

Molecular Diffusion

Types of Mass Transfer:

1. **Molecular diffusion** (or just diffusion).
Mass is transferred by the random motion of molecules across a concentration gradient. Sometimes, but not always, this is similar to heat transfer by conduction.
2. **Eddy diffusion** (mixing or dispersion or agitation).
Mass is transferred by finite parcels of fluids as in momentum and heat transfer.

Let us see now Molecular Diffusion.....

Molecular Diffusion

Typical e.g. for Molecular Diffusion:

Tea from a tea bag in hot water



To travel from high concentration to low concentration
(only true if medium is at stagnant or in laminar motion)

Vaporization of layer of water in lake:

If surrounding air is stagnant ➡ Diffusion is molecular! (slow process)

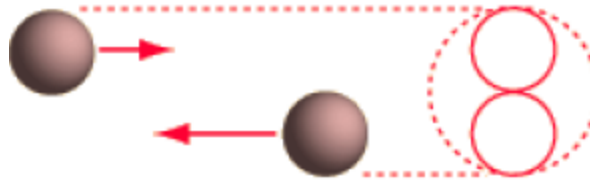
If surrounding air is turbulent ➡ Eddy Diffusion!

Rate of molecular diffusion = f (molecular velocity, conc.gradient)

Why molecular diffusion is a slow process?

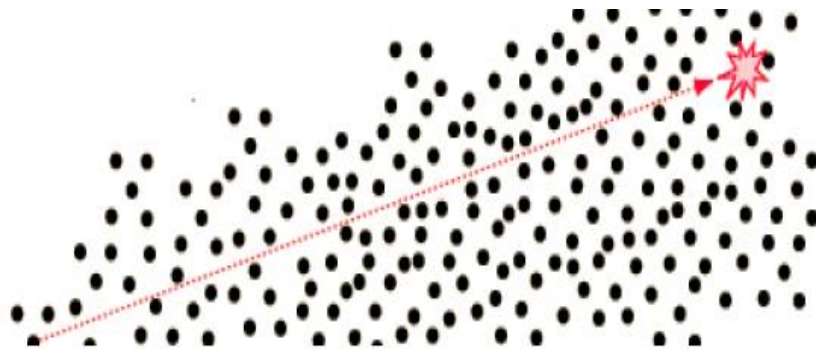
Molecular Diffusion – Depends on movement of individual molecules through a substance by virtue of their thermal energy.

Kinetic theory of gases:



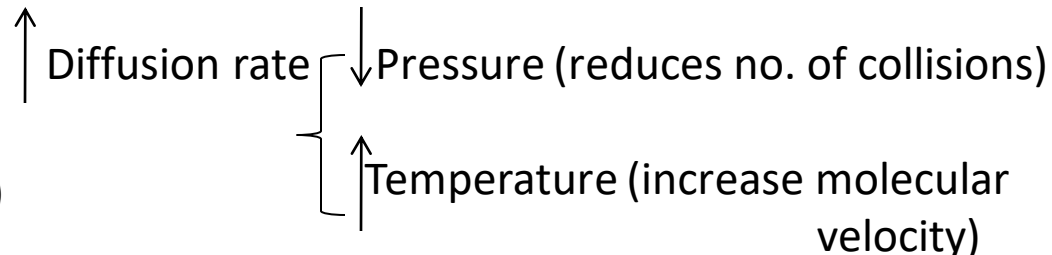
Simplified theory: Molecule is imagined to travel in a straight line at uniform velocity until it collides with another molecule.

Mean free path (λ): Average distance a molecule travels between collisions.



Average velocity = f (temperature)

At highly zig-zag path, the net distance in one direction, rate of diffusion is a small fraction to actual path and hence diffusion rate is slow.



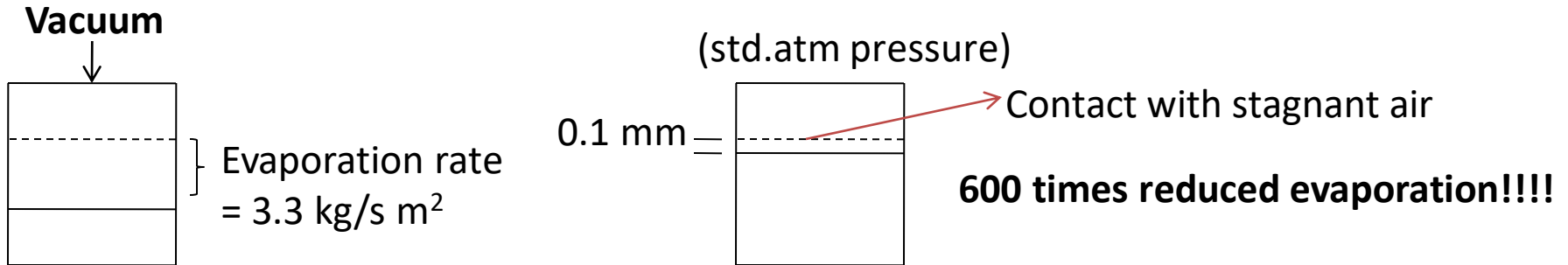
Approximate rates of diffusion in:

Gases: 10 cm/min (a nice perfume in a room).

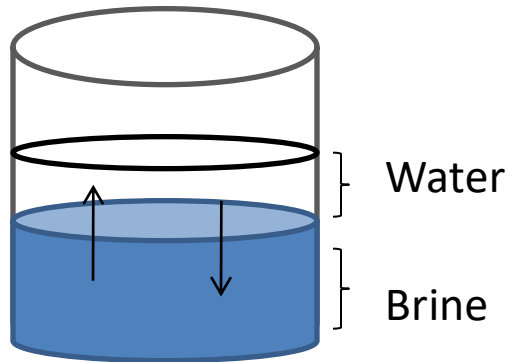
Liquids: 0.05 cm/min (stir cream into the coffee).

Solids: 0.00001 cm/min (takes long to rust an iron axe)

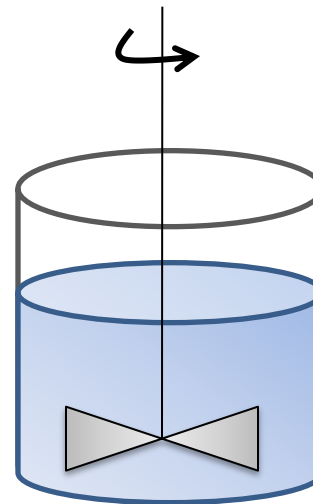
Evaporation of water:



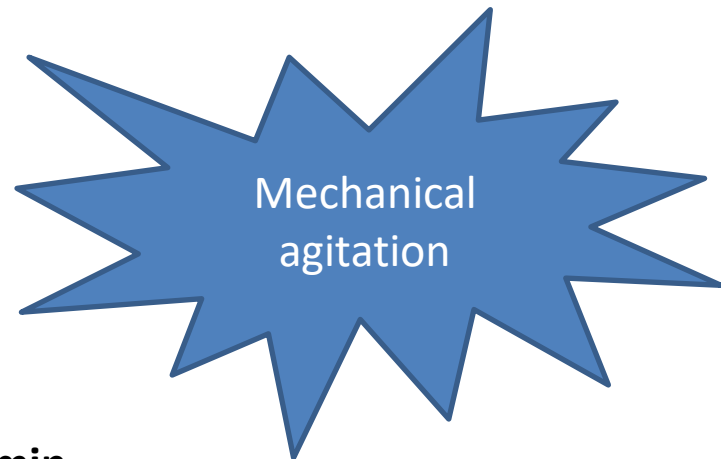
Brine solution:



28 years for a complete solution



Just 60s @ 22r/min
Eddy or Turbulent diffusion




Properties of Mixtures:

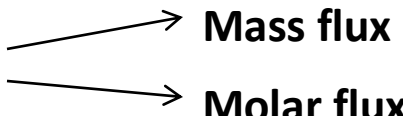
Mass transfer always involves mixtures. Consequently, we must account for the variation of physical properties which normally exist in a given system. The conventional engineering approach to problems of multicomponent system is to attempt to reduce them to representative binary (i.e., two component) systems.

The concentration, molecular velocity and flux of a species in mixture can be expressed in a number of ways as shown below:

(1) Concentration:-

**(a) Mass concentration (b) Total mass conc. (c) Mass fraction (d) Molar conc.,
(e) Total molar conc., (f) Mole fraction (liq) (g) Mole fraction (gas)**

(2) Velocity 
→ **Mass average velocity**
→ **Molar average velocity**

(3) Flux 
→ **Mass flux**
→ **Molar flux**

Concentration:

Concentration of species 'i' in multi component mixture can be expressed in many ways. For species i, mass concentration denoted by ρ_i is defined as the mass of i, m_i per unit volume of the mixture.

$$\rho_i = \frac{m_i}{V} \quad (2.1) \quad \text{SI Unit: kg/m}^3$$

The total mass concentration density ρ is the sum of the total mass of the mixture in unit volume:

$$\rho = \sum_i \rho_i \quad (2.2)$$

Molar concentration of, i, C_i is defined as the number of moles of 'i' present per unit volume of the mixture.

By definition,

$$\text{Number of moles} = \frac{\text{mass of } i}{\text{molecular weight of } i} \quad (2.3)$$

$$n_i = \frac{m_i}{M_i} \quad (2.4)$$

Therefore from (1) & (2)

$$C_i = \frac{n_i}{V} = \frac{\rho_i}{M_i} \quad (2.5) \quad \text{SI Unit: kmol/m}^3$$

For ideal gas mixtures,

$$n_i = \frac{p_i V}{RT} \quad [\text{from Ideal gas law } PV = nRT]$$

$$C_i = \frac{n_i}{V} = \frac{p_i}{RT} \quad (2.6)$$

where ' p_i ' is the partial pressure of species 'i' in the mixture. V is the volume of gas, T is the absolute temperature, and R is the universal gas constant.

The total **molar concentration or molar density** of the mixture is given by

$$C = \sum_i C_i \quad (2.7) \quad \text{SI Unit: kmol/m}^3$$

The mole fraction for liquid and solid mixture, x_i , and for gaseous mixtures, y_i , are the molar concentration of species 'i' divided by the molar density of the mixtures.

$$x_i = \frac{C_i}{C} \quad \text{(liquids and solids)} \quad (2.8)$$

$$y_i = \frac{p_i}{P} \quad \text{(gases)} \quad (2.9)$$

Where, P is total pressure

The sum of the mole fractions, by definition must equal 1;
(i.e.)

$$\sum_i x_i = 1 \quad \sum_i y_i = 1 \quad (2.10)$$

by similar way, mass fraction of 'i' in mixture is;

$$w_i = \frac{\rho_i}{\rho}$$

$$\sum_i w_i = 1 \quad (2.11)$$

Velocity

In a liquid (or) gaseous mixtures, the various species will normally move at different velocities; and evaluation of velocity of mixture requires the averaging of the velocities of each species present.

If u_i is the velocity of species 'i' with respect to stationary fixed coordinates, then mass-average velocity for a multi component mixture defined in terms of mass concentration is,

$$u = \frac{\sum_{i=1}^n \rho_i u_i}{\sum_{i=1}^n \rho_i} = \frac{\sum_{i=1}^n \rho_i u_i}{\rho} \quad (2.12)$$

$u_i \neq$ Instantaneous velocity
= Statistical mean of velocities
of comp 'i' in given direction

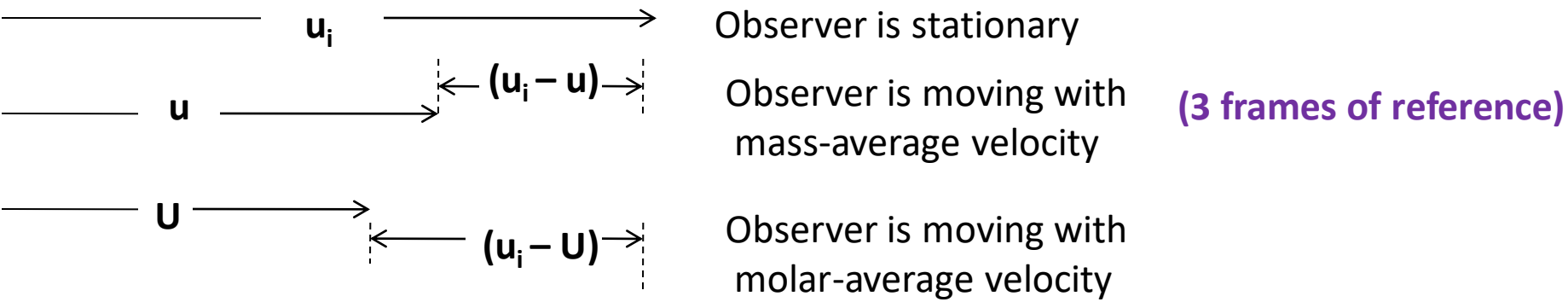
By similar way, molar-average velocity of the mixture 'U' is

$$U = \frac{\sum_{i=1}^n C_i u_i}{\sum_{i=1}^n C_i} = \frac{\sum_{i=1}^n C_i u_i}{C} \quad (2.13)$$

If C_i (solute) $\ll C_s$ (solution), $U = V_s$
 V_s – average velocity of solvent

If molecular weights of all species are equal, then $u = U$

Flux:
 The net rate at which a species in a solution passes through a unit area, which is normal to the direction of diffusion in unit time



Mass Flux (Kg/m ² s)	Molar Flux (kmol/m ² s)	
$n_i = \rho_i u_i$ (2.14)	$N_i = C_i u_i$ (2.17)	➡ Relative to observer
$i_i = \rho_i (u_i - u)$ (2.15)	$I_i = C_i (u_i - u)$ (2.18)	➡ Relative to observer moving with 'u'
$j_i = \rho_i (u_i - U)$ (2.16)	$J_i = C_i (u_i - U)$ (2.19)	➡ Relative to observer moving with 'U'

Fick's Law of Diffusion

Introduced by



Adolf Eugen Fick
– A German physiologist
(1885)

Fick's law states:

“the molar flux of a species relative to an observer moving with the molar average velocity is proportional to the concentration gradient of the species”

$$J_A = -D_{AB} \frac{dC_A}{dZ} \quad (2.20)$$

Diffusion occurs in decreasing conc.

where D_{AB} is diffusivity or diffusion coefficient for component A diffusing through component B, and dC_A / dZ is the concentration gradient in the Z-direction.

$$J_A = -D_{AB} \frac{dC_A}{dZ} \longleftrightarrow q_z = -k \frac{dT}{dZ} \longleftrightarrow \tau_{zx} = -\mu \frac{du_x}{dZ}$$

Mass Transfer

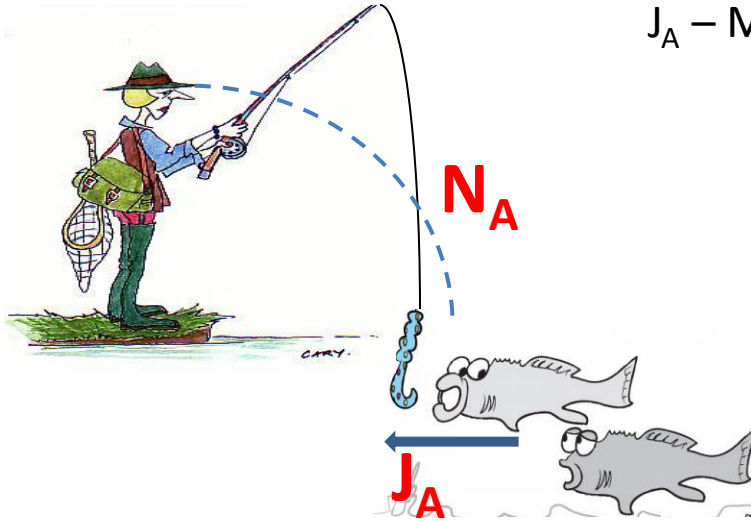
Fourier's law
- Heat Transfer

Newton's law of viscosity
- Momentum Transfer

Fick's Law of Diffusion

N_A – Molar flux relative to a fixed location in space

J_A – Molar flux of a constituent relative to avg. mol. velocity



How to express N_A ?

Using Eqs. (2.13) and (2.17)
$$U = \frac{1}{C} (N_A + N_B) \quad (2.21)$$

Fluxes of A and B:

$$N_A = C_A u_A \quad N_B = C_B u_B$$

Using Eqs. (2.19) and (2.20),

$$J_A = -D_{AB} \frac{dC_A}{dZ} = C_A (u_A - U) \quad (2.22)$$

$$-D_{AB} \frac{dC_A}{dZ} = C_A u_A - C_A U \quad (2.23)$$

$$-D_{AB} \frac{dC_A}{dZ} = N_A - \frac{C_A}{C} (C_A u_A + C_B u_B) \quad (2.24)$$

$$-D_{AB} \frac{dC_A}{dZ} = N_A - \frac{C_A}{C} (N_A + N_B) \quad (2.25)$$

$$N_A = \underbrace{(N_A + N_B) \frac{C_A}{C}}_{\text{Diffusion by bulk flow}} - \underbrace{D_{AB} \frac{dC_A}{dZ}}_{\text{Molecular diffusion}} \rightarrow \text{Molar flux of A in binary mixture w.r to stationary observer} \quad (2.26)$$

Diffusion by bulk flow **Molecular diffusion**

In case of dilute solutions, C_A is very small and its contribution to bulk flow is too small

$$N_A = -D_{AB} \frac{dC_A}{dZ}$$

Diffusing molecules move at a velocity greater than molar avg. velocity ($u_i > U$)

Diffusion velocity of species 'A' w.r.to observer moving with molar avg. velocity,

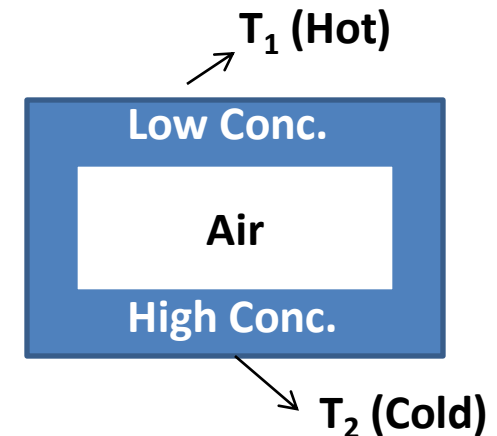
From Eq.(2.22)
$$v_{A,d} = u_A - U = \frac{J_A}{C_A} = \frac{D_{AB}}{C_A} \frac{dC_A}{dZ} \quad (2.27)$$

For gas phase diffusion (in terms of partial pressure):

$$N_A = (N_A + N_B) \frac{p_A}{P} - \frac{D_{AB}}{RT} \frac{d p_A}{d Z} \quad (2.28)$$

Significance of representation of flux in mole fraction:

$$C_{N_2,1} = \frac{p_{N_2,1}}{RT_1} \quad C_{N_2,2} = \frac{p_{N_2,2}}{RT_2}$$



If $T_1 > T_2$ $C_{N_2,2} > C_{N_2,1}$ \rightarrow

Eq. (2.20) $\rightarrow J_A = -CD_{AB} \frac{d y_A}{d Z} \quad (2.29)$

Eq. (2.28) $\rightarrow N_A = (N_A + N_B) y_A - CD_{AB} \frac{d y_A}{d Z} \quad (2.30)$

Fick's law misleads us to speculate on diffusion in this case, as total pressure is uniform and partial pressure of N_2 is uniform in enclosure. **No difference in mole fraction of N_2**

Diffusivity of ideal gas mixture

For a binary ideal gas mixture of A and B, the flux of B in mixture can be derived based on Eq. (2.30):

$$N_B = (N_A + N_B)y_B - CD_{BA} \frac{dy_B}{dZ} \quad (2.31)$$

Add (2.31) to (2.30)

$$(N_A + N_B) = (N_A + N_B)(y_A + y_B) - CD_{AB} \frac{dy_A}{dZ} - CD_{BA} \frac{dy_B}{dZ} \quad (2.32)$$

$$y_A + y_B = 1 \quad \Rightarrow \quad dy_A = -dy_B$$

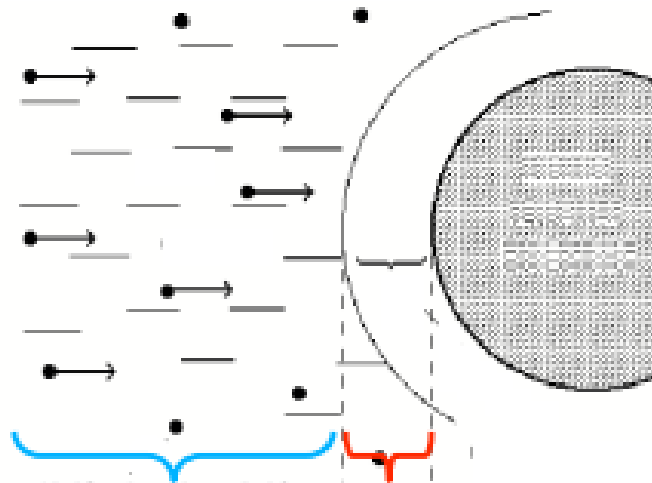
$$CD_{AB} \frac{dy_A}{dZ} = -CD_{BA} \frac{dy_B}{dZ}$$

$$\cancel{CD_{AB} \frac{dy_A}{dZ}} = \cancel{CD_{BA} \frac{dy_A}{dZ}}$$

$$D_{AB} = D_{BA} \quad (2.33)$$

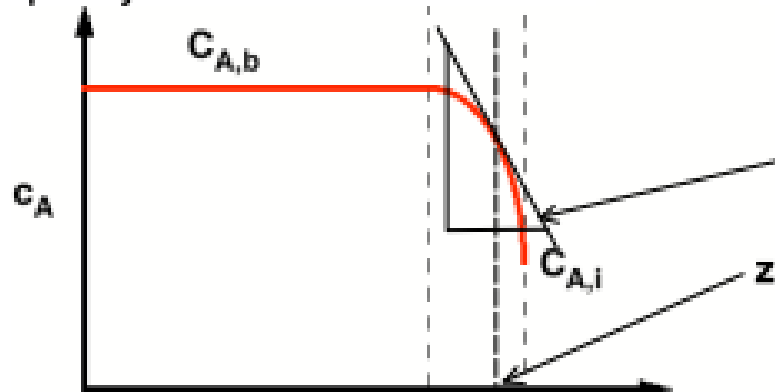
Mutual diffusivities are equal for ideal gas mixture

$$(2.26) \Rightarrow N_A = (N_A + N_B) \frac{C_A}{C} - D_{AB} \frac{dC_A}{dz}$$



But conc. difference is measurable
($C_{A1} - C_{A2}$) !!!!

Transport by: **Convection** **Diffusion**



$\frac{dc_A}{dz}$ is the concentration gradient
at a given location z .
It is the slope of this line!

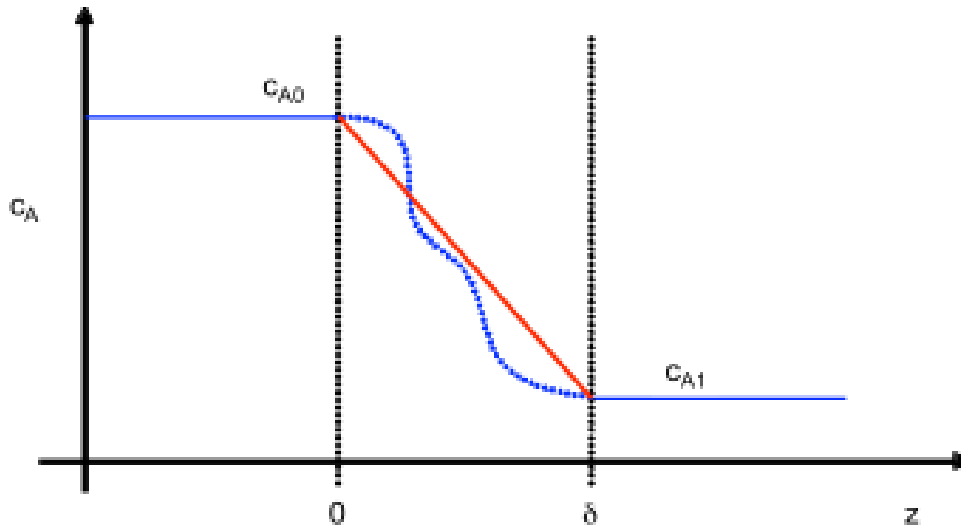
This cannot be measured!

Molecular diffusion in a binary gas mixture

A working formula for flux could be deduced by integrating the flux equation

1. Diffusion through a constant area

Assumptions: Area thru diffusion is constant, gas mixture is ideal, temperature is uniform and diffusion occurs in steady state.



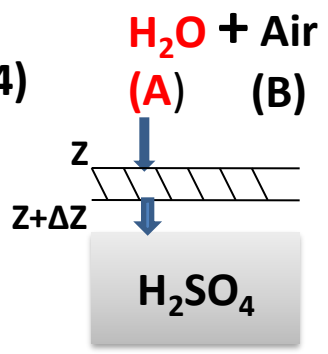
2. Diffusion in variable area of cross section

Diffusion of A through non-diffusing B (Constant Area)

Component A from gas to liq phase; the rate of diffusion may be expressed in terms of the molar flux. Consider the control volume $S \Delta z$, where S is the cross sectional area of the gas film. Mass balance on A over this control volume for a steady-state operation yields

[Moles of A leaving at $z + \Delta z$] – [Moles of A entering at z] = 0 (2.34)

$$S N_A \Big|_{z + \Delta z} - S N_A \Big|_z = 0. \quad (2.35)$$



Dividing through by the volume, $S\Delta Z$, and evaluating in the limit as ΔZ approaches zero, we obtain the differential equation

$$\frac{d N_A}{d z} = 0 \quad (2.36)$$

This relation stipulates a constant molar flux of A throughout the gas phase from Z_1 to Z_2 . A similar differential equation could also be written for component B as,

$$\frac{d N_B}{d Z} = 0, \quad (2.37)$$

and accordingly, the molar flux of B is also constant over the entire diffusion path from z_1 and z_2 .

Considering only at plane z_1 , and since the gas B is insoluble in liquid, we realize that N_B , the net flux of B, is zero throughout the diffusion path; accordingly B is a stagnant gas.

As per Eq. (2.30)

$$N_A = -C D_{AB} \frac{dy_A}{dz} + y_A (N_A + N_B)$$

Since $N_B = 0$,

$$N_A = -C D_{AB} \frac{dy_A}{dz} + y_A N_A \quad (2.38)$$

Rearranging,

$$N_A = \frac{-C D_{AB}}{1 - y_A} \frac{dy_A}{dz} \quad (2.39)$$

This equation may be integrated between the two boundary conditions:

$$\begin{array}{ll} \text{at } z = z_1 & Y_A = Y_{A1} \\ \text{And at } z = z_2 & Y_A = Y_{A2} \end{array}$$

Assuming the diffusivity is to be independent of concentration, and realizing that N_A is constant along the diffusion path, by integrating equation (2.39) we obtain

$$N_A \int_{Z_1}^{Z_2} dz = C D_{AB} \int_{Y_{A1}}^{Y_{A2}} \frac{-dy_A}{1 - y_A} \quad (2.40)$$

$$N_A = \frac{CD_{AB}}{Z_2 - Z_1} \ln \left(\frac{1 - y_{A2}}{1 - y_{A1}} \right) \quad (2.41)$$

The log mean average concentration of component B is defined as

$$y_{B,lm} = \frac{y_{B2} - y_{B1}}{\ln \left(\frac{y_{B2}}{y_{B1}} \right)} \quad (2.42)$$

Since $y_B = 1 - y_A$

$$y_{B,lm} = \frac{(1 - y_{A2}) - (1 - y_{A1})}{\ln \left(\frac{1 - y_{A2}}{1 - y_{A1}} \right)} = \frac{y_{A1} - y_{A2}}{\ln \left(\frac{1 - y_{A2}}{1 - y_{A1}} \right)} \quad (2.43)$$

Substituting from Eqn (2.43) in Eqn (2.41),

$$N_A = \frac{CD_{AB}}{Z_2 - Z_1} \frac{(y_{A1} - y_{A2})}{y_{B,lm}} \quad (2.44)$$

For an ideal gas $C = \frac{n}{V} = \frac{p}{RT}$ and for mixture of ideal gases $y_A = \frac{p_A}{P}$

Therefore, Eqn. (2.44) becomes

$$N_A = \frac{D_{AB}P}{RT(z_2 - z_1)} \frac{(p_{A1} - p_{A2})}{p_{B,lm}} \quad (2.45)$$

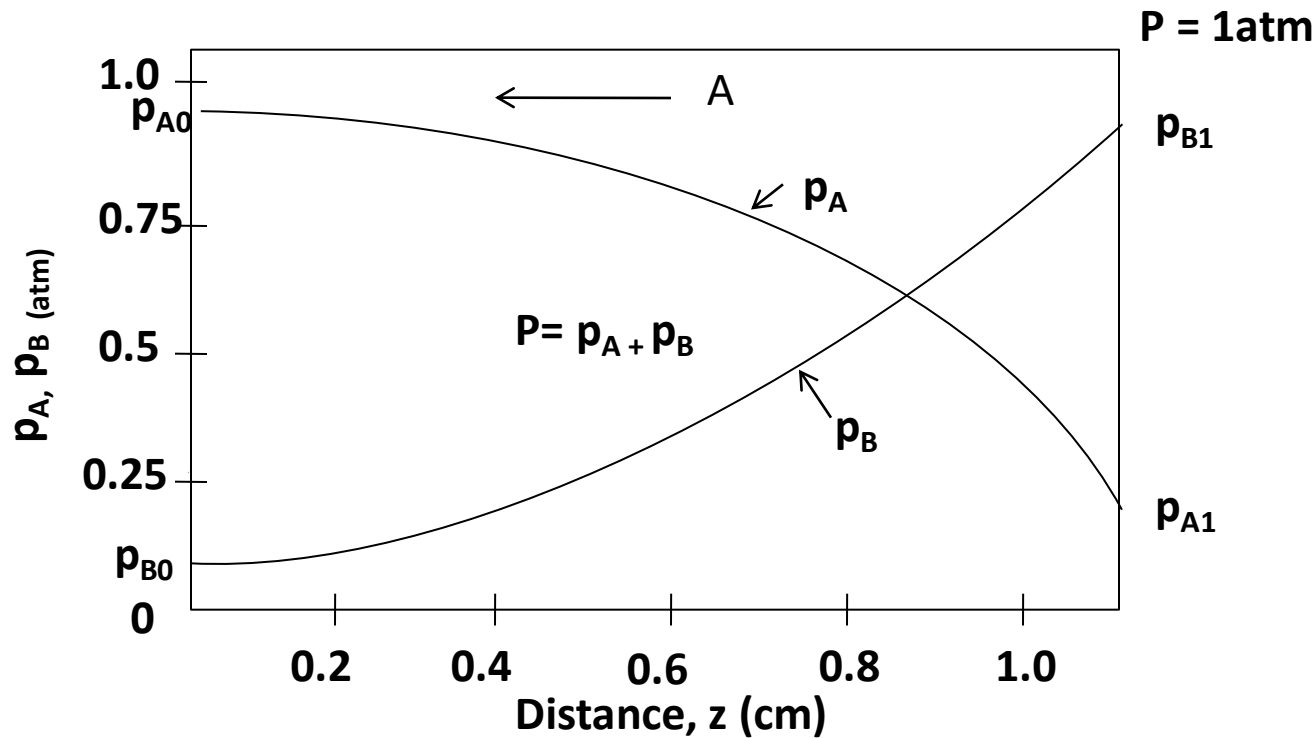
This is the equation of molar flux for steady state diffusion of one gas through a second stagnant gas.

Many mass-transfer operations involve the diffusion of one gas component through another non-diffusing component; absorption and humidification

Integrating Eq.(2.28)
$$N_A = (N_A + N_B) \frac{p_A}{P} - \frac{D_{AB}}{RT} \frac{d p_A}{d z}$$

in terms of partial pressure w.r.to limits $z = 0$ to $z = z$, $p_A = p_{A0}$, $p_A = p_A$ we get flux of A

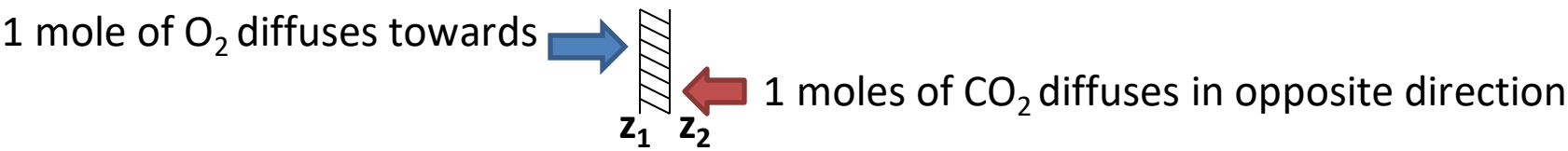
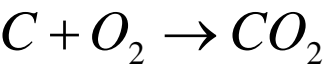
$$N_A = \frac{D_{AB} P}{RT z} \ln \frac{(P - p_A)}{(P - p_{A0})} \quad (2.46)$$



Why p_B increasing as we assumed B is non-diffusing???

- Recollect fishing illustration

Equimolar counter diffusion:



A physical situation which is encountered in the distillation of two constituents whose molar latent heats of vaporization are essentially equal, stipulates that the flux of one gaseous component is equal to but acting in the opposite direction from the other gaseous component; that is, $N_A = - N_B$.

The molar flux N_A , for a binary system at constant temperature and pressure is described by Eq.(2.30):

$$N_A = - C D_{AB} \frac{d y_A}{d z} + y_A (N_A + N_B)$$

or

$$N_A = - \frac{D_{AB}}{RT} \frac{d p_A}{d z} + \frac{p_A}{P} (N_A + N_B) \tag{2.47}$$

with the substitution of $N_B = - N_A$, Equation (2.47) becomes,

$$N_A = - \frac{D_{AB}}{RT} \frac{d p_A}{d z} \tag{2.48}$$

For steady state diffusion Equation. (2.48) may be integrated, using the boundary conditions:

$$\begin{array}{ll} \text{at } z = z_1 & p_A = p_{A1} \\ \text{and } z = z_2 & p_A = p_{A2} \end{array}$$

$$N_A \int_{z_1}^{z_2} dz = -\frac{D_{AB}}{RT} \int_{p_{A1}}^{p_{A2}} dp_A \quad (2.49)$$

from which

$$N_A = \frac{D_{AB}}{RT(z_2 - z_1)} (p_{A1} - p_{A2}) \quad (2.50)$$

This is the equation of molar flux for
steady-state equimolar counter diffusion.

Partial pressure profile in equimolar counter diffusion may be obtained from,

$$\frac{d}{dz} (N_A) = 0 \quad (2.51) \quad (\text{Since } N_A \text{ is constant over the diffusion path}).$$

Substituting for N_A from Eq. (2.48)

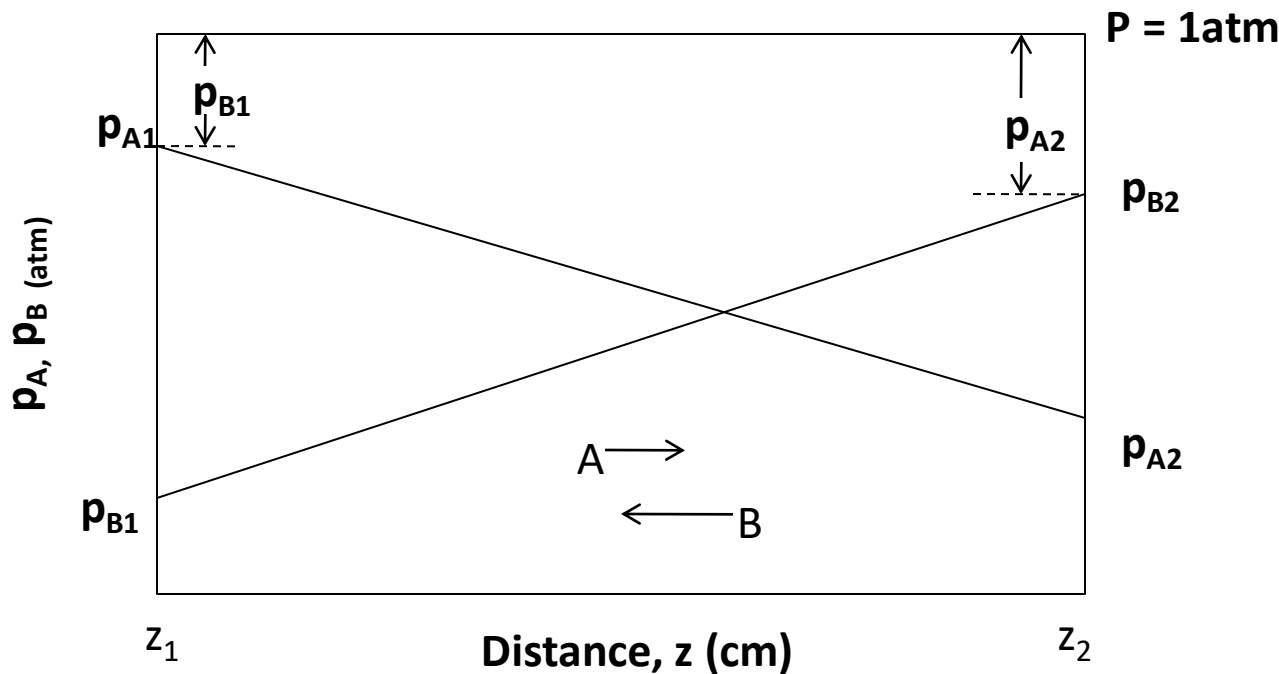
Therefore

$$\frac{d}{dz} \left(-D_{AB} \frac{dp_A}{dz} \right) = 0$$
$$\frac{d^2 p_A}{dz^2} = 0. \quad (2.52)$$

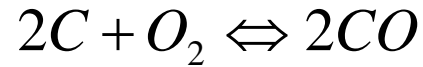
This equation may be solved using the boundary conditions to give

$$\frac{p_A - p_{A1}}{p_{A1} - p_{A2}} = \frac{z - z_1}{z_1 - z_2} \quad (2.53)$$

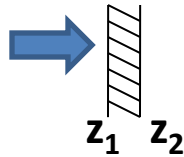
Linear concentration profile for equimolar counter diffusion.



Non-equimolar counter diffusion of A and B:



1 mole of O_2 diffuses towards



2 moles of CO diffuses in opposite direction

Molar latent heats of vaporization are not equal!

$$N_A \Delta H_A^v = -N_B \Delta H_B^v \quad (2.54)$$

Evaporation of a spherical Droplet:

As an example of such problems, we shall consider the evaporation of spherical droplet such as a raindrop or sublimation of naphthalene ball. The vapor formed at the surface of the droplet is assumed to diffuse by molecular motions into the large body of stagnant gas that surrounds the droplet.

Consider a raindrop, as shown in figure.
At any moment, when the radius of the drop is r_0 , the flux of water vapor at any distance r from the center is given by

$$N_A = -C D_{AB} \frac{d y_A}{d r} + y_A (N_A + N_B) \tag{2.55}$$

$$N_A = -C D_{AB} \frac{d y_A}{d r} + y_A N_A \tag{2.56}$$

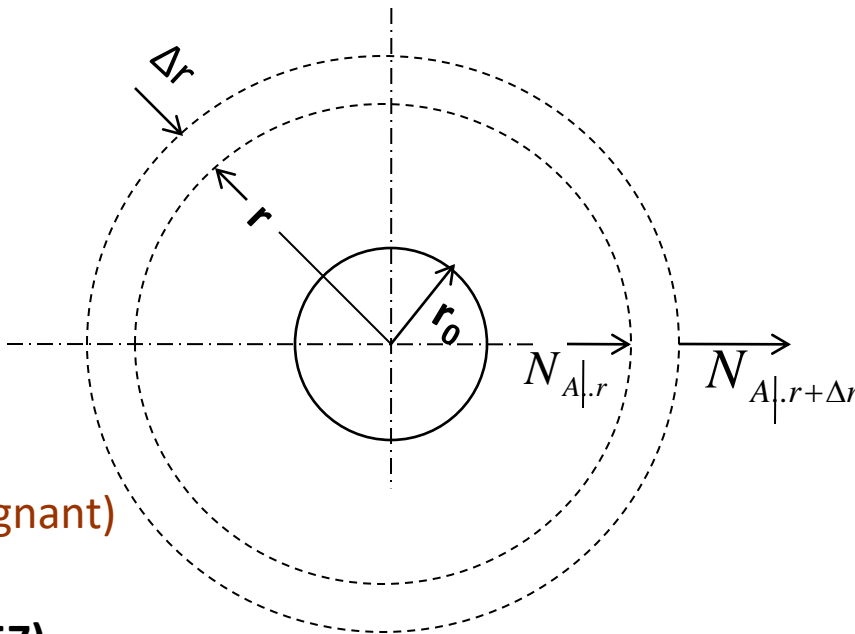
Here $N_B = 0$ (since air is assumed to be stagnant)
Therefore,

Rearranging,

$$N_A = \frac{-C D_{AB}}{1 - y_A} \frac{d y_A}{d r} \tag{2.57}$$

The flux N_A is not constant, because of the spherical geometry; decreases as the distance from the center of sphere increases. But the molar flow rate at r and $r + \delta r$ are the same. This could be written as,

$$A N_A|_r = A N_A|_{r + \delta r} \tag{2.58}$$



where A = surface area of sphere at r or $r + \delta r$.

Substituting for $A = 4 \pi r^2$ in equation (2.58),

$$4 \pi r^2 N_A \Big|_{r+\delta r} - 4 \pi r^2 N_A \Big|_r = 0 \quad (2.59)$$

$$\lim_{\delta r \rightarrow 0} \frac{r^2 N_A \Big|_{r+\delta r} - r^2 N_A \Big|_r}{\delta r} = 0$$

$$\frac{d}{dr} (r^2 N_A) = 0 \quad (2.60)$$

Integrating,

$$r^2 N_A = \text{constant} \quad (2.61)$$

From equation (2.61),

$$r^2 N_A = r_0^2 N_{A_0} \quad (2.62)$$

Substituting for N_A from equation (2.57),

$$\frac{-r^2 C D_{AB}}{1 - y_A} \frac{dy_A}{dr} = r_0^2 N_{A_0} \quad (2.63)$$

$$r_0^2 N_{A_0} \int \frac{dr}{r^2} = -C D_{AB} \int \frac{dy_A}{1-y_A} \quad (2.64)$$

Boundary condition :

At $r = r_0$ $y_A = y_{AS}$

and At $r = \infty$ $y_A = y_{A\infty}$

Therefore equation (2.64) becomes,

$$r_0^2 N_{A_0} \left(-\frac{1}{r} \right)_{r_0}^{\infty} = \left[C D_{AB} \ln(1-y_A) \right]_{y_{AS}}^{y_{A\infty}} \quad (2.65)$$

Simplifying

$$N_{A_0} = \frac{C D_{AB}}{r_0} \ln \left(\frac{1-y_{A\infty}}{1-y_{AS}} \right) \quad (2.66)$$

Time required for complete evaporation of the droplet may be evaluated from making mass balance.

$$\frac{\text{Moles of water diffusing}}{\text{unit time}} = \frac{\text{moles of water leaving the droplet}}{\text{unit time}} \quad (2.67)$$

$$4 \pi r_0^2 N_{A0} = - \frac{d}{dt} \left(\frac{4}{3} \pi r_0^3 \frac{\rho_A}{M_A} \right) = -4 \pi r_0^2 \frac{\rho_A}{M_A} \frac{d r_0}{d t} \quad (2.68)$$

Substituting for N_{A0} from equation (2.66) in equation (2.68),

$$\frac{C D_{AB}}{r_0} \ln \left(\frac{1 - y_{A\infty}}{1 - y_{AS}} \right) = \frac{-\rho_A}{M_A} \frac{d r_0}{d t} \quad (2.69)$$

Initial condition :

When $t = 0$ $r_0 = r_1$

Integrating equation (2.69) with these initial condition,

$$\int_0^t d t = \frac{-\rho_A}{M_A} \frac{1}{C D_{AB}} \frac{1}{\ln \left(\frac{1 - y_{A\infty}}{1 - y_{AS}} \right)} \int_{r_1}^0 r_0 d r_0 \quad (2.70)$$

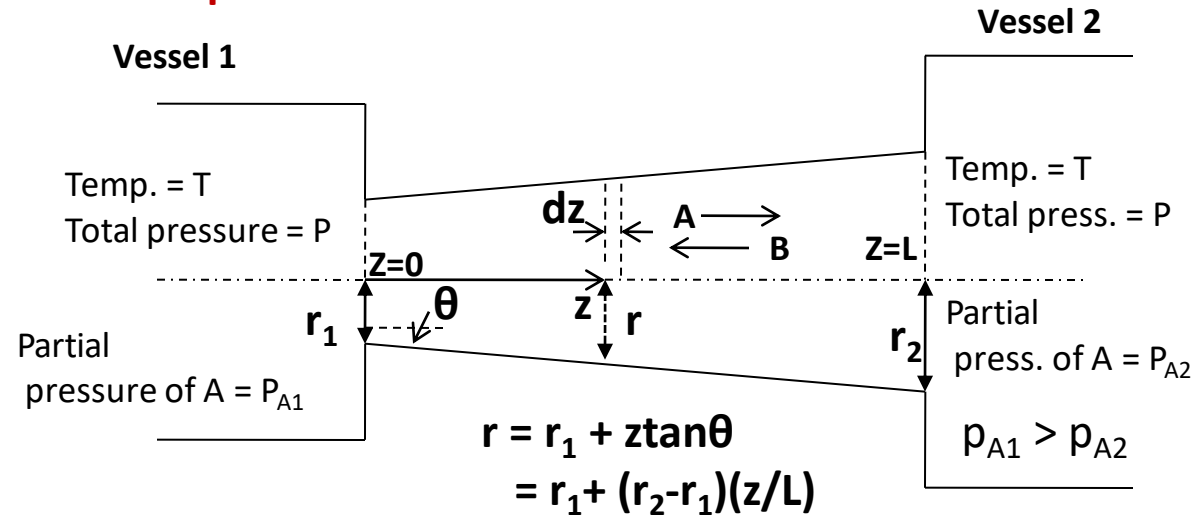
$$t = \frac{\rho_A}{M_A} \frac{1}{2 C D_{AB}} \frac{r_1^2}{\ln \left(\frac{1 - y_{A\infty}}{1 - y_{AS}} \right)} \quad (2.71)$$

In terms of partial pressure..

$$t = \frac{RT \rho_A r_1^2}{2 D_{AB} P M_A \ln \left(\frac{1 - p_{A\infty}}{1 - p_{AS}} \right)} \quad (2.72)$$

Equation (2.72) gives the total time t required for complete evaporation of spherical droplet of initial radius r_1 .

Diffusion thru a Tapered Tube



Consider two large vessels connected by a tapered tube of length L . The end Radii of the tubes are r_1 (**vessel 1**) and r_2 (**vessel 2**). Z-axis is taken as the axis of tube and $Z=0$ taken at vessel 1. Vessels contain mixture of gases A and B at same total Pressure P and temperature T . Partial pressure of A in vessel 1 and 2 are p_{A1} & p_{A2} .

Assumption: Composition of gases in two vessels are fairly constant

Rate of diffusion of A at steady state?

Since $p_{A1} > p_{A2}$, A diffuses from vessel 1 to vessel 2 & B diffuses in reverse direction
(Equimolar counter diffusion)

Consider a thin section of tube of thickness Δz at a distance z where local radius is r .

$$\text{Rate of input of A in to the section at } z = \pi r^2 N_A \Big|_z \quad (2.74)$$

$$\text{Rate of input of A in to the section at } z + \Delta z = \pi r^2 N_A \Big|_{z+\Delta z} \quad (2.75)$$

Since there is no accumulation within the section at steady state,

$$\pi r^2 N_A \Big|_{z+\Delta z} - \pi r^2 N_A \Big|_z = 0 \quad (2.76)$$

Dividing by Δz throughout and taking the limit $\Delta z \rightarrow 0$

$$\lim_{\Delta z \rightarrow 0} \frac{(\pi r^2) N_A \Big|_z - (\pi r^2) N_A \Big|_{z+\Delta z}}{\Delta z} = 0 \quad (2.77)$$

$$-\frac{d}{dz}(\pi r^2 N_A) = 0 \quad \pi r^2 N_A = W_1 = \text{constant} \quad (2.78)$$

Local flux of A for equimolar counter diffusion is given as:

$$N_A = -\frac{D_{AB}}{RT} \frac{dp_A}{dz} \quad (2.79) \quad \pi r^2 N_A = W_1 = -\pi r^2 \frac{D_{AB}}{RT} \frac{dp_A}{dz}$$

The local radius 'r' can be related to the axial position z by using the property of similar Δ 'les

$$r = r_1 + \left(\frac{r_2 - r_1}{L} \right) z \quad (2.80)$$

Substituting eq.(2.79) & eq.(2.80) in eq.(2.78), integrating & rearranging

$$-\int_{p_{A1}}^{p_{A2}} dp_A = \frac{W_1 RT}{\pi D_{AB}} \int_0^L \frac{dz}{\left[r_1 + \frac{(r_2 - r_1)z}{L} \right]^2} \quad (2.81)$$

$$W_1 = \frac{\pi D_{AB}}{RT} \frac{r_1 r_2}{L} (p_{A1} - p_{A2}) \quad (2.82)$$

Rate of diffusion $\propto (r_1 r_2)^{1/2}$

Rate of diffusion is equal to uniform
dia of tube with geometric mean of end radii

Diffusion in Liquids:

Equation derived for diffusion in gases equally applies to diffusion in liquids with some modifications. Mole fraction in liquid phases is normally written as 'x' (in gases as y). The concentration term 'C' is replaced by average molar density, $\left(\frac{\rho}{M}\right)_{av}$.

For steady – state diffusion of A through non diffusivity B: $N_A = \text{constant}$, $N_B = 0$

$$N_A = \frac{D_{AB}}{Z X_{BM}} \left(\frac{\rho}{M}\right)_{av} (x_{A1} - x_{A2}) \tag{2.83}$$

where $Z = Z_2 - Z_1$, the length of diffusion path; and

$$X_{BM} = \frac{X_{B2} - X_{B1}}{\ln\left(\frac{X_{B2}}{X_{B1}}\right)} \tag{2.84}$$

b) For steady – state equimolar counter diffusion : $N_A = - N_B$

$$N_A = \frac{D_{AB}}{Z} (C_{A1} - C_{A2}) = \frac{D_{AB}}{Z} \left(\frac{\rho}{M}\right)_{av} (x_{A1} - x_{A2}) \tag{2.85}$$

Fick's Law of Diffusion cannot account for:

- Multicomponent diffusion
- Non-ideal mixtures
- Driving forces other than concentration gradients, i.e.
 - Electrostatic force fields
 - Pressure gradients
 - Centrifugal forces

For these, you need

MAXWELL - STEFAN EQUATIONS!

Maxwell's Law of diffusion For Binary System

Maxwell's postulated that the pressure gradient (Δp_A) in the direction of diffusion for constituent of two components gaseous mixture is proportional to:

- A) Difference in velocities of the components in the direction of diffusion.
- B) The product of the molar concentration of the component.
- C) The length of the diffusion path (Δz)

$$-\Delta p_A \propto C_A C_B \Delta z (u_A - u_B) \quad (2.86)$$

$$-\frac{\Delta p_A}{\Delta z} = F C_A C_B (u_A - u_B) \quad (2.87)$$

$$-\frac{dp_A}{dz} = F C_A C_B (u_A - u_B) \quad (2.88)$$

u_A & u_B = velocities of A & B respectively

C_A & C_B = molar concentration of the component A & B respectively.

F = Coefficient

But, $u_A = N_A / C_A$ $u_B = N_B / C_B$

Also

$$P_A = C_A RT$$

Then

$$\frac{-dC_A}{dz} = \frac{F}{RT} (N_A \cdot C_B - N_B \cdot C_A) \quad (2.89)$$

Now, applying the two cases that have been considered before, *i.e.* equimolar diffusion, and diffusion through stagnant layer, then we can reach to the final equation to calculate the rate of mass transfer as shown below:

A) For equimolar diffusion

$$N_A = -N_B$$
$$\frac{-dC_A}{dz} = \frac{F \cdot N_A}{RT} (C_B + C_A) \quad (2.90)$$

$$N_A = -\frac{RT}{F \cdot C_T} \left(\frac{dC_A}{dz} \right) \quad (2.91)$$

$$C_T = C_A + C_B$$

Comparing with Fick's law, we find that

$$D_{AB} = \frac{RT}{FC_T}$$

Or

$$F_{AB} = \frac{RT}{D_{AB} C_T} \quad \text{General form } F = \frac{RT}{DC_T} \quad (2.92)$$

B) For diffusion through stagnant layer

$$N_B = 0$$

Then

$$\frac{-dC_A}{dz} = \frac{F}{RT} (N_A \cdot C_B) \quad (2.93)$$

And

$$N_A = -\frac{RT}{F \cdot C_B} \left(\frac{dC_A}{dz} \right) \quad (2.94)$$

Multiplying the right side of the equation by $\left(\frac{C_T}{C_B} \right)$ and by comparison we find that

$$N_A = -\frac{D \cdot C_T}{C_B} \left(\frac{dC_A}{dz} \right) \quad (2.95)$$

This finally will result:

$$N_A = \frac{C D_{AB}}{Z_2 - Z_1} \frac{(y_{A1} - y_{A2})}{y_{B,lm}} \quad (2.96)$$

Maxwell's Law for Multi-Component Diffusion

Consider the transfer of component A through a stationary gas consisting of component B, C, D ... Suppose that the total partial pressure gradient can be regarded as being made up of series of terms each represent the contribution of the individual component gases, the form of the binary system equation (Eq.2.93) can be written as follow:

$$\frac{-dC_A}{dz} = \frac{F_{AB} \cdot N_A \cdot C_B}{RT} + \frac{F_{AC} \cdot N_A \cdot C_C}{RT} + \frac{F_{AD} \cdot N_A \cdot C_D}{RT} \quad (2.97)$$

As found before for F

$$F = \frac{RT}{DC_T}$$

So, for diffusion of A through multi-component B, C, and D

$$F_{AB} = \frac{RT}{D_{AB}C_T}, F_{AC} = \frac{RT}{D_{AC}C_T}, F_{AD} = \frac{RT}{D_{AD}C_T} \text{ respectively}$$

Therefore:

$$\frac{-dC_A}{dz} = \frac{N_A}{C_T} \left(\frac{C_B}{D_{AB}} + \frac{C_C}{D_{AC}} + \frac{C_D}{D_{AD}} \right) \quad (2.98)$$

$$N_A = \frac{-C_T}{\left(\frac{C_B}{D_{AB}} + \frac{C_C}{D_{AC}} + \frac{C_D}{D_{AD}} + \Lambda \right)} \frac{dC_A}{dZ} \quad (2.99)$$

Multiplying the above equation by $\left(\frac{C_T - C_A}{C_T - C_A} \right)$, then

$$N_A = \frac{1}{\left(\left(\frac{1}{D_{AB}} \cdot \frac{C_B}{C_T - C_A} \right) + \left(\frac{1}{D_{AC}} \cdot \frac{C_C}{C_T - C_A} \right) + \left(\frac{1}{D_{AD}} \cdot \frac{C_D}{C_T - C_A} \right) \right)} \frac{-C_T}{C_T - C_A} \frac{dC_A}{dZ} \quad (2.100)$$

Define

$$y'_j = \frac{C_j}{C_T - C_A} \quad \text{then}$$

$$y'_B = \frac{C_B}{C_T - C_A}, \quad y'_C = \frac{C_C}{C_T - C_A} \quad \text{and} \quad y'_D = \frac{C_D}{C_T - C_A} \quad \text{Therefore}$$

$$N_A = \frac{1}{\left(\left(\frac{y'_B}{D_{AB}} \right) + \left(\frac{y'_C}{D_{AC}} \right) + \left(\frac{y'_D}{D_{AD}} \right) \right)} \frac{-C_T}{C_T - C_A} \frac{dC_A}{dZ} \quad (2.101)$$

Finally

$$N_A = D_{AM} \frac{-C_T}{C_T - C_A} \frac{dC_A}{dZ} \quad (2.102)$$

Where:

D_{AM} is defined as the diffusivity coefficient of component A through a mixture of B, C, D,

And

$$D_{AM} = \frac{1}{\left(\left(\frac{y'_B}{D_{AB}} \right) + \left(\frac{y'_C}{D_{AC}} \right) + \left(\frac{y'_D}{D_{AD}} \right) \right)} \quad (2.103)$$

Diffusivity (or) Diffusion Coefficient

Diffusion coefficient, also called Diffusivity, is an important parameter indicative of the diffusion mobility. Diffusion coefficient is generally prescribed for a given pair of species. For a multi-component system, it is prescribed for each pair of species in the system. **The higher the diffusivity (of one component with respect to another), the faster they diffuse into each other!**

D has the dimension of L^2/t , identical to the fundamental dimensions of the other transport properties:

Kinematic viscosity, $\nu = (\mu / \rho)$ in momentum transfer, and thermal diffusivity, $\alpha (= k / \rho C_p)$ in heat transfer.

Diffusivity is normally reported in cm^2/s ; the SI unit being m^2 / s .

Diffusivity depends on pressure, temperature, and composition of the system.

Diffusivities of gases at low density are almost composition independent, increase with the temperature and vary inversely with pressure.

Diffusivity strongly depends on intermolecular forces in a mixture. Rate of collision increases with decrease in mean free path and hence diffusivity of gas decreases with increase in pressure.

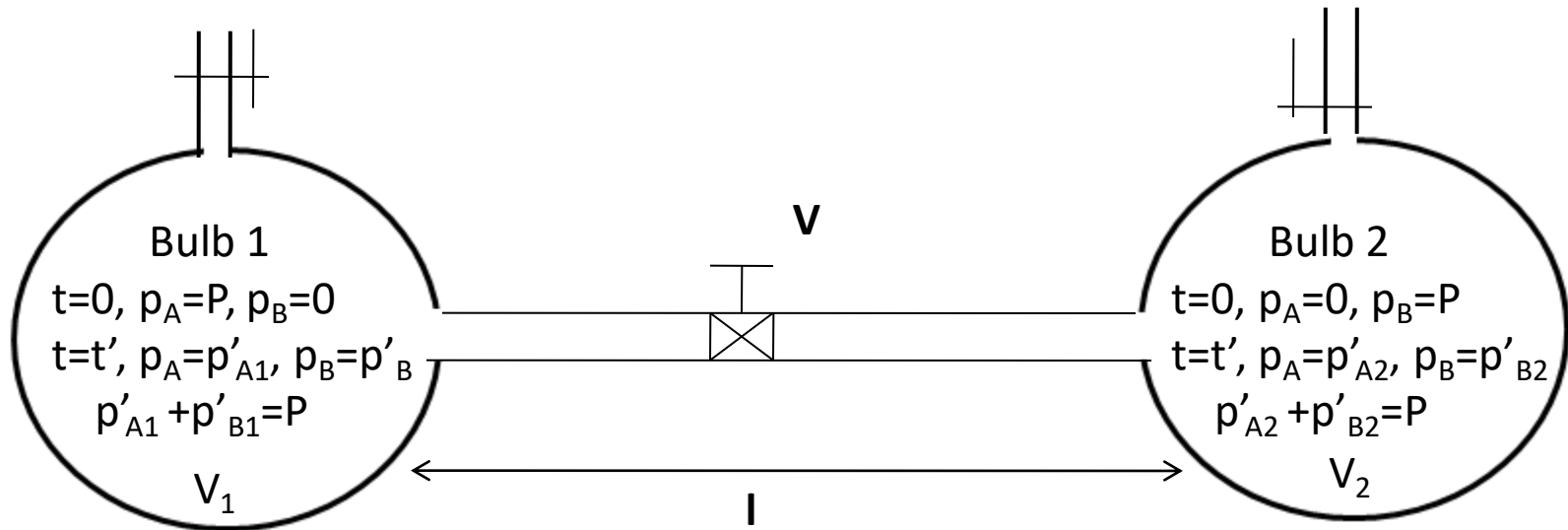
$$D_{AB} \propto \frac{1}{p} \qquad D_{AB} \propto T^{3/2}$$

Liquid and solid diffusivities are strongly concentration dependent and increase with temperature.

General range of values of diffusivity (at std atm pressure and temperature):

Gases :	5×10^{-6}	-----	1×10^{-5}	m ² /s.
Liquids :	10^{-6}	-----	10^{-9}	m ² /s.
Solids :	5×10^{-14}	-----	1×10^{-10}	m ² /s

Measurement of Diffusivity: Twin-bulb method



Two chambers of volume V_1 and V_2 connected by a narrow tube fitted with a plug-type valve or a stopcock.

Contents in the bulb are continuously stirred to ensure uniform concentration. Entire assembly should be maintained at constant temperature.

Two bulbs are evacuated initially and flushed repeatedly with pure gases A and B under same total pressure, P .

Valve is opened to allow diffusion for some time and at end again closed. Samples of gases were taken in both bulbs and analyzed for composition.

Since total pressure is constant, Equimolar counter diffusion occurs in connecting tube

Pseudo steady state assumption: In many mass transfer operations, one of the boundaries may move with time. If the length of the diffusion path changes a small amount over a long period of time, a pseudo steady state diffusion model may be used.

On twin-bulb method: Concentrations of components in bulbs will change rather slowly. i.e. time scale for change of conc. is considerably larger than time scale for attaining steady state diffusion thru connecting tube.

If 'a' is inner cross sec. area of tube, l its length, p_{A1} and p_{A2} partial pressures of A in bulbs at any time t, steady state rate of transport of A from bulb 1 to bulb 2 is:

$$aN_A = \frac{aD_{AB} P(p_{A1} - p_{A2})}{RTl} = -aN_B \quad (2.104)$$

If C_{A1} and C_{A2} are instantaneous conc. of A, the rate of change of conc. of A are:

$$-V_1 \frac{dC_{A1}}{dt} = -aN_A \qquad -\frac{V_1}{RT} \frac{dp_{A1}}{dt} = -aN_A \quad (2.105)$$

$$V_2 \frac{dC_{A2}}{dt} = aN_A \qquad \frac{V_2}{RT} \frac{dp_{A2}}{dt} = aN_A \quad (2.106)$$

$$-\frac{d}{dt}(p_{A1} - p_{A2}) = aRT \left[\frac{1}{V_1} + \frac{1}{V_2} \right] N_A = \frac{aD_{AB}(p_{A1} - p_{A2})}{l} \left[\frac{1}{V_1} + \frac{1}{V_2} \right] \quad (2.107)$$

$$-\frac{d(p_{A1} - p_{A2})}{(p_{A1} - p_{A2})} = \frac{aD_{AB}}{l} \left[\frac{1}{V_1} + \frac{1}{V_2} \right] dt \quad (2.108)$$

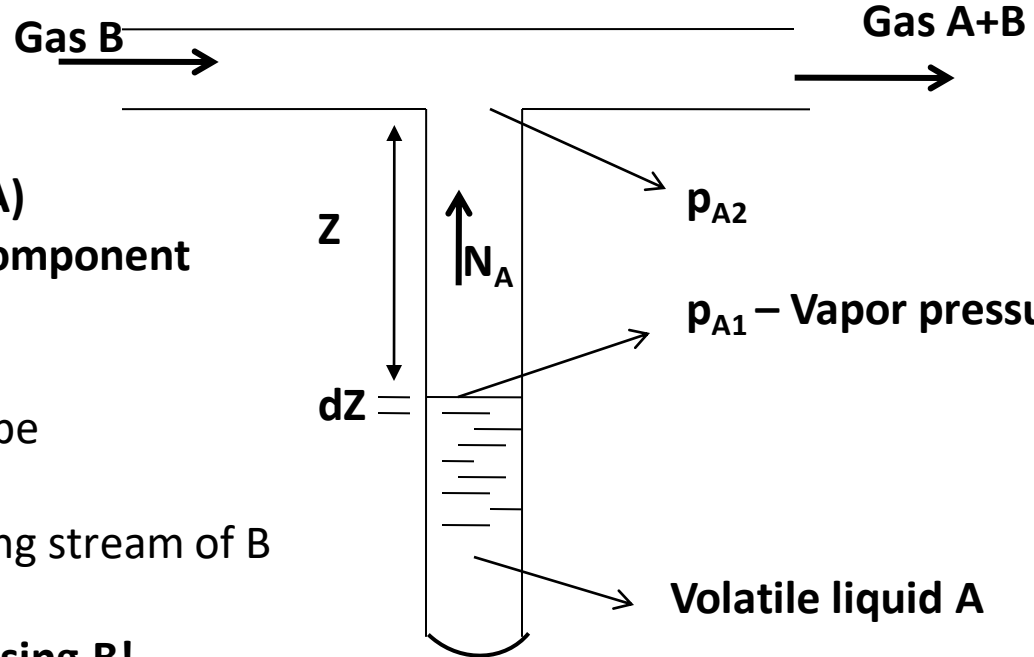
Boundary conditions: $t = 0$, $p_{A1} - p_{A2} = P - 0 = P$ and $t = t'$, $p_{A1} - p_{A2} = p_{A1}' - p_{A2}'$

$$-\ln \frac{P}{(p_{A1}' - p_{A2}')} = \frac{aD_{AB}}{l} \left[\frac{1}{V_1} + \frac{1}{V_2} \right] t' \quad (2.109)$$



Only to measure initial pressure
and partial pressure

Stefan Tube (or) Winkelmann Apparatus:



Suitable if **one component (A)**
Is volatile liquid and other **component**
(B) is a gas not soluble in A

A vertical 'T' shaped glass tube

Evaporated A swept by flowing stream of B

Diffusion of A thru non-diffusing B!

Eg: Diffusion of Napthalene (A) in supercritical CO₂ (B)

Let at time 't', the liquid level be at a distance 'z' from top of the vertical tube

p_{A1} – partial pressure of A at the liquid surface

p_{A2} – partial pressure of A at top

Pseudo steady state assumption: Liquid level in vertical tube will drop slowly as A diffuses thru tube virtually at steady state

Diffusional flux of A thru distance 'z',
$$N_A = \frac{D_{AB} P(p_{A1} - p_{A2})}{RTzp_{BM}} \quad (2.110)$$

If the fall in the liquid level is dz in time 'dt' the no. of moles of A that diffuse out is $\frac{adz\rho_A}{M_A}$

Material balance over time 'dt'

$$\frac{adz\rho_A}{M_A} = aN_A dt = \frac{aD_{AB} P(p_{A1} - p_{A2})}{RTzp_{BM}} dt \quad (2.111)$$

a is the inner cross sec. area of vertical tube. At time t = 0, the liquid level is z_0 from top and at time t' the level is z'

$$D_{AB} = \frac{RTzp_{BM}\rho_A(z'^2 - z_0^2)}{2PM_A(p_{A1} - p_{A2})t'} \quad (2.112)$$

p_{A1} is vapor pressure at prevailing temperature. At open top of tube, partial pressure of A is virtually zero ($p_{A2}=0$) because A is greatly diluted by gas B flowing at a high rate.

Chapman and Enskog equation

A reasonably accurate theoretical equ. based on kinetic theory of gases.
Diffusion coefficient strongly depends upon interaction parameters of A –B pair.

$$D_{AB} = \frac{1.858 \times 10^{-7} T^{3/2} (1/M_A + 1/M_B)^{1/2}}{P \sigma_{AB}^2 \Omega_D} \quad (2.113)$$

T absolute temperature, in K

M_A, M_B = molecular weight of components A and B

P=total pressure

σ_{AB}^2 = Characteristic length parameter of the binary (data available in literature)

Ω_D =Collision integral (data available in literature)