

## Chapter 5

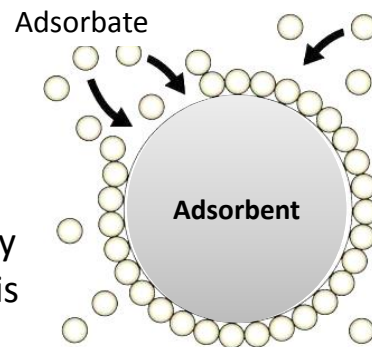
### Separation of Gases

- Adsorption
- Absorption

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### Adsorption

- The process by which gas is attracted to the **surfaces** of a solid or liquid and consequently separated from the air stream is referred to as **ad**sorption
- It takes place at the **interface** of the **adsorbent** and **adsorbate**
  - Adsorbent is the adsorbing material (e.g. A.C.)
  - Adsorbate is the gas being separated from the air stream.



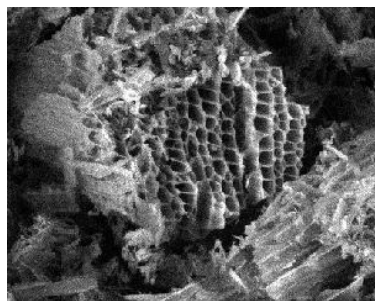
## Common Physical Adsorbents

- **Activated carbon** - a char-like material with high surface area.
- **Silica gel** - hard, granular, porous material made by precipitation from sodium silicate solutions treated with an acid.
- **Activated alumina** - aluminum oxide activated at high temperature and used primarily for moisture adsorption.
- **Aluminosilicates (molecular sieves)** - porous synthetic zeolites used primarily in separation processes.

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## Activated Carbon

- The most common adsorbent.
- Pore sizes: 10 - 10,000 Å in diameter.
  - Macropores: > 1000 Å
  - Micropores: <1000 Å
- Surface areas: 500-1500 m<sup>2</sup>/g



1 Angstrom (Å)=0.1 nm)

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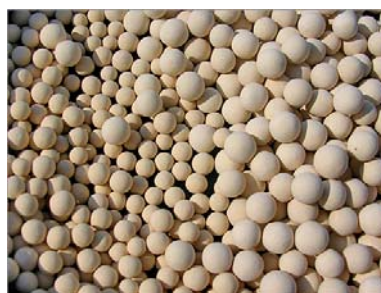
## Bulk Sizes of AC Particles

- Bulk dry density of granular AC: 0.22-0.5 kg/L.
- Bulk dry density powder AC: 0.34-0.74 kg/L.
- Real density: 2-2.1 kg/L.
- **Granules:** in millimeters.
  - Packed bed column
  - Easy regeneration
- **Powders:** in the order of tens of micrometers
  - need carrier
  - Disposable
- Bulk sizes of the AC particles do not affect maximum adsorption capabilities
- Affects the time to achieve equilibrium significantly.

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## Molecular Sieve

- a molecular sieve with pore diameter of 30 **Angstrom (1 Å=0.1 nm)** can adsorb light gases, such as NH<sub>3</sub> and H<sub>2</sub>O.
- a molecular sieve with pore diameter of 30 Å can adsorb light gases, such as NH<sub>3</sub> and H<sub>2</sub>O.
- when the diameter of the pores is increased to 40 Å, the sorbent is more effective on larger molecules such as CO<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>S.



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## Basics of Adsorption

- **Transport by diffusion** of gas molecules on to the surface of adsorbent pores
  - Larger AC particles means longer transport time to the deep pores
  - Large molecules may be too large to enter small pores. This may reduce adsorption.
- **Capture by affinity**
  - **Adsorbent affinity** is the attraction between the adsorbent and the adsorbate and it is a critical parameter for successful adsorption processes.
  - Affinities can be designed by adjusting the pore diameters of the adsorbent.

*Both the surface area of the adsorbent and the affinity of the adsorbent for the adsorbate affect adsorption efficiency.*

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## Adsorption Equilibrium

- An equilibrium is reached when a relationship exists between the concentration of the species in air and the amount of adsorbate in adsorbed per unit mass of adsorbent).
  - (Similar to Henry's Law? – think about it at molecular level)
- The adsorption equilibrium is a function of the temperature.
  - (How can temperature affect the adsorption?)

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## Adsorption Isotherm

- An adsorption isotherm is a relationship of adsorbent capability versus the adsorbate concentration at a **given temperature**.

$$M_{eq} = f(C)$$

– useful for design of adsorption systems.

- Typically equilibrium adsorption  $M_{eq}$  can be measured (*e.g. gram of adsorbate adsorbed per gram of adsorbent at equilibrium*), (kg adsorbate/kg adsorbent), while C can be  $\text{kg/m}^3$

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## Theoretical Isotherm

### 1. Langmuir Isotherm

- Assumptions
  - ❖ the adsorbed layer is made up of a single layer of molecules
  - ❖ adsorption is a reversible process
  - ❖ **The process is dynamic: the adsorbed molecules do not move on the surface of the adsorbent, but they may reenter the air stream**
  - ❖ the enthalpy of adsorption is the same for all molecules independently of how many have been adsorbed



The Nobel Prize in  
Chemistry 1932  
Irving Langmuir

[http://www.nobelprize.org/nobel\\_prizes/chemistry/laureates/1932/](http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1932/) 10

## Langmuir model (1918)

- At equilibrium the number of molecules being adsorbed will be equal to the number of molecules leaving the adsorbed state, i.e.

*Rate of adsorption = rate of desorption*

$$k_1 C (M_{max} - M_{eq}) = k_2 M_{eq}$$

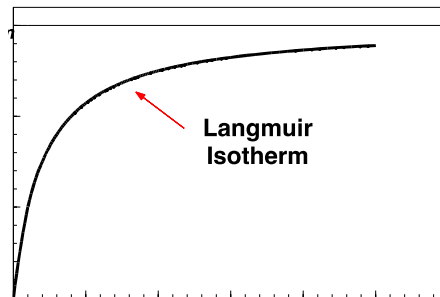
- Solve for  $M_{eq}$

$$\frac{M_{eq}}{M_{max}} = \frac{k_1 C}{k_1 C + k_2}$$

Define a new constant

$$K_L = k_1/k_2$$

$$\frac{M_{eq}}{M_{max}} = \frac{K_L C}{1 + K_L C}$$



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## Experimental Determination of Parameters in Langmuir Isotherm

- The Langmuir isotherm can be rearranged

$$M_{eq} = \frac{K_L C M_{max}}{1 + K_L C} \Rightarrow \left( \frac{C}{M_{eq}} \right) = \left( \frac{1}{M_{max}} \right) C + \left( \frac{1}{K_L M_{max}} \right)$$

- $C/M_{eq}$  vs.  $C$  is a linear relationship with  
Slope:  $1/M_{max}$  Intercept:  $1/K_L M_{max}$

OR 
$$M_{eq} = \frac{K_L C M_{max}}{1 + K_L C} \Rightarrow \left( \frac{1}{M_{eq}} \right) = \left( \frac{1}{M_{max}} \right) + \left( \frac{1}{K_L M_{max}} \right) \frac{1}{C}$$

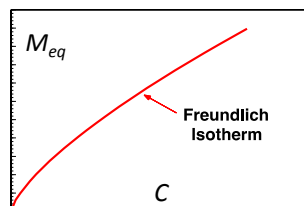
- $1/M_{eq}$  vs.  $1/C$  is a linear relationship with
  - Slope:  $1/K_L M_{max}$
  - Intercept:  $1/M_{max}$

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## 2. Freundlich Isotherm

$$M_{eq} = K_F C^{\frac{1}{n}}$$

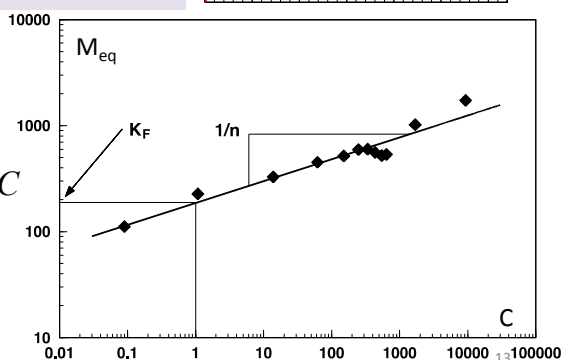
- An **empirical** equation
  - $K_F$  = constant (function of energy of adsorption and T)
  - $n$  = constant



- Determination of constants

$$M_{eq} = K_F C^{\frac{1}{n}}$$

$$\Rightarrow \log M_{eq} = \log K_F + \frac{1}{n} \log C$$



## Langmuir vs. Freundlich Isotherm

- The Langmuir isotherm is an empirical model with some theoretical basis.
- The Freundlich isotherm is an empirical model
- The Langmuir isotherm assumes reversible adsorption and desorption of the adsorbate molecules.
- No assumption is made for the Freundlich isotherm
- The Langmuir isotherm works well for typical single components, and high concentration
- The Freundlich isotherm can be used for mixtures of compounds and low concentration**

## Adsorption with Activated Carbon

$$\log M_{eq} = \log K_F + \frac{1}{n} \log C$$

Data for the adsorption of VOCs using activated carbon

- Empirical formula (Freundlich Isotherm) extended by Yaws et al. (1995)

$$\log_{10} M_{eq} = a + b \log_{10} C + d (\log_{10} C)^2$$

*a, b and d are coefficients are determined experimentally*

$M_{eq}$  is the adsorption capacity at equilibrium, in grams of adsorbate (VOC) **per 100 grams of adsorbent** (activated carbon),

$C$  = the concentration of VOC in the gas stream in **ppmv**

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**Table 5.4 /A.6** The values of coefficients *a*, *b*, and *d*

Formula	Name	<i>a</i>	<i>b</i>	<i>d</i>
CH <sub>4</sub>	Methane	-4.31008	0.77883	-0.00628
C <sub>2</sub> H <sub>6</sub>	Ethane	-2.40393	0.68107	-0.01925
C <sub>2</sub> H <sub>4</sub>	Ethylene	-2.27102	0.61731	-0.01467
C <sub>2</sub> H <sub>2</sub>	Acetylene	-2.24177	0.82454	-0.03390
C <sub>3</sub> H <sub>4</sub>	Methylacetylene	-2.52865	1.74715	-0.21635
C <sub>3</sub> H <sub>6</sub>	Propylene	-0.93674	0.57775	-0.03853
C <sub>3</sub> H <sub>8</sub>	Propane	-0.79460	0.49029	-0.02398
C <sub>4</sub> H <sub>10</sub>	n-Butane	0.03071	0.34304	-0.01596
C <sub>4</sub> H <sub>10</sub>	Isobutane	-0.01676	0.33495	-0.01274
CO	Carbon monoxide	-5.18782	0.90121	-0.01358
CO <sub>2</sub>	Carbon dioxide	-3.65224	0.80180	-0.00328
CS <sub>2</sub>	Carbon disulfide	-0.18899	0.47093	-0.01481
CH <sub>2</sub> O	Formaldehyde	-2.48524	0.69123	-0.00375

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## Example

In an automobile assembling shop, the concentration of *n*-butanol ( $C_4H_{10}O$ ) in the room air is 5 ppmv. The density of *n*-butanol is  $3.06 \text{ kg/m}^3$  under standard room air conditions.



A carbon filter bed is used for air cleaning, and the airflow rate is  $0.1 \text{ m}^3/\text{s}$  through the filter.

Determine the following:

- The equilibrium adsorption capacity of an activated carbon filter
- The total carbon mass needed for the bed, assuming the working adsorption capacity is 40% of the saturated adsorption and the bed service life is one year

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## Solution

$$\log_{10} M_{eq} = a + b \log_{10} C + d(\log_{10} C)^2$$

From Table 5-4, we have the adsorption constants of  $C_4H_{10}O$ :

$$a = 0.89881, b = 0.32534, d = -0.03648$$

Then we have

Formula	Name	a	b	d
$C_4H_{10}O$	n-Butanol	0.89881	0.32534	-0.03648

$$\begin{aligned} \log_{10} M_{eq} &= a + b \log_{10} C + d(\log_{10} C)^2 \\ &= 0.89881 + 0.32534 \log_{10}(5) - 0.03648[\log_{10}(5)]^2 \\ &= 0.89881 + 0.2274 - 0.0178 \\ &= 1.1084 \end{aligned}$$

$$M_{eq} = 10^{1.1084} = 12.8 \quad (\text{gram of } C_4H_{10}O \text{ per } 100 \text{ gram of carbon})$$

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- **The total amount of n-butanol passing through the carbon bed in one year is**

$$\begin{aligned}
 M &= QC\rho_g t \\
 &= 0.1 \frac{\text{m}^3 \text{ air}}{\text{s}} \times 0.000005 \frac{\text{m}^3 \text{ VOC}}{\text{m}^3 \text{ air}} \times 3.05 \frac{\text{kg}}{\text{m}^3 \text{ VOC}} \times (365 \times 24 \times 3600) \text{s} \\
 &= 48.1 \text{ kg}
 \end{aligned}$$

**The actual carbon mass needed is**

$$\begin{aligned}
 M_{\text{carbon}} &= \frac{M}{M_{\text{eq}}} \times \frac{100}{40} \\
 &= \frac{48.1 \text{ kg of } C_4H_{10}O}{0.128 \text{ kg of } C_4H_{10}O \text{ per kg of carbon}} \times \frac{100}{40} \\
 &= 939.5 \text{ kg of carbon}
 \end{aligned}$$

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## Simplified formula

- For many engineering processes, the term  $(\log_{10}C)^2$  in the equation is negligible

$$\log_{10}M_{\text{eq}} = a + b \log_{10}C + \cancel{d(\log_{10}C)^2}$$

$$\log_{10}M_{\text{eq}} = a + b \log_{10}C + d(\log_{10}C)^2$$

$$= 0.89881 + 0.32534 \log_{10}(5) - 0.03648[\log_{10}(5)]^2$$

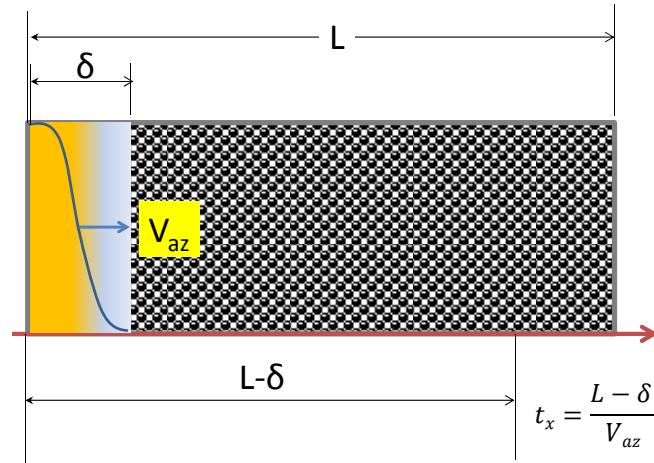
$$= 0.89881 + 0.2274 \quad \mathbf{-0.0178}$$

$$= 1.1084$$

Ignoring the third term results in a difference of <1.6%

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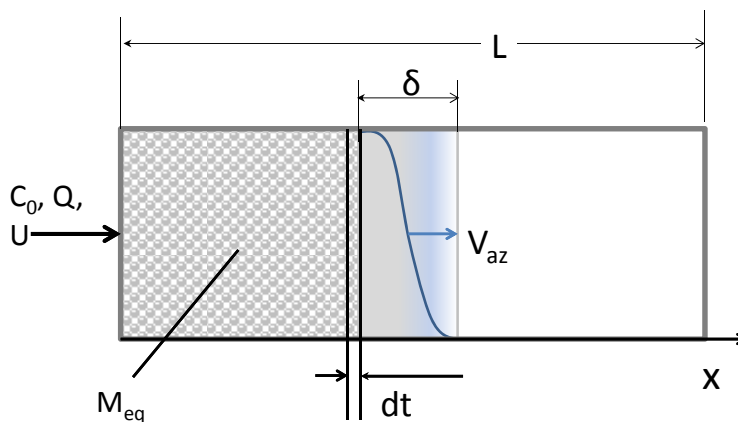
## Adsorption Wave



The wave could be steep or quite flat, depending on various factors including the adsorption capacity of the adsorbent, the flow rate, and the retention time of the flue gas stream.

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## Adsorption Wave Model



*Adsorbate mass entering bed  
= mass of adsorbate captured in the active zone*

$$QC_0 dt = M_{eq} (\rho_s AV_{az}) dt$$

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$$QC_0 = M_{eq}(\rho_s AV_{az})$$

$C_0$  = Mass concentration in air (kg adsorbate/m<sup>3</sup> air)

- **Not C in ppmv**

Q = Volumetric flow rate of the air (m<sup>3</sup> air /s)

$M_{eq}$  = equilibrium adsorption capacity (kg adsorbate/kg adsorbent)

- **Not  $M_{eq}$  in kg/100 kg AC**

$\rho_s$  = Density of the adsorbent (kg/m<sup>3</sup>)

A = Cross-sectional area of the adsorption column (m<sup>2</sup>)

$V_{az}$  = moving speed of the wave (m/s)

- In engineering practice where the specifications of the adsorption column and operation conditions are known, one can obtain the values of  $\rho_s, A, Q$  and  $C_0$

$$V_{az} = \frac{QC_0}{M_{eq}\rho_s A}$$

- $M_{eq}$  is required in order to solve the above equation for the wave speed  $V_{az}$

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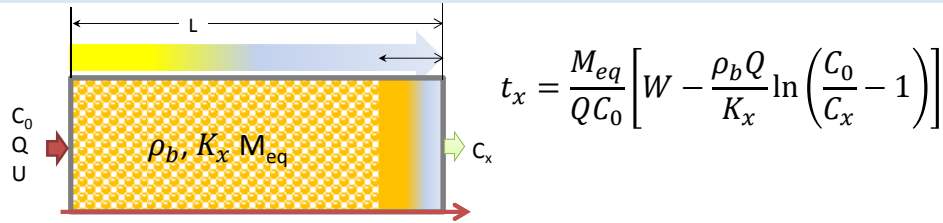
## Break through point or Break point



- **Almost** the entire adsorbent bed reaches equilibrium as the wave approaches the exit of the column.
- Then the penetration concentration will be greater than expected.
- **Breakthrough point** can also be defined as the ratio of the outlet to inlet concentrations, depending on the application and the threshold limits of allowable pollutant emission standards.
  - For many toxic chemicals, a measurable concentration at the exit, even if it is less than 1% of the inlet concentration, can be defined as the break point.

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### Wheeler equation for breakthrough time



$$t_x = \frac{M_{eq}}{QC_0} \left[ W - \frac{\rho_b Q}{K_x} \ln \left( \frac{C_0}{C_x} - 1 \right) \right]$$

$t_x$  = break through time (s)

$M_{eq}$  = adsorption capacity (g/g)

$C_0$  = inlet concentration (g/m<sup>3</sup>)

$W$  = weight of the adsorbent (g)

$\rho_b$  = bulk density of the packed adsorbent (g/m<sup>3</sup>)

$Q$  = gas phase volumetric flow rate (m<sup>3</sup>/s)

$K_x$  = mass transfer rate coefficient (1/s)

$C_x$  = exit concentration (g/m<sup>3</sup>).

This exit concentration is determined based on local emissions standard or air quality requirement.

### Example: Breakthrough time

If we have  $M_{eq} = 0.0128$  (kg VOC/kg AC),

$C_0 = 1.53 \times 10^{-5}$  (kg VOC/m<sup>3</sup>),  $Q = 0.1$  (m<sup>3</sup>/s),

$\rho_b = 400$  kg AC/m<sup>3</sup>.

- Now the mass transfer coefficient of the adsorbent  $K_x = 20$  s<sup>-1</sup>. The cross-sectional area of the bed is 1 m<sup>2</sup>. The designed adsorption efficiency is  $\eta_x = 0.9$ . That is, the breakthrough point of the bed is considered to be when the outlet *n*-butanol concentration reaches 10% of the inlet concentration.
- **Determine the length of the bed if the bed is to be regenerated or replaced every two months (assuming 60 days).**

## Solution

First we convert the breakthrough time unit from months to seconds.  $t_x = 60 \times 24 \times 3600 \text{ s} = 5,184,000 \text{ s}$

The weight of activated carbon in the filter as

$$\begin{aligned}
 W &= \frac{QC_0 t_x}{M_{eq}} + \frac{\rho_b Q}{K_x} \ln\left(\frac{\eta_x}{1 - \eta_x}\right) \\
 &= \frac{0.1(\text{m}^3/\text{s}) \times (1.53 \times 10^{-5} \text{ kg}/\text{m}^3) \times (5.184 \times 10^6 \text{ s})}{0.0128 \text{ (kg/kg)}} \\
 &\quad + \frac{(400 \text{ kg}/\text{m}^3) \times 0.1(\text{m}^3/\text{s})}{20 \text{ s}^{-1}} \ln\left(\frac{0.9}{0.1}\right) \\
 &= 619.65 \text{ (kg)} + 4.39 \text{ (kg)} = 624 \text{ kg}
 \end{aligned}$$

So, the needed length of the filter bed is

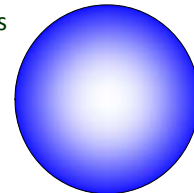
$$L = \frac{W}{A\rho_b} = \frac{624 \text{ kg}}{1 \text{ m}^2 \times 400 \text{ kg}/\text{m}^3} = 1.56 \text{ m}$$

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## ABsorption

- Absorption is a volumetric process where gases penetrate into the structure of the solid or liquid
- most likely by diffusion
- The absorption process involves a mass transfer by means of molecular and turbulent diffusion governed by Henry's law.

Gas molecules  
 $\text{SO}_2$



$$p_i = Hx_i$$

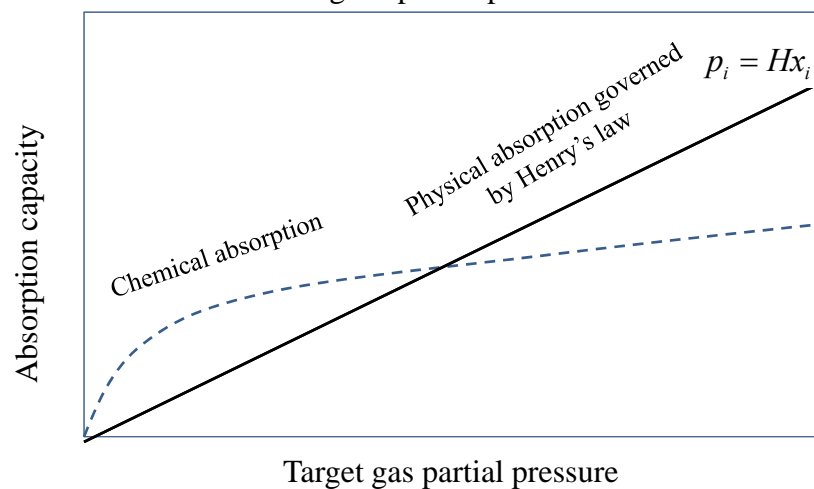
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## Absorption for Air Pollution Control

- Physical absorption and chemical absorption
- Physical absorption is a diffusional mass-transfer operation by which a soluble gaseous component is removed from a gas stream by dissolution in a liquid.
- Absorption is one of the most frequently used methods for removal of water-soluble gases.
- Acidic gases such as HCl can be absorbed in water efficiently and readily, especially if the last contact is made with water that has been made alkaline.
- Chemical absorption for acidic gases: Less soluble acidic gases such as SO<sub>2</sub> and H<sub>2</sub>S can be absorbed more readily in a dilute caustic solution.

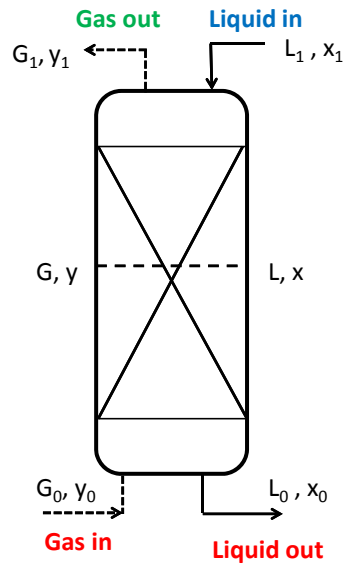
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Relative solvent loading vs. partial pressure of the absorbate gas



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## Countercurrent Absorption Model



- Mass balance around a cross-section through the tower  
*out of gas into liquid*

$$d(Gy) = d(Lx)$$

Integration from this point to top (1) gives

$$yG - y_1G_1 = xL - x_1L_1$$

- $L, G$ : mole flow rates (e.g. mole/s) - mixture
- $x, y$ : mole fractions in liquid and gas respectively
- 0: Bottom; 1: Top

## Simple mass balance

$$yG - y_1G_1 = xL - x_1L_1$$

- Gas phase include carrier gas and the soluble gas

$$(G = \bar{G} + x_A G)$$

☐ 1 mole of  $SO_2$  mixed with 9 moles of air

☐  $G = 10$  moles,  $G_B = 9$  moles and  $x_{SO_2} = 0.10$

- Similar to liquid phase: ( $L = \bar{L} + y_A L$ )

☐ 1 mole of  $SO_2$  dissolved in 9 moles of water

☐  $L = 10$  moles,  $L_B = 9$  moles and  $y_{SO_2} = 0.10$

- $\bar{G}$  and  $\bar{L}$  remain constant

$$G = \frac{\bar{G}}{1 - y}$$

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



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

Then  $yG - y_1G_1 = xL - x_1L_1$  becomes

$$\left(\frac{y}{1-y}\right)\bar{G} + \left(\frac{x_1}{1-x_1}\right)\bar{L} = \left(\frac{x}{1-x}\right)\bar{L} + \left(\frac{y_1}{1-y_1}\right)\bar{G}$$

↑ In gas
 ↑ In liquid

Applying this equation to the entire process from bottom (0) to top (1),

$$\left(\frac{y_0}{1-y_0} - \frac{y_1}{1-y_1}\right)\bar{G} = \left(\frac{x_0}{1-x_0} - \frac{x_1}{1-x_1}\right)\bar{L}$$

**General**

$$\left(\frac{y}{1-y}\right)\bar{G} + \left(\frac{x_1}{1-x_1}\right)\bar{L} = \left(\frac{x}{1-x}\right)\bar{L} + \left(\frac{y_1}{1-y_1}\right)\bar{G}$$

**A Special Case:**  
Diluted Solution and Low-concentration air pollutant

$$\begin{aligned} 1-x &= 1 \\ 1-y &= 1 \end{aligned}$$

$$\frac{\bar{L}}{\bar{G}} = \frac{(y - y_1)}{(x - x_1)}$$

Apply this equation to the entire process, from 0 to 1

**Liquid-gas flow ratio**  $\frac{\bar{L}}{\bar{G}} = \frac{(y_0 - y_1)}{(x_0 - x_1)}$  **NOTE: For dilute solution case**

### Example 1 (L/G ratio)

- A mixture of air and H<sub>2</sub>S is forced to pass through a single-stage counter flow water absorption scrubber.
- The inlet molar fraction of H<sub>2</sub>S in air is 50 ppmv. And outlet being 10 ppmv. Outlet H<sub>2</sub>S in water is 20 ppmv.
- The total pure air flow rate into the scrubber is 80 moles/s
- What is the pure water flow rate into the scrubber?

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$$\frac{\bar{L}}{\bar{G}} = \frac{(y_0 - y_1)}{(x_0 - x_1)}$$

$x_1 = 0$  (mole H<sub>2</sub>S/mole in fresh water)

$x_0 = 20 \times 10^{-6}$  (mole H<sub>2</sub>S/mole in fresh water)

$y_0 = 50 \times 10^{-6}$  (mole H<sub>2</sub>S/mole incoming air)

$y_1 = 10 \times 10^{-6}$  (mole H<sub>2</sub>S/mole incoming air)

$G = 80$  (mole air/s)

$$\frac{L}{80} = \frac{50 - 10}{20 - 0}$$

$L = 160$  (mole water/s)

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## Example 2. Performance evaluation

- A mixture of air and H<sub>2</sub>S is forced to pass through a single-stage counter flow water absorption scrubber.
- The inlet molar fraction of H<sub>2</sub>S in air is 50 ppmv.
- The total pure airflow rate into the scrubber is 80 moles/s and the pure water flow rate into the scrubber is 10 moles/s.
- Assuming that the gas-water system is at an equilibrium state, the temperature is 30 °C, and the atmospheric pressure is 101,325 Pa
- Find the mole fraction of H<sub>2</sub>S in gas phase at the exist.
- Assume that the system within the two is air-H<sub>2</sub>S for gas and water-H<sub>2</sub>S for liquid phases.

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### Solution 1

$$\frac{\bar{L}}{\bar{G}} = \frac{(y_0 - y_1)}{(x_0 - x_1)}$$

- Since it is a dilute solution, H<sub>2</sub>S in water is very low, the flow rate of water can be considered constant  
 $\bar{L}=10$  (mole water/s)
- Since pure water is used at the inlet  
 $x_1=0$  (mole H<sub>2</sub>S/mole water)
- The mole fraction of H<sub>2</sub>S in gas phase at inlet is 50 ppmv  
 $y_0=0.00005$  (mole H<sub>2</sub>S/mole air)
- The pure air flow rates at both inlet and exist of the scrubber:

$$\bar{G}=80 \text{ (mole air/s)}$$

$$8y_1 + x_0 = 0.0004$$

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$$8y_1 + x_0 = 0.0004$$

Two unknowns one equation. Need one more equation or one variable determined by other means

Assumed equilibrium state

Since H<sub>2</sub>S concentration is very low (<5%), Henry's Law applies to the bottom of the system

$$Py_1 = Hx_0$$

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## Henry's Law

$$H = \frac{\text{Partial pressure of gas in air}}{\text{Gas mole fraction in water}} = \frac{y_1 P_{total}}{x_0}$$

Temperature (°C)	$H$ ( $10^6 \text{ Pa} / \text{molar fraction of the system}$ )									
	CO <sub>2</sub>	CO	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	He	H <sub>2</sub>	H <sub>2</sub> S	CH <sub>4</sub>	N <sub>2</sub>	O <sub>2</sub>
0	72.8	3520	1260	552	12900	5790	26.8	2240	5290	2550
10	204	4420	1890	768	12600	6360	36.7	2970	6680	3270
20	142	5360	2630	1020	12500	6830	48.3	3760	8040	4010
30	186	6200	3420	1270	12400	7290	60.9	4490	9240	4750
40	233	6960	4230		12100	7510	74.5	5200	12400	5350

$$H = 60.9 \times 10^6 \text{ Pa /mole fraction in water}$$

$$(101,325)(50 \times 10^{-6}) = (60.9 \times 10^6)x_0$$

$$x_0 = 8.32 \times 10^{-8}$$

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Now two unknowns with two equations

$$8y_1 + x_0 = 0.0004$$

$$x_0 = 8.32 \times 10^{-8}$$

$$\Rightarrow y_1 \approx 50 \text{ ppmv} = y_0$$

### Comment

- Equilibrium state within the system does not allow absorption
- We cannot use the assumption of equilibrium to design an absorption process

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### Back to the general equation

$$\left(\frac{y}{1-y}\right)\bar{G} + \left(\frac{x_1}{1-x_1}\right)\bar{L} = \left(\frac{x}{1-x}\right)\bar{L} + \left(\frac{y_1}{1-y_1}\right)\bar{G}$$

Define: Mole ratios  $X, Y$

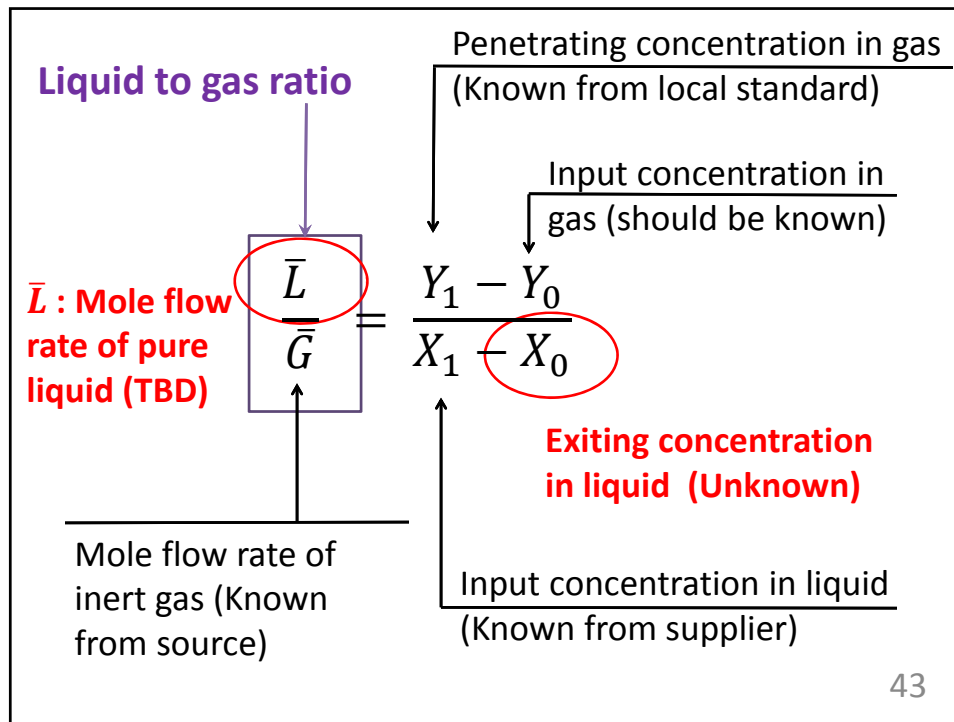
$$X = \frac{x}{1-x} = \frac{\text{Mole of target gas to be absorbed}}{\text{Mole of inert carrier liquid}}$$

$$Y = \frac{y}{1-y} = \frac{\text{Mole of target gas}}{\text{Mole of inert gas}}$$

- Note:  $x, y$  are mole fractions

$$(Y_0 - Y_1)\bar{G} = (X_0 - X_1)\bar{L}$$

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### Equilibrium Line

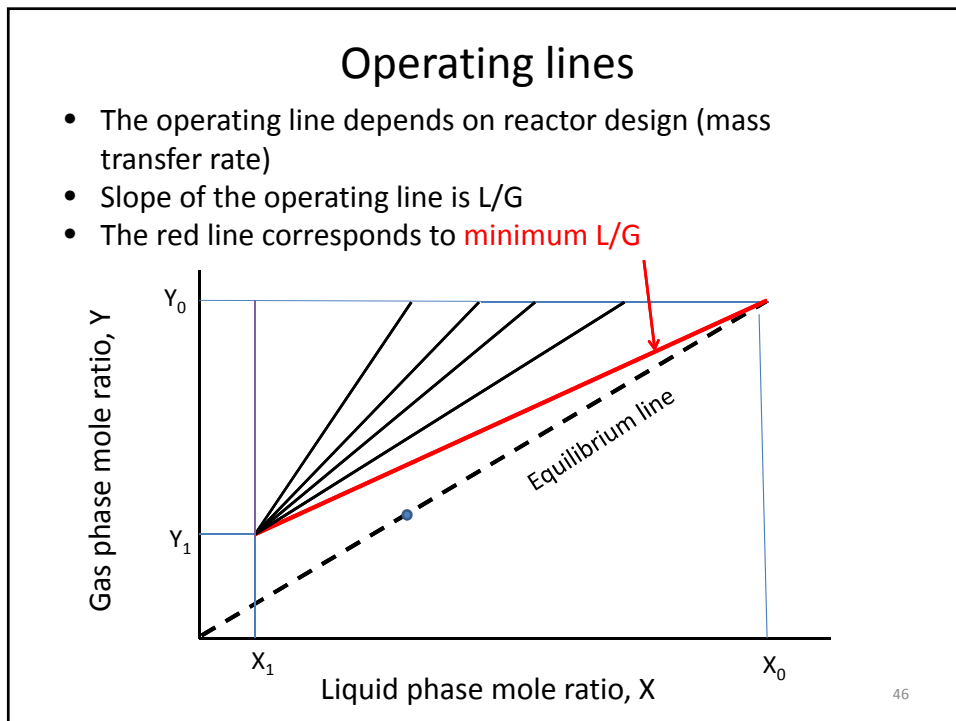
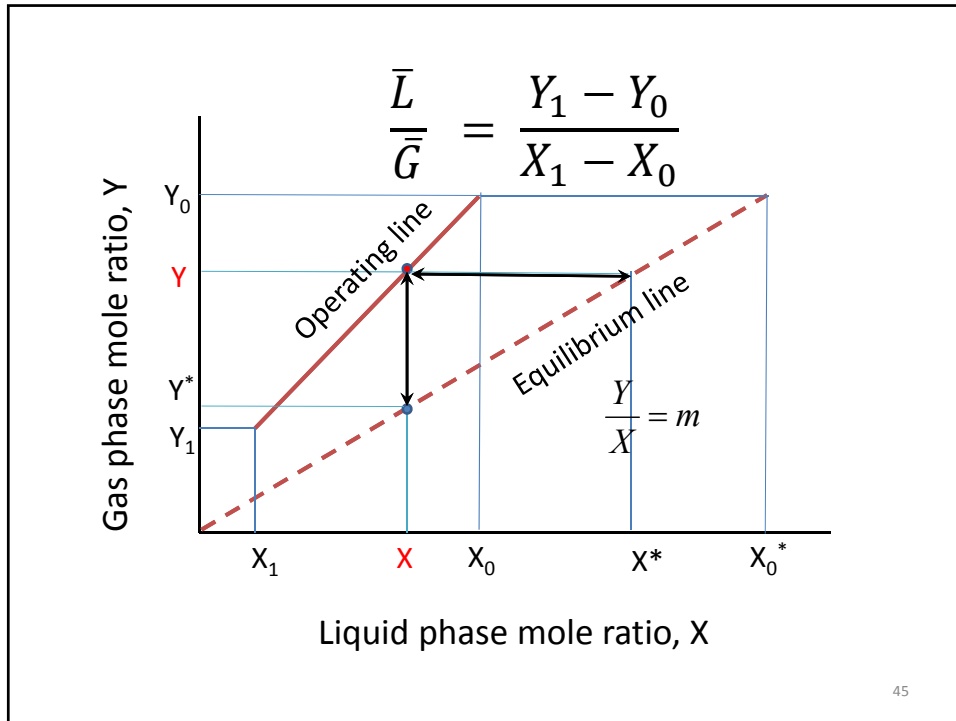
$$Py = Hx \quad \frac{Y}{1+Y} = \frac{H}{P} \left( \frac{X}{1+X} \right) \quad Y = \frac{H}{P} \left( \frac{1+Y}{1+X} \right) X$$

If  $X \ll 1, Y \ll 1$ , then  $\frac{Y}{X} = \left( \frac{P_t}{H} \right)$

### Actual Operating Line

$$\frac{\bar{L}}{\bar{G}} = \frac{Y_1 - Y_0}{X_1 - X_0}$$

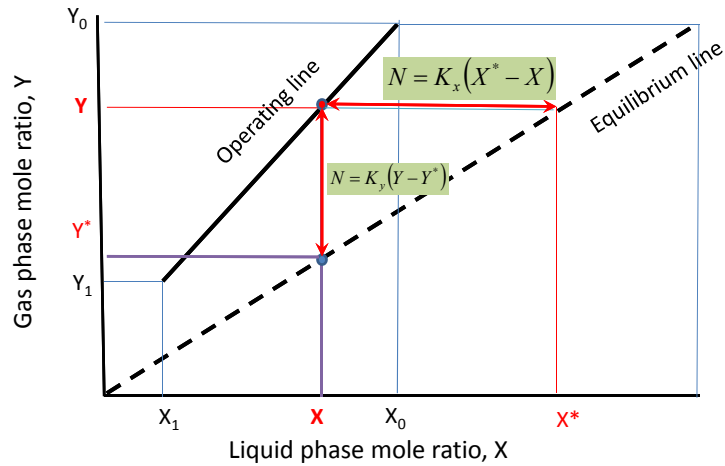
44



So redefine:  $N = K_x(X^* - X)$      $N = K_y(Y - Y^*)$

$X^*$ ,  $Y^*$ : Hypothetical mole ratio corresponding to  $X$ ,  $Y$  (actual mole ratios)

$K_x$ ,  $K_y$ : Overall mass transfer coefficient for the liquid and gas phases



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### Example 5.6: Absorption Operating Line

- A packed bed wet scrubber is designed to remove high concentration  $\text{SO}_2$  from the exhaust of a sulfuric acid plant.
- It is expected to achieve a removal efficiency of 95%.
- The incoming  $\text{SO}_2$  concentration is 10%.
- Pure water is used as an absorbent and the solute-free liquid to gas ratio is 1.5 times the minimum ratio.
- Assume that the system operates at 30 °C and 1 atm.
- The equilibrium data for  $\text{SO}_2$  in air and water at 30 °C are as follows

Partial pressure	0.6	1.7	4.7	8.1	11.8	19.7	36	52	79
$p_{\text{SO}_2}$ (mmHg)									
$c_{\text{SO}_2}$ (g $\text{SO}_2$ /100 g water)	0.02	0.05	0.1	0.15	0.2	0.3	0.5	0.7	1

Plot the *equilibrium line*, the *minimum operating line* and the *operating line* in the same figure



## Solution

- **Step 1:** Determine the equilibrium line by the mole fraction in gas by Dalton's law, Equation (2-40) and liquid phases, respectively

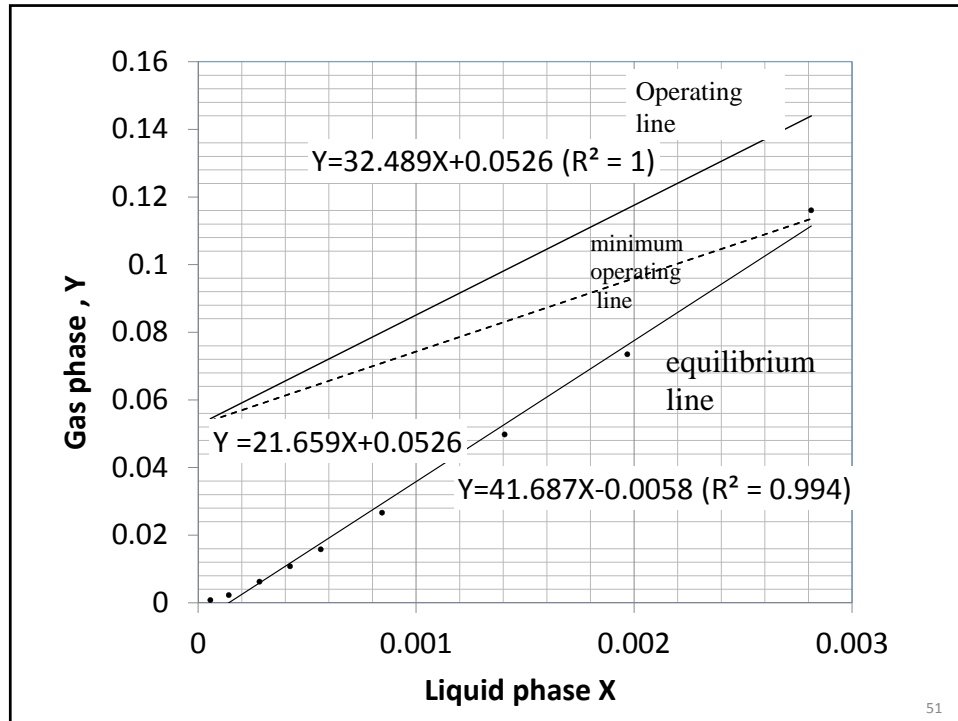
$$y = y_{SO_2} = \frac{P_{SO_2}}{P}$$

$$x = x_{SO_2} = \frac{\frac{c_{SO_2}}{64 \text{ g/mole}}}{\frac{c_{SO_2}}{64 \text{ g/mole}} + \frac{100 \text{ g}}{18 \text{ g/mole}}}$$

where 64 and 18 are the molar weights of  $SO_2$  and water, respectively, with the unit of g/mole. Using these equations, we can calculate the  $SO_2$  mole fractions in gas phase and liquid phase

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$p_{SO_2}$ (mmHg)	$c_{SO_2}$ (g $SO_2$ /100g water)	in gas	in liquid	mole ratio	mole ratio
		$y$	$x = x_{SO_2}$	$Y = \frac{y}{1-y}$	$X = \frac{x}{1-x}$
0.6	0.02	0.000789	0.00005625	0.00079	0.000056
1.7	0.05	0.00224	0.00014	0.00224	0.00014
4.7	0.1	0.00618	0.000281	0.00622	0.000281
8.1	0.15	0.01066	0.000422	0.01077	0.000422
11.8	0.2	0.0155	0.000562	0.01577	0.000563
19.7	0.3	0.0259	0.000843	0.0266	0.000844
36	0.5	0.04737	0.00140	0.0497	0.00141
52	0.7	0.06841	0.001965	0.07345	0.00197
79	1	0.104	0.0028	0.1160	0.00281



### Minimum L/G

$$\left(\frac{y}{1-y}\right)\bar{G} + \left(\frac{x_1}{1-x_1}\right)\bar{L} = \left(\frac{x}{1-x}\right)\bar{L} + \left(\frac{y_1}{1-y_1}\right)\bar{G}$$

with the

- inlet SO<sub>2</sub> mole fraction  $y_0=10\%=0.10$ ,
- exit SO<sub>2</sub> mole fraction  $y_1=0.10\times(1-95\%)=0.005$ .
- In the pure water entering the top of the tower,  $x_1=0$ ,
- at the bottom of tower, the SO<sub>2</sub> mole fraction in the air is  $y_0=0.1$
- the corresponding equilibrium mole fraction in the water exiting the bottom of the tower is determined from the equilibrium line,  
 $x_0^* = 0.0027(=0.0028 \text{ in Table})$
- Then the corresponding minimum liquid-to-gas ratio equilibrium operation is determined by substituting these values into Equation (5-35), together with  $x_1 = 0$ ,  $y_1 = 0.05$ ,

$$\left(\frac{\bar{L}}{\bar{G}}\right)_{min} = 21.67$$

- The actual operating liquid to gas ratio is 1.5 times of this liquid flow rate

$$\frac{\bar{L}}{\bar{G}} = 1.5 \times \left(\frac{\bar{L}}{\bar{G}}\right)_{min} = 32.49$$

- Then we can determine the actual operating line using Equation (5-21) again, with  $x_1 = 0$ , and  $y_1 = 0.05$ , and  $\left(\frac{\bar{L}}{\bar{G}}\right)_{min} = 32.49$

$$\left(\frac{y}{1-y}\right) + \left(\frac{x_1}{1-x_1}\right) \left(\frac{\bar{L}}{\bar{G}}\right) = \left(\frac{x}{1-x}\right) \left(\frac{\bar{L}}{\bar{G}}\right) + \left(\frac{y_1}{1-y_1}\right)$$

$$Y = 32.49 + 0.053$$

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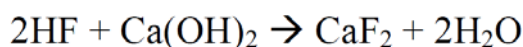
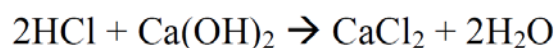
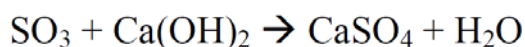
## Chemical Absorption

- An alkali addition system is used on wet scrubber systems that treat gas streams that have **acidic gases or vapors** that could absorb in the liquid stream.
  - The most common acid gases include sulfur dioxide (SO<sub>2</sub>), hydrogen chloride (HCl), and hydrogen fluoride (HF). Carbon dioxide formed in most combustion processes is also mildly acidic.
- Common alkalis include lime, soda ash, and sodium hydroxide. In some cases, limestone and nahcolite are used. Except for sodium hydroxide, all of these materials are typically stored and fed to the recirculation tank in a powder form.
- Sodium hydroxide is usually fed in solution.

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## Enhanced absorption factor, e

The alkali requirements are usually calculated based on the quantities of acidic gases captured and the molar ratios necessary for the following reactions:

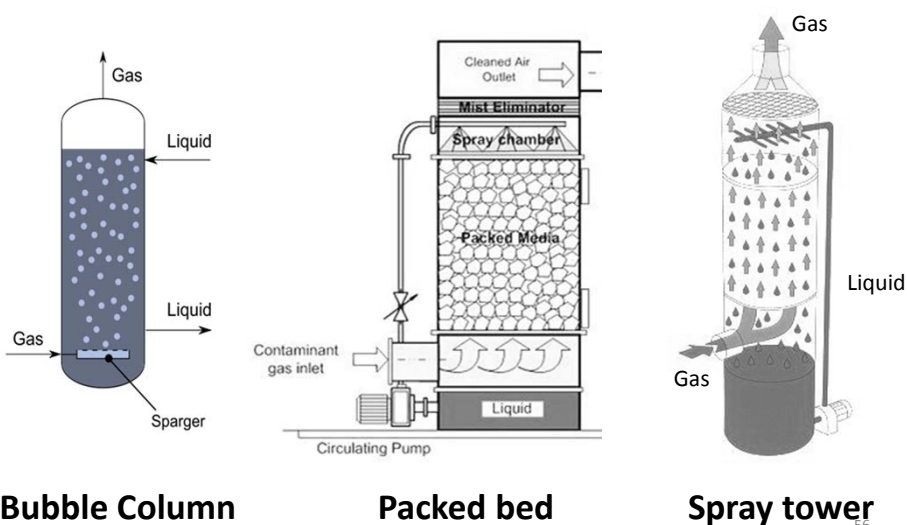


$$\frac{y}{1-y} - \frac{y_1}{1-y_1} = \left( \frac{x}{1-x} - \frac{x_1}{1-x_1} \right) \left( \frac{\bar{L}}{\bar{G}} \right) (1+e)$$

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## Engineering to Enhance Interfacial Contact Areas

**Can you rank their air handling capacity?**








Bubble Column

Packed bed

Spray tower

56

Packing type	Material	Nominal size (in.)	Area per volume (m <sup>2</sup> /m <sup>3</sup> )
(Berl saddle) 	Ceramic and porcelain	¼	899
		½	509
		1	259
		2	105
(Intalox saddle) 	Plastic	1	207
		2	108
		3	89
	Ceramic	¼	984
		½	623
		1	256
(Raschin ring) 	Ceramic and porcelain	2	118
		3	62
		5/8 x 0.018 thick	341
		1 ½ x 0.03 thick	128
		1	180
(Pall ring) 	Metal	1	180
		2	125
(Tellerette) 		1	180
		2	125
		3	98