

# CE407 SEPARATIONS

Lecture 18

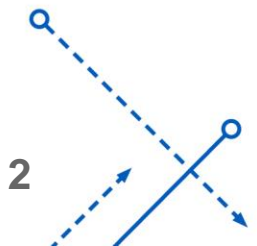
Instructor: Miao Yu

 University at Buffalo  
Department of Chemical  
and Biological Engineering  
School of Engineering and Applied Sciences



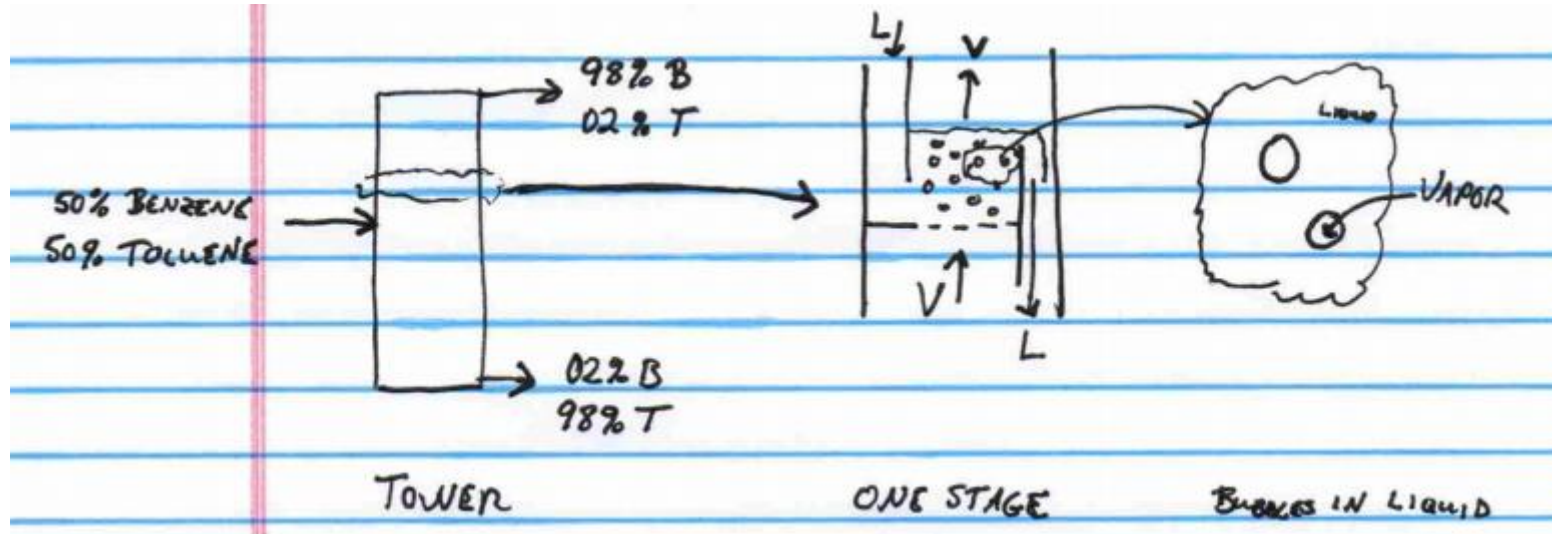
# Mass Transfer McSH pp 527-559

- Up to this point we have looked at absorption/stripping/rectification on terms of discrete stages and worked with the principle that each stage has 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



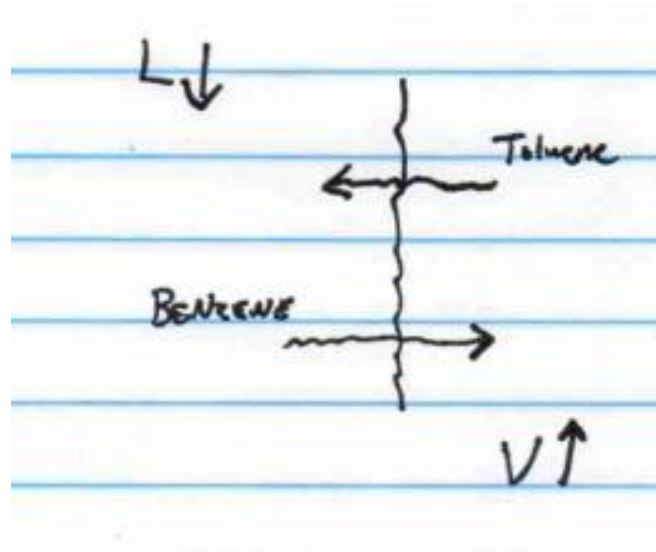
# Mass Transfer

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

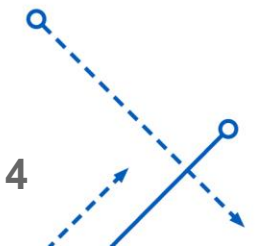


- Mass transfer occurs at the interface between vapor bubbles and continuous liquid
- The interface is distributed across the spherical surface of a very large number of bubbles

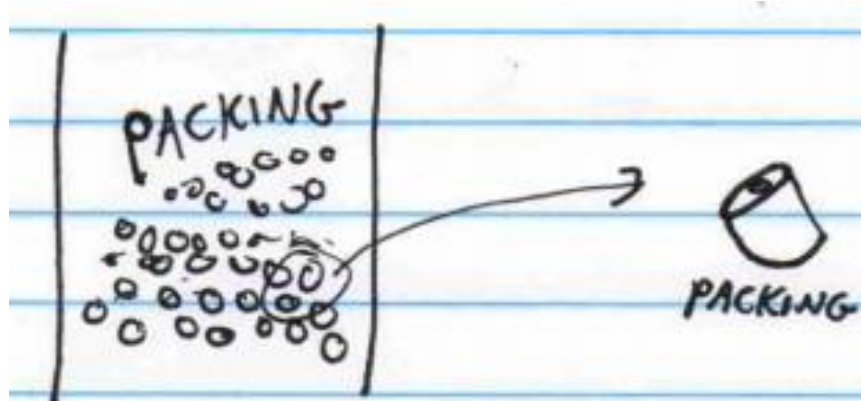
# Mass Transfer



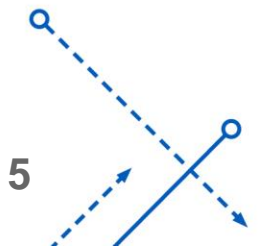
- Treat the interfacial surface as a plane
  - To an individual molecule the curvature of the bubble is not significant
- A toluene molecule must:
  - Diffuse through the vapor phase to reach the interface
  - Cross the interface (thus condensing)
  - Diffuse into the liquid phase
- A benzene molecule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



# Packed Absorption Tower

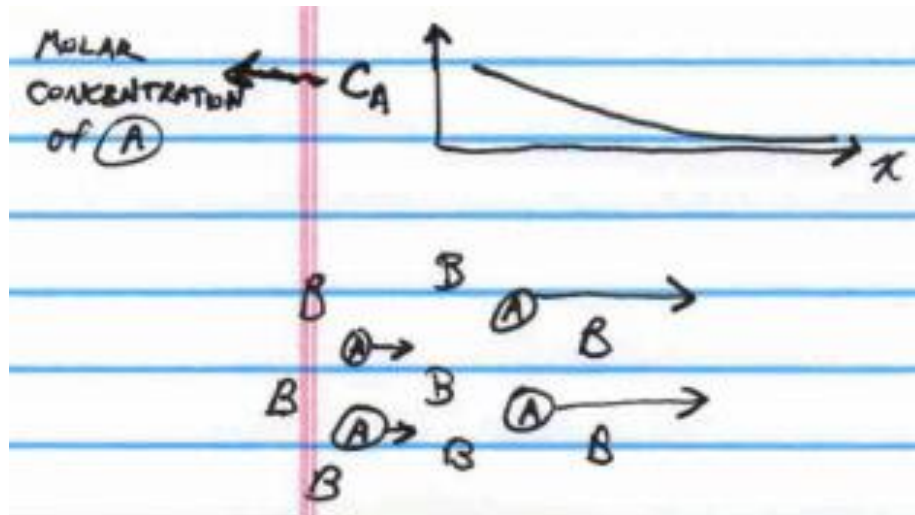


- The liquid wets out the packing in order to provide a large surface area
- Vapor flows up over the wetted packing
- Mass transfer occurs at the vapor/liquid interface
- There are no discrete stages to declare as having reached “equilibrium”
- The mass transfer is occurring in a continuous fashion
-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

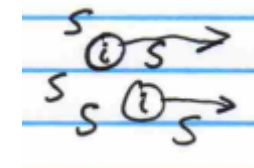


# Calculation of Diffusion Coefficients (CE 318)

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



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

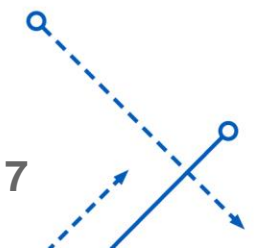


# Diffusion Coefficients - Diffusion in Liquids

- Wilke-Chang eq 17.32 McSH pp 538

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

- This approximation is good for small molecules (not polymers or protein molecules)
- This is a fitted approximation to experimental data
- $\psi_B M_B$  is an effective characterization of the molecular weight of solvent, B
  - $M_B$  is the molecular weight of component B
  - $\psi_B$  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
    - $\psi_B = 2.26$  for water and is approximately  $\psi_B = 1$  for many organic solvents
- $T$  is temperature in Kelvin
- $\mu$  is viscosity of the solution in cP, for dilute solutions this can often be approximated as the viscosity of the solvent

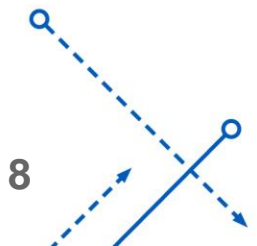


# Diffusion Coefficients - Diffusion in Liquids

- $V_A$  is the molar volume of the solute – the molar volume  $\left(\frac{\text{cm}^3}{\text{mol}}\right)$  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

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

- 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





# Diffusion Coefficients - Diffusion in Vapor Phase

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

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

- $D_{AB}$  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 7<sup>th</sup> 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)



## 1112 APPENDIX 19: Collision Integral and Lennard-Jones Force Constants

**Lennard-Jones force constants**

Compound	$\epsilon/k$ (K)	$\sigma$ (Å)
Acetone	560.2	4.600
Acetylene	231.8	4.033
Air	78.6	3.711
Ammonia	558.3	2.900
Argon	93.3	3.542
Benzene	412.3	5.349
Bromine	507.9	4.296
<i>n</i> -butane	310	5.339
<i>i</i> -butane	313	5.341
Carbon dioxide	195.2	3.941
Carbon disulfide	467	4.483
Carbon monoxide	91.7	3.690
Carbon tetrachloride	322.7	5.947
Carbonyl sulfide	336	4.130
Chlorine	316	4.217
Chloroform	340.2	5.389
Cyanogen	348.6	4.361
Cyclohexane	297.1	6.182
Cyclopropane	248.9	4.807
Ethane	215.7	4.443
Ethanol	362.6	4.530
Ethylene	224.7	4.163
Fluorine	112.6	3.357
Helium	10.22	2.551
<i>n</i> -Hexane	339.3	5.949
Hydrogen	59.7	2.827
Hydrogen cyanide	569.1	3.630
Hydrogen chloride	344.7	3.339
Hydrogen iodide	288.7	4.211
Hydrogen sulfide	301.1	3.623

**Collision integral  $\Omega_D$** 

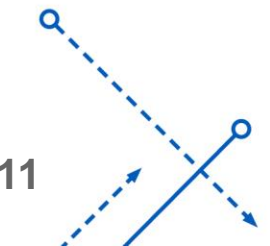
$\frac{kT}{\epsilon_{12}}$	$\Omega_D$	$\frac{kT}{\epsilon_{12}}$	$\Omega_D$	$\frac{kT}{\epsilon_{12}}$	$\Omega_D$
0.30	2.662	1.65	1.153	4.0	0.8836
0.35	2.476	1.70	1.140	4.1	0.8788
0.40	2.318	1.75	1.128	4.2	0.8740
0.45	2.184	1.80	1.116	4.3	0.8694
0.50	2.066	1.85	1.105	4.4	0.8652
0.55	1.966	1.90	1.094	4.5	0.8610
0.60	1.877	1.95	1.084	4.6	0.8568
0.65	1.798	2.00	1.075	4.7	0.8530
0.70	1.729	2.1	1.057	4.8	0.8492
0.75	1.667	2.2	1.041	4.9	0.8456
0.80	1.612	2.3	1.026	5.0	0.8422
0.85	1.562	2.4	1.012	6	0.8124
0.90	1.517	2.5	0.9996	7	0.7896
0.95	1.476	2.6	0.9878	8	0.7712
1.00	1.439	2.7	0.9770	9	0.7556
1.05	1.406	2.8	0.9672	10	0.7424
1.10	1.375	2.9	0.9576	20	0.6640
1.15	1.346	3.0	0.9490	30	0.6232
1.20	1.320	3.1	0.9406	40	0.5960
1.25	1.296	3.2	0.9328	50	0.5756
1.30	1.273	3.3	0.9256	60	0.5596
1.35	1.253	3.4	0.9186	70	0.5464
1.40	1.233	3.5	0.9120	80	0.5352
1.45	1.215	3.6	0.9058	90	0.5256
1.50	1.198	3.7	0.8998	100	0.5130
1.55	1.182	3.8	0.8942	200	0.4644
1.60	1.167	3.9	0.8888	400	0.4170

# Diffusion Coefficients - Diffusion in Vapor Phase

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

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

- Collision Integral  $\Omega_D = f(K_B T / \epsilon_{AB})$  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  $\Omega_D$  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

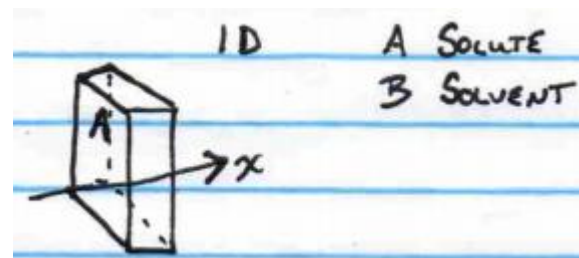


# Solute Flux

McSH pp 528-535

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

$$N_i = u_i c_i$$



# Solute Flux

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

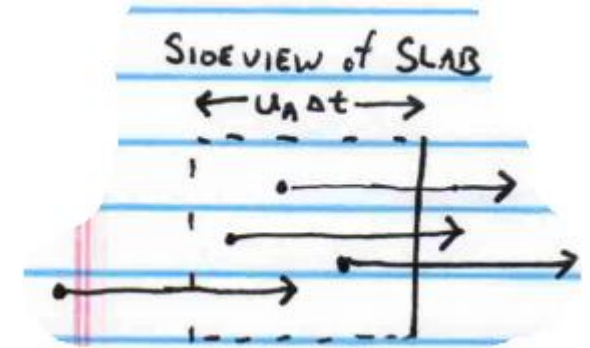
- An A molecule will travel the distance  $u_A \Delta t$
- Any molecules further to the left of the plane we are considering by a distance greater than  $u_A \Delta t$  will NOT cross the plane
- Any molecule that is within a distance of  $u_A \Delta t$  WILL cross the plane in the time period  $\Delta t$
- This defines a volume of  $u_A \Delta t A$  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  $u_A \Delta t A c_A$

- $c_A$  is  $\frac{\text{moles}}{\text{volume}}$

- This is the number of moles that will cross the plane during time  $\Delta t$

- $N_A = \frac{\text{moles}}{\text{area} \cdot \text{time}}$  crossing the plane

- $N_A = \frac{u_A \Delta t A c_A}{A \Delta t} = u_A c_A$  eq 17.3a

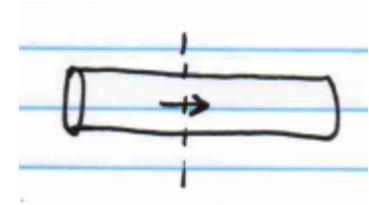


# Diffusion

- 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  $\left(\frac{\text{total moles}}{\text{volume}}\right)$  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
- $\bar{U} = x_A u_A + x_B u_B$  this is mole average velocity ( $U_0$  in textbook)

Flux relative to average motion of mixture is Diffusive Flux

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

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

- $J$  is the symbol for diffusive flux
- $J_A + J_B = u_A c_A + u_B c_B - \bar{U}(c_A + c_B)$   
 $= u_A x_A c + u_B x_B c - \bar{U}c = (u_A x_A + u_B x_B)c - \bar{U}c$   
 $= \bar{U}c - \bar{U}c = 0$

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

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

- 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

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

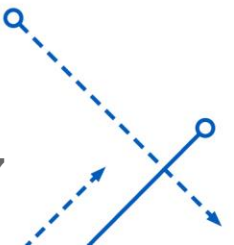
$$N_B = \bar{U}c_B - D_{BA} \frac{dc_B}{dx}$$

- 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

$$\begin{aligned}
 N_A &= \bar{U}c_A - D_{AB} \frac{dc_A}{dx} \\
 &= \bar{U}c x_A - D_{AB} \frac{d(c x_A)}{dx}
 \end{aligned}$$

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

$c$  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

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

## 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  $c_A + c_B = c = \text{constant}$

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

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

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

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

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

- Making substitutions

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

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

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

- Therefore:

$$\boxed{D_{BA} = D_{AB}}$$

eq 17.11

