2

Mass Transfer Coefficient & Interphase Mass Transfer

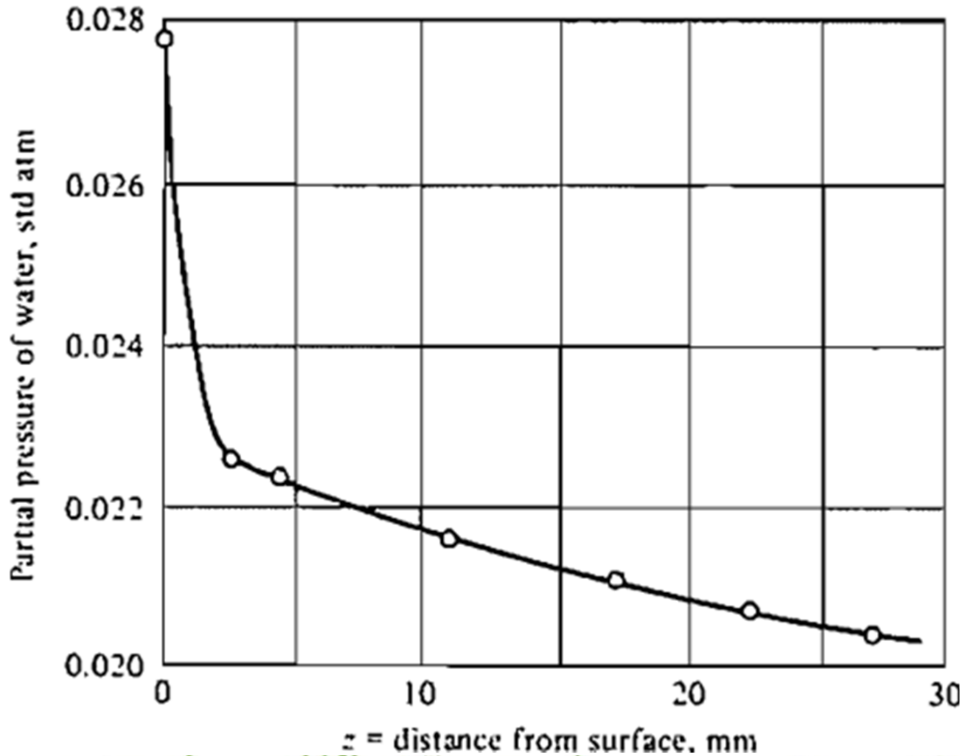
The rate of diffusion under molecular diffusion in stagnant fluids or fluids at laminar flow are very slow.

In the turbulent region, when a fluid flows past a solid surface, three regions for mass transfer can be visualized.

- Laminar or thin viscous sub layer very adjacent to the surface where most of the mass transfer occurs by molecular diffusion due to which a sudden concentration drop is seen.
- A gradual change in concentration of the diffusing substance is obtained in transition region.
- In the turbulent region, a very small variation in the concentration is observed since the eddies present, which tend to make the fluid in more uniform concentration.

Example:

Air in turbulent motion flowed past a water surface



Mass Transfer coefficient

Turbulent flow mechanism is yet to be understood, it is better to express the turbulent diffusion in similar manner as that of molecular diffusion.

Molecular diffusion is characterized by the term D_{AB} C/Z as in Equation, which is characteristic of molecular diffusion, is replaced by F, a mass transfer coefficient for binary system.

Flux depends upon the cross sectional surface area which may vary, the diffusional path which is not specifically known and the bulk average concentration difference.

Hence, Flux can be written using a convective mass transfer coefficient.

Flux = (coefficient) (concentration difference)

Since concentration can be expressed in many ways, different types of equation are possible as mentioned below.

1. For transfer of A through stagnant B [$N_B = 0$]

   For gases: $N_A = k_G (p_{A1} - p_{A2}) = k_y (y_{A1} - y_{A2}) = k_C (C_{A1} - C_{A2})$

   For liquids: $N_A = k_x (x_{A1} - x_{A2}) = k_L (C_{A1} - C_{A2})$

   Where k_G, k_y, k_C, k_x, and k_L are individual mass transfer coefficients.

2. For equimolar counter current diffusion [N_A = -N_B]

For gases: $N_A = k'_G (p_{A1} - p_{A2}) = k'_y (y_{A1} - y_{A2}) = k'_C (C_{A1} - C_{A2})$

For liquids: $N_A = k'_x (x_{A1} - x_{A2}) = k'_L (C_{A1} - C_{A2})$

Where k'_G, k'_y, k'_C, k'_x, and k'_L are individual mass transfer coefficients.

k_c is replacement of DAB C/Z used for low mass transfer rates.

F can be used for high mass transfer rates and it can be related to k's as F = $k_G(p_B)_{lm}$. The other relations of mass transfer coefficient and flux equation given in table.

The mass transfer coefficient can also be correlated as a dimensionless factor J_D by

$$J_D = \left(\frac{k'_c}{V}\right)(N_{SC})^{2/3}$$

Where V is the mass average velocity of the fluid, and

N_{SC} is Schmidt number i.e.

$$\left(\frac{\mu}{\rho D_{AB}}\right)$$

Where ρ and μ are density and viscosity of the mixture respectively.

Table Relations between mass transfer coefficient

Gases:

$$F = k_G \cdot (\bar{p}_B)_{lm} = k_y \cdot \frac{(\bar{p}_B)_{lm}}{P_t} = k_C \frac{(p_B)_{lm}}{RT} = \frac{k_Y}{M_B} = k'_G P_t = k'_C \cdot \frac{P_t}{RT} = k'_C C$$

$$= k_y(y_{BM}) = k'_y$$

Liquids:

$$F = k_x (x_B)_{lm} = k_L (x_B)_{lm}\, C = (k'_L)\; C = (k'_L)\left(\frac{\rho}{M}\right) = k'_x$$

Units of Mass Transfer Coefficient:

$$k'_G \text{ and } k_G = \frac{\text{Moles transferred}}{\text{(Area)(time)(pressure)}}$$

$$k'_x, k'_y, k_x \text{ and } k_y = \frac{\text{Moles transferred}}{\text{(Area)(time)(mole fraction)}}$$

$$k'_C, k_C, k'_L \text{ and } k_L = \frac{\text{Mole transferred}}{\text{(Area)(time)(mol/vol)}}$$

$$k_Y = \frac{\text{Mass transferred}}{\text{(Area)(time)(mass A/mass B)}}$$

Mass Transfer Coefficients in Laminar Flow

When mass transfer occurs in a fluid flowing in laminar flow, it follows the same phenomena of heat transfer by conduction in laminar flow. However, both heat and mass transfer are not always analogous since mass transfer involves multicomponent transport.

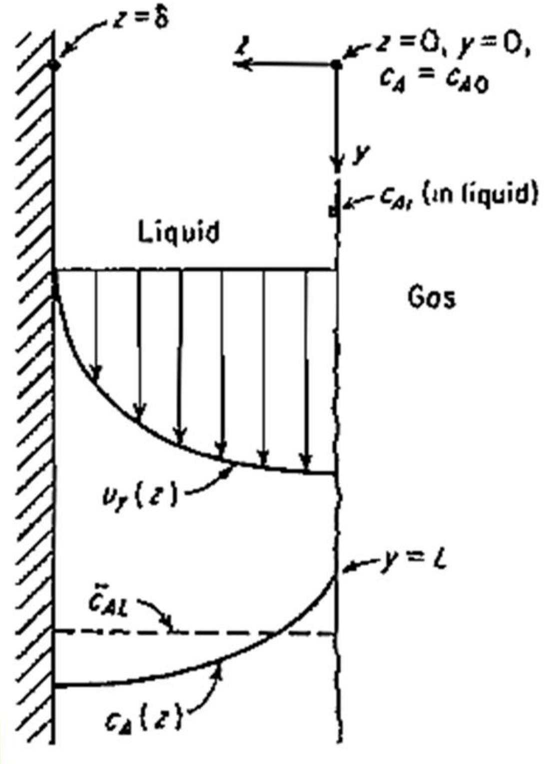
Thus, it needs some simplications to manipulate the mathematical equations for condition of laminar flow in many complex situations.

Mass transfer from gas into a falling liquid film

A liquid falling in a thin film in laminar flow down a vertical flat surface while being exposed to a gas A, which dissolves in the liquid shown in fig. This is similar to absorption of solute from gas into a falling liquid film as in wetted wall column.

Here the laminar flow of liquid and diffusion occur in such conditions that the velocity field can be virtually unaffected by the diffusion.

The liquid contains a uniform concentration C_{A0} of A at the top.



At the liquid surface, the concentration of the dissolved gas is $C_{A,i}$, in equilibrium with the pressure of A in the gas phase.

Since $C_{A,i} > C_{A0}$, gas dissolves in the liquid. The problem is to obtain the mass transfer coefficient k_L, with which the amount of gas dissolved after the liquid falls the distance L can be computed.

The problem is solved by simultaneous solution of the equation of continuity for component A with the equation describing the liquid motion (Navier-stokes equation).

Following assumption are taken to simplify the solution process:

1. There is no chemical reaction. $R_A = 0$
2. Conditions do not change in the x direction (perpendicular to the plane of slide). All derivatives with respect to x = 0.
3. Steady state conditions prevail. $\partial c_A/\partial \theta = 0$
4. The rate of absorption of gas is very small. This means that u_z due to diffusion of A is essentially zero.
5. Diffusion of A in the y direction is negligible in comparison with the movement of A downward due to bulk flow. Therefore, $D_{AB}\, \partial^2 c_A/\partial y^2 = 0$
6. Physical properties (D_{AB}, ρ, μ) are constant.

Equation of continuity for component A

$$u_x \frac{\partial c_A}{\partial x} + u_y \frac{\partial c_A}{\partial y} + u_z \frac{\partial c_A}{\partial z} + \frac{\partial c_A}{\partial \theta} = D_{AB}\left(\frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2} + \frac{\partial^2 c_A}{\partial z^2}\right) + R_A$$

After considering assumption equation reduces to

$$u_y \frac{\partial c_A}{\partial y} = D_{AB} \frac{\partial^2 c_A}{\partial z^2}$$

This signify that any A added to the liquid running down at any location z shows increment in y. The equations of motion under these condition reduces to

$$\mu \frac{d^2 u_y}{dz^2} + \rho g = 0$$

The solution of equation with the conditions that $u_y = 0$ at $z = \delta$ and that $du_y/dz = 0$ at $z = 0$, is well known

$$u_y = \frac{\rho g \delta^2}{2\mu}\left[1 - \left(\frac{z}{\delta}\right)^2\right] = \frac{3}{2}\bar{u}_y\left[1 - \left(\frac{z}{\delta}\right)^2\right]$$

Where u_y is the bulk average velocity. The film thickness is then

$$\delta = \left(\frac{3\bar{u}_y \mu}{\rho g}\right)^{1/2} = \left(\frac{3\mu\Gamma}{\rho^2 g}\right)^{1/3}$$

Where is the mass rate of liquid flow per unit of film width in the x direction. Substituting equation

$$\frac{3}{2}\bar{u}_y\left[1-\left(\frac{z}{\delta}\right)^2\right]\frac{\partial c_A}{\partial y} = D_{AB}\frac{\partial^2 c_A}{\partial z^2}$$

Which is to be solved under the following conditions:

1. At z = 0, $c_A = c_{A,i}$ at all values of y.
2. At z =δ , $\partial c_A/\partial z = 0$ at all values of y, siince no diffusion takes place into the solid wall.
3. At y = 0, $c_A = c_{A0}$ at all values of z.

Solution results a general expression (an infinite series) giving c_A for any z and y, thus providing a concentration distribution $c_A(z)$ at y = L as shown in fig. The bulk average $c_{A,L}$ at y = L can then be found in the manner.

$$\frac{c_{A,i} - \bar{c}_{A,L}}{c_{A,i} - c_{A0}} = 0.7857e^{-5.1213\eta} + 0.1001e^{-39.318\eta} + 0.03599e^{-105.64\eta} + \cdots$$

Where $\eta = 2D_{AB}L/3\delta^2\bar{u}_y$. the total rate of absorption is then $\bar{u}_y\delta(\bar{c}_{A,L} - c_{A0})$ per unit width of liquid film.

The local mass transfer coefficient can be obtained from molar flux of A, for the case of negligible bulk flow in the z direction ($N_A + N_B = 0$).

Mass transfer coefficient at the phase interphase (z = 0)

$$N_A = -D_{AB}\left(\frac{\partial c_A}{\partial z}\right)_{z=0} = k_L(c_{A,i} - \bar{c}_{A,L})$$

Nature of the c_A series shows derivative is undefined at z = 0. therefore, an average coefficient are considered for the entire liquid-gas surface.

The rate at which A is carried by the liquid at any y, per unit width in the x direction, is $\bar{u}_y \delta \hat{c}_A$ mol/time. The rate of solute absorption per unit width over a distance dy in mol/time

$$\bar{u}_y \delta \, d\bar{c}_A = k_L(c_{A,i} - \bar{c}_A)\, dy$$

$$\bar{u}_y \delta \int_{\bar{c}_A = c_{A0}}^{\bar{c}_A = \bar{c}_{A,L}} \frac{d\bar{c}_A}{c_{A,i} - \bar{c}_A} = \int_0^L k_L \, dy = k_{L,av} \int_0^L dy$$

$$k_{L,av} = \frac{\bar{u}_y \delta}{L} \ln \frac{c_{A,i} - c_{A0}}{c_{A,i} - \bar{c}_{A,L}}$$

Which defines the average coefficient.

Now for small flow rates or long time of contact of the liquid with the gas (usually for film Reynolds numbers Re = 4Γ/μ less than 100), only the first term of the series need be used. Substituting in Equation gives

$$k_{L,\,av} = \frac{\bar{u}_y \delta}{L} \ln \frac{e^{5.1213\eta}}{0.7857} = \frac{\bar{u}_y \delta}{L}(0.241 + 5.1213\eta) \approx 3.41 \frac{D_{AB}}{\delta}$$

$$\frac{k_{L,\,av}\delta}{D_{AB}} = Sh_{av} \approx 3.41$$

Where Sh represents the Sherwood number, the mass transfer analog to the Nusselt number of heat transfer.

A similar development for large Reynolds number or short contact time leads to

$$k_{L,\,av} = \left(\frac{6 D_{AB} \Gamma}{\pi \rho \delta L}\right)^{1/2}$$

$$Sh_{av} = \left(\frac{3}{2\pi} \frac{\delta}{L} \text{ Re Sc}\right)^{1/2}$$

The product Re Sc is Peclet number Pe. The average k_L's can be used to compute the total absorption rate.

Thus the average flux $N_{A,av}$ for the entire gas-liquid surface, per unit width, is the difference in rate of flow of A in the liquid at y = L and y = 0, divided by the liquid surface. This can be used with some mean concentration difference

$$N_{A,av} = \frac{\bar{u}_y \delta}{L}(\bar{c}_{A,L} - c_{A0}) = k_{L,av}(c_{A,i} - \bar{c}_A)_M$$

Substitution for kL,av from equation shows that the logarithmic average of the concentration difference at the top and bottom of the film is required

$$(c_{A,i} - \bar{c}_A)_M = \frac{(c_{A,i} - c_{A0}) - (c_{A,i} - \bar{c}_{A,L})}{\ln[(c_{A,i} - c_{A0})/(c_{A,i} - \bar{c}_{A,L})]}$$

Mass Transfer Coefficient in Turbulent Flow

Most practically useful situations involve turbulent flow, however, it is generally not possible to compute mass transfer coefficients because we can not describe the flow conditions mathematically.

Turbulent or Eddy Diffusion

Turbulent motion of a fluid is characterized by rapid and highly irregular fluctuation of the velocity at any point in the fluid.

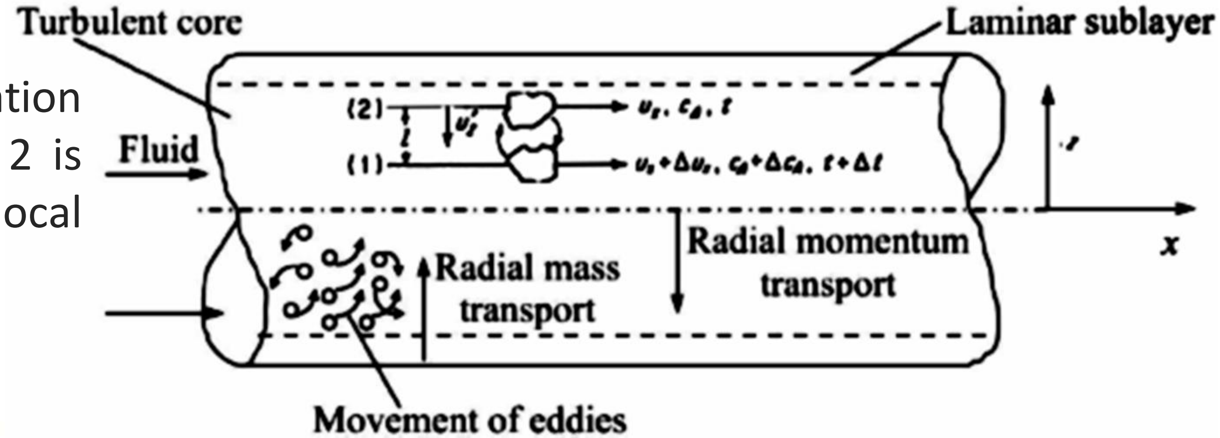
In a turbulent medium, tiny fluid elements move about randomly and are responsible for high rate of transport of momentum, heat or mass. These fluid elements, not necessarily of the same size, are called eddies.

The eddies are continually formed and they break up by interaction among themselves or even may disappear in the process. Eddies are, therefore, short-lived.

Mixing process caused by the movement of the eddies transfer the dissolved solute from a pipe wall to a flowing fluid. From figure it may be visualized that the effect of turbulence does not reach the wall.

Transport of momentum, mass or heat occurs by diffusion through a thin layer, called the laminar sublayer, at the wall. Beyond this layer, transport occurs predominantly by eddies.

The average concentration gradient between 1 and 2 is $\Delta c_A/l$ proportional to a local gradient , $-dc_A/dz$.



The flux of A due to the interchange, $u'_z \Delta c_A$, and the concentration gradient can be used to define an eddy diffusivity of mass E_D, length^2/time

$$E_D = \frac{b_1 u'_z \Delta c_A}{\Delta c_A / l} = \frac{J_{A,\,turb}}{-dc_A/dz}$$

Where b_1 is a proportionality constant. The total flux of A, due both to molecular and eddy diffusion, then will be

$$J_A = -(D_{AB} + E_D)\frac{dc_A}{dz}$$

As in the case of momentum transfer, D is a constant for particular solution at fixed conditions of temperature and pressure, while E_D depends on the local turbulence intensity. D predominates in the region near the wall, E_D in the turbulent core.

Theories of Mass Transfer

As we know that the mass transfer coefficient just a phenomenological quantity to be determined experimentally.

However, there are a number of theories of mass transfer which aim at visualizing the mechanism and developing the expressions for the mass transfer coefficient theoretically. In fact, any such theory is based on a conceptual model for mass transfer. These theories are old and rather simple.

These are considered very important in the study of mass transfer, particularly when the mass transfer is accompanied by chemical reaction.

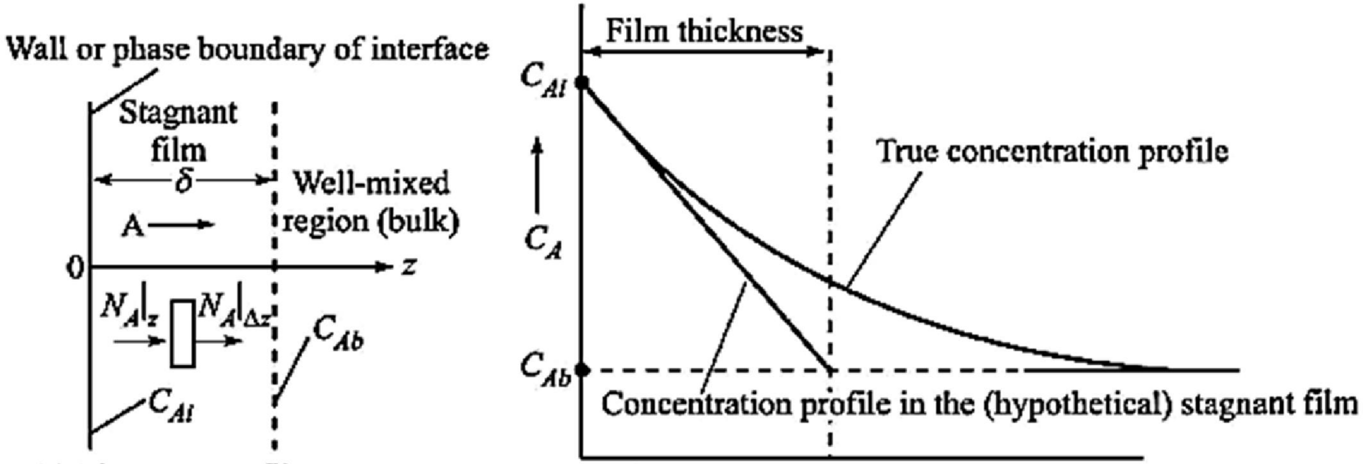
Film Theory

This theory represent the most obvious picture of the meaning of the mass transfer coefficient and having similar concept as used in convective heat transfer.

When a fluid flows turbulently past a solid surface, with mass transfer occurring from the surface to the fluid, the concentration-distance relation is as shown by figure

In a turbulent motion, the flow near the wall may be considered to be laminar. The concentration of the dissolved solid (A) will decrease from Cai at the solid-liquid interface to Cab at the bulk of liquid.

In reality the concentration profile will be very steep near the solid surface where the effect of turbulence is practically absent. Molecular diffusion is responsible near the wall while convection dominates a little away from it.



(a) The stagnant film
C_{Ai} = conc. at the interface
C_{Ab} = conc. at the bulk

(b) Concentration profiles of the solute near the phase boundary
(δ indicates the edge of the film)

Following assumption may be considered

1) Mass transfer through the film occurs at steady state.
2) The bulk flow term in the expression $(N_A + N_B)C_A/C$ for the Fick's law is small. So the flux can be written as $N_A = -D_{AB}(dC_A/dz)$.

Consider an elementary volume of thickness Δz and of unit area normal to the z-direction. A steady state mass balance over this element located at position z.

Rate of input of the solute at z $= N_A|_z$

Rate of input of the solute at z + Δz $= N_A|_{z+\Delta z}$

Rate of accumulation = 0 (at steady state)

Mass balance

$$N_A|_z - N_A|_{z+\Delta z} = 0$$

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

$$-dN_A/dz = 0$$

Putting $N_A = -D_{AB}(dC_A/dz)$ in preceding equation, we have

$$D_{AB}\frac{d^2C_A}{dz^2} = 0 \quad \text{i.e.} \quad \frac{d^2C_A}{dz^2} = 0$$

Integrating equation and using the following boundary conditions (i) and (ii),

(i) $z = 0, C_A = C_{Ai}$

(ii) $z = \delta, C_A = C_{Ab}$

We get

$$C_A = C_{Ai} - (C_{Ai} - C_{Ab})\frac{z}{\delta}$$

The above equation indicates that the theoretical concentration profile, according to film theory, is linear as shown in figure.

The mass transfer flux through the film is constant at steady state and is given as

$$N_A = -D_{AB}\left[\frac{dC_A}{dz}\right]_{z=0} = \frac{D_{AB}}{\delta}(C_{Ai} - C_{Ab})$$

Comparing with equation, the mass transfer coefficient is

$$k_L = \frac{D_{AB}}{\delta}$$

This theory does not help us in reality to predict the mass transfer coefficient because D_{AB} may be estimated by using a suitable correlation but δ is unknown. This theory predicts the linear dependency of k_L upon the diffusivity D_{AB}. However, Experimental data for diverse system show that the coefficient of mass transfer to a turbulent fluid varies as $(D_{AB})^n$ where n may have any value from 0 to 0.8 or 0.9, depending upon the circumstances.