CE407 SEPARATIONS

Lecture 18

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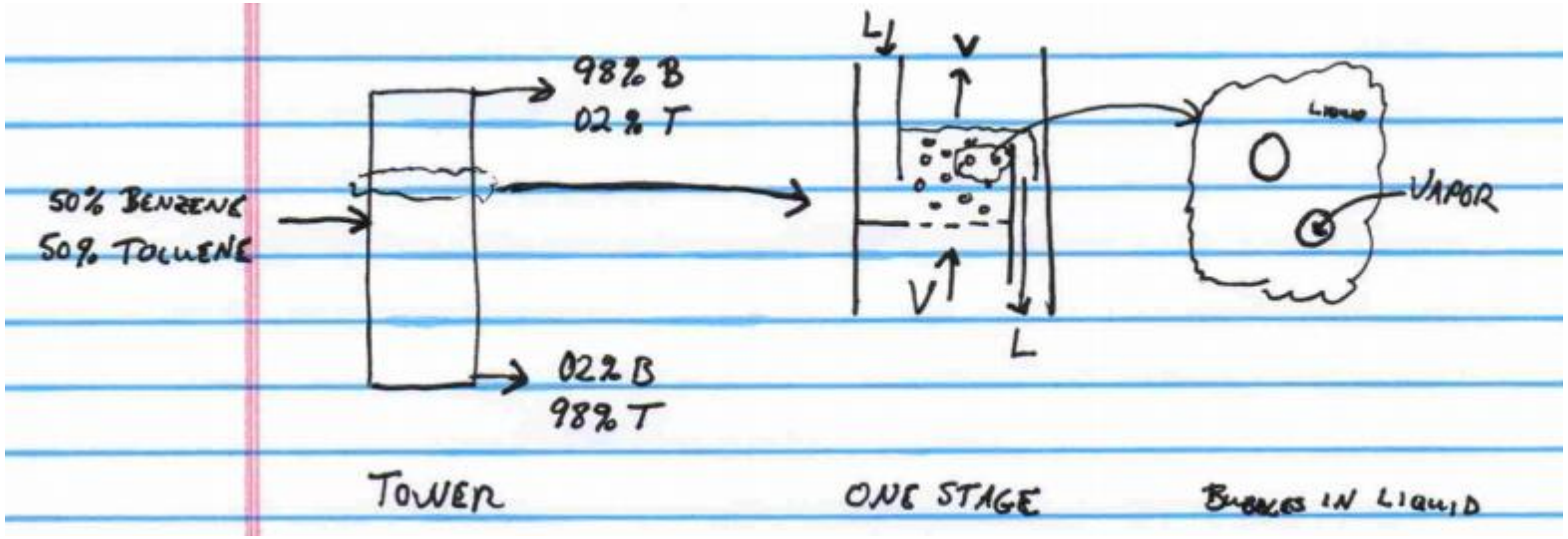
Mass Transfer McSH pp 527-559

- Up to this point we have looked at absorption/stripping/rectification on terms of discrete stages and worked with the principle that each stage had liquid and vapor exiting that stage in equilibrium
    - (or modified that assumption using efficiencies)
- Packed towers do not have discrete stages but rather a continuous array of objects that are wetted by the liquid in order to provide surface area for mass transfer
- Before we can analyze packed towers we need to begin to understand the actual mass transfer occurring between the two phases

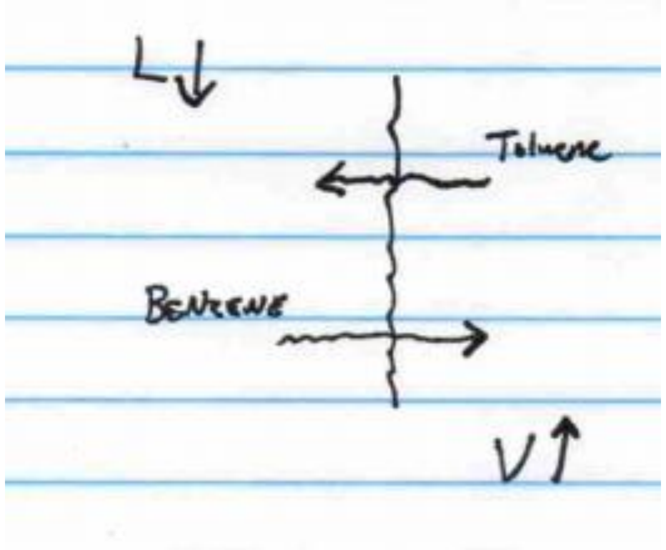
Mass Transfer

- Expand overall mass balance on tower to equilibrium stages to actual mass transfer



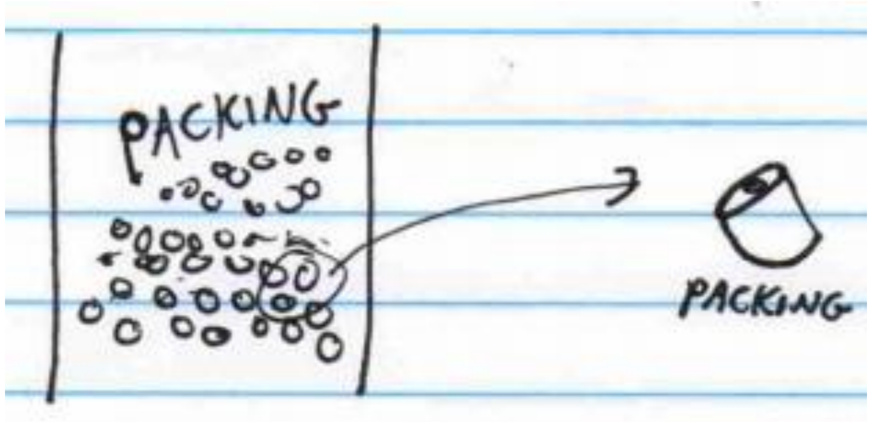
- Mass transfer occurs at the interface between vapor bubbles and continuous liquid
- The interface is distributed across the spherical surface of a very large number of bubbles

Mass Transfer



- Treat the interfacial surface as a plane
  - To an individual molecule the curvature of the bubble is not significant
- A toluene molecule must:
  - Diffuse through the vapor phase to reach the interface
  - Cross the interface (thus condensing)
  - Diffuse into the liquid phase
- A benzene molecule must follow a similar path in the opposite direction

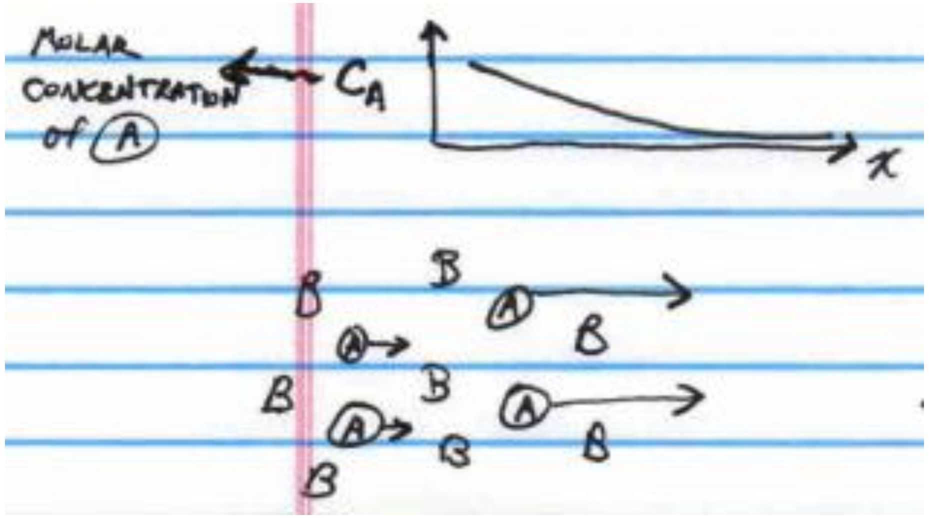
Packed Absorption Tower



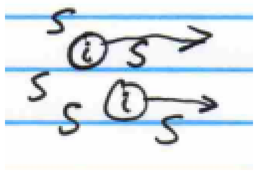
- The liquid wets out the packing in order to provide a large surface area
- Vapor flows up over the wetted packing
- Mass transfer occurs at the vapor/liquid interface
- There are no discrete stages to declare as having reached “equilibrium”
- The mass transfer is occurring in a continuous fashion
- We need to analyze this by looking at the actual diffusion of mass

Calculation of Diffusion Coefficients (CE 318)

- Binary mixture of $\boxed{A}$ and B molecules
- If there is a concentration gradient of $\boxed{A}$ then the $\boxed{A}$ molecules will travel in the direction of lower $\boxed{A}$ concentration



- $\boxed{\boldsymbol{J_A = -D_{AB}\frac{dc_A}{dx}} \qquad \textbf{Fick's Law}}$ J_A has units of $\frac{moles}{area * time}$
- For a generic solute, $\boxed{i}$, in solvent S $\boldsymbol{J_i = -D_i\frac{dc_i}{dx}}$
  - $D_i = D_{iS}$, it is specific to the given solvent



Diffusivity Coefficients - Diffusion in Liquids

- Wilke-Chang eq 17.32 McSH pp 538

$$\boldsymbol{D_{AB} = 7.4 * 10^{-8}\frac{(\psi_B M_B)^{1/2}\,T}{\mu\,V_A^{0.6}}} \text{ in units of } \frac{cm^2}{s}$$

- This approximation is good for small molecules (not polymers or protein molecules)
- This is a fitted approximation to experimental data
- $\boldsymbol{\psi_B M_B}$ is an effective characterization of the molecular weight of solvent, B
  - $\boldsymbol{M_B}$ is the molecular weight of component B
  - $\boldsymbol{\psi_B}$ is related to behavior of solvent B
    - For water the hydrogen bonds make the molecules act as though they are clumps of molecules relative to the solute diffusing through the solvent
    - $\boldsymbol{\psi_B}$ = 2.26 for water and is approximately $\boldsymbol{\psi_B}$= 1 for many organic solvents
- **T** is temperature in Kelvin
- $\boldsymbol{\mu}$ is viscosity of the solution in cP, for dilute solutions this can often be approximated as the viscosity of the solvent

Diffusivity Coefficients - Diffusion in Liquids

- **V**$_A$ is the molar volume of the solute – the molar volume $\left(\frac{cm^3}{mol}\right)$ of the solute as a LIQUID at its boiling point
- What if the solute is a solid that would decompose before reaching a melting point? Schroeder's Method

$$V_A = \left(N_C + N_H + N_O + N_N + N_{dbl} - N_{ring}\right) * 7\ \frac{cm^3}{mol}$$

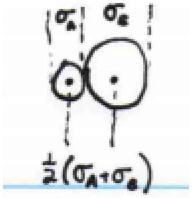
- Where:
  - N_C is the number of carbon atoms
  - N_H is the number of hydrogen atoms
  - N_O is the number of oxygen atoms
  - N_N is the number of nitrogen atoms
  - N_{dbl} is the number of double bonds
  - N_{ring} is the number of separate ring structures (fused rings count as 1)
- If you have data, always use data! Otherwise use the Schroeder method

Diffusivity Coefficients - Diffusion in Vapor Phase

- Chapman-Enskog (kinetic theory of gases) eq 17.28

$$D_{AB} = \frac{0.001858\, T^{3/2}\left[(M_A + M_B)/M_A M_B\right]^{1/2}}{P\, \sigma_{AB}^2\, \Omega_D}$$

- D_{AB} is in $\frac{cm^2}{s}$
- T is temperature in Kelvin
- M_A is the molecular weight of solute A
- M_B is the molecular weight of solvent B
- **P** is pressure in atmospheres
- Lennard-Jones parameters, Appendix 19, on pp 1111-1112 of McSH 7th Edition
    - $\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$ This is effective collision diameter in **Å**
    - $\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}$ This is a force constant, tabulated as $\frac{\epsilon}{K_B}$, with units of **K** (Kelvin)



Diffusivity Coefficients - Diffusion in Vapor Phase

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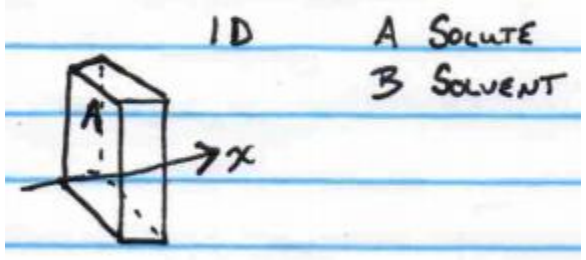
- Collision Integral $\Omega_D = f\left({K_B T}/{\epsilon_{AB}}\right)$ where K_B is Boltzmann's Constant
  - This function is tabulated on pp 1111 (Appendix 19)
- Diffusivity depends on temperature as $T^{3/2}$, BUT Ω_D also depends on temperature
- Typically $D_{AB} \propto T^{1.75}$ and depends on pressure as P^{-1}
- If you have D_{AB} at one temperature and pressure for a pair of components you can estimate at your temperature and pressure using $T^{1.75}$ and P^{-1}
- Correlations are a good resort if you do not have data, but USE EXPERIMENTAL DATA IF YOU HAVE IT

Solute Flux

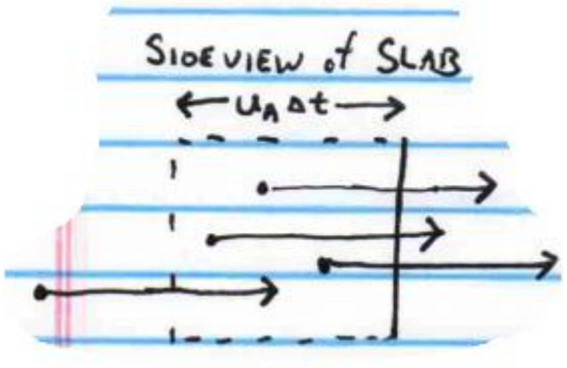
McSH pp 528-535

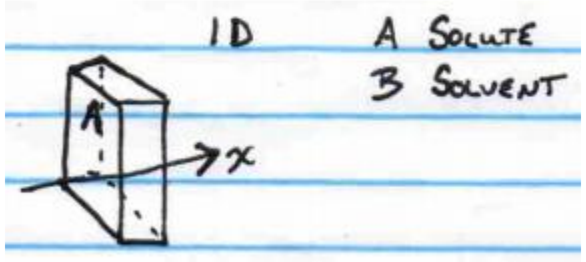
- 1D flow – one dimensional in that the flux is independent of the y and z axes
- Eq 17.3a $\boldsymbol{N_A = u_A c_A}$ Flux of A $\frac{mole}{area * time}$ of A passing through “window”
- Eq 17.3b $\boldsymbol{N_B = u_B c_B}$ Flux of B $\frac{mole}{area * time}$ of B passing through “window”
- $\boldsymbol{u_i}$ is the average speed of component i molecules
- $\boldsymbol{c_i}$ is the concentration of component i

$$\boldsymbol{N_i = u_i c_i}$$



Solute Flux





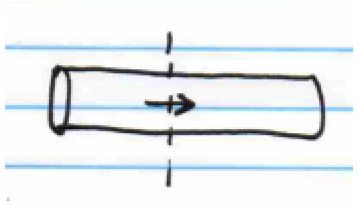
Side view of the slab, consider a time increment $\mathbf{\Delta t}$

- An A molecule will travel the distance $\boldsymbol{u_A}\ \mathbf{\Delta t}$
- Any molecules further to the left of the plane we are considering by a distance greater than $\boldsymbol{u_A}\ \mathbf{\Delta t}$ will NOT cross the plane
- Any molecule that is within a distance of $\boldsymbol{u_A}\ \mathbf{\Delta t}$ WILL cross the plane in the time period $\mathbf{\Delta t}$
- This defines a volume of $\boldsymbol{u_A}\ \boldsymbol{\Delta t}\ \boldsymbol{A}$ that contains all of the molecules that will cross the plane. (A is the cross-sectional area of the control volume.)
- The number of molecules within that volume is $\boldsymbol{u_A}\ \boldsymbol{\Delta t}\ \boldsymbol{A}\ \boldsymbol{c_A}$
  - $\boldsymbol{c_A}$ is $\frac{moles}{volume}$
- This is the number of moles that will cross the plane during time $\boldsymbol{\Delta t}$
- $N_A = \frac{moles}{area*time}$ crossing the plane
- $\boldsymbol{N_A} = \frac{\boldsymbol{u_A \Delta t\ A\ c_A}}{\boldsymbol{A\ \Delta t}} = \boldsymbol{u_A c_A}$ eq 17.3a

Diffusion

- When we talk about diffusion we are talking about the motion of a component relative to the mixture that it is in.

Mixture Flowing through a pipe



- We could measure the number of molecules of A passing a plane/(area*time)
- That is NOT diffusive flux
- Much of that flow of component A is from motion due to the flow of the mixture
- We want to determine motion of A relative to the motion of the mixture

Diffusion refers to the motion of a constituent in a mixture relative to the volume average velocity of the mixture

Diffusive Flux

- If molar density $\left(\frac{total\ moles}{volume}\right)$ is constant (or nearly constant) then the mole average velocity and volume average velocity are the same
- A derivation based on mole average velocity is more straightforward
- The results are the same for mole average as they are for volume average
- $\boldsymbol{\bar{U} = x_A u_A + x_B u_B}$ this is mole average velocity (U_o in textbook)

Flux relative to average motion of mixture is Diffusive Flux

$$\boldsymbol{J_A = (u_A - \bar{U})c_A}\ \frac{moles}{area * time}$$

$$\boldsymbol{J_B = (u_B - \bar{U})c_B}\ \frac{moles}{area * time}$$

$$c = \rho_M = \frac{total\ moles}{volume} = constant$$

$$c_A + c_B = x_A c + x_B c = (x_A + x_B)c = c$$

- $\boldsymbol{J}$ is the symbol for diffusive flux
- $\boldsymbol{J_A + J_B = u_A c_A + u_B c_B - \bar{U}(c_A + c_B)}$

$$\boldsymbol{= u_A x_A c + u_B x_B c - \bar{U}c = (u_A x_A + u_B x_B)c - \bar{U}c}$$

$$\boldsymbol{= \bar{U}c - \bar{U}c = 0}$$

- The motion of (A+B) relative to the average velocity of the mixture is zero – which makes sense

Flux

$$N_A = u_A c_A = \bar{U} c_A + u_A c_A - \bar{U} c_A$$

Overall flux of A eq 17.3a we just added and subtracted $\bar{U} c_A$

$$N_A = \bar{U} c_A + (u_A - \bar{U}) c_A$$

$$N_A = \bar{U} c_A + J_A = \bar{U} c_A - D_{AB} \frac{dc_A}{dx}$$

convective flux Diffusive flux definition Fick's Law

- Convective flux is the flux due to the overall flow of liquid as a whole
- D_{AB} is the diffusion coefficient of A diffusing through B

Flux

$$N_A = \bar{U}c_A - D_{AB}\frac{dc_A}{dx}$$

$$N_B = \bar{U}c_B - D_{BA}\frac{dc_B}{dx}$$

- Note that diffusivity in second equation is D_{BA}, for B diffusing through A
- Textbook uses “b” as the direction, not “x”
- One might be interested in either flow
- $N = N_A + N_B = u_A c_A + u_B c_B$ “the flux of everything”

$$= u_A x_A c + u_B x_B c$$

$$= (u_A x_A + u_B x_B)c$$

$$= \bar{U}c$$

Flux

$$N_A = \bar{U} c_A - D_{AB} \frac{dc_A}{dx}$$

$$= \bar{U} c\, x_A - D_{AB} \frac{d(c\, x_A)}{dx}$$

From previous slide $\mathrm{N} = N_A + N_B = \bar{U} c$

c can be taken out of derivative because it is constant

Note that x_A is a mole fraction while x in the denominator is just the x axis, a direction

$$N_A = (N_A + N_B) x_A - D_{AB}\, c\, \frac{dx_A}{dx}$$

- Similar steps for B lead to

$$\boxed{\begin{aligned} N_A &= (N_A + N_B) x_A - D_{AB}\, c\, \frac{dx_A}{dx} \\ N_B &= (N_A + N_B) x_B - D_{BA}\, c\, \frac{dx_B}{dx} \end{aligned}}$$

Reciprocal Relation of D_{AB} and D_{BA}

$$J_A = -D_{AB}\frac{dc_A}{dx} \qquad J_B = -D_{BA}\frac{dc_B}{dx}$$

- We know that $J_A + J_B = 0$ therefore $J_A = -J_B$
- Also $c_A + c_B = c = constant$

$$\frac{dc_A}{dx} + \frac{dc_B}{dx} = \frac{dc}{dx} = 0$$

$$\frac{dc_A}{dx} = -\frac{dc_B}{dx}$$

Reciprocal Relation of D_{AB} and D_{BA}

$$\frac{dc_A}{dx} = -\frac{dc_B}{dx} \qquad \text{and} \qquad J_A = -J_B$$

$$J_B = -D_{BA}\frac{dc_B}{dx}$$

- Making substitutions

$$J_B = -J_A = -D_{BA}\left(-\frac{dc_A}{dx}\right)$$ substitute $\frac{dc_A}{dx} = -\frac{dc_B}{dx}$

$$J_A = -D_{BA}\left(\frac{dc_A}{dx}\right)$$ drop a negative sign on each side

- But, by definition $J_A = -D_{AB}\left(\frac{dc_A}{dx}\right)$

- Therefore: $\boxed{D_{BA} = D_{AB}}$ eq 17.11