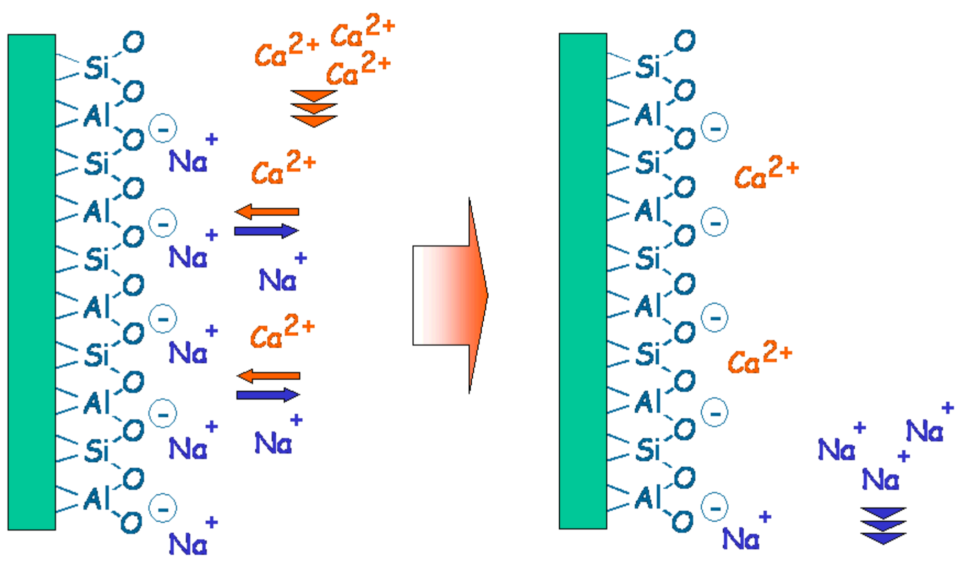


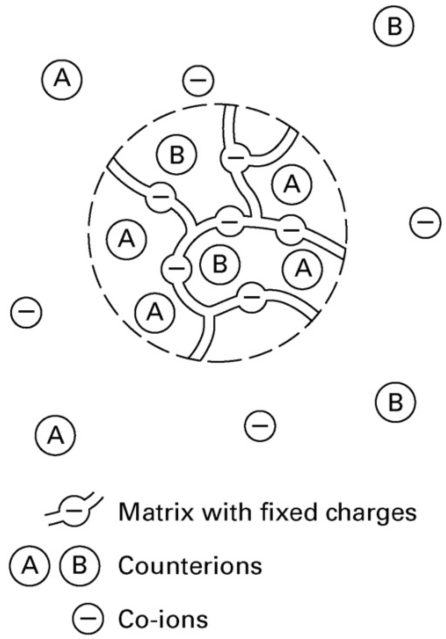


Ion–Exchange

- Ions of positive charge (cations) or negative charge (anions) in a liquid solution replace dissimilar and displaceable ions of the same charge contained in a solid ion exchanger
- Ion exchanger contains immobile, insoluble, and permanently bound co–ions of the opposite charge
- Water softening by ion exchange

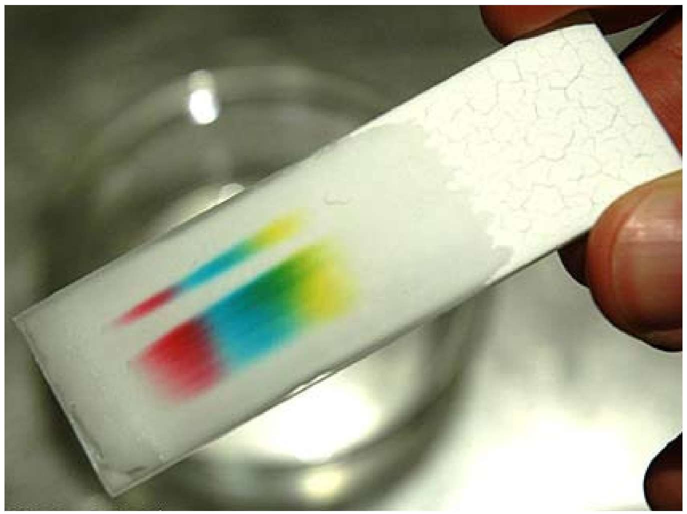
$$Ca^{2+}\ (aq) + 2NaR\ (s) \leftrightarrow CaR_2\ (s) + 2Na^{+}\ (aq)$$

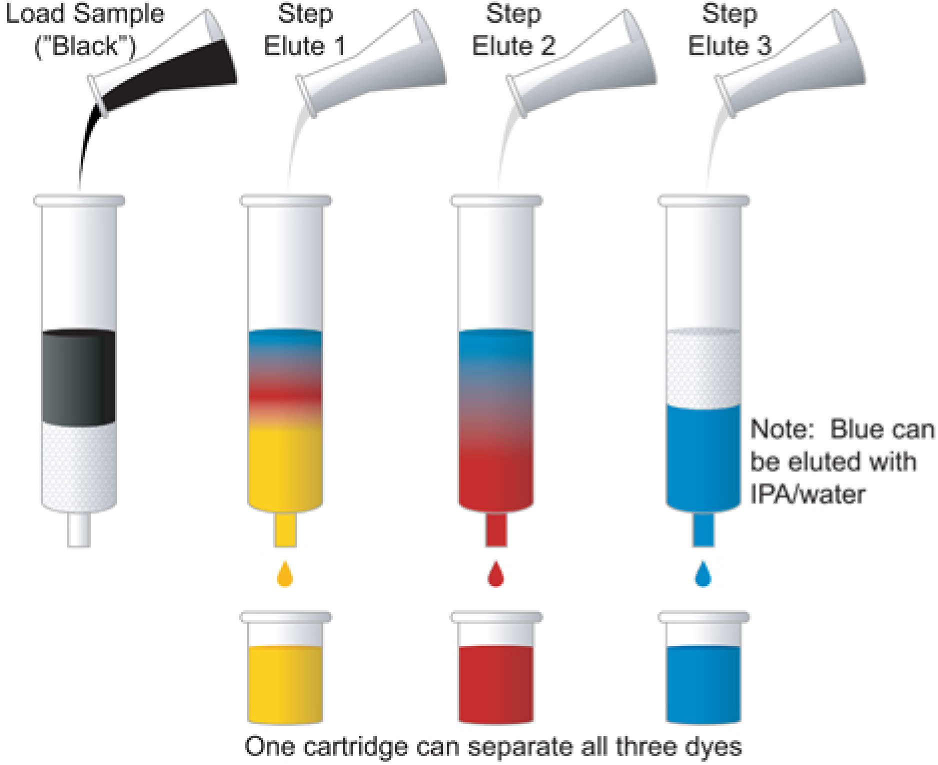




Chromatography

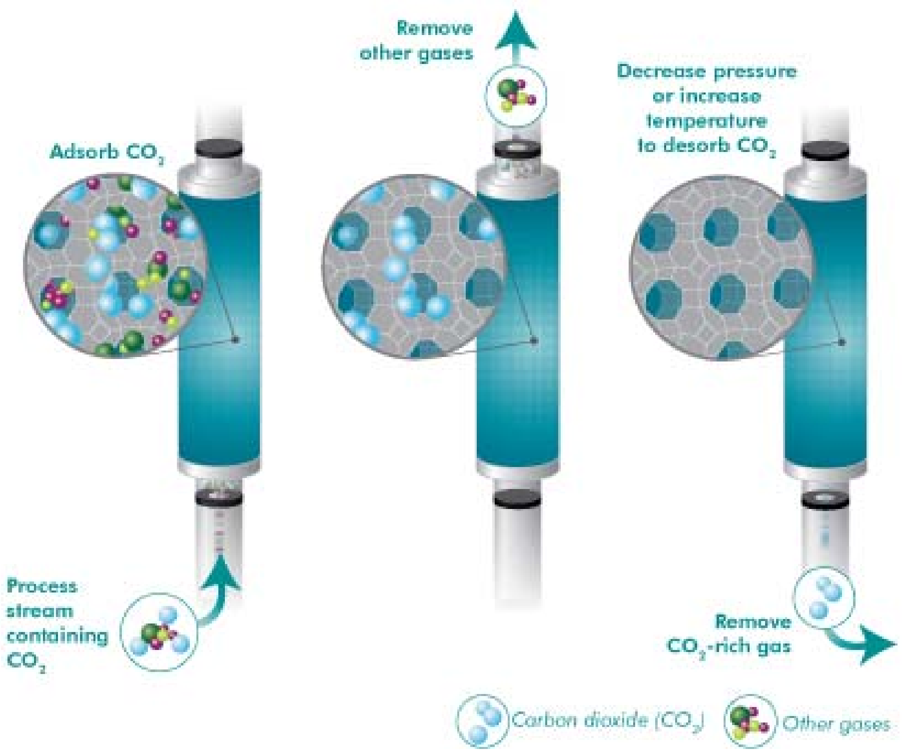
- The solutes move with an inert (eluting fluid) at different rates because of repeated sorption, desorption cycles
- The sorbent may be a solid adsorbent, an insoluble, nonvolatile, liquid absorbent contained in the pores of a granular solid support, or an ion exchanger





Regeneration

- Adsorption process: the sorbed substances are desorbed and recovered to reuse the adsorbent
- Ion-exchange process: replace ions using solutions (e.g. H_2SO_4 for cation, NaOH for anion resins)
- Chromatography: regeneration occurs continuously, but at changing locations



Sorbents

- Requirements for sorbents
  - High selectivity to enable sharp separations
  - High capacity to minimize the amount of sorbent needed
  - Favorable kinetic and transport properties for rapid sorption
  - Chemical and thermal stability
  - Hardness and mechanical strength to prevent crushing and erosion
  - Free-flowing tendency for ease of filling or emptying vessels
  - High resistance to fouling for long life
  - No tendency to promote undesirable chemical reactions
  - Capability of being regenerated
  - Low cost

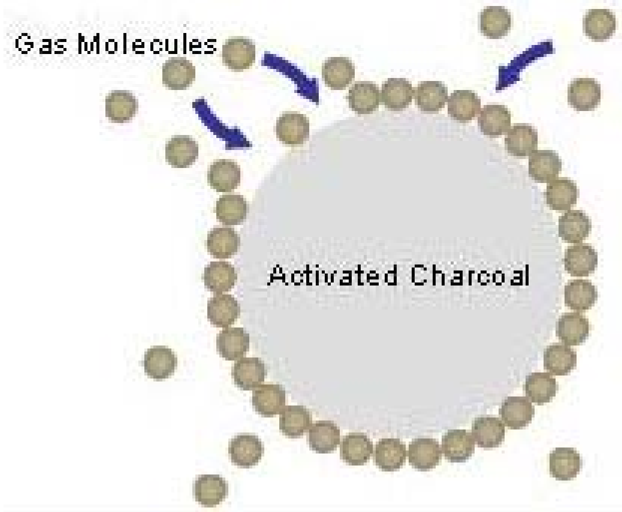
Adsorbents

- Commercial porous adsorbents

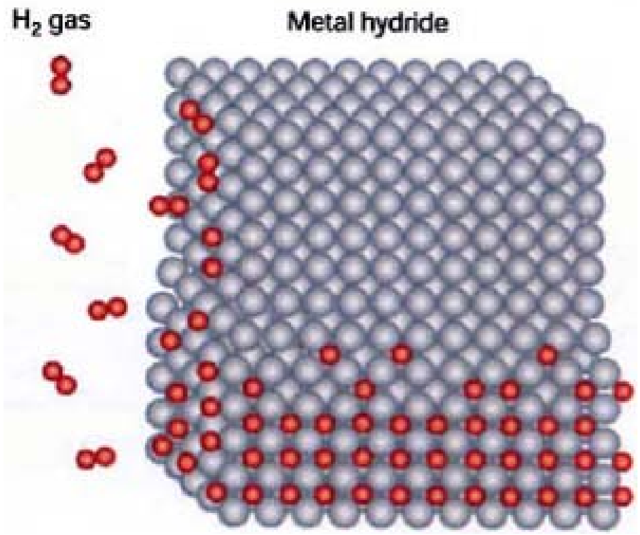
Adsorbent	Nature	Pore diameter d_p, Å	Surface area S_g, m^2/g
Activated alumina (Al_2O_3)	Great affinity for water	10–75	320
Silica gel (SiO_2) Small pore Large pore	High affinity for water and other polar compounds	 22–26 100–150	 750–850 300–350
Activated carbon Small pore Large pore	Hydrophobic (affinity for nonpolar and weakly polar compounds)	 10–25 >30	 400–1200 200–600
Molecular-sieve carbon	Hydrophobic	2–10	400
Molecular-sieve zeolites	Polar-hydrophilic, crystalline, highly selective $M_{x/m}[(AlO_2)_x(SiO_2)_y]zH_2O$	3–10	600–700

Physisorption *vs.* Chemisorption

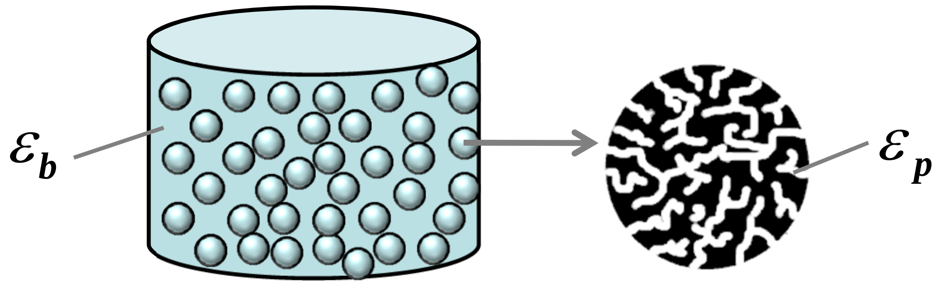
- Physisorption (physical adsorption)
  - Intermolecular attractive forces (van der Waals forces) between molecules of a solid and the gas are greater than those between molecules of the gas itself
  - The heat of adsorption is close to the heat of vaporization (in the region of 20 kJ/mol)



- Chemisorption (chemical adsorption)
  - Involves the formation of chemical bonds between the adsorbent and adsorbate in a monolayer
  - The heat of adsorption is much larger than the heat of vaporization (in the region of 200 kJ/mol)



Porosity



- Bed porosity (external porosity, interparticle porosity)

$$\varepsilon_b = \frac{\text{volume between particles}}{\text{volume of packed bed}} = 1 - \frac{\rho_b}{\rho_p}$$

- Particle porosity (intraparticle porosity)

$$\varepsilon_p = \frac{\text{volume of fluid inside particles}}{\text{volume of particles (solid + fluid)}} = 1 - \frac{\rho_p}{\rho_s}$$

- Specific pore volume $V_p = \varepsilon_p / \rho_p$
- Specific surface area $S_g = 4\varepsilon_p / \rho_p d_p$