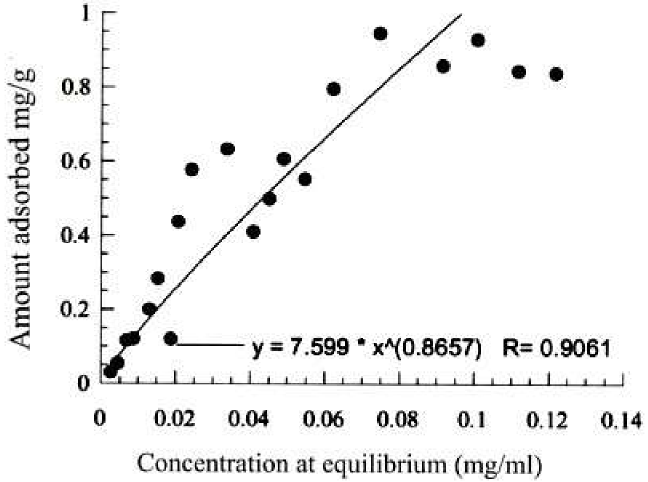
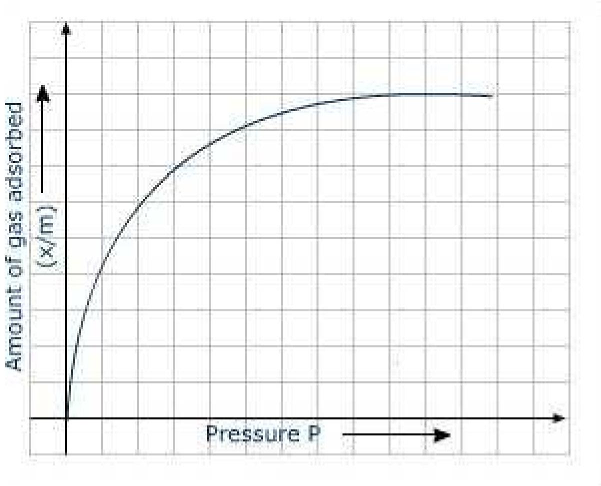
Lecture 3.
Sorption Equilibrium

- Pure Gas Adsorption
  - Linear isotherm
  - Freundlich isotherm
  - Langmuir isotherm
  - Other adsorption isotherms
  - BET isotherm
- Gas Mixtures and Extended Isotherms
- Liquid Adsorption
- Ion-Exchange Equilibria

Adsorption Equilibrium

- Dynamic equilibrium in adsorption: solute distribution between fluid and solid surface
  - [concentration (if the fluid is a liquid) or partial pressure (if the fluid is a gas) of the adsorbate in the fluid] vs. [solute loading on the adsorbent (mass, moles, or volume of adsorbate per unit mass or surface area)]

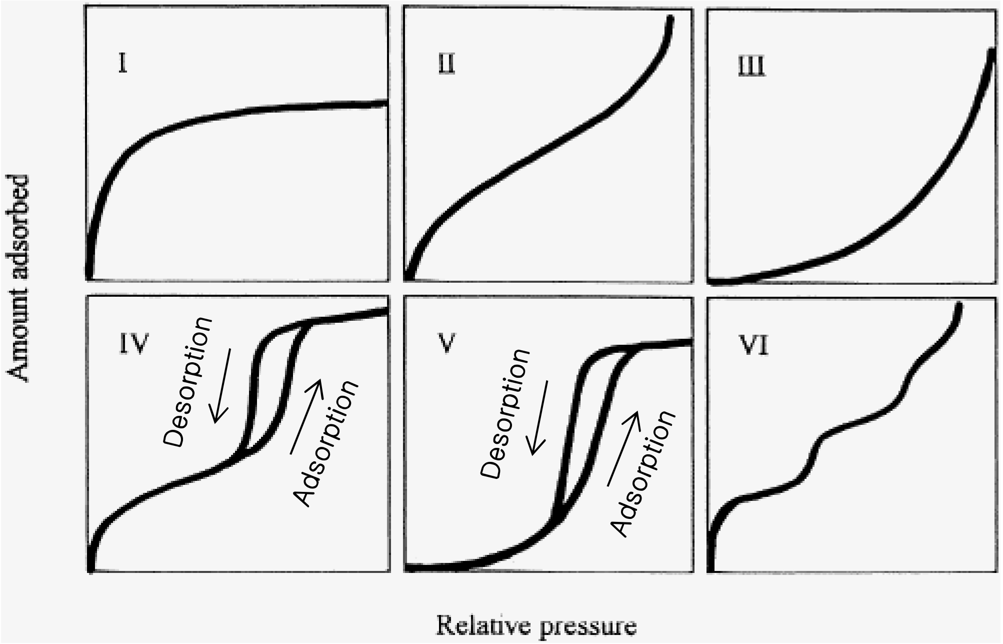




- Adsorption isotherm: equilibrium data at a constant temperature
  - A limit on the extent to which a solute is adsorbed from a specific fluid mixture on a given adsorbent for one set of conditions

Classification of Adsorption Isotherms (1)

Standard classification developed by IUPAC



- Type I isotherm
  - – Typical of adsorbents with a predominantly microporous structure
  - – Corresponds to unimolecular adsorption
  - – Maximum limit in the amount adsorbed
  - – Gases at temperatures above their critical temperature
  - – Example: nitrogen on carbon at 77K and ammonia on charcoal at 273K

Classification of Adsorption Isotherms (2)

- Type II isotherm
  - Physical adsorption of gases by non-porous solids
  - Corresponds to multimolecular BET adsorption (monolayer coverage followed by multilayering at high relative pressures)
  - Gases at temperatures below their critical temperature and pressures below, but approaching, the saturation pressure
  - The heat of adsorption for the first adsorbed layer is greater than that for the succeeding layers
  - Example: carbons with mixed micro- and meso-porosity
- Type III isotherm
  - Convex and undesirable (extent of adsorption is low except at high P)
  - Characteristic of weak adsorbate-adsorbent interactions
  - Corresponds to multimolecular adsorption
  - The heat of adsorption of the first adsorbed layer is less than that of succeeding layers
  - Example: adsorption of iodine vapor on silica gel

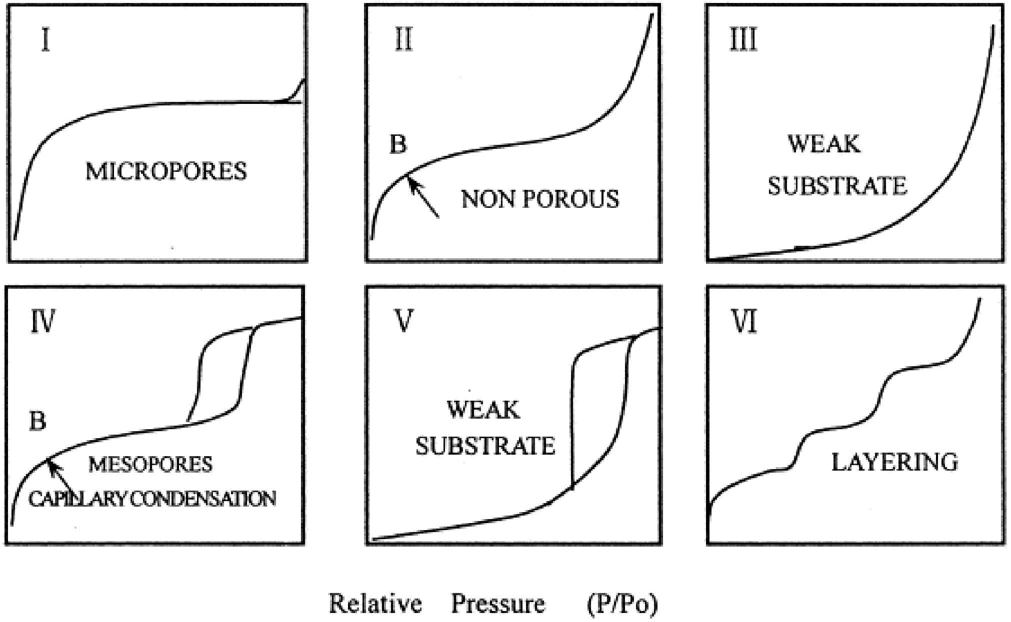
Classification of Adsorption Isotherms (3)

- Type IV isotherm
  - The maximum extent of adsorption occurs before the saturation pressure is reached
  - A hysteresis loop, which is commonly associated with the presence of mesoporosity
  - Capillary condensation gives rise to a hysteresis loop

- Type V isotherm
  - Convex to the relative pressure axis
  - Characteristic of weak adsorbate-adsorbent interactions at low relative pressures
  - Microporous or mesoporous solids
  - Hysteresis in multimolecular adsorption regions
  - Capillary condensation version of Type III

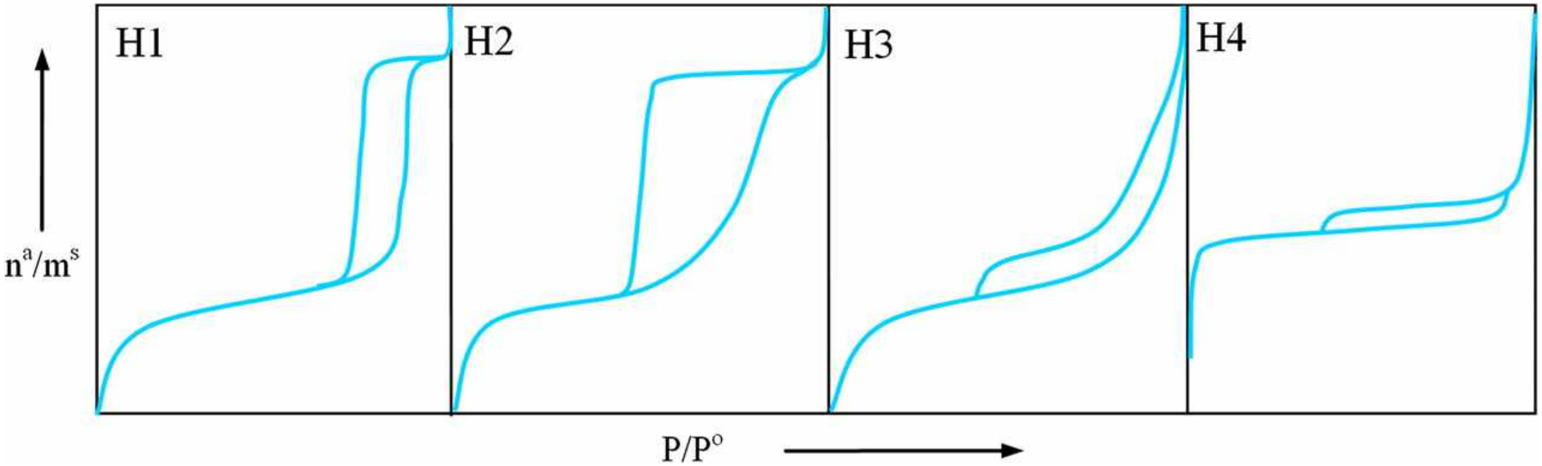
Classification of Adsorption Isotherms (4)

- Type VI isotherm
  - Complete formation of monomolecular layers before progression to a subsequent layer
  - Adsorption on extremely homogeneous, non-porous surfaces where the monolayer capacity corresponds to the step height
  - Example: adsorption of krypton on carbon black at 90 K



Classification of Adsorption Isotherms (5)

- Hysteresis loop
  - Occurs due to capillary condensation (gas adsorption in the pores at a low density → after a sufficient amount of gas has been supplied, it spontaneously condenses into a liquid-like state inside the pores)
  - Change of geometry during adsorption and desorption process



channels with uniform sizes and shapes

channels with a pore mouth smaller than pore body (ink-bottle-shaped pores)

solids with a very wide distribution of pore size

limited amounts of mesopores limited by micropores

Pure–Gas Adsorption

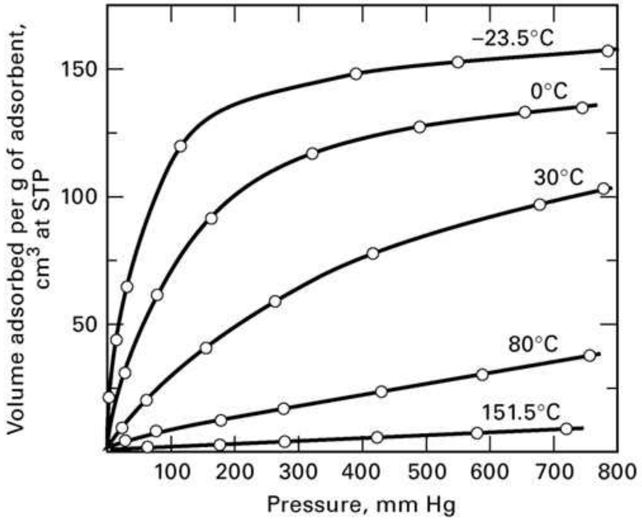
- Linear isotherm: a form of Henry's law

$$q = kp$$

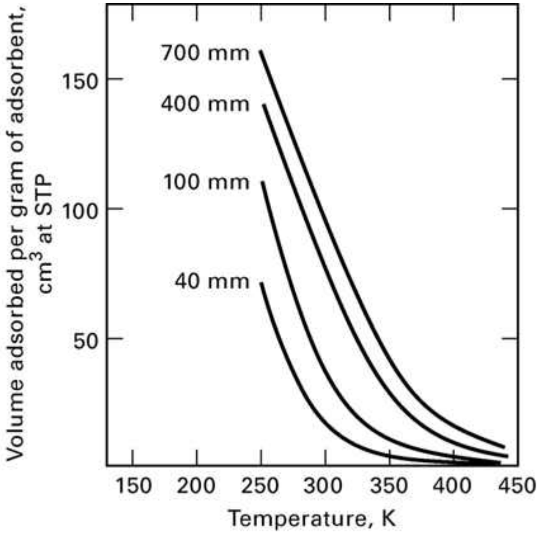
q : equilibrium loading
k : empirical, temperature–dependent constant for the component
p : partial pressure of the species

- As temperature increases, the amount adsorbed decreases because of Le Chatelier's principle for an exothermic process

Adsorption isotherms

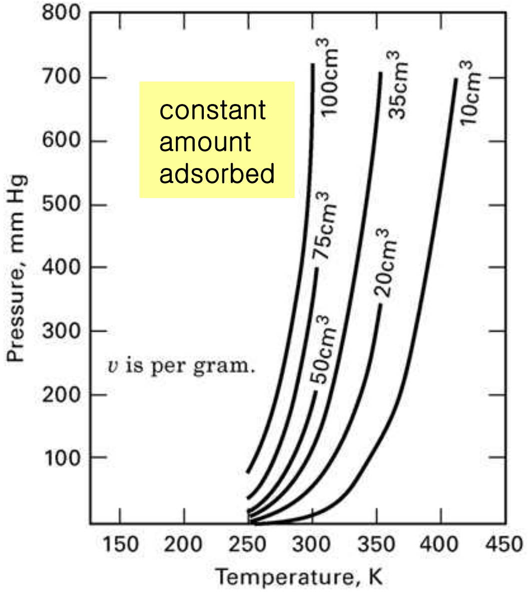


Adsorption isobars

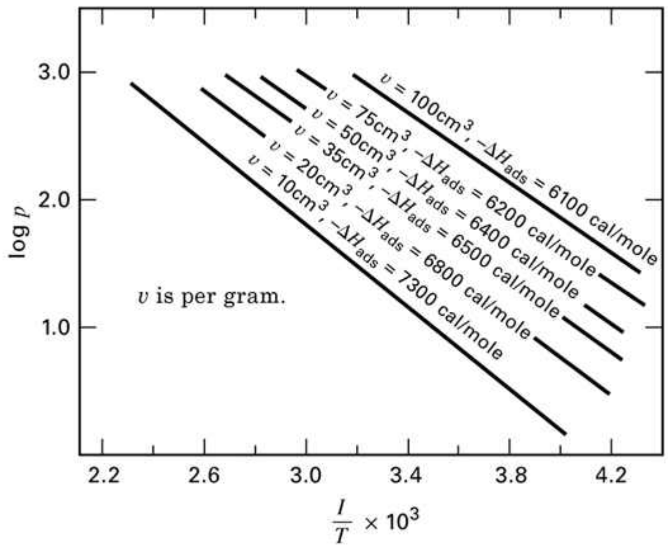


Isosteric Heat of Adsorption

Adsorption isosteres


constant amount adsorbed

Isosteric heats of adsorption



- Clausius–Clapeyron equation

$$\frac{d \ln p}{dT} = \frac{-\Delta H_{ads}}{RT^2} \qquad \frac{d \log p}{d(1/T)} = \frac{-\Delta H_{ads}}{2.303RT}$$

[Adsorption of NH_3 on charcoal]

$-\Delta H_{ads}$ is initially 7,300 cal/mol → 6,100 cal/mol at 100 cm^3/g

Heat of vaporization of HN_3 at 30°C: 4,600 cal/mol

Freundlich Isotherm

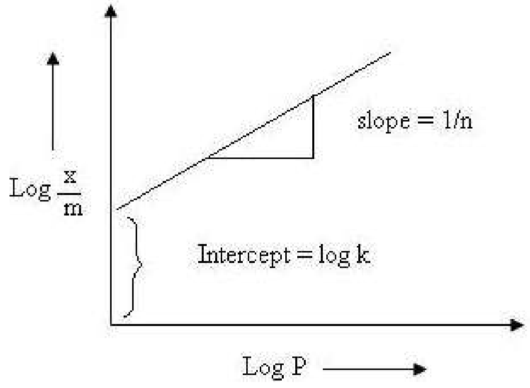
- Freundlich isotherm: empirical and nonlinear in pressure (Type I)

$$q = kp^{1/n}$$

  - k and n are temperature-dependent constants
  - n lies in the range of 1 to 5
  - In general, with T ↑ n ↑ but k ↓, approaching a value of 1 at high T
  - Can be derived by assuming a heterogeneous surface with a nonuniform distribution of heat of adsorption

- Fitting of experimental data to the Freundlich equation
  - By a nonlinear curve fit
  - By plotting log *q* vs. log *p* for the linear form

$$\log q = \log k + (1/n)\log p$$



Langmuir Isotherm (1)

- Basis of Langmuir equation
  - From mass-action kinetics, assuming chemisorption
  - The surface of adsorbent pores is homogeneous (ΔH_{ads} = constant)
  - Negligible interaction forces between adsorbed molecules

θ : fraction of surface covered by adsorbed molecules

$1 - \theta$: fraction of bare surface

- Net rate of adsorption

$$dq/dt = k_a p(1-\theta) - k_d\theta$$

k_a : adsorption kinetic constant

k_d : desorption kinetic constant

At equilibrium, dq/dt = 0

$$\theta = \frac{(k_a/k_d)p}{1+(k_a/k_d)p} = \frac{Kp}{1+Kp}$$

K : adsorption-equilibrium constant

$$\theta = q/q_m$$

q_m : maximum loading corresponding to complete surface coverage

Langmuir Isotherm (2)

Langmuir adsorption isotherm is restricted to a monomolecular layer

$$q = \frac{Kq_m p}{1 + Kp}$$

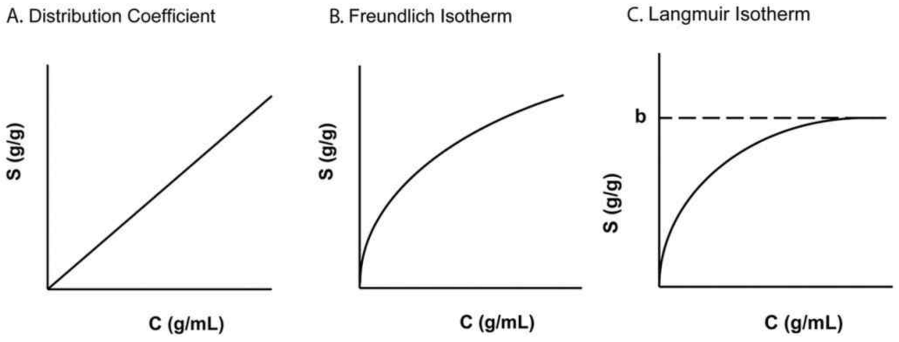
At low pressures ($Kp \ll 1$), $q=Kq_m p$ (linear isotherm)

At high pressures ($Kp \gg 1$), $q=q_m$

Although originally Langmuir adsorption isotherm is devised for chemisorption, it is widely applied to physical-adsorption data.

- Fitting of experimental data to the Langmuir equation
  - By a nonlinear curve fit
  - By plotting p/q vs. p for the linear form

$$\frac{p}{q} = \frac{1}{q_m K} + \frac{p}{q_m}$$



- Theoretically, K should change rapidly with T but q_m should not

Other Adsorption Isotherms

- Toth isotherm

$$q = \frac{mp}{\left(b + p^t\right)^{1/t}}$$

  - m, b, and t are constants for a given adsorbate-adsorbent and T
  - Obeys Henry's law at low P and reaches a maximum at high P
  - Reduce to the Langmuir isotherm for t = 1

- UNILAN isotherm

$$q = \frac{n}{2s} \ln\left[\frac{c + pe^{s}}{c + pe^{-s}}\right]$$

  - n, s, and c are constants for a given adsorbate-adsorbent and T
  - Based on a model of heterogeneous surfaces assuming a uniform distribution of adsorption energy
  - Reduce to the Langmuir isotherm for s = 0

BET Isotherm (1)

- BET theory: physical adsorption of gas molecules on a solid surface to form multilayer
- Number of adsorbed molecules

$$N = N_{\text{sites}}(\theta_1 + 2\theta_2 + 3\theta_3 + \cdots)$$

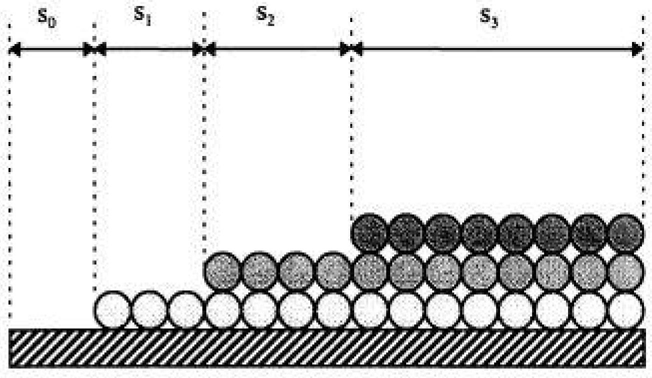
N_{sites} : total number of sites
θ_0 : fraction of surface sites unoccupied
θ_1 : fraction of surface sites covered by a monolayer
θ_2 : fraction of surface sites covered by a bilayer

- First layer

Rate of adsorption = $N k_{a,0} p \theta_0$

Rate of desorption = $N k_{d,0} \theta_1$

At equilibrium, $k_{a,0} p \theta_0 = k_{d,0} \theta_1$



BET Isotherm (2)

- Second layer

Rate of adsorption = $Nk_{a,1}p\theta_1$

Rate of desorption = $Nk_{d,1}\theta_2$

At equilibrium, $k_{a,1}p\theta_1 = k_{d,1}\theta_2$

- Third layer

Rate of adsorption = $Nk_{a,2}p\theta_2$

Rate of desorption = $Nk_{d,2}\theta_3$

At equilibrium, $k_{a,2}p\theta_2 = k_{d,2}\theta_3$

$$\vdots$$

Once a monolayer has been formed, all the rate constants involving adsorption and desorption from the physisorbed layers are assumed to be the same.

$$\begin{aligned}
k_{a,0}p\theta_0 = k_{d,0}\theta_1 \quad &\rightarrow \quad \theta_1 = (k_{a,0}/k_{d,0})\,p\theta_0 = K_0 p\theta_0 \\
k_{a,1}p\theta_1 = k_{d,1}\theta_2 \quad &\rightarrow \quad \theta_2 = (k_{a,1}/k_{d,1})\,p\theta_1 = (k_{a,0}/k_{d,0})(k_{a,1}/k_{d,1})\,p^2\theta_0 \\
&\qquad = K_0 K_1 p^2\theta_0 \\
k_{a,2}p\theta_2 = k_{d,2}\theta_3 \quad &\rightarrow \quad \theta_3 = (k_{a,2}/k_{d,2})\,p\theta_2 = (k_{a,0}/k_{d,0})(k_{a,1}/k_{d,1})^2\,p^3\theta_0 \\
&\qquad = K_0 K_1^2 p^3\theta_0
\end{aligned}$$

BET Isotherm (3)

Because $\theta_0 + \theta_1 + \theta_2 + \theta_3 + \cdots = \mathbf{1}$

$$1 = \theta_0 + \boldsymbol{K_0 p}\theta_0 + \boldsymbol{K_0 K_1 p^2}\theta_0 + \boldsymbol{K_0 K_1^2 p^3}\theta_0 + \cdots$$

$$= \theta_0 + \boldsymbol{K_0 p}\theta_0 \left\{\mathbf{1} + \boldsymbol{K_1 p} + \boldsymbol{K_1^2 p^2} + \cdots\right\}$$

$$= \left\{1 + \frac{\boldsymbol{K_0 p}}{\mathbf{1} - \boldsymbol{K_1 p}}\right\}\theta_0 = \left\{\frac{\mathbf{1} - \boldsymbol{K_1 p} + \boldsymbol{K_0 p}}{\mathbf{1} - \boldsymbol{K_1 p}}\right\}\theta_0$$

$$\theta_0 = \frac{\mathbf{1} - \boldsymbol{K_1 p}}{\mathbf{1} - \left(\boldsymbol{K_1} - \boldsymbol{K_0}\right)\boldsymbol{p}}$$

- Number of adsorbed species

$$N = N_{\mathbf{sites}}\boldsymbol{K_0 p}\theta_0 + \mathbf{2}N_{\mathbf{sites}}\boldsymbol{K_0 K_1 p^2}\theta_0 + \cdots$$

$$= N_{\mathbf{sites}}\boldsymbol{K_0 p}\theta_0\left(\mathbf{1} + \mathbf{2}\boldsymbol{K_1 p} + \mathbf{3}\boldsymbol{K_1^2 p^2} + \cdots\right)$$

$$= \frac{N_{\mathbf{sites}}\boldsymbol{K_0 p}\theta_0}{\left(\mathbf{1} - \boldsymbol{K_1 p}\right)^{\mathbf{2}}}$$

BET Isotherm (4)

$$N = \frac{N_{\text{sites}} K_0 p}{\left(1 - K_1 p\right)^2} \times \frac{1 - K_1 p}{1 - \left(K_1 - K_0\right) p}$$

$$= \frac{N_{\text{sites}} K_0 p}{\left(1 - K_1 p\right)\left\{1 - \left(K_1 - K_0\right) p\right\}}$$

The ratio N/N_{sites} is equal to the ratio v/v_{mon}

v : total volume adsorbed
v_{mon} : volume adsorbed for complete monolayer coverage

K_1 is the equilibrium constant for the reaction in which the reactant is a molecule physisorbed and the product is the molecule in the vapor.

$K = 1/P_0$ P_0 : vapor pressure of the liquid

$$\frac{v}{v_{\text{mon}}} = \frac{K_0 P}{\left(1 - P/P_0\right)\left\{1 - \left(1 - K_0/K_1\right) P/P_0\right\}}$$

Gas Mixtures and Extended Isotherms (1)

- One component can increase, decrease, or have no influence on adsorption of another, depending on interactions of adsorbed molecules.
- Data for binary and multi-component gas-solid adsorbent equilibria are scarce and less accurate than corresponding pure-gas data.
- Extended Langmuir isotherm
  - Neglect interactions
  - Assume the only effect is the reduction of the vacant surface area
  - For a binary gas mixture of A and B

θ_A : fraction of surface covered by A
θ_B : fraction of surface covered by B
$1 - \theta_A - \theta_B$: fraction of vacant surface

$$(k_A)_a p_A (1-\theta_A-\theta_B) = (k_A)_d \theta_A$$

$$(k_B)_a p_B (1-\theta_A-\theta_B) = (k_B)_d \theta_B$$

$$\theta_i = q_i/(q_i)_m$$

$(q_i)_m$: maximum amount of adsorption of species *i* for coverage of the entire surface

Gas Mixtures and Extended Isotherms (2)

$$q_{\mathrm{A}} = \frac{(q_{\mathrm{A}})_m K_{\mathrm{A}} p_{\mathrm{A}}}{1 + K_{\mathrm{A}} p_{\mathrm{A}} + K_{\mathrm{B}} p_{\mathrm{B}}} \qquad q_{\mathrm{B}} = \frac{(q_{\mathrm{B}})_m K_{\mathrm{B}} p_{\mathrm{B}}}{1 + K_{\mathrm{A}} p_{\mathrm{A}} + K_{\mathrm{B}} p_{\mathrm{B}}}$$

- For a mixture of *j* components

$$q_i = \frac{(q_i)_m K_i p_i}{1 + \sum_j K_j p_j}$$

- Extended Langmuir-Freundlich equation

$$q_i = \frac{(q_i)_0 k_i p_i^{1/n_i}}{1 + \sum_j k_j p_j^{1/n_j}}$$

Represents data for nonpolar, multicomponent mixtures in molecular sieves reasonably well

- Separation factor (selectivity)

$$\alpha_{i,j} = \frac{q_i / q_j}{p_i / p_j} = \frac{(q_i)_m K_i}{(q_j)_m K_j}$$

Liquid Adsorption (1)

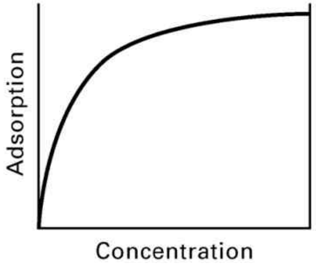
- Assumptions in a homogeneous binary liquid mixture adsorption
  - The composition change of the bulk liquid in contact with the porous solid is due entirely to adsorption of the solute
  - Solvent adsorption does not occur
- From a solute material balance

$$q_1^e = \frac{n^0(x_1^0 - x_1)}{m}$$

Assuming negligible change in the total moles of liquid mixture

n^0 : total moles of binary liquid contacting the adsorbent
m : mass of adsorbent
$x_1{}^0$: mole fraction of solute before contact with adsorbent
x_1 : mole fraction of solute after adsorption equilibrium is achieved
$q_1{}^e$: apparent moles of solute adsorbed per unit mass of adsorbent

- Isotherms in the dilute region
  - Solvent adsorption, if any, may be constant
  - All changes in total amount adsorbed are due to solute

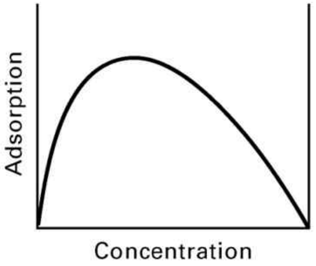


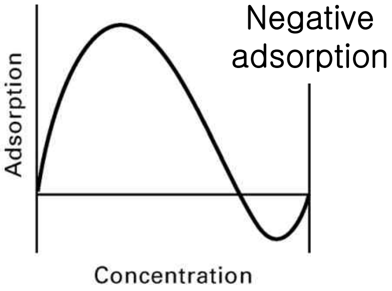
$$q = kc^{1/n}$$

$$q = \frac{Kq_m c}{1 + Kc}$$

Liquid Adsorption (2)

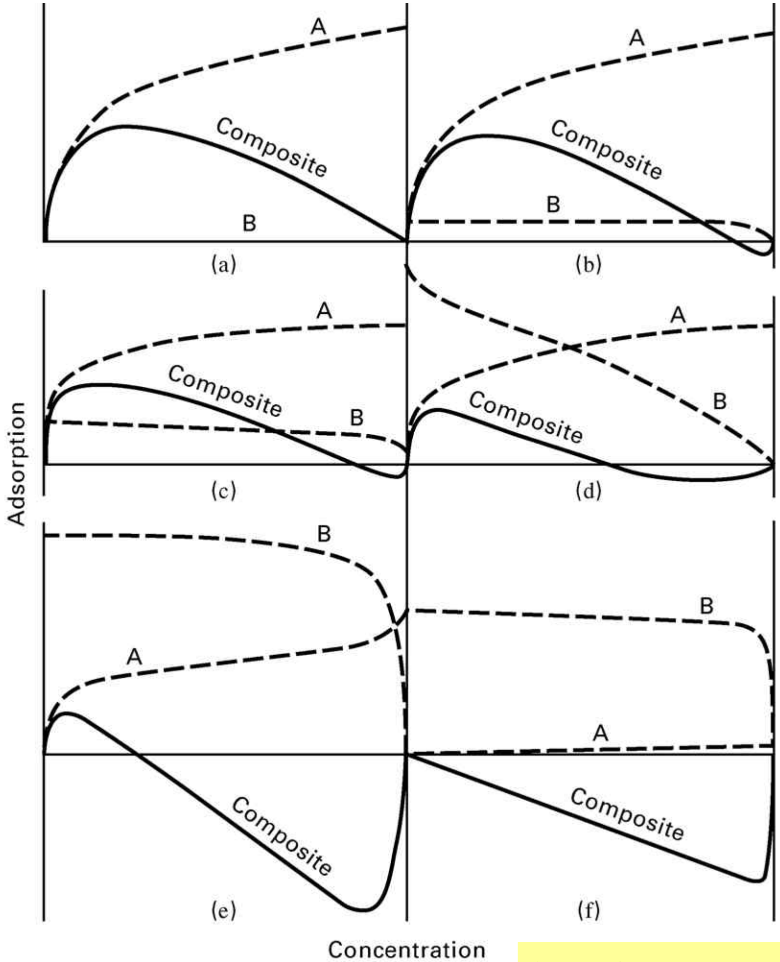
- Isotherms over entire concentration range





  - Composite isotherms or isotherms of concentration change
  - q_1^e : surface excess
  - When the solvent is not adsorbed, a composite curve without negative adsorption is obtained

- Origin of various types of composite isotherms



A: solute, B: solvent

Ion-Exchange Equilibria (1)

- Ion exchange
  - One sorbate (a counterion) is exchanged for a solute ion, the process being governed by a reversible, stoichiometric, chemical-reaction equation
  - Selectivity of the ion exchanger for one counterion over another may be just as important as the ion-exchanger capacity
  - The law of mass action is used to obtain an equilibrium ratio

(1) Case 1. The counterion initially in the ion exchanger is exchanged with a counterion from an acid or base solution

$$\mathrm{Na}^{+}_{(\mathrm{aq})} + \mathrm{OH}^{-}_{(\mathrm{aq})} + \mathrm{HR}_{(\mathrm{s})} \leftrightarrow \mathrm{NaR}_{(\mathrm{s})} + \mathrm{H_2O}_{(\mathrm{l})}$$

Leaving no counterion

(2) Case 2. The counterion being transferred from exchanger to fluid remains as an ion

$$\mathrm{A}^{n\pm}_{(\mathrm{l})} + n\mathrm{BR}_{(\mathrm{s})} \leftrightarrow \mathrm{AR}_{n(\mathrm{s})} + n\mathrm{B}^{\pm}_{(\mathrm{l})}$$

Molar selectivity coefficient for A displacing B

$$K_{\mathrm{A,B}} = \frac{q_{\mathrm{AR}_n} c^{n}_{\mathrm{B}^{\pm}}}{q^{n}_{\mathrm{BR}} c_{\mathrm{A}^{n\pm}}}$$

Ion–Exchange Equilibria (2)

- The total concentrations, C and Q, in equivalents of counterions in the solution and the resin, remain constant during exchange

$$c_i = C\,x_i / z_i$$

$$q_i = Q\,y_i / z_i$$

x_i and y_i : equivalent fractions ($x_A + x_B = 1$, $y_A + y_B = 1$)
z_i : valence of counterion *i*

- For counterions A and B of equal charge

$$K_{\mathrm{A,B}} = \frac{y_{\mathrm{A}} x_{\mathrm{B}}}{y_{\mathrm{B}} x_{\mathrm{A}}} = \frac{y_{\mathrm{A}}(1 - x_{\mathrm{A}})}{x_{\mathrm{A}}(1 - y_{\mathrm{A}})}$$

- For counterions A and B of unequal charge

$$K_{\mathrm{A,B}} = \left(\frac{C}{Q}\right)^{n-1} \frac{y_{\mathrm{A}}(1 - x_{\mathrm{A}})^n}{x_{\mathrm{A}}(1 - y_{\mathrm{A}})^n}$$

Ion–Exchange Equilibria (3)

- Estimation of $K_{A,B}$

$$K_{ij} = K_i / K_j$$

K_i **and** K_i : relative selectivities

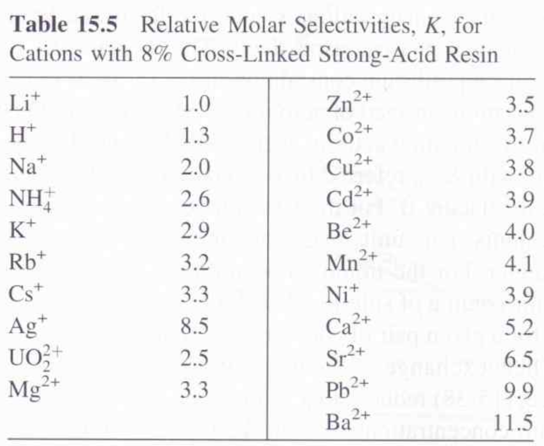


Table 15.5 Relative Molar Selectivities, *K*, for Cations with 8% Cross-Linked Strong-Acid Resin

Li^+	1.0	Zn^{2+}	3.5
H^+	1.3	Co^{2+}	3.7
Na^+	2.0	Cu^{2+}	3.8
NH_4^+	2.6	Cd^{2+}	3.9
K^+	2.9	Be^{2+}	4.0
Rb^+	3.2	Mn^{2+}	4.1
Cs^+	3.3	Ni^+	3.9
Ag^+	8.5	Ca^{2+}	5.2
UO_2^{2+}	2.5	Sr^{2+}	6.5
Mg^{2+}	3.3	Pb^{2+}	9.9
		Ba^{2+}	11.5

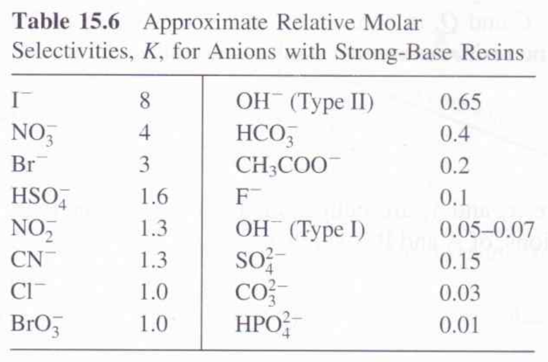


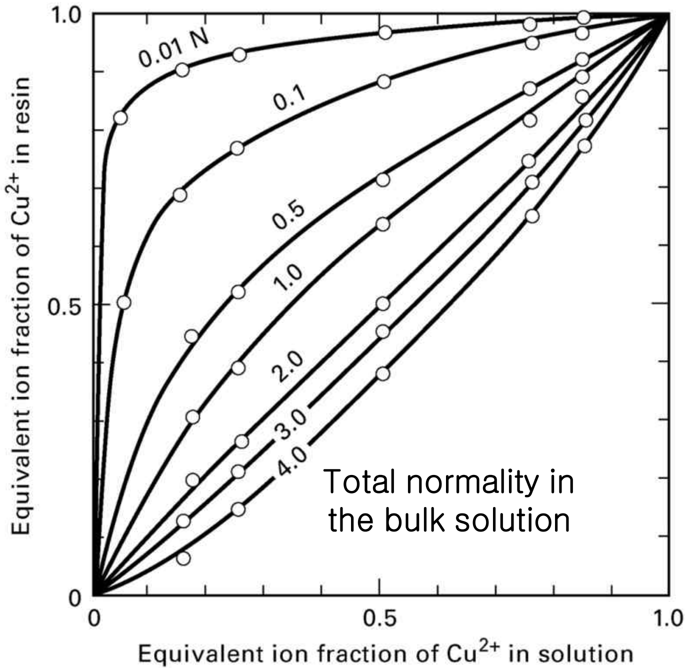
Table 15.6 Approximate Relative Molar Selectivities, *K*, for Anions with Strong-Base Resins

I^-	8	OH^- (Type II)	0.65
NO_3^-	4	HCO_3^-	0.4
Br^-	3	CH_3COO^-	0.2
HSO_4^-	1.6	F^-	0.1
NO_2^-	1.3	OH^- (Type I)	0.05–0.07
CN^-	1.3	SO_4^{2-}	0.15
Cl^-	1.0	CO_3^{2-}	0.03
BrO_3^-	1.0	HPO_4^{2-}	0.01

- Separation factor, SP (ignoring the valence of the exchange ions)

$$S_{A,B} = \frac{y_A(1 - x_A)}{x_A(1 - y_A)}$$

- Isotherms for ion exchange of Cu^{2+} and Na^+



At low total-solution concentration, the resin is highly selective for Cu^{2+}, whereas at high total-solution concentration, the selectivity is reversed to slightly favor Na^+