



Spring Semester course

CH31010: Mass Transfer II

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L4: Diffusion

- Mass transfer may occur in a gas mixture, a liquid solution or solid.
- Mass transfer occurs whenever there is a **gradient in the concentration** of a species.
- The basic mechanisms are the same whether the phase is a gas, liquid, or solid.

Diffusion phenomena

Mass diffusion – Fickian type (molecular diffusion)

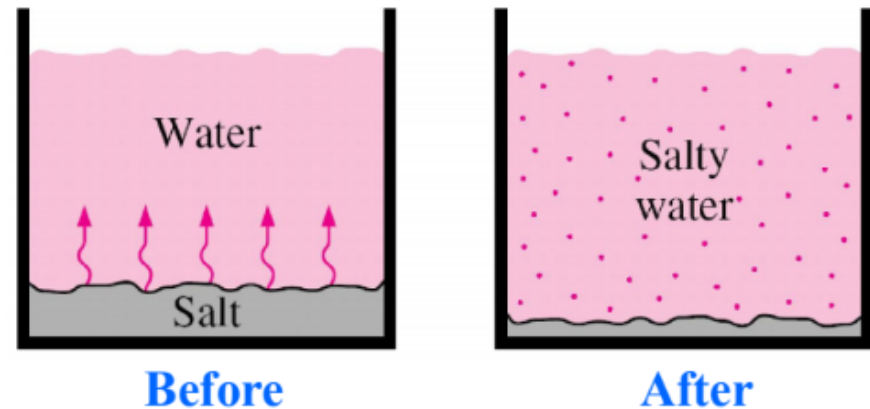
Brownian diffusion

Turbulent / eddy diffusion

Diffusion in electrolytic solution

Knudsen diffusion

- Whenever there is concentration difference in a medium, nature tends to equalize things by forcing a flow from the high to the low concentration region.



- The molecular transport process of mass is characterized by the general equation:

$$\text{Rate of transfer process} = \frac{\text{driving force}}{\text{resistance}}$$



Molecular Diffusion Equation

- Fick's Law

$$J_{AZ}^* = -D_{AB} \frac{dc_A}{dz}$$

$$J_{AZ}^* = -\nabla (D_{AB} c_A)$$

J_A^* is the molar flux of component A in the z direction in kg mol A/s.m².

D_{AB} is the molecular diffusivity of the molecule A in B in m²/s

c_A is the concentration of A in kg mol/m³.

z is the distance of diffusion in m

Fick's Law of Diffusion

- Molecular diffusion or molecular transport can be defined as the transfer or movement of individual molecules through a fluid by mean of the random, individual movements of the molecules.

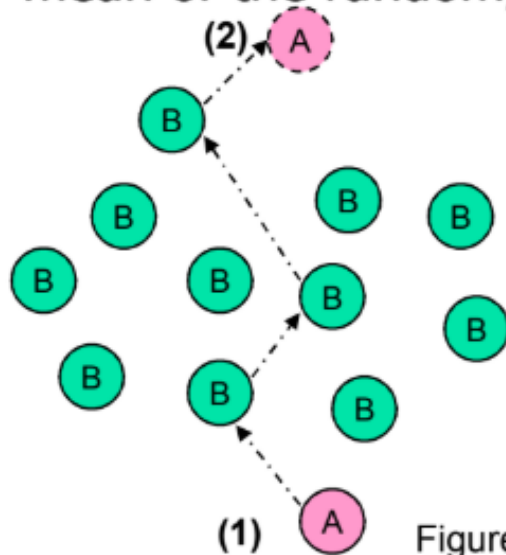


Figure 3: Schematic diagram of molecular diffusion process

- If there are greater number of A molecules near point (1) than at (2), then since molecules diffuse randomly in both direction, more A molecules will diffuse from (1) to (2) than from (2) to (1).
- The net diffusion of A is from high to low concentration regions.



Molecular diffusion

The diffusion of molecules when the whole bulk fluid is not moving but stationary. Diffusion of molecules is due to a concentration gradient.

The general Fick's Law Equation for **binary mixture of A and B**

$$J_{AZ}^* = -cD_{AB} \frac{dx_A}{dz}$$

c = total concentration of A and B [kgmol (A + B)/m³]

x_A = mole fraction of A in the mixture of A and B

Example:

A mixture of He and N₂ gas is contained in a pipe at 298 K and 1 atm total pressure which is constant throughout. At one end of the pipe at point 1 the partial pressure p_{A1} of He is 0.6 atm and at the other end 0.2 m $p_{A2} = 0.2$ atm.

Calculate the flux of He at steady state if D_{AB} of the He-N₂ mixture is $0.687 \times 10^{-4} \text{ m}^2/\text{s}$.

Solution:

- Since a total pressure P is constant, the c is constant, where c is as follows for a gas according to the perfect gas law:

$$PV = nRT$$

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

- Where n is kg mol A plus B , V is volume in m^3 , T is temperature in K, R is $8314.3 \text{ m}^3 \cdot \text{Pa} / \text{kg mol} \cdot \text{K}$ or R is $82.057 \times 10^{-3} \text{ cm}^3 \cdot \text{atm} / \text{g. mol. K}$, and c is kg mol A plus B / m^3 .
- For steady state the flux J_{Az}^* is constant. Also D_{AB} for gas is constant.

$$J_{Az}^* \int_{z_1}^{z_2} dz = -D_{AB} \int_{c_{A1}}^{c_{A2}} dc_A$$

$$J_{Az}^* = \frac{D_{AB}(c_{A1} - c_{A2})}{z_2 - z_1}$$

- Also, from the perfect gas law, $p_A V = n_A RT$, and

$$c_{A1} = \frac{p_{A1}}{RT} = \frac{n_A}{V}$$

- Substituting

$$J_{Az}^* = \frac{D_{AB}(p_{A1} - p_{A2})}{RT(z_2 - z_1)}$$

- This is the final equation to use, which is in a form eqsily used for gases. Partial pressures are $p_{A1} = 0.6 \text{ atm} = 0.6 \times 1.01325 \times 10^5 = 6.04 \times 10^4 \text{ Pa}$ and $p_{A2} = 0.2 \text{ atm} = 0.2 \times 1.01325 \times 10^5 = 2.027 \times 10^4 \text{ Pa}$. Then, using SI units,


$$\begin{aligned} J_{Az}^* &= \frac{(0.687 \times 10^{-4})(6.08 \times 10^4 - 2.027 \times 10^4)}{8314(298)(0.20 - 0)} \\ &= 5.63 \times 10^{-6} \text{ kg mol } A/\text{s} \cdot \text{m}^2 \end{aligned}$$

Mass transfer driving force

At constant T & P, species i experiences a force (per mole), acting in the direction of z

$$F_i = - \left(\frac{\partial \mu_i}{\partial z} \right)_{T,P}$$

The chemical potential for component i in ideal phases:

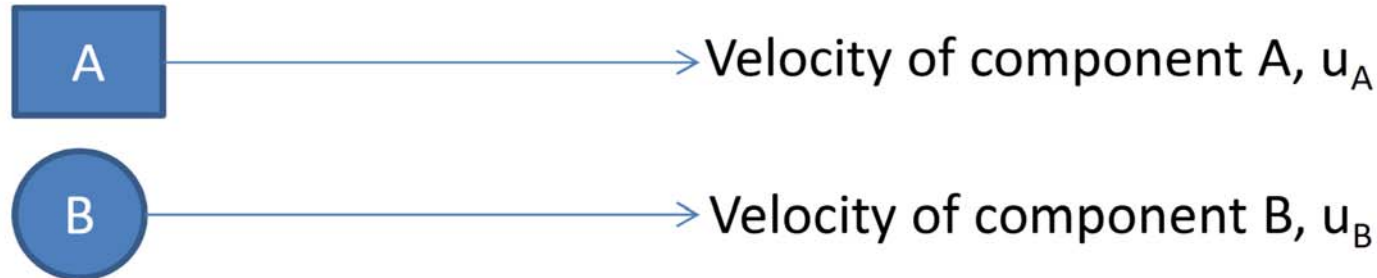
For gas: $\mu_i = \mu_i^0 + RT \ln P_i = \mu_i^0 + RT \ln y_i P$  $d\mu_i = RT \frac{dy_i}{y_i}$

For liquid: $\mu_i = \mu_i^* + RT \ln x_i$  $d\mu_i = RT \frac{dx_i}{x_i}$

For non-ideal phases: use fugacity (gas) or activity (liquid) coefficients for correction.

Frictional resistance

Consider two components A and B:



Frictional resistance exerted by A to one mole of B, F_B , is found to be proportional to difference in the velocities:

$$F_B = -RT \frac{x_A}{D_{BA}} (u_B - u_A)$$

We will see that the constant D is in fact diffusion coefficient.

Similarly, for the force exerted by B to 1 mole of A:

$$F_A = -RT \frac{x_B}{D_{AB}} (u_A - u_B)$$

Generalising to multi-components: $F_i = -RT \sum_{j=1}^{n-1} \frac{x_j}{D_{ij}} (u_i - u_j)$

In a unit volume of the mixture, the forces will be:

$$\text{On A: } x_A C_T F_A = -RT \frac{x_B x_A C_T}{D_{AB}} (u_A - u_B)$$

$$\text{On B: } x_B C_T F_B = -RT \frac{x_A x_B C_T}{D_{BA}} (u_B - u_A)$$

Complete picture



$$-\left(\frac{\partial \mu_i}{\partial \mathbf{z}}\right)_{T,P} - RT \sum_{j=1}^{n-1} \frac{\mathbf{x}_j}{D_{ij}} (\mathbf{u}_i - \mathbf{u}_j) = 0$$

Use fluxes and
concentrations
instead of velocities
and mol fractions

$$-\left(\frac{\partial \mu_i}{\partial \mathbf{z}}\right)_{T,P} = -RT \frac{1}{\mathbf{x}_i} \frac{\partial \mathbf{x}_i}{\partial \mathbf{z}} = -RT \frac{1}{\mathbf{c}_i} \frac{\partial \mathbf{c}_i}{\partial \mathbf{z}}$$

$$\mathbf{x}_i = \mathbf{c}_i / \mathbf{c}_T, \mathbf{c}_T = \mathbf{c}_A + \mathbf{c}_B$$

$$\mathbf{N}_i = \mathbf{c}_i \mathbf{u}_i$$

$$-\frac{\partial \mathbf{c}_i}{\partial \mathbf{z}} = \sum_{j=1}^{n-1} \frac{1}{\mathbf{c}_T D_{ij}} (\mathbf{c}_j \mathbf{N}_i - \mathbf{c}_i \mathbf{N}_j)$$

Diffusion in a binary mixture

$$-\frac{\partial \mathbf{c}_i}{\partial \mathbf{z}} = \sum_{j=1}^{n-1} \frac{1}{\mathbf{c}_T \mathbf{D}_{ij}} (\mathbf{c}_j \mathbf{N}_i - \mathbf{c}_i \mathbf{N}_j)$$



$$-\frac{\partial \mathbf{c}_B}{\partial \mathbf{z}} = \frac{1}{\mathbf{c}_T \mathbf{D}_{AB}} (\mathbf{c}_A \mathbf{N}_B - \mathbf{c}_B \mathbf{N}_A)$$

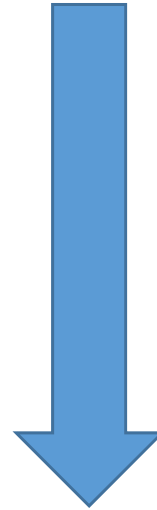
$$-\frac{\partial \mathbf{c}_A}{\partial \mathbf{z}} = \frac{1}{\mathbf{c}_T \mathbf{D}_{AB}} (\mathbf{c}_B \mathbf{N}_A - \mathbf{c}_A \mathbf{N}_B)$$

Note that the interaction (frictional) term involves the knowledge of *relative velocities*.

We need therefore to specify another *single piece of information*, which will fix the velocity or flux relative to a fixed reference frame.

Specification 1: Equimolar counter-diffusion

$$-\frac{\partial C_A}{\partial z} = \frac{1}{C_T D_{AB}} (C_B N_A - C_A N_B) \quad \text{and} \quad -\frac{\partial C_B}{\partial z} = \frac{1}{C_T D_{BA}} (C_A N_B - C_B N_A)$$



The fluxes of A & B are equal
and opposite (e.g. distillation)

$$N_A = -N_B$$

Therefore, $N_A = -D_{AB} \frac{\partial C_A}{\partial z}$ and $N_B = -D_{BA} \frac{\partial C_B}{\partial z}$

This looks like the Fick's law, but here we do not have the condition of being dilute or stagnant!

Specification 2: Stagnant component (Stefan's condition)

$$-\frac{\partial C_A}{\partial z} = \frac{1}{C_T D_{AB}} (C_B N_A - C_A N_B) \quad \text{and} \quad -\frac{\partial C_B}{\partial z} = \frac{1}{C_T D_{BA}} (C_A N_B - C_B N_A)$$

The fluxes one component, say B is zero (e.g. membrane separation)

$$N_B = 0$$

$$\frac{\partial C_A}{\partial z} = -\frac{C_B}{C_T D_{AB}} N_A \quad \text{and} \quad \frac{\partial C_B}{\partial z} = \frac{C_B}{C_T D_{AB}} N_A$$

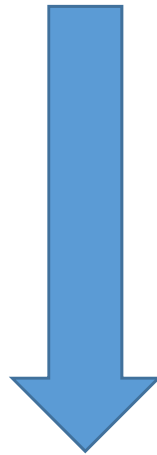
Stefan's law

$$N_A = -\frac{C_T}{C_T - C_A} D_{AB} \frac{\partial C_A}{\partial z}$$

Note that even $N_B = 0$, the spatial gradient of B $\left(\frac{\partial C_B}{\partial z}\right)$ still exists, in the positive direction of the diffusion of A

Specification 3: Stagnant & dilute component (Fick's law)

Stefan's law: $N_A = -\frac{C_T}{C_T - C_A} D_{AB} \frac{\partial C_A}{\partial z}$ considering the flux of one component to be zero, $N_B = 0$



Considering A to be dilute, $C_A \ll C_T$

$$N_A = -D_{AB} \frac{\partial C_A}{\partial z} \text{ (Fick's law)}$$

Understanding the diffusion coefficient

A typical diffusion coefficient for a molecule in the gas phase is in the range of 10^{-6} to $10^{-5} \text{ m}^2/\text{s}$. By contrast, diffusion for molecules dissolved in liquids is far slower. In an aqueous (water) solution, typical diffusion coefficients are in the range of 10^{-10} to $10^{-9} \text{ m}^2/\text{s}$. As a result, diffusion in liquids is very slow over everyday length scales and is almost always dominated by convection.

Solids: $10^{-12} - 10^{-14} \text{ m}^2/\text{s}$

Formally, the diffusion coefficient can be understood as parameterizing the area of a spherical surface, defined as the surface of root-mean-square displacement of material diffusing away from an infinitesimal point where a mass is initially concentrated. Since the statistics of diffusion cause this area to grow linearly in time, the diffusion coefficient is a quantity described by area per time.

Diffusion in gas

Considering the values for the mean free path and average velocity for molecules in an **ideal gas from the Maxwell-Boltzmann distribution**, it follows that the diffusion coefficient obeys the following relation to temperature and pressure:

$$D \propto \frac{T^{\frac{3}{2}}}{P}$$

That is, diffusion is faster in both **hotter and more rarefied gases**.

Nature of kinetic theories (molecular motion in dilute gases)

Gas of rigid spheres of very small dimensions, the diffusion flux is

$$\text{Flux} = - \underbrace{\frac{1}{3} \tilde{v} l}_{\substack{\text{mol. diffusion} \\ \text{avg. mol. velocity.}}} \nabla c + \underbrace{c v^0}_{\substack{\text{convection} \\ \text{mean free path}}} \leftarrow \text{bulk velocity}$$

[RE Cunningham, RJJ Williams (1980) "Diffusion in Gases & Porous Media". New York: Plenum]

Comparing this with Fick's law,

$$D \approx \frac{1}{3} \tilde{v} l$$

From statistical mechanics, $\tilde{v} = \sqrt{\frac{8 k_B T N_A}{\pi M_w}}$

$$\text{and } l = \frac{k_B T}{P \sqrt{2} \pi d^2} \leftarrow \text{diameter of the spheres.}$$

$N_A P / RT \rightarrow$ conc. in molecules/volume

$$\text{Combining} \Rightarrow D = \left[\frac{2}{3} \left(\frac{k_B}{\pi} \right)^{3/2} \sqrt{N_A} \right] \frac{T^{3/2}}{P d^2 \sqrt{M_w}}$$

Diffusion coefficient for gases

1. Chapman & Enskog

$$D_{AB} = \frac{1.8583 \times 10^{-7} T^{3/2}}{P \sigma_{AB}^2 \Omega_{D,AB}} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2}$$

P = absolute pressure in atm

σ_{AB} = average collision diameter

$\Omega_{D,AB}$ = collision integral based on Lennard-Jones potential;
is a ratio giving the deviation of a gas with interaction as
compared to a gas rigid, elastic spheres.

Diffusion in liquid

For particles or large molecules in a viscous fluid (usually a liquid solution), the Stokes-Einstein equation can be applied:

$$D = \frac{kT}{6\pi\mu a}$$

Here, k is the Boltzmann constant, μ is the solvent viscosity, and r is the radius of the diffusing particle. This equation is derived on the assumption that the particles obey Stokes' law for drag, such that the drag exerted on diffusing molecules, by the solvent molecules.

Derivation of the Stokes-Einstein Equation :

Molecular motion is not accounted for as in gases (kinetic theory)

Assumption: Dilute solution \rightarrow isolated single rigid sphere moving slowly in a continuum of solvent.

$$\therefore \text{force} = \eta \cdot v$$

\nwarrow friction coefficient

$$\eta = 6\pi\mu r \leftarrow \text{Stokes law}$$

$$\text{Now, force} \equiv -\nabla\mu_p = (6\pi\mu r) v$$

\nwarrow chemical potential defined per molecule (not per mole)

Ideal solution assumption, since it is dilute,

$$\mu_p = \mu_p^0 + k_B T \ln x$$

$$\cong \mu_p^0 + k_B T \ln c/c_{\text{solvent}}$$

$$\left[x = \frac{c}{c + c_{\text{solvent}}} \right]$$

Since, soln is dilute

$$c_{\text{sol}} \gg c, \text{ so } x \sim c/c_{\text{sol}}$$

$$\therefore \nabla\mu_p = \frac{k_B T}{c} \nabla c$$

$$\therefore \text{Flux} \equiv c v = - \frac{k_B T}{6\pi\mu r} \nabla c$$

$\underbrace{\hspace{1.5cm}}$
Diffusion coefficient
comparing with fick's law

$$\therefore \nabla \mu_p = \frac{k_B T}{c} \nabla c$$

$$\therefore \text{Flux} \equiv c v = - \underbrace{\frac{k_B T}{6\pi\mu r}}_{\text{Diffusion coefficient}} \nabla c$$

Diffusion coefficient
comparing with fick's law

this expression is valid when

$$1. \frac{r_{\text{solute}}}{r_{\text{solvent}}} \gg 5 \quad \left[\text{for smaller solutes, often } 6\pi \text{ is replaced by } 4\pi \right]$$

2. low viscosity of the solvent

$$\left[\text{For high viscosity, } D \sim \frac{1}{\mu^{2/3}} \text{ (instead of } \frac{1}{\mu} \text{) } \right]$$

Extreme high viscosity, $D \sim \mu^0$

Modified Stokes-Einstein equation for (regular)
non-spherical solutes/macromoles:

Prolate ellipsoid (rugby ball)

$$D = \frac{k_B T}{6\pi\mu \left[\frac{(a^2 - b^2)^{1/2}}{\ln \left(\frac{a + (a^2 - b^2)^{1/2}}{b} \right)} \right]}$$

Oblate ellipsoid (disc-shaped)

$$D = \frac{k_B T}{6\pi\mu \left[\frac{(a^2 - b^2)^{1/2}}{\tan^{-1} \left[\frac{(a^2 - b^2)^{1/2}}{b} \right]} \right]}$$

equivalent radius
of some average
over this shape

where a & b are the major & minor axes of the ellipsoid.
when $a = b (= r)$ this reduces to the ~~ex~~ expression
for a sphere.

In case of concentrated solutions:

$$D \approx \frac{k_B T}{6\pi\mu r} (1 + 1.5\phi + \dots)$$

volume fraction of the
solute (related to conc.)

The Stokes-Einstein equation is limited to cases in which the solute is larger than the solvent. Thus investigators have developed correlations for cases in which solute and solvent are similar in size.

Authors	Origin	Basic equation	Viscosity variation	Solute size variation	Remarks
Sutherland (1905)	Parallel to Stokes-Einstein, but "no stick" at sphere's surface	$D = \frac{k_B T}{4\pi \mu R_0}$	μ^{-1}	R_0^{-1}	Always mentioned but rarely used
Glasstone et al. (1941)	Diffusion as a rate process	$D = \frac{k_B T}{2\mu R_0}$	μ^{-1}	R_0^{-1}	Closer to some experimental results
Scheibel (1954) ^{c,d}	Empirical	$D = \frac{AT}{\mu(\bar{V}_1)^{1/3}} \left[1 + \left(\frac{3\bar{V}_2}{\bar{V}_1} \right)^{2/3} \right]$ \uparrow solute	μ^{-1}	R_0^{-1} for large solutes and R_0^{-3} for small ones	Variation with solute size is the interesting feature
Wilke and Chang (1955) ^{c,e}	Empirical	$D = \frac{7.4 \cdot 10^{-8} (\phi \bar{M}_2)^{1/2} T}{\mu \bar{V}_1^{0.6}}$ $D = 4.4 \cdot 10^{-8} \frac{T}{\mu} \left(\frac{\bar{V}_2}{\bar{V}_1} \right)^{1/6} \left(\frac{\Delta \tilde{H}_{\text{vap},2}}{\Delta \tilde{H}_{\text{vap},1}} \right)$	μ^{-1}	Equivalent to $R_0^{-1.8}$	Factor ϕ for solute solvent interaction
King, Hsueh, and Mas (1965) ^c	Empirical	$\left(\frac{\bar{V}_2}{\bar{V}_1} \right)^{1/6} \left(\frac{\Delta \tilde{H}_{\text{vap},2}}{\Delta \tilde{H}_{\text{vap},1}} \right)$	μ^{-1}	$R_0^{-0.5}$	Not suitable for viscous solvents or aqueous systems

Notes: ^aThe subscripts 1 and 2 indicate the solute and solvent, respectively.

^bThese relations are accurate within about ten percent for water and twenty percent for most organics, but they are often inaccurate for alcohols and other hydrogen-bonded solvents.

^cSpecific units implied are $D[=] \text{cm}^2/\text{sec}$; $T[=]^\circ\text{K}$; $\mu[=] 10^{-2} \text{g/cm-sec}$; $V_i[=] \text{cm}^3/\text{g-mol}$.

^dThe \bar{V} are the molar volumes at the boiling points. The constant A equals $8.2 \cdot 10^{-8}$, except as follows: $25.2 \cdot 10^{-8}$ for water if $\bar{V}_1 < \bar{V}_2$; $18.9 \cdot 10^{-8}$ for benzene when $\bar{V}_1 < 2\bar{V}_2$; $17.5 \cdot 10^{-8}$ for others if $\bar{V}_1 < 2.5\bar{V}_2$.

^eThe factor ϕ has the following values: 2.26 for water, 1.9 for methanol, 1.5 for ethanol, and 1.0 for non-hydrogen-bonded solvents.

Summary

Comparison of diffusion coefficients :

<u>Phase</u>	<u>Magnitude (m^2/s)</u>	<u>Temp.</u>	<u>Pr.</u>	<u>Solute size</u>	<u>Viscosity</u>
Gas	$10^{-6} - 10^{-5}$	$T^{3/2}$	P^{-1}	d^{-2}	μ^1
Liquid	$10^{-10} - 10^{-9}$	T^1	(small)	d^{-1}	μ^{-1} ($\mu^{-2/3}$ for high viscosities)

Diffusion Coefficient in Porous Media

$$\mathbf{N}_i = -D_{i,eff} \nabla c_i = -\frac{\epsilon}{\tau} D_i \nabla c_i$$

The tortuosity (τ) is, the ratio of the actual distance a molecule must travel between two points by following the fluid channel to the straight-line distance between those points.

Millington-Quirk: $\tau = \epsilon^{-1/3}$

Bruggeman: $\tau = \epsilon^{-1/2}$

In some types of porous media, the (effective) **diffusion coefficient may also be anisotropic**, so that the rate of diffusion depends on the direction of the concentration gradient. In this case, the **diffusivity is a tensor**.

How do we measure diffusion coefficients experimentally ?

Stefan's tube

Diaphragm Cell

Taylor dispersion

Spin Echo Nuclear Magnetic Resonance

Dynamic Light Scattering

Gouy interferometer

Extra reading

Convection Mass Transfer

- When a fluid flowing outside a solid surface in forced convection motion, rate of convective mass transfer is given by:

$$N_A = k_c (c_{L1} - c_{Li})$$

- k_c - mass transfer coefficient (m/s)
- c_{L1} - bulk fluid conc.
- c_{Li} - conc of fluid near the solid surface

- k_c depend on:
 1. system geometry
 2. Fluid properties
 3. Flow velocity

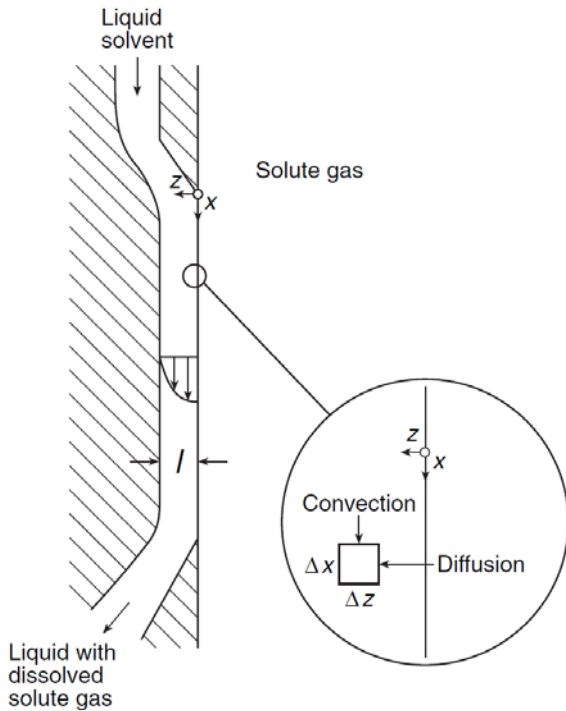
Mass transfer coefficients (MTC)

We would like to predict the mass transfer coefficient k as a function of the diffusion coefficient D and the fluid velocity v .

We look at MTC's for fluid-fluid systems that are VERY important in industrial applications.

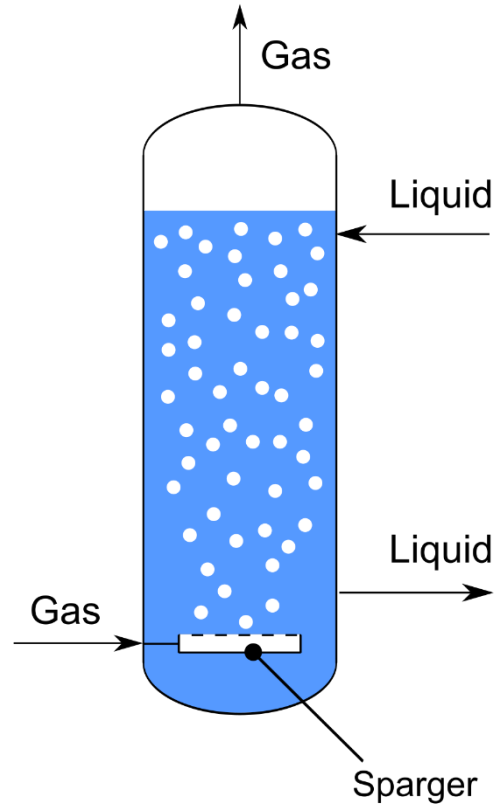
Fluid-Fluid Interfaces, e.g.

Falling film



Source: Cussler, Chapter 2.5.2

Gas bubbles in tank



Source: Wikipedia, "Blasensäule"

Liquid in packed tower

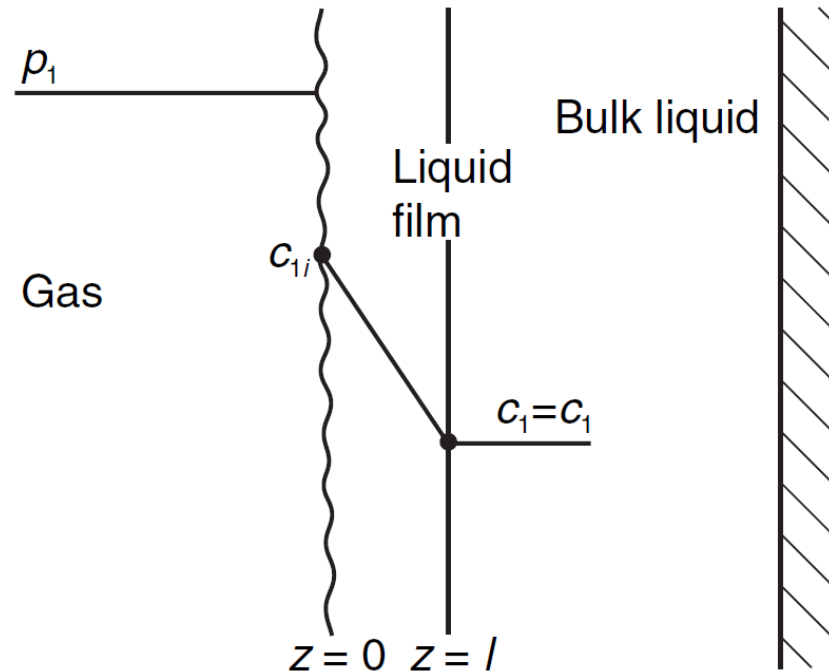


Source: Büchi Glas, Uster

Falling film	Gas bubbles in tank	Liquid in packed tower
Evaporation, Gas scrubbing	Aereation, Gas ab- and desorption, Bioreaktors	Extraction, Distillation
$\frac{kz}{D} = 0.69 \cdot \left(\frac{z \cdot v^0}{D} \right)^{0.5}$	$\frac{kd}{D} = 0.31 \cdot \left(\frac{d^3 \cdot g \cdot \Delta\rho / \rho}{v^2} \right)^{1/3} \left(\frac{v}{D} \right)^{1/3}$	$k \left(\frac{1}{vg} \right)^{1/3} = 0.0051 \left(\frac{v^0}{av} \right)^{0.67} \left(\frac{D}{v} \right)^{0.5} (ad)^{0.4}$
$k \sim D^{0.5}, \sim v^{0.5}$	$k \sim D^{2/3}$	$k \sim D^{0.5}, \sim v^{0.67}$

Why is $k \sim D^{1/2}$ or $k \sim D^{2/3}$ or $k \sim v^{0.67}$??

The Film Theory (Nernst, 1904)



Assumptions:

- All action (fluid flow and mass transfer) occurs in a thin film at the interface
- Bulk fluid (e.g. gas) – FILM – bulk fluid (e.g. liquid)
- Steady-state flux across film

$$n_1|_{z=0} = N_1 = k(c_{1i} - c_1)$$

This flux can be obtained also in terms of D
(for dilute concentrations)

$$N_1 = j_1|_{z=0} = \frac{D}{\ell}(c_{1i} - c_1)$$

Comparing the above equation gives $k = \frac{D}{\ell}$

Or by rewriting gives $\frac{k\ell}{D} = 1 = Sh$

This simple theory gives $k \propto D^1$ BUT all fluid characteristics (e.g. fluid velocity due to stirring) are in the unknown film thickness ℓ .

This simple theory provides the FRAMEWORK of most MTC's as follows:

$$\text{Sh} = \frac{\left(\begin{array}{c} \text{mass transfer} \\ \text{coefficient} \end{array} \right) \left(\begin{array}{c} \text{characteristic} \\ \text{length} \end{array} \right)}{\left(\begin{array}{c} \text{diffusion} \\ \text{coefficient} \end{array} \right)} = F \left(\begin{array}{c} \text{other} \\ \text{system} \\ \text{variables} \end{array} \right)$$

Applications:

The film theory is used in some practical cases to determine the ℓ .

Example:

CO₂ is being scrubbed out of a gas by water flowing through a packed bed. Calculate the film thickness if $2.3 \cdot 10^{-6} \text{ mol}/(\text{cm}^2 \cdot \text{s})$ of CO₂ are adsorbed when

$$p_{\text{CO}_2} = 10 \text{ atm}, \quad H = 600 \text{ atm} \quad \text{and} \quad D_{\text{CO}_2/\text{H}_2\text{O}} = 1.9 \cdot 10^{-5} \text{ cm}^2/\text{s}.$$

Solution:

First find the interfacial concentration c_{1i} :

$$p_1 = H \cdot x_1 = H \frac{c_{1i}}{c}$$

$$10 \text{ atm} = 600 \text{ atm} \left(\frac{c_{1i}}{(1 \text{ mol})/(18 \text{ cm}^3)} \right) \Rightarrow$$

$$c_{1i} = 9.3 \cdot 10^{-4} \text{ mol}/\text{cm}^3$$

Calculate k from equation (9.1-1):

$$N_1 = k(c_{1i} - c_1)$$



$$2.3 \cdot 10^{-6} \text{ mol}/(\text{cm}^2 \text{ s}) = k (9.3 \cdot 10^{-4} \text{ mol}/\text{cm}^3 - 0)$$

$$k = 2.5 \cdot 10^{-3} \text{ cm/s}$$

Now

$$\ell = \frac{D}{k} = \frac{1.9 \cdot 10^{-5} \text{ cm}^2 / \text{s}}{2.5 \cdot 10^{-3} \text{ cm}^2 / \text{s}} = 0.76 \cdot 10^{-2} \text{ cm}$$

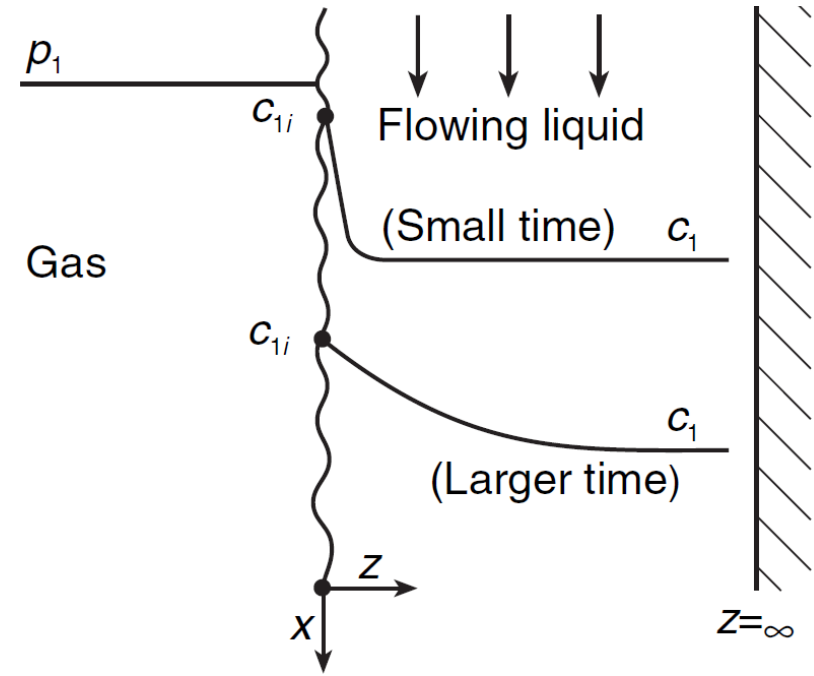
Typically $\ell \cong 10^{-2} \text{ cm}$ ← VERY IMPORTANT

The Penetration Theory (Higbie, 1935)

Assumptions:

- Same as in “Film-theory” but the film is VERY thick
- Diffusion is important in z-direction
- Convection is important in x-direction

Equation: $N_1 = k(c_{1i} - c_1)$



The solution to this problem was given before in the context of the semi-infinite slab (Cussler p. 46):

$$N_1 = j_1|_{z=0} = \sqrt{Dv_{\max}} / (\pi x) (c_{1i} - c_1)$$

where N_1 is the flux and v_{\max} is the velocity of the liquid at the interface

Note that this flux at the interface is valid at a specific x . To find the average flux, $N_1(x)$ has to be averaged over the entire surface:

$$N_1 = \frac{1}{W \cdot L} \int_0^L \int_0^W n_1|_{z=0} dy \cdot dx$$

where L is the length of the film in x and W is its width in y . Since n_1 does not vary in y :

$$N_1 = \frac{1}{L} \int_0^L \sqrt{\frac{D \cdot v_{\max}}{\pi \cdot x}} \cdot \Delta c \, dx \quad \rightarrow \quad N_1 = \frac{2}{L} \sqrt{\frac{D \cdot v_{\max} \cdot x}{\pi}} \Big|_0^L \Delta c$$

$$N_1 = \frac{2}{L} \sqrt{\frac{D \cdot v_{\max} \cdot L}{\pi}} \cdot \Delta c$$

or

$$N_1 = 2 \sqrt{\frac{D \cdot v_{\max}}{\pi \cdot L}} \cdot (c_{1i} - c_1)$$

so

$$k = 2 \cdot \sqrt{\frac{D \cdot v_{\max}}{\pi \cdot L}}$$

The L/v_{\max} is called contact time and is not known a priori in complex situations, as was ℓ in the film theory.

Compare:

$$k \propto D^{1/2}$$

(penetration theory)

$$k \propto D$$

(film theory)

These two theories bracket the experimental data very well, almost too well to be accepted.

The previous equation can be rewritten, assuming that the average velocity is $v^0 = 2/3 v_{\max}$ (true for a laminar slit flow, Newtonian fluid).

$$k \frac{L}{D} = 2 \frac{L}{D} \left(\frac{3}{2} \right)^{1/2} \left(\frac{D v^0}{\pi L} \right) = \left(\frac{6}{\pi} \right)^{1/2} \left(\frac{L v^0}{v} \right)^{1/2} \left(\frac{v}{D} \right)^{1/2} = \left(\frac{6}{\pi} \right)^{1/2} \underbrace{\text{Re}^{1/2} \text{Sc}^{1/2}}_{\text{Pe}^{1/2}}$$

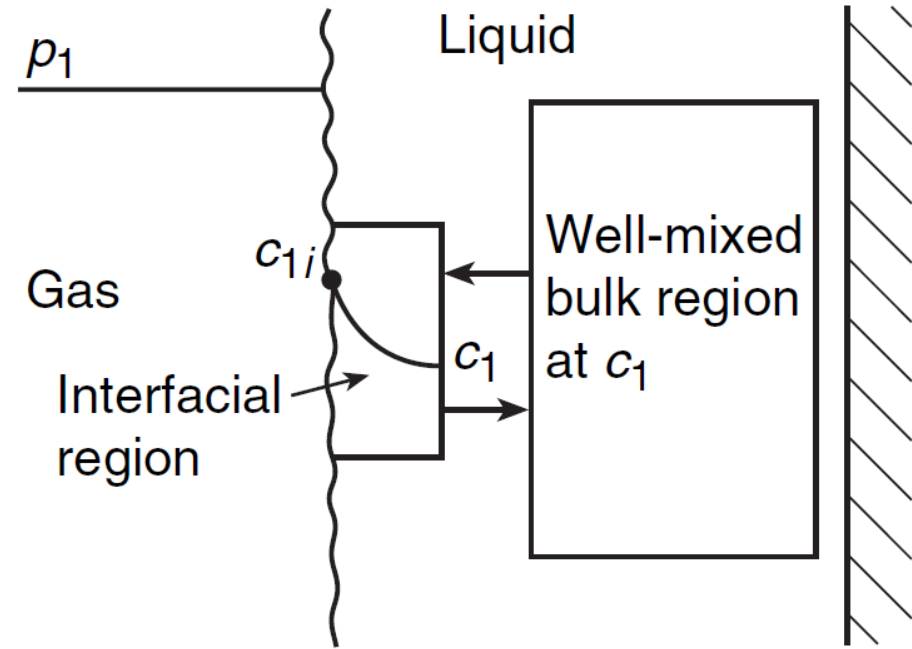
The Surface Renewal Theory (Dankwerts, 1951)

The success of the penetration theory with data despite its restrictive assumption motivated scientists and engineers to propose alternative and more realistic models leading, however, to the same variable dependencies at the end.

Assumption:

The thick film framework is replaced by TWO regions: interface and bulk.

In the interfacial region mass transfer takes place according to penetration theory. Then elements of this region ARE EXCHANGED with the bulk region. This is the so-called surface-renewal process.



The issue is how long the fluid elements stay in the interfacial region “exposed to penetration”.

$$E(t)dt = \left(\begin{array}{c} \text{probability of a surface} \\ \text{element to be at the} \\ \text{surface for time } t \end{array} \right)$$

$E(t)$ is the residence time distribution, RTD, and $\int_0^{\infty} E(t) dt = 1$

The transfer of interfacial elements into the bulk is random and any surface element is equally likely to be withdrawn.

By definition the fraction of surface elements at time t is :

$$\theta = \exp[-t / \tau]$$

where τ is a characteristic constant equivalent to the average residence time of an element in the interfacial (surface) region.

Now the fraction θ is also the sum of probabilities $\theta = \int_t^\infty E(t) dt$

Thus the residence time distribution of surface elements is:

$$\frac{d}{dt} \left(\int_t^\infty E(t) dt \right) = \frac{d\theta}{dt} = -\frac{1}{\tau} \exp\left(-\frac{t}{\tau}\right) = \frac{d}{dt} \left(\underbrace{\int_0^\infty E(t) dt}_{=1} - \int_0^t E(t) dt \right) = -E(t)$$

So,
$$E(t) = \frac{1}{\tau} \exp\left(-\frac{t}{\tau}\right)$$

The mass transfer coefficient at the interfacial region is obtained from the semi-infinite slab model (Cussler p. 28) as:

$$n_1|_{z=0} = N_1 = \sqrt{\frac{D}{\pi t}} \cdot (c_{1i} - c_1)$$

The semi-infinite slab model is used here even though the interfacial region is not infinite. But if the surface is rapidly renewed and the τ is small, then the interfacial region appears as infinite.

The average flux (over all surface elements) is:

$$\begin{aligned} N_{1,av} &= \int_0^{\infty} \mathbf{E}(t) \cdot \mathbf{n}_1|_{z=0} dt \\ &= \int_0^{\infty} \left(\frac{\exp[-t/\tau]}{\tau} \cdot \sqrt{\frac{D}{\pi t}} \cdot (c_{1i} - c_1) \right) dt \\ &= \sqrt{\frac{D}{\pi}} \frac{(c_{1i} - c_1)}{\tau} \cdot \int_0^{\infty} \frac{\exp[-t/\tau]}{\sqrt{t}} dt \\ &= \sqrt{\frac{D}{\pi}} \frac{(c_{1i} - c_1)}{\tau} \cdot \left(\frac{\sqrt{\pi} \cdot \operatorname{erf}(\sqrt{t/\tau})}{\sqrt{1/\tau}} \right) \Bigg|_0^{\infty} \end{aligned}$$

$$N_{1,av} = \sqrt{\frac{D}{\pi}} \frac{(c_{1i} - c_1)}{\tau} \cdot \sqrt{\pi\tau} \cdot \left(\underbrace{\text{erf}\left(\sqrt{\infty/\tau}\right)}_{=1} - \underbrace{\text{erf}\left(\sqrt{0/\tau}\right)}_{=0} \right)$$

$$N_{1,av} = \sqrt{\frac{D}{\tau}} (c_{1i} - c_1) \quad \text{Thus, } k = \sqrt{D / \tau}$$

As in the penetration theory, here $k \propto D^{1/2}$

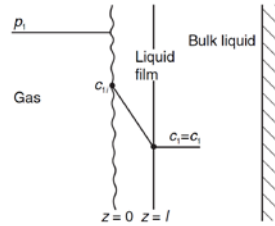
Again the residence time τ is as unknown as the ℓ in film theory or the L/v_{\max} (contact time) in the penetration theory.

The major contribution of the surface renewal theory is that it gives a more REALISTIC physical situation. This gives a better starting point for development of effective correlations and better models.

Summary:

The Film Theory

$$\frac{k\ell}{D} = 1$$



Advantages

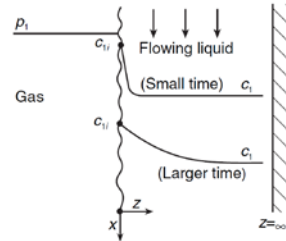
Simple;
good base for
extension

Disadvantages

Film thickness ℓ
is unknown

The Penetration Theory

$$k = 2 \cdot \sqrt{\frac{D \cdot v_{\max}}{\pi \cdot L}}$$

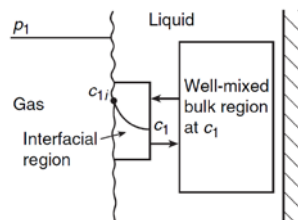


Simplest
including flow

Contact time
(L/v_{\max}) usually
unknown

The Surface-Renewal Theory

$$k = \sqrt{D / \tau}$$



Similar math to
penetration theory,
but better physical
picture

Surface-renewal
rate (τ) is
unknown

The dependencies of k on D and v , like $k \sim D^{1/2}$, $k \sim D^{2/3}$ or $k \sim v^{0.67}$, observed in the experimentally-based MTCs are typically not well reflected by the simple mass transfer models.

These simple models for fluid-fluid interfaces pretend that fluid motion is incorporated in diffusion and everything is treated as a thin film or semi-infinite slab problem.

In principle, these two extreme cases should bracket all possible geometries. Yet, especially the effect of flow (velocity) is usually not well reflected.

One reason is that the simple theories assume a homogeneous system while real systems are heterogeneous with respect to concentration and flow (Schlünder, 1977).