



Molecular diffusion in fluids

Mass Transfer II 

Diffusion

When transfer of the component from one phase to the other occurs due to concentration gradient, the phenomena is called diffusion. The diffusion stops once equilibrium is attained.

Two types of diffusion

- Molecular diffusion
- Eddy diffusion or turbulent diffusion

Molecular diffusion

Movement of individual molecules in a highly zigzag manner through another fluid by virtue of their thermal energy.

In the case of simplified kinetic theory, a molecule is imagined to travel in a straight line at a uniform velocity until it collides with another molecule, whereupon its velocity changes both in magnitude and direction.

The average distance the molecule travels between collision is its mean free path, and the average velocity is dependent upon the temperature.

Net distance travel in one direction is small fraction of the length of its actual path therefore, diffusion rate is very slow.

For Example: If a coloured solution is introduced in a pool of water, it begins slowly to diffuse into the entire liquid which is termed as molecular diffusion.

Eddy or turbulent or convective diffusion

The mechanical agitation produces rapid movement of relatively large chunks, or eddies and this will cause a turbulent motion which enhances rate of mixing. This method of mass transfer is known as eddy or turbulent diffusion.

Diffusion rate in molecular diffusion

The rate at which a solutes moves at any point in any direction must therefore depend on the concentration gradient at that point, and in that direction.

Rates will be most conveniently described in terms of a molar flux, or mol/(area)(time) the area being measured in a direction normal to the diffusion.

In a nonuniform solution containing two constituents, both constituents diffuses and two fluxes use to describe the motion of one constituent:

N , the flux relative to fixed location in space (important in the application to design of equipment)

J , the flux of a constituent relative to the average molar velocity of all constituents. (represent the more characteristic of the nature of the constituent)

For Example:

A fisherman is most interested in the rate at which a fish swims upstream against the flowing current to reach his baited hook (analogous to N)

The velocity of the fish relative to the stream (analogous to J) is more characteristic of the swimming ability of the fish.

Diffusivity or diffusion coefficient

D_{AB} of a constituent A in solution in B, which is a measure of its diffusive mobility, is then defined as the ratio of its flux J_A to its concentration gradient

$$J_A = -D_{AB} \left(\frac{\partial C_A}{\partial Z} \right) = -C D_{AB} \left(\frac{\partial x_A}{\partial Z} \right)$$

This is Fick's law written for the z direction. The negative sign emphasizes that diffusion occurs in the direction of a drop in concentration.

The diffusivity is characteristic of a constituent and its environment (temp, pr, concⁿ, whether in liquid, gas, or solid solution, and the nature of the other constituents).

Consider two gases A and B of equal volume placed in two boxes connected by a tube and maintained at a constant total pressure. Now gases are allowed to diffuse. Since the total pressure P remains constant throughout the process. If the direction to the right is taken as positive, the flux N_A of A relative to the fixed position X has been positive and the flux N_B of B has been negative.

For a condition of steady state, the net flux is

$$N_A + N_B = N$$

The movement of A is made up of two parts from the bulk motion and the fraction x_A of N (molecular diffusion)

$$N_A = Nx_A + J_A$$

$$N_A = (N_A + N_B) \frac{c_A}{c} - D_{AB} \frac{\partial c_A}{\partial z}$$

Similarly for B

$$N_B = (N_A + N_B) \frac{c_B}{c} - D_{BA} \frac{\partial c_B}{\partial z}$$

Adding these gives

$$-D_{AB} \frac{\partial c_A}{\partial z} = D_{BA} \frac{\partial c_B}{\partial z}$$

the net moles of A diffused in one direction must be equal to net moles of B diffused in opposite direction.

If $c_A + c_B = \text{constant}$, it follows that $D_{AB} = D_{BA}$ at the prevailing concentration and temperature.

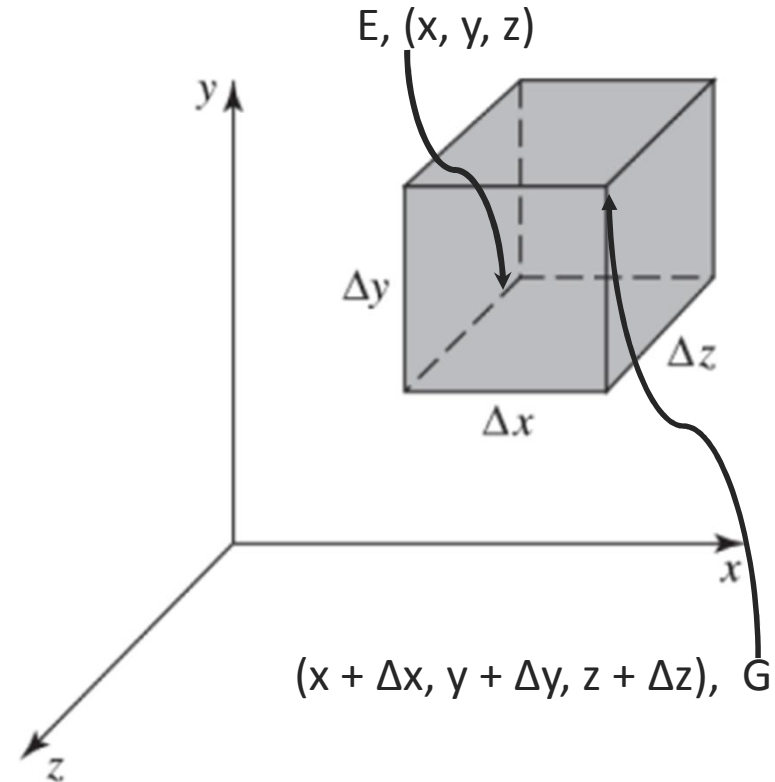
All the above has considered diffusion in only one direction, but in general concentration gradients, velocities, and diffusional fluxes exist in all directions.

3 Dimensional Equation of continuity

Consider two gases A and B of equal volume placed in two boxes connected by a tube and maintained at a constant total pressure. Now gases are allowed to diffuse. Since the total pressure P remains constant throughout the process. Consider the volume element of fluid of volume $\Delta x \Delta y \Delta z$ in the flowing fluid.

Material balance for a component A flowing through volume element

The mass rate of flow of component A into three faces with a common corner at E



$$M_A \left[(N_{A,x})_x \Delta y \Delta z + (N_{A,y})_y \Delta x \Delta z + (N_{A,z})_z \Delta x \Delta y \right]$$

Where $N_{A,x}$ signifies the x-directed flux and $(N_{A,x})_x$ its value at location x. Similarly the mass rate of flow out of the three faces with a common corner at G is

$$M_A \left[(N_{A,x})_{x+\Delta x} \Delta y \Delta z + (N_{A,y})_{y+\Delta y} \Delta x \Delta z + (N_{A,z})_{z+\Delta z} \Delta x \Delta y \right]$$

The total component A in the element is $\Delta x \Delta y \Delta z \rho_A$, and its rate of accumulation is therefore $\Delta x \Delta y \Delta z \partial \rho_A / \partial \theta$. If, A is generated by chemical reaction at the rate R_A mol/(volume)(time), its production rate is $M_A R_A \Delta x \Delta y \Delta z$, mass/time. In general,

Rate out – rate in + rate of accumulation = rate of generation

Then

$$M_A \left\{ [(N_{A,x})_{x+\Delta x} - (N_{A,x})_x] \Delta y \Delta z + [(N_{A,y})_{y+\Delta y} - (N_{A,y})_y] \Delta x \Delta z + [(N_{A,z})_{z+\Delta z} - (N_{A,z})_z] \Delta x \Delta y \right\} + \Delta x \Delta y \Delta z \frac{\partial \rho_A}{\partial \theta} = M_A R_A \Delta x \Delta y \Delta z$$

Dividing by and taking the limit as three distance become zero gives

$$M_A \left(\frac{\partial N_{A,x}}{\partial x} + \frac{\partial N_{A,y}}{\partial y} + \frac{\partial N_{A,z}}{\partial z} \right) + \frac{\partial \rho_A}{\partial \theta} = M_A R_A$$

Similarly for component B

$$M_B \left(\frac{\partial N_{B,x}}{\partial x} + \frac{\partial N_{B,y}}{\partial y} + \frac{\partial N_{B,z}}{\partial z} \right) + \frac{\partial \rho_B}{\partial \theta} = M_B R_B$$

The total material balance is obtained by adding those for A and B

$$\frac{\partial (M_A N_A + M_B N_B)_x}{\partial x} + \frac{\partial (M_A N_A + M_B N_B)_y}{\partial y} + \frac{\partial (M_A N_A + M_B N_B)_z}{\partial z} + \frac{\partial \rho}{\partial \theta} = 0$$

Where $\rho = \rho_A + \rho_B$ = the solution density, since the mass rate of generation of A and B must equal zero.

Now molar flux of A in terms of masses and in the x direction is

$$M_A N_{A,x} = u_x \rho_A + M_A J_{A,x}$$

Where u_x is the mass average velocity such that

$$\rho u_x = u_{A,x} \rho_A + u_{B,x} \rho_B = M_A N_{A,x} + M_B N_{B,x}$$

Therefore

$$\frac{\partial (M_A N_A + M_B N_B)_x}{\partial x} = \rho \frac{\partial u_x}{\partial x} + u_x \frac{\partial \rho}{\partial x}$$

Then equation becomes

$$\rho \left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \right) + u_x \frac{\partial \rho}{\partial x} + u_y \frac{\partial \rho}{\partial y} + u_z \frac{\partial \rho}{\partial z} + \frac{\partial \rho}{\partial \theta} = 0$$

This is *equation of continuity*, or a mass balance, for total substance. If the solution density is constant, it becomes

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} = 0$$

Returning to the balance for component A

$$M_A \frac{\partial N_{A,x}}{\partial x} = u_x \frac{\partial \rho_A}{\partial x} + \rho_A \frac{\partial u_x}{\partial x} + M_A \frac{\partial J_{A,x}}{\partial x} = u_x \frac{\partial \rho_A}{\partial x} + \rho_A \frac{\partial u_x}{\partial x} - M_A D_{AB} \frac{\partial^2 c_A}{\partial x^2}$$

Equation then becomes

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

This is the equation of continuity for substance A. For a solution of constant density,

equation same as previous only multiple by ρ_A . Dividing by M_A , then

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

reaction, it reduces to Fick's second law

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

This is frequently applicable to diffusion in solids and to limited situations in fluids.

Steady state molecular diffusion in fluids at rest and in laminar flow

For steady state molecular diffusion between two gases A and B, the net flux is given by

$$N = N_A + N_B$$

Hence the molar flux N_A can be expressed as

$$N_A = (N_A + N_B) x_A - D_{AB} \left(\frac{\partial C_A}{\partial Z} \right)$$

Applying this equation to the case of diffusion in z direction between the diffusional path Z_1 and Z_2 , where concentration are C_{A1} and C_{A2} respectively. Equation can also be written as

$$N_A = (N_A + N_B) \frac{C_A}{C} - D_{AB} \left(\frac{\partial C_A}{\partial Z} \right), \text{ since } x_A = \frac{C_A}{C}$$

Rearranging the above equation and integrating

$$\int_{C_{A1}}^{C_{A2}} \frac{-dC_A}{N_A C - C_A (N_A + N_B)} = \frac{1}{C D_{AB}} \int_{Z_1}^{Z_2} dZ$$

$$\frac{1}{N_A + N_B} \ln \frac{N_A C - C_{A2} (N_A + N_B)}{N_A C - C_{A1} (N_A + N_B)} = \frac{z}{C D_{AB}}$$

$$N_A = \frac{N_A}{N_A + N_B} \frac{D_{AB} C}{z} \ln \frac{N_A / (N_A + N_B) - C_{A2} / C}{N_A / (N_A + N_B) - C_{A1} / C}$$

Molecular diffusion in gases

Molecular diffusion in gases is caused by random movement of molecules due to their thermal energy and hence the kinetic theory of gases helps to understand the mechanism of molecular diffusion in gases.

In case of diffusion in gases, molar flux may be expressed in terms of partial pressure gradient.

Assuming the gas mixture to be ideal,

$$\frac{c_A}{c} = \frac{p_A}{p_t} = y_A$$

Where p_A is the partial pressure of component A, p_t is the total pressure and y_A is mole fraction of component A. Further,

$$C = \frac{n}{V} = \frac{P_t}{RT}$$

So that previous equation becomes

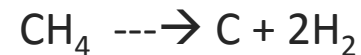
$$N_A = \left[\frac{N_A}{N_A + N_B} \right] \left[D_{AB} \frac{P_t}{RTZ} \right] \ln \left[\frac{\left\{ \left(\frac{N_A}{N_A + N_B} \right) P_t - p_{A2} \right\}}{\left\{ \left(\frac{N_A}{N_A + N_B} \right) P_t - p_{A1} \right\}} \right]$$

or

$$N_A = \left[\frac{N_A}{N_A + N_B} \right] \left[D_{AB} \frac{P_t}{RTZ} \right] \ln \left[\frac{\frac{N_A}{N_A + N_B} - y_{A2}}{\frac{N_A}{N_A + N_B} - y_{A1}} \right]$$

In order to use these equations the relation between N_A and N_B must be known. This is usually fixed by other considerations.

For Example: Methane is being cracked on a catalyst,



Under circumstances such that CH_4 (A) diffuses to the cracking surface and H_2 (B) diffuses back, the reaction stoichiometry fixes the relationship $N_B = -2N_A$ and

$$\frac{N_A}{N_A + N_B} = \frac{N_A}{N_A - 2N_A} = -1$$

On the occasion, in the absence of chemical reaction, the ratio can be fixed by enthalpy consideration.

Steady-state diffusion of A through non-diffusing B

For Example: If ammonia (A) were being absorbed from air (B) into water. In the gas phase, since air does not dissolve appreciably in water, and if we neglect the evaporation of water, only the ammonia diffuses. Thus $N_B = 0$, $N_A = \text{const}$,

$$\text{Hence, } \frac{N_A}{N_A + N_B} = 1$$

Substituting this in equation

$$N_A = \left(\frac{D_{AB} P_t}{RTZ} \right) \ln \left[\frac{P_t - p_{A2}}{P_t - p_{A1}} \right]$$

Since $P_t - p_{A2} = p_{B2}$, $P_t - p_{A1} = p_{B1}$, $p_{B2} - p_{B1} = p_{A1} - p_{A2}$.

Equation becomes

$$N_A = \left(\frac{D_{AB} P_t}{RTZ} \right) \left[\frac{p_{A1} - p_{A2}}{p_{B2} - p_{B1}} \right] \ln \left(\frac{p_{B2}}{p_{B1}} \right)$$

Let

$$p_{B,M} = \frac{p_{B2} - p_{B1}}{\ln \left(\frac{p_{B2}}{p_{B1}} \right)}$$

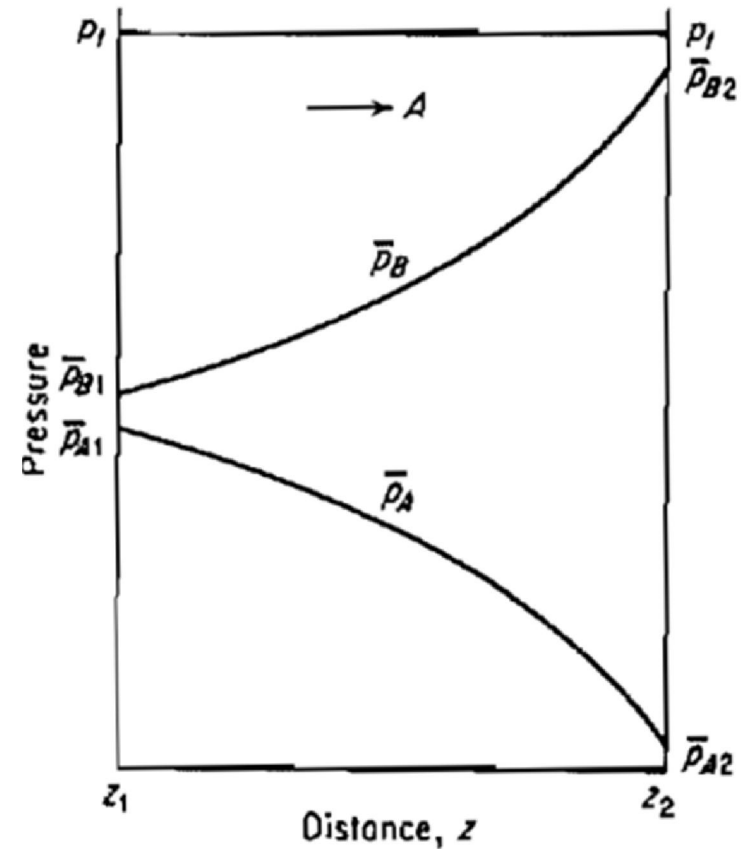
Then

$$N_A = \left[\frac{D_{AB} P_t}{RTZ p_{B,M}} \right] (p_{A1} - p_{A2})$$

Or

$$N_A = \left[\frac{D_{AB} P_t}{RTZ} \right] \ln \left[\frac{1 - y_{A2}}{1 - y_{A1}} \right]$$

This equation is shown in figure. Substance A diffuse by virtue of its concentration gradient $-dp_A/dz$. Substance B is also diffusing relative to the average molar velocity at a flux J_B , which depends on $-dp_B/dz$



Steady state equimolar counter-diffusion

This is a situation which frequently pertains in distillation operations.

$$N_A = -N_B = \text{const.}$$

$$N_A = (N_A + N_B) \frac{\bar{p}_A}{p_t} - \frac{D_{AB}}{RT} \frac{d\bar{p}_A}{dz}$$

Or, for this case

$$N_A = - \frac{D_{AB}}{RT} \frac{d\bar{p}_A}{dz}$$
$$\int_{z_1}^{z_2} dz = - \frac{D_{AB}}{RT N_A} \int_{\bar{p}_{A1}}^{\bar{p}_{A2}} d\bar{p}_A$$

$$N_A = \frac{D_{AB}}{RT z} (\bar{p}_{A1} - \bar{p}_{A2})$$

