\[ T \equiv J \text{ K} \]

\[ M_{AB} = \text{average molecular weight} = \frac{2}{\left( \frac{1}{M_A} \right) + \left( \frac{1}{M_B} \right)} \]

\[ \Sigma_V = \text{sum of diffusion volumes from Table 3.1} \]

(SEADER + HENLEY)

\[ \Rightarrow \text{Empirical} \Rightarrow \text{Good Estimate (\pm 5\%)} \]

---

**TRENDS + DEPENDENCE ON T + P**

1) if small molecules & similar, then \[ M_{AB} + \Sigma_V \] will have negligible change.

2) \[ D_{AB} \propto \frac{1}{P} \]

3) \[ D_{AB} \propto T^{1.75} \]

\[ \Rightarrow \text{much higher dependence on } T. \]
Also, have a way to convert $D_{AB}(T_1, P_1)$

$\Rightarrow D_{AB}(T_2, P_2)$

**Example:** Air (21% O₂, 79% N₂) @ 1 atm, 298 K

$D_{O_2, N_2} =$ ?

Use Chapman-Enskog

$$D_{AB} = \frac{0.00143 T^{1.75}}{P M_{AB}^{\frac{1}{2}} \left[ (\Sigma_v)_{A}^{\frac{1}{2}} + (\Sigma_v)_{B}^{\frac{1}{2}} \right]^2}$$

$$M_{AB} = \frac{2}{\left( \frac{1}{32} \right) + \left( \frac{1}{28} \right)} = 29.8$$

$$(\Sigma_v)_{O_2} = 16.3 \quad (\Sigma_v)_{N_2} = 18.5$$

(from Table 3.1)
\[ P = 1 \text{ atm} \]

\[ T = 298 \text{ K} \]

\[ D_{AB} = \frac{0.00143 \ (298)^{1.75}}{(1 \text{ atm})(298)^{1/2} \left[ 16.2^{1/3} + 18.5^{1/3} \right]^2} \]

\[ D_{AB} = 0.209 \frac{\text{cm}^2}{\text{s}} \quad @ \quad 1 \text{ atm} \]

\[ 298 \text{ K} \]

\[ 0_2/\text{N}_2 \]

**WHAT IF...**

\[ P = 2 \text{ atm} \]

\[ T = 398 \text{ K} \]

Everything else is the same

\[ D_{AB}^\text{new} = D_{AB} \left| \frac{P_1}{P_2} \right| \left( \frac{T_2}{T_1} \right)^{1.75} = 0.174 \frac{\text{cm}^2}{\text{s}} \]

if only \( T \) changed (\( \Rightarrow P = 1 \text{ atm} \))

\[ D_{AB}^\text{new} = 0.347 \frac{\text{cm}^2}{\text{s}} \]
Also can use correlations, see p. 101.

Nice thing about gases...

Not a lot of interactions

(large V, low P)

However, Liquids are not so lucky

Liquid diffusivities:

Creeping flow w/ drag on molecules of A.
\[ (D_{AB})_{\infty} = \frac{RT}{6\pi \eta B R_A} \]

- \( (D_{AB})_{\infty} \):
  - Infinite dilution diffusivity

- \( R \):
  - Gas constant

- \( T \):
  - Temperature (K)

- \( \eta_B \):
  - Viscosity of B

- \( R_A \):
  - Radius of molecule A

- \( \Rightarrow \) No A-A interactions

Lots of limitations here:

- \( \Rightarrow \) Size of A >> Size of B

- \( \Rightarrow \) No interactions A-A

- \( \Rightarrow \) Dilute (very) solution

- \( \Rightarrow \) If diffusion by random motion, tough to do with really large molecules.

(\( + \) all the interaction with solvent \( B \))
ASIDE:

Notice how nothing is averaged in Stokes-Einstein.
All subscripted for solute or solvent.
(individual component properties)

Consequence:

\[ D_{AB} \neq D_{BA} \quad \text{LIQUIDS} \]

Why? Difference in density of A vs. B,

OK... can still calculate \( D_{AB} + D_{BA} \)

Stokes-Einstein can be extended
to include more properties of the mixture. (again, pure component properties, but catch smaller molecules)
MOST COMMONLY USED:

WILKE - CHANG:

Good for dilute solution (< 5 mol%) 

**Biggest mistake here**

\[ D_{AB} = \frac{7.4 \times 10^{-8} \left( \Phi_B M_B \right)^{1/2}}{M_B \sqrt{V_A}} \]

Note: No pressure dependence.

\[ \Phi_B \] = association parameter \rightarrow Gives measure of interactions

<table>
<thead>
<tr>
<th>( \Phi_B )</th>
<th>Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>( \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>1.9</td>
<td>Methanol</td>
</tr>
<tr>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>1.0</td>
<td>Benzene, Ether, Heptane</td>
</tr>
</tbody>
</table>
*Note: These are non-dissociating solutes.

(≠ not salts)

\[ M_B = \text{molecular weight of solvent} \]

\[ T = \text{temperature (K)} \]

\[ \mu_B = \text{solvent viscosity (cP)} \]

\[ V_A = \text{molar volume @ normal boiling point} \]

\[ \text{(cm}^3/\text{mol)} \]

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

\[ D_{AB} \approx 10^{-6} - 10^{-4} \frac{\text{cm}^2}{s} \quad \text{(binary)} \]

for \( MW < 200 \quad \text{and} \quad \text{viscosity} < 10 \text{cP} \)

Remember, Wilke-Chang for solute concentration less than \( 5-10 \text{ mol}\% \).
DISSOCIATING SOLUTES (Ions/Salts)

- Need to look at each ion.
  
  e.g.: HCl

  \[ D_{H^+}, D_{Cl^-} \]

- Electroneutrality must exist
  
  \( \Rightarrow \text{Total charge} = 0 \)

  \( \Rightarrow \text{Transport of } H^+ \text{ is coupled to transport of } Cl^- \)

\[
D_{12} = \frac{|Z_1| + |Z_2|}{\frac{|Z_1|}{D_1} + \frac{|Z_2|}{D_2}}
\]

Get \( D_1 + D_2 \) from tables.

(e.g., "Diffusion" by E.L. Cussler, 1997)
EXAMPLE: $H_2SO_4$

$H^+ (1)$

$\Rightarrow Z_1 = +1$

$SO_4^{2-} (2)$

$Z_2 = -2$

From Cussler,

$D_1 = 9.31 \times 10^{-5} \frac{cm^2}{s}$ in water

$D_2 = 1.06 \times 10^{-5} \frac{cm^2}{s}$ @ 25°C

$D_{12} = D_{H_2SO_4} = \frac{|+1| + | -2 |}{\frac{|+1|}{9.31 \times 10^{-5}} + \frac{| -2 |}{1.06 \times 10^{-5}}}$

\[ D_{H_2SO_4} = 1.50 \times 10^{-5} \frac{cm^2}{s} \]

**SOLIDS:**

**RANGE:** $10^{-4}$ - $10^{-12} \frac{cm^2}{s}$

Typical gas in polymer: $\sim 10^{-9} \frac{cm^2}{s}$

$\Rightarrow$ MAss transfer in solids **very slow.**
MASS TRANSFER COEFFICIENTS:

FIRST, WHY DO WE NEED THESE?

→ FLOWING SYSTEMS

→ DIFFUSION DISTANCE NOT KNOWN.

EXAMPLES:

1) NON-FLOW w/ B_T KNOWN

&m_capillary

MEMBRANE

BALLOON

HERE, \[ N_A = y_a (N_a + N_B) + J_A \]
2) **Flowing Systems w/ $B_T$ unknown**

- **Turbulent Flow**
  - $B_T$ close to wall

- **Laminar Flow**
  - $B_T$ in radial direction

- **Fixed Particle**

- **Particle Flowing**
  - $\vec{V}_{particle} \neq \vec{V}_{fluid}$

- **Air**
  - Evap liq. from large area.

- **Gas Bubbles**
  - Rising in liquid.

$\Rightarrow$ Use $N_A = k_c A \rho_a$
Using mass transfer coefficients...

\[ N_A = \frac{R_c}{k_v} \Delta C_A \]

Total molar flux \( "A" \)

\[ N_A = k_y \Delta Y_A \]

Mole fraction based mass transfer coefficient

Difference?

\( \frac{R_c}{k_v} \)

Based on concentration

\( k_y \)

Based on mole fraction

In both cases, these are mass transfer coefficients.
CONTAIN:
1) DIFFUSIVITY \( (D_{AB}) \)
2) DIFFUSION DISTANCE \( (B_t) \)

STILL MOLECULAR DIFFUSION

\[ \Rightarrow \text{NOT BULK FLOW.} \]

UNITS:

\[ R_c = \frac{\text{molar flux}}{\Delta \text{conc}} \]

\[ \Rightarrow \frac{\text{mol}}{\text{cm}^2 \cdot \text{s}} \left| \frac{\text{cm}^2}{\text{mol}} \right| \Rightarrow \left| \frac{\text{cm}}{\text{s}} \right| \]

Recall, \( D_{AB} \Rightarrow \frac{\text{cm}^2}{\text{s}} \)

\[ k_y \text{ or } k_x : \]

Mole fractions have no units

\[ \Rightarrow N_A = k_y \Delta y_A \]
$$k_y [\equiv \frac{\text{mol}}{\text{cm}^2 \cdot \text{s}} \iff \text{same as } N_A]$$

As you might imagine, $k_c$ and $k_y$ are related...

**How? DENSITY**

**Gas Phase:**

$$k_y = \frac{k_c \, P}{RT}$$

**Liquid Phase:**

$$k_x = \frac{k_c \, p_x}{M_{av} \cdot \text{solution density}}$$

average molecular weight
BACK TO GAS PHASE...

Common to use partial pressure

\[ k_g = \frac{N_A}{P_{A_i} - P_A} \]

\[ \Rightarrow k_g = \frac{k_g}{p} = \frac{k_c}{RT} \]

WHAT IS THE COMMONALITY?

CAN PUT EVERYTHING IN TERMS OF \( k_c \)

\[ k_c = \frac{N_A}{C_{A_i} - C_A} = \frac{D_{AB} (C_{A_i} - C_A)}{(z - z_i)} \]

\[ \Rightarrow k_c = \frac{D_{AB}}{B_T} \]

NEXT TIME:
- Mass transfer theories
- Correlations for \( k_c \), etc.
MASS TRANSFER THEORIES:

1) FILM THEORY

$$k_c \propto D_{AB}$$

In film theory, $B_T$ is effective film thickness

$B_T = f(Re, D_{AB}, \text{others})$

**Note:** $B_T \neq$ thickness of laminar layer
2) **Two-Film Theory**: (Changing Phases)

\[ y_A \quad \text{interface} \]

\[ \text{Discontinuity @ interface} \]

\[ y_A^* \quad \text{EQ value} \]

\[ y_A \quad \text{GA} \]

\[ x_A \quad \text{LIQUID} \]

\[ x_{A_i} \quad \text{equilibrium} \]

\[ @ \text{interface} \]

\[ N_{A_g} = k_y (y_A - y_A^*) \]

**WHAT DOES THIS LOOK LIKE?**

**Distillation**
Getting mass transfer resistance at the interface in each phase.

Concentration gradients in both phases.

$N_A$ in each phase toward or away from interface.

Discontinuity at interface.

EQ relationship.

If none $\Rightarrow$ No separation.

(Recall, add a phase to get separation)

How do we use THIS for DESIGN?

Add mass transfer resistances in each phase & take reciprocal to get

OVERALL MASS TRANSFER COEFFICIENT
TRANSFER TO/FROM INTERFACE:

To interface:

\[ \Gamma = k_x (x_A - x_{A_i}) \]  

From interface:

\[ \Gamma = k_y (y_{A_i} - y_A) \]  

These are equal.

Why?

MASS CONSERVATION

\[ k_x + k_y \] are mass transfer coefficients in the liquid and gas phases, respectively.

CAN ALSO WRITE WITH OVERALL MASS TRANSFER COEFFICIENT:

\[ \Gamma = k_y (y^*_A - y_A) \] \( \leq \) EQUILIBRIUM.

DIVIDE BOTH SIDES BY \( r k_y \)

\[ \frac{1}{k_y} = \frac{(y^*_A - y_A)}{\Gamma} \]
\[
\frac{1}{K_y} = \frac{(y_A^* - y_{A_i}) + (y_{A_i} - y_A)}{r} \\
\frac{1}{K_y} = \frac{y_A^* - y_{A_i}}{r} + \frac{y_{A_i} - y_A}{r}
\]

Substitute for \( r \)

\[
\frac{1}{K_y} = \frac{(y_A^* - y_{A_i})}{k_x (X_A - X_{A_i})} + \frac{(y_{A_i} - y_A)}{k_y (y_{A_i} - y_A)}
\]

and \( \frac{y_A^* - y_{A_i}}{X_A - X_{A_i}} = \text{slope of eq. line} = m \)

\[
\frac{1}{K_y} = \frac{m}{k_x} + \frac{1}{k_y}
\]

overall resistance

liquid film resistance

gas film resistance
**Cases:**

1) Liquid resistance controls

\[ k_x << k_y \]

\[ \Rightarrow \frac{m}{k_x} \gg \frac{1}{k_y} \]

\[ \Rightarrow \frac{1}{k_y} \approx \frac{m}{k_x} \quad \Rightarrow \quad k_y \approx \frac{k_x}{m} \]

2) Gas resistance controls

*Vice versa*

\[ k_y \approx k_y \]

Look at rates for each to see what driving force to use.

\[ N_A = k_y \left( y_A^* - y_A \right) \]

\[ \rightleftharpoons \quad \text{eq} \quad \uparrow \text{bulk} \]

\[ \Rightarrow \text{Don't need to know } y \ldots \]
PREDICTING MASS TRANSFER COEFFICIENTS

\[ k = f \left( D_{AB}, D, u, \mu, \ell \right) \]

volume diffusivity \( \rightarrow \) linear dimension \( \rightarrow \) density \( \rightarrow \) viscosity

\[ \text{velocity} \]

\[ \Rightarrow \text{DIMENSIONLESS GROUPS} \]

Reynolds #: \[ Re = \frac{Du\ell}{\mu} \]

viscous

Schmidt #: \[ Sc = \frac{\mu}{\ell D_{AB}} \]

diffusive

Sherwood #: \[ Sh = \frac{Re D}{D_{AB}} \]

mass diffusion

\[ Sh = f \left( Re, Sc \right) \]

Based on situation...
CASE 1: MASS TRANSFER w/ FLOW INSIDE PIPES

2) LAMINAR FLOW

GRAETZ #: \( G'_3 = \frac{\dot{m}}{D_{AB} L \rho} = \frac{\dot{m}}{4} \text{Re} Sc \frac{D}{L} \uparrow \text{pipe length} \)

\[ Sh = 1.62 \left( G'_3 \right)^{1/3} \]

b) TURBULENT FLOW

\[ Sh = 0.023 \text{Re}^{0.8} \text{Sc}^{1/3} \left( \frac{\dot{m}}{\dot{m}_w} \right)^{0.14} \approx 1 \text{ for mass transfer} \]

c) Variations for ranges of Sc

i) \( 0.6 \leq Sc \leq 2.5 \)

\[ Sh = 0.023 \text{Re}^{0.81} \text{Sc}^{0.44} \]

ii) \( 430 \leq Sc \leq 100,000 \)

\[ Sh = 0.0096 \text{Re}^{0.913} \text{Sc}^{0.346} \]
EXAMPLE:

\[ \text{Flow in pipe with } Re = 10,000 \]

\[ \text{Sc} = ? \quad (\text{Sc} = \frac{\mu}{\ell D_{ab}}) \quad (Re = \frac{DuP}{\mu}) \]

\[ \text{BT of gas film} = ? \]

\[ \text{Need to get } k_c \]

\[ \text{Let's fill out the equation.} \]
\[ p = \frac{29 \text{ g}}{\text{ mol}} \times \frac{\text{kmol}}{22.4 \text{ mol}} \times \frac{1 \text{ L}}{10^3 \text{ cm}^3} \times \frac{273 \text{ K}}{313 \text{ K}} = 0.00129 \text{ g cm}^3 \] @ STP

\( \Rightarrow \) Need to correct for \( T \)

From App. 8 in McCabe, Smith, & Harriott

\[ \mu = 0.019 \text{ cP} \]

\( (x = 11, \ y = 20) \)

\[ \text{Sc} = \frac{0.019 \text{ cP cm}^3 \text{ s}}{(0.00129 \text{ g})(0.288 \text{ cm}^2)} \times \frac{1 \times 10^{-3} \text{ kg}}{\text{cP m s}} \times \frac{10^3 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ m}}{100 \text{ cm}} \]

\[ \text{Sc} = 0.584 \]

fits case 1c.

\[ \text{Sh} = 0.023 \text{ Re}^{0.81} \text{ Sc}^{0.44} \]

\[ = 0.023 \times (10,000)^{0.81} \times (0.584)^{0.44} \]

\[ \text{Sh} = 31.55 \]
$$\text{but } \text{Sh} = \frac{k_c \cdot D}{D_{AB}} \Rightarrow k_c = \frac{\text{Sh} \cdot D_{AB}}{D}$$

$$k_c = (31.55) \left( 0.288 \, \text{cm}^2 \right) \frac{1}{5} \frac{1}{2 \text{ in.}} \frac{1}{2.54 \text{ cm}}$$

$$k_c = 1.79 \, \text{cm} \frac{1}{5}$$

$$k_c = \frac{D_{AB}}{B_T} \Rightarrow B_T = \frac{D_{AB}}{k_c}$$

$$B_T = 0.288 \, \text{cm}^2 \frac{1}{5} \frac{5}{1.79 \text{ cm}}$$

$$B_T = 0.16 \, \text{cm}$$

**WHAT IF ETHANOL INSTEAD?**

$$D_{AB} = 0.145 \, \text{cm}^2$$

ethanol in air
Sc = \frac{0.019 \text{e}}{(0.001129 \text{ g}) (0.145 \text{ cm}^2)} \left| \frac{1}{100} = 1.16 \right.

Sh = 0.023 (10,000) (1.16) = 42.7

\begin{align*}
R_c &= \frac{Sh D_{AB}}{D} = (42.7) (0.145 \text{ cm}^2) \left( \frac{1}{2 \text{ in}} \right) \left( \frac{1 \text{ in}}{2.54 \text{ cm}} \right) \\
R_c &= 1.22 \text{ cm} \left( \frac{\text{ cm}}{\text{s}} \right)
\end{align*}

B_T = \frac{D_{AB}}{R_c} = 0.145 \text{ cm}^2 \left| \frac{\text{s}}{1.22 \text{ cm}} \right.

B_T = 0.12 \text{ cm}

CASE 2: FLOW OUTSIDE TUBES PARALLEL TO AXIS:

\text{for hollow fiber membrane module}

\begin{align*}
\frac{d_e}{\text{effective diameter}} &= \frac{4 \text{ flow area}}{\text{wetted perimeter}} = 4 \frac{\epsilon}{(4/\pi)(1-\epsilon)} \text{ fiber diameter} \\
\frac{d}{\text{void fraction}} &= \frac{\epsilon}{1-\epsilon} \text{ fiber diameter}
\end{align*}
then use model from above.

\[ \text{CASE 3: FLOW NORMAL TO CYLINDERS} \]

\[ \text{\rightarrow Single cylinder} \]

\[ Sh = 0.61 \, Re^{\frac{1}{2}} \, Sc^{\frac{1}{3}} \]

for \( Re = 10^{-4} \)

\[ \text{CASE 4: FLOW NORMAL TO TUBE BUNDLE} \]

\[ \text{\rightarrow Varies, but for O}_2 \text{ removal from H}_2\text{O} \]

\[ Sh = 1.28 \, Re^{0.4} \, Sc^{0.33} \]

\[ \text{CASE 5: FLOW PAST SINGLE SPHERES} \]

\[ Sh \rightarrow 2 \quad \text{as} \quad Re \rightarrow 0 \]

\[ Re < 1000 \quad Sh = 2.0 + 0.6 \, Re^{\frac{1}{2}} \, Sc^{\frac{1}{3}} \]
CREEPING FLOW

(Low Re, High Peclet # = ReSc)

\[ Sh = \left( 4.0 + 1.21 \text{Pe}^{2/3} \right)^{1/2} \]

w/ Effective film thickness = \( \frac{D_p}{2} \)

CASE 6: MASS TRANSFER IN PACKED BEDS

\[ Sh = 1.17 \text{Re}^{0.585} \text{Sc}^{1/2} \]

Good for beds w/ up to 40-45% voids

for cylindrical particles, use D as characteristic length.

Other correlations for different packings and higher void space

Good for Re > 10
NOTE: PACKED BEDS GIVE MUCH BETTER $\text{Sh}$ THAN SINGLE SPHERES.

CASE 7: MASS TRANSFER TO SUSPENDED PARTICLES

$\rightarrow$ use terminal velocity to get $\text{Re}$.

$\rightarrow$ this gives worse case scenario

$k'_c \geq k'_{c\text{,TV}}$.

CASE 8: MASS TRANSFER TO DROPS $+$ BUBBLES

$\rightarrow$ Penetration Theory

$\text{Sh} = 1.13 \text{Re}^{\frac{1}{2}} \text{Sc}^{\frac{1}{2}}$

NEXT TIME: ABSORBERS