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Multicomponent Diffusion and Adsorption in Porous Solid Adsorbents with Maxwell-Stefan Framework

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In memory of Professor Giorgio Zgrabich (1942-2012)

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  - Adsorption of Hydrocarbon Mixtures in Activated Carbon

Design of Adsorber for
Separation and Purification
-- Equilibria
-- Dynamics

Diffusion in Porous Media

A brief Historical Survey

1827	Navier –	Momentum equation
1829	Graham –	Mass diffusion in gas
1839	Hagen, Poiseuille –	Flow in pipe
1845	Stokes –	Momentum equation
1855	Fick –	Law of mass transport
1856	Darcy –	Empirical flow equation
1859	Maxwell –	Distribution of velocity in gas
1870	Kelvin –	Capillary condensation
1878	Gibbs –	Thermodynamics treatment of interfaces
1885	Boltzmann –	General transport equation
1905	Einstein –	Random walk diffusion equation
1909	Knudsen –	Flow of rarified gases

Some Classical Devices

for diffusion measurements

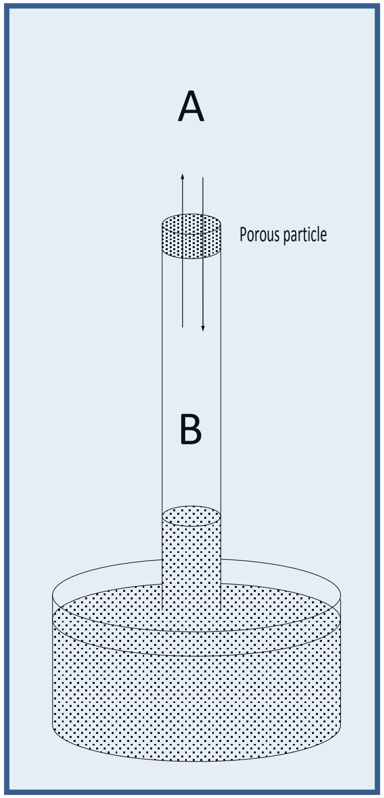
- Graham system
- Hoogschagen system
- Two-bulb devices of Loschmidt and Graham
- Wicke and Kallanbach diffusion cell
- Perturbation Chromatography
- Time lag method
- Differential adsorption bed
  - Very effective in dealing with diffusion and adsorption of mixtures

Devices

Graham system (1829)

- In the Graham experiment, a tube containing gas B is immersed in a water bath with the porous media mounted at the upper end of the tube, exposing to gas A.

- Gas B diffuses out, and gas A diffuses in.
- Because the net transport of gas is not zero, the water level inside the tube will either rise or fall. If gas B is heavier, the water level will fall, and if the gas B is lighter the level will rise.



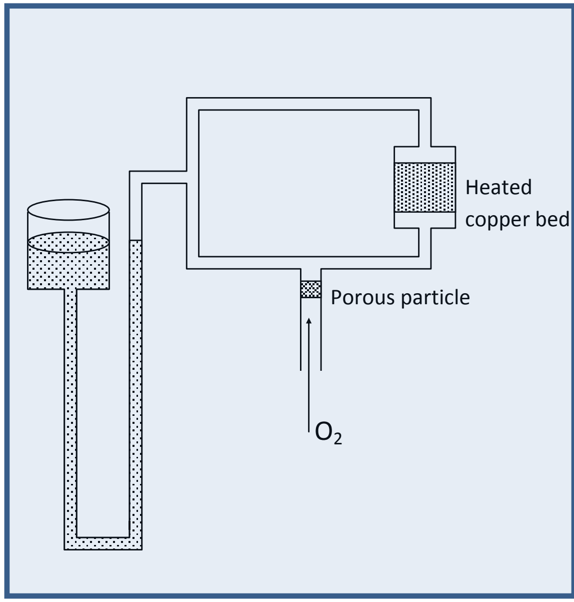
$$\frac{N_A}{N_B} = -\sqrt{\frac{M_B}{M_A}}$$

Devices

Hoogschagen system (1953)

- Diffusion of oxygen and other gases: Oxygen is supplied at the bottom of the porous plug, and diffuses in exchange for the other gas. Oxygen molecules entering the loop will be taken up completely by the copper bed at 480 ^{0}C.

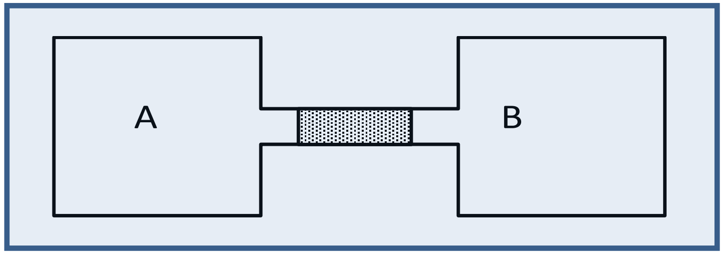
- The pressure inside the loop is maintained atmospheric with the burette. The flux of the outgoing gas is calculated from the change in the liquid level in the burette, and the incoming oxygen flux is measured by weighing the copper.



$$\frac{N_A}{N_B} = -\sqrt{\frac{M_B}{M_A}}$$

Devices

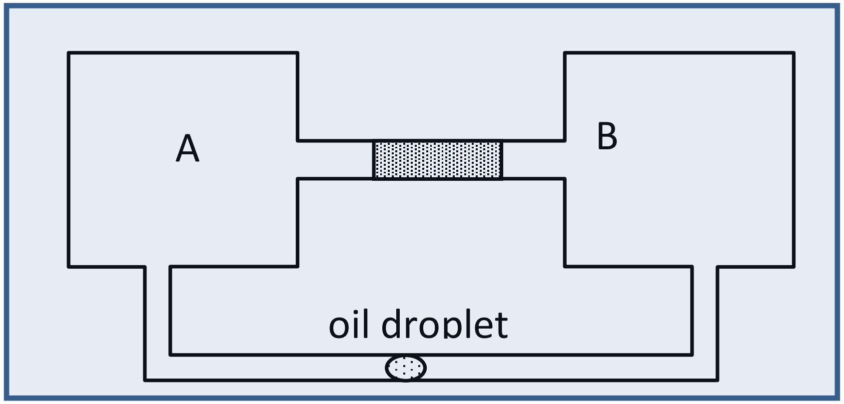
Loschmidt and Graham



- The flow of gas A will move to the right while gas B diffuses to the left. This type of set up has a pressure gradient build-up in the system because the flows of A and B are generally not equimolar.
  - Let us take an example where A is the heavier gas, the left bulb pressure increases while the right bulb pressure decreases because the diffusion rate of A through the capillary is slower than the diffusion rate of B. The resulting pressure gradient will then cause a viscous flow from the left to the right retarding the rate of molar flux of B to the left.
  - This induced viscous flow will complicate the study of diffusion phenomena.

Devices

Loschmidt and Graham

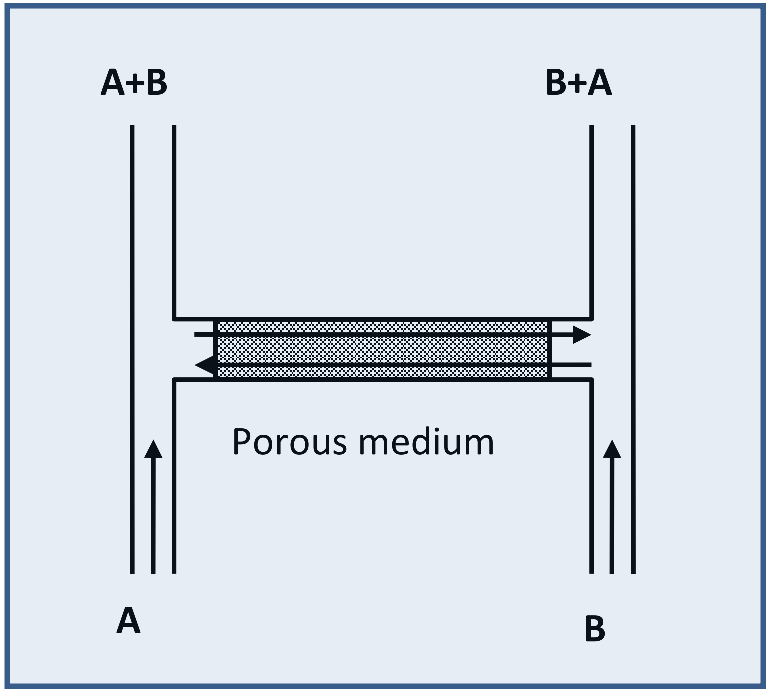


- To avoid the viscous flow, they later developed a system, where the two bulbs are connected to each other through a small tube containing a drop of oil acting as a "frictionless" piston.

  – Take the last case where gas B is the lighter gas; hence the molar diffusion flux of A is less than the flux of B, leading the increase in pressure in the left bulb. Due to this increase in pressure in the left bulb, the oil droplet moves to the right, resulting in a balance in the pressures of the bulbs. The rate of movement of this oil piston provides the net flux of A and B through the porous plug.

Devices

Wicke and Kallanbach's diffusion cell

- This diffusion cell is introduced by Buckingham in 1904 and later exploited by Wicke (1940) and Wicke and Kallanbach (1941).
- 

Devices

Perturbation Chromatography

- A flow of a gaseous mixture is passed through the bed packed with porous solid adsorbent until equilibrium is reached.

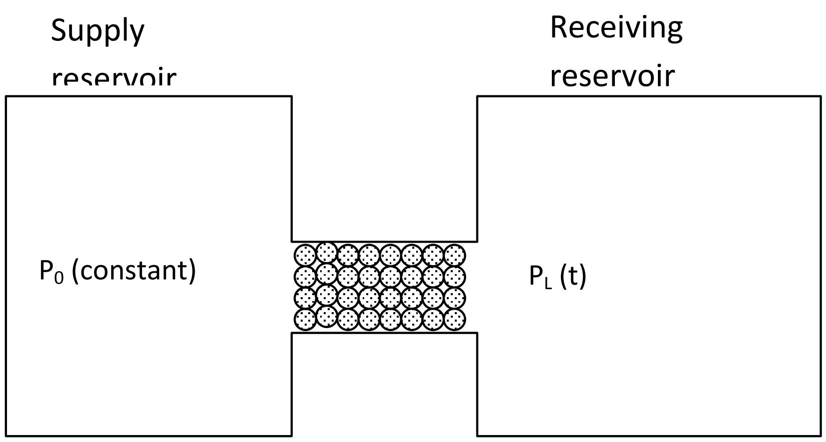
- The concentration of one component is perturbed as a pulse or step increment, and then its concentration is analysed at the exit of the bed. Theoretical solution is used to derive the transport properties in the bed as well as in the porous solids

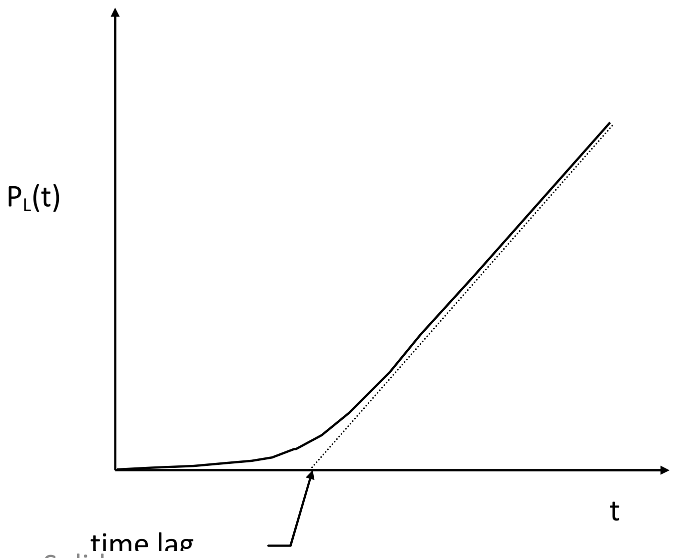
Devices

Time Lag Method (Daynes, 1920)

- Very simple to set up; It involves two reservoirs: the left reservoir is large so that the concentration is practical unchanged. The porous medium and the receiving reservoir are initially free of adsorbate. Once the diffusion is started adsorbate molecules will take a finite time to travel to the receiving reservoir.

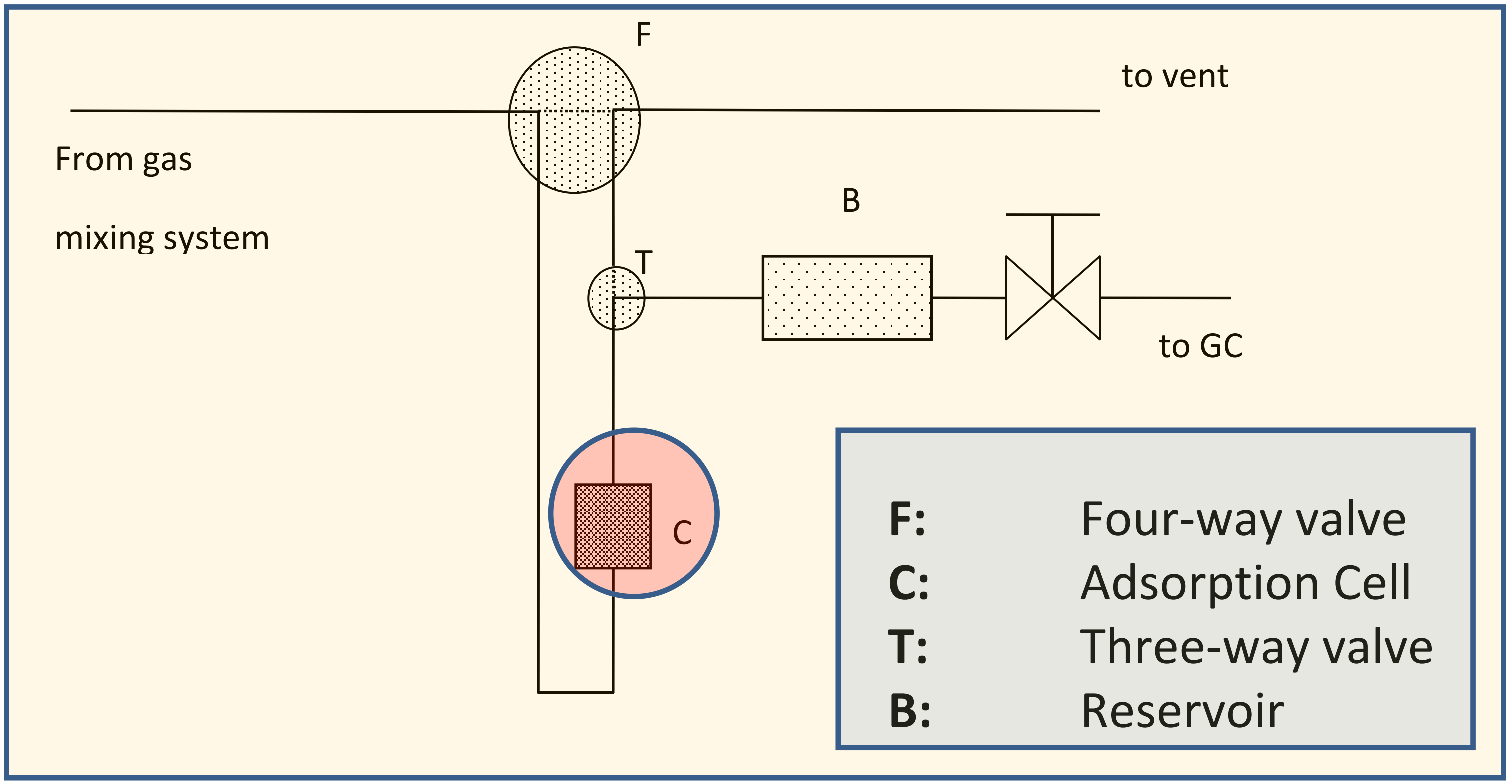
- The nice feature of this setup is that the time lag is directly inversely proportional to the transport diffusivity





Devices

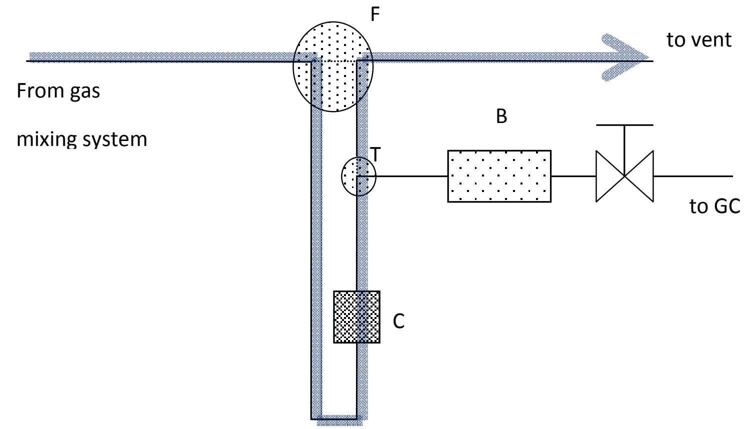
- Differential adsorption bed (DAB)
  - Very effective device to study **mixture** adsorption

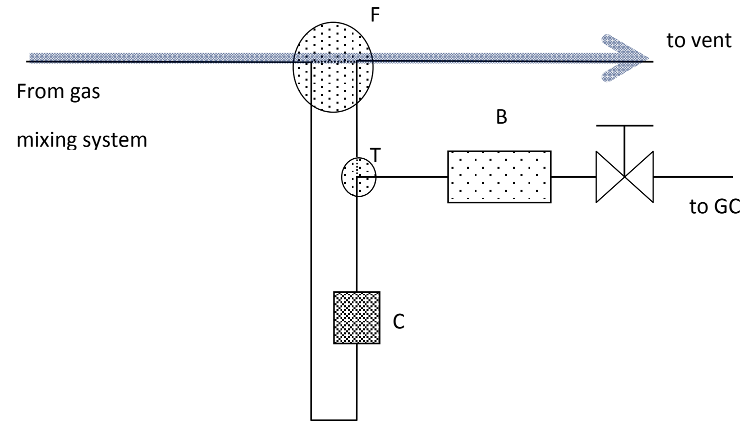


Devices

Differential Adsorption Bed

- After the bed is cleaned, the three way valve is set to the position to isolate the cell from the reservoir B, and the adsorption cell is brought to the adsorption temperature with an aid of a flowing inert gas.
- Once this has been done, the cell is isolated from the flowing gas by using the four way valve F.

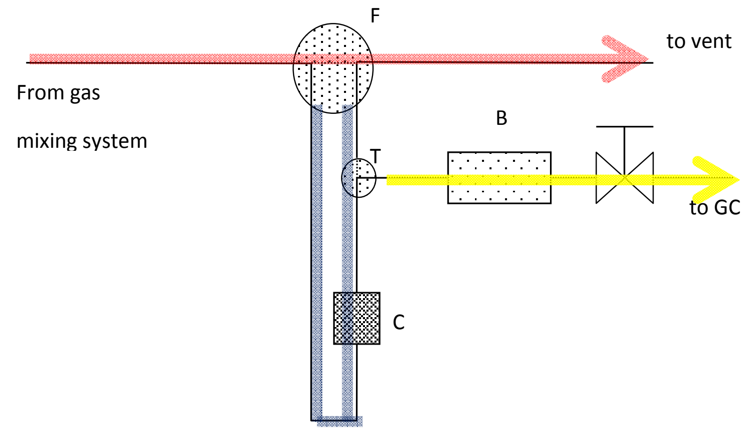


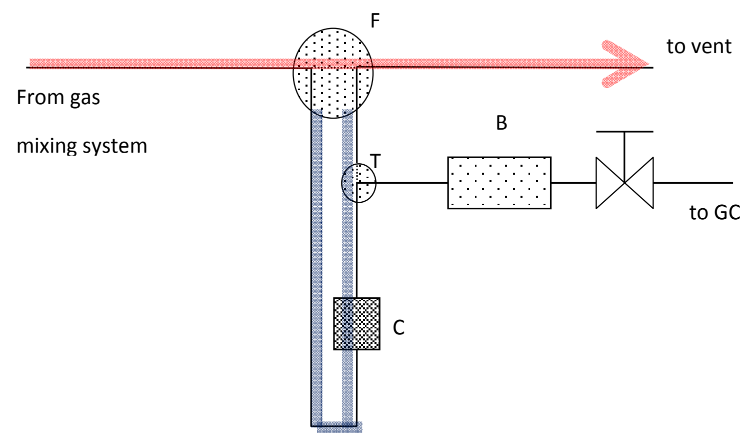


Devices

Differential Adsorption Bed

- <u>Step 1</u>:
- With the adsorption cell isolated, mix the adsorbates to the desired concentration. While this is done, the reservoir B is evacuated.
- Once this is done, it is isolated from the cell as well as the vacuum.

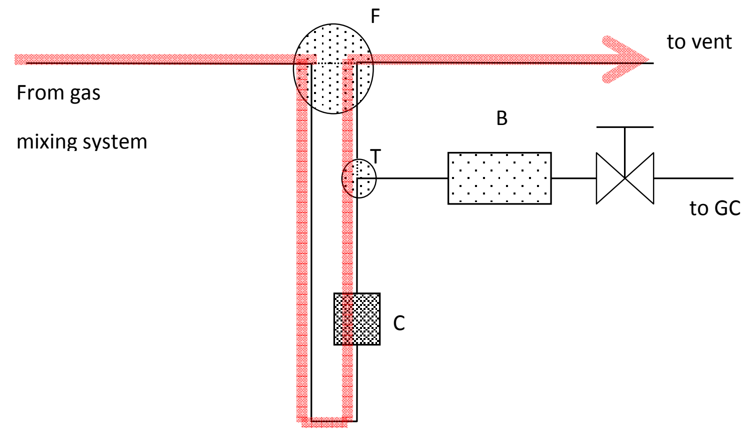


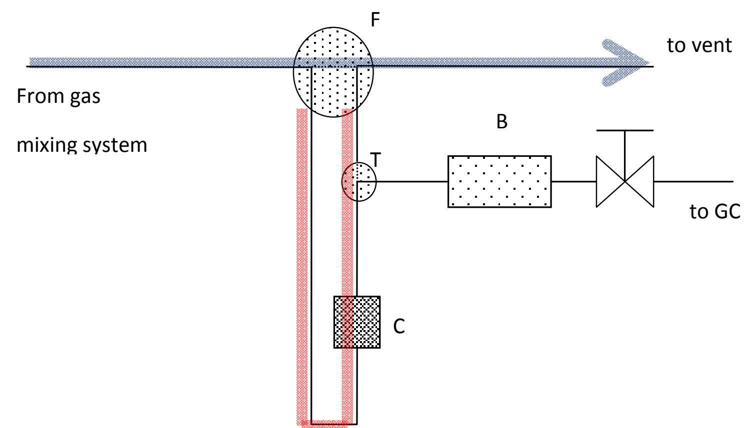


Devices

Differential Adsorption Bed

- <u>Step 2</u>:
- At time t=0, the adsorbate stream is allowed to pass through the adsorption cell. Adsorption is allowed to occur over a period of t*, and then the adsorption cell is isolated.
- During the period of exposure t*, the total amount inside the cell will be the amount adsorbed by the solid up to time t* plus the amount in the dead volume of the cell.



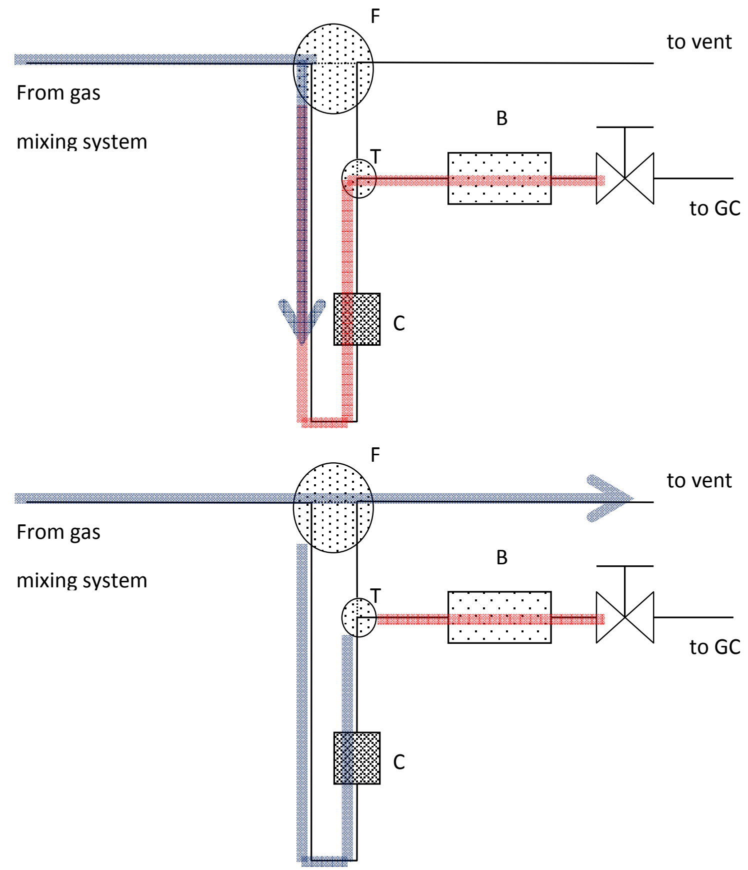


Devices

Differential Adsorption Bed

- <u>Step 3</u>:
- Next, turn the three way valve T to connect the adsorption cell to the pre-evacuated reservoir B. Adsorbate in the cell will desorb into the reservoir.

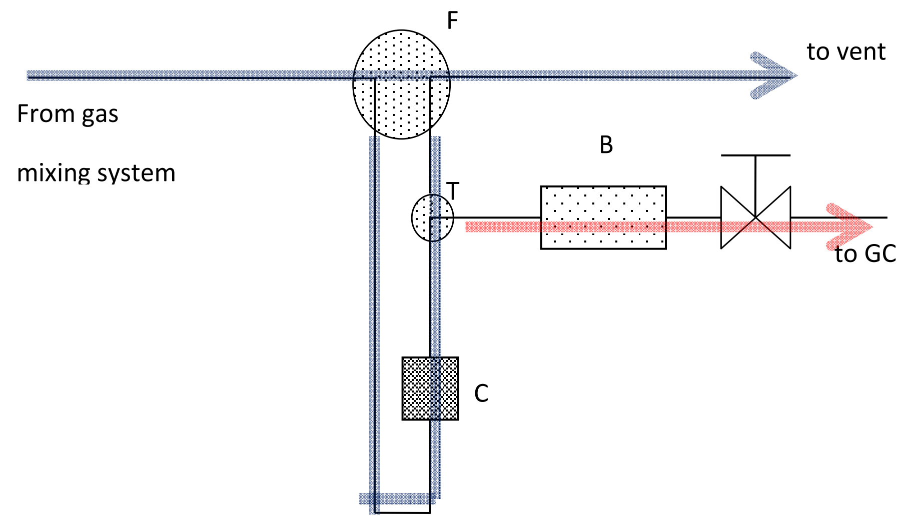
- After this desorption step is completed, the three way valve is switched to isolate the reservoir. Pressure and temperature of the reservoir are then recorded; hence the total number of moles is calculated.



Devices

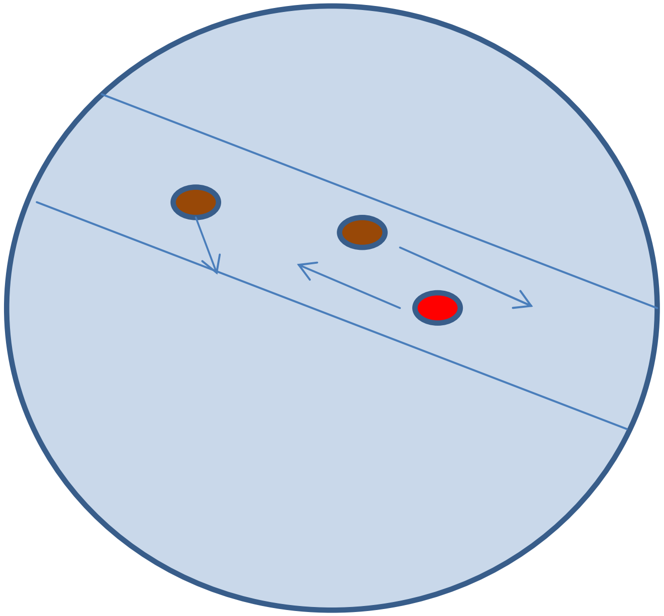
Differential Adsorption Bed

- Step 4:
- Pass the gas in the reservoir to the GC for the analysis of the adsorbate concentration, from which we can calculate the number of moles of adsorbates in the reservoir.



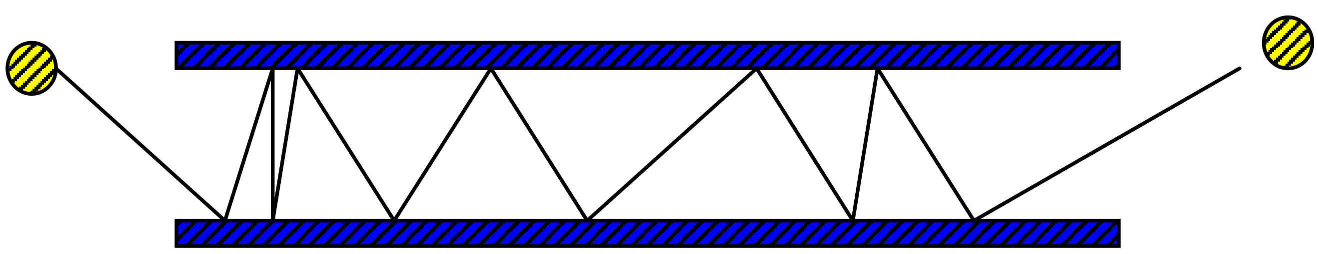
Modes of Transport

- Knudsen diffusion
- Viscous flow
- Continuum diffusion
- Surface diffusion



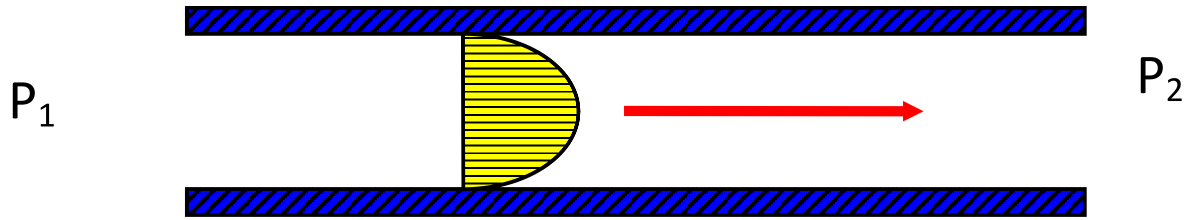
Modes of Transport

- <u>Free molecular diffusion (Knudsen):</u>
  - This type of diffusion is sometimes called molecular streaming. This flow is induced by collision of gaseous molecules with the pore wall of the capillary (that is when the mean free path is greater than the capillary diameter). Because of the collision of gaseous molecules with the wall of the capillary being the driving force for the Knudsen diffusion, transport of molecules of different type are independent of each other.



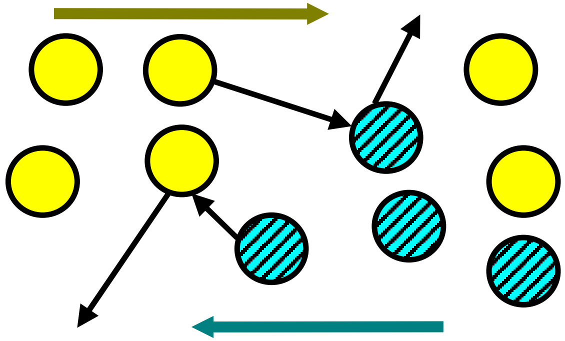
Modes of Transport

- <u>Viscous flow (streamline flow):</u>
  - This is also called the Poiseuille flow. This flow is driven by a <u>total pressure gradient</u>, and as a result the fluid mixture moves through the capillary without separation because all species move at the same speed.



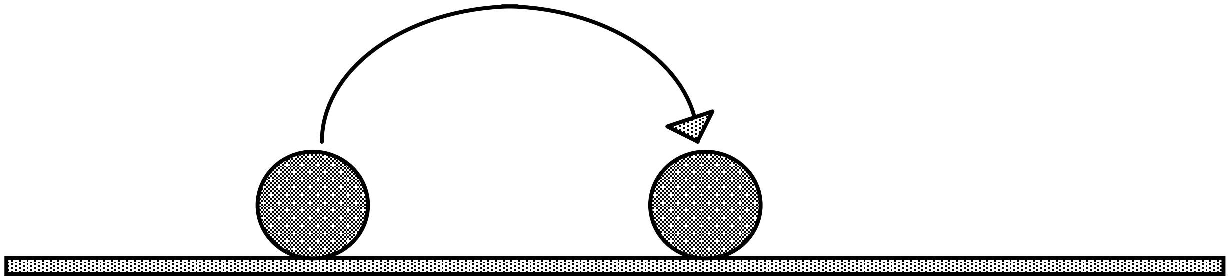
Modes of Transport

- Continuum diffusion:
  - This flow is resulting from the collisions among molecules of different type, not of the same type because there is no net momentum change due to the collisions among molecules of the same type. This situation happens when the mean free path is much less than the diameter of the capillary.



Modes of Transport

- <u>Surface diffusion</u>:
  - Different molecules have different mobility on the surface of the capillary due to their different extent of interaction with the surface. Hence a binary mixture can be separated using this type of flow, like the Knudsen diffusion.



Theories of Diffusion

- Fickian diffusion

$$J = -cD\nabla y = -cD\frac{\partial y}{\partial z}$$

  - Simple, but can't handle multicomponent systems

- Maxwell-Stefan diffusion
  - More complicated, but its utilization can be made simple with vector manipulation
  - Consistent treatment of diffusion of mixtures

Maxwell-Stefan Framework

- General and self-consistent
- Can handle non-ideal fluids
- Can incorporate Knudsen diffusion, viscous flow and surface diffusion into a single framework

D. D. Do, "Adsorption Analysis: Equilibria and Kinetics", Imperial College Press, 1998

Maxwell-Stefan Diffusion

Derivation

- For a multicomponent system containing "**n**" species, the diffusion flux equation for the component "**i**" is (Do, 1998, pg. 416)

Velocity difference

$$\frac{1}{P}\nabla p_i = -\sum_{j=1}^{n} \frac{y_i y_j \left(u_i - u_j\right)}{D_{ij}}$$

- This equation is the Maxwell-Stefan equation (credited to the Scottish physicist James Clerk Maxwell and the Austrian scientist Josef Stefan), and $D_{i,j}$ is the binary diffusion coefficient.

D. D. Do, "Adsorption Analysis: Equilibria and Kinetics", Imperial College Press, 1998

Maxwell-Stefan Diffusion

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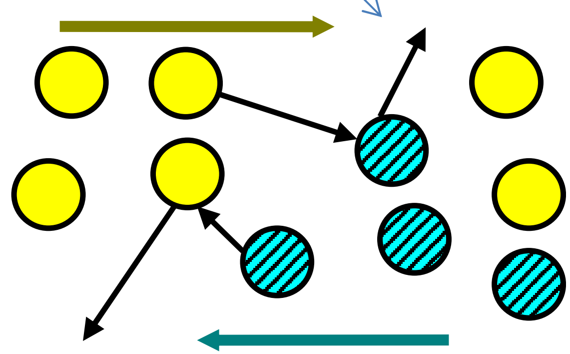
Velocity difference

$$\frac{1}{P}\nabla p_i = -\sum_{j=1}^{n} \frac{y_i y_j \left(u_i - u_j\right)}{D_{ij}}$$

Driving force due to the momentum exchange



Friction between species "i" and species "j"

Maxwell-Stefan Diffusion

Derivation

- The Maxwell-Stefan equation is more useful when written in terms of **fluxes**, which are useful to engineers and scientists

$$\frac{1}{P}\nabla p_i = \sum_{j=1}^{n}\frac{\left(y_i N_j - y_j N_i\right)}{cD_{ij}} \qquad \frac{1}{P}\nabla p_i = \sum_{j=1}^{n}\frac{\left(x_i J_j - x_j J_i\right)}{cD_{ij}}$$

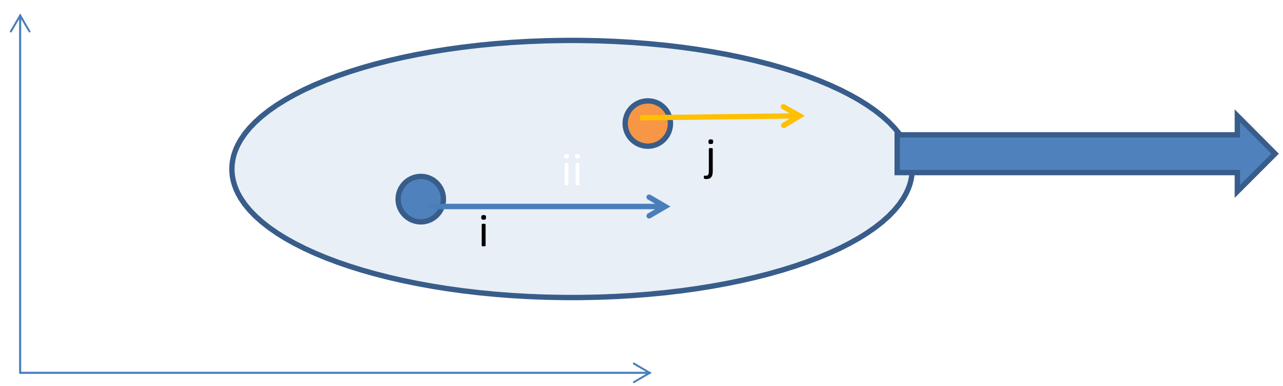
- These "**n**" equations *__are not independent__* because of the requirement of constant total pressure of the system. This is so because we are dealing with the *relative* motion of n different molecules, that is there are only (n-1) relative velocities.
  - Therefore we need a physical constraint $N_n = -\sum_{j=1}^{n-1} \nu_j N_j$

Maxwell-Stefan Diffusion

Derivation

- The Maxwell-Stefan equation is more useful when written in terms of **fluxes**, which are useful to engineers and scientists

$$\frac{1}{P}\nabla p_i = \sum_{j=1}^{n} \frac{\left(y_i N_j - y_j N_i\right)}{cD_{ij}} \qquad \frac{1}{P}\nabla p_i = \sum_{j=1}^{n} \frac{\left(x_i J_j - x_j J_i\right)}{cD_{ij}}$$



Maxwell-Stefan Diffusion

Derivation

- The Maxwell-Stefan equation seems to be complicated, BUT...

- It can be cast into the following vector format, which has a similar form as the classical Fickian equation

$$\boxed{\underline{N} = -c\left[\underline{\underline{B}}\right]^{-1} \nabla \underline{y}}$$

$$J = -cD\nabla y$$

  - The difference is in the concentration dependence of the **diffusivity matrix**

$$\underline{\underline{B}} = \begin{cases} \dfrac{y_i \nu_i}{D_{i,n}} + \displaystyle\sum_{\substack{k=1 \\ k \neq i}}^{n} \dfrac{y_k}{D_{i,k}} & \text{for} \quad i = j \\ y_i \left(\dfrac{\nu_j}{D_{i,n}} - \dfrac{1}{D_{i,j}} \right) & \text{for} \quad i \neq j \end{cases}$$

It means that the presence of other species can influence the diffusion of a given species

Maxwell-Stefan Diffusion

Example 1: Loschmidt tube

- The Loschmidt tube is simply a tube with an impermeable partition separating the two sections of the tube. At time t=0, the partition is removed and the diffusion process is started.

$$c\frac{\partial \underline{y}}{\partial t} = -\frac{\partial}{\partial z}\left(\underline{N}\right)$$

$$c\frac{\partial \underline{y}}{\partial t} = -\frac{\partial}{\partial z}\left(\underline{N}\right)$$

- Using the constitutive equation leads to the following equation

$$\underline{N} = -c\left[\underline{\underline{B}}\right]^{-1}\nabla \underline{y} \quad \Longrightarrow \quad \frac{\partial \underline{y}}{\partial t} = \frac{\partial}{\partial z}\left\{\left[\underline{\underline{B}}(\underline{y})\right]^{-1}\frac{\partial \underline{y}}{\partial z}\right\}$$

Maxwell-Stefan Diffusion

Example 1: Loschmidt tube

- Methane (**1**)/argon (**2**)/hydrogen (**3**) diffusion at 307K.

$$c\frac{\partial \underline{y}}{\partial t} = -\frac{\partial}{\partial z}\left(\underline{N}\right) \qquad\qquad c\frac{\partial \underline{y}}{\partial t} = -\frac{\partial}{\partial z}\left(\underline{N}\right)$$

- At t = 0
- **Methane**: y(1) = 0 $\longleftarrow$ y(1) = 0.515
- **Argon**: y(2) = 0.509 $\longrightarrow$ y(2) = 0.485
- **Hydrogen**: y(3) = 0.491 $\longrightarrow$ y(3) = 0

- The directions of transport are predicted by the Fickian law of diffusion
- **BUT**

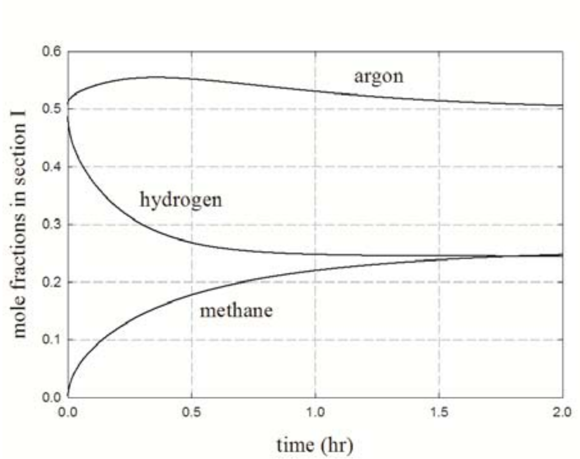
Maxwell-Stefan Diffusion

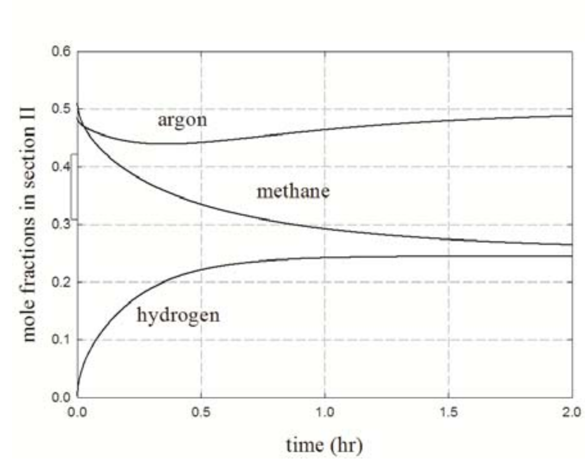
Example 1: Loschmidt tube

- Methane (**1**)/argon (**2**)/hydrogen (**3**) diffusion at 307K.

• **Methane**:	$y(1) = 0$	$y(1) = 0.515$
• **Argon**:	$y(2) = 0.509$	$y(2) = 0.485$
• **Hydrogen**:	$y(3) = 0.491$	$y(3) = 0$

- Maxwell-Stefan diffusion equation:



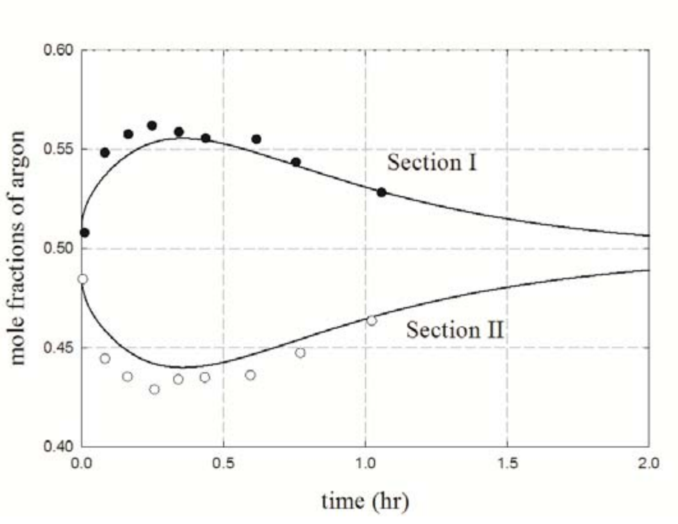


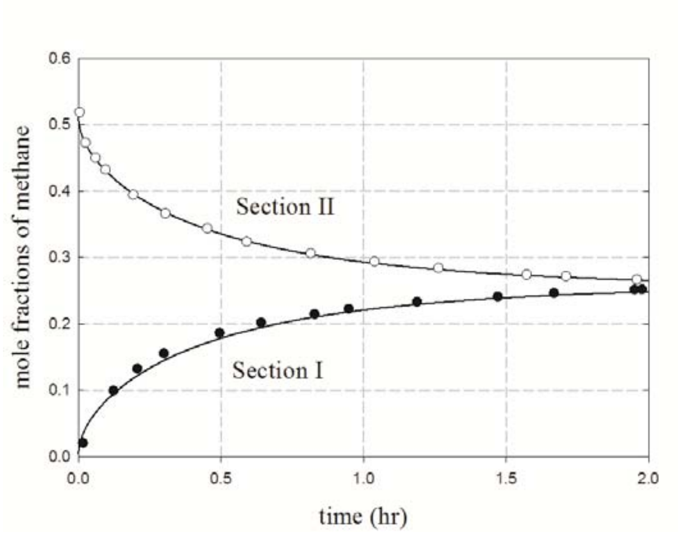
Maxwell-Stefan Diffusion

Example 1: Loschmidt tube

- Methane (**1**)/argon (**2**)/hydrogen (**3**) diffusion at 307K.

- Experimental data of Arnold and Toor, *AIChE* J, 13 (1967) 909.
- Uphill diffusion of argon, which is due to the drag effects of methane diffusion from Section II to Section I, a phenomenon that can’t be described by Fickian law of diffusion

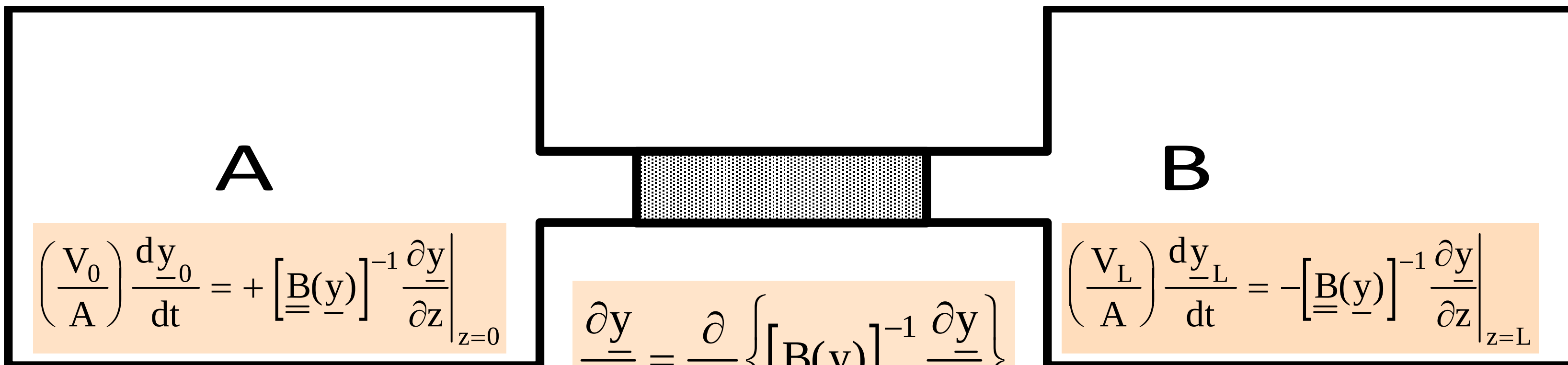




Maxwell-Stefan Diffusion

Example 2: Two-bulb system

- This system has two reservoirs connected together with a capillary. The mass balance equations are:



$$\left(\frac{V_0}{A}\right)\frac{d\underline{y}_0}{dt} = +\left[\underline{\underline{B}}(\underline{y})\right]^{-1}\frac{\partial \underline{y}}{\partial z}\bigg|_{z=0}$$

$$\frac{\partial \underline{y}}{\partial t} = \frac{\partial}{\partial z}\left\{\left[\underline{\underline{B}}(\underline{y})\right]^{-1}\frac{\partial \underline{y}}{\partial z}\right\}$$

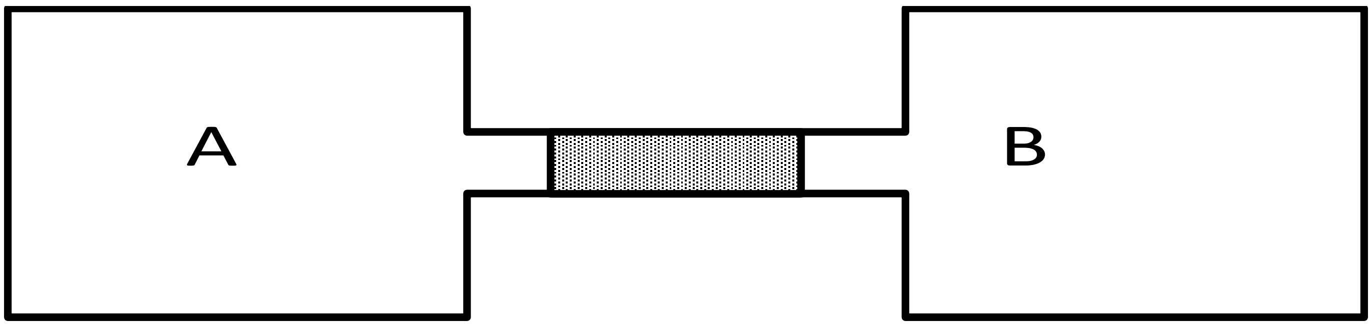
$$\left(\frac{V_L}{A}\right)\frac{d\underline{y}_L}{dt} = -\left[\underline{\underline{B}}(\underline{y})\right]^{-1}\frac{\partial \underline{y}}{\partial z}\bigg|_{z=L}$$

$$\underline{\underline{B}}\left(\underline{y}\right) = \begin{cases} \dfrac{y_i}{D_{i,n}} + \displaystyle\sum_{\substack{k=1 \\ k\neq i}}^{n}\dfrac{y_k}{D_{i,k}} & i = j \\ y_i\left(\dfrac{1}{D_{i,n}} - \dfrac{1}{D_{i,j}}\right) & i \neq j \end{cases}$$

Maxwell-Stefan Diffusion

Example 2: Two-bulb system

- Experimental data of Duncan and Toor, AIChEJ, 8 (1962) 38:
- Ternary system: hydrogen (**1**), nitrogen (**2**) and carbon dioxide (**3**)



A		B
y(1) = 0	←	y(1) = 0.50121
y(2) = 0.50086	→	y(2) = 0.49879
y(3) = 0.49914	→	y(3) = 0

- We expect hydrogen to diffuse to the left and carbon dioxide to diffuse to the right; and nitrogen to go to the right, **BUT**…

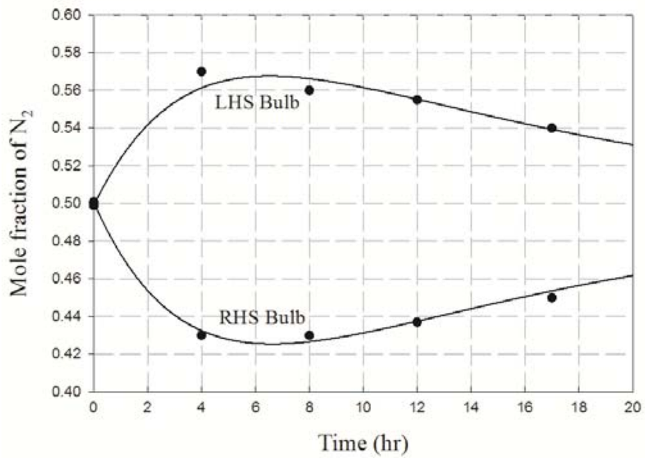
Maxwell-Stefan Diffusion

Example 2: Two-bulb system

- Ternary system: hydrogen (**1**), nitrogen (**2**) and carbon dioxide (**3**)

• y(1) = 0	y(1) = 0.50121
• y(2) = 0.50086	y(2) = 0.49879
• y(3) = 0.49914	y(3) = 0

- We expect hydrogen to diffuse to the left and carbon dioxide to diffuse to the right; and nitrogen to go to the right, BUT… we see the uphill diffusion of nitrogen and this is due to the **drag effects** of hydrogen



Maxwell-Stefan Diffusion

Constitutive Relations for non-ideal fluids

- The generalised Maxwell-Stefan equation for the case of non-ideal fluids containing n species is given below:
- $$\frac{y_i}{R_g T}\frac{d\mu_i}{dz} = \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{y_i N_j - y_j N_i}{cD_{ij}}$$
- for i = 1, 2, ..., n-1.
- Only (n-1) above equations are independent because of the Gibbs-Duhem restriction on the chemical potential.

$$\sum_{i=1}^{n} y_i \nabla\mu_i = 0$$

Maxwell-Stefan Diffusion & Knudsen

Constitutive Relations

- The generalised Maxwell-Stefan equation for the case of non-ideal fluids containing “n” species in a confined space is given below:
- $$-\frac{y_i}{R_g T}\frac{d\mu_i}{dz} = \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{y_j N_i - y_i N_j}{cD_{ij}} + \frac{N_i}{cD_{i,K}}$$

Friction of all species on component “i”

Knudsen diffusion:
Collision of molecules with the wall

Maxwell-Stefan Diffusion & Knudsen & Viscous Flow

- The generalised Maxwell-Stefan equation for the case of non-ideal fluids containing **n** species is given below:

$$\sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{y_j N_i - y_i N_j}{D_{ij}} + \frac{N_i}{D_{K,i}} = -\frac{1}{R_g T}\frac{dp_i}{dz} - \frac{y_i}{R_g T}\frac{B_0 P}{\mu D_{K,i}}\frac{dP}{dz}$$

Continuum diffusion

Knudsen

Viscous

- It looks complicated?

Maxwell-Stefan Diffusion & Knudsen & Viscous Flow

- The generalised Maxwell-Stefan equation for the case of non-ideal fluids containing n species is given below:

$$\underline{N} = -\frac{1}{R_g T}\left[\underline{\underline{B}}\left(\underline{y}\right)\right]^{-1}\frac{d\underline{p}}{dz} - \frac{B_0}{\mu R_g T}\frac{dP}{dz}\left[\underline{\underline{B}}\left(\underline{y}\right)\right]^{-1}\underline{\underline{\Lambda}}\,\underline{p}$$

$$\underline{\underline{B}} = \begin{cases} \dfrac{1}{D_{K,i}} + \displaystyle\sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{y_j}{D_{ij}} & \text{for} \quad i = j \\ -\dfrac{y_i}{D_{ij}} & \text{for} \quad i \neq j \end{cases}$$

$$\underline{\underline{\Lambda}} = \left\{ \Lambda_{ii} = \frac{1}{D_{K,i}} \right.$$

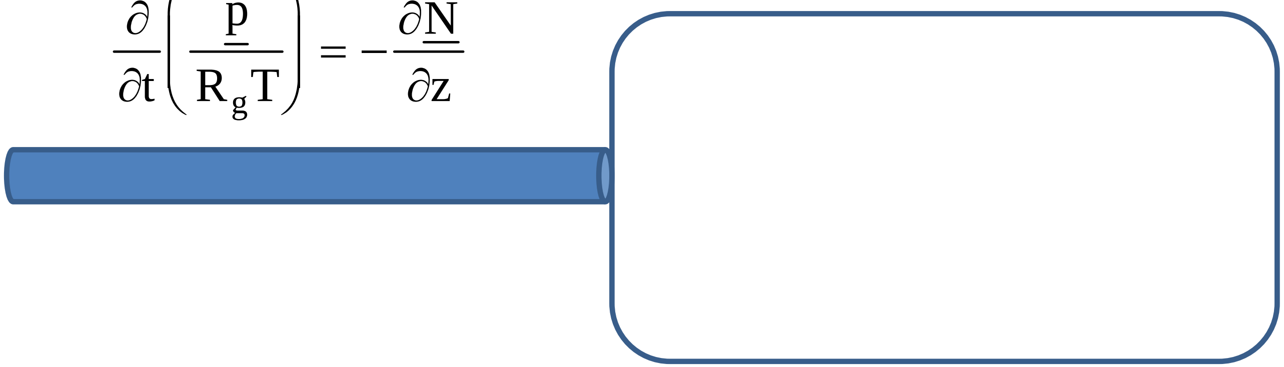
- Now it looks similar to a Fickian form with a viscous contribution

Applications

Transient Diffusion of methane/argon/hydrogen in a capillary

- Methane (**1**); argon (**2**); hydrogen (**3**)

$$\frac{\partial}{\partial t}\left(\frac{\underline{p}}{R_g T}\right) = -\frac{\partial \underline{N}}{\partial z}$$



Initial partial pressures		Bulk partial pressures
p(1) = 0.515		p(1) = 0
p(2) = 0.485	?	p(2) = 0.509
p(3) = 0		p(3) = 0.491

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Bulk partial pressures

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? p(2) = 0.509

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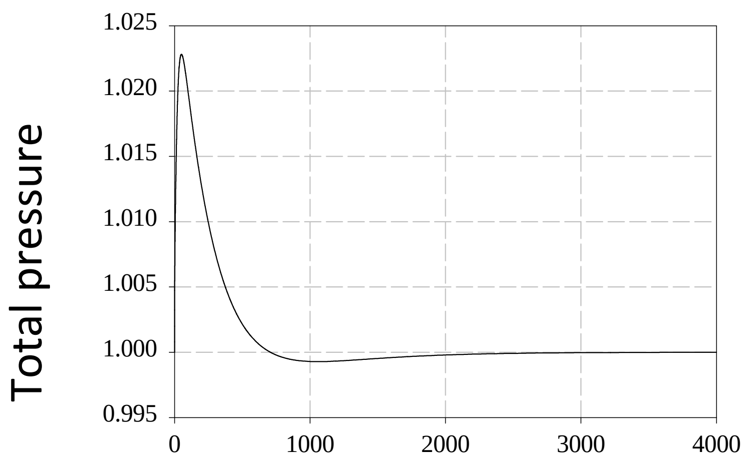

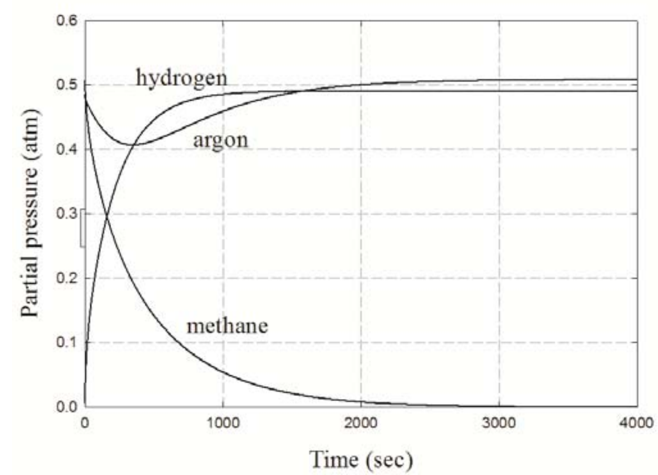

Applications

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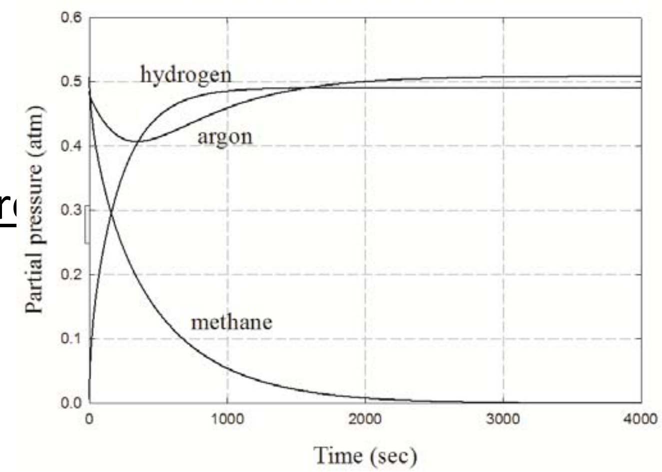

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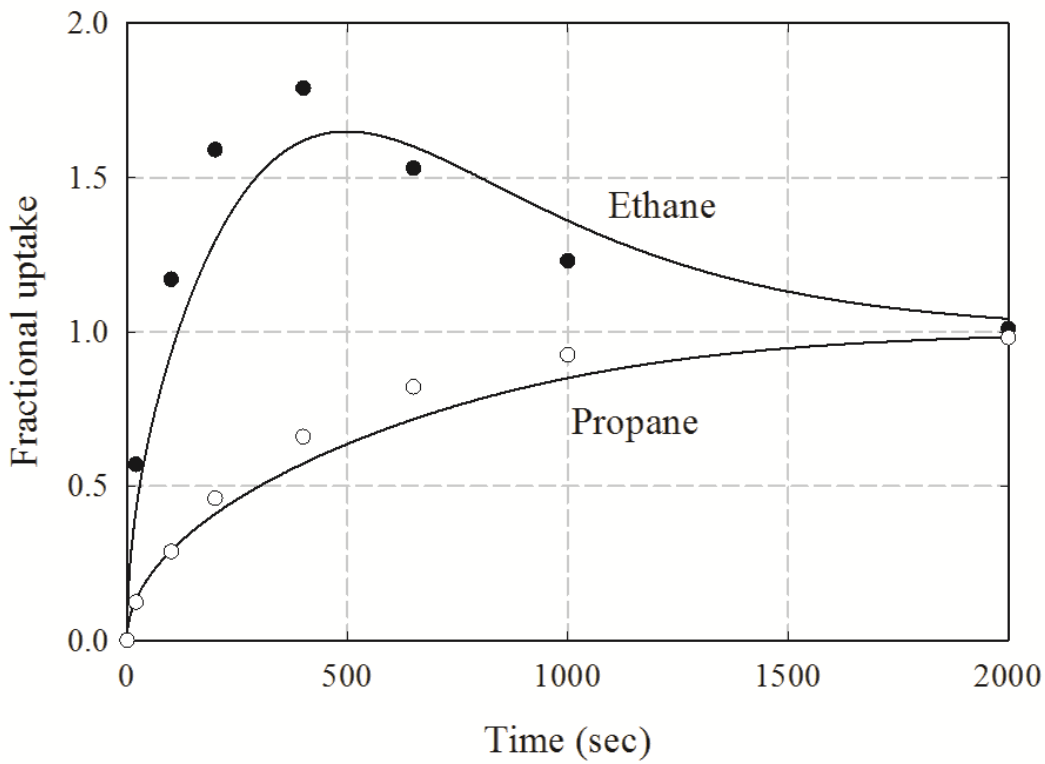
- Methane and hydrogen: downhill diffusion.
- The behaviour of argon is interesting. Instead of going up from the initial pressure of 0.485 to a final bulk pressure of 0.509 atm, the argon mean partial pressure decreases with time during the early stage of diffusion. This behaviour is due to the outflux of methane and it drags argon to the bulk, resulting in the initial drop of argon pressure.

Applications

Adsorption of Hydrocarbons in Activated Carbon

- Adsorption of ethane/propane/nitrogen in activated carbon at 298K
  - Roll-over phenomenon



References

D. D. Do, "Adsorption Analysis-Equilibria and Kinetics", Imperial College Press, 1998

- Relevant reading

- Chapter 7: Basic diffusion
- Chapter 8: Maxwell-Stefan diffusion theory for mixtures
- Chapter 9: Adsorption Kinetics in a Single Particles
- Chapter 11: Surface Heterogeneity on Adsorption Kinetics

In Memory of Prof. Giorgio Zgrablich 1942-2012

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