Transport Phenomena

Section 3: Mass Transfer

Modes of mass transfer

1. **Diffusion**
   - **1a. Molecular diffusion**
   - **1b. Knudsen diffusion (Gas)**
2. **Convection**

Diffusion is more complicated than viscous flow or heat conduction because we have to deal with mixtures (more than one component)

Definitions of C, u, J

1. Concentrations

Mass concentration	$\rho_j = \dfrac{\text{mass of j}}{\text{volume of solution}}$
Molar concentration	$C_j = \dfrac{\rho_j}{M_j} = \dfrac{\text{mole of j}}{\text{volume of solution}}$
Mass fraction	$\omega_j = \dfrac{\rho_j}{\rho} = \dfrac{\rho_j}{\sum_{k=1}^{n} \rho_k} = \dfrac{\text{mass of j}}{\text{total mass}}$
Mole fraction	$x_j = \dfrac{C_j}{C} = \dfrac{C_j}{\sum_{k=1}^{n} C_k} = \dfrac{\text{mole of j}}{\text{total moles}}$

The word "solution" means one phase gaseous, liquid or solid mixtures

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2. Velocities and average velocities

a. **Various species move at different velocities.**

b. **Let v_j be the velocity of the species j relative to the stationary coordinate.**

c. **The local *mass* average velocity is defined as:**

$$v = \frac{\sum_{k=1}^{n} \rho_k v_k}{\sum_{k=1}^{n} \rho_k} = \frac{\sum_{k=1}^{n} \rho_k v_k}{\rho} = \sum_{k=1}^{n} \frac{\rho_k}{\rho} v_k = \sum_{k=1}^{n} \omega_k v_k$$

Note that

$\rho v = \left(\dfrac{\text{total mass}}{\text{volume}}\right) \times \left(\dfrac{\text{distance}}{\text{time}}\right)$ **is the local mass rate through a unit cross section placed perpendicular to the velocity v**

This mass average velocity is the local velocity one would measured by a pitot tube.

d. The local *molar* average velocity is defined as:

$$v^* = \frac{\sum_{k=1}^{n} C_k v_k}{\sum_{k=1}^{n} C_k} = \frac{\sum_{k=1}^{n} C_k v_k}{C} = \sum_{k=1}^{n} \frac{C_k}{C} v_k = \sum_{k=1}^{n} x_k v_k$$

Note that

$$Cv^* = \left(\frac{\text{total mole}}{\text{volume}}\right) \times \left(\frac{\text{distance}}{\text{time}}\right)$$

is the local molar rate through a unit cross section placed perpendicular to the velocity v^*.

3. Diffusion velocities

In flow systems, very often that we are interested in the velocity of species j with respect to v or v^*,

rather than

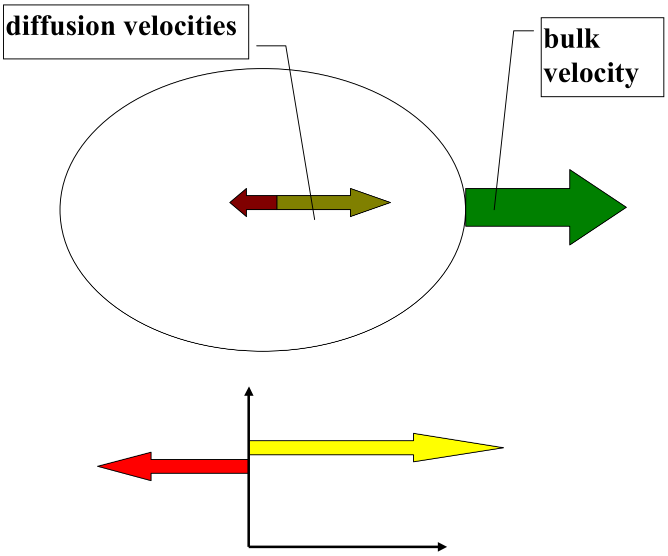
with respect to the stationary coordinates.

Here, we talk of the diffusion velocities, and there are two diffusion velocities:

$$v_j - v \equiv \begin{pmatrix} \text{diffusion velocity of species j} \\ \text{with respect to v} \end{pmatrix}$$

and

$$v_j - v^* \equiv \begin{pmatrix} \text{diffusion velocity of species j} \\ \text{with respect to } v^* \end{pmatrix}$$



There are two diffusion velocities. In applications where we deal with molar flow, the diffusion velocities with respect to v^* will be used.

4. Mass and molar fluxes relative to stationary coordinates

a. *Mass flux*

$$n_j = \rho_j v_j = \left(\frac{\text{mass of species j}}{\text{volume}}\right) \times \left(\frac{\text{distance}}{\text{time}}\right)$$

which is the mass of species j transferred per unit time and per unit area perpendicular to the velocity v_j.

b. *Molar flux*

$$N_j = C_j v_j = \left(\frac{\text{mole of species j}}{\text{volume}}\right) \times \left(\frac{\text{distance}}{\text{time}}\right)$$

which is the moles of species j transferred per unit time and per unit area perpendicular to the velocity v_j.

5. Diffusive mass and molar fluxes

a. *Mass fluxes relative to the local mass average velocity*

$$j_j = \rho_j \left(v_j - v\right)$$

b. *Molar fluxes relative to the local molar average velocity*

$$J_j = C_j \left(v_j - v^*\right)$$

6. Properties of diffusive fluxes

$$\boxed{\sum_{k=1}^{n} j_k = 0; \qquad \sum_{k=1}^{n} J_k = 0}$$

Proof:

By definition:

$$\sum_{k=1}^{n} J_k = \sum_{k=1}^{n} C_k \left(v_k - v^*\right)$$

$$\sum_{k=1}^{n} J_k = \sum_{k=1}^{n} C_k v_k - v^* \sum_{k=1}^{n} C_k$$

$$\sum_{k=1}^{n} J_k = \sum_{k=1}^{n} C_k v_k - v^* C$$

$$\boxed{v^* = \frac{\sum_{k=1}^{n} C_k v_k}{C}}$$

$$\Downarrow$$

$$\sum_{k=1}^{n} J_k = 0$$

$$\sum_{k=1}^{n} J_k = 0$$

This equation means that within the movement of the bulk fluid mixture, the sum of all the diffusive fluxes must be zero so that the pressure is maintained constant.

For a binary mixture, we have:

$$\mathbf{J_1 = - J_2}$$

Two species move in the opposite direction (relative to the movement of the mixture).

7. Diffusive molar fluxes versus molar fluxes

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

Proof:

$$J_k = C_k \left(v_k - v^*\right) = C_k v_k - C_k \frac{\sum_{j=1}^{n} C_j v_j}{C}$$

$$J_k = C_k \left(v_k - v^*\right) = C_k v_k - \frac{C_k}{C} \sum_{j=1}^{n} C_j v_j$$

Therefore

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

This equation simply states that the *diffusive* molar flux of species j is equal to the molar flux minus its contribution in the total flux.

8. Diffusive mass flux versus mass flux

$$j_k = n_k - \omega_k \sum_{j=1}^{n} n_j$$

Fick's law of diffusion for binary mixtures

Here, we first study the diffusion law for binary mixtures: The *Fick's law*

For multicomponent mixtures, the correct law is the Stefan-Maxwell's law. This is more complicated, and will be dealt with much later.

1. The Fick's law:

The basic equation for Fick's law for an isobaric and isothermal system is:

$$\boxed{J_1 = -cD_{12}\frac{dx_1}{dz}}$$

which is the diffusive molar flux along the z direction.

Similarly, we can write an equation for the second species.

$$J_2 = -cD_{21}\frac{dx_2}{dz}$$

But

$$J_1 + J_2 = 0 \quad \text{and} \quad x_1 + x_2 = 1$$

we must have the following important relation:

$$\mathbf{D_{12} = D_{21}}$$

Note: The two diffusion equations are linearly dependent. So only ONE is independent.

For three dimensional coordinates, the general Fick's law equation is:

$$\underline{J}_1 = -cD_{12}\underline{\nabla}x_1$$

and

$$\underline{J}_1 + \underline{J}_2 = \underline{0}$$

2. Equation in terms of the molar flux

The desired equation is:

$$N_1 = J_1 + x_1(N_1 + N_2)$$

$$J_1 = -cD_{12}\frac{dx_1}{dz}$$

$$\boxed{N_1 = -cD_{12}\frac{dx_1}{dz} + x_1(N_1 + N_2)}$$

Similarly, the equation for the species 2:

$$N_2 = -cD_{21}\frac{dx_2}{dz} + x_2(N_2 + N_1)$$

These two equations are not linearly independent. Thus, only ONE is needed, but here we have two fluxes.

More about this later.

For three dimensional coordinates, the general equation involving molar fluxes is:

$$\underline{N}_1 = -cD_{12}\underline{\nabla}x_1 + x_1\left(\underline{N}_1 + \underline{N}_2\right)$$

diffusive term**: resulting from concentration gradient, superimposed on the bulk flow**

convective term**: resulting from the bulk motion of the fluid**

For rectangular coordinates, the equations in component form are:

$$N_{x,1} = -cD_{12}\frac{dx_1}{dx} + x_1\left(N_{x,1} + N_{x,2}\right)$$

$$N_{y,1} = -cD_{12}\frac{dx_1}{dy} + x_1\left(N_{y,1} + N_{y,2}\right)$$

$$N_{z,1} = -cD_{12}\frac{dx_1}{dz} + x_1\left(N_{z,1} + N_{z,2}\right)$$

For cylindrical coordinates, the equations in component form are:

$$N_{z,1} = -cD_{12}\frac{dx_1}{dz} + x_1\left(N_{z,1} + N_{z,2}\right)$$

$$N_{r,1} = -cD_{12}\frac{dx_1}{dr} + x_1\left(N_{r,1} + N_{r,2}\right)$$

3. Diffusion coefficient

a. Units

$$D_{12} \equiv \left[\frac{m^2}{sec}\right]$$

b. Order of magnitude

State	Order of magnitude (cm^2/sec)
Gas	0.1 - 1
Liquid	1×10^{-7} - 1×10^{-5}
Solid	1×10^{-12} - 1×10^{-7}

c. Temperature and pressure dependence

For gases at low density, D increases with T and decreases with pressure.

For liquids and solids, D increases with temperature.

Stefan-Maxwell's law for multicomponent mixtures

The Stefan-Maxwell equation derived for multicomponent gases at low density is:

$$-c\underline{\nabla}x_i = \sum_{j=1}^{n}\frac{\left(x_j\underline{N}_i - x_i\underline{N}_j\right)}{D_{ij}}$$

for i=1, 2, 3, ..., n-1, as only (n-1) above equations are linearly independent. This can be proved by summing the above with respect to i from 1 to n.

Another form of the Stefan-Maxwell equation is:

$$-c\underline{\nabla}x_i = \sum_{j=1}^{n}\frac{\left(x_j\underline{J}_i - x_i\underline{J}_j\right)}{D_{ij}}$$

Theory of D for low density gases

Procedures for binary mixtures

Similar to those we learnt earlier for momentum and energy transfers.

Steps 1 to 4: involve draw a physical diagram and a thin shell with surfaces perpendicular to transport directions.

Step 5: Set up mass balance equation of the thin shell

$$\begin{pmatrix}\text{Rate of}\\ \text{mass in}\end{pmatrix} - \begin{pmatrix}\text{Rate of}\\ \text{mass out}\end{pmatrix} + \begin{pmatrix}\text{Rate of mass}\\ \text{production}\end{pmatrix} = (\text{Accummulation})$$

Taking the shell as thin as possible will yield a first order differential equation in terms of molar flux.

Step 6: Apply the Fick's law

$$N_1 = -cD_{12}\frac{dx_1}{dz} + x_1\left(N_1 + N_2\right)$$

or in three dimensional coordinates

$$\underline{N}_1 = -cD_{12}\underline{\nabla}x_1 + x_1\left(\underline{N}_1 + \underline{N}_2\right)$$

Depending on the physical system, N_2 must be determined based on the physical ground. We see this in a number of simple examples.

Step 7: Impose physical constraints

Step 8: Solve for concentration distribution

Step 9: Solve for desired quantity, such as average concentration, molar fluxes.

Boundary conditions

Generally, there are five boundary conditions:

B.C. of the first kind:

Concentration is specified at the boundary

B.C. of the second kind:

Molar flux is specified at the boundary

B.C. of the third kind:

Molar flux into the medium is the same as the flux through a stagnant film surrounding the medium

B.C. of the fourth kind:

Concentrations and fluxes are continuous across the interface of two adjoining media.

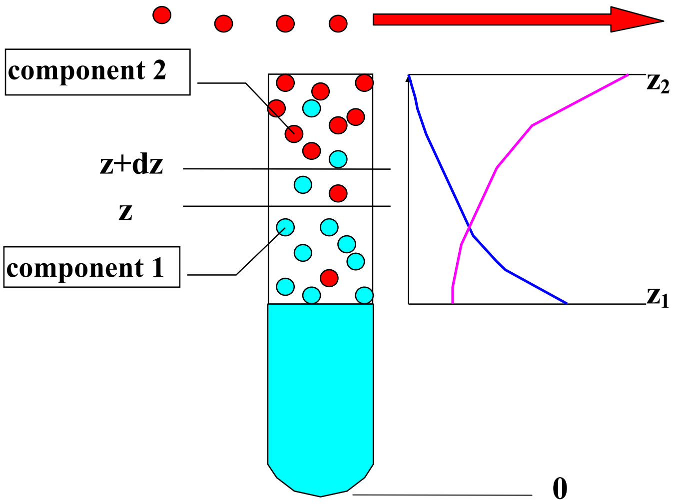
B.C. of the fifth kind:

Molar flux is equal to the surface reaction

Simple problems

1. Diffusion in a Stefan tube
2. Dissolution of a spherical object
3. Diffusion with heterogeneous reaction at surface
4. Diffusion with homogeneous reaction
5. Diffusion into a falling film
6. Gas absorption from a rising bubble
7. Diffusion and reaction in a porous catalyst
8. Transient diffusion through a polymer film
9. Transient diffusion in a finite environment

Diffusion in a Stefan tube



Physical system

1. Liquid 1 in the tube
2. Gas 2 flowing across the mouth of the tube
3. Gas 2 is nonsoluble in liquid 1

Step 5: Shell mass balance

$$\begin{pmatrix}\text{Rate of}\\ \text{mass in}\end{pmatrix}-\begin{pmatrix}\text{Rate of}\\ \text{mass out}\end{pmatrix}+\begin{pmatrix}\text{Rate of mass}\\ \text{production}\end{pmatrix}=(\text{Accummulation})$$

$$S\cdot N_1\big|_z - S\cdot N_1\big|_{z+\Delta z} + 0 = 0$$

Taking the shell as thin as possible:

$$-\frac{dN_1}{dz}=0$$

which simply states that the molar flux is constant along the tube.

Step 6: Apply the Fick's law

$$N_1=-cD_{12}\frac{dx_1}{dz}+x_1(N_1+N_2)$$

is *equal to zero* as the species 2 is nonsoluble in liquid 1. This is called the bootstrap condition.

Thus, we solve for N_1 in terms of the concentration gradient.

$$N_1=-\frac{cD_{12}}{1-x_1}\frac{dx_1}{dz}$$

Substitute this into the mass balance equation:

$$-\frac{dN_1}{dz}=0$$

we get

$$\frac{d}{dz}\left(\frac{cD_{12}}{1-x_1}\frac{dx_1}{dz}\right)=0$$

For constant total pressure and constant diffusion coefficient, we have:

$$\frac{d}{dz}\left(\frac{1}{1-x_1}\frac{dx_1}{dz}\right)=0$$

which is a second-order differential equation in terms of mole fraction.

Step 7: Physical constraint

The two boundary conditions are:

$$z = z_1; \qquad x_1 = x_{1,0} = \frac{p_1^0}{P}$$

vapor pressure

total pressure

$$z = z_2; \qquad x_1 = x_{1,L}$$

Step 8: Concentration distribution

$$\frac{d}{dz}\left(\frac{cD_{12}}{1-x_1}\frac{dx_1}{dz}\right) = 0$$

that is

$$\frac{cD_{12}}{1-x_1}\frac{dx_1}{dz} = K_1 (\text{constant})$$

and hence

$$cD_{12}\ln\left(\frac{1}{1-x_1}\right) = K_1 z + K_2$$

Here, we have two constants K_1 and K_2, so apply the two boundary conditions:

$$@ z = z_1; \quad cD_{12}\ln\left(\frac{1}{1-x_{1,0}}\right) = K_1 z_1 + K_2$$

$$@ z = z_2; \quad cD_{12}\ln\left(\frac{1}{1-x_{1,L}}\right) = K_1 z_2 + K_2$$

Solving for K_1 and K_2, we get:

$$K_1 = \frac{cD_{12}}{z_2 - z_1}\ln\left(\frac{1-x_{1,0}}{1-x_{1,L}}\right)$$

$$K_2 = cD_{12}\ln\left(\frac{1}{1-x_{1,L}}\right) - \frac{cD_{12} z_1}{z_2 - z_1}\ln\left(\frac{1-x_{1,0}}{1-x_{1,L}}\right)$$

Thus, the concentration profile is:

$$\boxed{\left(\frac{1-x_1}{1-x_{1,0}}\right) = \left(\frac{1-x_{1,L}}{1-x_{1,0}}\right)^{(z-z_1)/(z_2-z_1)}}$$

Step 9: Molar flux

The quantity of interest is the molar flux from the liquid surface (evaporation rate):

$$N_1 = -\frac{cD_{12}}{1-x_1}\frac{dx_1}{dz}$$

Where should we evaluate the above derivative to obtain the evaporation rate? At the liquid surface?

Answer:

It is fine at the liquid surface if we wish to obtain the molar flux from the liquid, BUT in this problem it can be evaluated anywhere as the molar flux is constant along the tube.

During the integration for the concentration profile, we see that:

$$\frac{cD_{12}}{1-x_1}\frac{dx_1}{dz} = K_1$$

Thus, the evaporation rate is:

$$N_1 = \frac{cD_{12}}{z_2 - z_1}\ln\left(\frac{1-x_{1,L}}{1-x_{1,0}}\right)$$

This is the desired relation.

If the gas 2 is sweeping past the mouth fast enough, the concentration of the species 1 at the mouth will be effectively zero; hence the evaporation rate is:

$$N_1 = \frac{cD_{12}}{z_2 - z_1}\ln\left(\frac{1}{1-x_{1,0}}\right)$$

Written in terms of pressure, we get:

$$N_1 = \frac{(P/RT)D_{12}}{z_2 - z_1}\ln\left(\frac{1}{1-p_i^0/P}\right)$$

The total molar rate is:

$$N_1 + \overset{\boxed{0}}{\cancel{N_2}} = \frac{(P/RT)D_{12}}{z_2 - z_1}\ln\left(\frac{1}{1 - p_i^0/P}\right)$$

We note that the molar flux of the species 2 is:

$$N_2 = \overbrace{-cD_{12}\frac{dx_2}{dz}}^{\text{diffusive flux down the tube}} + \underbrace{x_2\frac{(P/RT)D_{12}}{z_2 - z_1}\ln\left(\frac{1}{1 - p_i^0/P}\right)}_{\text{convective flux up the tube}} = 0$$

Drop in liquid level

Due to evaporation, the liquid level will drop, and to determine this drop in level versus time, we have to do the mass balance equation around the liquid.

$$\frac{d(Sz_1\rho_L)}{dt} = -SM_1\frac{(P/RT)D_{12}}{z_2 - z_1}\ln\left(\frac{1}{1 - p_1^0/P}\right)$$

The initial condition is:

t=0; $z_1 = z_{10}$

Integration gives the solution:

$$[z_2 - z_1(t)]^2 - (z_2 - z_{10})^2 = \left[2\frac{M_1(P/RT)D_{12}}{\rho_L}\ln\left(\frac{1}{1 - p_1^0/P}\right)\right]t$$

The time it takes to empty the tube is:

$$t^* = \frac{z_2^2 - (z_2 - z_{10})^2}{\left[2\frac{M_1(P/RT)D_{12}}{\rho_L}\ln\left(\frac{1}{1 - p_1^0/P}\right)\right]}$$

Example:

Species 1: Carbon tetrachloride

Species 2: Air

R = 82.05 cm^3-atm/mole/K

Operating conditions

P = 760 mmHg

T = 273 K

Species characteristics

p_1^0 = 33 mmHg

M_1 = 154 g/mole

ρ_L = 1.59 g/cc

D_{12} = 0.0636 cm^2/sec

Tube height and initial liquid level

z_2 = 40 cm

z_{10} = 25 cm

Answer:

t^* = 651 days

Reasons for this extremely long time required to empty the tube:

a. low vapor pressure

b. very long diffusion path in the tube

c. very low diffusion coefficient

Conclusion:

Diffusion is a very slow process. It is always advisable to speed up this process. One way of doing is to reduce the diffusion path length.

Achievable in practice by mixing.

More about Stefan tube

Summary:

$$N_1 = \frac{(P/RT)D_{12}}{z_2 - z_1}\ln\left(\frac{1}{1-p_i^0/P}\right)$$

If we ignore the bulk flow term in the Fick's law equation, that is

$$N_1 = -cD_{12}\frac{dx_1}{dz} + \boxed{x_1(N_1+N_2)}$$

ignore this convective term

then the evaporation flux will be:

$$N_1^0 = \frac{(P/RT)D_{12}(p_1^0/P)}{z_2 - z_1}$$

compared with

To show how much error when the convective term is neglected, we use the example of benzene evaporation at 6 and 60 ^{0}C, and compute:

$$\frac{N_1}{N_1^0} = \frac{\ln\left(\frac{1}{1-p_i^0/P}\right)}{p_i^0/P}$$

Data

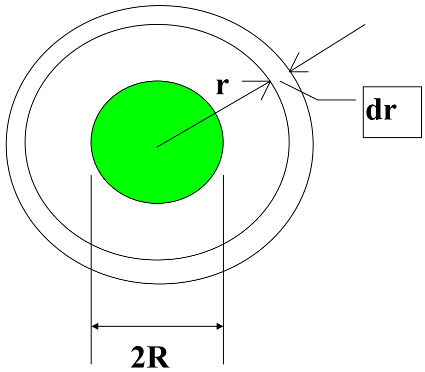
$p_1^0 = 37$ at 6 ^{0}C, 395 mmHg at 60 ^{0}C.

T (^{0}C)	N_1/N_1^0
6	1.025
60	1.41

For low temperature, the convective flux can be ignored but for high temperature it can not be ignored as error is 41%.

Dissolution of a sphere

Sparingly soluble sphere in a surrounding fluid of infinite extent.



The object (species 1) dissolves in surrounding fluid 2 with the solubility of C_{10}.

Step 5: Shell mass balance

The mass balance equation around the thin shell at r and having a thickness of dr is:

$$\left(4\pi r^2 N_1\right)\Big|_r - \left(4\pi r^2 N_1\right)\Big|_{r+\Delta r} + 0 = 0$$

Divide the equation by 4πΔr, and take the limit of the result when Δr approaches zero, we get

$$\lim_{\Delta r\to 0}\frac{\left(r^2N_1\right)\Big|_r - \left(r^2N_1\right)\Big|_{r+\Delta r}}{\Delta r} = -\frac{d}{dr}\left(r^2N_1\right) = 0$$

Step 6: Fick's law equation:

$$N_1 = -cD_{12}\frac{dx_1}{dr} + x_1(N_1 + N_2)$$

can be taken as zero as the species 1 (object) is only sparingly soluble in liquid 2

Thus, the mass balance equation will become:

$$\frac{d}{dr}\left(r^2 cD_{12}\frac{dx_1}{dr}\right) = 0$$

Step 7: Physical constraints

r=R (surface of object); $C_1 = C_{10}$

$r \to \infty$; $C_1 = 0$

Step 8: Concentration distribution

$$C_1 = C_{10}\frac{R}{r}$$

Step 9: Dissolution rate

$$N_1\big|_{r=R} = \frac{D_{12}C_{10}}{R}$$

To increase the dissolution rate:

1. smaller object
2. larger solubility
3. larger diffusivity

If we define the mass transfer coefficient as:

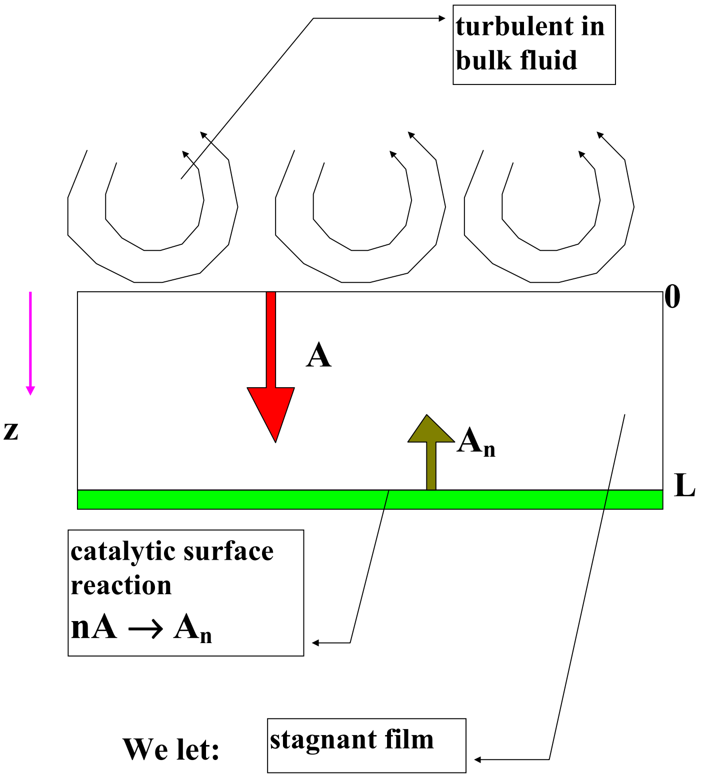
$$N_1\big|_{r=R} = k_m(C_{10} - 0)$$

Matching this with the solution obtained from first principles, we get:

$$\frac{k_m(2R)}{D_{12}} = 2$$

this is known as the Schmidt number, which is equal to 2 for stagnant environment

Diffusion with heterogeneous reaction



We let:

The species A as 1

The species A_n as 2

According to the surface chemical reaction, we must have:

$$N_1 = - n N_2$$

This is the bootstrap condition, needed in addition to the Fick's law equation.

Recall that the bootstrap condition in the last example of the Stefan tube is:

$$N_2 = 0$$

Step 5: Shell mass balance equation

$$-\frac{dN_1}{dz} = 0$$

Step 6: Fick's law

The Fick's law equation is:

$$N_1 = -cD_{12}\frac{dx_1}{dz} + x_1\left(N_1 + N_2\right)$$

But the bootstrap relation is:

$$N_2 = -\frac{1}{n}N_1$$

Thus, solving for N_1 in terms of the concentration gradient gives:

$$N_1 = -\frac{cD_{12}}{\left[1 - \frac{(n-1)}{n}x_1\right]}\frac{dx_1}{dz}$$

Substitute this Fick's law into the mass balance equation, we have:

$$\frac{d}{dz}\left\{\frac{cD_{12}}{\left[1 - \frac{(n-1)}{n}x_1\right]}\frac{dx_1}{dz}\right\} = 0$$

Step 7: Physical constraints

The boundary conditions will be at two ends of the stagnant film:

$$z = 0; \qquad x_1 = x_{10}$$

$$z = L; \qquad N_1\big|_{z=L} = kcx_1\big|_{z=L}$$

where L is the thickness of the film.

The surface chemical reaction rate is:

$$kcx_1\big|_{z=L} \equiv \frac{\text{moles of A reacted}}{\text{area of catalyst} - \text{time}}$$

Observing the boundary condition at the surface of the catalyst, we see that when $k \to \infty$ (very fast chemical reaction), the surface concentration of the species 1 will be practically zero.

Thus, the boundary condition at the surface in the case of fast reaction is:

$$z = L; \qquad x_1\big|_{z=L} = 0$$

We will now solve for the case of fast reaction first, and then return to the case of finite reaction later.

Step 8: Concentration distribution

Recall the mass balance equation

$$\frac{d}{dz}\left\{\frac{cD_{12}}{\left[1-\frac{(n-1)}{n}x_1\right]}\frac{dx_1}{dz}\right\}=0$$

Integrating once:

$$\frac{cD_{12}}{\left[1-\frac{(n-1)}{n}x_1\right]}\frac{dx_1}{dz}=K_1$$

Integrating once more:

$$cD_{12}\ln\left[\frac{1}{1-(n-1)x_1/n}\right]=\frac{(n-1)}{n}K_1z+K_2$$

Two unknown constants of integration with two boundary conditions.

Apply the boundary conditions:

@ z = 0;

$$cD_{12}\ln\left[\frac{1}{1-(n-1)x_{10}/n}\right]=K_2$$

@ z = L; $\frac{(n-1)}{n}K_1L+K_2=0$

from which we can solve for K_1 and K_2.

The concentration distribution:

$$\left[1-\frac{(n-1)}{n}x_1\right]=\left[1-\frac{(n-1)}{n}x_{10}\right]^{(1-z/L)}$$

This equation shows how the concentration of the species 1 will distribute itself in the stagnant film.

The distribution of the species 2 is simply:

$$x_2 = 1 - x_1$$

Step 9: Reaction rate

To calculate the reaction rate, we simply calculate the Fickian flux at the catalytic surface.

$$N_1\Big|_{z=L}=-\frac{cD_{12}}{\left[1-\frac{(n-1)}{n}x_1\right]}\frac{dx_1}{dz}\Bigg|_{z=L}$$

But remember that during the integration, we have:

$$N_1\Big|_{z=L}=-\frac{cD_{12}}{\left[1-\frac{(n-1)}{n}x_1\right]}\frac{dx_1}{dz}\Bigg|_{z=L}=-K_1$$

that is:

$$N_1\Big|_{z=L}=\frac{[n/(n-1)]cD_{12}}{L}\ln\left[\frac{1}{1-(n-1)x_{10}/n}\right]$$

This flux at the surface is exactly the same as the chemical reaction rate.

What do we observe from this?

The chemical reaction rate is:

1. **independent of the reaction rate (system is diffusion controlled)**
2. **a function of the diffusivity**
3. **inversely proportional to the film thickness**
4. **proportional to the total concentration, c**
5. **a function of the bulk mole fraction**

Now we turn to the case when the chemical reaction is finite.

Step 8': Concentration distribution

Recall the mass balance equation and the boundary conditions are:

$$\frac{d}{dz}\left\{\frac{cD_{12}}{\left[1-\frac{(n-1)}{n}x_1\right]}\frac{dx_1}{dz}\right\}=0$$

$$z=0; \qquad x_1 = x_{10}$$

$$z=L; \qquad N_1\big|_{z=L} = kcx_1\big|_{z=L}$$

Integrating the mass balance once:

$$\frac{cD_{12}}{\left[1-\frac{(n-1)}{n}x_1\right]}\frac{dx_1}{dz}=K_1$$

Integrating once more:

$$cD_{12}\ln\left[\frac{1}{1-(n-1)x_1/n}\right]=\frac{(n-1)}{n}K_1 z+K_2$$

Apply the boundary conditions:

$$@\,z=0;$$

$$cD_{12}\ln\left[\frac{1}{1-(n-1)x_{10}/n}\right]=K_2$$

$$@\,z=L; \qquad K_1=-kcx_{1,L}$$

The concentration distribution is:

$$\ln\left[\frac{1-(n-1)x_{1,0}/n}{1-(n-1)x_1/n}\right]=-\frac{(n-1)}{n}\cdot\frac{kx_{1,L}}{D_{12}}z$$

where $x_{1,L}$ is still an unknown mole fraction at the catalytic surface. It is determined by setting z = L

$$\ln\left[\frac{1-(n-1)x_{1,L}/n}{1-(n-1)x_{1,0}/n}\right]=\frac{(n-1)}{n}\cdot\left(\frac{kL}{D_{12}}\right)x_{1,L}$$

which is a nonlinear algebraic equation in terms of the mole fraction at the catalytic surface.

Knowing the mole fraction at the catalytic surface

$$\ln\left[\frac{1-(n-1)x_{1,L}/n}{1-(n-1)x_{1,0}/n}\right]=\frac{(n-1)}{n}\cdot\left(\frac{kL}{D_{12}}\right)x_{1,L}$$

the chemical reaction rate can be obtained from:

$$N_1\big|_{z=L}=\frac{[n/(n-1)]cD_{12}}{L}\ln\left[\frac{1-(n-1)x_{1,L}/n}{1-(n-1)x_{1,0}/n}\right]$$

$$=kcx_{1,L}$$

What do we observe here?

We see that the nonlinear algebraic equation for $x_{1,L}$ involves a dimensionless group

$$\left(\frac{kL}{D_{12}}\right)\equiv\frac{\text{chemical reaction rate}}{\text{diffusion rate}}$$

Case 1: If this group is very large, that is the chemical reaction rate is much larger than the diffusion rate, we get:

$$x_{1,L}=0$$

and the chemical reaction rate is:

$$N_1\big|_{z=L}=\frac{[n/(n-1)]cD_{12}}{L}\ln\left[\frac{1}{1-(n-1)x_{1,0}/n}\right]$$

which is exactly the equation we obtained earlier for fast reaction.

<u>Case 2:</u> When the dimensionless group is less than unity, that is the reaction is very slow compared to the diffusion rate, we have:

$$x_{1,L} = x_{1,0}$$

Thus, the chemical reaction rate is:

$$N_1 = kcx_{1,0}$$

The chemical reaction in the case of fast diffusion is dominated entirely by chemical kinetics.

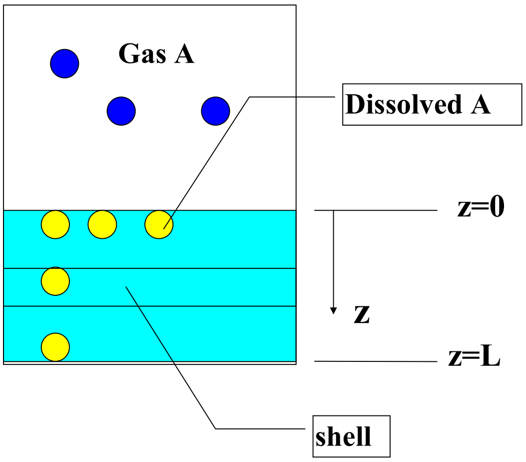
Diffusion & homogeneous reaction

What we have seen so far:

1. Diffusion with bulk flow in a Stefan tube
2. Diffusion with chemical reaction at catalytic surface.

Now we deal with diffusion and homogeneous reaction within the medium.

The difference between this and the last two examples is the appearance of the reaction term in the mass balance equation, in contrast to the second example where the reaction term appears in the boundary condition.



<u>Physical system</u>

1. Gas A dissolves sparingly in liquid B
2. Dissolved A reacted with B, following a first order kinetics with expression

$$\left(\frac{\text{moles of A reacted}}{\text{volume} - \text{time}}\right) = kC_1$$

3. Isothermal system
4. Let species A be 1, and species B be 2

<u>Gas solubility (King, 273)</u>

@ 1 atm and 20 ^{0}C

Gas	mole fraction
SO_2	0.03
Cl_2	0.0017
H_2S	0.002
CO_2	0.00062
C_2H_4	0.0001
CO	0.000018

Solubility, in general, increases linearly with pressure and decreases with temperature.

Step 5: Shell mass balance

$$\begin{pmatrix}\text{Rate of}\\ \text{mass in}\end{pmatrix}-\begin{pmatrix}\text{Rate of}\\ \text{mass out}\end{pmatrix}+\begin{pmatrix}\text{Rate of mass}\\ \text{production}\end{pmatrix}=(\text{Accummulation})$$

$$\left(SN_1\right)\Big|_z-\left(SN_1\right)\Big|_{z+\Delta z}-\left(S\Delta z\right)kC_1=0$$

Divide the shell mass balance by SΔz, and then take the limit when Δz → 0:

$$-\frac{dN_1}{dz}-kC_1=0$$

chemical reaction appearing in the mass balance equation

Step 6: Fick's law

Apply the Fick's law

negligible because A is sparingly soluble in B

$$N_1=-cD_{12}\frac{dx_1}{dz}+\cancel{x_1\left(N_1+N_2\right)}$$

Thus

$$N_1=-D_{12}\frac{dC_1}{dz}$$

Substitute this into the mass balance equation, we get:

$$D_{12}\frac{d^2C_1}{dz^2}-kC_1=0$$

This is a typical form of simultaneous diffusion and reaction equation.

Step 7: Physical constraints

At the gas-liquid interface, we have the solubility condition:

@ z = 0; $C_1 = C_{10}$ (solubility)

For constant T and P, this solubility is a constant.

The other boundary condition is at the bottom of the liquid pool.

At the bottom, mass can not penetrate,

thus:

@ z = L; $N_1 = 0$

Using the Fick's law at this point (z=L), we have:

$$@\,z=L;\quad N_1\Big|_{z=L}=-D_{12}\frac{dC_1}{dz}\bigg|_{z=L}=0$$

Step 8: Concentration distribution

$$\frac{C_1}{C_{10}}=\frac{\cosh\left[\left(1-\frac{z}{L}\right)\sqrt{\frac{kL^2}{D_{12}}}\right]}{\cosh\left(\sqrt{\frac{kL^2}{D_{12}}}\right)}$$

Note that the three parameters of the system, namely

1. **reaction rate constant, k**
2. **depth of the liquid pool, L**
3. **diffusion coefficient, D_{12}**

are grouped together.

It is dimensionless. It is known as the Damkohler* number (1937).

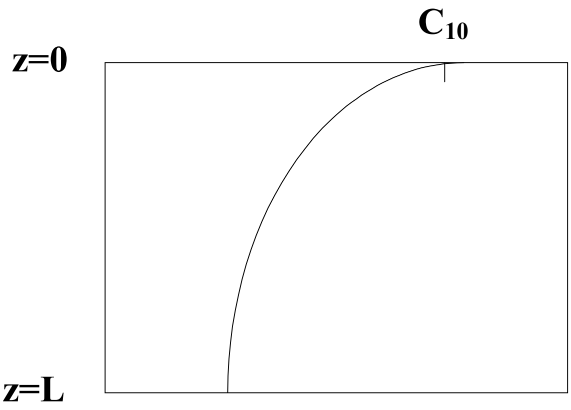
$$Da=\frac{kL^2}{D_{12}}$$

***: German chemist (1908-1944)**

The solution:

$$\frac{C_1}{C_{10}} = \frac{\cosh\left[\left(1-\frac{z}{L}\right)\sqrt{Da}\right]}{\cosh\left(\sqrt{Da}\right)}$$

The good thing about the dimensionless group is that systems having the same value of the dimensionless will behave identically.



Step 9: Mass transfer

To calculate the mass transfer of A (gas absorption rate) into the liquid B, we simply apply the Fick's law and evaluate at the gas-liquid interface.

$$N_1\Big|_{z=0} = -D_{12}\frac{dC_1}{dz}\Big|_{z=0}$$

$$N_1\Big|_{z=0} = \frac{C_{10}D_{12}}{L}\sqrt{Da}\cdot\tanh\left(\sqrt{Da}\right)$$

$$N_1\Big|_{z=0} = \frac{C_{10}D_{12}}{L}\sqrt{\frac{kL^2}{D_{12}}}\cdot\tanh\left(\sqrt{\frac{kL^2}{D_{12}}}\right)$$

This is the gas absorption rate per unit interfacial area.

Let's have a look at the Damkohler number:

$$Da = \frac{kL^2}{D_{12}} \equiv \frac{\left(L^2/D_{12}\right)}{\left(1/k\right)} \equiv \frac{\text{diffusion time}}{\text{reaction time}}$$

There are two extreme cases:

Case 1:

When Da << 1, the diffusion time is very short compared to the reaction time.

Case 2:

When Da >> 1, the diffusion time is much larger than the reaction time.

Case 1: Da << 1

This means that dissolved A will have time to penetrate throughout the liquid B before reaction could take place. One expects:

$$C_1(z) = C_{10}$$

and

$$N_1 = LkC_{10}$$

To prove this expectation, we take the limit of the solution

$$\lim_{Da\to 0} N_1\Big|_{z=0} = \frac{C_{10}D_{12}}{L}Da = LkC_{10}$$

In this case, there is no diffusivity term as the system is *kinetically controlled*

Also the limit of the concentration distribution will give:

$$C_1(z) = C_{10}$$

<u>Case 2:</u> Da >> 1

In this case, the reaction is so fast, so the penetration of the dissolved A can not go far into the liquid pool.

The gas absorption rate is:

$$\lim_{Da>>1} N_1\Big|_{z=0} = \frac{C_{10}D_{12}}{L}\sqrt{Da} = C_{10}\sqrt{k\cdot D_{12}}$$

Observation:

1. Rate is proportional to the solubility
2. Rate is proportional to square root of chemical reaction rate
3. Rate is proportional to square root of diffusivity
4. Rate is independent of the depth of the liquid pool (is this expected?).

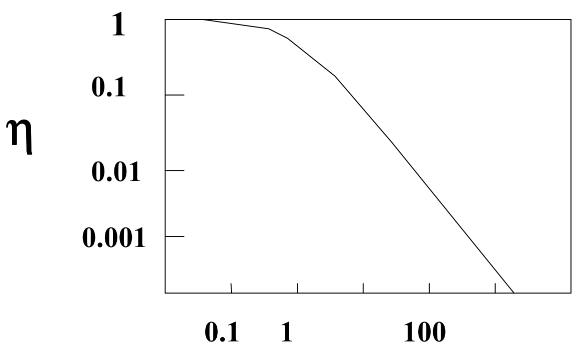
This case is the diffusion-controlled case.

Before we leave this example, there is a quantity that engineers use to quantify the influence of diffusion.

This is the ratio of the true absorption rate to the ideal absorption rate (in the absence of diffusion):

$$\eta = \frac{N_1\big|_{z=0}}{N_1^{\text{no diffusion}}\big|_{z=0}} = \frac{\tanh\left(\sqrt{Da}\right)}{\sqrt{Da}} = \frac{\tanh\left(\sqrt{\frac{kL^2}{D_{12}}}\right)}{\sqrt{\frac{kL^2}{D_{12}}}}$$

This ratio is known as the effectiveness factor.



Diffusion into a falling film

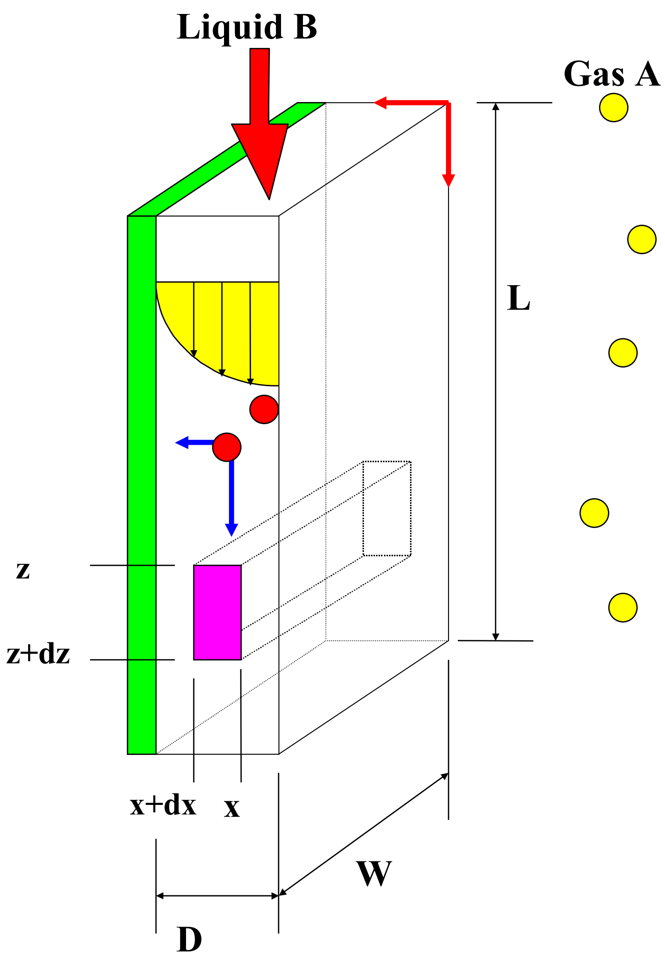
All the examples:

1. Diffusion Stefan tube
2. Diffusion & heterogeneous rxn
3. Diffusion & homogeneous rxn

deal only with diffusion and bulk flow induced by the mass transfer.

Now we deal with mass transfer caused by diffusion and forced convection.

<u>Gas absorption in a falling liquid film.</u>



Step 5: Shell mass balance

$$\underbrace{\begin{pmatrix}\text{Rate of}\\ \text{mass in}\end{pmatrix}}_{\boxed{\left(W\Delta z N_{x,1}\right)\Big|_{x}+\left(W\Delta x N_{z,1}\right)\Big|_{z}}}-\underbrace{\begin{pmatrix}\text{Rate of}\\ \text{mass out}\end{pmatrix}}_{\boxed{\left(W\Delta z N_{x,1}\right)\Big|_{x+\Delta x}+\left(W\Delta x N_{z,1}\right)\Big|_{z+\Delta z}}}+\begin{pmatrix}\text{Rate of mass}\\ \text{production}\end{pmatrix}=\left(\text{Accummulation}\right)$$

$$\boxed{\left(W\Delta z N_{x,1}\right)\Big|_{x}+\left(W\Delta x N_{z,1}\right)\Big|_{z}}-\boxed{\left(W\Delta z N_{x,1}\right)\Big|_{x+\Delta x}+\left(W\Delta x N_{z,1}\right)\Big|_{z+\Delta z}}$$

$$+0=0$$

where

$N_{x,1}$ is the molar flux in the x-direction

$N_{z,1}$ is the molar flux in the z-direction

In the limit of very thin shell

$$\frac{\partial N_{x,1}}{\partial x}+\frac{\partial N_{z,1}}{\partial z}=0$$

Step 6: Fick's law

1. The molar flux in the x-direction

$$N_{x,1}=-D_{12}\frac{\partial C_1}{\partial x}+x_1\left(N_{x,1}+N_{x,2}\right)$$

Since most gases dissolve sparingly in liquid, that is the bulk flow term (second term) is negligible compared to the diffusive term, i.e.

$$N_{x,1}\approx -D_{12}\frac{\partial C_1}{\partial x}$$

The flux in the direction into the bulk liquid to controlled by diffusion.

2. The molar flux in the z-direction

$$N_{z,1}=-D_{12}\frac{\partial C_1}{\partial z}+x_1\left(N_{z,1}+N_{z,2}\right)$$

By definition of the flux:

$$N_{z,1}=C_1 v_{z,1};\qquad N_{z,2}=C_2 v_{z,2}$$

the above equation will become:

$$N_{z,1}=-D_{12}\frac{\partial C_1}{\partial z}+x_1\left(C_1 v_{z,1}+C_2 v_{z,2}\right)$$

Rearrange the above equation as:

$$N_{z,1}=-D_{12}\frac{\partial C_1}{\partial z}+x_1\left(\frac{C_1 v_{z,1}+C_2 v_{z,2}}{C_1+C_2}\right)\left(C_1+C_2\right)$$

But

$$\left(\frac{C_1 v_{z,1}+C_2 v_{z,2}}{C_1+C_2}\right)=\underbrace{v_z(x)}_{\boxed{\textbf{liquid bulk velocity}}}$$

Thus, the molar flux in the z-direction is:

$$N_{z,1}=-D_{12}\frac{\partial C_1}{\partial z}+v_z(x)C_1$$

The second term is simply the convection flux term, and we could have written that term without going through the first principles.

Usually, the diffusion term in the z direction is much smaller in magnitude than the convection term, except in cases where the flow velocity is very slow.

Thus, the molar flux in the z direction is:

$$N_{z,1}\approx v_z(x)C_1$$

Substitute the two fluxes equations

$$N_{x,1} \approx -D_{12}\frac{\partial C_1}{\partial x}\ ; \quad N_{z,1} \approx v_z(x)C_1$$

into the mass balance equation, we get:

$$D_{12}\frac{\partial^2 C_1}{\partial x^2} = v_z(x)\frac{\partial C_1}{\partial z}$$

This is the typical form of diffusion-convection equation.

Recall the conduction-convection equation in a tube is:

$$\alpha\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) = v_z(x)\frac{\partial T}{\partial z}$$

If we deal with heat conduction-convection in a parallel plate system, we will have:

$$\alpha\frac{\partial^2 T}{\partial x^2} = v_z(x)\frac{\partial T}{\partial z}$$

An extreme similarity

Now coming back to our mass balance equation:

$$\boxed{D_{12}\frac{\partial^2 C_1}{\partial x^2}} = \boxed{v_{max}\left[1-\left(\frac{x}{D}\right)^2\right]\frac{\partial C_1}{\partial z}}$$

in which we have used the velocity distribution from the results of momentum analysis done earlier.

diffusion term in x direction

convection term in z direction

All this equation says is that the amount of dissolved A diffusing in the x direction is balanced by the amount of A carried downstream by the fluid.

Step 7: Physical constraints

1. **At entrance of the liquid film:**

   @ z = 0; $C_1 = 0$

2. **At the gas-liquid interface:**

   @ x = 0; $C_1 = C_{10}$ **(solubility)**

   Solubility is constant for a given temperature and pressure in the gas phase.

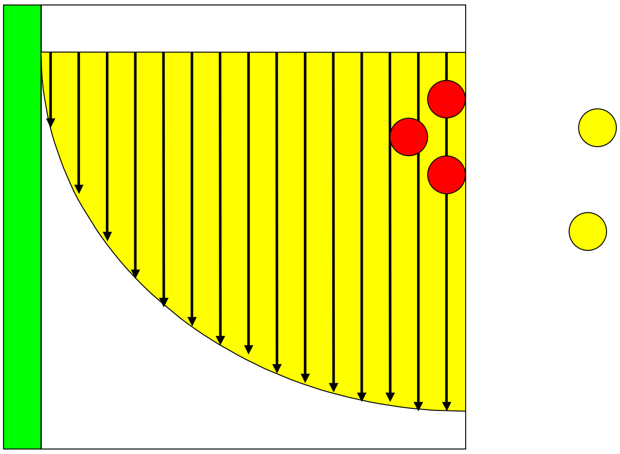
3. **At the liquid-solid surface, there is no penetration of mass in the x-direction:**

   @ x = D; $N_{x,1} = -D_{12}dC_1/dx = 0$

Step 8: Concentration distribution

The mass balance equation together with the three boundary conditions can be readily solved by the separation of variables method.

However, we will deal with the case of short contact time, that is dissolved only travels a short distance into the bulk liquid



Because of the short contact time, the dissolved molecules A will not travel far into the bulk, so:

1. **they will experience only the velocity v_{max}**
2. **the solid surface seems like too far away from them.**

The mass balance and BCs for this short contact time situation are:

$$D_{12}\frac{\partial^2 C_1}{\partial x^2} \approx v_{max}\frac{\partial C_1}{\partial z}$$

**@ $z = 0$;	$C_1 = 0$**

**@ $x = 0$;	$C_1 = C_{10}$**

**@ $x \to \infty$;	$C_1 = 0$**

This set of equations is simpler than the original set, and it can be readily solved by the method of combination of variables ⇒ *<u>Analytical Solutions</u>*

In this method, the concentration distribution of dissolved A behaves like:

$$C_1 = f\left(\frac{x}{\sqrt{z}}\right)$$

instead of

$$C_1 = g(x,z)$$

The solution is:

$$C_1 = C_{10}\left[1 - \mathrm{erf}\left(\frac{x}{\sqrt{4D_{12}z/v_{max}}}\right)\right]$$

where erf is the error function.

This solution is analytical and compact, and is useful in obtaining quantities such as mass transfer rate.

The error function is defined as:

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-x^2}dx$$

and it has the following properties:

1. **erf(0) = 0;**
2. **erf(∞) = 1**
3. $\frac{d}{dz}(\mathrm{erf}(z)) = \frac{2}{\sqrt{\pi}}e^{-z^2}$

You have encounterred the error function when dealing with heat transfer into a semi-infinite object.

<u>Step 9: Desired quantities</u>

The molar flux into the bulk liquid can be calculated from the Fick's law:

$$N_{x,1}\Big|_{x=0} = -D_{12}\frac{\partial C_1}{\partial x}\Big|_{x=0}$$

that is:

$$N_{x,1}\Big|_{x=0} = C_{10}\sqrt{\frac{D_{12}v_{max}}{\pi z}} \qquad \left[\frac{\text{moles of A absorbed}}{\text{int erfacial area} - \text{time}}\right]$$

<u>Observation</u>

1. **This molar flux is decreasing with respect to distance x as the driving force is lower.**
2. **This flux is infinite @ z = 0, because of the infinite driving force at that point.**

   Infinite flux? Does this worry us?

Answer:

No it should not worry us, because we are interested in the amount of moles absorbed over a certain length of the film, which is:

$$M_1 = W\int_0^L N_{x,1}\Big|_{x=0} dz = W\int_0^L C_{10}\sqrt{\frac{D_{12}v_{max}}{\pi z}}dz$$

$$M_1 = (WL)C_{10}\sqrt{\frac{4D_{12}v_{max}}{\pi L}}$$

Observation

The mass transfer is proportional to:

1. **solubility**
2. **square root of the diffusivity**
3. **the width of the film**
4. **square root of the length**

and it is inversely proportional to

5. **square root of the exposure (contact) time between the gas and liquid. The exposure time is**

$$\frac{L}{v_{max}}$$

Another quantity of interest is the average exit concentration. It is defined as:

$$F\cdot\overline{C}_{1,exit} = M_1$$

where F is the volumetric flow rate, which is:

$$F = (WD)\overline{v} = (WD)\frac{2}{3}v_{max}$$

Thus

$$\overline{C}_{1,exit} = C_{10}\sqrt{\frac{3}{\pi}}\cdot\sqrt{\frac{D_{12}L}{D^2 v_{max}}}$$

Observation of the average exit conc.

$$\overline{C}_{1,exit} = C_{10}\sqrt{\frac{3}{\pi}}\cdot\sqrt{\frac{D_{12}L}{D^2 v_{max}}}$$

Rearrange it as follows:

$$\overline{C}_{1,exit} = C_{10}\sqrt{\frac{3}{\pi}}\cdot\sqrt{\frac{(L/v_{max})}{(D^2/D_{12})}}$$

But

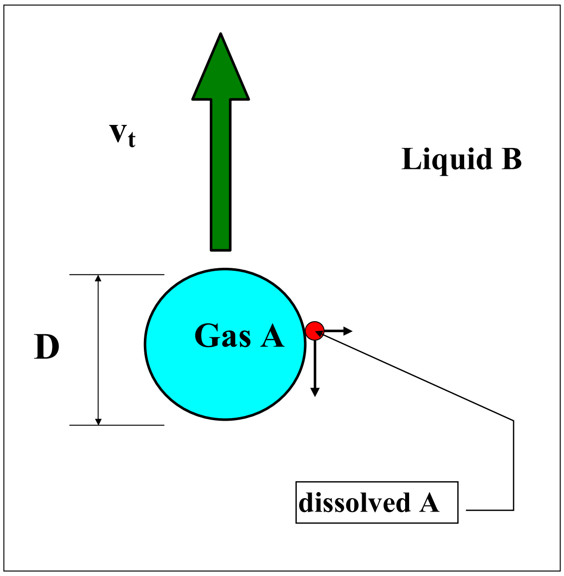
L/v_{max} = exposure time

D^2/D_{12} = diffusion time

This means that how much we have at the exit depends on the ratio of these two time scales, i.e.

$$\overline{C}_{1,exit} = C_{10}\sqrt{\frac{3}{\pi}}\cdot\sqrt{\frac{\text{exposure time}}{\text{diffusion time}}}$$

Gas absorption from rising bubble



The physical situation of gas absorption from a rising bubble is very complicated, but

we can apply the result of the previous analysis into this problem:

$$\begin{pmatrix}\text{Average}\\ \text{molar flux}\end{pmatrix}=\frac{M_1}{WL}=C_{10}\sqrt{\frac{4D_{12}v_{\max}}{\pi L}}$$

In the context of the rising bubble, we have the following variable transformation.

Falling film	**Rising bubble**
v_{max}	v_t
L	**D**

where v_t is the terminal velocity, and D is the bubble diameter.

Thus, the average molar flux out of the bubble is:

$$\overline{N}_1=C_{10}\sqrt{\frac{4D_{12}v_t}{\pi D}}$$

To find out how quick the bubble would deplete, we do a mass balance around a bubble, i.e.

$$\frac{d}{dt}\left(\frac{\pi D^3}{6}\frac{p_0}{RT}\right)=-\left(\pi D^2\right)C_{10}\sqrt{\frac{4D_{12}v_t}{\pi D}}$$

where p_0 is the bubble pressure.

But the terminal velocity v_t is a function of bubble diameter, as shown below:

$$v_t=\frac{g\Delta\rho D^2}{18\mu}$$

So the mass balance equation of a bubble is:

$$\frac{dD}{dt}=-2D\cdot\left(\frac{C_{10}}{p_0/RT}\right)\sqrt{\frac{4D_{12}}{\pi}}\sqrt{\frac{g\Delta\rho}{18\mu}}$$

This is a first-order ODE in terms of diameter D. The initial condition is:

@ t = 0; D = D_0 (initial size)

Integrate the above equation, we get:

$$\sqrt{D}=\sqrt{D_0}-\gamma t$$

where

$$\gamma=\left(\frac{C_{10}}{p_0/RT}\right)\sqrt{\frac{4D_{12}}{\pi}}\sqrt{\frac{g\Delta\rho}{18\mu}}$$

This equation will describe how the bubble diameter changes with time.

The time it takes for the bubble to disappear is:

$$t^*=\frac{1}{\gamma}\sqrt{D_0}$$

The time it takes for the bubble to disappear is not of too much interest to engineers. What we want is the height required for the bubble to disappear.

This height can be calculated from:

$$H=\int_0^{t^*}v_t\,dt$$

But

$$v_t=\frac{g\Delta\rho D^2}{18\mu}=\frac{g\Delta\rho}{18\mu}\left[\sqrt{D_0}-\gamma t\right]^2$$

Therefore, the height can be calculated as follows:

$$H = \left(\frac{g\Delta\rho}{18\mu}\right)\left(\frac{1}{5\gamma}\right)D_0^{5/2}$$

or

$$H = \left(\frac{\sqrt{\pi}}{30\sqrt{2}}\right)\cdot\left(\sqrt{\frac{g\Delta\rho}{\mu D_{12}}}\right)\cdot\left(\frac{p_0/RT}{C_{10}}\right)\cdot D_0^{5/2}$$

Observation:

The height required to rid of bubble is proportional to:

1. **$D_0^{5/2}$**
2. **bubble pressure, p_0**
3. **square root of density difference**

and is inversely proportional to:

4. **square root of diffusivity**
5. **solubility**

Example:

Chlorine gas absorption in water.

D_{12} = 1.55×10^{-8} ft^2/sec
ρ = 59.4 lb/ft^3
μ = 6.73×10^{-4} lb/ft/sec
g = 32.17 ft/sec^2

p_0 = 1 atm
R = 0.73 atm-ft^3/lbmole/R
T = 528 R

D_0 = 0.00328 ft
C_{10} = 0.01412 lbmole/ft^3

The height required is

2

The height is 2 cm. It is so short because of the small size of the bubble.

If the initial bubble size is 1 cm, the height required is 6.6 m!

This is to show that how quick the height will increase with the bubble size. Remember the functional dependence on the bubble size is

$$D^{5/2}$$

Equations of change for binary mixtures

1. Mass units

We apply the law of conservation of mass to an element of volume ΔxΔyΔz, fixed in space and through which a mixture (species 1 and 2) is flowing.

Also in this volume, there is a chemical reaction per unit volume:

$$r_1 \ \& \ r_2 \equiv \left[\frac{\text{g produced}}{\text{cm}^3 - \text{sec}}\right]$$

The mass balance equations are:

$$\boxed{\frac{\partial \rho_1}{\partial t} + \left(\underline{\nabla} \bullet \underline{n}_1\right) = r_1, \quad \frac{\partial \rho_2}{\partial t} + \left(\underline{\nabla} \bullet \underline{n}_2\right) = r_2}$$

where n_1 and n_2 are mass flux of 1 and 2.

Summing the two equations, we get:

$$\frac{\partial (\rho_1 + \rho_2)}{\partial t} + \left(\underline{\nabla} \bullet \left(\underline{n}_1 + \underline{n}_2\right)\right) = r_1 + r_2$$

But

$r_1 + r_2 = 0$ (conservation of mass)

and

$$\left(\underline{\nabla} \bullet \left(\underline{n}_1 + \underline{n}_2\right)\right) = \left(\underline{\nabla} \bullet \left(\rho_1 \underline{v}_1 + \rho_2 \underline{v}_2\right)\right) = \left(\underline{\nabla} \bullet \rho \underline{v}\right)$$

we have the following equation of continuity for the mixture:

$$\boxed{\frac{\partial \rho}{\partial t} + \left(\underline{\nabla} \bullet \rho \underline{v}\right) = 0}$$

The mass balance equations written in terms of the mass flux are not useful in getting the concentration profiles.

SO

We have to use the relationship between the mass flux and the mass conc.

$$\underline{n}_1 = -\rho D_{12} \underline{\nabla} \omega_1 + \omega_1 \left(\underline{n}_1 + \underline{n}_2\right)$$

$$\underline{n}_2 = -\rho D_{12} \underline{\nabla} \omega_2 + \omega_2 \left(\underline{n}_1 + \underline{n}_2\right)$$

and get:

$$\boxed{\begin{aligned} \frac{\partial \rho_1}{\partial t} + \left(\underline{\nabla} \bullet \rho_1 \underline{v}\right) &= \left(\underline{\nabla} \bullet \rho D_{12} \underline{\nabla} \omega_1\right) + r_1 \\ \frac{\partial \rho_2}{\partial t} + \left(\underline{\nabla} \bullet \rho_2 \underline{v}\right) &= \left(\underline{\nabla} \bullet \rho D_{12} \underline{\nabla} \omega_2\right) + r_2 \end{aligned}}$$

Summing these two equations, we get:

$$\frac{\partial \rho}{\partial t} + \left(\underline{\nabla} \bullet \rho \underline{v}\right) = 0$$

which is the total mass balance.

1. Mole units

We have obtained necessary equations written in mass units. Now let apply the same procedure to obtain the mass balance in mole units.

The chemical reaction rates per unit volume are:

$$R_1 \ \& \ R_2 \equiv \left[\frac{\text{moles produced}}{\text{cm}^3 - \text{sec}}\right]$$

The mass balance equations are:

$$\frac{\partial c_1}{\partial t} + \left(\underline{\nabla} \bullet \underline{N}_1\right) = R_1$$

$$\frac{\partial c_2}{\partial t} + \left(\underline{\nabla} \bullet \underline{N}_2\right) = R_2$$

where N_1 and N_2 are *molar* flux vectors of 1 and 2.

Summing the two equations, we get:

$$\frac{\partial c}{\partial t} + \left(\underline{\nabla} \bullet \left(\underline{N}_1 + \underline{N}_2\right)\right) = R_1 + R_2$$

But

$$\left(\underline{\nabla} \bullet \left(\underline{N}_1 + \underline{N}_2\right)\right) = \left(\underline{\nabla} \bullet \left(c_1 \underline{v}_1 + c_2 \underline{v}_2\right)\right) = \left(\underline{\nabla} \bullet c \underline{v}^*\right)$$

we have the following equation of continuity for the mixture:

$$\frac{\partial c}{\partial t} + \left(\underline{\nabla} \bullet c \underline{v}^*\right) = R_1 + R_2$$

Since moles are generally not conserved, $R_1 + R_2$ is not zero unless one mole of species 2 is produced for every mole of species 1 consumed (or vice versa).

Now we relate the molar fluxes in terms of the mole fractions, using:

$$\underline{N}_1 = -cD_{12}\underline{\nabla}y_1 + y_1\left(\underline{N}_1 + \underline{N}_2\right)$$

$$\underline{N}_2 = -cD_{12}\underline{\nabla}y_2 + y_2\left(\underline{N}_1 + \underline{N}_2\right)$$

we get:

$$\boxed{\begin{aligned} \frac{\partial c_1}{\partial t} + \left(\underline{\nabla} \bullet c_1\underline{v}^*\right) &= \left(\underline{\nabla} \bullet cD_{12}\underline{\nabla}y_1\right) + R_1 \\ \frac{\partial c_2}{\partial t} + \left(\underline{\nabla} \bullet c_2\underline{v}\right) &= \left(\underline{\nabla} \bullet cD_{12}\underline{\nabla}y_2\right) + R_2 \end{aligned}}$$

Summing the two equations, we have:

$$\frac{\partial c}{\partial t} + \left(\underline{\nabla} \bullet c\underline{v}^*\right) = R_1 + R_2$$

Special case: Constant mixture density & D

The starting equations are:

$$\frac{\partial \rho_1}{\partial t} + \left(\underline{\nabla} \bullet \rho_1\underline{v}\right) = \left(\underline{\nabla} \bullet \rho D_{12}\underline{\nabla}\omega_1\right) + r_1$$

$$\frac{\partial \rho_2}{\partial t} + \left(\underline{\nabla} \bullet \rho_2\underline{v}\right) = \left(\underline{\nabla} \bullet \rho D_{12}\underline{\nabla}\omega_2\right) + r_2$$

At constant density of the mixture, the above equations become:

$$\frac{\partial \rho_1}{\partial t} + \left(\underline{v} \bullet \underline{\nabla}\rho_1\right) = D_{12}\left(\nabla^2\rho_1\right) + r_1$$

$$\frac{\partial \rho_2}{\partial t} + \left(\underline{v} \bullet \underline{\nabla}\rho_2\right) = D_{12}\left(\nabla^2\rho_2\right) + r_2$$

in which we have used the continuity equation for a constant density mixture:

$$\left(\underline{\nabla} \bullet \underline{v}\right) = 0$$

Furthermore, if we divide the mass balance equations by their molecular weights, we get:

$$\frac{\partial c_1}{\partial t} + \left(\underline{v} \bullet \underline{\nabla}c_1\right) = D_{12}\left(\nabla^2 c_1\right) + R_1$$

$$\frac{\partial c_2}{\partial t} + \left(\underline{v} \bullet \underline{\nabla}c_2\right) = D_{12}\left(\nabla^2 c_2\right) + R_2$$

This equation is used for:

1. **dilute liquid solutions at constant T and pressure.**

Special case: Constant c & D

The starting equations are:

$$\frac{\partial c_1}{\partial t} + \left(\underline{\nabla} \bullet c_1\underline{v}^*\right) = \left(\underline{\nabla} \bullet cD_{12}\underline{\nabla}y_1\right) + R_1$$

$$\frac{\partial c_2}{\partial t} + \left(\underline{\nabla} \bullet c_2\underline{v}\right) = \left(\underline{\nabla} \bullet cD_{12}\underline{\nabla}y_2\right) + R_2$$

At constant c and D$_{12}$, they become:

$$\frac{\partial c_1}{\partial t} + \left(\underline{v}^* \bullet \underline{\nabla} \bullet c_1\right) = D_{12}\nabla^2 c_1 + R_1 - \frac{c_1}{c}\left(R_1 + R_2\right)$$

$$\frac{\partial c_2}{\partial t} + \left(\underline{v}^* \bullet \underline{\nabla} \bullet c_2\right) = D_{12}\nabla^2 c_2 + R_2 - \frac{c_2}{c}\left(R_1 + R_2\right)$$

in which we have used the continuity equation for the mixture:

$$\cancel{\frac{\partial c}{\partial t}} + \left(\underline{\nabla} \bullet c\underline{v}^*\right) = R_1 + R_2$$

0 because of constant c

These eqns are used for low density gases at constant T and pressure.

Special case: No reaction & zero velocity

In this case, the mass balance equations are:

$$\frac{\partial c_1}{\partial t} = D_{12} \nabla^2 c_1$$

$$\frac{\partial c_2}{\partial t} = D_{12} \nabla^2 c_2$$

which are now well known in the literature as the Fick's second law of diffusion.

These equations are valid in:

1. **Solids or stationary liquids**
2. **equimolar, counter-diffusion of gas**

Equations of change for multicomponent systems

The equation of continuity for each species

$$\boxed{\frac{D}{Dt}\rho_i = -\rho_i (\underline{\nabla} \bullet \underline{v}) - (\underline{\nabla} \bullet \underline{j}_i) + r_i}$$

for i=1,2, ..., n.

Here, r_i is the mass rate of reaction per unit volume, i.e.

$$\sum_{i=1}^{n} r_i = 0$$

which is the law of conservation of mass.

Also, according to the definition of the diffusive fluxes:

$$\sum_{i=1}^{n} \underline{j}_i = \underline{0}$$

Summing the individual mass balance equations wrt i=1,...,n, gives:

$$\frac{\partial \rho}{\partial t} + (\underline{\nabla} \bullet \rho \underline{v}) = 0$$

which is the continuity eqn for mixture

For fluids of constant mass density ρ, the continuity equation of the mixture is:

$$(\underline{\nabla} \bullet \underline{v}) = 0$$

Unsteady state evaporation

Take the example of Stefan tube.

<u>Liquid A</u>: Species 1

<u>Gas B</u>: Species 2

<u>1. Mass balance equations:</u>

Carrying out the mass balance on an element, we get the following two equation for species 1 and 2:

$$\frac{\partial c_1}{\partial t} = -\frac{\partial N_1}{\partial z}; \qquad \frac{\partial c_2}{\partial t} = -\frac{\partial N_2}{\partial z}$$

Adding the two equations gives the total mass balance:

$$\frac{\partial c}{\partial t} = -\frac{\partial (N_1 + N_2)}{\partial z}$$

2. Evaluation of total flux

Since the system is at constant pressure, the total mass balance eqn become:

$$\frac{\partial(N_1+N_2)}{\partial z}=0$$

which simply means that N_1 + N_2 is a function of time only, that is:

$$(N_1+N_2)=f(t)=N_{1,0}+N_{2,0}$$

At the liquid-gas interface (z=0), gas B is not soluble, i.e. $N_{2,0}$ = 0; hence

$$(N_1+N_2)=N_{1,0}$$

Using the Fick's law equation, we have:

$$N_{1,0}=-\frac{cD_{12}}{1-y_{1,0}}\frac{\partial y_1}{\partial z}\bigg|_{z=0}$$

Thus, the total flux is:

$$N_1+N_2=N_{1,0}=-\frac{cD_{12}}{1-y_{1,0}}\frac{\partial y_1}{\partial z}\bigg|_{z=0}$$

3. The Fick's law equation

Substitute the total flux to the Fick's law equation, we get:

$$N_1=-cD_{12}\frac{\partial y_1}{\partial z}+y_1\left(\frac{cD_{12}}{1-y_{1,0}}\frac{\partial y_1}{\partial z}\bigg|_{z=0}\right)$$

4. The final form of governing equation

Finally, put this Fick's law into the mass balance equation, we have:

$$\frac{\partial y_1}{\partial t}=D_{12}\frac{\partial^2 y_1}{\partial z^2}+\left(\frac{D_{12}}{1-y_{1,0}}\frac{\partial y_1}{\partial z}\bigg|_{z=0}\right)\frac{\partial y_1}{\partial z}$$

The initial and boundary conditions are:

@ t = 0; $y_1 = 0$

@ z = 0; $y_1 = y_{1,0}$

@ z → ∞; $y_1 = 0$

5. Combination of variables

Introduce:

$$Y=\frac{y_1}{y_{1,0}};\qquad Z=\frac{z}{\sqrt{4D_{12}t}}$$

the mass balance will become:

$$\frac{d^2Y}{dZ^2}+2(Z-\varphi)\frac{dY}{dZ}=0$$

subject to:

@ Z = 0; Y = 1

@ Z = ∞; Y = 0

where φ is:

$$\varphi=-\frac{1}{2}\frac{y_{1,0}}{1-y_{1,0}}\frac{\partial Y}{\partial Z}\bigg|_{z=0}$$

We have reduced a partial differential equation to a second order ODE!

6. Solution for concentration profiles:

Solution is:

$$Y=\frac{1-\mathrm{erf}(Z-\varphi)}{1+\mathrm{erf}(\varphi)}$$

Remember that φ is still an unknown. Differentiate the above equation

$$\frac{dY}{dZ}=-\frac{2}{\sqrt{\pi}}\frac{\exp\left[-(Z-\varphi)^2\right]}{1+\mathrm{erf}(\varphi)}$$

Substitute this into

$$\varphi=-\frac{1}{2}\frac{y_{1,0}}{1-y_{1,0}}\frac{\partial Y}{\partial Z}\bigg|_{z=0}$$

to get:

$$\frac{1}{y_{1,0}}=1+\frac{1}{\sqrt{\pi}(1+\mathrm{erf}\varphi)\varphi e^{\varphi^2}}$$

This is a nonlinear equation in terms of φ, and it can be solved for a given $y_{1,0}$.

7. The evaporation rate:

From the Fick's law

$$N_{1,0} = -\frac{cD_{12}}{1-y_{1,0}}\left.\frac{\partial y_1}{\partial z}\right|_{z=0}$$

Written in terms of Y and Z:

$$N_{1,0} = -\frac{cy_{1,0}}{1-y_{1,0}}\frac{\sqrt{D_{12}}}{\sqrt{4t}}\left.\frac{\partial Y}{\partial Z}\right|_{z=0}$$

We then finally get:

$$N_{1,0} = c\varphi\sqrt{\frac{D_{12}}{t}} \quad \equiv \left[\frac{\text{moles evaporated}}{\text{area} - \text{time}}\right]$$

The rate of volume of evaporation is:

$$c\frac{dV_1}{dt} = Ac\varphi\sqrt{\frac{D_{12}}{t}}$$

Integrating will give:

$$V_1 = A\varphi\sqrt{4D_{12}t}$$

8. Diffusivity determination

The useful equation is:

$$V_1 = A\varphi\sqrt{4D_{12}t}$$

The volume of evaporation can be measured as function of time. Thus, a plot of $V_1/(2A)$ versus square root of time will give a slope:

$$\varphi\sqrt{D_{12}}$$

from which the diffusivity can be calculated.

Note: Again we see the square root of time dependence. This is the property of diffusion process.