

$$m_{N_2}^* = \frac{C_{N_2}}{C} = \frac{0.0363}{0.046} = 0.79 \text{ (Ans.)}$$

(The molar fractions are equal to the partial pressures fraction).

### 13.4. FICK'S LAW

In order to understand the “*mass diffusion*” (a transport process originating from molecular activity), consider a chamber in which two different gas species A and B, at the same temperature and pressure are initially separated by a partition. The left compartment has a high concentration (i.e., more molecules per unit volume) of gas A (open circles) whereas the right compartment is rich in gas B (dark circles). When the partition wall is removed a driving potential comes into existence which tends to equalize the concentration difference. Mass transfer by diffusion will be in the direction of decreasing concentration and subsequently there will be a net transport of species A to the right and of species B to the left. After a sufficiently long period, equilibrium conditions prevail i.e., uniform concentrations of species A and B are achieved and then the mass diffusion ceases.

It has been observed through experiments that *molecular diffusion* is governed by Fick’s law which is expressed as

$$N_A = \frac{m_A}{A} = - D_{AB} \frac{dC_A}{dx} \quad \dots(13.19)$$

where,

$m_A$  = Mass flow rate of species A by diffusion, kg/s,

$A$  = Area through which mass is flowing,  $m^2$ ,

$N_A = \frac{m_A}{A}$  = Mass flux of species A i.e., amount of species A that is transferred per unit time and per unit area perpendicular to the direction of transfer,  $kg/s\cdot m^2$  or  $kg \text{ mole}/s\cdot m^2$ ,

$D_{AB}$  = Diffusion coefficient or mass diffusivity for binary mixture of species A and B,  $m^2/s$ ,

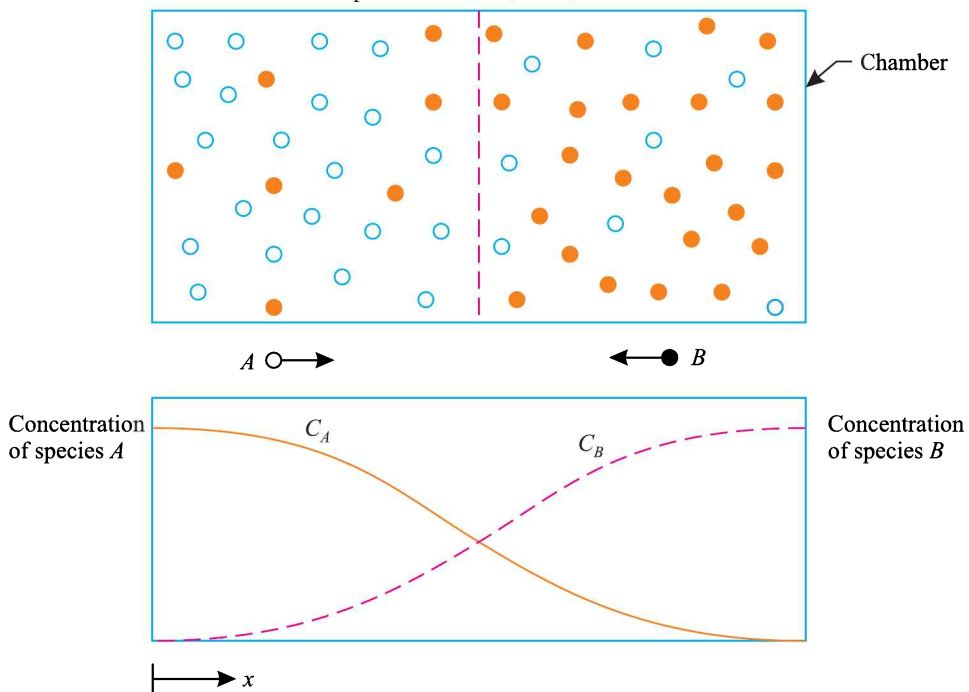


Fig. 13.1. Mass transfer by diffusion in a binary gas mixture

$C_A$  = Concentration or molecules per unit volume of species A, kg/m<sup>3</sup>, and  
 $\frac{dC_A}{dx}$  = Concentration of gradient for species A; this acts as driving potential, kg/m<sup>3</sup>.

In Eqn. (13.19) – ve sign indicates that diffusion takes place in the direction *opposite* to that of increasing concentration.

The diffusion rate for species B is given by

$$N_B = \frac{m_B}{A} = - D_{BA} \frac{dC_B}{dx} \quad \dots(13.20)$$

It may be noted that “diffusion coefficient D” (i.e.,  $D_{AB}$  or  $D_{BA}$  in this case) is dependent upon the temperature, pressure and nature of the components of the system.

The Fick’s law of diffusion is analogous to:

(i) Fourier law of heat conduction:

$$\frac{Q}{A} = - k \frac{dt}{dx}; \text{ and}$$

(ii) Newton’s law of viscosity :

$$\tau = \mu \frac{du}{dy}$$

By comparison of the above equations, we find that the Fourier equation describes the transport of heat energy due to temperature gradient, the shear equation describes the transport of momentum due to velocity gradient while the Fick’s law describes the mass transport due to concentration gradient.

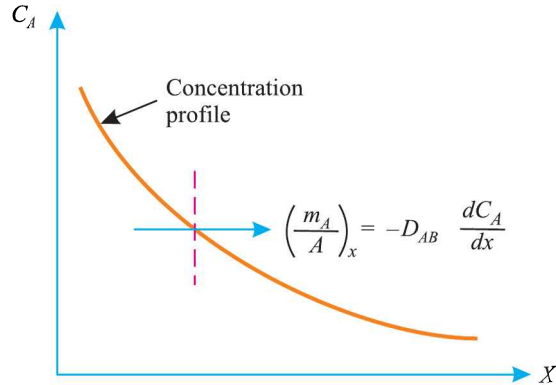


Fig. 13.2. Concentration profile.

As per Eqn. (13.19), the dimensions of diffusion coefficient  $D$  are

$$D = - \frac{N}{\left(\frac{dC}{dx}\right)} = \frac{(M / L^2 T)}{[(M / L^3) \times (1 / L)]} = \frac{L^2}{T} = m^2 / s$$

Thus units of mass diffusion coefficient are identical to those of thermal diffusivity ( $\alpha$ ) and kinematic viscosity ( $\nu$ ). Thus, *diffusion coefficient is a transport property of the fluid.*

Further, by using perfect gas equation the Fick’s law may be expressed in terms of partial pressures of species as follows:

For species A:  $p_A = \rho_A R_A T = \rho_A \frac{GT}{M_A}$

where,

$p_A$  = Partial pressure of species A,

$\rho_A$  = Density of species A,

$G$  = Universal gas constant (= 8314 J/kg mole-K), and

$M_A$  = Molecular weight of species A.

$\therefore \rho_A = C_A = \frac{p_A M_A}{GT}$

Substituting the value of  $\rho_A$  in eqn. (13.19), we get

$$N_A = \frac{m_A}{A} = - D_{AB} \frac{d}{dx} \left[ \frac{p_A M_A}{GT} \right]$$

or, 
$$N_A = \frac{m_A}{A} = - D_{AB} \frac{M_A}{G.T} \cdot \frac{dp_A}{dx} \quad \dots(13.21)$$

Similarly, for species B:

$$N_B = \frac{m_B}{A} = - D_{AB} \frac{M_B}{G.T} \cdot \frac{dp_B}{dx} \quad \dots(13.22)$$

It may be noted that Eqns. (13.21) and (13.22) are *valid only for isothermal diffusion*.

Eqns. (13.19) and (13.20) entail the following *restrictive conditions*:

- (i) These are valid only when diffusion occurs due to concentration gradient and fail when diffusion occurs due to a temperature gradient, pressure gradient or an external force.
- (ii) The mass or molar fluxes are measured *relative to coordinates which move with some average velocity* of the mixture. These equations become invalid if the flux (mass or molar) is expressed *relative to a fixed set of coordinates*.



Determination of diffusion coefficient

**Some important aspects of Fick’s law of diffusion:**

1. Fick’s law is based on experimental evidence and cannot be derived from first principles.
2. Fick’s law is *valid for all matter* irrespective of its state (e.g., solid, liquid or gas).
3. The mass diffusion, besides *concentration gradient*, may occur due to a temperature gradient, a pressure gradient or an external force; however, while applying Fick’s law it is assumed that these additional effects are either absent or negligibly small.
4. The movement of a diffusion substance is *in the direction of decreasing concentration*. In a diffusion process, the concentration difference is similar to temperature difference in a heat transfer process.
5. Diffusion coefficient (*D*), in general, is dependent upon temperature, pressure and nature of the system component; however, for ideal gases and dilute liquids it can be assumed to remain practically constant for a given range of temperature and pressure.

**Mass diffusion coefficient (D):**

**For gases/gas mixtures:**

By using kinetic theory of gases it is possible to predict the mass diffusion coefficient  $D_{AB}$ , for the binary mixture of two gases, A and B; it is of the form given below:

$$D_{AB} \sim \frac{T^{3/2}}{p} \quad \dots(13.23)$$

or, 
$$D_{AB} = 0.0043 \frac{(T^{3/2})}{p (V_A^{1/3} + V_B^{1/3})^2} \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2} \text{ cm}^2/\text{s} \quad \dots(13.24)$$

$p$  = Total pressure in atmosphere (=  $p_A + p_B$ ),

$T$  = Absolute temperature of the binary gas mixture,  $K$ ,

$V_A, V_B$  = Molecular volumes of constituent species at normal boiling points,  $\text{cm}^3/\text{gm-mole}$ , and

$M_A, M_B$  = Molecular weights of species  $A$  and  $B$ .

It is evident from the above equation that diffusion coefficient ( $D$ ) for gases depends upon temperature, pressure and other molecular properties of diffusing gases. At other temperature and pressure, we have

$$\frac{D_1}{D_2} = \left(\frac{T_1}{T_2}\right)^{3/2} \left(\frac{p_2}{p_1}\right) \quad \dots(13.25)$$

$D_{AB}$ , for liquids is wholly available from experiments. *Liquid mass diffusivities are considerably smaller than those for the gases.* This is due to high molecular density in the liquid phase. However, increase in  $D_{AB}$  with increase in temperature has been observed. *Diffusion in solids is even slower than in liquids*, only very little information in the experimental form is available.

An effective diffusivity in case of steady state diffusion through a non-diffusing, multicomponent mixture of constant composition is given by:

$$D = \frac{1}{\left(\frac{x_B}{D_{AB}}\right) + \left(\frac{x_C}{D_{AC}}\right) + \left(\frac{x_D}{D_{AD}}\right)} \quad \dots(13.26)$$

where,  $x_B, x_C, x_D$  = Mole fraction composition of the mixture on a free basis, and

$D_{AB}, D_{AC}, D_{AD}$  = Diffusivities of species  $A$  through  $B, C, D$ , etc.

For gas pairs of non-polar, non-reacting molecules, the diffusion coefficient is given by:

$$D_{AB} = 0.001858 \frac{T^{3/2}}{p (\sigma_{AB})^2 \Omega} \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2} \quad \dots(13.27)$$

where,  $D_{AB}$  = Mass diffusivity of gas species  $B$  diffusing through another gas species  $A$ ,  $\text{cm}^2/\text{s}$ ,

$T$  = Absolute temperature,  $K$

$p$  = Total pressure in atmospheres ( $= p_A + p_B$ ),

$\sigma_{AB}$  = Collision diameter in  $\text{\AA}$  (Angstroms),

$\Omega$  = Collision integral, a dimensionless function of the temperature and the intermolecular potential field for one molecule of  $A$  and one molecule of  $B$ , and

$M_A, M_B$  = Molecular weights of gas species  $A$  and  $B$  respectively.

The value of  $\Omega$  (collision integral) is, in general, compiled as a function of  $\frac{KT}{\epsilon_{AB}}$ , where  $K$  is Boltzmann's constant and  $\epsilon_{AB}$  is the energy of molecular interaction for this binary system  $AB$ .

In case of a binary system, composed of non-polar molecule pairs, we have:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

$$\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}$$

**For dilute liquids:**

The diffusion coefficient for “dilute liquids” is calculated from the following empirical relation:

$$D_{AB} = \frac{T}{F \mu_B} \quad \dots(13.28)$$

where,

$D_{AB}$  = Diffusivity of solute  $A$  through a solvent  $B$ ,  $\text{m}^2/\text{s}$ ,

$T$  = Absolute temperature,  $K$ ,

$\mu_B$  = Viscosity of solvent *B*, centipoise, and

$F$  = A function of the molar volume of solute *A*, K.s/cm<sup>2</sup>; centipoise

The values of  $F$  may be obtained from the charts available.

**For solids:**

Diffusion in solids occurs still at a *lower rate* as compared to that in gases and solids.

**Example 13.3.** From the data given below, calculate the diffusion coefficient for  $NH_3$  in air at 27°C temperature and atmospheric pressure:

$NH_3$  (Gas A) : Molecular weight = 17                      Molecular volume = 26.43 cm<sup>3</sup>/gm mole

Air (Gas B): Molecular weight = 29                      Molecular volume = 30.6 cm<sup>3</sup>/gm mole.

**Solution.** Given:  $M_A = 17$ ,  $V_A = 26.43$  cm<sup>3</sup>/gm mole;  $M_B = 29$ ,  $V_B = 30.6$  cm<sup>3</sup>/gm mole,  $T = 27 + 273 = 300$  K,  $p = 1$  atmosphere.

**Diffusion coefficient,  $D_{AB}$ :**

The diffusion coefficient for binary gaseous mixture is calculated from the relation:

$$D_{AB} = 0.0043 \frac{(T)^{3/2}}{p (V_A^{1/3} + V_B^{1/3})^2} = \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2} \quad \dots[\text{Eqn. (13.24)}]$$

Substituting the appropriate values, we obtain,

$$\begin{aligned} D_{AB} &= 0.0043 \frac{(300)^{3/2}}{1 (26.43^{1/3} + 30.6^{1/3})^2} \left[ \frac{1}{17} + \frac{1}{29} \right]^{1/2} \\ &= 0.0043 \times \frac{5196.15}{(2.978 + 3.128)^2} [(0.0588 + 0.0345)]^{1/2} = \mathbf{0.183 \text{ cm}^2/\text{s}. \quad (\text{Ans.})} \end{aligned}$$

**Example 13.4.** From the following data calculate the diffusion coefficient of  $CO_2$  in air at a temperature of 25°C and atmospheric pressure.

$CO_2$  (Gas A):  $\sigma = 3.996 \text{ \AA}$  ;                       $\frac{\epsilon}{K} = 190 \text{ K}$

Air (Gas B):  $\sigma = 3.167 \text{ \AA}$  ;                       $\frac{\epsilon}{K} = 97 \text{ K}$

The table given below may be used to estimate collision integral  $\Omega$ .

$\frac{kT}{\epsilon}$	2.00	2.10	2.20	2.30
$\Omega$	1.075	1.057	1.041	1.026

**Solution.** Given:  $\sigma_A = 3.996 \text{ \AA}$ ,  $\frac{\epsilon_A}{K} = 190 \text{ K}$ ,  $M_A = 44$ ;  $\sigma_B = 3.167 \text{ \AA}$ ,  $\frac{\epsilon_B}{K} = 97 \text{ K}$ ,  $M_B = 29$

**Diffusion Coefficient,  $D_{AB}$ :**

The diffusion coefficient may be calculated using the following relation :

$$D_{AB} = 0.001858 \frac{T^{3/2}}{p (\sigma_{AB})^2 \Omega} \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2} \quad \dots[\text{Eqn. (13.27)}]$$

Here, 
$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} = \frac{3.996 + 3.167}{2} = 3.5815 \text{ \AA}$$

$$\frac{\epsilon_{AB}}{K} = \sqrt{\frac{\epsilon_A}{K} \times \frac{\epsilon_B}{K}} = \sqrt{190 \times 97} = 135.76 \text{ K}$$

$$\text{or, } \frac{\epsilon_{AB}}{KT} = \frac{135.76}{(25 + 273)} = 0.4556$$

$$\text{or, } \frac{KT}{\epsilon_{AB}} = \frac{1}{0.4556} = 2.195$$

Corresponding to  $\frac{KT}{\epsilon_{AB}} = 2.195$ , the collision integral  $\Omega$

$$= 1.057 - \left[ \frac{1.057 - 1.041}{2.20 - 2.10} \right] \times (2.195 - 2.10) = 1.0418$$

Substituting the various values in the above equation, we get

$$\begin{aligned} D_{AB} &= 0.001858 \times \frac{(298)^{3/2}}{1 \times (3.5815)^2 \times 1.0418} \left[ \frac{1}{44} + \frac{1}{29} \right]^{1/2} \\ &= 0.001858 \times \frac{5144.28}{13.363} (0.02273 + 0.03448)^{1/2} = \mathbf{0.171 \text{ cm}^2/\text{s}} \text{ (Ans.)} \end{aligned}$$

### 13.5. GENERAL MASS DIFFUSION EQUATION IN STATIONARY MEDIA

The general differential equation for mass transfer of any species can be derived on the similar lines as outlined in chapter 2 for the derivation of heat transfer equations.

Consider a homogeneous medium consisting of binary mixture of species A and B. Let the medium be stationary (*i.e.*, the mass average or molar average velocity of the mixture is zero) and mass transfer may occur only by diffusion. Now, consider a differential control volume  $dx dy dz$  as shown in Fig. 13.3. The mass balance of species A diffusing through the control volume in the stationary medium B is given by:

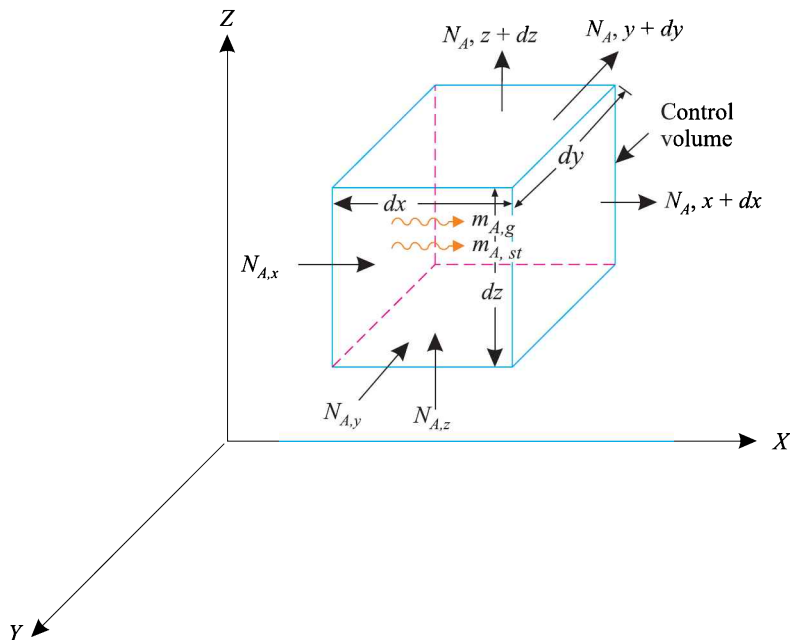


Fig. 13.3. Control volume for species conservation equation.