CHEN3001-TP
Mass Transport - 1

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Outline

- Mass transfer by diffusion
  - Fick's law of diffusion
  - Values of diffusivity
  - Units of concentration
  - Component velocity and average velocity
  - Case-1: equimolar counter diffusion
  - Case-2: Component-A diffuses through non-diffusing component-B
- Steady-state mass transfer: Shell balance approach
  - Mass balance equation
  - Case study-1: Diffusion through stagnant gas film
  - Case study-2: Steady state diffusion from a suspended droplet

Fick's law of diffusion

"The molar flux of a species relative to an observer moving with the molar average velocity of the medium is proportional to the concentration gradient of the species."

- It is only applicable to a BINARY mixture
- For mixtures of three of more components, the proper law is the Maxwell-Stefan law

- For A diffuses in a binary mixture (liquid or gas) of A and B,

$$J_A = -D_{AB} \frac{dc_A}{dz}$$

- Where
  - J_A – the molar flux of a species relative to an observer moving with the molar average velocity in the positive z direction, kmol/m^2·s;
  - D_{AB} – the mutual diffusion coefficient (or diffusivity) of A in B, m^2/s;
  - dc_A/dz – the concentration gradient, dc_A/dz is < 0 as diffusion spontaneously takes place in the direction of decreasing concentration

Diffusivity or Diffusion coefficient

- Highest in gases, lowest in solids
- Increases with temperature
- In gases → Roughly constant at constant temperature
- In liquids/solids → a function of concentration too…..

- D_{AB} is function of temperature and pressure

$$D_{AB} \propto \frac{T^{3/2}}{P} \qquad \text{or} \qquad \frac{D_{AB,1}}{D_{AB,2}} = \frac{P_2}{P_1}\left(\frac{T_1}{T_2}\right)^{3/2}$$

- or

$$\frac{p\mathcal{D}_{AB}}{(p_{cA}p_{cB})^{1/3}(T_{cA}T_{cB})^{5/12}(1/M_A + 1/M_B)^{1/2}} = a\left(\frac{T}{\sqrt{T_{cA}T_{cB}}}\right)^b$$

$a = 2.745 \times 10^{-4}$ and $b = 1.823$ for nonpolar gas pairs, excluding helium and hydrogen

$a = 3.640 \times 10^{-4}$ and $b = 2.334$ for pairs consisting of H_2O and a nonpolar gas.

Diffusivity or Diffusion coefficient

Binary diffusion coefficients of some gases in air at 1 atm pressure (from Mills, Ref. 13, Table A.17a, p. 869)

	Binary Diffusion Coefficient, $m^2/s \times 10^5$*			
T, K	O_2	CO_2	H_2	NO
200	0.95	0.74	3.75	0.88
300	1.88	1.57	7.77	1.80
400	5.25	2.63	12.5	3.03
500	4.75	3.85	17.1	4.43
600	6.46	5.37	24.4	6.03
700	8.38	6.84	31.7	7.82
800	10.5	8.57	39.3	9.78
900	12.6	10.5	47.7	11.8
1000	15.2	12.4	56.9	14.1
1200	20.6	16.9	77.7	19.2
1400	26.6	21.7	99.0	24.5
1600	33.2	27.5	125	30.4
1800	40.3	32.8	152	37.0
2000	48.0	39.4	180	44.8

*Multiply by 10.76 to convert to ft^2/s.

Diffusivity or Diffusion coefficient

Binary diffusion coefficients of dilute gas mixtures at 1 atm
(from Barrer, Ref. 2; Geankoplis, Ref. 5; Perry, Ref. 14; and Reid et al., Ref. 15)

Substance A	Substance B	T, K	D_{AB} or D_{BA}, m^2/s	Substance A	Substance B	T, K	D_{AB} or D_{BA}, m^2/s
Air	Acetone	273	1.1×10^{-5}	Argon, Ar	Nitrogen, N_2	293	1.9×10^{-5}
Air	Ammonia, NH_3	298	2.6×10^{-5}	Carbon dioxide, CO_2	Benzene	318	0.72×10^{-5}
Air	Benzene	298	0.88×10^{-5}	Carbon dioxide, CO_2	Hydrogen, H_2	273	5.5×10^{-5}
Air	Carbon dioxide	298	1.6×10^{-5}	Carbon dioxide, CO_2	Nitrogen, N_2	293	1.6×10^{-5}
Air	Chlorine	273	1.2×10^{-5}	Carbon dioxide, CO_2	Oxygen, O_2	273	1.4×10^{-5}
Air	Ethyl alcohol	298	1.2×10^{-5}	Carbon dioxide, CO_2	Water vapor	298	1.6×10^{-5}
Air	Ethyl ether	298	0.93×10^{-5}	Hydrogen, H_2	Nitrogen, N_2	273	6.8×10^{-5}
Air	Helium, He	298	7.2×10^{-5}	Hydrogen, H_2	Oxygen, O_2	273	7.0×10^{-5}
Air	Hydrogen, H_2	298	7.2×10^{-5}	Oxygen, O_2	Ammonia	293	2.5×10^{-5}
Air	Iodine, I_2	298	0.83×10^{-5}	Oxygen, O_2	Benzene	296	0.39×10^{-5}
Air	Methanol	298	1.6×10^{-5}	Oxygen, O_2	Nitrogen, N_2	273	1.8×10^{-5}
Air	Mercury	614	4.7×10^{-5}	Oxygen, O_2	Water vapor	298	2.5×10^{-5}
Air	Napthalene	300	0.62×10^{-5}	Water vapor	Argon, Ar	298	2.4×10^{-5}
Air	Oxygen, O_2	298	2.1×10^{-5}	Water vapor	Helium, He	298	9.2×10^{-5}
Air	Water vapor	298	2.5×10^{-5}	Water vapor	Nitrogen, N_2	298	2.5×10^{-5}

Note: The effect of pressure and temperature on D_{AB} can be accounted for through $D_{AB} \sim T^{3/2}/P$. Also, multiply D_{AB} values by 10.76 to convert them to ft^2/s.

Diffusivity or Diffusion coefficient

Binary diffusion coefficients of dilute liquid solutions and solid solutions at 1 atm
(from Barrer, Ref. 2; Reid et al., Ref. 15; Thomas, Ref. 19; and van Black, Ref. 20)

(a) Diffusion through Liquids

Substance A (Solute)	Substance B (Solvent)	T, K	D_{AB}, m^2/s
Ammonia	Water	285	1.6×10^{-9}
Benzene	Water	293	1.0×10^{-9}
Carbon dioxide	Water	298	2.0×10^{-9}
Chlorine	Water	285	1.4×10^{-9}
Ethanol	Water	283	0.84×10^{-9}
Ethanol	Water	288	1.0×10^{-9}
Ethanol	Water	298	1.2×10^{-9}
Glucose	Water	298	0.69×10^{-9}
Hydrogen	Water	298	6.3×10^{-9}
Methane	Water	275	0.85×10^{-9}
Methane	Water	293	1.5×10^{-9}
Methane	Water	333	3.6×10^{-9}
Methanol	Water	288	1.3×10^{-9}
Nitrogen	Water	298	2.6×10^{-9}
Oxygen	Water	298	2.4×10^{-9}
Water	Ethanol	298	1.2×10^{-9}
Water	Ethylene glycol	298	0.18×10^{-9}
Water	Methanol	298	1.8×10^{-9}
Chloroform	Methanol	288	2.1×10^{-9}

(b) Diffusion through Solids

Substance A (Solute)	Substance B (Solvent)	T, K	D_{AB}, m^2/s
Carbon dioxide	Natural rubber	298	1.1×10^{-10}
Nitrogen	Natural rubber	298	1.5×10^{-10}
Oxygen	Natural rubber	298	2.1×10^{-10}
Helium	Pyrex	773	2.0×10^{-12}
Helium	Pyrex	293	4.5×10^{-15}
Helium	Silicon dioxide	298	4.0×10^{-14}
Hydrogen	Iron	298	2.6×10^{-13}
Hydrogen	Nickel	358	1.2×10^{-12}
Hydrogen	Nickel	438	1.0×10^{-11}
Cadmium	Copper	293	2.7×10^{-19}
Zinc	Copper	773	4.0×10^{-18}
Zinc	Copper	1273	5.0×10^{-13}
Antimony	Silver	293	3.5×10^{-25}
Bismuth	Lead	293	1.1×10^{-20}
Mercury	Lead	293	2.5×10^{-19}
Copper	Aluminum	773	4.0×10^{-14}
Copper	Aluminum	1273	1.0×10^{-10}
Carbon	Iron (fcc)	773	5.0×10^{-15}
Carbon	Iron (fcc)	1273	3.0×10^{-11}

Diffusivity or Diffusion coefficient

TABLE 5-14 Correlations of Diffusivities for Gases From Perry's handbook

Authors*	Equation		Error
1. Binary Mixtures—Low Pressure—Nonpolar			
Chapman-Enskog	$D_{AB} = \frac{0.001858 T^{3/2} M_{AB}^{1/2}}{P \sigma_{AB}^2 \Omega_D}$	(5-194)	7.3%
Wilke-Lee [65]	$D_{AB} = \frac{(0.0027 - 0.0005 M_{AB}^{1/2}) T^{3/2} M_{AB}^{1/2}}{P \sigma_{AB}^2 \Omega_D}$	(5-195)	7.0%
Fuller-Schettler-Giddings [19]	$D_{AB} = \frac{0.001 T^{1.75} M_{AB}^{1/2}}{P [(\sum v)_A^{1/3} + (\sum v)_B^{1/3}]^2}$	(5-196)	5.4%
2. Binary Mixtures—Low Pressure—Polar			
Brokaw [4]	$D_{AB} = \frac{0.001858 T^{3/2} M_{AB}^{1/2}}{P \sigma_{AB}^2 \Omega_D}$	(5-197)	9.0%
3. Self-Diffusivity—High Pressure			
Mathur-Thodos [37]	$D_{AA} = \frac{10.7 \times 10^{-5} T_r}{\beta \rho_r}$ $\{\rho_r \le 1.5\}$	(5-198)	5%
Lee-Thodos [31]	$D_{AA} = \frac{0.77 \times 10^{-5} T_r}{\rho_r \delta}$ $\{\rho_r \le 1\}$	(5-199)	0.5%
Lee-Thodos [32]	$D_{AA} = \frac{(0.007094 G + 0.001916)^{2.5} T_r}{\delta}$, $[\rho_r > 1, G < 1]$	(5-200)	17%
4. Supercritical Mixtures			
Sun and Chen [56]	$D_{AB} = \frac{1.23 \times 10^{-10} T}{\mu^{0.799} V_{C_A}^{0.49}}$	(5-201)	5%
Catchpole and King [6]	$D_{AB} = 5.152 D_c T_r \frac{(\rho^{-0.667} - 0.4510)(1 + M_A/M_B) R}{(1 + (V_{cB}/V_{cA})^{0.333})^2}$	(5-202)	10%

Diffusivity or Diffusion coefficient

From Perry's handbook

TABLE 5-13 Rules of Thumb for Diffusivities (See Cussler, Reid et al., Schwartzberg and Chao)

Continuous phase	D_i magnitude		D_i range		Comments
	m^2/s	cm^2/s	m^2/s	cm^2/s	
Gas at atmospheric pressure	10^{-5}	0.1	10^{-4}–10^{-6}	1–10^{-2}	Accurate theories exist, generally within ±10%; $D_iP \cong$ constant; $D_i \propto T^{1.66 \text{ to } 2.0}$
Liquid	10^{-9}	10^{-5}	10^{-8}–10^{-10}	10^{-4}–10^{-6}	Approximate correlations exist, generally within ±25%
Liquid occluded in solid matrix	10^{-10}	10^{-6}	10^{-8}–10^{-12}	10^{-4}–10^{-8}	Hard cell walls: $D_{eff}/D_i = 0.1$ to 0.2. Soft cell walls: $D_{eff}/D_i = 0.3$ to 0.9
Polymers and glasses	10^{-12}	10^{-8}	10^{-10}–10^{-14}	10^{-6}–10^{-10}	Approximate theories exist for dilute and concentrated limits; strong composition dependence
Solid	10^{-14}	10^{-10}	10^{-10}–10^{-34}	10^{-6}–10^{-30}	Approximate theories exist; strong temperature dependence

Units of concentration terms

Mass concentrations

ρ = total mass density of the mixture

ρ_A = mass density of species A

ρ_B = mass density of species B

ω_A = mass fraction of species A = ρ_A/ρ

ω_B = mass fraction of species B = ρ_B/ρ

$$\rho = \rho_A + \rho_B$$

$$1 = \omega_A + \omega_B$$

Molar concentrations

Liquid or solid mixture

c = molar density of mixture = n/V

c_A = molar density of species $A = n_A/V$

c_B = molar density of species $B = n_B/V$

x_A = mole fraction of species $A = c_A/c = n_A/n$

x_B = mole fraction of species $B = c_B/c = n_B/n$

$$c = c_A + c_B$$

$$1 = x_A + x_B$$

Gas mixture

$$c = n/V = P/RT$$

$$c_A = n_A/V = p_A/RT$$

$$c_B = n_B/V = p_B/RT$$

$$y_A = c_A/c = n_A/n = p_A/p$$

$$y_B = c_B/c = n_B/n = p_B/p$$

$$c = c_A + c_B = \frac{p_A}{RT} + \frac{p_B}{RT} = \frac{P}{RT}$$

$$1 = y_A + y_B$$

Interrelations

$$\rho_A = c_A M_A$$

$$x_A \quad \text{or} \quad y_A = \frac{\omega_A/M_A}{\omega_A/M_A + \omega_B/M_B} \tag{24-10}$$

$$\omega_A = \frac{x_A M_A}{x_A M_A + x_A M_A} \quad \text{or} \quad \frac{y_A M_A}{y_A M_A + y_B M_B} \tag{24-11}$$

Units of concentration terms

The concentration of a species *i* in a solution:

ρ_i – "mass concentration" of the species *i* in a solution, kg/m^3

ρ – "total mass concentration" of all species in a solution, kg/m^3

$w_i = \rho_i / \rho$ – "mass fraction" of the species *i* in a solution

c_i – "molar concentration" of the species *i* in a solution, kmol/m^3

c – "total molar concentration" of the solution, kmol/m^3

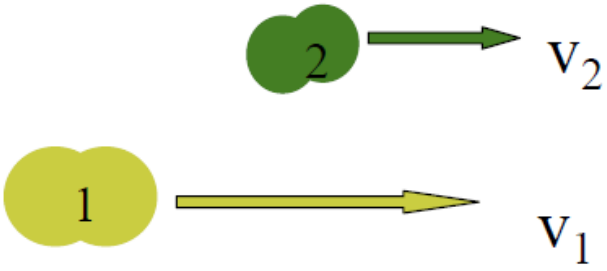
$x_i = c_i / c$ – "mole fraction" of the species *i* in a solution.

If there are *n* species in a solution, we have

$$\sum_{i=1}^{n} \rho_i = \rho; \quad \sum_{i=1}^{n} c_i = c\,; \quad \sum_{i=1}^{n} w_i = 1; \quad \sum_{i=1}^{n} x_i = 1;$$

Component velocity in a mixture

Two components in a mixture have two different velocity (v_1 and v_2)



Mass flux (mass flow rate per unit cross section area perpendicular to the flow):

$$n_i = \sum \rho_i v_i = \rho_1 v_1 + \rho_2 v_2$$

Molar flux (mass flow rate per unit cross section area perpendicular to the flow):

$$N_i = \sum C_i v_i = C_1 v_1 + C_2 v_2$$

ρ represents density (kg/m^3) and *C* represents molar concentration (kmol/m^3)

Component velocity in a mixture

Mass average velocity of a mixture:

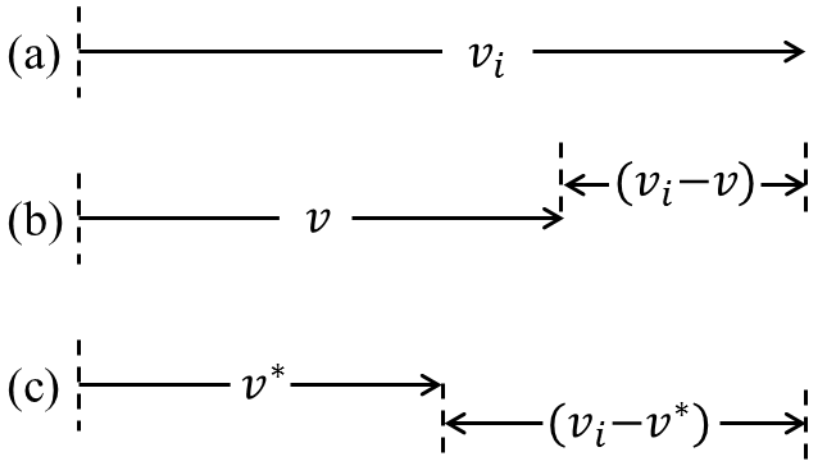
$$v = \frac{\sum \rho_i v_i}{\sum \rho_i} = \frac{\rho_1 v_1 + \rho_2 v_2}{\rho_1 + \rho_2}$$

Mass average velocity of a mixture:

$$v^* = \frac{\sum C_i v_i}{\sum C_i} = \frac{C_1 v_1 + C_2 v_2}{C_1 + C_2}$$

Component velocity in a mixture

- There are 3 frames of reference commonly used for expressing the flux of a diffusing species.



(a) The observer is stationary, then component velocity = v_i
(b) The observer is moving with the mass average velocity of the medium, then component velocity = $(v_i - v)$
(c) The observer is moving with the molar average velocity of the medium, then component velocity = $(v_i - v^*)$

Component velocity in a mixture

- A diffusing species moves with a velocity greater than the average velocity of the medium.

- There are two diffusion velocities.
  - Diffusion velocity relative to average mass velocity or diffusion velocity when an observer is moving with average mass velocity

$$V_{j,d} = v_j - v$$

  - Diffusion velocity relative to average molar velocity or diffusion velocity when an observer is moving with average molar velocity

$$V^*_{j.d} = v_j - v^*$$

Bulk flux and diffusion flux

- Bulk flux of a component i
  - Mass flux = $n_i = \rho_i v_i$
  - Molar flux = $N_i = c_i v_i$

- Diffusion flux a component i
  - Relative to average mass velocity
    - Mass flux = $i_i = \rho_i (v_i - v)$
    - Molar flux = $I_i = c_i (v_i - v)$

  - Relative to average molar velocity
    - Mass flux = $j_i = \rho_i (v_i - v^*)$
    - Molar flux = $J_i = c_i (v_i - v^*)$

Fick's law:
"The molar flux of a species relative to an observer moving with the molar average velocity of the medium is proportional to the concentration gradient of the species."

- Relationship between bulk flux and molar diffusion flux

$$J_k = N_k - x_k \sum_{j=1}^{n} N_j$$

Diffusion flux

For a binary system A + B

Bulk flux: $N_A = c_A v_A$; $N_B = c_B v_B$

$c = \frac{P}{RT}\ for\ gas\ or\ \frac{\rho}{M}\ for\ liquid$

$$v^* = \frac{1}{c}(c_A v_A + c_B v_B) = \frac{1}{c}(N_A + N_B)$$

$$J_A = -D_{AB}\frac{dc_A}{dz} = c_A(v_A - v^*) = c_A v_A - c_A v^* = N_A - \frac{c_A}{c}(N_A + N_B)$$

$$N_A = (N_A + N_B)\frac{c_A}{c} - D_{AB}\frac{dc_A}{dz}$$ ——— Expressed on molar concentration, **for liquid or gas**

$$N_A = (N_A + N_B)y_A - cD_{AB}\frac{dy_A}{dz}$$ ——— Expressed on molar fraction, **for gas**

$$N_A = (N_A + N_B)x_A - cD_{AB}\frac{dx_A}{dz}$$ ——— Expressed on molar fraction, **for liquid**

Diffusion flux – two limiting cases

We will consider two cases

Equimolar counter-diffusion of gases A and B
Example, diffusion of O_2 and CO_2 in the air-film during carbon combustion (assuming the CO_2 is the only combustion product)

A diffusing through stagnant, non-diffusing B
For example, during air drying using concentrated sulphuric acid, the diffusion of moisture in air through a film of air (treated as a single component) and then absorbed by concentrated sulphuric acid

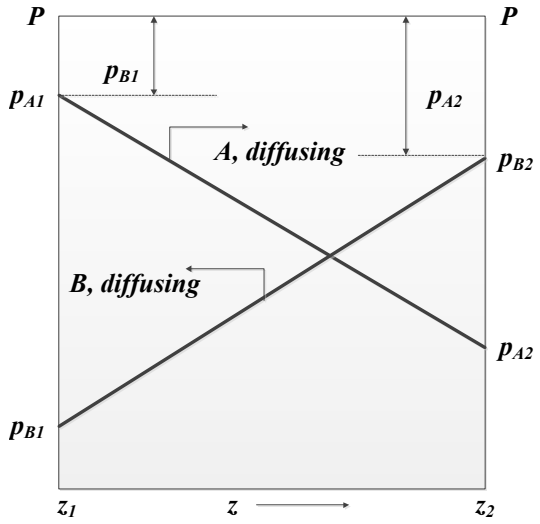
Equimolar counter-diffusion of gases A and B

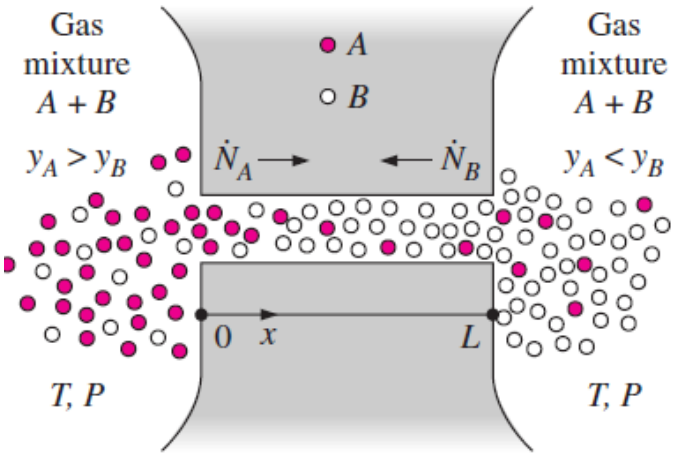
- In equimolar counter-diffusion of A and B, the components A and B both diffuse at equal rates but in opposite direction.

$$N_A + N_B = 0$$

$$N_A = -\frac{D_{AB}}{RT}\frac{dp_A}{dz}$$

$$\int_0^l N_A dz = \int_{p_{A0}}^{p_{Al}} -\frac{D_{AB}}{RT} dp_A \quad \Rightarrow \quad N_A = \frac{D_{AB}(p_{A0} - p_{Al})}{RTl}$$





A diffusing through stagnant, non-diffusing B

When B is non-diffusing. We have $N_B = 0$

$$N_A = N_A \frac{p_A}{P} - \frac{D_{AB}}{RT}\frac{dp_A}{dz}$$

$$N_A = -\frac{D_{AB}P}{RT(P-p_A)}\frac{dp_A}{dz}$$

$$\int_0^l N_A dz = \int_{p_{A0}}^{p_{Al}} -\frac{D_{AB}P}{RT(P-p_A)}dp_A \quad \Rightarrow \quad N_A = \frac{D_{AB}P}{RTl}\ln\frac{P-p_{Al}}{P-p_{A0}}$$

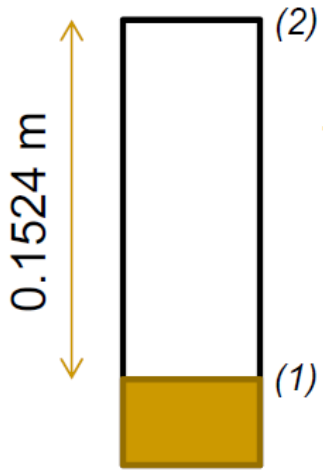
$$N_A = \frac{D_{AB}(p_{A0}-p_{Al})}{RTl}\frac{P}{p_{BM}} \quad where \quad p_{BM} = \frac{(p_{Bl}-p_{B0})}{\ln(p_{Bl}/p_{B0})}$$

A diffusing through stagnant, non-diffusing B

Special case: Pseudo steady-state analysis: what if the boundary moves with time?

$$N_A = \frac{D_{AB}P}{RT(z_2 - z_1)p_{BM}}(p_{A1} - p_{A2}) \quad \text{OR} \quad N_A = \frac{cD_{AB}}{(z_2 - z_1)y_{BM}}(y_{A1} - y_{A2})$$

$D_{AB} = 0.25 \times 10^{-4}$ m^2/s



N_A = ?

T = 293 K

P = 1.01325×10^5 Pa

The molar flux above is balanced by the amount of A leaving the liquid (per unit surface area):

$$N_A = \frac{\rho_{A,L}}{M_A}\frac{dz}{dt}$$

molar density of A in the liquid phase

A diffusing through stagnant, non-diffusing B

Special case: Pseudo steady-state analysis: what if the boundary moves with time?

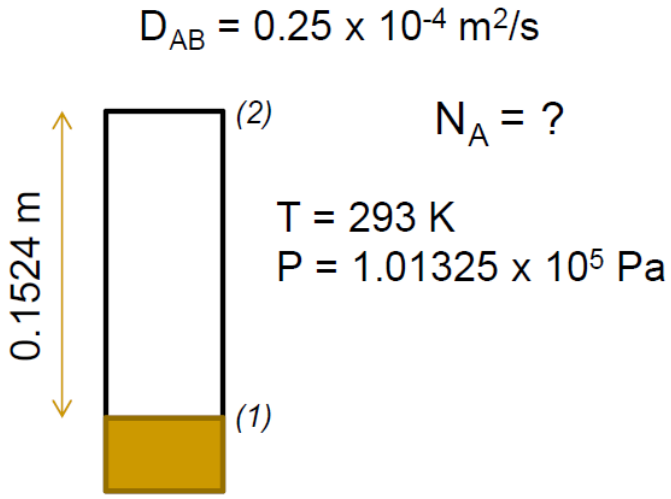
$$N_A = \frac{\rho_{A,L}}{M_A}\frac{dz}{dt} = \frac{cD_{AB}}{z\, y_{BM}}\left(y_{A1} - y_{A2}\right)$$

$$\int_0^t dt = \int_{z_0}^{z_f} \frac{\rho_{A,L} z\, y_{BM}}{cD_{AB}M_A\left(y_{A1} - y_{A2}\right)} dz$$

$$t = \frac{\rho_{A,L} y_{BM}}{cD_{AB}M_A\left(y_{A1} - y_{A2}\right)}\left[\frac{z^2}{2}\right]_{z_0}^{z_f}$$

Classroom example-1:

Water in the bottom of a narrow metal tube is held at a constant temperature of 293 K. The total pressure of air (assumed dry) is 1.01325 x 105 Pa and the temperature is 293 K. Water evaporates and diffuses through the air in the tube, and the diffusion path $z_2 - z_1$ is 0.1524 m. Calculate the rate of evaporation at steady state in kgmol/s.m2. The diffusivity of water vapour at 293 K and 1 atm pressure is 0.250 x 10-4 m^2/s. Assume that the system is isothermal. The vapour pressure of water at 1 atm and 293 K is 17.535 mmHg.



Additional note:
Moving boundaries or pseudo-steady state diffusion. How long would it take for the water level to decrease by 0.1 m?

Classroom example-2:

Calculate the rate of diffusion of butanol at 20 °C under unidirectional steady state conditions through a 0.1 cm thick film of water when the concentrations of butanol at the opposite sides of the film are, 10% and 4% butanol by weight, respectively.

DAB (butanol in water solution)= 5.9×10^{-6} cm^2/s. The densities of 10% and 4% butanol solutions at 20 °C may be taken as 0.971 and 0.992 g/cc, respectively. Molecular weight of Butanol is 74, and that of water is 18.

Steady-state M.T.: Shell balance approach

Mass balance equation:

$$\left\{\begin{array}{c}\text{Rate of}\\ \text{mass of}\\ \text{A } \textit{in}\end{array}\right\} - \left\{\begin{array}{c}\text{Rate of}\\ \text{mass of}\\ \text{A } \textit{out}\end{array}\right\} + \left\{\begin{array}{l}\text{Rate of production of}\\ \text{mass of A by}\\ \textit{homogeneous} \text{ reaction}\end{array}\right\} = 0$$

Mass of A in/out by:

Molecular diffusion
Motion of fluid (convective mass transfer)

} N_A (molar flux) or n_A (mass flux)

Rate of mass in/out = S. N_A

Diffusion of A in z-direction (Cartesian coordinate) = (Δx. Δy). N_A

Equation for molar flux = $N_A = (N_A + N_B)x_A - cD_{AB}\frac{dx_A}{dz}$

Steady-state M.T.: Shell balance approach

Mass balance equation:

$$\left\{\begin{array}{c}\text{Rate of}\\ \text{mass of}\\ \text{A } \textit{in}\end{array}\right\} - \left\{\begin{array}{c}\text{Rate of}\\ \text{mass of}\\ \text{A } \textit{out}\end{array}\right\} + \left\{\begin{array}{l}\text{Rate of production of}\\ \text{mass of A by}\\ \textit{homogeneous} \text{ reaction}\end{array}\right\} = 0$$

Homogeneous reaction → Chemical rxn in *entire* volume of fluid

Molar rate production by homogeneous reaction = $R_A(\frac{moles}{cm^3}s) = {k_n}'''{C_A}^n$

For shell balance, rate of production of A = ($\Delta x.\ \Delta y.\ \Delta z$). R_A

Heterogeneous reaction → Chemical rxn at a restricted region, e.g. the surface of a catalyst (Not included in the equation, but as a boundary condition at the region on which the reaction takes place)

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$$\left\{\begin{array}{c}\text{Rate of}\\ \text{mass of}\\ \text{A } in\end{array}\right\}-\left\{\begin{array}{c}\text{Rate of}\\ \text{mass of}\\ \text{A } out\end{array}\right\}+\left\{\begin{array}{l}\text{Rate of production of}\\ \text{mass of A by}\\ homogeneous \text{ reaction}\end{array}\right\}=0$$

Boundary conditions:

- Concentration at a surface → $x_A = x_{A0}$
- Mass flux at a surface → $N_{Az} = N_{A0}$; N_{Bz}/N_{Az}
- Diffusion in a solid (e.g. when solid surface substance A is lost to a surrounding stream) → $N_{A0} = k_c(c_{A0} - c_{Ab})$

Surface conc. *Concentration in the bulk fluid stream*

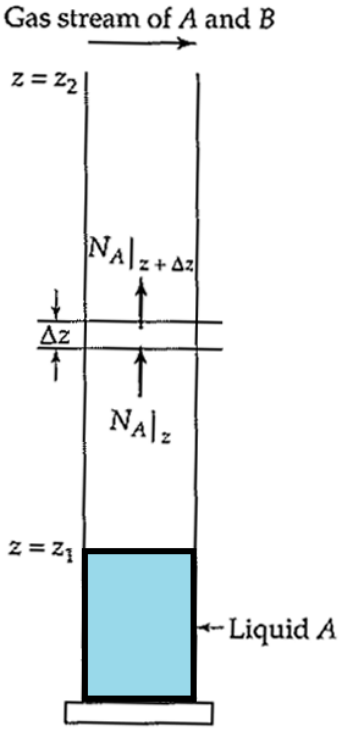
- Rate of chemical reaction (heterogeneous) → $N_{A0} = k_n'' c_{A0}^n$

Case study-1: Diffusion through stagnant gas film

Consider the diffusion of species A (in vapour form) through a stagnant species B

Species B is insoluble in in liquid A, so:

- Downward motion by diffusion must be balanced by upward bulk motion (advection) such that the absolute flux is everywhere zero. → $N_{Bz} = 0$
- Only need to do shell balance on species A



Non-reacting system

$$\left\{\begin{matrix}\text{Rate of}\\ \text{mass of}\\ \text{A } in\end{matrix}\right\} - \left\{\begin{matrix}\text{Rate of}\\ \text{mass of}\\ \text{A } out\end{matrix}\right\} + \left\{\begin{matrix}\text{Rate of production of}\\ \text{mass of A by}\\ homogeneous \text{ reaction}\end{matrix}\right\} = 0$$

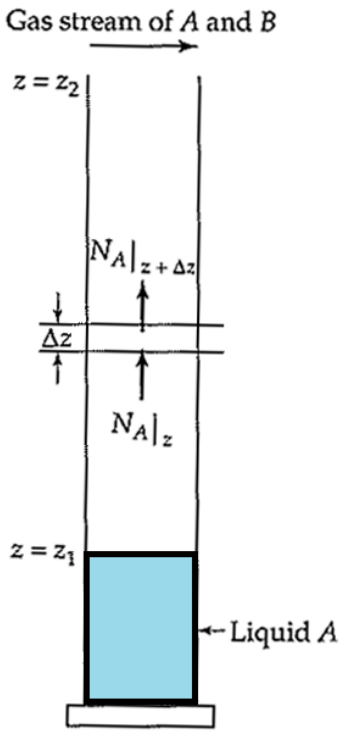
$$SN_{Az}\big|_z - SN_{Az}\big|_{z+\Delta z} = 0$$

S → cross sectional area of column

Shell balance approach → Divide by $S\Delta z$, take limit to $\Delta z \to 0$

$$\frac{N_{Az}\big|_z - N_{Az}\big|_{z+\Delta z}}{\Delta z} = 0 \quad \Rightarrow \quad -\frac{dN_{Az}}{dz} = 0$$

Case study-1: Diffusion through stagnant gas film



Equation for N_{Az}: $N_{Az} = -cD_{AB}\frac{dx_A}{dz} + \frac{c_A}{c}(N_{Az} + N_{Bz})$

At steady state, there is a net motion of A away from the interface, while species B is stationary (as B is insoluble in the liquid) → N_{Bz} = 0

$$N_{Az} = -cD_{AB}\frac{dx_A}{dz} + \frac{c_A}{c}N_{Az} = -cD_{AB}\frac{dx_A}{dz} + x_A N_{Az}$$

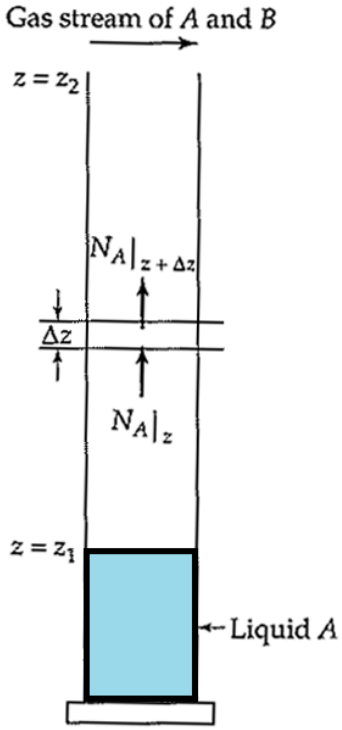
$$\Leftrightarrow N_{Az}(1-x_A) = -cD_{AB}\frac{dx_A}{dz}$$

$$\Leftrightarrow N_{Az} = -\frac{cD_{AB}}{(1-x_A)}\frac{dx_A}{dz}$$

Substitute into differential equation for N_{Az}:

$$\frac{d}{dz}\left(\frac{cD_{AB}}{(1-x_A)}\frac{dx_A}{dz}\right) = 0$$

Case study-1: Diffusion through stagnant gas film



$$\frac{d}{dz}\left(\frac{cD_{AB}}{(1-x_A)}\frac{dx_A}{dz}\right)=0$$

- For gases, D_{AB} is constant
- As P is constant, w/ ideal gas law (c = n/V = P/RT) → c is constant
- Therefore:

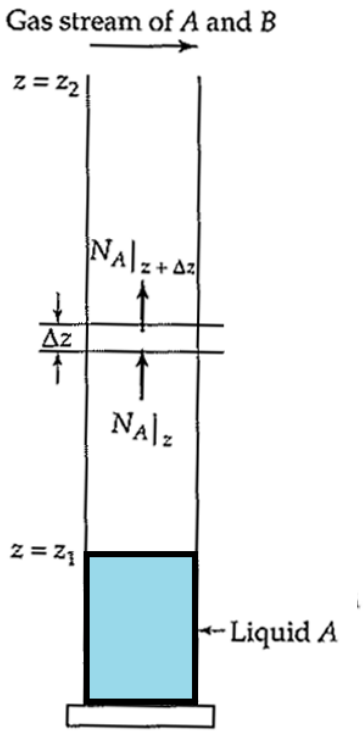
$$\frac{d}{dz}\left(\frac{cD_{AB}}{(1-x_A)}\frac{dx_A}{dz}\right)=cD_{AB}\frac{d}{dz}\left(\frac{1}{(1-x_A)}\frac{dx_A}{dz}\right)=0$$

$$\Rightarrow \quad \frac{d}{dz}\left(\frac{1}{(1-x_A)}\frac{dx_A}{dz}\right)=0$$

- Integrate: $$\frac{1}{(1-x_A)}\frac{dx_A}{dz}=C_1$$

- Integrate again: $$-\ln(1-x_A)=C_1z+C_2$$

Case study-1: Diffusion through stagnant gas film



$$-\ln(1-x_A) = C_1 z + C_2$$

- Standard procedure: $C_1 = -lnK_1$; $C_2 = -lnK_2$

$$-\ln(1-x_A) = -\ln(K_1)z - \ln(K_2)$$

$$\Rightarrow \quad (1-x_A) = K_1^{z} K_2$$ *maths 101…*

- Boundary conditions:
  - At $z = z_1$, $x_A = x_{A1}$

$$(1-x_{A1}) = K_1^{z_1} K_2$$

  - At $z = z_2$, $x_A = x_{A2}$

$$(1-x_{A2}) = K_1^{z_2} K_2$$

$$K_1^{z_2 - z_1} = \frac{1-x_{A2}}{1-x_{A1}}$$

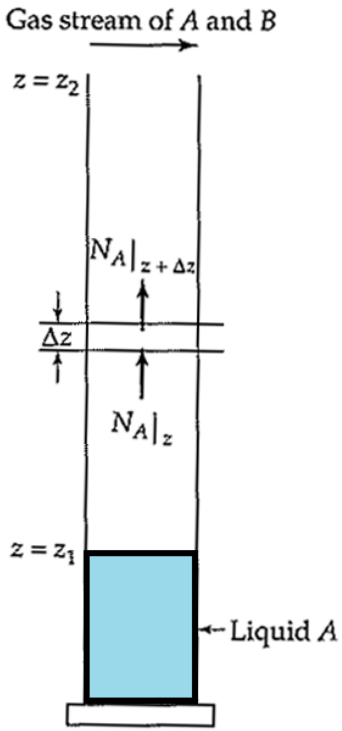
$$\Leftrightarrow K_1 = \left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{\frac{1}{z_2 - z_1}}$$

- Evaluate K_2 from B.C. 1:

$$K_2 = (1-x_{A1})K_1^{-z_1}$$

$$= (1-x_{A1})\left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{-\frac{z_1}{z_2 - z_1}}$$

Case study-1: Diffusion through stagnant gas film



$$(1-x_A) = K_1^{z} K_2$$

$$\Rightarrow \quad (1-x_A) = \left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{\frac{z}{z_2-z_1}} (1-x_{A1}) \left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{-\frac{z_1}{z_2-z_1}}$$

$$\Leftrightarrow \quad \left(\frac{1-x_A}{1-x_{A1}}\right) = \left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{\frac{z-z_1}{z_2-z_1}}$$

Case study-2:
Steady state diffusion from a suspended droplet

See handwritten derivation on BB!