

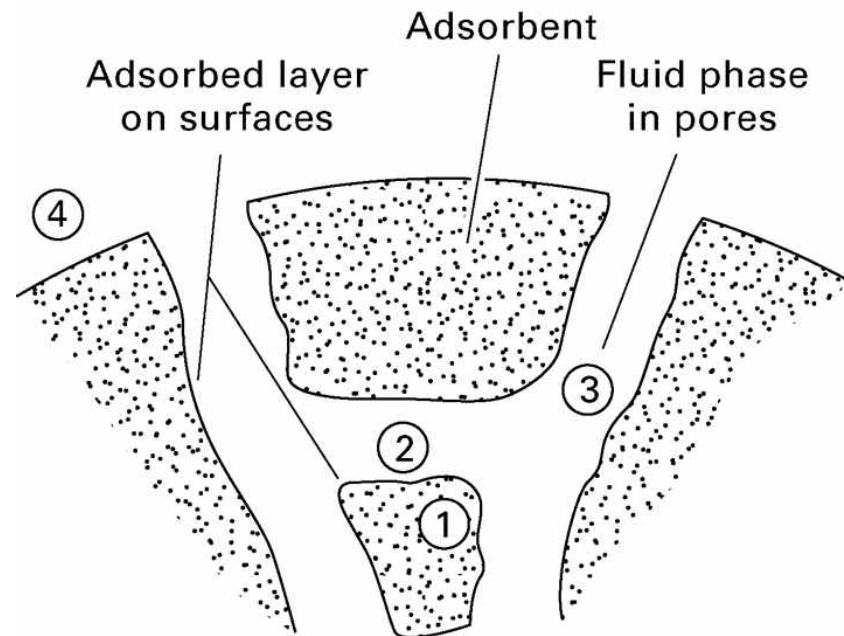
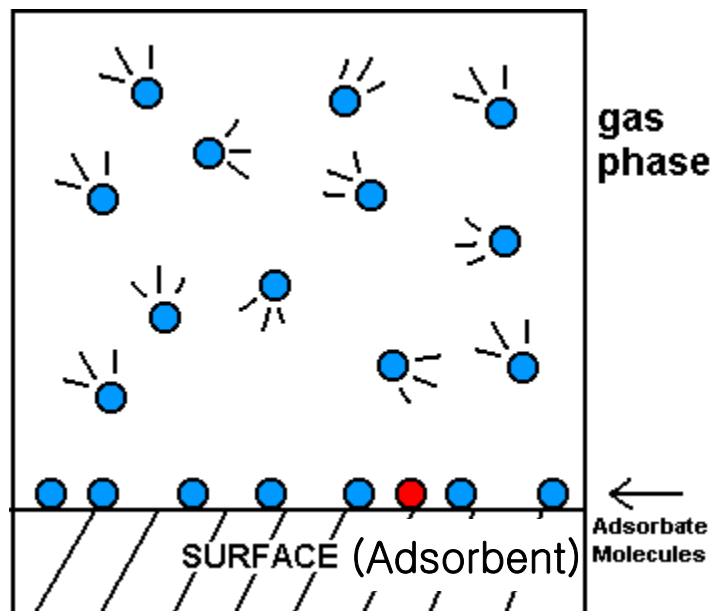
# Lecture 2.

## Sorption and Sorbents

- Sorption
  - Adsorption
  - Ion-exchange
  - Chromatography
- Regeneration
- Sorbents
  - Adsorbents
  - Ion exchangers
  - Sorbents for chromatography

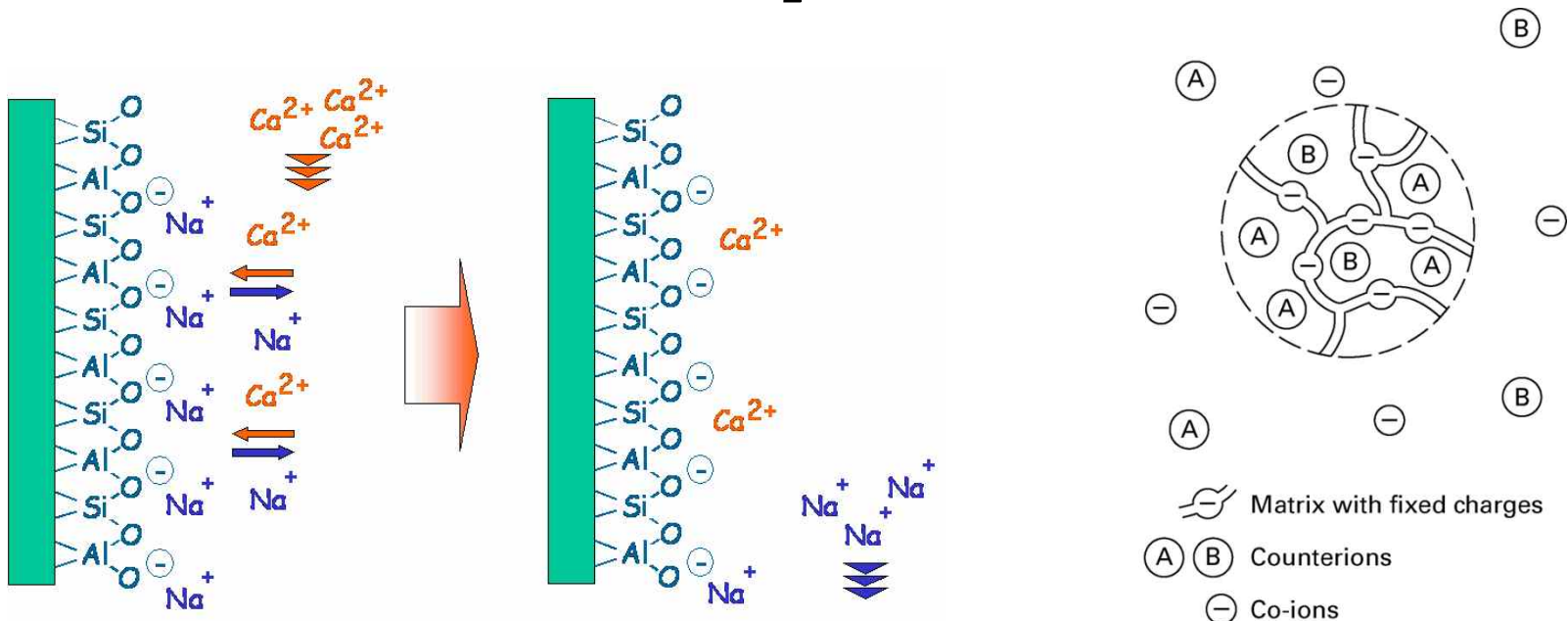
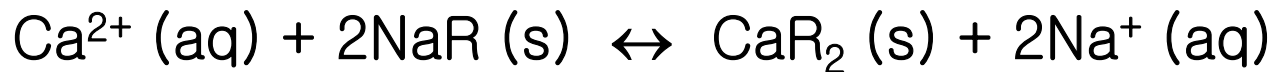
# Adsorption

- 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



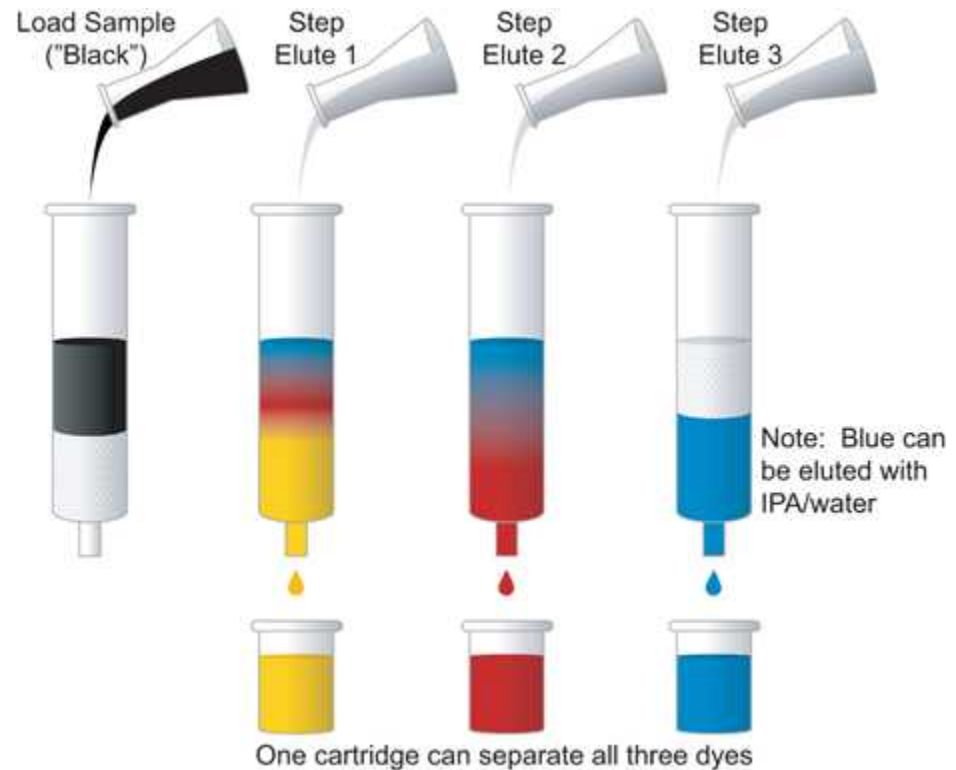
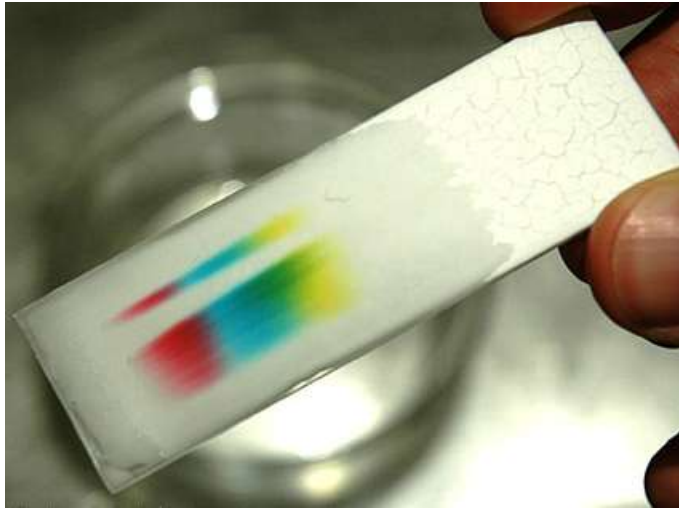
# Ion-Exchange

- 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



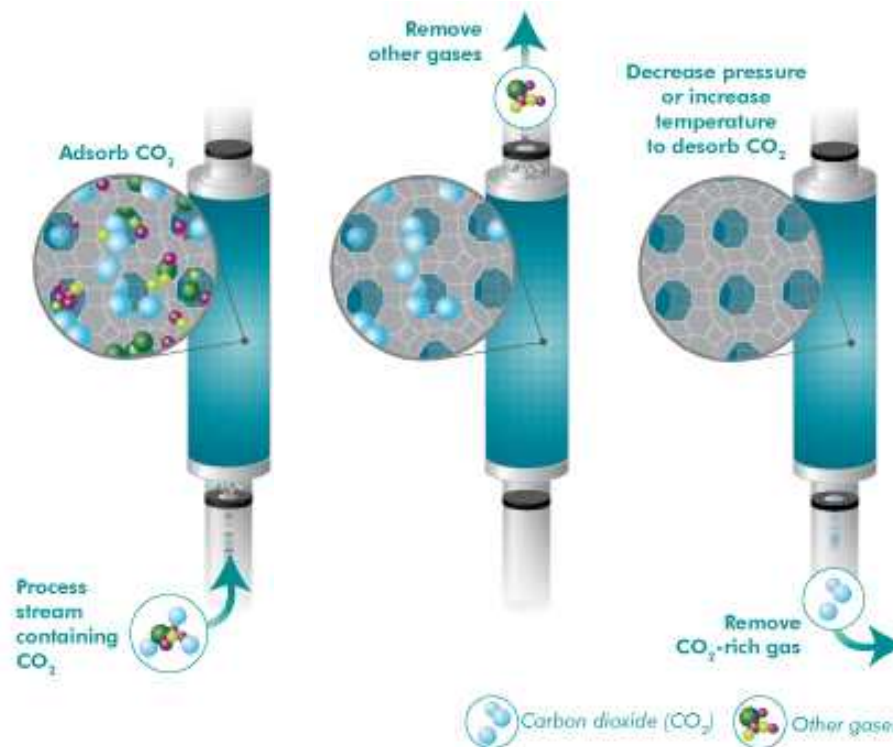
# Chromatography

- 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.  $\text{H}_2\text{SO}_4$  for cation,  $\text{NaOH}$  for anion resins)
- **Chromatography:** regeneration occurs continuously, but at changing locations



# Sorbents

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- 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

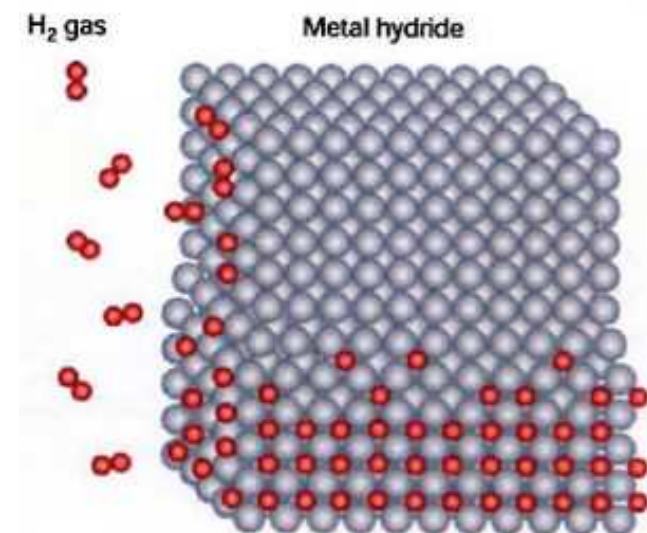
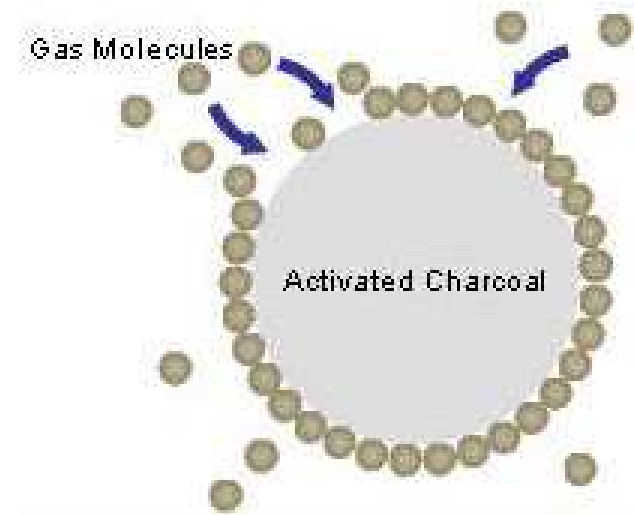
# Adsorbents

- Commercial porous adsorbents

Adsorbent	Nature	Pore diameter $d_p$ , Å	Surface area $S_g$ , m <sup>2</sup> /g
Activated alumina (Al <sub>2</sub> O <sub>3</sub> )	Great affinity for water	10–75	320
Silica gel (SiO <sub>2</sub> ) 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	<b>Hydrophobic</b> (affinity for nonpolar and weakly polar compounds)	10–25 >30	400–1200 200–600
Molecular-sieve carbon	<b>Hydrophobic</b>	<b>2–10</b>	400
Molecular-sieve zeolites	Polar-hydrophilic, crystalline, highly selective $M_{x/m}[(AlO_2)_x(SiO_2)_y]zH_2O$	<b>3–10</b>	600–700

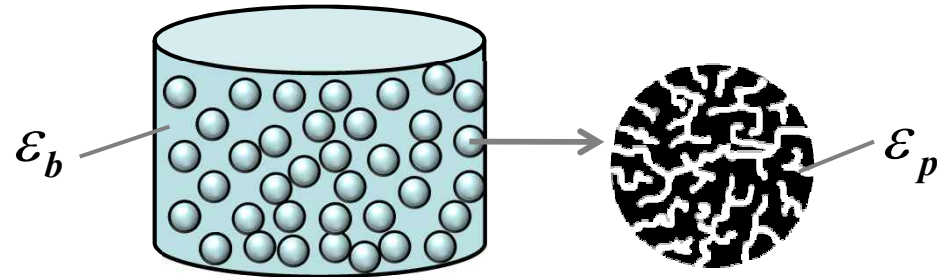
# Physisorption vs. Chemisorption

- **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  $S_g = 4\varepsilon_p / \rho_p d_p$

# Surface Area and BET Equations (1)

- BET (Brunauer, Emmett, and Teller) method
  - Specific surface area ( $S_g$ ) can be measured by adsorbing  $N_2$  gas
  - The BET apparatus operates at the normal boiling point of  $N_2$  (77 K)
  - Measuring the equilibrium volume of pure  $N_2$  physically adsorbed at different total pressures
- BET equation

$$\frac{P}{v(P_0 - P)} = \frac{1}{v_m c} + \frac{(c-1)}{v_m c} \left( \frac{P}{P_0} \right)$$

$P$  : total pressure

$P_0$  : vapor pressure of adsorbate

$v$  : volume of gas adsorbed at STP (0°C, 1 atm)

$v_m$  : volume of monomolecular layer of gas adsorbed at STP

$$\frac{P}{v(P_0 - P)} \text{ vs. } \left( \frac{P}{P_0} \right) \rightarrow v_m \text{ and } c$$

# Surface Area and BET Equations (2)

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$$S_g = \frac{\alpha v_m N_A}{V}$$

$N_A$  : Avogadro's number ( $6.023 \times 10^{23}$  molecules/mol)  
 $V$  : volume of gas per mole at STP (22.4 L/mol)  
 $\alpha$  : surface area per adsorbed molecule

$$\alpha = 1.091 \left( \frac{M}{N_A \rho_L} \right)^{2/3} \quad \text{for spherical molecules}$$

$M$  : molecular weight of the adsorbate  
 $\rho_L$  : density of the adsorbate in liquid at the test temperature (g/cm<sup>3</sup>)

- The BET surface area may not always represent the surface area available for adsorption
- The BET test is reproducible and widely used to characterize adsorbents

# Pore Volume

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- Specific pore volume

$$V'_p = \frac{(V_{\text{Hg}} - V_{\text{He}})}{m_p}$$

- Helium is not adsorbed but fills the pores
- At ambient pressure, mercury cannot enter the pore because of unfavorable interfacial tension and contact angle

- Particle density

$$\rho_p = \frac{m_p}{V_{\text{Hg}}}$$

- True solid density

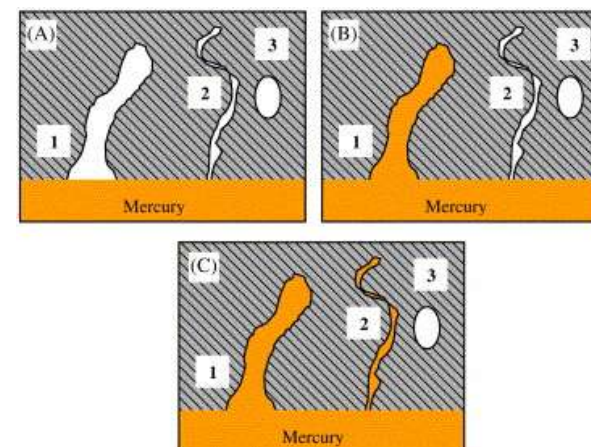
$$\rho_s = \frac{m_p}{V_{\text{He}}}$$

# Pore Volume Distribution

- Measurement of pore volume distribution

- Large-diameter pores (>100 Å): mercury porosimetry

- the extent of mercury penetration into the pores is measured as a function of applied hydrostatic pressure)



- Pores of 15–250 Å: gaseous nitrogen desorption

- an extension of the BET method
- at  $P/P_0 = 1$ , the entire pore volume is filled with nitrogen
- by reducing the pressure in steps, nitrogen is desorbed selectively, starting with larger pores
- Kelvin equation

$$P_p^s = P^s \exp\left(-\frac{4\sigma v_L \cos \theta}{RTd_p}\right)$$

$P_p^s$  : vapor pressure of liquid in pore  
 $P^s$  : normal vapor pressure of liquid on a flat surface  
 $\sigma$  : surface tension of liquid in pore  
 $v_L$  : molar volume of liquid in pore

- Pores of <15 Å: molecular sieving, using molecules of different size

# Adsorbents (1)

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- Activated alumina ( $\text{Al}_2\text{O}_3$ )
  - Made by removing water from hydrated colloidal alumina
  - Moderately high  $S_g$
  - The surface has a strong affinity for water: used for removal of water from gases and liquids
  - Not harmed by immersion in liquid water



- Silica gel ( $\text{SiO}_2$ )
  - Amorphous solid made from colloidal silica
  - High  $S_g$
  - High affinity for water and other polar compounds
  - Can be damaged by liquid water

# Adsorbents (2)

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- Activated carbon
  - Made by carbonizing coconut shells, fruit nuts, wood, coal, lignite, peat, petroleum residues, and bones → partially gasified in a mild oxidizing gas such as  $\text{CO}_2$  and steam (activation process: creates desired porosity and surface area, and oxidizes the surface)
  - Two commercial grade are available: one with large pores for processing liquids, one with small pores for gas adsorption
  - Large  $S_g$ , hydrophobic (nonpolar surface)
  - Used for purification and separation of gas and liquid mixtures containing nonpolar and weakly polar organic compounds
  - The bonding strength of adsorption on activated carbon is low → low heat of adsorption and ease of regeneration
- Molecular-sieve carbon
  - Pores ranging 2–10 Å
  - Used for separating  $\text{O}_2$  and  $\text{N}_2$  based on the different diffusion rates
  - Small pores can be made by depositing coke in the pore mouths of AC



# Adsorbents (3)

- Molecular-sieve zeolite
  - Crystalline, three-dimensional cage structure, inorganic polymers of aluminosilicates and alkali or alkali-earth elements (Na, K, and Ca)
  - Formula:  $M_{x/m}[(AlO_2)_x(SiO_2)_y] \cdot zH_2O$   
(M is the cation with valence m,  $y \geq x$ )
  - The cations balance the charge of the  $AlO_2$  groups (net charge of  $-1$ )
  - Types based on Si/Al ratio:  $\sim 1$  A type,  $1-1.5$  X type,  $1.5-3$  Y type
  - To activate zeolite, water molecules are removed
  - Highly selective due to the same size apertures ( $3.8-10 \text{ \AA}$ )
  - Separation by not only molecular size and shape but also polarity  $\rightarrow$  can separate molecules of similar size



Molecular Sieve Type A

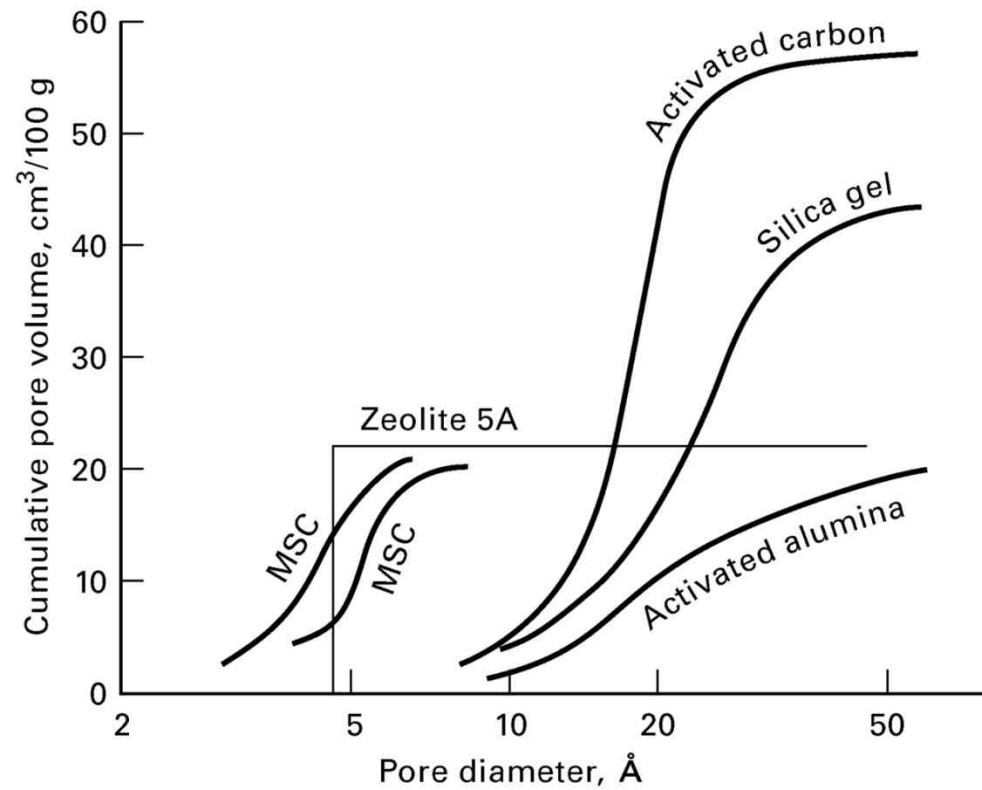


Molecular Sieve Type X



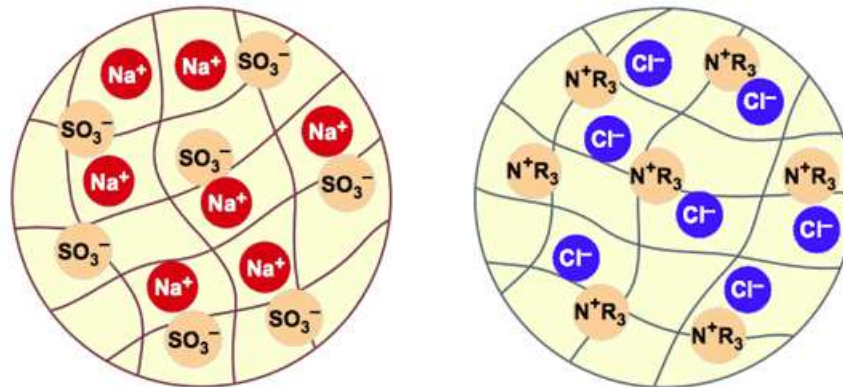
# Adsorbents (4)

- Cumulative pore-size distributions of adsorbents



# Ion Exchangers (1)

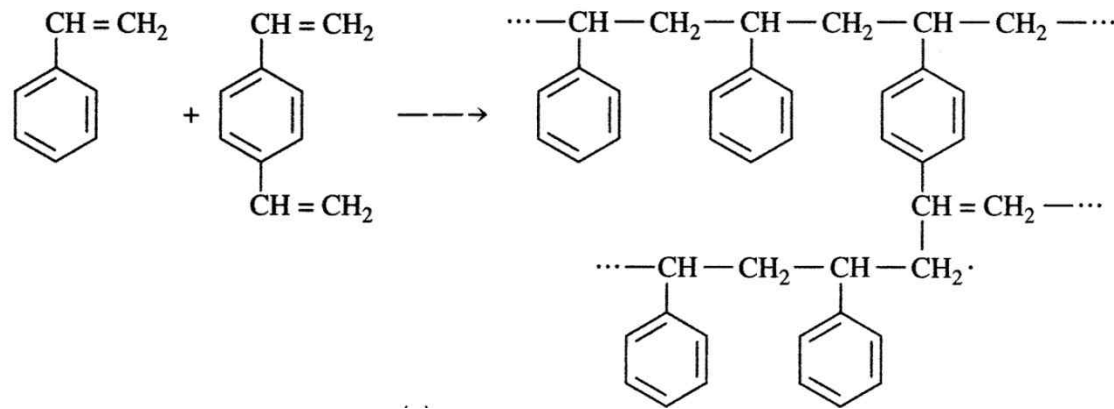
- About 1910, water softeners using zeolites were introduced
  - Unstable in the presence of mineral acids
- In 1935, organic-polymer ion-exchange resins were synthesized
  - Polycondensation of phenol and aldehydes
  - Resin contains either sulfonic ( $-\text{SO}_3^-$ ) or amine ( $-\text{NH}_3^+$ ) groups
- Today, synthetic, organic-polymer resins based on styrene- or acrylic-acid-type monomers are most widely used



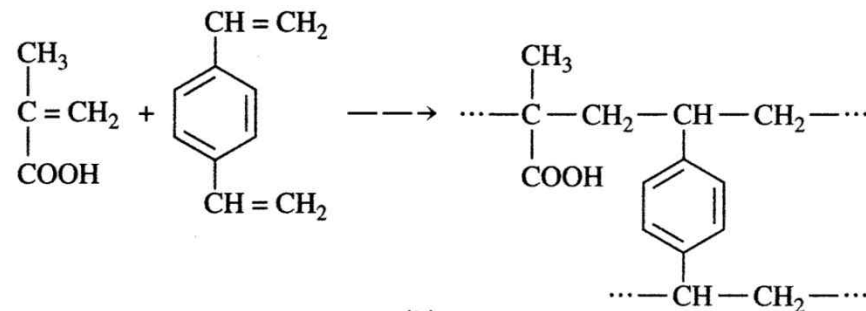
- Ion-exchange resins: generally solid gels in spherical or granular form, consisting of (1) a three-dimensional polymeric network, (2) ionic functional groups, (3) counterions, and (4) a solvent

# Ion Exchangers (2)

- Strong-acid, cation-exchange resins and strong-base, anion-exchange resins: based on the copolymerization of styrene and a cross-linking agent, divinylbenzene



- Weakly acid, cation exchangers: sometimes based on the copolymerization of acrylic acid and methacrylic acid





# Ion Exchangers (4)

- When saturated with water, ion exchange beads have typical moisture contents from 40 to 65 wt%
- Ion-exchange capacity
  - The maximum value is based on the number of equivalents of mobile charge in the resin
  - 1 mol H<sup>+</sup>: one equivalent, 1 mol Ca<sup>2+</sup>: two equivalents
  - Dry capacity (eq/kg) is fixed, wet capacity (eq/L) depends on water content and degree of swelling



[Example] A commercial ion-exchange resin is made from 88 wt% styrene and 12 wt% divinylbenzene. Estimate the maximum ion-exchange capacity in eq/kg resin.

	M	g	mol
Styrene	104.14	88	0.845
Divinylbenzene	130.18	12	0.092
Total		100	0.937

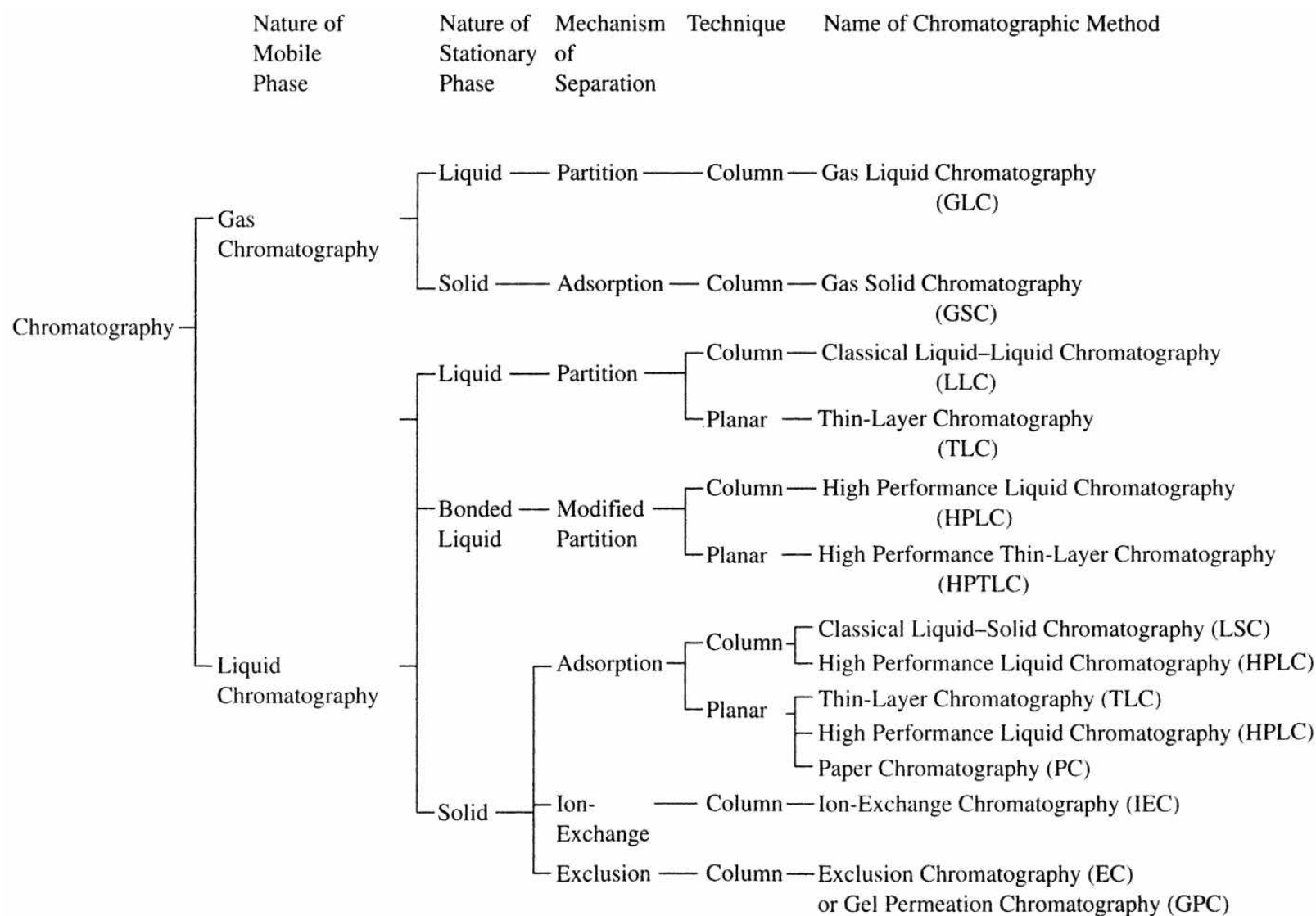
0.937 equivalent,  $0.937 \times 81.07 = 76 \text{ g}$

Sulfonation on each benzene requires 0.937 mol of H<sub>2</sub>SO<sub>4</sub>

→ a sulfonic acid group (M = 81.07) and one water molecule

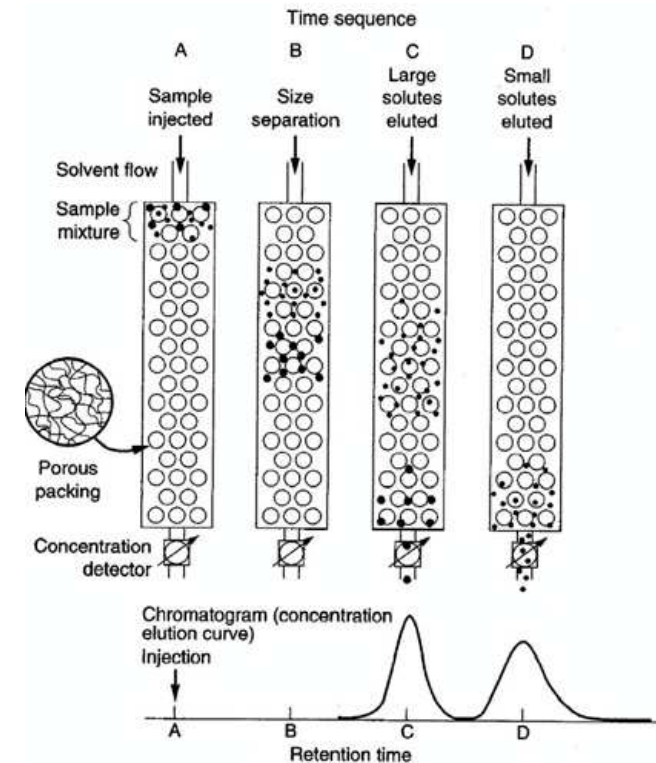
$0.937 / (100 + 76) \text{ g} = 5.3 \text{ eq/kg (dry)}$

# Classification of Analytical Chromatographic systems



# Chromatographic Separation

- Carrier fluid: mobile phase
  - Gas chromatography: gas carriers are inert and do not interact
  - Liquid chromatography: liquid carriers (solvents) can interact
- Sorbent: stationary phase
  - A solid, a liquid supported on or bonded to a solid, or a gel
- Mechanisms of chromatographic separation
  - Adsorption
  - Ion-exchange
  - Exclusion (sieving)
  - Absorption (partition chromatography)



# Sorbents for Chromatography (1)

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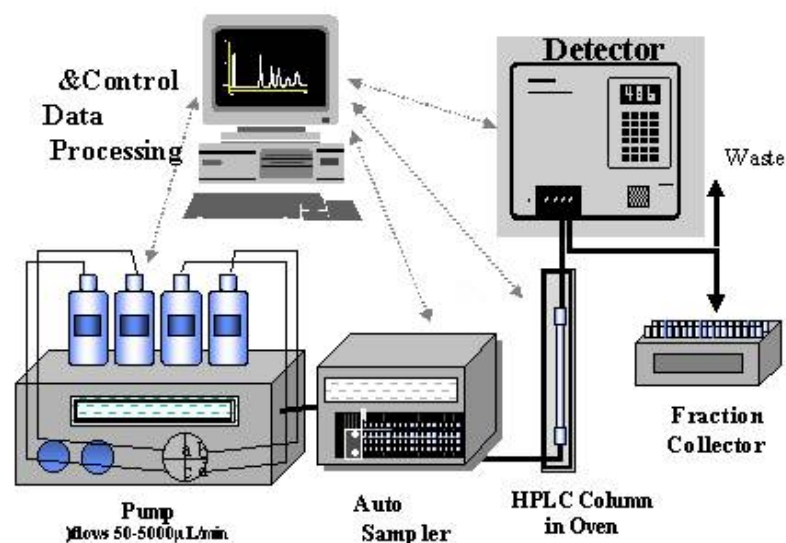
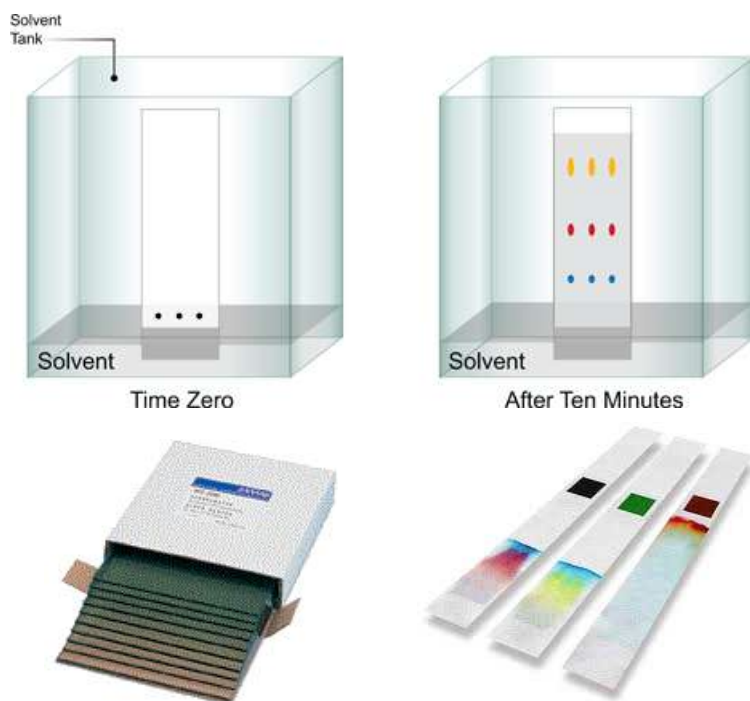
- Chromatographic column
  - Packed column (>1 mm inside diameter): particle type sorbents
  - Capillary column (<0.5 mm inside diameter): sorbent is the inside wall or a coating on the wall
    - Wall-coated, open-tubular (WCOT): coated capillary column
    - Support-coated, open-tubular (SCOT): the coating is a layer of fine particulate support material
    - Porous-layer, open-tubular (PLOT): the wall is coated with a porous adsorbent only





# Sorbents for Chromatography (2)

- Type of chromatography
  - Thin-layer (planar) chromatography: sheets of glass, plastic, or aluminum for sorbent
  - Paper chromatography: a sheet of cellulose material for sorbent
  - High-performance liquid chromatography (HPLC): a pump, rather than gravity, is used to pass a liquid mobile phase



# Sorbents for Chromatography (3)

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- Adsorbents used in chromatography
  - Porous alumina: polar adsorbent, preferred for the separation of components that are weakly or moderately polar, with more polar compounds; basic adsorbent, preferentially retaining acidic compounds
  - Porous silica gel: less polar than alumina; acidic adsorbent, preferentially retaining basic compounds
  - Carbon: nonpolar (apolar), highest attraction for nonpolar molecules
- Liquid chromatography
  - Normal-phase chromatography: stationary phase is more polar than the mobile phase
  - Reverse-phase chromatography (hydrophobic chromatography)
  - The order of elution of solutes can be influenced by the solvent carrier by matching the solvent polarity with the solutes and using more-polar adsorbents for less-polar solutes and less-polar adsorbents for more-polar solutes