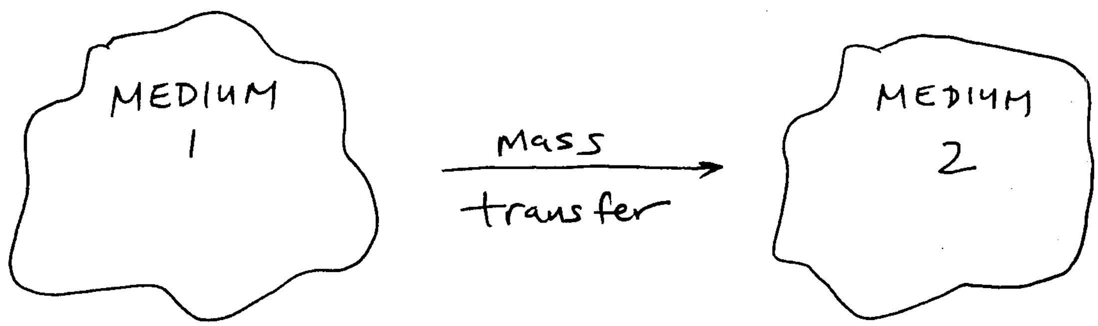
CHAPTER 3 - MASS TRANSFER + DIFFUSION

WHAT IS MASS TRANSFER?



→ Motion of molecules from medium 1 to medium 2 under some driving force.

EXAMPLES:

→ ONE PHASE (NOT WELL MIXED)

→ TWO PHASES (ACROSS AN INTERFACE)

→ SOLID ADSORBENT (INTO POROUS MATERIAL)

→ MEMBRANE (ACROSS "DENSE" FILM)

WHAT MASS TRANSFER IS <u>NOT</u>:

1) Flow in a pipe

2) Flow of solids on a conveyor

⇒ THESE ARE BULK FLUID FLOW

• WHAT IS DIFFUSION?

MOVEMENT OF MOLECULES BY <u>RANDOM</u>, <u>MICROSCOPIC</u> CHANGES DUE TO THERMAL MOTION

(MOLECULAR DIFFUSION)

OR

MOVEMENT BY <u>RANDOM</u>, <u>MACROSCOPIC</u> FLUID MOTION.

(EDDY DIFFUSION)

DEMONSTRATION IN CLASS

MECHANISMS OF DIFFUSION —

→ MOLECULAR

→ RANDOM WALK BY THERMAL MOTION

SLOW

→ EDDY

→ TURBULENT FLOW WITH RANDOM MACROSCOPIC FLUID MOTION.

FAST (RELATIVE)

→ NET FLOW

⇒ CONVECTION

(MORE LIKE FLUID FLOW)

CONSEQUENCE?

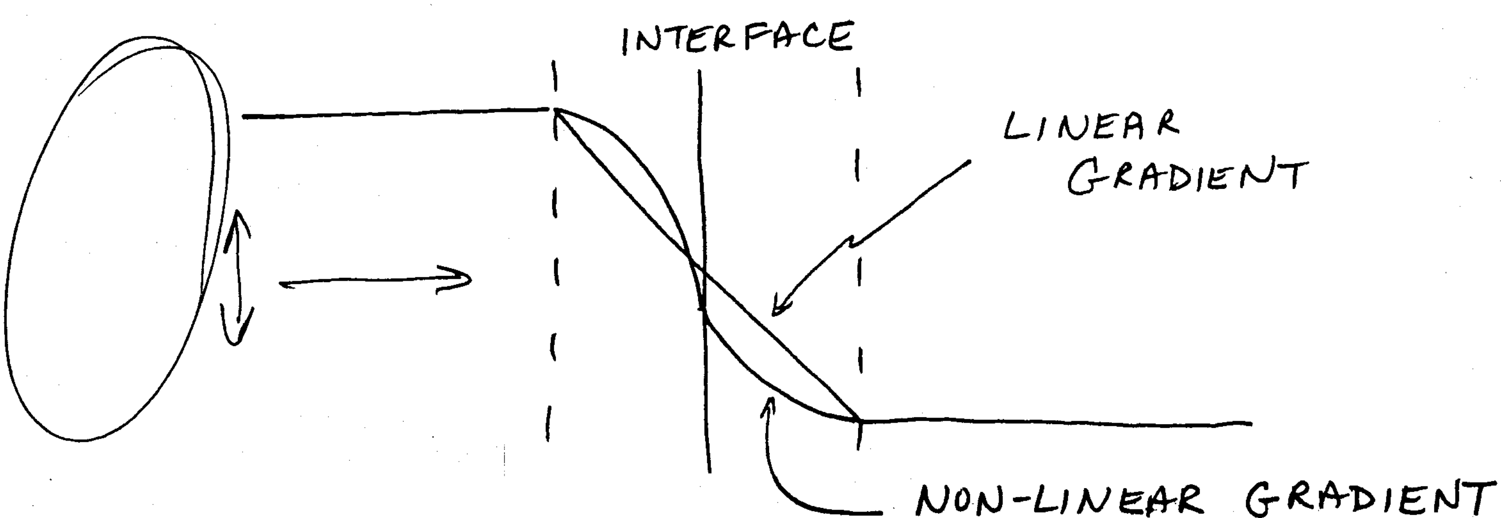
BECAUSE DIFFUSION PROCESSES ARE SLOW AND ON SHORT LENGTH SCALES, FOR LARGE EQUIPMENT, NEED TO AGITATE TO REDUCE THE DISTANCE

DRIVING FORCES FOR DIFFUSION:

1) CONCENTRATION GRADIENT (OUR FOCUS HERE)
   ABSORPTION
2) PRESSURE GRADIENT
   CENTRIFUGATION
3) TEMPERATURE GRADIENT
   LIQUID/GAS CASCADES
4) EXTERNAL FORCE FIELDS
   ELECTRIC FIELDS
   (w/ different effects on different solutes)

WHAT IS THE COMMON THREAD?

* GRADIENT *



WHEN DO YOU GET DIFFERENT MODES OF DIFFUSION?

MOLECULAR DIFFUSION

→ STAGNANT FILMS

→ LAMINAR FLOW

→ TURBULENT FLOW

⇒ THIS IS EVERYWHERE!

EDDY DIFFUSION

→ TURBULENT FLOW <u>ONLY</u>

GENERAL STATEMENTS ON DIFFUSION

→ DIFFUSION IS ADDITIVE

→ EDDY DIFFUSION <u>DAMPED</u> AT INTERFACES + SOLID SURFACES

→ MASS TRANSFER ANALYZED IN <u>ONE</u> DIRECTION RELATIVE TO A PLANE OR FIXED COORDINATE SYSTEM.

→ A NET FLUX CARRIES **ALL** SPECIES

HOW DO WE PUT THIS IN THE FORM OF AN EQUATION?

$$N_i = X_i\,N + \left\{\begin{matrix}\text{MOLECULAR}\\ \text{DIFFUSIONAL}\\ \text{FLUX}\\ \text{COMPONENT}\\ \text{"}i\text{"}\end{matrix}\right\} + \left\{\begin{matrix}\text{EDDY}\\ \text{DIFFUSIONAL}\\ \text{FLUX}\\ \text{COMPONENT}\\ \text{"}i\text{"}\end{matrix}\right\}$$

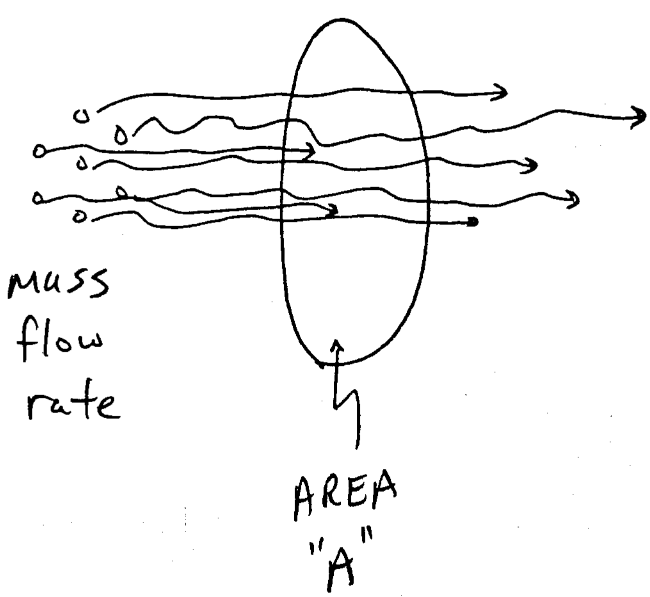
N_i: molar flux component "i"

X_i: mole fraction

N: total molar flux

DIRECTION DICTATES **SIGN** (+ or −)

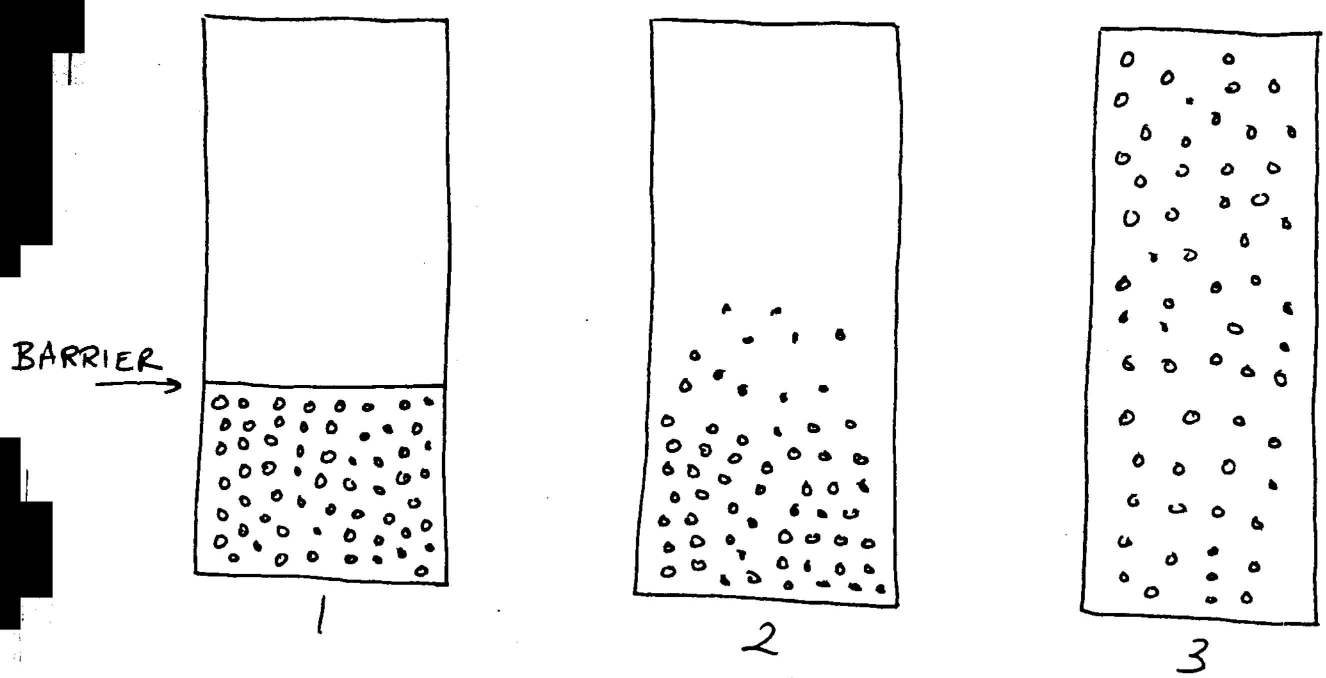
WHAT IS A FLUX?



$$\text{MASS FLUX} = \frac{(\text{mass})}{(\text{area})(\text{time})}$$

$$\text{MOLE FLUX} = \frac{(\text{moles})}{(\text{area})(\text{time})}$$

STEADY STATE ORDINARY MOLECULAR DIFFUSION :



3 COLUMNS OF WATER

① RED DYE IN LOWER SECTION

$$\frac{60 \text{ molecules}}{\tfrac{1}{3} \text{ volume}} \Rightarrow \underset{\text{IN LOWER}}{\text{Concentration}} \text{ is } \frac{180 \text{ molecules}}{\text{volume}}$$

CONCENTRATION IN UPPER SECTION (COL. 1)

$$= \frac{0 \text{ molecules}}{\frac{2}{3} \text{ volume}} = \frac{0 \text{ molecules}}{\text{volume}}$$

Total Concentration (c)

$$= \frac{\left(\frac{180 \text{ molecules}}{\text{volume}}\right)\left(\frac{1}{3} \text{ volume}\right) + \left(\frac{0 \text{ molecules}}{\text{volume}}\right)\left(\frac{2}{3} \text{ volume}\right)}{\text{volume}}$$

$$= \boxed{\frac{60 \text{ molecules}}{\text{volume}} = C}$$

REMOVE BARRIER ...

(2) RED DYE STILL ESSENTIALLY IN LOWER SECTION

$\Rightarrow$ NOT WELL MIXED

$\Rightarrow$ CONCENTRATION GRADIENT (DRIVING FORCE FOR MASS TRANSFER)

TOTAL CONCENTRATION

$$= \boxed{\frac{60 \text{ molecules}}{\text{volume}} = C}$$

ALLOW SUFFICIENT TIME...

(LET THE THERMAL MOTION DO ITS JOB)

3 RED DYE UNIFORMLY DISTRIBUTED

⇒ WELL MIXED

⇒ UNIFORM CONCENTRATION

(SAME CONCENTRATION EVERYWHERE)

→ TOTAL CONCENTRATION = ?

$$C = \frac{60 \text{ molecules}}{\text{volume}}$$

FICK'S LAW OF DIFFUSION:

Similar to heat transfer

$$q_z = -k \frac{dT}{dz}$$

heat transfer rate

thermal Conductivity

TEMPERATURE GRADIENT

ANALOG FOR MASS TRANSFER

(ORDINARY MOLECULAR DIFFUSION)

$$J_{A_z} = -D_{AB} \frac{dc_A}{dz}$$

molecular flux of component "A" in "z" direction

Diffusion coefficient of "A" in "B"

AKA: DIFFUSIVITY

CONCENTRATION GRADIENT COMPONENT "A"

CAN WRITE SIMILAR EXPRESSION FOR OTHER COMPONENTS...

GENERALLY CAN SHORTHAND TO...

$$\boxed{J_A = -c\, D_{AB} \frac{dx_A}{dz}}$$

RECALL FROM OUR 3 COLUMNS,

$C =$ constant

$C_A = x_A C$, so pull c out of derivative & write in terms of mole fraction.

C: total molar concentration

D_{AB}: Diffusivity of component "A" in "B"

D_{BA}: Diffusivity of component "B" in "A"

x_A: mole fraction of component "A"

z: direction in which diffusion takes place.

J_A: Molecular diffusive flux of "A"

N = Total molar flux

BINARY (A & B)

$$N = N_A + N_B$$

N_A = BULK FLOW A + MOLECULAR DIFFUSIVE FLUX OF A + EDDY DIFFUSIVE FLUX OF A

RECALL EDDY DIFFUSION ~ ELIMINATED NEAR AN INTERFACE

$$\Rightarrow \quad N_A = \underbrace{X_A N}_{\text{BULK FLOW}} + \underbrace{- c D_{AB} \frac{d x_A}{d z}}_{J_A}$$

LIKEWISE...

$$N_B = X_B N - c D_{BA} \frac{d x_B}{d z}$$

NOTE THE DIFFERENCES

$$N_A = \frac{n_A}{A} = \frac{\text{molar flow rate } \left(\frac{\text{moles}}{\text{time}}\right)}{\text{mass transfer area}}$$

$$N_B = \frac{n_B}{A}$$

TWO LIMITING CASES:

1) EQUIMOLAR COUNTER DIFFUSION

2) UNIMOLECULAR DIFFUSION.

WE'LL HIT THESE IN THE NEXT SET OF NOTES.

MORE ON MASS TRANSFER

TWO IMPORTANT CASES FOR MOLECULAR DIFFUSION -

1) EQUIMOLAR COUNTER DIFFUSION

2) UNIMOLECULAR DIFFUSION

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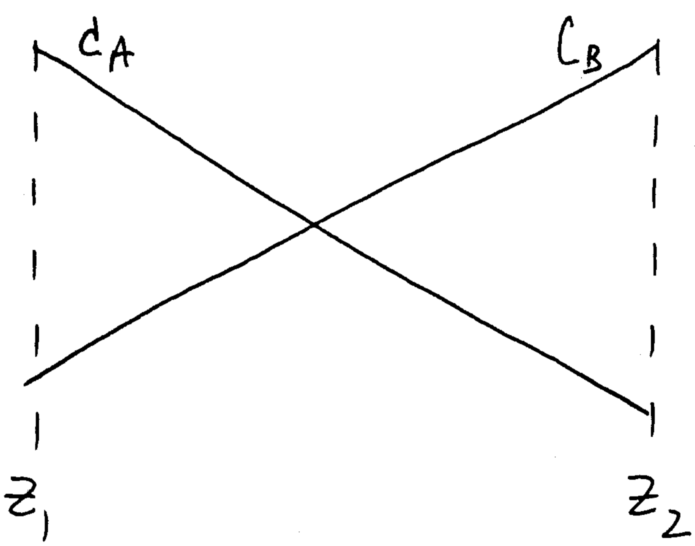
1) EQUIMOLAR COUNTER DIFFUSION



LINEAR CONCENTRATION GRADIENTS

EQUIMOLAR

$\Rightarrow$ MOLES A TRANSFERRED

= MOLES B TRANSFERRED

$\Rightarrow$ $|N_A| = |N_B|$ (equal magnitudes)

COUNTER

$\Rightarrow$ MOLES OF A + B MOVE IN OPPOSITE DIRECTIONS

$\Rightarrow$ $N_A = -N_B$

DIFFUSION

$\Rightarrow$ MECHANISM OF TRANSPORT BY RANDOM MOVEMENT OF MOLECULES (THERMAL MOTION)

$$N = N_A + N_B = 0$$

EQUIMOLAR COUNTER DIFFUSION

BUT
$$N_A = \cancel{x_A N}^{\,0} - c\, D_{AB} \frac{d x_A}{dz}$$

$$N_B = \cancel{x_B N}^{\,0} - c\, D_{BA} \frac{d x_B}{dz}$$

$$\Rightarrow \quad N_A = J_A$$

$$N_B = J_B$$

$$J_A + J_B = 0$$

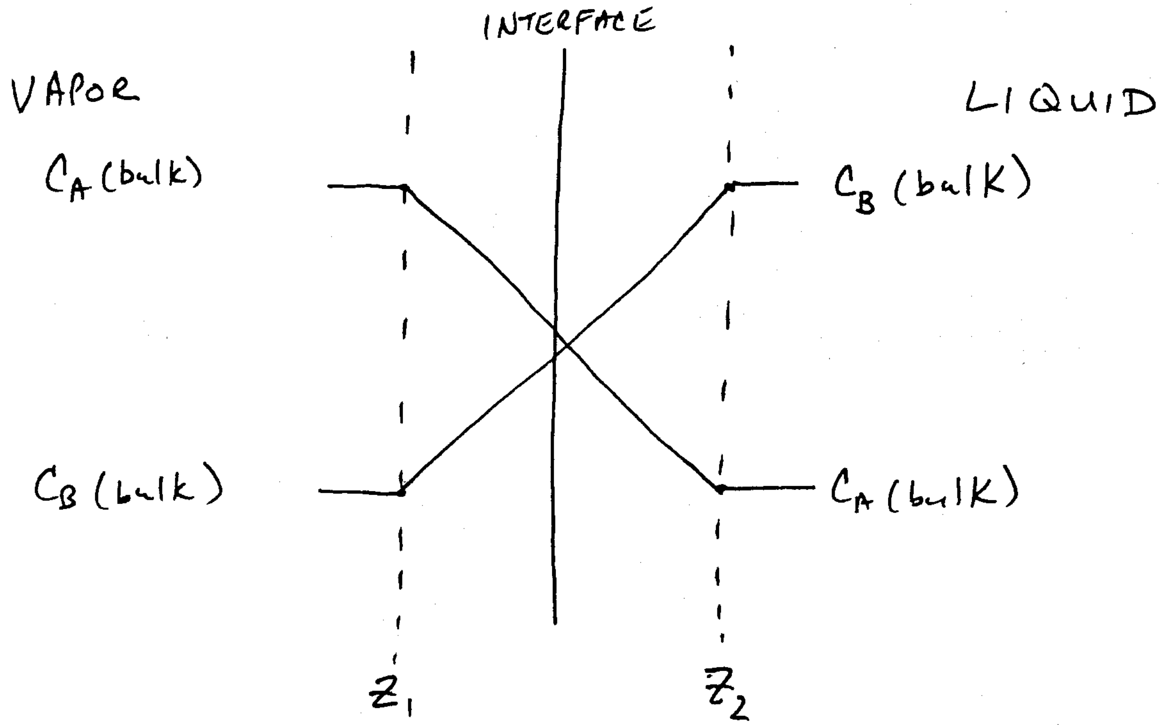
$$\boxed{J_A = -J_B}$$ ← Molecular Diffusive Fluxes

EQUAL MAGNITUDE, OPPOSITE DIRECTION

(EQUIMOLAR COUNTER DIFFUSION)

⇒ GOOD MODEL FOR DISTILLATION

WHY?



A is the light Key

B is the heavy Key

AT ANY PARTICULAR STAGE –

– EQUILIBRIUM

→ CONSTANT T

→ CONSTANT P

→ CONSTANT X_i (composition)

Both phases

$$J_A = -c D_{AB} \frac{dx_A}{dz}$$

Separate + Integrate

$$J_A \int_{z_1}^{z} dz = -c D_{AB} \int_{x_{A_1}}^{x_A} dx_A = -D_{Ac} \int_{c_{A_1}}^{c_A} dc_A$$

$$\frac{J_A (z - z_1)}{z - z_1} = \frac{-c D_{AB} (x_A - x_{A_1})}{z - z_1}$$

$$\boxed{J_A = \frac{c D_{AB}}{(z - z_1)} (x_{A_1} - x_A)}$$

mole fractions of A

C: total molar concentration

D_{AB}: diffusivity A in B

$z - z_1$: diffusion distance

Likewise...

$$J_B = \frac{c D_{BA}}{(z - z_1)} (x_{B1} - x_B)$$

How ARE D_{AB} & D_{BA} RELATED?

1) Remember that c is constant

2) $C = C_A + C_B$ (binary)

3) $\underbrace{dc = 0}_{C \text{ is constant}} = dc_A + dc_B$

$$\Rightarrow \quad dc_A = -dc_B$$

4) Gradients in z-direction

$$\Rightarrow \quad \boxed{\frac{dc_A}{dz} = -\frac{dc_B}{dz}}$$

(Recall graph)

5) But, this is EQUIMOLAR COUNTER-DIFFUSION

$$N = N_A + N_B = 0$$

$$0 = -c D_{AB} \frac{dx_A}{dz} - c D_{BA} \frac{dx_B}{dz}$$

$$0 = D_{AB} \frac{dc_A}{dz} + D_{BA} \frac{dc_B}{dz}$$

Substitute for $\frac{dc_B}{dz}$

$$0 = D_{AB} \frac{dc_A}{dz} - D_{BA} \frac{dc_A}{dz}$$

$\Rightarrow \boxed{D_{AB} = D_{BA}}$ for EQUIMOLAR COUNTER DIFFUSION

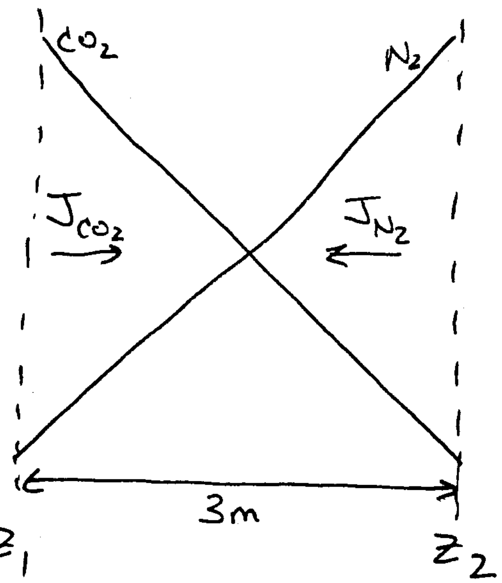
EXAMPLE:

$P = 1\,atm$

$T = 0\,^{\circ}C$

$D_{CO_2-N_2} = 0.144\ \frac{cm^2}{s}$

$N = N_A + N_B = 0$



$y_{CO_2} = 0.2$ $\qquad$ $y_{CO_2} = 0.02$

a) WHAT IS THE FLUX OF CO_2?

b) WHAT IS THE FLUX OF N_2?

(in $mol/m^2 \cdot hr$)

→ Got a picture already

→ Have a list of what we know

→ $$J_{CO_2} = \frac{c\, D_{CO_2-N_2}}{(z_2 - z_1)} \left(y_{CO_2,1} - y_{CO_2,2} \right)$$

GAS PHASE ⇒ GAS MOLE FRACTIONS

HAVE THE EQUATION...

LET'S FILL OUT THE TERMS...

C: GAS PHASE, 1 ATM $\Rightarrow$ IDEAL GAS OK

$$C = \frac{n}{V} = \frac{P}{RT}$$

$P = 1 \text{atm}$

$T = 0°C = 273.15 K$

$R = 0.08206 \frac{L \cdot atm}{mol \cdot K}$

$$\Rightarrow \boxed{C = 0.0446 \frac{mol}{L}}$$

Moles of what? EVERYTHING

$$D_{CO_2 - N_2} = 0.144 \frac{cm^2}{s}$$

$$z_2 - z_1 = 3m$$

$y_{CO_2,1} = 0.2$ $y_{CO_2,2} = 0.02$

PLUG + CHUG...

$$J_{CO_2} = \frac{0.0446\ mol}{L}\left|\frac{0.144\ cm^2}{s}\right|\frac{1}{3\ m}\left|\frac{(0.2-0.02)}{1}\right|$$

$$\left|\frac{3600\ sec}{1\ hr}\right|\frac{1\ L}{1000\ cm^3}\left|\frac{100\ cm}{1\ m}\right|$$

$$\boxed{J_{CO_2} = \frac{0.138\ moles\ CO_2}{m^2 \cdot hr}}$$

WHAT IS THE FLUX OF N_2?

$$J_{N_2} = \frac{0.138\ moles\ N_2}{m^2 \cdot hr}$$

in opposite direction

UNIMOLECULAR DIFFUSION:

→ COMPONENT A DIFFUSES THROUGH

STAGNANT LAYER OF B.

$\Rightarrow \quad N_B = 0$ Total Molar Flux of B.

$$N = N_A + \cancel{N_B}^{\,0}$$

$$\Rightarrow \quad \boxed{N = N_A}$$ Unimolecular Diffusion

Recall...

$$N_A = X_A N - c D_{AB} \frac{dx_A}{dz}$$

BUT $N = N_A$

$$N_A = X_A N_A - c D_{AB} \frac{dx_A}{dz}$$

[redacted]

SOLVE FOR N_A ...

$$\boxed{N_A = \frac{-\,c\,D_{AB}}{(1-x_A)} \frac{dx_A}{dz}}$$

Total Molar Flux of $\underline{\underline{A}}$

WHAT ABOUT B?

$$N_B = x_B N - c\,D_{BA} \frac{dx_B}{dz}$$

BUT, $N_B = 0$

$N = N_A$

$$0 = x_B N_A - c\,D_{BA} \frac{dx_B}{dz}$$

$$\Rightarrow \quad x_B N_A = c\,D_{BA} \frac{dx_B}{dz}$$

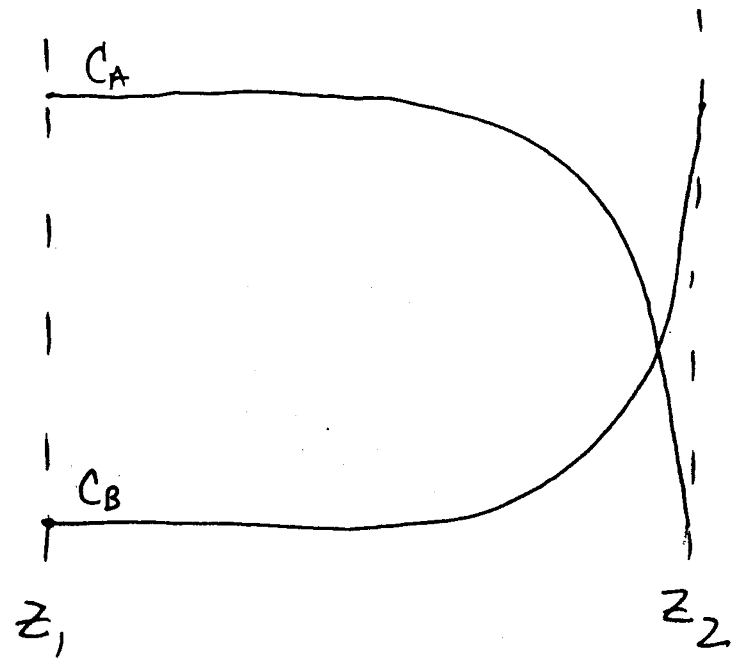
EQUAL, BUT OPPOSITE DIRECTIONS

$$\Rightarrow \underline{\underline{N_B = 0}}$$

<u>OK</u>, BUT WHAT IS THE FLUX OF A?

SEPARATE & INTEGRATE

$$N_A \, dz = -c D_{AB} \frac{dx_A}{(1-x_A)}$$



$$N_A \int_{z_1}^{z} dz = -c D_{AB} \int_{x_{A_1}}^{x_A} \frac{dx_A}{1-x_A}$$

$$N_A (z - z_1) = -c D_{AB} \ln (1 - x_A) \Big|_{x_{A_1}}^{x_A} \quad (-1)$$

$$N_A\,(z-z_1) = +\,c\,D_{AB}\,\ln\left(\frac{1-x_A}{1-x_{A_1}}\right)\ (+1)$$

$$\Rightarrow \quad \boxed{N_A = \frac{c\,D_{AB}}{(z-z_1)}\,\ln\left(\frac{1-x_A}{1-x_{A_1}}\right)}$$

Total Molar Flux A for

UNIMOLECULAR DIFFUSION.

NEXT TIME...

HOW DO I GET D_{AB}?

DIFFUSION COEFFICIENTS:

→ MOLECULAR

$$\Rightarrow \quad J_A = -c \boxed{D_{AB}} \frac{dx_A}{dz}$$

OUR FOCUS IS ON BINARY DIFFUSIVITIES

MEASURED EXPERIMENTALLY

⇒ HOWEVER, NEED TO MAKE SURE
NO BULK FLOW
(So that all mass transfer is by diffusion)

DIFFUSION IN GAS, LIQUID, SOLIDS

→ IN EACH CASE, LARGE MAGNITUDE DIFFERENCE

GAS: $\quad D_{AB} \approx 0.1 - 10 \ \frac{cm^2}{s}$

LIQUID: $D_{AB} \approx 1 \times 10^{-5} \frac{cm^2}{s}$

SOLID: $D_{AB} \approx 1 \times 10^{-9} \frac{cm^2}{s}$ (gas in polymer)

Varies the most
$10^{-4} - 10^{-12} \frac{cm^2}{s}$

BIGGEST CHANGE IN DIFFUSIVITY BY:

<u>TEMPERATURE !</u>

WHY? $T \uparrow \Rightarrow$ more energy in system

Recall: Molecular diffusion is random movement of molecules by <u>thermal</u> motion.

Also, changes in Gas phase by pressure.

Why?

Gases: High Pressure $\Rightarrow$

more interaction between gases (molecules)

$\Rightarrow$ Not going as far between collisions.

Liquids + Solids: INCOMPRESSIBLE

$\Rightarrow$ NEGLIGIBLE PRESSURE EFFECT.

GAS DIFFUSION COEFFICIENTS (DIFFUSIVITIES)

Remember for binary, $D_{AB} = D_{BA}$

Why? Density same for different compositions

@ low $\rightarrow$ moderate Pressure:

$$D_{AB} \propto \frac{1}{P} \qquad (\sim 1:1)$$

$$D_{AB} \neq f(\text{composition})$$

$D_{AB} \propto T \qquad (> 1:1)$

Consequence?

$P_{new} = 2P \qquad D_{AB}^{New} = \frac{1}{2} D_{AB}$

$P_{New} = \frac{1}{2} P \qquad D_{AB}^{New} = 2 D_{AB}$

$X_A = X_B$

$\rightarrow X_A = \frac{X_B}{10} \qquad D_{AB}^{New} = D_{AB}$

WHAT ABOUT Temperature?

→ Chapman - Enskog

$$D_{AB} = D_{BA} = \frac{0.00143\, T^{1.75}}{P\, M_{AB}^{1/2} \left[(\Sigma_v)_A^{1/3} + (\Sigma_v)_B^{1/3} \right]^2}$$

$D_{AB} \; [=] \; \frac{cm^2}{s}$

$P \; [=] \; atm$