Lecture 10

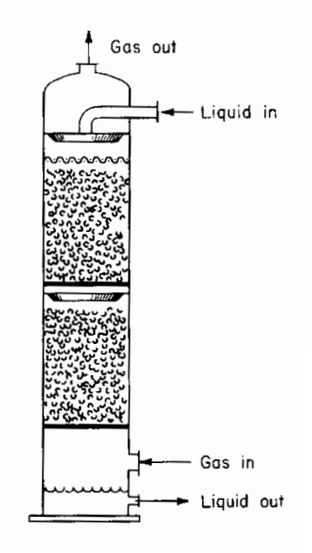
Continuation of absorption process

HTU vs HETP

HTU: Height of transfer unit

HETP: Height Equivalent to a Theoretical Plate

$$Height \quad of \quad packed \quad column = h = HTU * NTU = HETP * n$$



Kremser Equation

$$n = \frac{\ln\left[\frac{1}{A} + \left(1 - \frac{1}{A}\right)\left(\frac{y_{N+1} - y_0}{y_1 - y_0}\right)\right]}{\ln A}$$

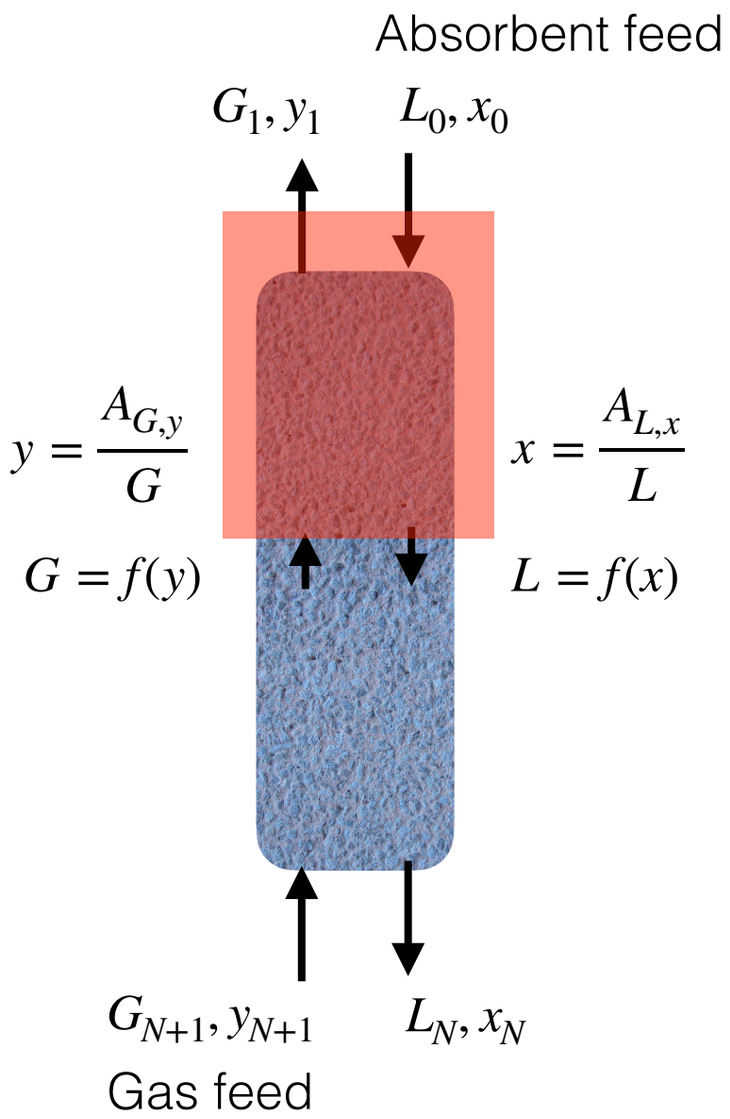
$$NTU = \left(\frac{1}{1 - \frac{mG}{L}}\right) \ln\left(\frac{y_{N+1} - mx_N}{y_1 - mx_0}\right)$$

$$y_0 = mx_0$$

$$A = \frac{L}{mG}$$

Unlike HTU, HETP has no theoretical basis.

Concentrated absorption in packed column



Absorbent: L_0
Gas dissolved: $A_{L,0}$

$$L_0 = L_A + A_{L,0}$$

Carrier gas: Gc
Gas to be removed: $A_{G,N+1}$

$$G_{N+1} = G_C + A_{G,N+1}$$

$$G = f(y)$$

$$G = G_C + A_{G,y}$$

$$y = \frac{A_{G,y}}{G}$$

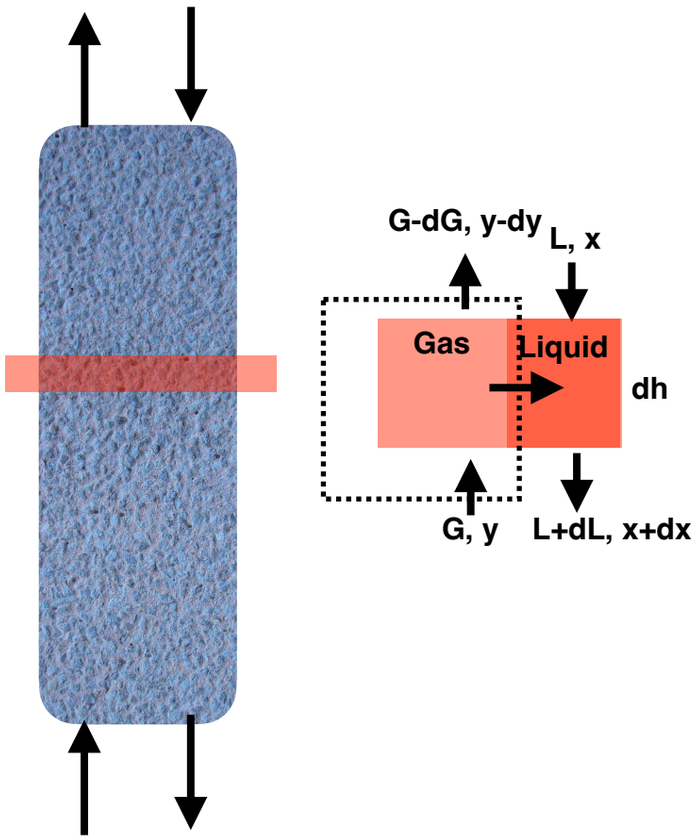
$$\Rightarrow G = G_C + Gy$$

$$\Rightarrow G = \frac{G_C}{1 - y}$$

Similarly

$$L = \frac{L_A}{1 - x}$$

Concentrated absorption in packed column



$$G = \frac{G_C}{1-y} \qquad L = \frac{L_A}{1-x}$$

Applying mass transfer concept

Accumulation = in - out

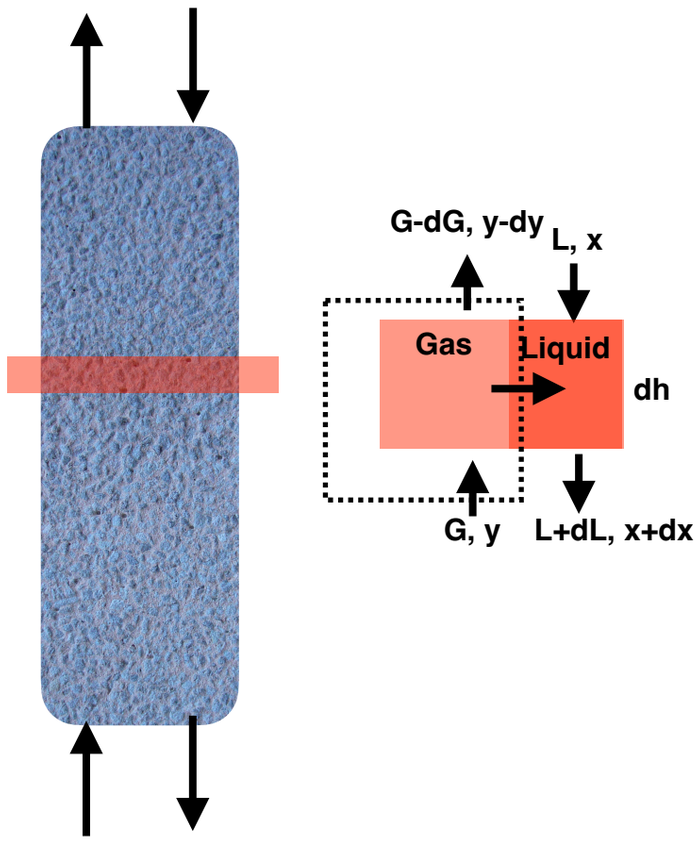
$$0 = Gy - \left(G-dG\right)\left(y-dy\right) - K_y\left(y-y^*\right)aAdh$$

$$\Rightarrow \quad Gdy + ydG - dGdy = K_y aA\left(y-y^*\right)dh$$

$$\Rightarrow \quad Gdy + ydG = K_y aA\left(y-y^*\right)dh$$

$$\Rightarrow \quad \frac{G_C}{1-y}dy + yd\left(\frac{G_C}{1-y}\right) = K_y aA\left(y-y^*\right)dh$$

Concentrated absorption in packed column



$$\frac{G_C}{1-y}dy + yd\left(\frac{G_C}{1-y}\right) = K_y aA\left(y - y^*\right)dh$$

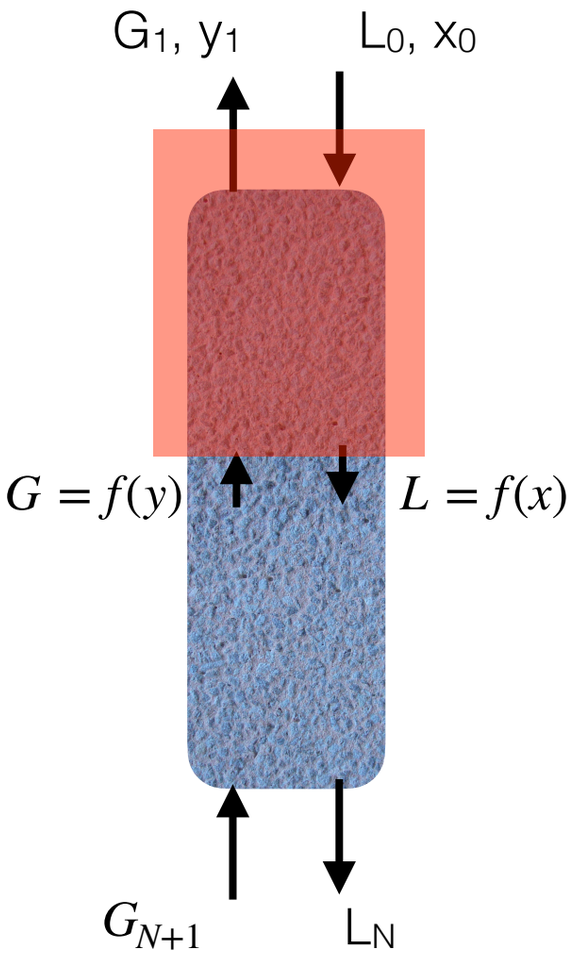
$$\frac{G_C}{1-y}dy + \frac{G_C y}{\left(1-y\right)^2}dy = K_y aA\left(y - y^*\right)dh$$

$$\frac{G_C}{\left(1-y\right)^2}dy = K_y aA\left(y - y^*\right)dh$$

$$\frac{G_C}{K_y aA}\frac{dy}{\left(1-y\right)^2\left(y - y^*\right)} = dh$$

$$\int_0^h dh = h = \frac{G_C}{K_y aA}\int_{y_{N+1}}^{y_1}\frac{dy}{\left(1-y\right)^2\left(y - y^*\right)}$$

Concentrated absorption in packed column



$$\int_0^h dh \quad = \quad h \quad = \quad \frac{G_C}{K_y a A} \int_{y_{N+1}}^{y_1} \frac{dy}{(1-y)^2 (y-y^*)}$$

$$y^* = f(x)$$

Use operating line to get x as a function of y

In = out

$$Gy + L_0 x_0 = Lx + G_1 y_1$$

$$\Rightarrow y = \frac{L}{G} x + \frac{G_1}{G} y_1 - \frac{L_0}{G} x_0$$

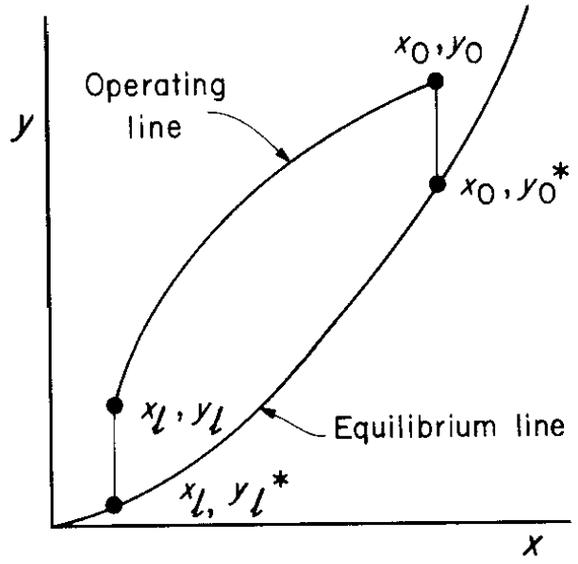
$$L = \frac{L_A}{1-x} \qquad G = \frac{G_C}{1-y}$$

$$\Rightarrow y = \frac{L_A}{G_C} \frac{x(1-y)}{1-x} + \frac{G_1}{G_c}(1-y) y_1 - \frac{L_0}{G_C}(1-y) x_0$$

Get x as a function of y, and then solve numerically

Concentrated absorption in packed column

$$\int_0^h dh \quad = \quad h \quad = \quad \frac{G_C}{K_y a A} \int_{y_{N+1}}^{y_1} \frac{dy}{(1-y)^2 (y-y^*)}$$



Equilibrium line $y^* = f(x)$

Operating line $$y = \frac{L_A}{G_C} \frac{x(1-y)}{1-x} + \frac{G_1}{G_c}(1-y)y_1 \; - \; \frac{L_0}{G_C}(1-y)x_0$$

Numerically integrate once the equilibrium curve is known

Concentrated absorption: simplification

$$\int_0^h dh \quad = \quad h \quad = \quad -\frac{G_C}{K_y a A}\int_{y_{N+1}}^{y_1}\frac{dy}{(1-y)^2(y-y^*)}$$

$$h = \left(\frac{G_C}{K_y a A}\right)\frac{y_{N+1}-y_1}{(y-y^*)_{N+1}-(y-y^*)_1}\ln\left[\frac{(y-y^*)_{N+1}}{(y-y^*)_1}\right]$$

HTU **NTU**

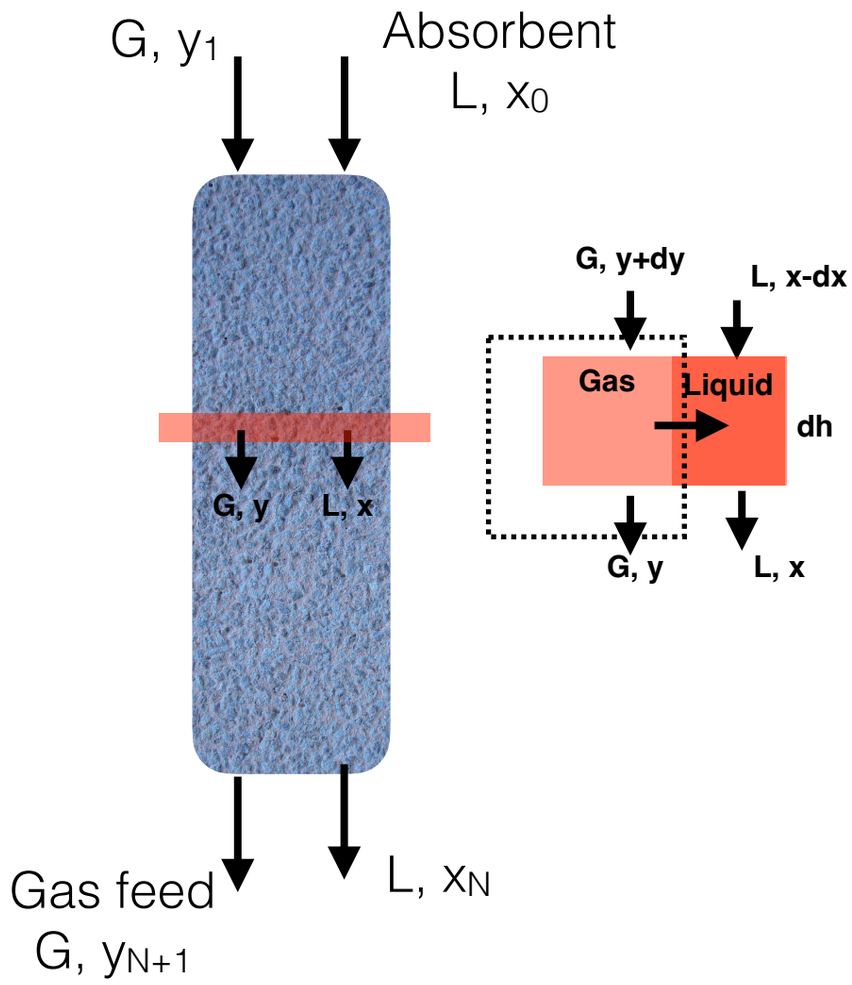
Concentrated absorption in packed column

Key assumptions that may break down

1. Carrier gas does not dissolve
2. Mass transfer coefficient is independent of concentration

In general, $mass\ \ transfer\ \ rate\ \ =\ \ K_y\left(y-y^*\right)+K_y^{'}\left(y-y^*\right)^2+...$

Co-current packed column absorber



Applying mass transfer concept

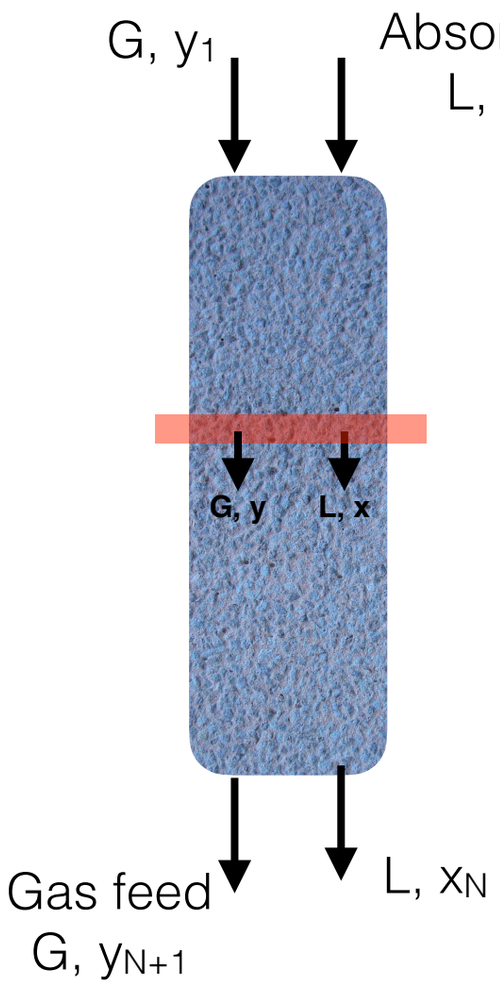
Accumulation = in - out

$$0 = G\left(y+dy\right) - Gy - K_y\left(y-y^*\right)aAdh$$

$$Gdy = K_y aA\left(y-y^*\right)dh$$

$$\frac{G}{K_y aA}\frac{dy}{\left(y-y^*\right)} = dh$$

Co-current packed column absorber



$$\int_{y_{N+1}}^{y_1} \frac{G}{K_y aA} \frac{dy}{\left(y - y^*\right)} = \int_0^h dh$$

$$\int_{y_{N+1}}^{y_1} \frac{G}{K_y aA} \frac{dy}{\left(y - mx\right)} = h$$

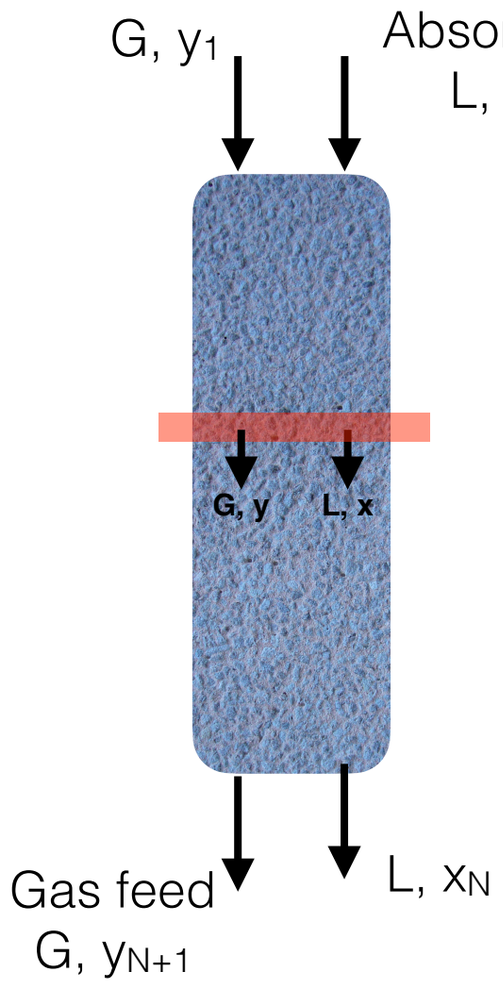
$$Gy + Lx = Gy_1 + Lx_0$$

$$x = -\frac{G}{L} y + \left(x_0 + \frac{G}{L} y_1 \right)$$

$$\int_{y_{N+1}}^{y_1} \frac{G}{K_y aA} \frac{dy}{\left[y - m\left\{ -\frac{G}{L} y + \left(x_0 + \frac{G}{L} y_1 \right) \right\} \right]} = h$$

$$h = \frac{G}{K_y aA} \left[\left(\frac{1}{1 + \frac{mG}{L}} \right) \ln \left(\frac{y_1 - mx_0}{y_{N+1} - mx_N} \right) \right]$$

Co-current packed column absorber



$$h = \frac{G}{K_y a A}\left[\left(\frac{1}{1+\frac{mG}{L}}\right)\ln\left(\frac{y_1 - mx_0}{y_{N+1} - mx_N}\right)\right]$$

$$Height \quad of \quad packed \quad column = h = HTU * NTU$$

$$HTU = \frac{G}{K_y a A}$$

$$NTU = \left(\frac{1}{1+\frac{mG}{L}}\right)\ln\left(\frac{y_1 - mx_0}{y_{N+1} - mx_N}\right)$$

Adsorption-based separation processes

Where adsorption stands with other MSA process

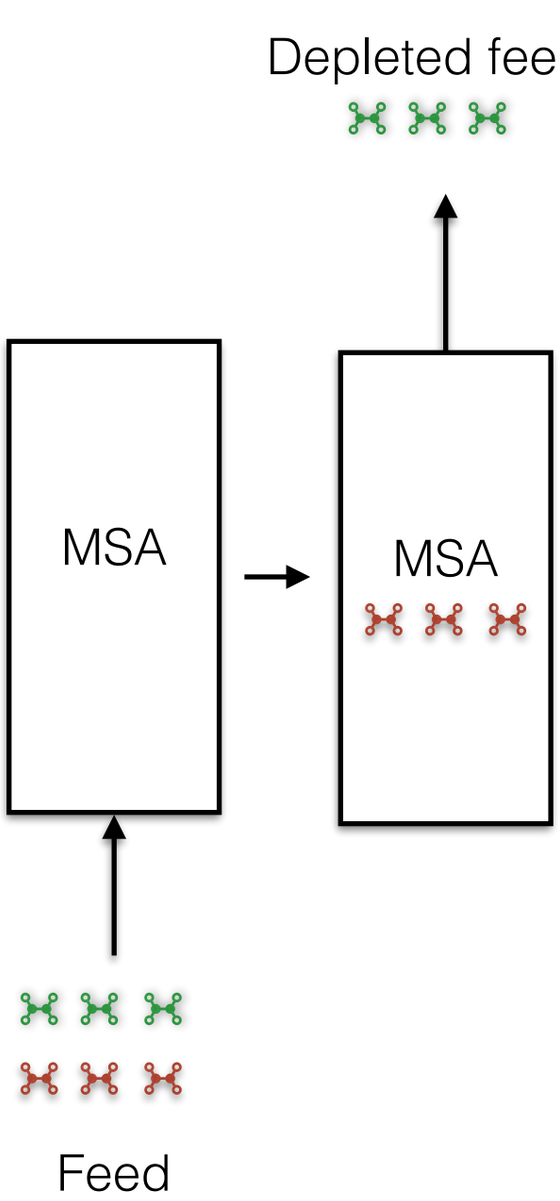
Separation Process	Feed	MSA	Regeneration Step
Liquid-Liquid Extraction	Liquid (solute)	Liquid (solvent)	Distillation, Crystallization
Absorption	Gas/vapor	Liquid (low-volatility)	Stripping
Stripping	Liquid	Gas (Steam)	Condensation
Adsorption	Gas/vapor/liquid	Porous solid	Desorption

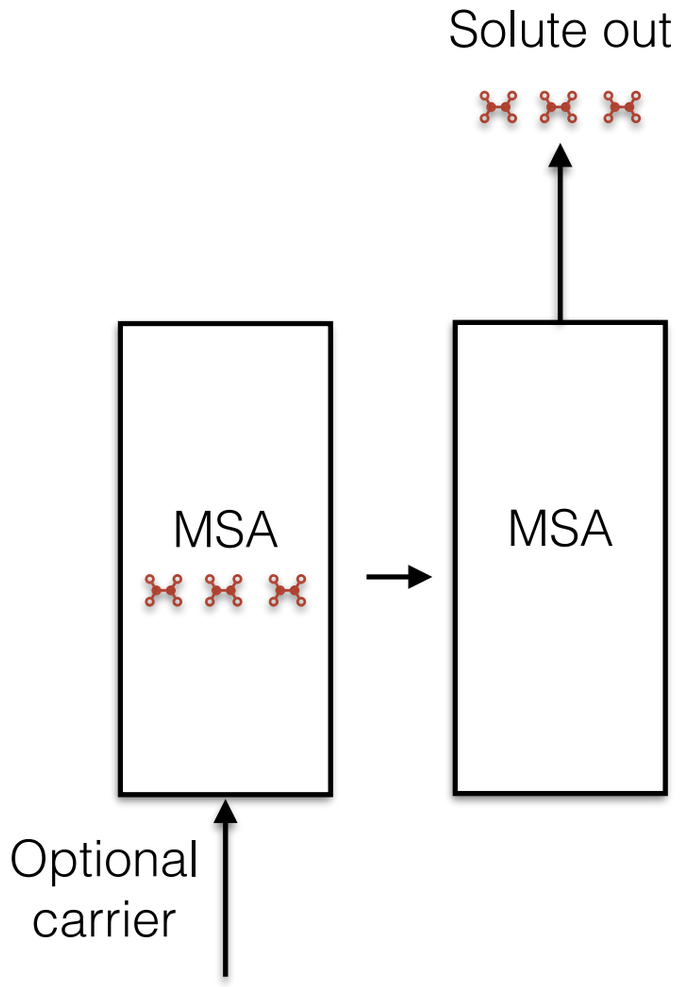
Adsorption

Separation process	Equilibrium-stage	Steady-state
Distillation	Yes	Yes
Liquid-Liquid Extraction	Yes	Yes
Absorption	Yes	Yes
Membranes	No (diffusion)	Yes
Adsorption	No (diffusion, convection)	No (MSA does not move)

Adsorption is like a batch process and takes place in cycles (adsorption cycle, regeneration cycle)

Phase creation by adding mass separating agent (MSA)

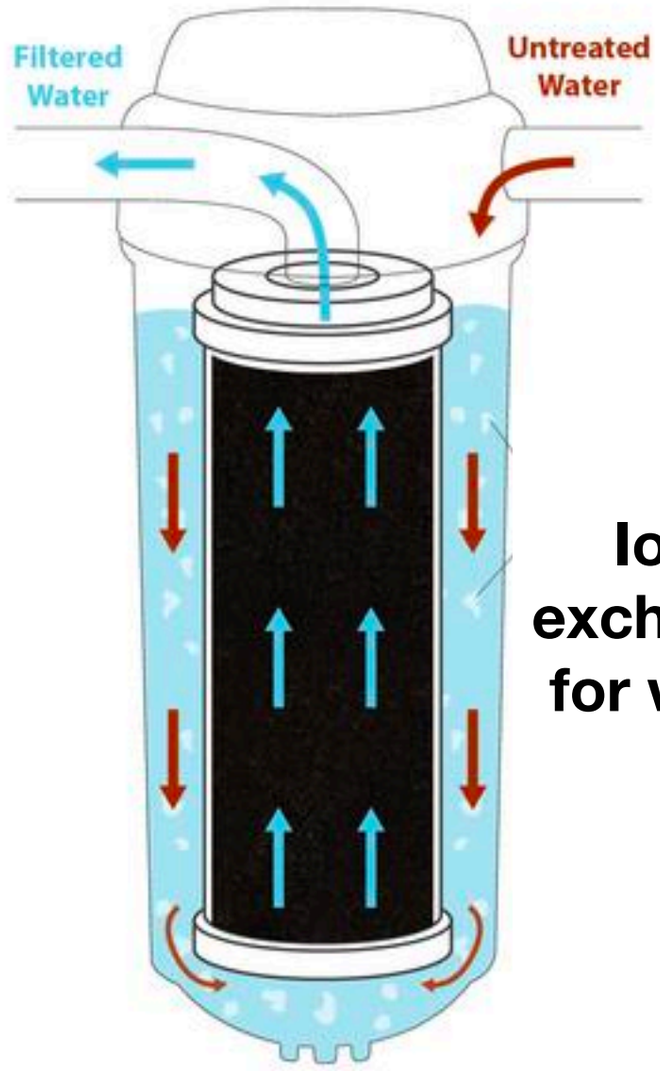




Regeneration
Temperature increase
Pressure decrease

Did you interact with an adsorbent today?

Ion-exchange



Ion-exchange for water

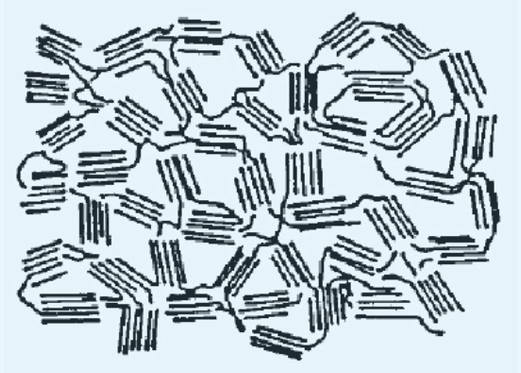
Vapor sorption (masks, odor removers)

Moisture sorption

Popular molecular and ionic absorbents

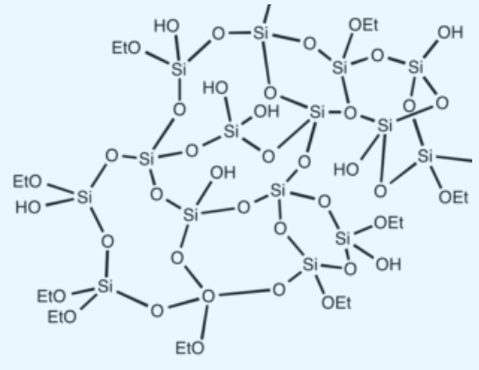
Amorphous

Activated carbon



Pore size: 1 - 20 nm
Surface area: up to 2000 m^2/g
ε_P: 0.6 - 0.85
Tortuosity: 5-65

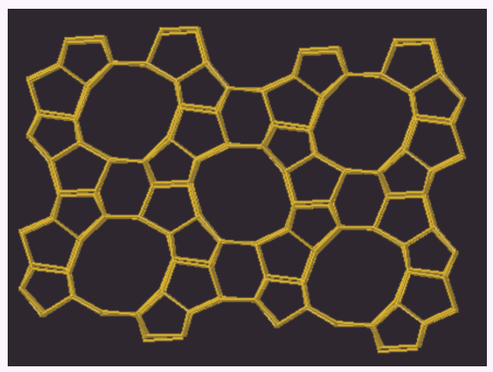
Silica, alumina



Pore size: 1 - 20 nm
Surface area: up to 800 m^2/g
ε_P: 0.4-0.6
Tortuosity: 2-6

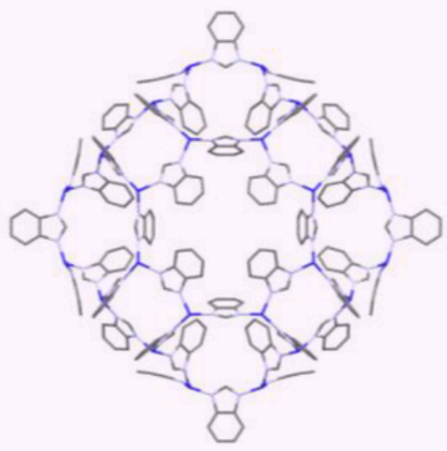
Crystalline

Zeolites



Pore size: 0.3 - 1 nm
Surface area: up to 500 m^2/g
ε_P: 0.3-0.4
Tortuosity: 1.7-4.5

Metal-organic frameworks (MOFs)



Pore size: 0.3 - 2 nm
Surface area: up to 5000 m^2/g
ε_P: similar to zeolites
Tortuosity: similar to zeolites

Tortuosity

Straight pores

Zig-zag pores

$$\tau = \frac{L_t}{L}$$

Type of adsorption

Physisorption

1. Adsorption due to van der Waals and electrostatic interaction.
2. Heat of adsorption: < 50 kJ/mole.
3. Reversible

Chemisorption

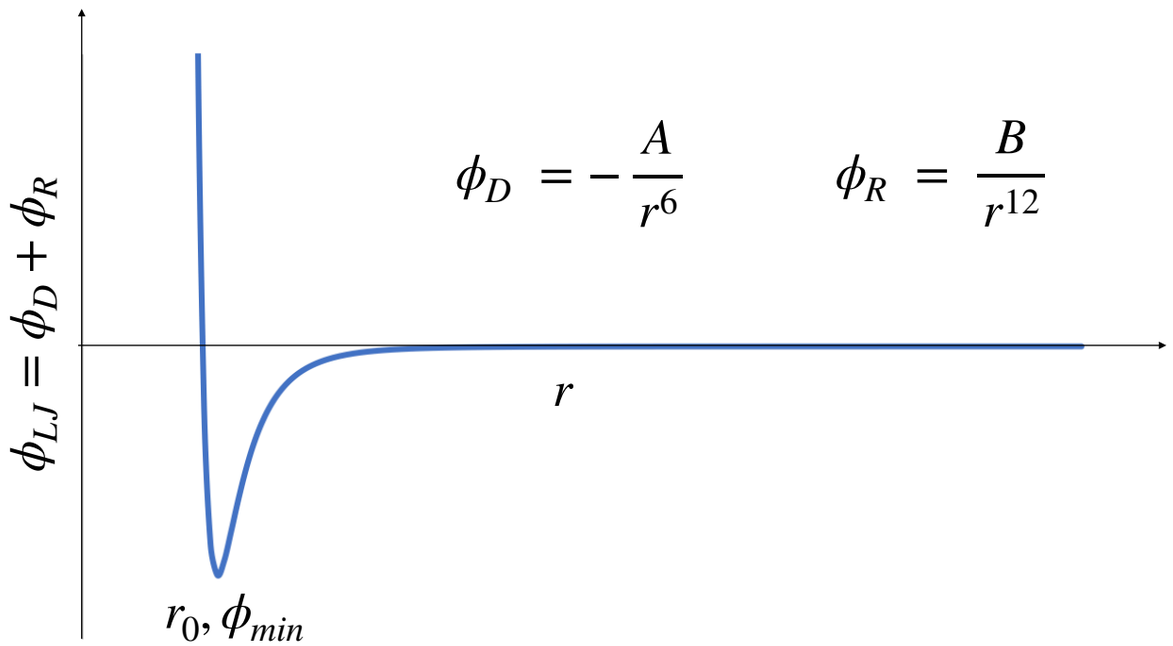
1. Physisorption followed by chemical reaction.
2. Heat of adsorption: 80-240 kJ/mole.
3. Irreversible (bond formation)

Understanding physisorption

Adsorbate-adsorbent interaction potential

$$\phi = \phi_D + \phi_R$$

Dispersion Attractive **Repulsive**



By minimizing at r_0

$$B = A\frac{r_0^6}{2}$$

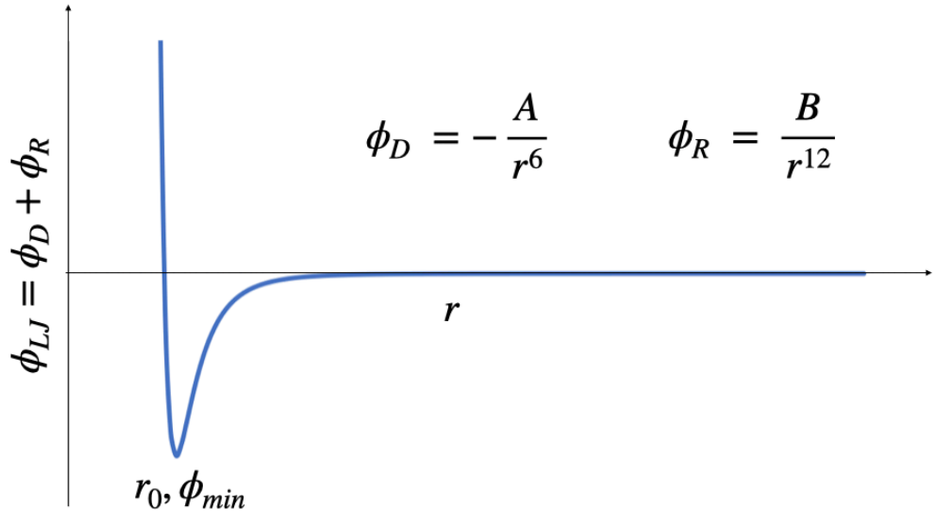
$$\phi = A\left[-\frac{1}{r^6} + \frac{r_0^6}{2r^{12}}\right]$$

Lennard-Jones Potential

6-12 potential

Understanding physisorption

$$\phi = A\left[-\frac{1}{r^6} + \frac{r_0^6}{2r^{12}}\right]$$



A is given by the Kirkwood-Müller formula

$$A = \frac{6mc^2\alpha_i\alpha_j}{\alpha_i/\chi_i + \alpha_j/\chi_j}$$

m = mass of the electron

c = speed of light

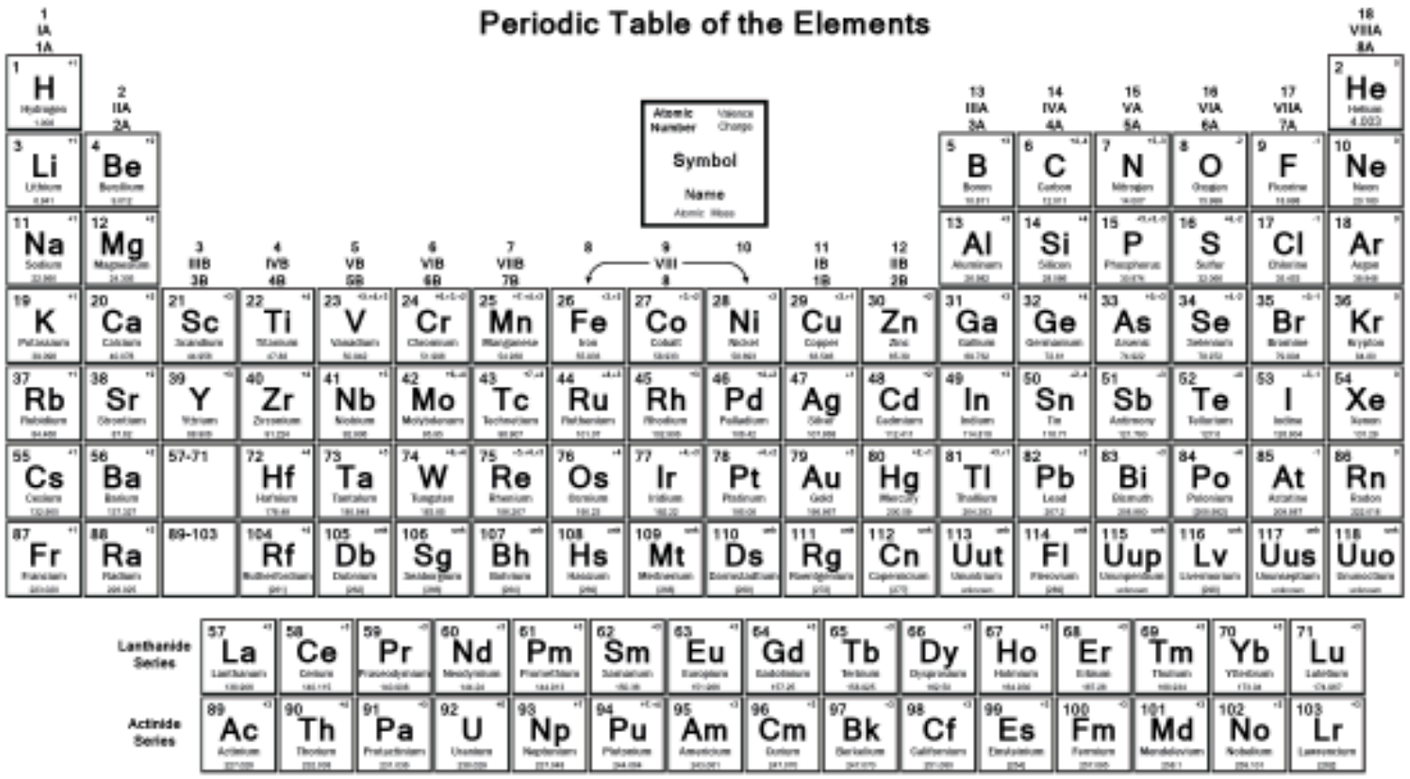
α_i = polarizibility of the i^{th} atom

χ_i = magnetic susceptibility

Table 2.2. Polarizabilities (α) of ground state atoms and ions (in 10^{-24} cm^3)

Atom	α	Atom	α	Atom	α
C	1.76	K	43.4	Co	7.5
N	1.10	Rb	47.3	Ni	6.8
O	0.802	Cs	59.6		
F	0.557	Mg	10.6	Li^+	0.029
S	2.90	Ca	22.8	Na^+	0.180
Cl	2.18	Sr	27.6	K^+	0.840
Br	3.05	Ba	39.7	Ca^{2+}	0.471
I	5.35	Al	6.8	Sr^{2+}	0.863
		Si	5.38	Ba^{2+}	1.560
Li	24.3	Fe	8.4		
Na	24.08				

Polarizability increases with increasing molecular weight (in the same periodic table group) ↓



Polarizability decreases with increasing molecular weight (in the same periodic table row) →

Heat of adsorption

$$\Delta H = \phi - RT + F(T)$$

$F(T)$ = vibrational and translational energy of the adsorbed molecule

For monoatomic classical oscillator

$$F(T) = \frac{3}{2}RT$$

$$\Rightarrow \Delta H \approx \phi + \frac{RT}{2}$$

At room temperature

$RT = 8.314 * 300$ J/mol $\approx$ 2.5 kJ/mole

ΔH can be estimated by microcalorimetry, and therefore, ϕ can also be estimated

System with charge

$$\phi = \phi_D + \phi_R + \phi_{induced-dipole} + \phi_{permanent-dipole} + \phi_{quadrupole}$$

$$\phi_{LJ} = \phi_D + \phi_R$$

Energetic interaction between Field and dipole

Energetic interaction between Field gradient and quadrupole

$$\phi_{induced} = -\frac{1}{2}\alpha F^2 = -\frac{\alpha q^2}{2r^4(4\pi\varepsilon_0)^2}$$

$$\phi_{F\mu} = -F\mu\cos\theta = -\frac{q\mu\cos\theta}{r^2(4\pi\varepsilon_0)}$$

$$\phi_{\dot{F}\mu} = \frac{1}{2}Q\dot{F} = -\frac{Qq(3\cos^2\theta - 1)}{4r^3(4\pi\varepsilon_0)}$$

q = elctronic charge of ion on surface

ε = permittivity of vacuum

μ = permanent dipole moment

θ = angle between field (or field gradient) and the axis of dipole (or linear quadrupole)

$$\phi = \phi_D + \phi_R + \phi_{Induced} + \phi_{F\mu} + \phi_{\dot{F}Q}$$

$$\phi = \frac{6mc^2\alpha_i\alpha_j}{(\alpha_i/\chi_i + \alpha_j/\chi_j)}\left[-\frac{1}{r^6} + \frac{r_o^6}{r^{12}}\right] - \frac{\alpha q^2}{2r^4(4\pi\epsilon_o)^2} - \frac{q\mu cos\theta}{r^2(4\pi\epsilon_o)} - \frac{Qq(3cos^2\theta - 1)}{4r^3(4\pi\epsilon_o)}$$

Table 2.1. Contributions (theoretical) to initial (near zero loading) heat of adsorption

Sorbent	Sorbate*	$\alpha \times 10^{24}$ cm^3/molec.	$-\Delta H$	$-(\phi_D + \phi_R + \phi_{Ind})$**	$-(\phi_{F\mu} + \phi_{\dot{F}Q})$
Graphitized Carbon	Ne	0.396	0.74	0.73	0
	Ar	1.63	2.12	1.84	0
	Kr	2.48	2.8	2.48	0
	Xe	4.04	3.7	3.1	0
Chabazite	N_2	1.74	8.98	6.45	2.55
	N_2O	3.03	15.3	9.07	6.18
	NH_3	2.2	31.5	7.5	23.8
Na-Mordenite	N_2	1.74	7.0	4.5	2.50
	CO_2	2.91	15.7	6.73	8.93
Na-X	N_2	1.74	6.5	3.10	3.4
	CO_2	2.91	12.2	4.20	7.98
	NH_3	2.2	17.9	3.75	14.2
	H_2O	1.45	≈33.9	2.65	≈31.3

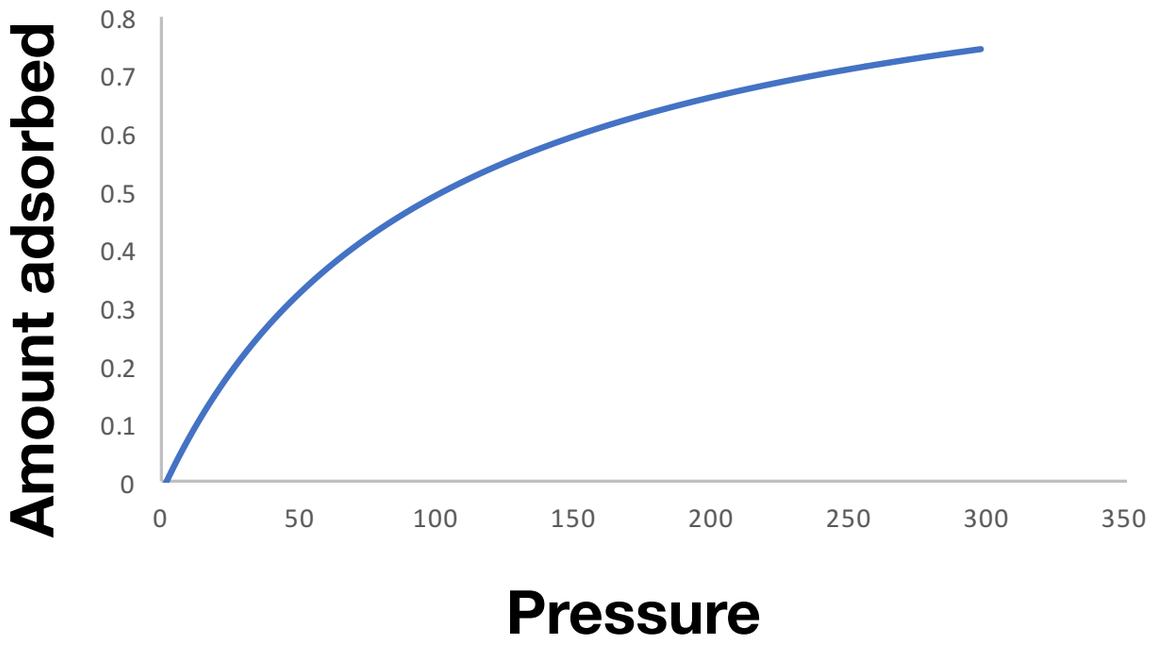
*Permanent dipole moments (μ, debye): $N_2O = 0.161$, $NH_3 = 1.47$, $H_2O = 1.84$, all others $= 0$.
Quadrupole moments (Q, erg$^{1/2}$ cm$^{5/2}$ $\times 10^{26}$): $N_2 = -1.5$, $N_2O = -3.0$, $NH_3 = -1.0$, $CO_2 = -4.3$, all others ≈0.
**For graphitized carbon, $\phi_{Ind} = 0$.
Experimental, $-\Delta H$, kcal/mol (Barrer, 1978; Ross and Olivier, 1964).

How can we measure adsorption?

How can we learn important parameters of adsorption?

How do we measure adsorption: Adsorption isotherms

- Equilibrium behavior is determined as constant temperature isotherms (long waiting time).
- Equilibrium between solute (also known as sorbent) pressure and adsorbed amount.
- At low pressure, isotherms are usually linear (Henry regime)
- At moderate to high pressure, isotherms curve (nonlinear regime).



Langmuir isotherm

Assumptions

1. The surface is homogeneous (flat surface).
2. All sites are equivalent.
3. Each site can only adsorb one molecule.
4. Adsorption is limited to monolayer coverage.
5. There are no interactions between adsorbed molecules.

Irving Langmuir

Nobel prize in chemistry (1934)

$$\theta = \frac{q}{q_{max}} = \frac{KP}{1+KP}$$

θ is site occupancy

K is the equilibrium constant for adsorption

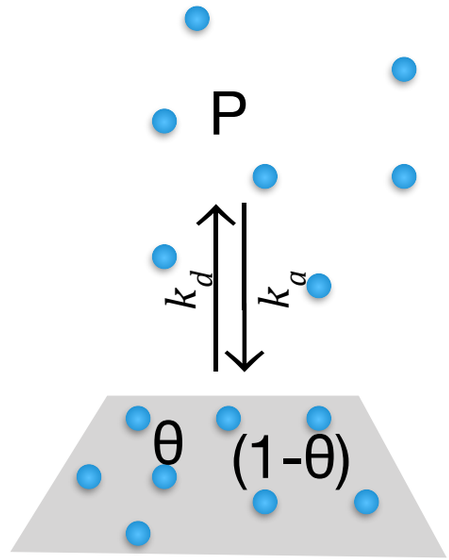
P is pressure

EPFL

Langmuir isotherm

Net rate of adsorption = rate of adsorption - rate of desorption

At equilibrium, rate of adsorption = rate of desorption



$$k_a P(1-\theta) = k_d \theta$$

$$\theta = \frac{q}{q_{max}} = \frac{\left(\frac{k_a}{k_d}\right)P}{1+\left(\frac{k_a}{k_d}\right)P}$$

$$K = \left(\frac{k_a}{k_d}\right)$$

$$\theta = \frac{q}{q_{max}} = \frac{KP}{1+KP}$$

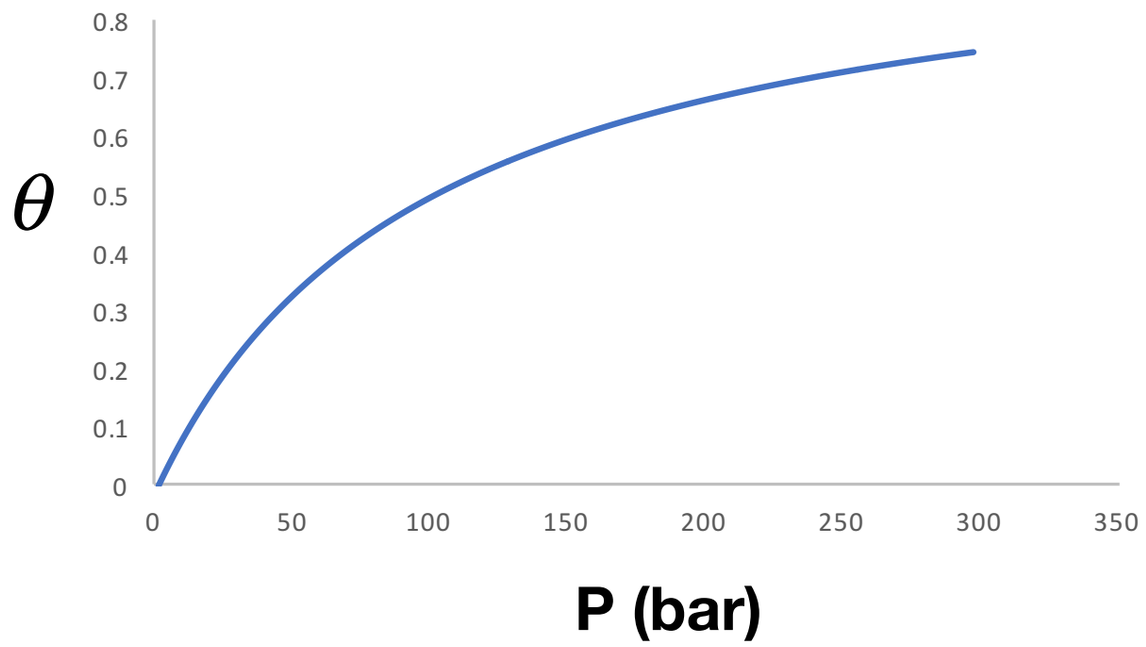
$$\theta = \frac{site\ \ occupied}{total\ \ site}$$

Langmuir isotherm

$$\theta = \frac{KP}{1+KP}$$

At low pressure $1+KP \approx 1$ $\theta = KP$

At high pressure $1+KP \approx KP$ $\theta = 1$

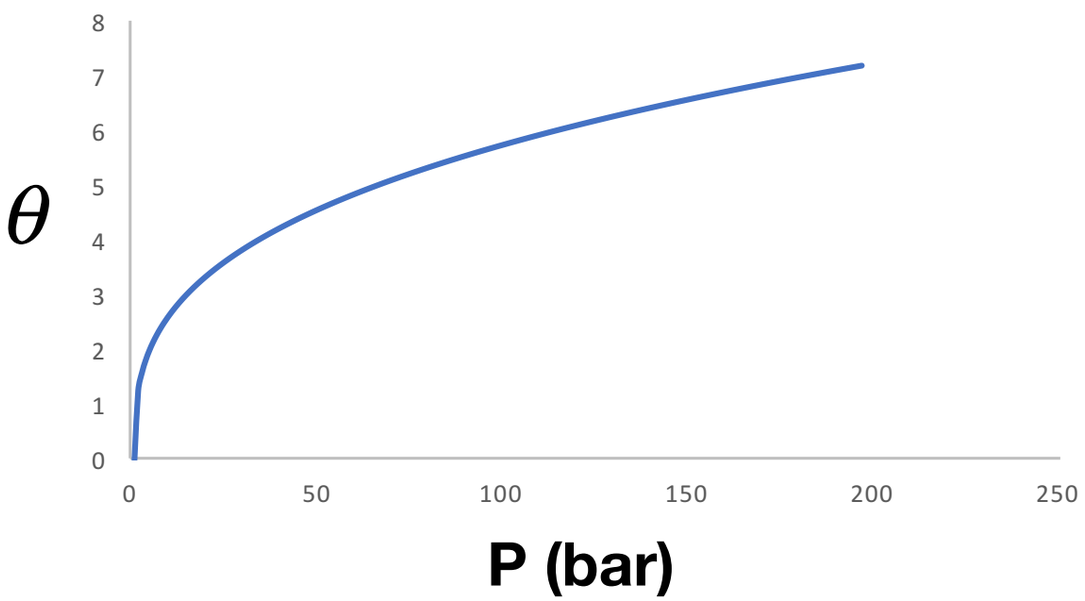


Freundlich isotherm

The assumptions of Langmuir adsorption often break down

1. The surface is seldom homogeneous (flat surface).
2. Interactions between adsorbed molecules (heat of adsorption is not independent of coverage).

$$\theta = KP^{\frac{1}{n}}$$ **Derived empirically**



- k and n are temperature-dependent constants.
- n lies in the range of 1 to 5.
- n increases with temperature.
- K decreases with temperature.
- K approaches 1 at high T

Other isotherms

Toth isotherm

$$q = \frac{KP}{\left(1+KP^{t}\right)^{\frac{1}{t}}}$$

- K and t are temperature-dependent constants.
- Reduces to 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 temperature-dependent constants.
- Reduces to Langmuir isotherm for s =0.

Several other isotherms

Some examples

Adsorbate	*Carrier*	*Adsorbent*	*Form*
Gas Systems			
Methane	None	Activated carbon	~ Langmuir
Methane	Helium	5A zeolite	Linear
Methane	H_2, N_2, CO_2	BPL activated carbon	Langmuir
Nitrogen	None	5A zeolite	Linear
Liquid Systems			
Acetic acid	Water	Activated carbon	Freundlich
Bovine serum albumin	Buffered water	DEAE Sephadex A-50	Langmuir
Fructose	Water	IEX resin in	Linear
Glucose	Water	Ca^{+2} form	
Anthracene	Cyclohexane	Activated alumina	Langmuir

What are factors affecting adsorption process

1. Chemical nature of adsorbent and solute (physisorption, chemisorption)
2. Temperature
3. Pressure
4. Physical structure of adsorbent

- Porosity (pore-density)
- Mean pore-size
- Pore-size-distribution (micropores, mesopores)
- Pore-shape (circular, elliptical, slit like)
- Tortuosity

} **Surface area**