

# Lecture 10

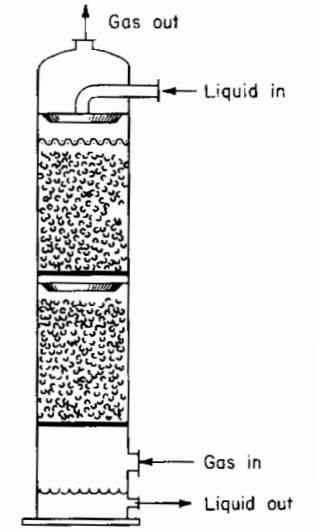
# Continuation of absorption process

# HTU vs HETP

HTU: Height of transfer unit

HETP: Height Equivalent to a Theoretical Plate

$$\text{Height of packed column} = h = \text{HTU} * \text{NTU} = \text{HETP} * n$$



**Kremser Equation**

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

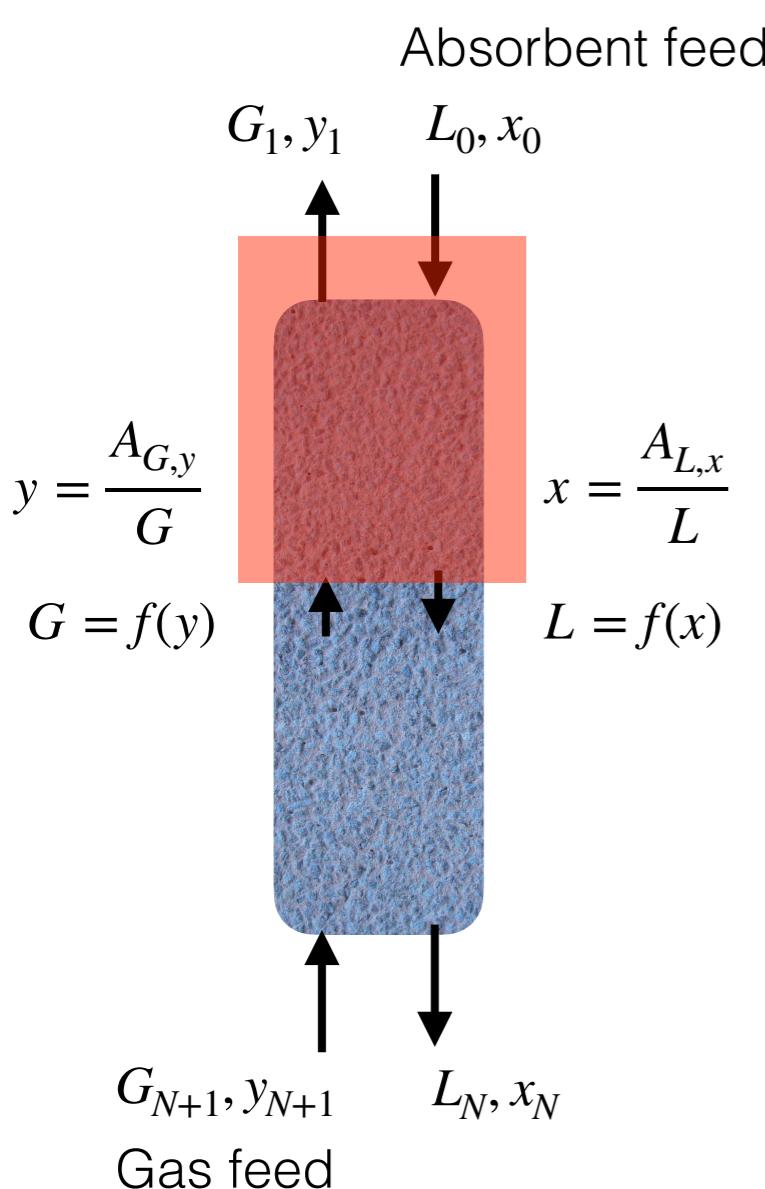
$$\text{NTU} = \left( \frac{1}{1 - \frac{mG}{L}} \right) \ln \left( \frac{y_{N+1} - mx_N}{y_1 - mx_0} \right)$$

$$y_0 = mx_0$$

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

**Unlike HTU, HETP has no theoretical basis.**

# Concentrated absorption in packed column



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

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

$$G = f(y)$$

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

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

$$\Rightarrow G = G_C + Gy$$

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

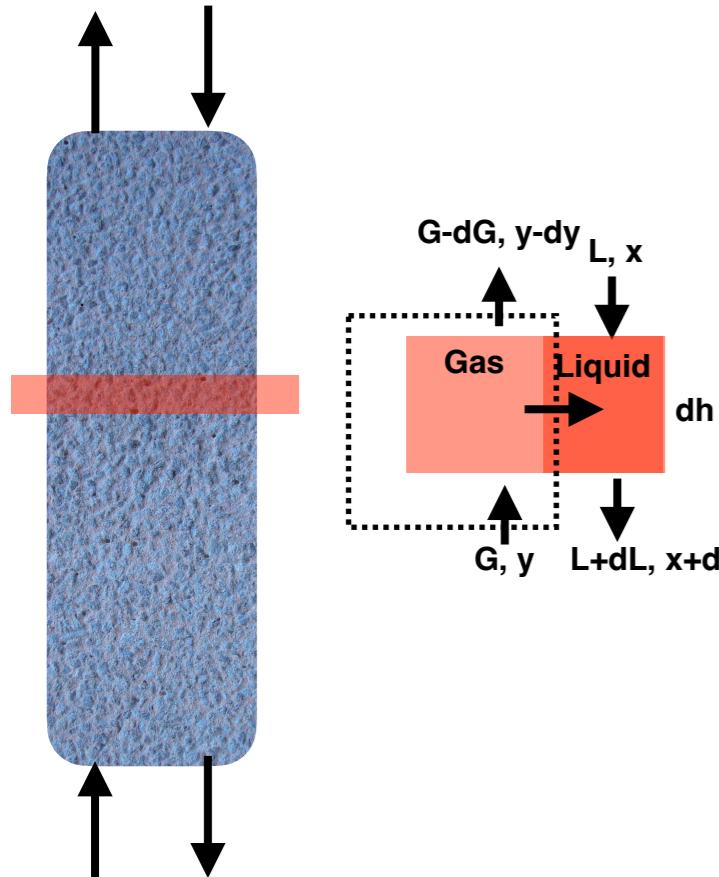
**Similarly**

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

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

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

# Concentrated absorption in packed column



$$G = \frac{G_c}{1-y} \quad L = \frac{L_A}{1-x}$$

## Applying mass transfer concept

Accumulation = in - out

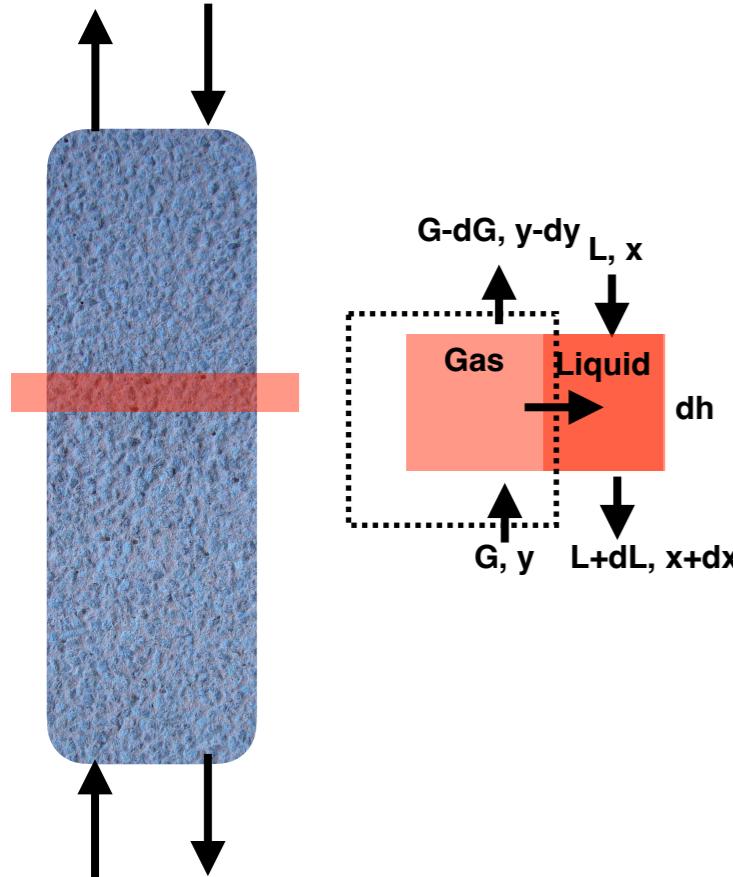
$$0 = Gy - (G - dG)(y - dy) - K_y(y - y^*)aAdh$$

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

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

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

# Concentrated absorption in packed column



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

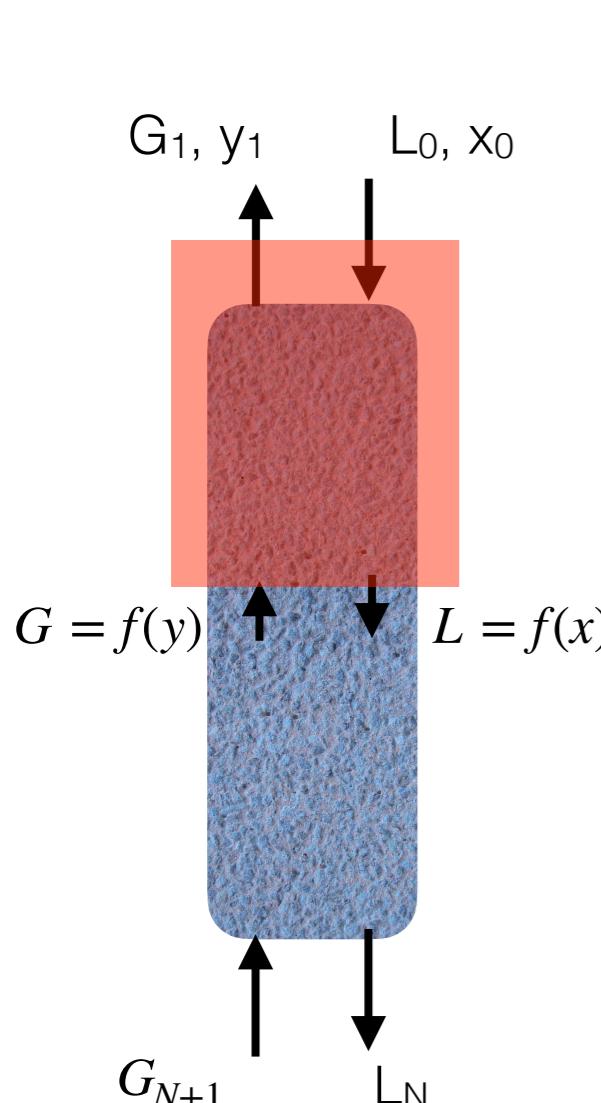
$$\frac{G_c}{1-y} dy + \frac{G_c y}{(1-y)^2} dy = K_y a A (y - y^*) dh$$

$$\frac{G_c}{(1-y)^2} dy = K_y a A (y - y^*) dh$$

$$\frac{G_c}{K_y a A (1-y)^2 (y - y^*)} dy = dh$$

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

# Concentrated absorption in packed column



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

$y^* = f(x)$

**Use operating line to get x as a function of y**

in = out

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

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

$$L = \frac{L_A}{1-x} \quad G = \frac{G_c}{1-y}$$

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

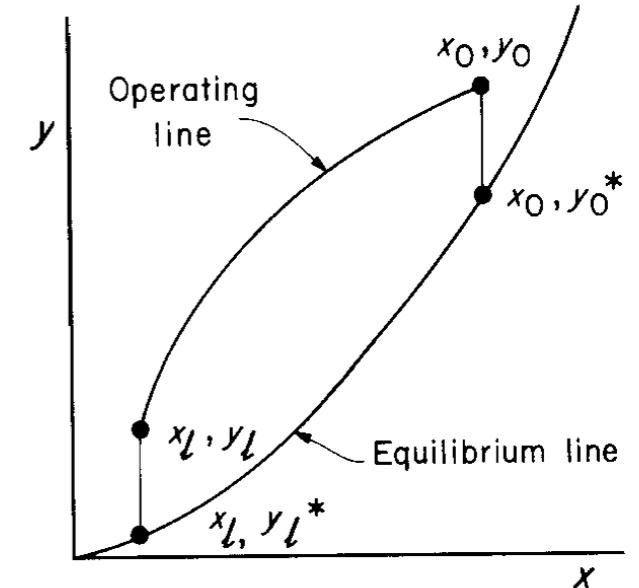
**Get x as a function of y, and then solve numerically**

# Concentrated absorption in packed column

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

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

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

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

**HTU**

**NTU**

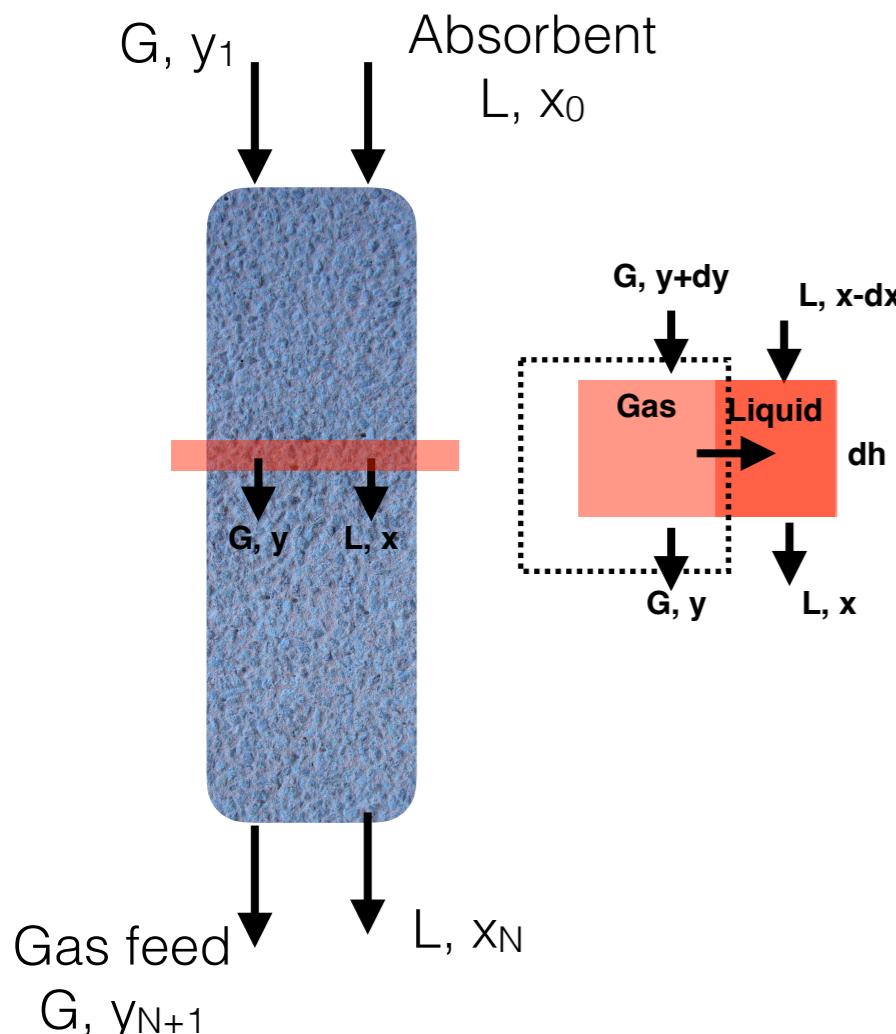
# Concentrated absorption in packed column

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* =  $K_y(y - y^*) + K'_y(y - y^*)^2 + \dots$

# Co-current packed column absorber



## Applying mass transfer concept

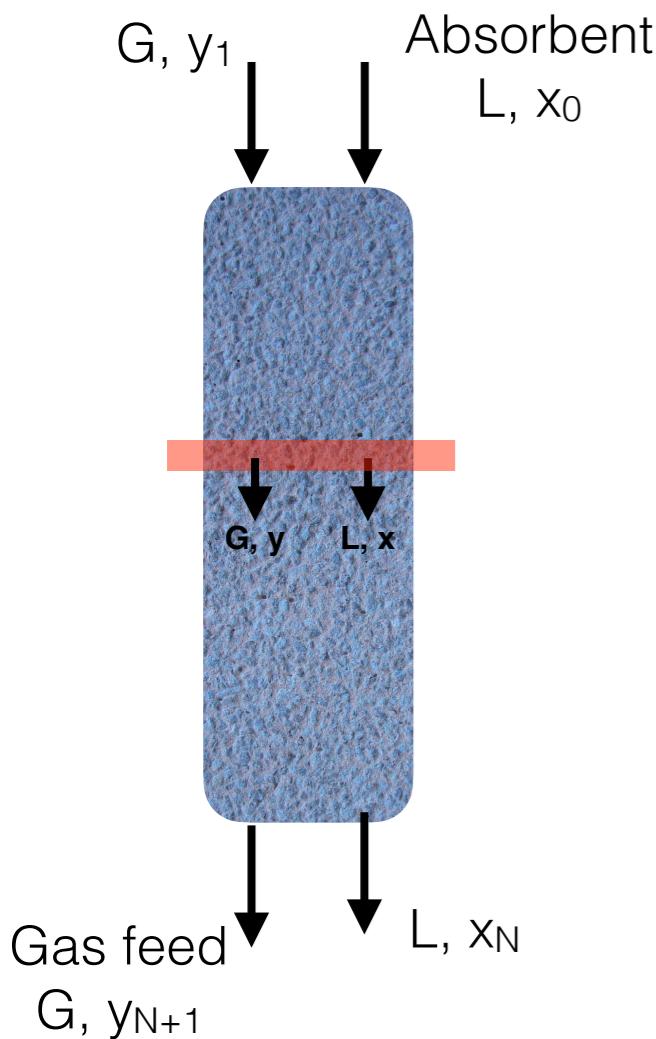
Accumulation = in - out

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

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

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

# Co-current packed column absorber



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

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

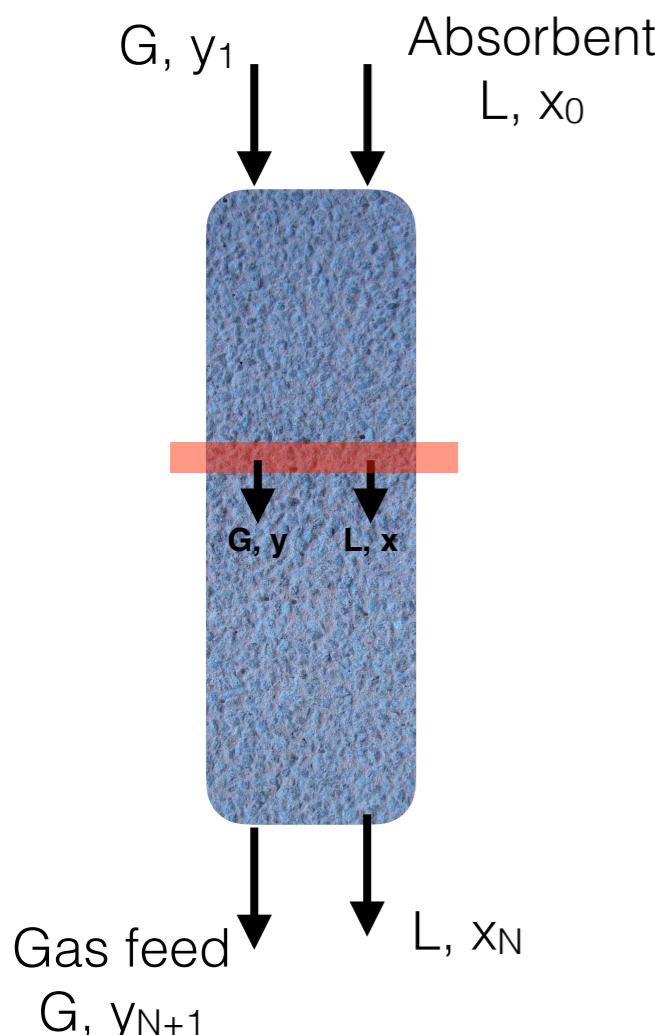
$$Gy + Lx = Gy_1 + Lx_0$$

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

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

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

# Co-current packed column absorber



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

$$\text{Height of packed column} = h = HTU * NTU$$

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

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

# Adsorption-based separation processes

# Where adsorption stands with other MSA process

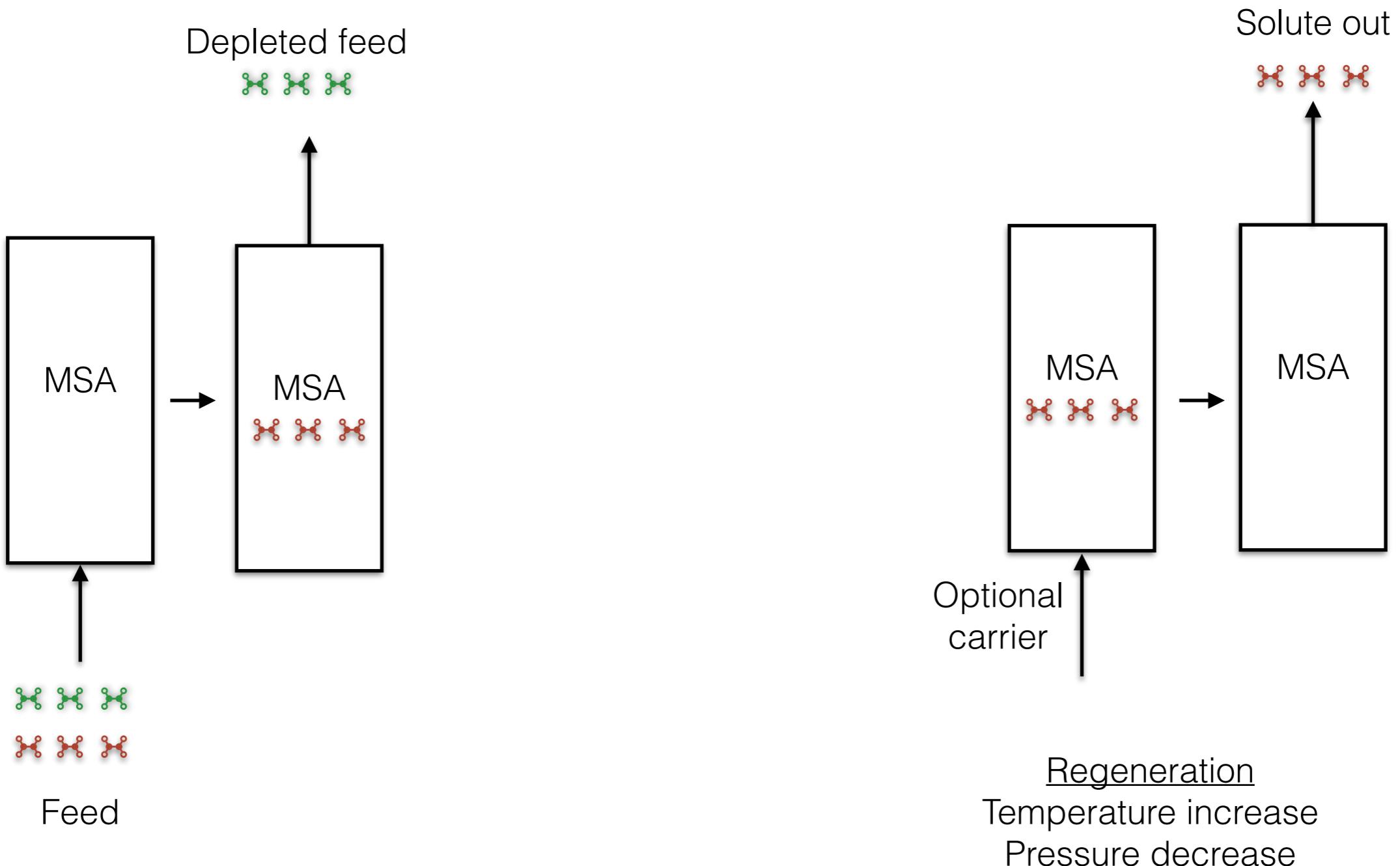
Separation Process	Feed	MSA	Regeneration Step
Liquid-Liquid Extraction	Liquid (solute)	Liquid (solvent)	Distillation, Crystallization
Absorption	Gas/vapor	Liquid (low-volatility)	Stripping
Stripping	Liquid	Gas (Steam)	Condensation
Adsorption	Gas/vapor/liquid	Porous solid	Desorption

# 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)**

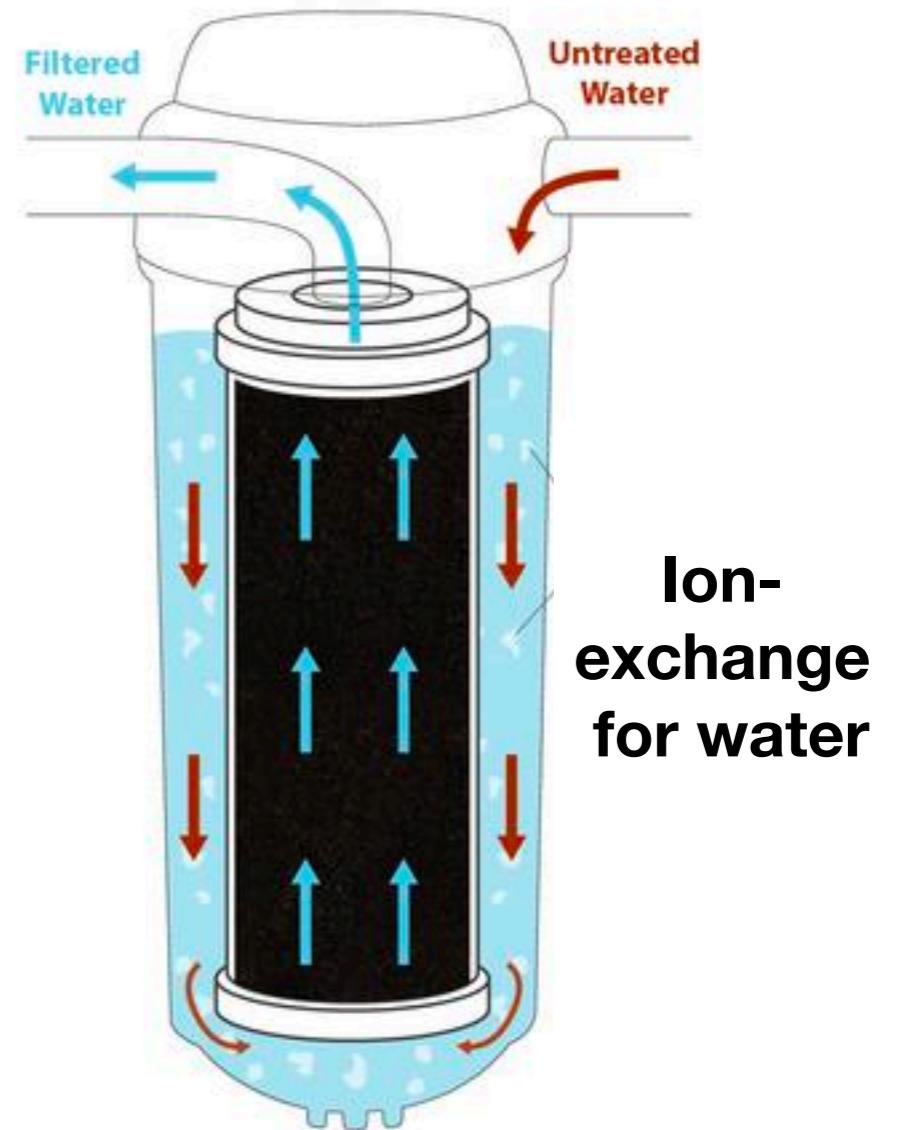
# Phase creation by adding mass separating agent (MSA)



# Did you interact with an adsorbent today?



Ion-exchange



Ion-exchange  
for water



Vapor sorption  
(masks, odor removers)

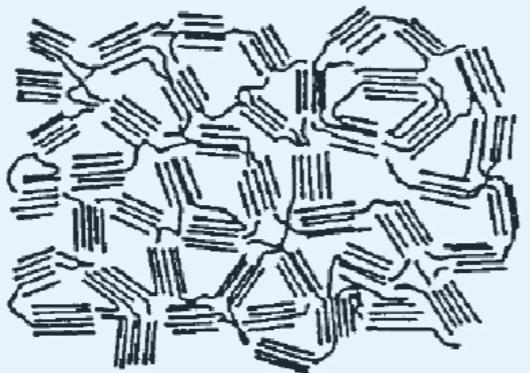
EPFL



Moisture sorption

# Popular molecular and ionic absorbents

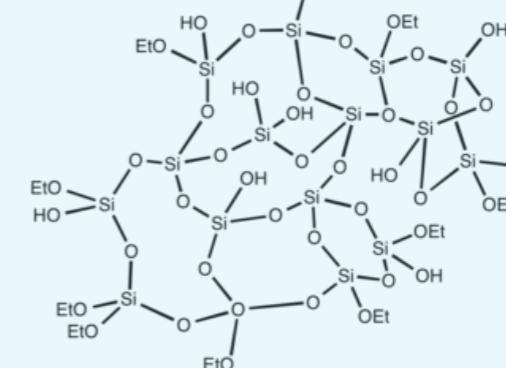
## Activated carbon



**Amorphous**

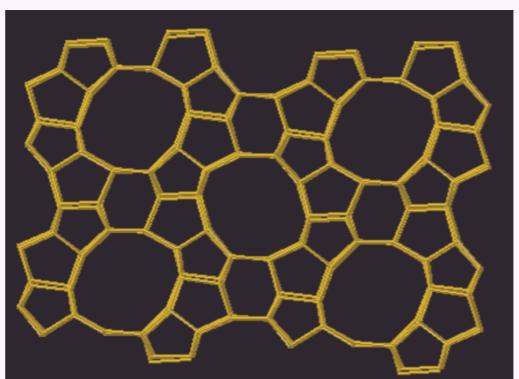
Pore size: 1 - 20 nm  
Surface area: up to 2000 m<sup>2</sup>/g  
 $\epsilon_P$ : 0.6 - 0.85  
Tortuosity: 5-65

## Silica, alumina



Pore size: 1 - 20 nm  
Surface area: up to 800 m<sup>2</sup>/g  
 $\epsilon_P$ : 0.4-0.6  
Tortuosity: 2-6

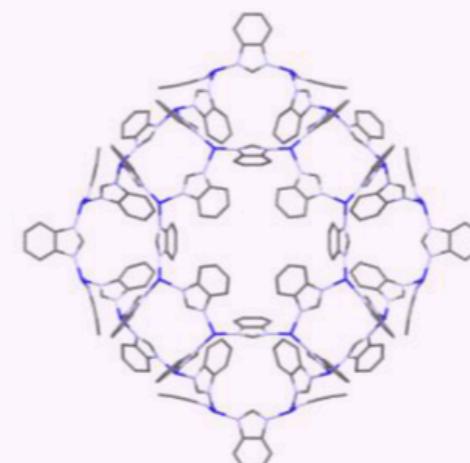
## Zeolites



**Crystalline**

Pore size: 0.3 - 1 nm  
Surface area: up to 500 m<sup>2</sup>/g  
 $\epsilon_P$ : 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<sup>2</sup>/g  
 $\epsilon_P$ : 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

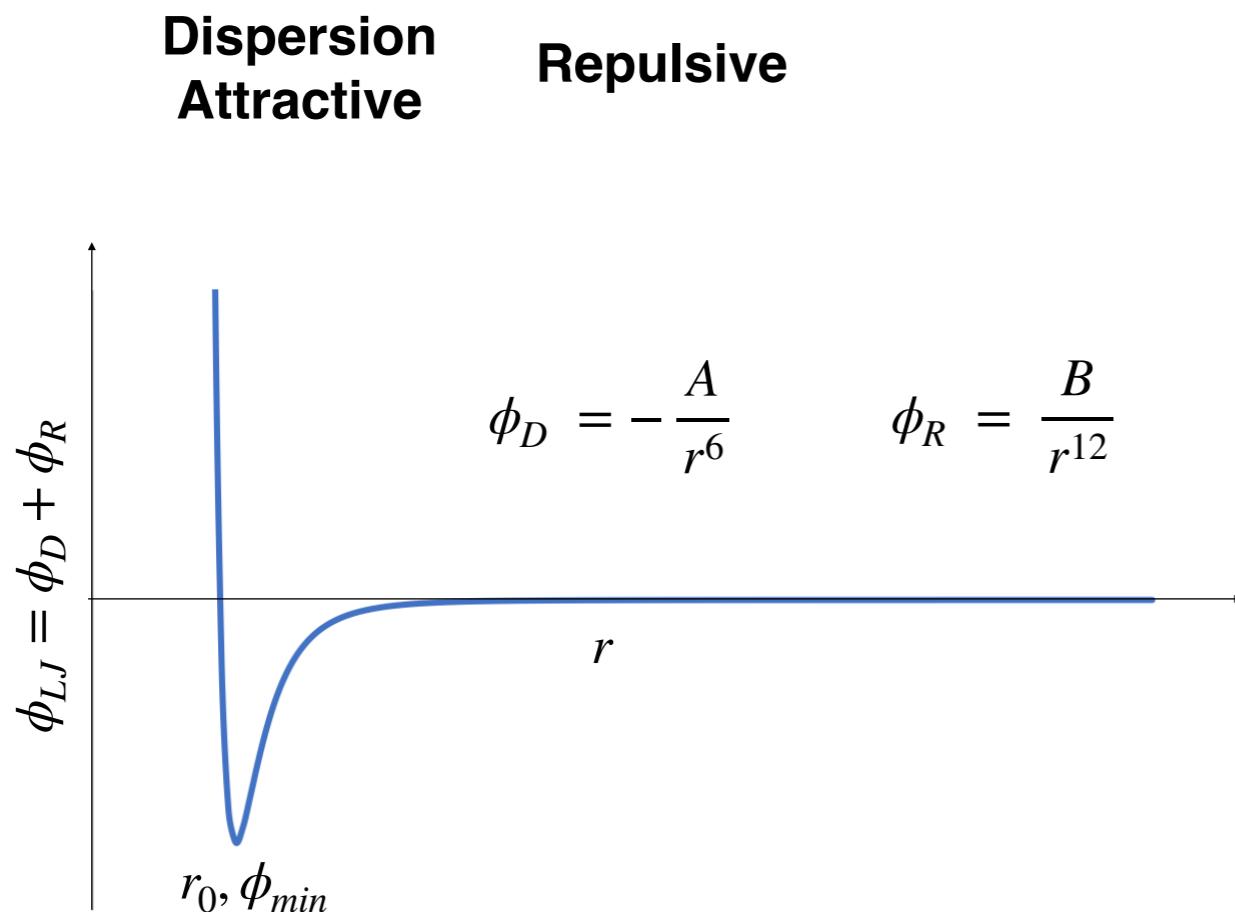
## **Chemisorption**

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

# Understanding physisorption

## Adsorbate-adsorbent interaction potential

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



By minimizing at  $r_0$

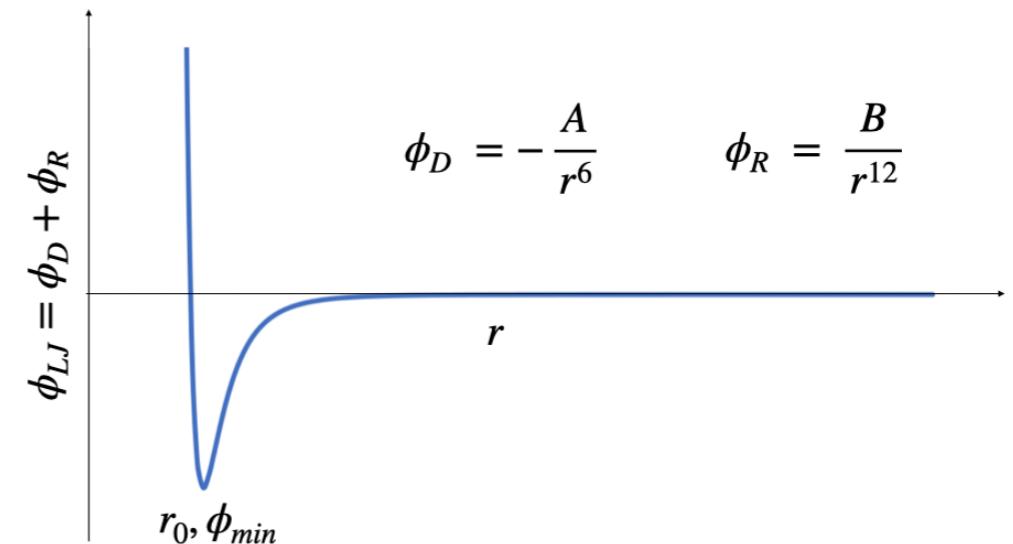
$$B = A \frac{r_0^6}{2}$$

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

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

$\alpha_i$  = polarizability of the  $i^{\text{th}}$  atom

$\chi_i$  = magnetic susceptibility

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

Atom	$\alpha$	Atom	$\alpha$	Atom	$\alpha$
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 <sup>+</sup>	0.029
S	2.90	Ca	22.8	Na <sup>+</sup>	0.180
Cl	2.18	Sr	27.6	K <sup>+</sup>	0.840
Br	3.05	Ba	39.7	Ca <sup>2+</sup>	0.471
I	5.35	Al	6.8	Sr <sup>2+</sup>	0.863
		Si	5.38	Ba <sup>2+</sup>	1.560
Li	24.3	Fe	8.4		
Na	24.08				

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

Periodic Table of the Elements																																																																																								
1 IA 1A		Periodic Table of the Elements														18 VIIA 1A																																																																								
1 H Hydrogen 1.008	2 IIA 2A															13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	2 He Helium 4.003																																																																			
3 Li Lithium 6.941	4 Be Boron 9.012															13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	2 He Helium 4.003																																																																			
11 Na Sodium 22.990	12 Mg Magnesium 24.312	3 B Boron 9.012	4 NB Boron 9.012	5 VB Boron 9.012	6 VIB Boron 9.012	7 VIIIB Boron 9.012	8 VIII Boron 9.012	9 VIIIA Boron 9.012	10 VIIIA Boron 9.012	11 IB Boron 9.012	12 IB Boron 9.012	13 IB Boron 9.012	14 VA Boron 9.012	15 VIA Boron 9.012	16 VIA Boron 9.012	17 VIIA Boron 9.012	18 VIIA Boron 9.012	19 K Potassium 39.098	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.86	23 V Vanadium 50.94	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.847	27 Co Cobalt 58.931	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.40	31 Ga Gallium 69.721	32 Ge Germanium 72.61	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80	37 Rb Rubidium 84.998	38 Sr Strontium 87.62	39 Y Yttrium 88.902	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 95.94	44 Ru Ruthenium 95.94	45 Rh Rhodium 95.94	46 Pd Palladium 95.94	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.904	54 Xe Xenon 131.33	55 Cs Cesium 132.90	56 Ba Barium 137.367	57-71 57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.85	75 Re Rhenium 186.20	76 Os Osmium 190.23	77 Ir Iridium 192.20	78 Pt Platinum 190.98	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.20	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium 209.98	85 At Astatine 209.97	86 Rn Radium 226.02	87 Fr Francium 223.02	88-103 88-103	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Sodium-90 263	107 Bh Berkelium 264	108 Hs Hassium 265	109 Mt Mendelevium 268	110 Ds Darmstadtium 281	111 Rg Roentgenium 282	112 Cn Copernicium 285	113 Uut Ununtrium 287	114 Fl Florium 289	115 Uup Ununpentium 291	116 Lv Livermorium 293	117 Uus Ununseptium 294	118 Uuo Ununoctium 295
Lanthanide Series		57 La Lanthanum 138.905	58 Ce Cerium 138.91	59 Pr Praseodymium 138.91	60 Nd Neodymium 140.91	61 Pm Promethium 141.91	62 Sm Samarium 144.91	63 Eu Europium 147.91	64 Gd Gadolinium 157.26	65 Tb Terbium 158.925	66 Dy Dysprosium 162.93	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.93	71 Lu Lutetium 174.93																																																																								
Actinide Series		89 Ac Actinium 227.02	90 Th Thorium 232.03	91 Pa Protactinium 231.03	92 U Uranium 231.03	93 Np Neptunium 231.03	94 Pu Plutonium 234.034	95 Am Americium 243.031	96 Cm Curium 243.031	97 Bk Berkelium 247.031	98 Cf Californium 251.031	99 Es Einsteinium 252.031	100 Fm Fermium 257.031	101 Md Mendelevium 258.031	102 No Nobelium 259.031	103 Lr Lawrencium 258.031																																																																								

**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

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

At room temperature

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

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

$\Delta H$  can be estimated by microcalorimetry, and therefore,  $\phi$  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**

$$\phi_{induced} = -\frac{1}{2}\alpha F^2 = -\frac{\alpha q^2}{2r^4(4\pi\epsilon_0)^2}$$

$q$  = electronic charge of ion on surface

$\epsilon$  = permittivity of vacuum

$\mu$  = permanent dipole moment

$\theta$  = angle between field (or field gradient)

and the axis of dipole (or linear quadrupole)

$$\phi_{F\mu} = -F\mu \cos \theta = -\frac{q\mu \cos \theta}{r^2(4\pi\epsilon_0)}$$

$$\phi_{\dot{F}\mu} = \frac{1}{2}Q\dot{F} = -\frac{Qq(3\cos^2 \theta - 1)}{4r^3(4\pi\epsilon_0)}$$

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

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

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

Sorbent	Sorbate*	$\alpha \times 10^{24}$ cm <sup>3</sup> /molec.	$-\Delta H$	$-(\phi_D + \phi_R + \phi_{Ind})^{**}$	$-(\phi_{F\mu} + \phi_{FQ})$
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 <sub>2</sub>	1.74	8.98	6.45	2.55
	N <sub>2</sub> O	3.03	15.3	9.07	6.18
	NH <sub>3</sub>	2.2	31.5	7.5	23.8
Na-Mordenite	N <sub>2</sub>	1.74	7.0	4.5	2.50
	CO <sub>2</sub>	2.91	15.7	6.73	8.93
Na-X	N <sub>2</sub>	1.74	6.5	3.10	3.4
	CO <sub>2</sub>	2.91	12.2	4.20	7.98
	NH <sub>3</sub>	2.2	17.9	3.75	14.2
	H <sub>2</sub> O	1.45	≈33.9	2.65	≈31.3

\*Permanent dipole moments ( $\mu$ , debye): N<sub>2</sub>O = 0.161, NH<sub>3</sub> = 1.47, H<sub>2</sub>O = 1.84, all others = 0. Quadrupole moments (Q, erg<sup>1/2</sup> cm<sup>5/2</sup> × 10<sup>26</sup>): N<sub>2</sub> = -1.5, N<sub>2</sub>O = -3.0, NH<sub>3</sub> = -1.0, CO<sub>2</sub> = -4.3, all others ≈ 0.

\*\*For graphitized carbon,  $\phi_{Ind} = 0$ .

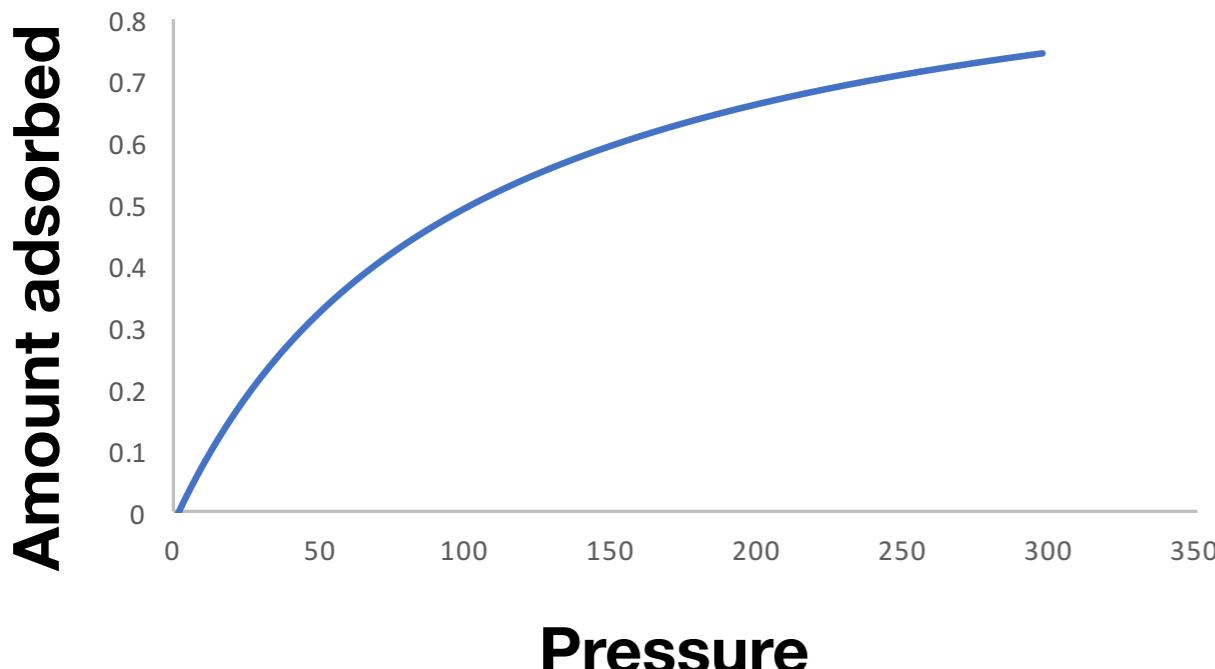
Experimental,  $-\Delta H$ , kcal/mol (Barrer, 1978; Ross and Olivier, 1964).

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)

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

$\theta$  is site occupancy

K is the equilibrium constant for adsorption

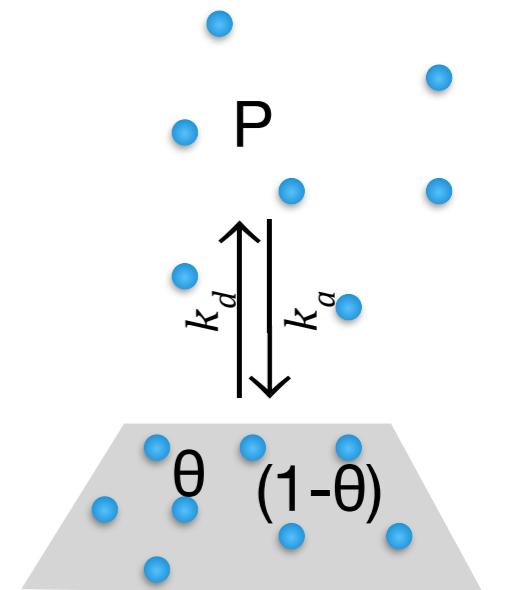
P is pressure

# Langmuir isotherm

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

At equilibrium, rate of adsorption = rate of desorption

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



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

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

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

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

# Langmuir isotherm

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

At low pressure

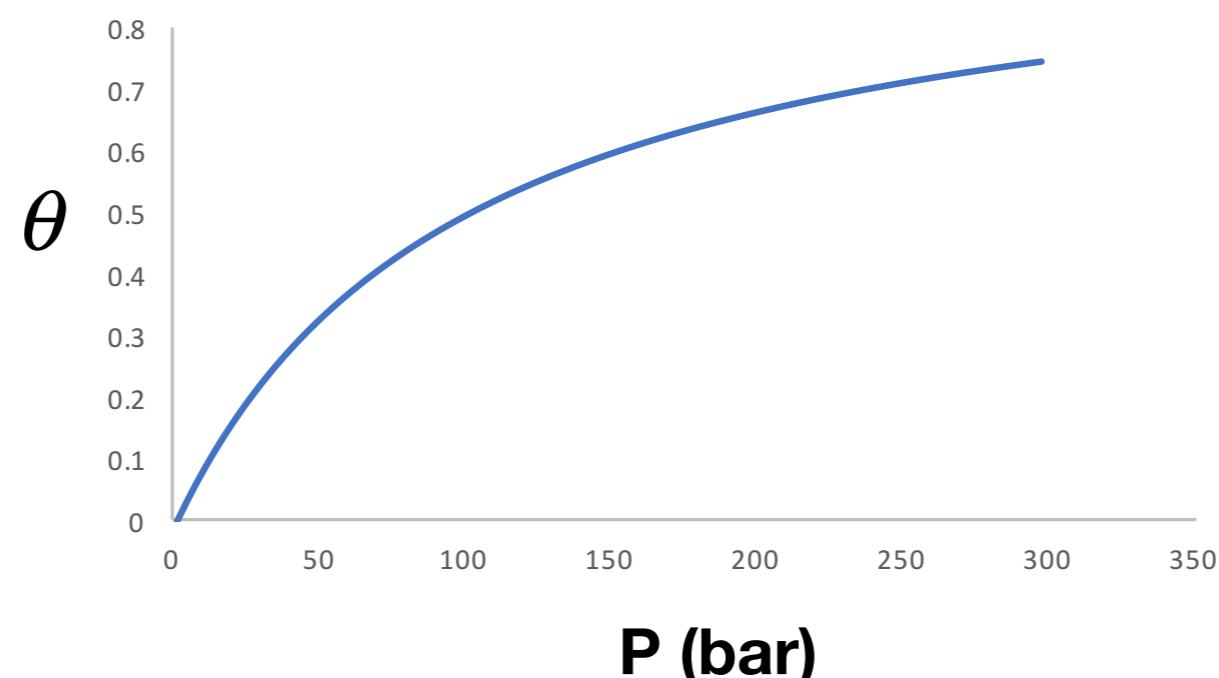
$$1+KP \approx 1$$

$$\theta = KP$$

At high pressure

$$1+KP \approx KP$$

$$\theta = 1$$



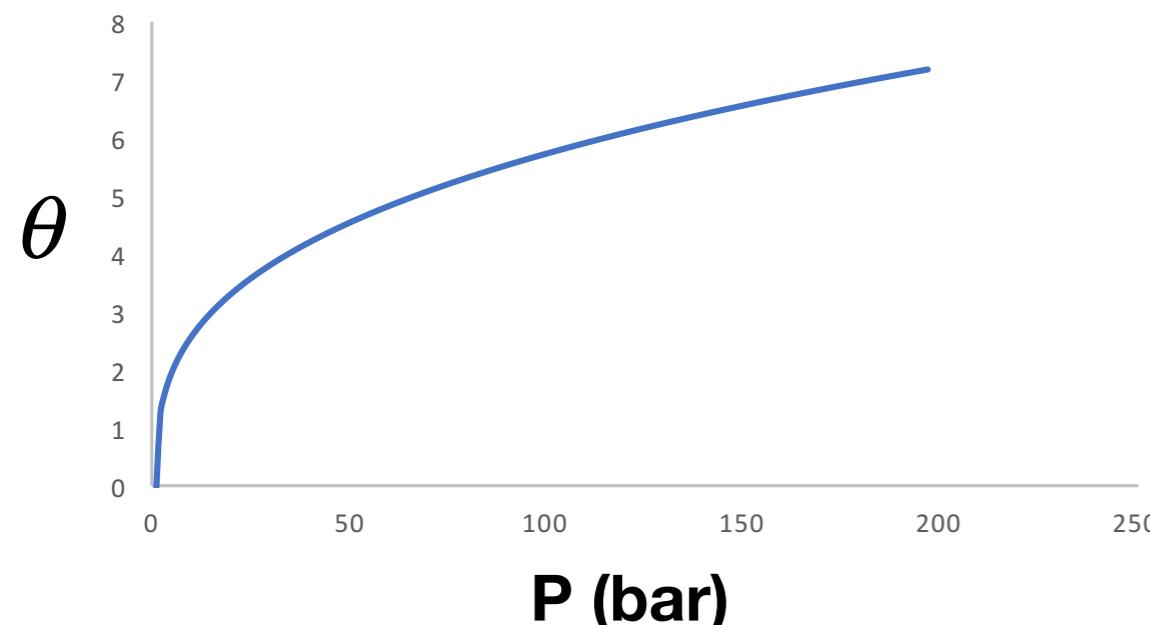
# Freundlich isotherm

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

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

- 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.

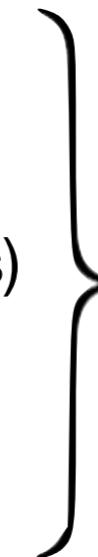
## Several other isotherms

# Some examples

<i>Adsorbate</i>	<i>Carrier</i>	<i>Adsorbent</i>	<i>Form</i>
<i>Gas Systems</i>			
Methane	None	Activated carbon	~ Langmuir
Methane	Helium	5A zeolite	Linear
Methane	H <sub>2</sub> , N <sub>2</sub> , CO <sub>2</sub>	BPL activated carbon	Langmuir
Nitrogen	None	5A zeolite	Linear
<i>Liquid Systems</i>			
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 <sup>+2</sup> 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**