CH351 Mass Transfer

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9/26/07
Fick’s First Law: Steady State Molecular Diffusion

\[ J_{A,z} = -D_{AB} \frac{\partial c_A}{\partial z} \]

\( J_{A,z} \) = flux of component A along z - axis, mol/(cm\(^2\) · s)

\( D_{AB} \) = diffusion coefficient, cm\(^2\)/s

\( \frac{\partial c_A}{\partial z} \) = concentration gradient along z - axis
From Kinetic Theory or Low Density Gases:

\[ D_{AA^*} = \frac{2}{3\pi^{\frac{3}{2}}d^2P} \left( \frac{\kappa^3 T^3}{m} \right)^{\frac{1}{2}} \]

\[ D_{AA^*} = \text{self diffusion coefficient} \]

\[ d = \text{diameter of (spherical) molecules} \]

\[ m = \text{mass of a molecule} \]

Fuller, Schetler and Giddings equation:

\[ D_{AB} = \frac{0.00143T^{1.75}}{P(M_{AB})^{\frac{1}{2}} \left[ (\Sigma_v)_A^{\frac{1}{3}} + (\Sigma_v)_B^{\frac{1}{3}} \right]^2} \]
Wilke - Chang Equation for Diffusion in Liquids:

$$D_{AB} = \frac{7.4 \times 10^{-8} (\Phi_B M_B)^{1/2} T}{\eta_B V_A^{0.6}}$$

Species A is diffusing in solvent B
Partial Pressures, Molar Concentrations, Total Pressure

\[ p_A V = n_A RT \Rightarrow p_A = \frac{n_A}{V} RT \]

- \( p_i \) = partial pressure of component \( i \)
- \( c_i \) = molar conc. of component \( i \)
- \( P \) = total pressure (atm, bar, N/m², mmHg, Torr)
- \( c \) = total molar concentration of gas (mol/cm³, mol/m³, …)

\[ p_A = c_A RT \]
\[ p_B = c_B RT \]
\[ (p_A + p_B) = (c_A + c_B)RT \]
\[ P = cRT \]
Concentrations, Partial Pressures, and Mole Fractions

\[ p_A = c_A RT \quad \text{Mole fraction of } A = y_A = \frac{c_A}{c} = \frac{p_A}{P} \]

\[ p_B = c_B RT \quad \text{Mole fraction of } B = y_B = \frac{c_B}{c} = \frac{p_B}{P} \]

- At constant total pressure, \( P \), and constant temperature, \( T \), total molar concentration, \( c \), is constant.
- For each species, mole fraction \( \propto \) concentration \( \propto \) partial pressure
Fick’s First Law in terms of Mole Fractions

\[ J_{A,z} = -D_{AB} \frac{\partial c_A}{\partial z} = -cD_{AB} \frac{\partial y_A}{\partial z} = -\frac{D_{AB} P}{RT} \frac{\partial y_A}{\partial z} \]

\[ J_{B,z} = -D_{BA} \frac{\partial c_B}{\partial z} = -cD_{BA} \frac{\partial y_B}{\partial z} = -\frac{D_{BA} P}{RT} \frac{\partial y_B}{\partial z} \]
What is the net molar flux of A that a stationary observer would measure?

\[ N_{A,z} = c_A v_{A,z} \]

\[ v_{A,z} = \text{velocity of A relative to stationary observer} \]
What is the net molar flux of A that an observer who moves with the fluid element would measure?

Moving observer will measure only flux due to diffusion.

\[
J_{A,z} = c_A (v_{A,z} - v_z^*)
\]

\[
= -D_{AB} \frac{\partial c_A}{\partial z}
\]
Total Flux, $N_{A,z} = J_{A,z} + c_A v_z^*$

$J_{A,z} = c_A (v_{A,z} - v_z^*)$

$v_z^* = y_A v_{A,z} + y_B v_{B,z}$

$N_{A,z} = c_A v_{A,z}$

- $v_{A,z}$ = velocity of A measured by a stationary observer
- $v_{B,z}$ = velocity of B measured by a stationary observer
- $v_z^*$ = molar average velocity

$mol \times \frac{cm}{cm^3} \times \frac{s}{s} = \frac{mol}{cm^2 \cdot s}$
General Form of Fick’s First Law

\[ N_{A,z} = J_{A,z} + c_A v_z \]

= diffusive flux + flux due to bulk motion

\[ N_{A,z} = J_{A,z} + y_A (N_A + N_B) \]

\[ N_{A,z} = -c_{D_{AB}} \frac{\partial y_A}{\partial z} + y_A (N_{A,z} + N_{B,z}) \]
Equimolar Counter Diffusion (EMCD)

\[ N_{A,z} = -N_{B,z} \]

\[ \therefore N_{A,z} = J_{A,z} + \gamma_A \left( N_{A,z} + N_{B,z} \right) \]

\[ N_{A,z} = J_{A,z} = -D_{AB} \frac{\partial c_A}{\partial z} \]

- A simplifying assumption that
  - allows easier solution of the general form of Fick’s first law
  - makes analytical solution possible
Problem 1 (EMCD assumption)

Mixture of two gases, A and B, in a tube with conc. gradient

\[ \frac{\partial y_A}{\partial z} = 0 \]

\[ p_{A,1} \]

\[ y_{A,1} \]

\[ p_{A,2} \]

\[ y_{A,2} \]

\[ z = z_1 = 0 \]

\[ z = z_2 \]

\[ N_{A,z} = J_{A,z} = -\frac{D_{AB}p}{RT} \frac{\partial y_A}{\partial z} \]

\[ N_{A,z} = \frac{D_{AB}p}{RT} \left( \frac{y_{A,1} - y_{A,2}}{z_2 - z_1} \right) \]

\[ \text{FLUX} \]

\[ y_A = y_{A,1} - \left( \frac{y_{A,1} - y_{A,2}}{z_2 - z_1} \right) (z - z_1) \]

\[ \text{CONCENTRATION PROFILE} \]
Problem 2 (EMCD assumption)

Evaporation from surface of naphthalene ball

\[ c_A \bigg|_{r \to \infty} = c_A^b \approx 0 \]

At steady state, \( N_A \big|_r = -D_{AB} \frac{\partial c_A}{\partial r} \big|_r \)

\[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_A}{\partial r} \right) = 0 \quad \Rightarrow \quad \frac{c_A - c_A^b}{c_A^s - c_A^b} = \frac{R}{r} \]

\[ N_A \big|_{r=R} = D_{AB} \frac{c_A^s - c_A^b}{R} \left( \frac{\text{mol}}{\text{cm}^2 \ \text{s}} \right) \]

Evaporation rate = \( 4\pi R^2 \times D_{AB} \frac{c_A^s - c_A^b}{R} \left( \frac{\text{mol}}{\text{s}} \right) \)

\[ c_A \big|_{r=R} = \frac{p_A^{vp}}{RT} = c_A^s \]

Air near surface is saturated with naphthalene

\[ \therefore p_A \big|_{r=R} = p_A^{vp} \]
Unimolecular Diffusion

\[ N_{A,z} = J_{A,z} + y_A(N_{A,z} + N_{B,z}) \]

\[ N_{B,z} = 0 \]

\[ \therefore N_{A,z} = J_{A,z} + y_A N_{A,z} \]

\[ N_{A,z} = \frac{J_{A,z}}{1 - y_A} = -\left(\frac{D_{AB}P}{RT}\right)\left(\frac{1}{1 - y_A}\right) \frac{\partial y_A}{\partial z} \]
Solvent Evaporation (UMD)

- At $z = z_1 = 0$, air is saturated with liquid: $p_{A1} = \text{vap. pressure}$
- At $z = z_2$, all A carried away by air: $p_{A2} \sim 0$
Solvent Evaporation

\[ N_{A,z} = -\left( \frac{D_{AB}P}{RT} \right) \left( \frac{1}{y_B} \right) \frac{\partial y_A}{\partial z} \]

\[ N_A = \left( \frac{D_{AB}P}{RT} \right) \left( \frac{1}{y_{B,lm}} \right) \left( \frac{y_{A,1} - y_{A,2}}{z_2 - z_1} \right) \]

\[ y_{B,lm} = \frac{y_{B,2} - y_{B,1}}{\ln \left( \frac{y_{B,2}}{y_{B,1}} \right)} \]

CONC. PROFILE

FLUX
Evaporation of Benzene (bp 80 °C) at 25 °C and 70 °C

25 °C

70 °C
Flux Profiles (UMD)
Evaporation of Dichloromethane (bp 40 °C) at 25 °C
Diffusion Into a Falling Liquid Film

\[ v_y(z) = \frac{\rho g \delta^2}{2\mu} \left[ 1 - \left(\frac{z}{\delta}\right)^2 \right] \]

**OBJECTIVE:**

- To determine molar flux \((\text{mol cm}^{-1} \text{ s}^{-1})\) at the gas–liquid interface.
- The overall rate of mass transfer (mol/s).

\[ N_A(y)_{z=0} = \text{local molar flux at interface} \ (z = 0) \]

at position \(y\) from the top entrance.
\[ N_{A,y}\bigg|_{y} \cdot (W\Delta z) - N_{A,y}\bigg|_{y+\Delta y} \cdot (W\Delta z) + N_{A,z}\bigg|_{z} \cdot (W\Delta y) - N_{A,z}\bigg|_{z+\Delta z} \cdot (W\Delta y) = 0 \]

\[ \frac{N_{A,y}\bigg|_{y+\Delta y} - N_{A,y}\bigg|_{y}}{\Delta y} + \frac{N_{A,z}\bigg|_{z+\Delta z} - N_{A,z}\bigg|_{z}}{\Delta z} = 0 \]

\[ \frac{\partial N_{A,y}}{\partial y} + \frac{\partial N_{A,z}}{\partial z} = 0 \]

\[ N_{A,y} = -D_{AB} \frac{\partial c_A}{\partial y} + c_A v_y \]

\[ N_{A,z} = -D_{AB} \frac{\partial c_A}{\partial z} + c_A v_z \]

\[ v_y \frac{\partial c_A}{\partial y} = D_{AB} \frac{\partial^2 c_A}{\partial z^2} \]
Liquid
\[ v_y \frac{\partial c_A}{\partial y} = D_{AB} \frac{\partial^2 c_A}{\partial z^2} \]

Approximate solution:
\[ c_A(y, z) = c_{A,i} \operatorname{erfc} \left( \frac{z}{\sqrt{4D_{AB}} \frac{y}{v_{y,\max}}} \right) \]
\[ N_{A,z} \bigg|_{z=0} = -D_{AB} \frac{\partial c_A}{\partial z} \bigg|_{z=0} = c_{A,i} \sqrt{\frac{D_{AB} v_{y,\max}}{\pi y}} \]
\[ N_{A,z} \bigg|_{z=0} = -D_{AB} \left. \frac{\partial c_A}{\partial z} \right|_{z=0} = c_{A,i} \sqrt{\frac{D_{AB} v_{y,max}}{\pi y}} \]

Moles of \( A \) transferred per second at position \( y \)
\[ = (\text{flux}) \times (\text{area}) \]
\[ = (N_{A,z} \bigg|_{z=0}) \times (\mathcal{W} \cdot d\,y) \]
\[ = \left( c_{A,i} \sqrt{\frac{D_{AB} v_{y,max}}{\pi y}} \right) \times (\mathcal{W} \cdot d\,y) \]
\[ \vdots \text{total moles of } A \text{ transferred per second over length } L \text{ of the tower} \]

\[ = \int_0^L \left( c_{A,i} \sqrt{\frac{D_{AB}v_{y,\text{max}}}{\pi y}} \right) \times (W \cdot dy) \]

\[ = Wc_{A,i} \sqrt{\frac{D_{AB}v_{y,\text{max}}}{\pi}} \int_0^L \frac{1}{\sqrt{y}} \, dy \]

\[ = 2Wc_{A,i} \sqrt{\frac{D_{AB}v_{y,\text{max}} L}{\pi}} \]

\[ = WL \times 2c_{A,i} \sqrt{\frac{D_{AB}v_{y,\text{max}}}{\pi L}} \]

\[ = WL \times 2c_{A,i} \sqrt{\left( \frac{D_{AB}}{\pi} \right) \frac{1}{\tau}} \]

where \( \tau = \text{time of contact between liquid element and gas} \)
Mass Transfer Coefficient

- Fick’s law: flux \( \propto \) conc. gradient
  - const. of proportionality = diffusion coefficient
- Another approach to quantify flux:
  - Flux \( \propto \) conc. driving force, \( \Delta c_A \)
  - const. of proportionality = mass transfer coefficient, \( k \)
  - Similar to Newton’s “law” of cooling
Fick's law: \[ N_A = D_{AB} \frac{\Delta c_A}{\Delta z} \]

Engineering approach: \[ N_A = k \cdot \Delta c_A \]

\( k \) = mass transfer coefficient

\( k \) has units of \( \frac{\text{cm}}{\text{s}} \)

\[ N_A \left( \frac{\text{mol}}{\text{cm}^2 \cdot \text{s}} \right) = k \left( \frac{\text{cm}}{\text{s}} \right) \cdot \Delta c_A \left( \frac{\text{mol}}{\text{cm}^3} \right) \]
Evaporation from surface of naphthalene ball

Conc. driving force for mass transfer

\[ \Delta c = \left( c_A^s - c_A^b \right) \]

Mass transfer coefficient, \( k = \frac{N_A}{\Delta c} \)

Solution of Fick's law had given us:

\[ N_A \bigg|_{r=R} = D_{AB} \frac{\left( c_A^s - c_A^b \right)}{R} \]

\[ k = \frac{N_A}{\Delta c_A} = \frac{D_{AB} \left( c_A^s - c_A^b \right)}{R} = \frac{D_{AB}}{R} \]

\[ c_A \bigg|_{r=R} = \frac{p_A^{vp}}{RT} = c_A^s \]

\[ c_A \bigg|_{r=\infty} = c_A^b \]
Sherwood Number

• For evaporation from surface of a sphere, we obtained:

\[ k = \frac{D_{AB}}{R} = 2 \frac{D_{AB}}{D} \quad (D = \text{sphere diameter}) \]

\[ \therefore \frac{k \cdot D}{D_{AB}} = 2 \]

• \( kD/D_{AB} \) is a dimensionless quantity that often appears in mass transfer calculations.

• It is called the Sherwood number and is denoted by \( Sh \).

• For diffusion from surface of a sphere into a stagnant fluid, \( Sh = 2 \)
Convective Mass Transfer

• Material is transported between
  – a solid surface and a moving fluid (gas or liquid)
  – two relatively immiscible moving fluids (gas and liquid, or liquid and liquid)

• Examples
  – Mass-transfer of gas into a falling liquid film
  – Mass-transfer of naphthalene into a flowing gas stream
  – Mixing in a stirred vessel
Turbulent Flow

- Laminar flow is characterized by streamlines
- Turbulent flow is characterized by chaotic flow of packets of fluid called “eddies”
- Rate of mass transfer in laminar flow is determined by molecular diffusivity, $D_{AB}$
- Rate of mass transfer in turbulent flow is determined by both molecular diffusivity, $D_{AB}$ and turbulent diffusivity, $D_t$
Mass Transfer Correlations for Convective Flows

• **Dimensional Analysis**

• **Example**
  
  – The inner wall of a circular tube is coated with species A (e.g., naphthalene)
  
  – Mass transfer occurs to a fluid flowing through the tube (e.g., air)
\[ N_A = k_c \cdot \left( c_A^s - c_A^b \right) \]

\[ k_c = \text{convective mass transfer coefficient} \]

\[ k_c = [\text{constant}] (D)^a (\rho)^b (\mu)^c (\nu)^d (D_{AB})^e \]

<table>
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<th>( k_c )</th>
<th>( D )</th>
<th>( \rho )</th>
<th>( \mu )</th>
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</table>

\[ b + c = 0 \]
\[ a - 3b - c + d + 2e = 1 \]
\[ -c - d - e = -1 \]

5 variables, 3 equations
\[
\begin{bmatrix}
1 & 0 & 0 \\
-3 & 1 & 2 \\
0 & -1 & -1
\end{bmatrix}
\begin{bmatrix}
b \\
d \\
e
\end{bmatrix}
=
\begin{bmatrix}
-1 + c \\
1 - a + c \\
-1 + c
\end{bmatrix}
\]

\[Ax = B\]

\[
\begin{bmatrix}
b \\
d \\
e
\end{bmatrix}
=
\begin{bmatrix}
1 & 0 & 0 \\
-3 & -1 & -2 \\
3 & 1 & 1
\end{bmatrix}
\begin{bmatrix}
-1 + c \\
1 - a + c \\
-1 + c
\end{bmatrix}
\]

\[A^{-1}Ax = x = A^{-1}B\]
\[ k_c = \text{[constant]} (D)^a (\rho)^b (\mu)^c (\nu)^d (D_{AB})^e \]
\[ = \text{[constant]} (D)^a (\rho)^{-c} (\mu)^c (\nu)^{a+1} (D_{AB})^{-a-c} \]
\[ = \text{[constant]} \left( \frac{D\nu\rho}{\mu} \right)^{a+1} (\mu)^{a+c+1} (D_{AB})^{-a-c} \frac{1}{D} \]
\[ \left( \frac{k_c D}{D_{AB}} \right) = \text{[constant]} \left( \frac{D\nu\rho}{\mu} \right)^{a+1} \left( \frac{\mu}{\rho D_{AB}} \right)^{a+c+1} \]

\[ Sh = \text{[constant]} Re^\alpha Sc^\beta \]

\[ Sc = \text{Schmidt number} = \frac{(\mu/\rho)}{D_{AB}} = \frac{\text{momentum diffusivity}}{\text{mass diffusivity}} \]
\[ k_c = \left[ \text{constant} \right] (D)^a (\rho)^{-c} (\mu)^c (\nu)^{a+1} (D_{AB})^{-a-c} \]

\[ = \left[ \text{constant} \right] \left( \frac{D\nu \rho}{\mu} \right)^a (\rho)^{-a-c} (\mu)^{a+c} (D_{AB})^{-a-c} \nu \]

\[ \left( \frac{k_c}{\nu} \right) = \left[ \text{constant} \right] \left( \frac{D\nu \rho}{\mu} \right)^a \left( \frac{\mu}{\rho D_{AB}} \right)^{a+c+1} \]

\[ k_c = \left[ \text{constant} \right] Re^\gamma Sc^\delta \]

\[ \frac{k_c}{\nu} Sc^{2/3} = \left[ \text{constant} \right] Re^\gamma Sc^{\delta + (2/3)} \]

\[ \frac{k_c}{\nu} Sc^{2/3} = J_D = \text{Chilton and Colburn J-factor} \]
Turbulent Flow Inside Pipes

\[ Sh = \frac{k_c D}{D_{AB}} \quad Re = \frac{Dv \rho}{\mu} \quad Sc = \frac{\mu}{\rho D_{AB}} \]

When \( Re > 2100 \) and \( 0.6 < Sc < 3000 \):

\[ Sh = 0.023 Re^{0.83} Sc^{0.33} \]

In general, \( Sc \) for gases is in the range 0.5–3, and for liquids, \( Sc > 100 \).
Flow Past Single Spheres

\[ Sh = \frac{k_c D}{D_{AB}} \quad Re = \frac{D v \rho}{\mu} \quad Sc = \frac{\mu}{\rho D_{AB}} \]

For gases, when \( 1 < Re < 48000 \), and \( 0.6 < Sc < 2.7 \)

\[ Sh = 2 + 0.552 Re^{0.53} Sc^{1/3} \]

For liquids, when \( 2 < Re < 2000 \) : \( Sh = 2 + 0.95 Re^{0.5} Sc^{1/3} \)

For liquids, \( 2000 < Re < 17000 \) : \( Sh = 0.347 Re^{0.62} Sc^{1/3} \)
Naphthalene Evaporation

• A sphere of naphthalene having a diameter of 1 cm is suspended in air at 1 atm, and flowing at a velocity of 0.3 m/s. The diffusion coefficient of naphthalene in air at this temperature is $6.92 \times 10^{-6}$ m²/s. The molar density of naphthalene solid is $8.86 \times 10^{-3}$ mol/cm³. Calculate the initial rate of evaporation of naphthalene from the surface. Estimate the time required to reduce the diameter from 1 to 0.5 cm.
For gases in a packed bed of spheres, when \( 10 < Re < 10000 \),

\[
J_D = \frac{0.4548}{\varepsilon} Re^{-0.4069}
\]

\[
J_D = \frac{k_c}{v'} Sc^{2/3} \quad Re = \frac{D_p v' \rho}{\mu} \quad Sc = \frac{\mu}{\rho D_{AB}}
\]

\( \varepsilon \) = void fraction in the bed = \( \frac{\text{volume of void space}}{\text{total volume of void space plus solid}} \)

The value of \( \varepsilon \) is usually between 0.3 and 0.5.

\( D_p \) = diameter of the spheres

\( v' \) = superficial velocity of gas

= average velocity in the empty tube without packing

= \( \frac{\text{volumetric flow rate}}{\text{cross-sectional area of tube}} \)
Mass Transfer in Packed Beds

For liquids, when $0.0016 < Re < 55$, and $165 < Sc < 70000$

$$J_D = \frac{1.09}{\varepsilon} Re^{-2/3} \quad \text{(Wilson and Geankoplis)}$$

For liquids, when $55 < Re < 1500$, and $165 < Sc < 10690$

$$J_D = \frac{0.250}{\varepsilon} Re^{-0.31}$$

For non-spherical particles, $D_p = \text{dia. of a sphere with the same surface area as the given solid particle}$

To calculate flux, use the surface area of the non-spherical particles.
Packed Bed of Benzoic Acid Spheres

- Water at 26.1 °C flows at a rate of $5.514 \times 10^{-7}$ m$^3$/s through a packed bed of benzoic acid spheres having a diameter of 6.375 mm. The void fraction of the bed is 0.436. The tower diameter is 0.0667 m and the tower height is 0.1 m. The solubility of benzoic acid in water is $2.948 \times 10^{-2}$ kg mol/m$^3$. Predict the mass transfer coefficient $k_c$ and the outlet concentration of benzoic acid in water.
Water flow rate, \( Q = 5.514 \times 10^{-7} \text{ m}^3/\text{s} \)
\( \mu = 0.8718 \times 10^{-3} \text{ Pa} \cdot \text{s}, \rho = 996.7 \text{ kg/m}^3 \)

\( \varepsilon = 0.436 \)

\( D_p = 6.375 \times 10^{-3} \text{ m}, A_p = 0.01198 \text{ m}^2 \)

Tower dia. \( T = 0.0667 \text{ m}; \) Height \( H = 1 \text{ m} \)

\( D_{AB} = 1.25 \times 10^{-9} \text{ m}^2/\text{s} \) (Wilke-Chang)

\[ c_{A,1} = 0 \]

\[ c_{A,2} = ? \]

\[ S_c = \frac{\mu}{\rho D_{AB}} = \frac{0.8718 \times 10^{-3}}{996.7 \left(1.245 \times 10^{-9}\right)} = 702.6 \]

\[ \nu' = \frac{Q}{\frac{\pi T^2}{4}} = \frac{5.514 \times 10^{-7}}{\frac{\pi}{4} \left(0.0667\right)^2} = 1.578 \times 10^{-4} \text{ m/s} \]

\[ Re = \frac{D_p \nu' \rho}{\mu} = \frac{\left(6.375 \times 10^{-3}\right) \left(1.578 \times 10^{-4}\right) (996.7)}{0.8718 \times 10^{-3}} = 1.150 \]
\[ Sc = 702.6 \quad Re = 1.150 \quad v' = 1.578 \times 10^{-4} \text{ m/s} \]

\[ J_D = \frac{1.09}{\varepsilon} Re^{-2/3} = \frac{1.09}{0.0436} (1.150)^{-2/3} = 2.277 \]

\[ k_c = J_D \cdot v' \cdot Sc^{-2/3} = (2.277) (1.578 \times 10^{-4}) (702.6)^{-2/3} = 4.447 \times 10^{-6} \text{ m/s} \]

Total volume of bed \( V_b = \frac{\pi}{4} T^2 H = \frac{\pi}{4} (0.0667)^2 (0.1) = 3.494 \times 10^{-3} \text{ m}^3 \)

Void fraction \( \varepsilon \)

\( \therefore \) volume of spheres in the bed \( = V_b \cdot (1 - \varepsilon) \)

Let number of spheres in the bed \( = N_p \)

\( \therefore N_p \cdot \left( \frac{\pi}{6} D_p^3 \right) = V_b \cdot (1 - \varepsilon) \)

Total surface area of spheres \( = A = N_p \cdot \left( \pi D_p^2 \right) \)

\[ \frac{6V_b \cdot (1 - \varepsilon)}{D_p} = \frac{6(3.494 \times 10^{-3})(1 - 0.436)}{6.375 \times 10^{-3}} = 0.1855 \text{ m}^2 \]
Mole balance:

\[ k_c \cdot A \cdot (c_A^s - c_A^b)_{\text{im}} = Q \cdot (c_{A,2} - c_{A,1}) \]

\[
\frac{m}{s} \cdot \frac{m^2}{m^3} \cdot \frac{\text{kg mol}}{m^3} = \frac{m^3}{s} \cdot \frac{\text{kg mol}}{m^3}
\]

\[
(c_A^s - c_A^b)_{\text{im}} = \frac{(c_A^s - c_A^b)_1 - (c_A^s - c_A^b)_2}{\ln \left( \frac{(c_A^s - c_A^b)_1}{(c_A^s - c_A^b)_2} \right)}
\]

\[ c_A^s = 2.948 \times 10^{-2} \text{ kg mol/m}^3 \]

\[ (c_A^b)_1 = \text{conc. of benzoic acid at inlet} = c_{A,1} = 0 \text{ kg mol/m}^3 \]

\[ (c_A^b)_2 = \text{conc. of benzoic acid at outlet} = c_{A,2} \]
\[ k_c \cdot A \cdot \frac{(c_{A,2} - c_{A,1})}{\ln \left( \frac{c_A^s - c_{A,1}}{c_A^s - c_{A,2}} \right)} = Q \cdot (c_{A,2} - c_{A,1}) \]

\[ \therefore c_{A,2} = c_A^s - \left( c_A^s - c_{A,1} \right) \exp \left( -\frac{k_c A}{Q} \right) \]

\[ = 2.948 \times 10^{-2} - \left( 2.948 \times 10^{-2} - 0 \right) \times \exp \left( -\frac{4.447 \times 10^{-6} \times 0.1855}{5.514 \times 10^{-7}} \right) \]

\[ = 2.287 \times 10^{-2} \text{ kg mol/m}^3 \]
Mass Transfer to Bubbles and Particles

- Small particles in suspension
  - Mass transfer from small gas bubbles to liquid phase
  - Mass transfer from liquid phase to the surface of catalyst particles, microorganisms, liquid drops, etc.
  - Mass transfer coefficient depends on free fall or rise of particles due to gravitational forces
Mass transfer coefficient, $k_c$, in mass transfer to small particles is affected by natural convection. Natural convection occurs when there is significant density difference between the particles of the dispersed phase (gas bubbles or liquid drops) and the fluid (continuous phase). In such cases, $k_c$ is expected to depend on:
- diameter $D_p$ of the particles of dispersed phase (e.g., O$_2$ bubble)
- density $\rho_c$ of the continuous phase (e.g., water)
- viscosity $\mu_c$ of the continuous phase (e.g., water)
- the buoyant force $g\Delta\rho$ where $\Delta\rho$ is the density difference between the dispersed and continuous phases, and $g$ is the acceleration due to gravity (9.81 m/s$^2$)
- the diffusion coefficient of the molecules of dispersed phase (oxygen) in the continuous phase (water).

Using dimensional analysis, derive an expression for the mass transfer coefficient in terms of the dimensionless numbers $Sh$ and $Sc$. The dimensionless group with the buoyant force variable, $g\Delta\rho$, is called the Grashof number, $Gr$. Derive an expression for $Gr$. 
Mass Transfer to Small Particles
(< 0.6 mm)

\[ k_L = \frac{2D_{AB}}{D_p} + 0.31Sc^{-2/3} \left( \frac{\Delta \rho \mu_c g}{\rho_c^2} \right)^{1/3} \]

- \( k_L \) = 'liquid - side' mass transfer coefficient
- \( D_{AB} \) = diffusivity of the solute A in solution
- \( D_p \) = diameter of the gas bubble or solid particle
- \( Sc = \mu_c / (\rho_c D_{AB}) \)
- \( \mu_c \) = viscosity of the solution
- \( g = 9.81 \text{ m/s}^2 \)
- \( \Delta \rho \) = magnitude of the density difference between the dispersed and continuous phases (always positive)

LOW DENSITY SOLIDS OR SMALL GAS BUBBLES IN AGITATED SYSTEMS
Mass Transfer to Large Gas Bubbles or Liquid Drops (> 2.5 mm)

\[ k_L = 0.42Sc^{-0.5} \left( \frac{\Delta \rho \mu_c g}{\rho_c^2} \right)^{1/3} \]

AERATION OF PURE LIQUIDS IN MIXING VESSELS; SIEVE-PLATE COLUMNS

\[ k_L \] = 'liquid - side' mass transfer coefficient

\[ Sc = \frac{\mu_c}{\rho_c D_{AB}} \]

\( \mu_c \) = viscosity of the solution

\( g = 9.81 \text{m/s}^2 \)

\( \Delta \rho \) = magnitude of the density difference between the dispersed and continuous phases (always positive)
Mass Transfer to Particles in Highly Turbulent Mixers

- Turbulent forces become larger than gravitational forces. Mass transfer coefficient is determined primarily by agitation power-input and not by buoyant forces (natural convection).

\[ k_L = 0.13 \text{Sc}^{-2/3} \left( \frac{P/V}{\rho_c} \right)^{1/3} \]

\[ k_L = \text{'liquid - side' mass transfer coefficient} \]

\[ \text{Sc} = \frac{\mu_c}{\rho_c D_{AB}} \]

\[ \mu_c = \text{viscosity of the solution} \]

\[ \rho_c = \text{density of the solution} \]
Inter-phase Mass Transfer

• Mass transfer at gas–liquid or liquid–liquid interfaces

• Consider mass transfer from naphthalene to air, or from benzoic acid to water
  – Mass transfer rate is determined by concentration gradients in air or water

• In mass transfer at interface of two immiscible liquids A and B (or gas A and liquid B)

• Mass transfer rate is determined by concentration gradients on both sides of the interface (in phase A and phase B)
Concentration Profile at Interface

- Consider evaporation of napthalene from surface of a sphere (1 cm dia.) at 45 °C and 1 atm total pressure.

\[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_A}{\partial r} \right) = 0 \]

\[ c_A \bigg|_{r=R} = c_A^s \]

\[ c_A \bigg|_{r \to \infty} = c_A^b \]

\[ \frac{c_A - c_A^b}{c_A^s - c_A^b} = \frac{R}{r} \]

\[ c_A^s = 2.798 \times 10^{-8} \text{ mol/cm}^3 \]

\[ c_A^b \approx 0 \text{ mol/cm}^3 \]

\[ R = 0.5 \text{ cm} \]
‘Two-Film’ Theory & Overall Mass Transfer Coefficient

Gas phase

Liquid phase

\[ p_A^b \]

\[ p_A^i \]

\[ c_A^i \]

\[ c_A^b \]

Mass transfer from gas to liquid

gas–liquid interface
Flux on 'gas - side' = $k_g \left( p_A^b - p_A^i \right)$ \( \text{mol cm}^2 \cdot \text{s} \)

$k_g = \text{gas - side mass transfer coefficient} \quad \left( \text{mol atm} \cdot \text{cm}^2 \cdot \text{s} \right)$

Flux on 'liquid - side' = $k_l \left( c_A^i - c_A^b \right)$ \( \text{mol cm}^2 \cdot \text{s} \)

$k_l = \text{liquid - side mass transfer coefficient} \quad \left( \text{cm s} \right)$

The two fluxes across the interface are equal.

\[ \Rightarrow N_A = k_g \left( p_A^b - p_A^i \right) = k_l \left( c_A^i - c_A^b \right) \]
Assume that, at the interface, there is equilibrium between the gas mixture and the liquid solution

\[ \therefore c_A^i = H_A \cdot p_A^i \]

\( H_A \) is the equilibrium constant (e.g., Henry's constant) for species A

\[ \left( \frac{\text{mol}}{\text{atm} \cdot \text{cm}^3} \right) \]
Now, \( c_A^i = \left( c_A^b + \frac{N_A}{k_l} \right) \) and \( p_A^i = \left( p_A^b - \frac{N_A}{k_g} \right) \)

\[
\therefore H_A \left( p_A^b - \frac{N_A}{k_g} \right) = \left( c_A^b + \frac{N_A}{k_l} \right)
\]

Solving for \( N_A \):

\[
N_A = \frac{H_A p_A^b - c_A^b}{\frac{H_A}{k_g} + \frac{1}{k_l}}
\]

Define concentration \( c_A^* = H_A p_A^b \)

\( c_A^* \) = saturation conc. of A in the liquid when the partial pressure of A in the gas phase is \( p_A^b \).
\[ N_A = \frac{c_A^* - c_A^b}{H_A + \frac{1}{k_g} + \frac{1}{k_l}} \]

'Over-all' mass transfer coefficient, \( K_L = \frac{N_A}{c_A^* - c_A^b} = \frac{1}{\left( \frac{H_A}{k_g} + \frac{1}{k_l} \right)} \)

\[ \therefore \frac{1}{K_L} = \frac{H_A}{k_g} + \frac{1}{k_l} \]

\[ \frac{1}{\text{mass transfer coefficient}} = \text{'mass transfer resistance'} \]

Thus, mass transfer resistances across an interface are additive.
Laminar Boundary Layer on a Flat Plate \((Re_x < 5 \times 10^5)\)

- Velocity boundary layer
- Flat plate

\[
Re_x = \frac{xv_0\rho}{\mu}
\]

\[
\frac{\delta_x}{x} = \frac{4.96}{Re_x^{0.5}}
\]

\[
\frac{v_x}{v_0} = 1.5 \left( \frac{y}{\delta_x} \right) - 0.5 \left( \frac{y}{\delta_x} \right)^3
\]
Laminar Boundary Layer on a Flat Plate

\[ \frac{\partial c_A}{\partial y} \bigg|_{y=0} = \left( c_A^b - c_A^s \right) \left( \frac{0.332}{x} Re_x^{1/2} Sc^{1/3} \right) \]

where \( Re_x = \frac{x v_0 \rho}{\mu} \)
Local convection mass transfer coefficient is given by:

\[ k_{c,x} \equiv \left( \frac{N_{A,y}}{c_A^s - c_A^b} \right) = \frac{-D_{AB}\left( \frac{\partial c_A}{\partial y} \right)_{y=0}}{c_A^s - c_A^b} \]  

(definition)

\[
\frac{k_{c,x} x}{D_{AB}} = 0.332 \left( \frac{xv_0 \rho}{\mu} \right)^{1/2} \left( \frac{\mu}{\rho D_{AB}} \right)^{1/3} \iff Sh_x = 0.332 Re_x^{1/2} Sc^{1/3}
\]

Mean mass - transfer coefficient for laminar flow over

a flat plate of width \( W \) and length \( L \) : 

\[
k_c = \frac{1}{L} \int_0^L k_{c,x} \, dx
\]

\[
\left( \frac{k_c L}{D_{AB}} \right) = 0.664 \left( \frac{Lv_0 \rho}{\mu} \right)^{1/2} \left( \frac{\mu}{\rho D_{AB}} \right)^{1/3} \Rightarrow Sh_L = 0.664 Re_L^{1/2} Sc^{1/3}
\]
PROBLEM 18

\[ k_c = [\text{constant}] (D)^a (\rho)^b (\mu)^c (g\Delta\rho)^d (D_{AB})^e \]

<table>
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<tr>
<th></th>
<th>(k_c)</th>
<th>(D)</th>
<th>(\rho)</th>
<th>(\mu)</th>
<th>(g\Delta\rho)</th>
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<td>-1</td>
<td>-2</td>
<td>-1</td>
</tr>
</tbody>
</table>

\(b + c + d = 0\)  \(b = -c - d\)
\(a - 3b - c - 2d + 2e = 1\)  \(a - 3b + 2e = 1 + c + 2d\)
\(-c - 2d - e = -1\)  \(e = 1 - c - 2d\)

5 variables, 3 equations
\[
\begin{bmatrix}
0 & 1 & 0 \\
1 & -3 & 2 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
a \\
b \\
e
\end{bmatrix}
= \begin{bmatrix}
-c - d \\
1 + c + 2d \\
1 - c - 2d
\end{bmatrix}
\]
\(A\mathbf{x} = \mathbf{B}\)

\[
\begin{bmatrix}
a \\
b \\
e
\end{bmatrix}
= \begin{bmatrix}
3 & 1 & -2 \\
1 & 0 & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
-c - d \\
1 + c + 2d \\
1 - c - 2d
\end{bmatrix}
\]
\[A^{-1}\mathbf{x} = \mathbf{x} = A^{-1}\mathbf{B}\]
\[ k_c = [\text{constant}] (D)^a (\rho)^b (\mu)^c (g\Delta\rho)^d (D_{AB})^e \]

\[ = [\text{constant}] (D)^{3d-1} (\rho)^{-c-d} (\mu)^c (g\Delta\rho)^d (D_{AB})^{1-c-2d} \]

\[ \therefore \frac{k_c D}{D_{AB}} = [\text{constant}] (D)^{3d} (\rho)^{-c-d} (\mu)^c (g\Delta\rho)^d (D_{AB})^{-c-2d} \]

\[ = [\text{constant}] \left( \frac{\mu}{\rho D_{AB}} \right)^{c+2d} (D)^{3d} (\rho)^{-c-d+c+2d} (\mu)^{c-c-2d} (g\Delta\rho)^d (D_{AB})^{-c-2d+c+2d} \]
\[
\left( \frac{k_c D}{D_{AB}} \right) = \left[ \text{constant} \right] \left( \frac{\mu}{\rho D_{AB}} \right)^{c+2d} (D)^3 (\rho)^d (\mu)^{-2d} (g \Delta \rho)^d (D_{AB})^0
\]

\[
\left( \frac{k_c D}{D_{AB}} \right) = \left[ \text{constant} \right] \left( \frac{\mu}{\rho D_{AB}} \right)^{c+2d} \left( \frac{D^3 \rho g \Delta \rho}{\mu^2} \right)^d
\]

\[Sh = \left[ \text{constant} \right] Sc^\alpha Gr^\beta\]

\[Gr = \text{Grashof number} = \frac{D^3 \rho g \Delta \rho}{\mu^2}\]
PROBLEM 17

Flux at surface = \( k_c \left( c_A^s - c_A^b \right) \approx k_c \left( c_A^s - 0 \right) = k_c c_A^s \)

\[ c_A^s = \left( \frac{0.555}{760} \right) \text{atm} \times \frac{1}{82.06 \frac{\text{cm}^3 \text{ atm}}{\text{K mol}}} \times (273.15 + 45) \text{K} \]

\[ = 2.797 \times 10^{-8} \frac{\text{mol}}{\text{cm}^3} \]
Initially, $D = 1\, \text{cm}$

$$\text{Re} = \frac{D v \rho}{\mu} = \frac{D v}{\nu} = \frac{1\, \text{cm} \times 30\, \frac{\text{cm}}{\text{s}}}{0.174\, \frac{\text{cm}^2}{\text{s}}} = 172.41$$

$$\text{Sc} = \frac{\mu}{\rho D_{AB}} = \frac{\nu}{D_{AB}} = \frac{0.174\, \frac{\text{cm}^2}{\text{s}}}{0.0692\, \frac{\text{cm}^2}{\text{s}}} = 2.514$$

FLOW PAST A SINGLE SPHERE:

For gases, when $1 < \text{Re} < 48000$, and $0.6 < \text{Sc} < 2.7$

$$\text{Sh} = 2 + 0.552 \text{Re}^{0.53} \text{Sc}^{1/3} = 13.503$$
\[ Sh = \frac{k_c D}{D_{AB}} = 13.503 \]

\[ \therefore k_c = \frac{Sh \cdot D_{AB}}{D} = \frac{13.503 \times 0.0692 \, \text{cm}^2}{1 \, \text{cm}} = 0.934 \, \text{cm/s} \]

Initial rate of evaporation \( \left( \frac{\text{mol}}{\text{s}} \right) = k_c c_A^s \times \pi D^2 \)

\[ = 0.934 \, \text{cm/s} \times \left( 2.797 \times 10^{-8} \right) \frac{\text{mol}}{\text{cm}^3} \times \pi \times (1.0)^2 \, \text{cm}^2 \]

\[ = 8.211 \times 10^{-8} \, \frac{\text{mol}}{\text{s}} \]
Initial rate of evaporation \( \left( \frac{\text{cm}^3}{\text{s}} \right) \)

\[
\begin{align*}
&= k_C c_A^s \times \pi D^2 \\
&= \frac{k_C c_A^s \times \pi D^2}{\rho_m} \\
&= 8.211 \times 10^{-8} \text{ mol s}^{-1} \\
&= \frac{8.211 \times 10^{-8} \text{ mol}}{8.86 \times 10^{-3} \text{ mol cm}^3} \\
&= 9.267 \times 10^{-6} \text{ cm}^3 \text{s}^{-1}
\end{align*}
\]
\[ V = \frac{4\pi}{3} R^3 \]
\[ \frac{dV}{dt} = 4\pi R^2 \frac{dR}{dt} \]
\[ \frac{dV}{dt} = -Q = -\frac{k_c c_A^s \times \pi D^2}{\rho_m} = -\frac{k_c c_A^s \times 4\pi R^2}{\rho_m} \]
\[ \therefore 4\pi R^2 \frac{dR}{dt} = -\frac{k_c c_A^s \times 4\pi R^2}{\rho_m} \]
\[ \Rightarrow \frac{dR}{dt} = -\frac{k_c c_A^s}{\rho_m} \]
\[
\frac{dR}{dt} = -\frac{k_c c_A}{\rho_m} \\
\]
\[
k_c = \frac{Sh \cdot D_{AB}}{D} = \frac{D_{AB}}{2R} \quad Sh = \frac{D_{AB}}{2R} \left\{ 2 + 0.552 \left( \frac{2R \nu}{\nu} \right)^{0.53} \left( \frac{\nu}{D_{AB}} \right)^{0.33} \right\} \\
\]
\[
:\therefore \frac{dR}{dt} = \left( \frac{D_{AB} c_A}{\rho_m} \right) \cdot \left( \frac{1}{2R} \right) \cdot \left\{ 2 + 0.552 \left( \frac{2R \nu}{\nu} \right)^{0.53} \left( \frac{\nu}{D_{AB}} \right)^{0.33} \right\} \\
\]
\[
:\therefore dt = -\left( \frac{\rho_m}{D_{AB} c_A} \right) \left\{ 2 + 0.552 \left( \frac{2R \nu}{\nu} \right)^{0.53} \left( \frac{\nu}{D_{AB}} \right)^{0.33} \right\} \frac{2R}{dR} \\
\]
\[ t = \left( \frac{\rho_m}{D_{AB} c_A} \right) \cdot \int_{R_1}^{R_2} \frac{2R}{\left( 2 + 0.552 \left( \frac{2R \nu}{v} \right)^{0.53} \left( \frac{\nu}{D_{AB}} \right)^{0.33} \right)} \, dR \]

\[ t = \left( \frac{\rho_m}{D_{AB} c_A} \right) \cdot \int_{R_1}^{R_2} \frac{2R}{Sh} \, dR \]

\[ R_1 = 1 \text{ cm and } R_2 = 0.5 \text{ cm} \]
<table>
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<tr>
<th>$D$</th>
<th>$R$</th>
<th>$Re$</th>
<th>$Sc$</th>
<th>$Sh$</th>
<th>$2R/\text{Sh}$</th>
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\[
\int_{x_1}^{x_n} y \, dx = \left\{ \frac{1}{2} \left( y_1 + y_n \right) + \left( y_2 + y_3 + \cdots + y_{n-1} \right) \right\} \cdot (\Delta x)
\]

<table>
<thead>
<tr>
<th>$D$</th>
<th>$R$</th>
<th>$Re$</th>
<th>$Sc$</th>
<th>$Sh$</th>
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Integral 0.0157 cm

t 71875.03 s

1197.92 min

19.97 h
Evaporation in Stagnant Air

\[ V = \frac{4\pi}{3} R^3 \]
\[ \frac{dV}{dt} = 4\pi R^2 \frac{dR}{dt} \]
\[ \frac{dV}{dt} = -Q = -\frac{4\pi D_{AB} c_A^s R}{\rho_m} \]
\[ \therefore 4\pi R^2 \frac{dR}{dt} = -\frac{4\pi D_{AB} c_A^s R}{\rho_m} \]
\[ \Rightarrow R \frac{dR}{dt} = -\frac{D_{AB} c_A^s}{\rho_m} \]
\[
\left[ \frac{R^2}{2} \right]_{R_1}^{R_2} = -\frac{D_{AB}c_A^s}{\rho_m} (t - 0)
\]

\[
\therefore t = \frac{\rho_m}{2D_{AB}c_A^s} \left( R_1^2 - R_2^2 \right)
\]

\[
8.86 \times 10^{-3} \left( \frac{\text{mol}}{\text{cm}^3} \right)
\]

\[
= \frac{2 \times 0.0692 \left( \frac{\text{cm}^2}{\text{s}} \right) \times 2.797 \times 10^{-8} \left( \frac{\text{mol}}{\text{cm}^3} \right)}{(0.5^2 - 0.25^2) \left( \text{cm}^2 \right)}
\]

\[
= 429147.35 \text{ s}
\]

\[
= 4.97 \text{ days}
\]
• Dimensional analysis
  – Application in developing correlations
• Correlations for convective mass transfer coefficients
• Mass transfer calculations for packed beds
• **Inter-phase mass transfer**
  – Two-Film theory
  – Gas-side and liquid-side mass transfer coefficients
  – Overall mass transfer coefficient

• **Review**
  – Dimensional analysis (HW Problem 18)
  – Mass transfer coefficient (HW Problem 17)
    • Use of correlation
HW Problems

- Mass transfer in packed beds (benzoic acid): Problem 19, HW # 5
- Kinematic viscosity (slide 35):
  - \( \nu = \frac{\mu}{\rho} \text{ (cm}^2/\text{s)} \)
  - \( \text{Re} = D \frac{\nu \rho}{\mu} = D \frac{\nu}{\nu} \)
  - \( \text{Sc} = \frac{\mu}{(\rho D_{AB})} = \frac{\nu}{D_{AB}} \)
- Problem 14: “Write 3 sentences explaining the answers to part 3 of problems 11 and 13.”
10/5/07

• Inter-phase mass transfer
• Review of topics covered
• Simple quiz on fundamental concepts?
  – Definitions, units, < 5-min problems, etc.
Review

- Slides 42 to 46
- Correlations

\[ Sh = [\text{constant}] Re^\alpha Sc^\beta \]

Turbulent flow through pipes:

\[ Sh = 0.023 Re^{0.83} Sc^{0.33} \]
• Quiz
  – 16 questions, < 40 min
  – Questions at the beginning require less time than those at the end

• Course evaluation
  – CH351: Mass Transfer and Stagewise Operations
  – Instructor: Sitaraman Krishnan
Benzoic acid spheres in a packed bed

Saturation solubility of benzoic acid in water = \( c_A^s \)

Mass transfer driving force at inlet = \( c_A^s - c_{A,1} \)
= \( (2.948 \times 10^{-5} - 0) \) mol/cm\(^3\)

Mass transfer driving force at outlet = \( c_A^s - c_{A,2} \)
= \( (2.948 \times 10^{-5} - c_{A,2}) \) mol/cm\(^3\)