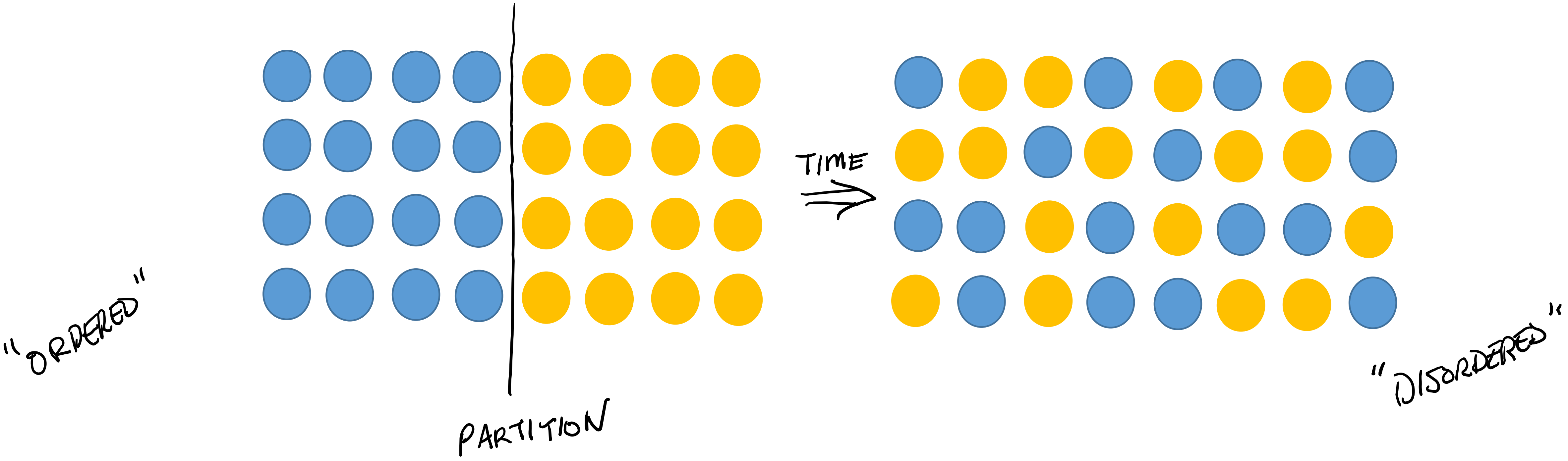
4) MOLECULAR MASS TRANSPORT

A. INTRODUCTION

MOLECULAR MASS TRANSPORT IS THE MOVEMENT OF INDIVIDUAL MOLECULES THROUGH A MEDIUM BY RANDOM MOTION



DIFFUSION IS THE PHYSICAL TENDENCY OF MOLECULES TO MOVE BY RANDOM MOTION TOWARD CONDITIONS OF "EQUILIBRIUM". THERE MUST BE SOME MOLECULAR "DRIVING FORCE" FOR DIFFUSION TO OCCUR, THIS DRIVING FORCE IS THE DIFFERENCE BETWEEN THE PRESENT STATE AND THE EQUILIBRIUM STATE.

"DRIVING FORCES"

1) CONCENTRATION DIFFERENCE - "ORDINARY DIFFUSION"
2) TEMPERATURE DIFFERENCE - "THERMAL DIFFUSION"
3) PRESSURE DIFFERENCE - "PRESSURE DIFFUSION"
4) UNEQUAL EXTERNAL FORCES - "FORCED DIFFUSION" (e.g., EXTERNAL CHARGE)

B) VELOCITIES

i. PARTICLES (SUCH AS PARTICLES) TRAVELLING THROUGH SPACE HAVE A VELOCITY DENOTED BY A VECTOR:

$$\vec{V_i} = V_{i1}\vec{\varepsilon}_1 + V_{i2}\vec{\varepsilon}_2 + V_{i3}\vec{\varepsilon}_3$$

i = ith component

$\vec{\varepsilon}_1, \vec{\varepsilon}_2, \vec{\varepsilon}_3$ = UNIT VECTORS IN DIRECTION OF THE 1, 2, 3 AXES.

IN RECT. COORDINATES

$$\vec{V_i} = V_{ix}\vec{\varepsilon}_x + V_{iy}\vec{\varepsilon}_y + V_{iz}\vec{\varepsilon}_z$$

VELOCITY HAS A MAGNITUDE & DIRECTION.

ii. THE MEAN VELOCITY OF A K-COMPONENT SYSTEM CAN BE DESCRIBED BY A MASS AVERAGE OR A MOLE-AVERAGE VELOCITY. EITHER ONE COULD BE TERMED THE "BULK VELOCITY"

MASS AVERAGE (LOWER CASE v)

$$\vec{v} = \frac{\sum m_i \vec{v}_i}{\sum m_i} = \sum w_i \vec{v}_i = \frac{\sum \rho_i \vec{v}_i}{\sum \rho_i}$$

MOLE AVERAGE (UPPER CASE V)

$$\vec{V} = \frac{\sum n_i \vec{V}_i}{\sum n_i} = \sum x_i \vec{V}_i = \frac{\sum c_i \vec{V}_i}{\sum c_i}$$

NOTE:

USUALLY IT IS CONVENIENT TO USE CONCENTRATIONS (ρ_i OR c_i) INSTEAD OF MASS OR MOLES (m_i OR n_i) BECAUSE CONCENTRATIONS ARE KNOWN.

iii) IN GENERAL A GIVEN COMPONENT DOES NOT HAVE THE SAME VELOCITY AS THE BULK FLUID. THAT IS,

$$\vec{V}_i \neq \vec{v}$$

$$\vec{v}_i \neq \vec{V}$$

THE DIFFERENCE BETWEEN THE VELOCITY OF A PARTICULAR COMPONENT AND THE BULK VELOCITY IS CALED THE DIFFUSION VELOCITY, AND IT CAN BE RELATIVE TO EITHER THE MASS-AVERAGE OR MOLE-AVERAGE VELOCITIES

MASS:
(LOWER CASE u)

$$\vec{u}_i = \vec{v}_i - \vec{v}$$

MOLE:

$$\vec{U} = \vec{v}_i - \vec{V}$$

NOTES:

1) COMPONENT VELOCITY = BULK VELOCITY + DIFFUSION VELOCITY

2) DIFFUSION VELOCITY IS THE VELOCITY OF THE COMPONENT RELATIVE TO THE MOVING COORDINATES OF THE BULK FLUID.

EXAMPLE 1

A GAS MIXTURE CONTAINS 80% He AND 20% Ar (MOLE BASIS). THESE PARTICLES MOVE WITH THE FOLLOWING VELOCITY VECTORS:

$$\vec{V}_{He} = 2.0\,\vec{\varepsilon}_x \qquad \vec{V}_{Ar} = -1.2\,\vec{\varepsilon}_x \qquad (\mu m/s)$$

a) FIND MASS- & MOLE- AVERAGE VELOCITIES

b) FIND MASS- & MOLE- BASIS DIFFUSION VELOCITIES.

$$y_{He} = 0.80 \qquad y_{Ar} = 0.20$$

$$w_{He} = \frac{(0.80)(4)}{(0.80)(4) + (0.20)(40)} = 0.286 \qquad w_{Ar} = 0.714$$

a) MASS AVERAGE VELOCITY:

$$\vec{v} = \sum \omega_i \vec{v}_i$$

$$= \omega_{He} \vec{v}_{He} + \omega_{Ar} \vec{v}_{Ar}$$

$$= (0.286)(2.0\,\vec{e}_x) + (0.714)(-1.2\,\vec{e}_x)$$

$$\underline{\vec{v} = -0.285\,\vec{e}_x} \quad (\mu m/s)$$

MOLE-AVERAGE VELOCITY

$$\vec{V} = \sum y_i \vec{v}_i$$

$$= y_{He} \vec{v}_{He} + y_{Ar} \vec{v}_{Ar}$$

$$= (0.80)(2.0\,\vec{e}_x) + (0.20)(-1.2\,\vec{e}_x)$$

$$\underline{\vec{V} = +1.36\,\vec{e}_x} \quad (\mu m/s)$$

b) DIFFUSION VELOCITIES

RELATIVE TO MASS-AVERAGE VELOCITY: $\vec{u}_i = \vec{v}_i - \vec{v}$

$$\vec{u}_{He} = \vec{v}_{He} - \vec{v} = 2.0\,\vec{\varepsilon}_x - (-0.285\,\vec{\varepsilon}_x) = \underline{+2.285\,\vec{\varepsilon}_x}$$

$$\vec{u}_{Ar} = \vec{v}_{Ar} - \vec{v} = -1.2\,\vec{\varepsilon}_x - (-0.285\,\vec{\varepsilon}_x) = \underline{-0.915\,\vec{\varepsilon}_x}$$

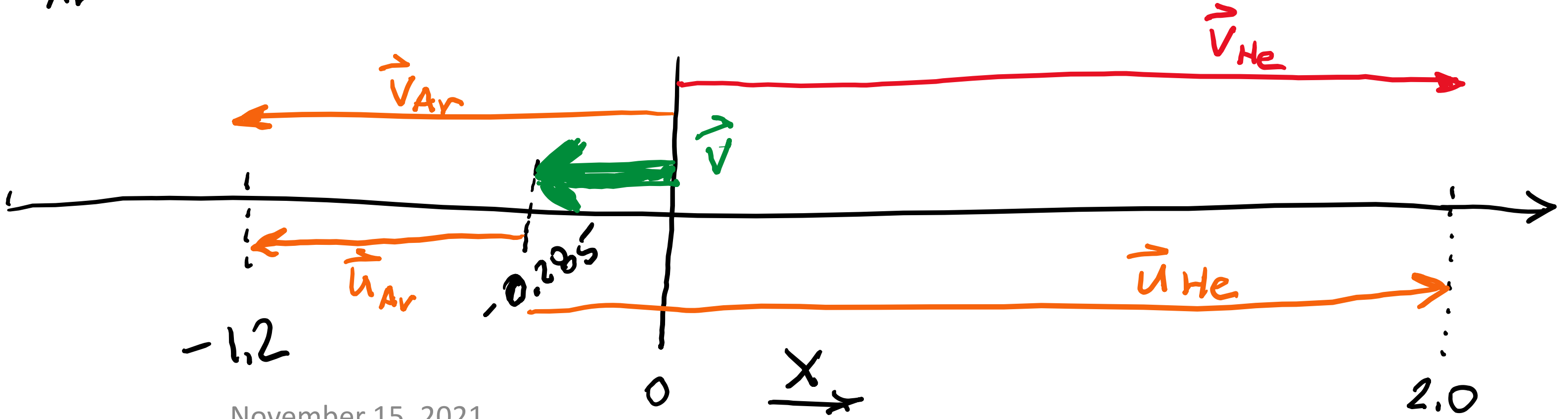
(μm/s)

RELATIVE TO MOLE-AVERAGE VELOCITY: $\vec{U}_i = \vec{v}_i - \vec{V}$

$$\vec{U}_{He} = \vec{v}_{He} - \vec{V} = 2.0\,\vec{\varepsilon}_x - (1.36\,\vec{\varepsilon}_x) = \underline{+0.64\,\vec{\varepsilon}_x}$$

$$\vec{U}_{Ar} = \vec{v}_{Ar} - \vec{V} = -1.2\,\vec{\varepsilon}_x - (1.36\,\vec{\varepsilon}_x) = \underline{-2.56\,\vec{\varepsilon}_x}$$

MASS BASIS



C. FLUXES

FLUX IS THE QUANTITY OF A COMPONENT (MASS OR MOLAR BASIS) FLOWING THROUGH A UNIT AREA IN A UNIT TIME (QTY/AREA·TIME)

EXAMPLE UNITS

$$\left.\begin{array}{l} mol/m^2s \\ kmol/m^2s \end{array}\right\} \text{MOLAR}$$

$$\left.\begin{array}{l} g/cm^2s \\ kg/m^2s \end{array}\right\} \text{MASS}$$

FLUX HAS DIRECTION & MAGNITUDE

$$\text{MASS FLUX} = \frac{\text{MASS}}{\text{AREA} \cdot \text{TIME}} = \frac{\text{MASS FLOWRATE}}{\text{AREA}}$$

$$\text{MOLAR FLUX} = \frac{\text{MOLES}}{\text{AREA} \cdot \text{TIME}} = \frac{\text{MOLAR FLOWRATE}}{\text{AREA}}$$

MASS FLOWRATE = MASS FLUX * AREA

MOLAR FLOWRATE = MOLAR FLUX * AREA

USEFUL!

i. A COMPONENT'S FLUX ("TOTAL FLUX") IS THE QUANTITY OF A COMPONENT FLOWING THROUGH A STATIONARY AREA IN A GIVEN AMOUNT OF TIME.

MASS: $\vec{\phi}_i = \rho_i \vec{V}_i$

$$\frac{g}{cm^2 s} = \left(\frac{g}{cm^3}\frac{cm}{s}\right)$$

MOLAR: $\vec{\Phi}_i = c_i \vec{V}_i$

ii. THE COMPONENT FLUX DUE TO THE BULK FLUID IS MERELY THE CONCENTRATION OF THAT COMPONENT TIMES THE BULK VELOCITY

MASS: $\rho_i \vec{V}$ NO SYMBOL IS USED

MOLAR: $c_i \vec{V}$

OTHER WAYS TO WRITE THIS VALUE (MASS - EXAMPLE)

$$\rho_i \vec{V} = \rho_i \left(\sum w_j \vec{v}_j \right) = \frac{\rho_i}{\rho} \left(\rho \sum w_j \vec{v}_j \right) = \frac{\rho_i}{\rho} \sum \left(\rho w_j \vec{v}_j \right)$$

$$= w_i \underline{\sum \rho_j \vec{v}_j} = \underline{w_i \sum \vec{\phi}_j}$$

SIMILARLY $c_i \vec{V} = y_i \sum \vec{\Phi}_j$

iii) FOR A GIVEN COMPONENT, THE FLUX NOT DUE TO BULK FLOW MUST BE DUE TO THAT COMPONENT'S DIFFUSION

Recall from velocity: COMPONENT VELOCITY = BULK VELOCITY + DIFFUSION VELOCITY

SIMILARLY, DIFFUSIONAL FLUX IS A COMPONENT'S FLUX RELATIVE TO THE COORDINATES MOVING AT THE AVERAGE VELOCITY OF THE BULK

MASS DIFFUSIONAL FLUX $\vec{j}_i$

MOLAR DIFFUSIONAL FLUX $\vec{J}_i$

SO, THERE ARE LOTS OF WAYS TO WRITE $\vec{j}_i =$ ___ & $\vec{J}_i =$ ___

MASS

$$\vec{j}_i = \vec{\phi}_i - \rho_i \vec{v}$$

$$= \rho_i \vec{v}_i - \rho_i \vec{v}$$

$$= \rho_i (\vec{v}_i - \vec{v})$$

$$= \rho_i \vec{u}_i$$

$$= \rho_i \vec{v}_i - w_i \sum \vec{\phi}_j$$

$$= \vec{\phi}_i - w_i \sum \vec{\phi}_j \; *$$

MOLAR

$$\vec{J}_i = \vec{\Phi}_i - c_i \vec{V}$$

$$\vec{J}_i = c_i (\vec{v}_i - \vec{V})$$

$$\vec{J}_i = c_i \vec{U}_i$$

$$\vec{J}_i = \vec{\Phi}_i - y_i \sum \vec{\Phi}_j \; *$$

D. FICK'S LAW

IN 1855, ADOLPH EUGEN FICK (26 yr old) CONCEPTUALIZED MOLECULAR DIFFUSION, PROPOSING THAT DIFFUSIONAL FLUX WAS PROPORTIONAL TO THE CONCENTRATION GRADIENT OF THAT COMPONENT. PROPORTIONALITY CONSTANT IS CALLED THE DIFFUSION COEFFICIENT.

FOR A STEADY-STATE MOLAR CONCENTRATION PROFILE IN ONE-DIMENSION (z)

$$\boxed{J_{iz} = -D \frac{dc_i}{dz}}$$

FICK'S FIRST LAW

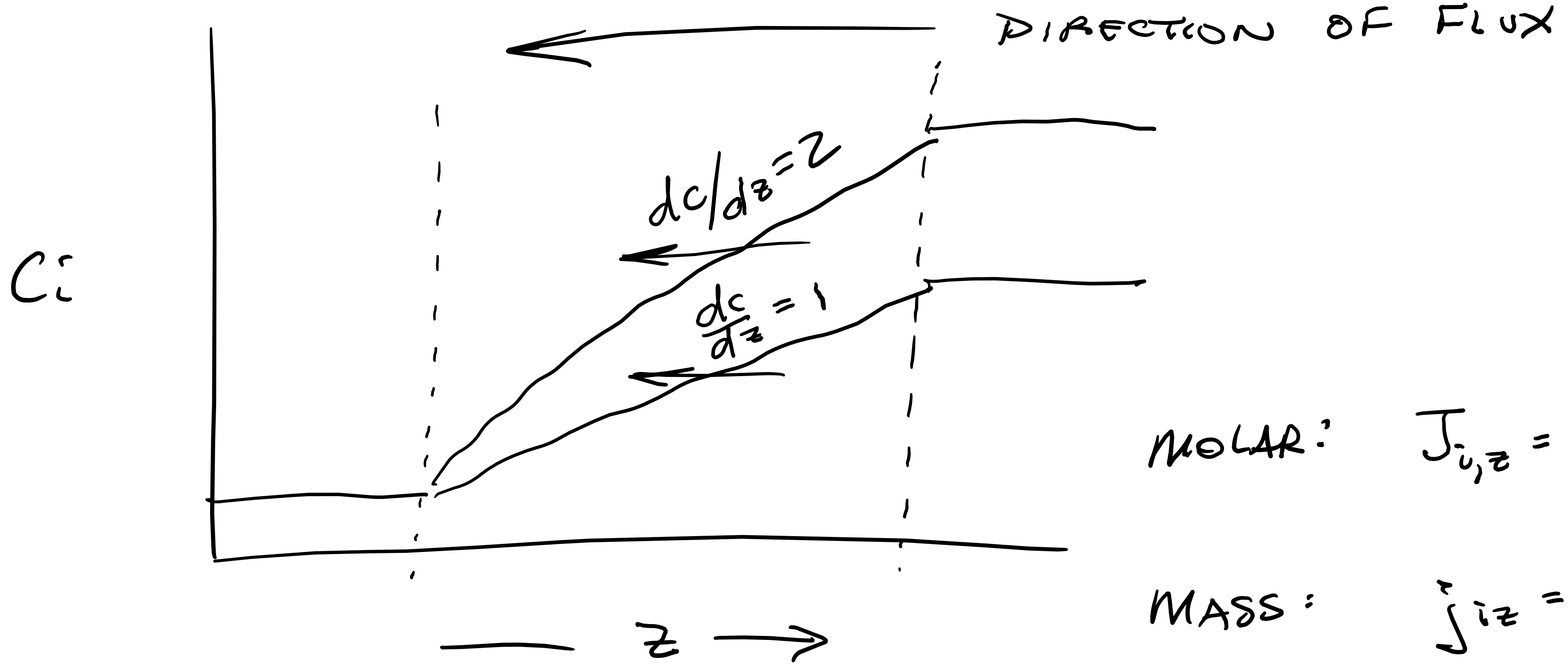
NEGATIVE SIGN INDICATES THAT DIFFUSIONAL FLUX OCCURS IN THE OPPOSITE DIRECTION TO THE CONCENTRATION GRADIENT, THAT IS, DIFFUSION OCCURS FROM HIGH CONCENTRATION TO LOW CONCENTRATION.

PREPARATION FOR TEST #4

1) MAKE SURE YOU UNDERSTAND TEST #3.
2) MAKE SURE YOU UNDERSTAND HOMEWORK.
3) MAKE SURE YOU UNDERSTAND PROBLEMS DONE IN CLASS
4) BONUS: WORK ON ADDITIONAL HOMEWORK PROBLEMS (THOSE NOT ASSIGNED).*

* YOU WILL NOT HAVE A "COMPLEX" DIFFERENTIAL EQUATION TO SOLVE, INVOLVING INTEGRATING FACTORS, ETC.

- PAY ATTENTION TO UNITS & INITIAL CONDITIONS.



MOLAR: $J_{i,z} = -c D_{is} \frac{dx_i}{dz}$

MASS: $j_{iz} = -\rho D_{is} \frac{dw_i}{dz}$

X, W = MOLE, MASS FRACTIONS

WHERE D_{is} IS THE DIFFUSION COEFFICIENT OF i IN BACKGROUND SOLVENT "S"

IN VECTOR NOTATION:

MASS: $\vec{j}_i = -\rho D_{is} \vec{\nabla} w_i$

MOLAR $\vec{J}_i = -c D_{is} \vec{\nabla} x_i$

$\vec{\nabla}$ IS CALLED THE DEL OPERATOR

WHEN OPERATING ON A SCALAR QUANTITY THE DEL OPERATOR YIELDS A VECTOR CALLED A <u>GRADIENT</u>.

RECTANGULAR $$\vec{\nabla} s = \frac{\partial s}{\partial x} \vec{\varepsilon}_x + \frac{\partial s}{\partial y} \vec{\varepsilon}_y + \frac{\partial s}{\partial z} \vec{\varepsilon}_z$$

CYLINDRICAL $$\vec{\nabla} s = \frac{\partial s}{\partial r} \vec{\varepsilon}_r + \frac{1}{r} \frac{\partial s}{\partial \theta} \vec{\varepsilon}_\theta + \frac{\partial s}{\partial z} \vec{\varepsilon}_z$$

SPHERICAL $$\vec{\nabla} s = \frac{\partial s}{\partial r} \vec{\varepsilon}_r + \frac{1}{r} \frac{\partial s}{\partial \theta} \vec{\varepsilon}_\theta + \frac{1}{r \sin\theta} \frac{\partial s}{\partial \phi} \vec{\varepsilon}_\phi$$

EXAMPLE 2

MOLAR ONE-DIMENSIONAL FLUX OF A BINARY MIXTURE CONSIDERING

1) MOTION OF "A" THROUGH A STAGNANT MEDIUM
2) EQUIMOLAR COUNTERDIFFUSION

A) MOLAR FLUX $\vec{\Phi}_i$

B) ONE-DIMENSION (RECTANGULAR)

$$\vec{\Phi}_i = \cancel{\Phi_{ix}\vec{\varepsilon}_x} + \cancel{\Phi_{iy}\vec{\varepsilon}_y} + \Phi_{iz}\vec{\varepsilon}_z$$

C) BINARY MIXTURE (A & B)

$$\Phi_{Az} = \Phi_A$$

$$\Phi_{Bz} = \Phi_B$$

MOLAR

$$\vec{J}_i = \vec{\Phi}_i - x_i \sum \vec{\Phi}_j$$

$$\vec{\Phi}_i = \vec{J}_i + x_i \sum \vec{\Phi}_j$$

FICK'S LAW...

$$\vec{\Phi}_i = -c D_{is} \vec{\nabla} x_i + x_i \sum \vec{\Phi}_j$$

$$\boxed{\begin{aligned} \Phi_A &= -c D_{AB} \frac{dx_A}{dz} + x_A (\Phi_A + \Phi_B) \\ \Phi_B &= -c D_{BA} \frac{dx_B}{dz} + x_B (\Phi_A + \Phi_B) \end{aligned}}$$

CASE I

"A" IS MOVING THROUGH STAGNANT "B"

$$\Phi_B = 0$$

$$\Phi_A = -cD_{AB}\frac{dx_A}{dz} + x_A\left(\Phi_A + \cancel{\Phi_B}^{\,0}\right)$$

$$\Phi_A = -cD_{AB}\frac{dx_A}{dz} + x_A\Phi_A$$

$$\boxed{\Phi_A = -\frac{cD_{AB}}{1-x_A}\frac{dx_A}{dz}}$$

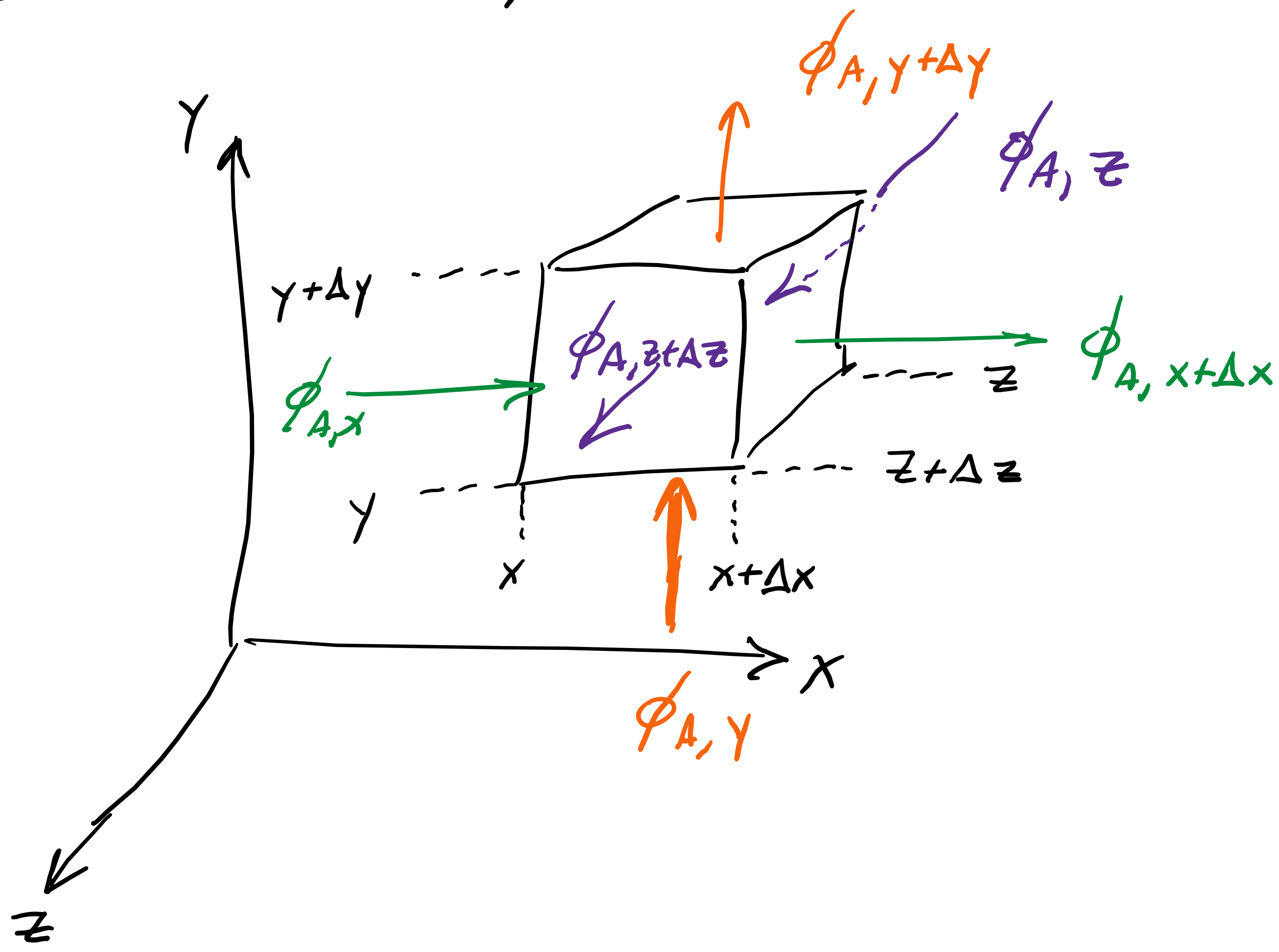
CASE II EQUIMOLAR COUNTERDIFFUSION

$$\Phi_A = -\Phi_B$$

$$\Phi_A = -cD_{AB}\frac{dx_A}{dz} + x_A\underbrace{\left(\Phi_A + \Phi_B\right)}_{=0}$$

$$\boxed{\Phi_A = -cD_{AB}\frac{dx_A}{dz}}$$

E. GENERAL MASS BALANCE SPECIES "A"
(RECTANGULAR COORDINATES)



ACC = IN − OUT + GEN

$$\frac{\partial(\rho_A V)}{\partial t} = \phi_{A,x}\Delta y\Delta z + \phi_{A,y}\Delta x\Delta z + \phi_{A,z}\Delta x\Delta y$$

$$- \phi_{A,x+\Delta x}\Delta y\Delta z - \phi_{A,y+\Delta y}\Delta x\Delta z - \phi_{A,z+\Delta z}\Delta x\Delta y$$

$$+ r_A\Delta x\Delta y\Delta z$$

$V = \Delta x\Delta y\Delta z$

DIVIDE BY $\Delta x, \Delta y, \Delta z$ AND TAKE LIMIT AS $\Delta x, \Delta y, \Delta z \rightarrow 0$

$$\boxed{\frac{\partial \rho_A}{\partial t} = -\frac{\partial \phi_{A,x}}{\partial x} - \frac{\partial \phi_{A,y}}{\partial y} - \frac{\partial \phi_{A,z}}{\partial z} + r_A}$$

$$\boxed{\frac{\partial \rho_i}{\partial t} = -\vec{\nabla}\,\vec{\phi}_A + r_A}$$

GENERAL MICROSCOPIC MATERIAL BALANCE

$$\vec{\nabla}\cdot\vec{\phi}_A = \frac{\partial \phi_{A,x}}{\partial x} + \frac{\partial \phi_{A,y}}{\partial y} + \frac{\partial \phi_{A,z}}{\partial z} \quad \text{(RECT)}$$

$$= \frac{1}{r}\frac{\partial}{\partial r}\left(r\,\phi_{A,r}\right) + \frac{1}{r}\frac{\partial \phi_{A,\theta}}{\partial \theta} + \frac{\partial \phi_{A,z}}{\partial z} \quad \text{(CYL)}$$

$$= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\phi_{A,r}\right) + \frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}\left(\phi_{A,\theta}\sin\theta\right) + \frac{1}{r\sin\theta}\frac{\partial \phi_{A,\phi}}{\partial \phi}$$

(SPHERICAL)

APPLICATION OF FICK'S LAW

$$\vec{\phi}_A = \underbrace{-D_{AS}\vec{\nabla}\rho_A}_{\vec{J}_A} + \underbrace{\rho_A\vec{v}}_{\Sigma}$$

$$\frac{\partial \rho_A}{\partial t} = -\vec{\nabla}\left(-D_{AS}\vec{\nabla}\rho_A + \rho_A\vec{v}\right) + r_A$$

$$\frac{\partial \rho_A}{\partial t} = D_{AS}\vec{\nabla}^2\rho_A - \vec{\nabla}\left(\underline{\rho_A\vec{v}}\right) + r_A$$

$$\vec{\nabla}(\rho_A\vec{v}) = \rho_A\vec{\nabla}\vec{v} + \vec{v}\,\vec{\nabla}\rho_A$$

PRODUCT RULE

FOR CONSTANT DENSITY SYSTEMS $\vec{\nabla}\vec{v} = 0$

$$\boxed{\frac{\partial \rho_A}{\partial t} = D_{AS} \vec{\nabla}^2 \rho_A - \vec{v} \nabla \rho_A + r_A}$$

FOR CONSTANT DENSITY SYSTEM & WHERE FICK'S LAW APPLIES

ACC = DIFFUSIVE TRANSPORT + CONVECTIVE TRANSPORT + GENERATION

FOR EXAMPLE, IN RECTANGULAR COORDINATES:

$$\frac{\partial \rho_A}{\partial t} = D_{AS}\left(\frac{\partial^2 \rho_A}{\partial x^2} + \frac{\partial^2 \rho_A}{\partial y^2} + \frac{\partial^2 \rho_A}{\partial z^2}\right) - v_x \frac{\partial \rho_A}{\partial x} - v_y \frac{\partial \rho_A}{\partial y} - v_z \frac{\partial \rho_A}{\partial z} + r_A$$