CHAPTER

# 14

# Mass Transfer

## 14.1 Introduction

Mass transfer is an important topic with vast industrial applications in varied fields such as: mechanical, chemical and aerospace engineering, physics, chemistry, biology, etc. Few of the applications involving mass transfer are:

(i) absorption and desorption (e.g. ammonia refrigeration systems)
(ii) solvent extraction
(iii) humidification (e.g. cooling towers and air-conditioning applications)
(iv) oxygenation of blood, food, etc.
(v) evaporation of petrol in internal combustion engines
(vi) neutron diffusion in nuclear reactors
(vii) distillation columns to separate components in a mixture.

Numerous every day applications such as dissolving of sugar in tea, drying of wood or clothes, evaporation of water vapour into dry air, diffusion of smoke from a chimney into atmosphere, etc., are also examples of mass diffusion.

Our aim in this introductory chapter on mass diffusion is, primarily, to show the similarity between the heat transfer and mass transfer processes. For an in-depth study of this topic, one should consult specialised books in the field.

**Modes of mass transfer** Mass transfer occurs whenever there is a concentration gradient between two fluids, just as heat transfer occurs when there is a temperature gradient. Three modes of mass transfer may be distinguished:

(i) **Molecular mass diffusion** This occurs when mass transfer takes place in a fluid at rest, as a result of concentration gradient and is analogous to diffusion heat transfer in conduction due to temperature gradients.
(ii) **Convective mass transfer** This occurs when the fluid is in motion. Now, the effect of velocity field also comes into picture. Mass transfer may be between a moving fluid and a surface or between two moving fluids, which do not mix with each other. In fact, now, the mass transfer is by both by molecular diffusion and convective motion of the fluid. This process is analogous to convective heat transfer process and for low concentrations and low mass transfer rates, many of the equations for convective mass transfer will be identical to those derived for convective heat transfer.
(iii) **Mass transfer by change of phase** Here, again, both convection and diffusion are involved. Boiling of water in an open pan, evaporation of a cryogenic liquid from its container, diffusion of smoke from a chimney, etc., are familiar examples.

## 14.2 Concentrations, Velocities and Fluxes

It is necessary to define a few terms:

### 14.2.1 Concentrations

**Mass concentration (or mass density)** Mass concentration or mass density $\rho_A$ of a species A in a mixture is defined as mass of component A per unit volume of the mixture. It is expressed in kg/m$^3$ units. Often, mass concentration is also denoted by C; thus, $C_A = \rho_A$.

**Molar concentration (or molar density)** Molar concentration or molar density $n_A$ of a species A in a mixture is defined as the number of moles of component A per unit volume of the mixture. It is expressed in kg moles/m$^3$ units.

These two concentrations are related to each other as follows:

$$n_A = \frac{\rho_A}{M_A} \qquad \text{...(14.1)}$$

where, $M_A$ = molecular weight of species A.

**Mass fraction** It is the ratio of mass concentration of species A to the total mass density of the mixture, i.e.

$$w_A = \frac{\rho_A}{\rho} \qquad \text{...(14.2)}$$

**Mole fraction** It is the ratio of molar density of species A to the total molar density of the mixture, i.e.

$$y_A = \frac{n_A}{n} \qquad \text{...(14.3)}$$

For a binary mixture of two components, A and B, we have, by definition:

$$\rho_A + \rho_B = \rho \qquad \text{...(14.4)}$$

$$n_A + n_B = n \qquad \text{...(14.5)}$$

$$w_A + w_B = 1 \qquad \text{...(14.6)}$$

$$y_A + y_B = 1 \qquad \text{...(14.7)}$$

**Ideal gas mixtures** At low pressures, a gas or gas mixture can be considered as an ideal gas. Familiar example of such a case is the mixture of dry air and water vapour existing under atmospheric conditions. Then, by Dalton's law, total pressure of the mixture is equal to the sum of the partial pressures of each component, and is given by:

$$P = \Sigma P_i \qquad \text{...(14.8)}$$

Here, $P_i$ is the partial pressure of component $i$ and it is the pressure that would be exerted by the component $i$ if it alone occupied the whole mixture volume. Then, using the ideal gas relation (i.e. $P.V = n.R_u.T$, where $R_u$ = universal gas constant = 8314 J/kg mole K), we can write:

$$\frac{P_i}{P} = \frac{\dfrac{N_i \cdot R_u \cdot T}{V}}{\dfrac{N \cdot R_u \cdot T}{V}} = \frac{N_i}{N} = y_i \qquad \text{...(14.9)}$$

i.e. pressure fraction is equal to the mole fraction.

### 14.2.2 Velocities

Mass diffusion may occur in a stationary medium or a moving medium. In a staionary medium, the components in a mixture move because of the concentration gradients only and the velocity of each species is equal to the 'diffusion velocity' only. However, if the medium is also moving, then, the absolute velocity of a species is equal to the sum of the bulk flow velocity and the diffusion velocity.

Remembering that, $m = \rho.V.A$, we can write for a mixture of two components A and B:

$$m = m_A + m_B$$

i.e.

$$\rho \cdot V_{\text{mass}} \cdot A = \rho_A \cdot V_A \cdot A + \rho_B \cdot V_B \cdot A$$

Therefore,

$$V_{\text{mass}} = \frac{\rho_A \cdot V_A + \rho_B \cdot V_B}{\rho} = w_A \cdot V_A + w_B \cdot V_B \qquad \text{...(14.10)}$$

Here, $V_{\text{mass}}$ is called the mass–average velocity of flow.

In the case of a stationary medium, mass–average velocity is equal to zero.

When there is no concentration gradient, velocity of all species is equal to the mass–average velocity of flow; and when there is a concentration gradient, average velocity of each component is given by:

$$V_A = V_{\text{mass}} + V_{\text{diff\_A}} \quad \text{...(14.11a)}$$

and,

$$V_B = V_{\text{mass}} + V_{\text{diff\_B}} \quad \text{...(14.11b)}$$

Similarly, molar average velocity is defined by:

$$V_{\text{molar}} = \frac{n_A \cdot V_A + n_B \cdot V_B}{n} = y_A \cdot V_A + y_B \cdot V_B \quad \text{...(14.12)}$$

And, molar average velocity of each component is given by:

$$V_A = V_{\text{molar}} + V_{\text{diff\_A}} \quad \text{...(14.13a)}$$

and,

$$V_B = V_{\text{molar}} + V_{\text{diff\_B}} \quad \text{...(14.13b)}$$

From Eqs. 14.11 and 14.13, we can write:

Mass diffusion velocities of A and B:

$$V_{\text{diff\_A}} = V_A - V_{\text{mass}} \quad \text{...(14.14a)}$$

$$V_{\text{diff\_B}} = V_A - V_{\text{mass}} \quad \text{...(14.14b)}$$

Molar diffusion velocities of A and B:

$$V_{\text{diff\_A}} = V_A - V_{\text{molar}} \quad \text{...(14.15a)}$$

$$V_{\text{diff\_B}} = V_A - V_{\text{molar}} \quad \text{...(14.15b)}$$

### 14.2.3 Fluxes

*For species A*: Absolute flux = $\rho_A . V_A$.

Bulk motion flux = $\rho_A . V_{\text{mass}}$.

Diffusion flux = $m_A / A$ = mass flow per unit time per unit area.

Absolute flux of a component is as seen by a stationary observer.

It is equal to diffusion flux + bulk motion flux

i.e.

$$\rho_A \cdot V_A = \frac{m_A}{A} + \rho_A \cdot V_{\text{mass}}$$

i.e. Diffusion flux $= \dfrac{m_A}{A} = \rho_A \cdot V_A - \rho_A \cdot V_{\text{mass}} = \rho_A \cdot (V_A - V_{\text{mass}})$ ...(14.16)

Similarly, on molar basis:

Diffusion flux $= n_A \cdot (V_A - V_{\text{molar}})$ ...(14.17)

## 14.3 Fick's Law of Diffusion

Consider a chamber, containing a mixture of two gases B and C, divided into two volumes by a partition in the middle, as shown in Fig. 14.1.

To start with, let the gas mixture in volume B be rich in species B, and the volume C be rich in species C. Now, if the partition is removed, molecules of B would diffuse to the right, i.e. in the direction of decreasing concentration of B, and the molecules of C would diffuse to the left. Lower part of Fig. 14.1 shows the concentration profiles of B and C shortly after the partition is removed. After sufficient time has elapsed, equilibrium conditions would be achieved, i.e. uniform concentrations of B and C would be attained and there would be no more mass diffusion. Fick's law relates the mass flux by diffusion to the concentration gradient. It is stated as: **'Diffusion mass flux of a species through a medium is proportional to the concentration gradient"**, i.e.

$$j_B = \frac{m_B}{A} = -D_{BC} \cdot \frac{dC_B}{dx} \ \text{kg/(sm}^2) \quad \text{...(14.18)}$$

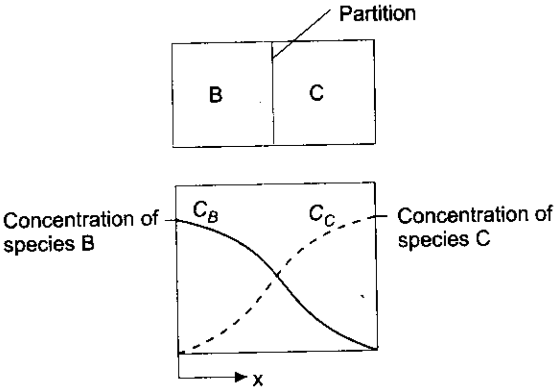


**FIGURE 14.1** Fick's law of diffusion for a binary gas mixture

where,

$j_B = m_B/A$ = mass flux, kg/(sm$^2$)
$A$ = area normal to the line of propagation of mass, m$^2$
$C_B$ = concentration of species B which is diffusing, kg/m$^3$
$dC_B/dx$ = concentration gradient for species B
$D_{BC}$ = diffusion coefficient or 'diffusivity' for the binary mixture of B and C, m$^2$/s

The negative sign in Eq. 14.18 signifies the fact that diffusion takes place in the direction of decreasing concentration, so that mass flux is a positive quantity.

Observe that unit of diffusivity is : m$^2$/s.

Molar flux would be obtained by simply dividing $j_B$ by the molecular weight of species B, i.e.

$$J_B = \frac{j_B}{M_B} \text{ kg moles(sm}^2) \qquad \text{...(14.19)}$$

Note the close similarity of Fick's law as given by Eq. 14.18 to the Fourier's law of heat conduction and to the Newton's law of viscosity, i.e.

$$q = \frac{Q}{A} = -k\cdot\frac{dT}{dx} = \alpha\cdot\frac{d}{dx}(\rho\cdot C_p\cdot T) \qquad \textit{(Fouier's law of heat conduction)}$$

$$\tau = \mu\cdot\frac{du}{dy} = \nu\cdot\frac{d}{dy}(\rho\cdot u) \qquad \textit{(Newton's law of viscosity)}$$

We can state that:

Fourier's law ...describes transport of energy due to temperature gradient
Newton's law...describes transport of momentum due to velocity gradient, and
Fick's law...describes transport of mass due to concentration gradient.

Further, units of mass diffusivity ($D$), thermal diffusivity ($\alpha$), and kinematic viscosity ($\nu$) are all same, i.e. m$^2$/s.

*Now, while dealing with perfect gases,* we can express the concentration gradient appearing in Fick's Eq. 14.18, in terms of partial pressures, as follows:

For species B:

$$p_B = \rho_B\cdot R_B\cdot T \qquad \textit{(Perfact gas law)}$$

i.e.

$$p_B = \rho_B\cdot\frac{R_u\cdot T}{M_B} \qquad \textit{(where, } R_u = \textit{Universal gas constant} = 8314 \text{ J}/(\textit{kg mole K}))$$

In the above, $p_B$ = partial pressure of species B,
$\rho_B$ = density of species B,
$M_B$ = the molecular weight of species B,

and, $T$ is the absolute temperature in Kelvin.

Remembering that density is nothing but concentration, i.e. $\rho_B = C_B$, we write, substituting for $\rho_B$ in Eq. 14.18:

$$j_B = \frac{m_B}{A} = -D_{BC}\cdot\frac{dC_B}{dx}$$

i.e.

$$j_B = \frac{m_B}{A} = -D_{BC}\cdot\frac{d}{dx}\left(\frac{p_B\cdot M_B}{R_u\cdot T}\right)$$

i.e.

$$j_B = \frac{m_B}{A} = -D_{BC}\cdot\frac{M_B}{R_u\cdot T}\cdot\frac{dp_B}{dx} \qquad \text{...(14.20)}$$

Similarly, for species C, we can write:

$$j_C = \frac{m_C}{A} = -D_{CB}\cdot\frac{M_C}{R_u\cdot T}\cdot\frac{dp_C}{dx} \qquad \text{...(14.21)}$$

Note that Eqs. 14.20 and 14.21 are valid for isothermal conditions only.

Following points must be noted well in connection with the Fick's law equation 14.18:

(i) This law is valid for mass diffusion, only due to concentration gradient. It is not applicable to the case of mass diffusion occurring due to other reasons such as pressure gradients, temperature gradients or other external forces.

(ii) Fick's law, like Fourier's law, is derived as a result of experimental observations; it is not derived from first principles analytically.

(iii) Mass diffusion occurs in the direction of decreasing concentration, just as heat transfer occurs in the direction of decreasing temperature.

(iv) Diffusion coefficient ($D$) depends upon pressure, temperature and the nature of the component concerned; however, it may be assumed as constant for ideal gases and dilute liquids for a given range of temperature and pressure.

**Diffusion coefficient ($D$):**

***For gases/gas mixtures:***

From kinetic theory of gases, it can be shown that at ordinary pressures, diffusion coefficient is independent of mixture composition, but increases with temperature and decreases with pressure, i.e. for a binary gas mixture of two components $B$ and $C$, we have:

$$D = 0.0043 \cdot \frac{T^{\frac{3}{2}}}{p_t \cdot \left( V_b^{\frac{1}{3}} + V_c^{\frac{1}{3}} \right)^2} \cdot \left( \frac{1}{M_B} + \frac{1}{M_C} \right)^{\frac{1}{2}} \text{cm}^2/\text{s} \qquad \text{...(14.22)}$$

where,

$p_t$ = total pressure (atm.)

$T$ = absolute temperature (K)

$M_B$, $M_C$ = molecular weights of gas species

$V_b$, $V_c$ = molecular volumes of B and C at normal boiling points, cm$^3$/gm. mole

Molecular weights and molecular volumes of a few gases are given in Table 14.1.

Data in Table 14.1 is useful to estimate the diffusion in binary gas mixtures.

From Eq. 14.22, it is clear that:

$$\frac{D_1}{D_2} = \left( \frac{T_1}{T_2} \right)^{\frac{3}{2}} \cdot \left( \frac{P_1}{P_2} \right) \qquad \text{...(14.23)}$$

i.e. if the diffusion coefficient at a certain temperature and pressure are known, then the diffusion coefficient at any other pressure and temperature can be estimated using Eq. 14.23. Note that the temperatures must be expressed in Kelvin.

Table 14.2 gives values of Diffusion coefficient and Schmidt numbers for a few substances diffusing through air at 25°C and 1 atm. Eq. 14.23 may be used to get values of diffusion coefficient at any other desired temperature and pressure.

**TABLE 14.1** Molecular weights and molecular volumes for a few gases

| Gas | Molecular weight | Molecular volume at normal boiling point (cm$^3$/gm.mole) |
|---|---|---|
| Air | 29 | 29.89 |
| Ammonia ($NH_3$) | 17 | 25.81 |
| Carbon dioxide ($CO_2$) | 44 | 34.00 |
| Carbon monoxide ($CO$) | 28 | 30.71 |
| Hydrogen ($H_2$) | 2 | 14.28 |
| Nitrogen ($N_2$) | 28 | 31.20 |
| Oxygen ($O_2$) | 32 | 25.63 |
| Sulphur dioxide ($SO_2$) | 64 | 44.78 |

**TABLE 14.2** Mass diffusivity and Schmidt number for a few gases and vapours diffusing through air at 25°C and 1 atm.

| *Substance* | *Mass diffusivity, $D$(m$^2$/s)* | *Schmidt number, $Sc = \nu/D$* |
|---|---|---|
| Ammonia | $0.280 \times 10^{-4}$ | 0.78 |
| Carbon dioxide | $0.164 \times 10^{-4}$ | 0.94 |
| Hydrogen | $0.410 \times 10^{-4}$ | 0.22 |
| Oxygen | $0.206 \times 10^{-4}$ | 0.75 |
| Water | $0.256 \times 10^{-4}$ | 0.60 |
| Methanol | $0.159 \times 10^{-4}$ | 0.97 |
| Ethyl alcohol | $0.119 \times 10^{-4}$ | 1.30 |
| Acetic acid | $0.133 \times 10^{-4}$ | 1.16 |
| Benzene | $0.088 \times 10^{-4}$ | 1.76 |
| Toluene | $0.084 \times 10^{-4}$ | 1.84 |

For the practically important case of diffusion of water vapour in air, following formula has been proposed by Marrero and Mason:

$$D_{H_2O\_air} = 1.87 \times 10^{-10} \cdot \frac{T^{2.072}}{P} \text{ m}^2/\text{s} \qquad ...280 \text{ K} < T < 450 \text{ K}...(14.24)$$

where, $P$ is the total pressure in atm. and $T$ is the temperature in Kelvin.

Values of $D$ at 1 atm., as calculated from Eq. 14.24, are given in Table 14.3:

**TABLE 14.3** Diffusion coefficient for water vapour in air at 1 atm.

| *T (deg.C)* | *D (m$^2$/s)* |
|---|---|
| 0 | 2.09E-05 |
| 5 | 2.17E-05 |
| 10 | 2.25E-05 |
| 15 | 2.33E-05 |
| 20 | 2.42E-05 |
| 25 | 2.5E-05 |
| 30 | 2.59E-05 |
| 35 | 2.68E-05 |
| 40 | 2.77E-05 |
| 45 | 2.86E-05 |
| 50 | 2.96E-05 |
| 55 | 3.05E-05 |
| 60 | 3.15E-05 |
| 65 | 3.25E-05 |
| 70 | 3.35E-05 |
| 75 | 3.45E-05 |
| 80 | 3.55E-05 |
| 85 | 3.66E-05 |
| 90 | 3.77E-05 |
| 95 | 3.88E-05 |
| 100 | 3.98E-05 |
| 105 | 4.1E-05 |
| 110 | 4.21E-05 |
| 115 | 4.32E-05 |
| 120 | 4.44E-05 |
| 125 | 4.56E-05 |

*Contd.*

*Contd.*

| | |
|---|---|
| 130 | 4.68E-05 |
| 135 | 4.8E-05 |
| 140 | 4.92E-05 |
| 145 | 5.05E-05 |
| 150 | 5.17E-05 |

For steady state diffusion through a non-diffusing, *multi-component mixture*, an 'effective diffusivity' is defined as:

$$D = \frac{1}{\frac{y_b}{D_{ab}} + \frac{y_c}{D_{ac}} + \frac{y_d}{D_{ad}}} \qquad \text{...(14.25)}$$

where,

$y_b, y_c, y_d, \ldots$ = mole fractions of components on a free basis

$D_{ab}, D_{ac}, D_{ad}, \ldots$ = diffusivities of species A through B, C, D ...

***For dilute liquids:***

Following semi-empirical relation is suggested to estimate the diffusion coefficient of dilute liquids:

$$F = \frac{T}{D_{AB} \cdot \mu_B} \qquad \text{...(14.26)}$$

where,

$T$ = absolute temperature (K)

$D_{AB}$ = diffusivity of solute A through a solvent B, ($m^2/s$)

$\mu_B$ = viscosity of solvent B (centipoises), and

$F$ = a function of molal volume of solute A, Ks/cm$^2$.centipoise...determined from charts

Table 14.4 gives mass diffusivity values of a few liquids at 20°C with water as solvent:

Observe that mass diffusivity in liquids is much lower than in gases; therefore, diffusion in liquids occurs at a much slower rate than in gases.

***For solids:***

Diffusion in solids occurs still at a lower rate as compared to that in gases and liquids. This is evident from the Table 14.5, which gives mass diffusivity values for a few substances diffusing through some solids.

## 14.4 General Differential Equation for Diffusion in Stationary Media

This equation for mass transfer of any species is derived in a manner analogous to the derivation of general differential equation for conduction.

**TABLE 14.4** Mass diffusivity of liquids at 20 deg.C, with water as solvent

| *Solute* | *D, ($m^2/s$)* | *Schmidt number, $Sc = \nu/D$* |
|---|---|---|
| Oxygen | $1.80 \times 10^{-9}$ | 558 |
| Carbon dioxide | $1.77 \times 10^{-9}$ | 559 |
| Ammonia | $1.76 \times 10^{-9}$ | 570 |
| Hydrogen | $5.13 \times 10^{-9}$ | 196 |
| Chlorine | $1.22 \times 10^{-9}$ | 824 |
| Hydrochloric acid | $2.64 \times 10^{-9}$ | 381 |
| Sulphuric acid | $1.73 \times 10^{-9}$ | 580 |
| Acetic acid | $0.88 \times 10^{-9}$ | 1140 |
| Ethanol | $1.00 \times 10^{-9}$ | 1005 |
| Urea | $8.06 \times 10^{-9}$ | 946 |
| Glucose | $0.60 \times 10^{-9}$ | - |

**TABLE 14.5** Diffusion through solids at 1 atm.

| Substance A (Solute) | Substance B (Solvent) | T, (K) | $D_{AB}$, (m²/s) |
|---|---|---|---|
| Carbon dioxide | Natural rubber | 298 | $1.1 \times 10^{-10}$ |
| Nitrogen | Natural rubber | 298 | $1.5 \times 10^{-10}$ |
| Oxygen | Natural rubber | 298 | $2.1 \times 10^{-10}$ |
| Helium | Pyrex | 773 | $2.0 \times 10^{-12}$ |
| Helium | Pyrex | 293 | $4.5 \times 10^{-15}$ |
| Helium | Silicon dioxide | 298 | $4.0 \times 10^{-14}$ |
| Hydrogen | Iron | 298 | $2.6 \times 10^{-13}$ |
| Hydrogen | Nickel | 358 | $1.2 \times 10^{-12}$ |
| Hydrogen | Nickel | 438 | $1.0 \times 10^{-11}$ |
| Cadmium | Copper | 293 | $2.7 \times 10^{-19}$ |
| Zinc | Copper | 773 | $4.0 \times 10^{-18}$ |
| Zinc | Copper | 1273 | $5.0 \times 10^{-13}$ |
| Antimony | Silver | 293 | $3.5 \times 10^{-25}$ |
| Bismuth | Lead | 293 | $1.1 \times 10^{-20}$ |
| Mercury | Lead | 293 | $2.5 \times 10^{-19}$ |
| Copper | Aluminium | 773 | $4.0 \times 10^{-14}$ |
| Copper | Aluminium | 1273 | $1.0 \times 10^{-10}$ |
| Copper | Iron (fcc) | 773 | $5.0 \times 10^{-15}$ |
| Carbon | Iron (fcc) | 1273 | $3.0 \times 10^{-11}$ |

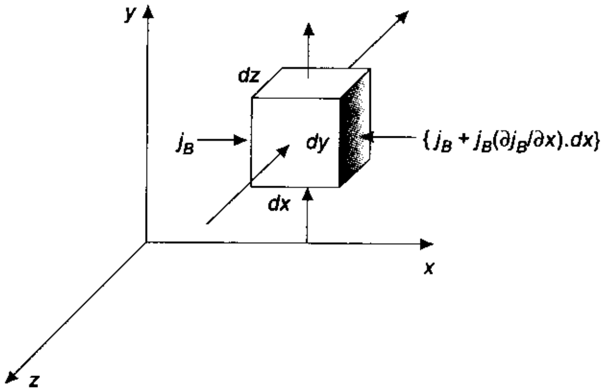


**FIGURE 14.2** General differential equation for mass diffusion

Consider a differential control volume in a given stationary medium (i.e. mass average velocity of the mixture is zero) as shown in Fig. 14.2.

**Assumptions:**

(i) Species B is diffusing through a solid or through a stationary fluid medium C

(ii) Mass transfer is by concentration difference only, and influence of other effects such as pressure, temperature or other forces is negligible

(iii) Diffusivity is constant in all directions (Isotropic).

Consider the mass balance of species B:

Along the X-direction:

Mass influx at the left surface = $(m_b/A).dy.dz$

Mass efflux at the right surface = $\{(m_b/A) + (\partial/\partial x)(m_b/A).dx\}.dy.dz$

Therefore, accumulation of species B in the elemental volume due to diffusion in X-direction =

$$(m_b/A).dy.dz - \{(m_b/A) + (\partial/\partial x)(m_b/A).dx\}.dy.dz = -(\partial/\partial x)(m_b/A).dx.dy.dz$$

Similarly, accumulation of species B due to diffusion in the Y and Z directions are:

Y-direction: $-(\partial/\partial y)(m_b/A).dx.dy.dz$

Z-direction: $-(\partial/\partial z)(m_b/A).dx.dy.dz$

Therefore, net accumulation of species B =

$$-\{(\partial/\partial x)(m_b/A) + (\partial/\partial y)(m_b/A) + (\partial/\partial z)(m_b/A)\}.\mathrm{dx.dy.dz} \quad \text{...(i)}$$

Let $q_b$ be the generation of mass species per unit volume (say, due to some chemical reaction). Then, total mass of species generated =

$$q_b.dx.dy.dz \quad \text{...(ii)}$$

Now, net effect of the mass accumulation due to diffusion and mass generation in the volume is an increase in the mass concentration of species B; this results in a time rate of change of mass concentration in the control volume, and is given by:

$$(\partial C_b/\partial \tau).dx.dy.dz \qquad \text{...(iii)}$$

Then, writing the mass balance,

$$-\{(\partial/\partial x)(m_b/A) + (\partial/\partial y)(m_b/A) + (\partial/\partial z)(m_b/A)\}.dx.dy.dz + q_b.dx.dy.dz = (\partial C_b/\partial \tau).dx.dy.dz$$

Cancelling $(dx.dy.dz)$ throughout and using Fick's law, i.e. $(m_b/A) = -D.(\partial C_b/\partial x)$,

$$(\partial C_b/\partial \tau) = (\partial/\partial x)\{D.(\partial C_b/\partial x)\} + (\partial/\partial y)\{D.(\partial C_b/\partial y)\} + (\partial/\partial z)\{D.(\partial C_b/\partial z)\} + q_b \qquad \text{...(14.27)}$$

Eq. 14.27 is the general differential equation for mass transfer by diffusion in a solid or stationary medium, with constant $D$ and with internal mass generation.

With no internal mass generation ($q_b = 0$), and constant $D$, we have:

$$(\partial C_b/\partial \tau) = D.\{(\partial^2 C_b/\partial x^2) + (\partial^2 C_b/\partial y^2) + (\partial^2 C_b/\partial z^2)\} = D.\nabla^2 C_b \qquad \text{...(14.28)}$$

To obtain the concentration gradient, and the mass diffusion rate, Eq. 14.28 has to be solved with the appropriate boundary conditions.

Eq. 14.28 can be written as:

$$\nabla^2 C_b = (1/D).(\partial C_b/\partial \tau) \qquad \text{...(14.29)}$$

Observe that Eq. 14.29 is similar in form to the heat conduction equation, i.e.

$$\nabla^2 T = (1/\alpha).(\partial T/\partial \tau) \qquad \textit{(differential equation of heat conduction)}$$

Boundary conditions generally encountered in practice are:

1. Specified concentrations at the boundary: $C_b = C_{b0}$ at $x = 0$ and $C_b = C_{bL}$ at $x = L$
2. Impermeable surface at the boundary: $\partial C_b/\partial x = 0$ at $x = 0$
3. Specified mass flux at the surface: $j_b = (m_b/A) = -D_{bc}.(\partial C_b/\partial x)$ at $x = 0$
4. Specified mass transfer coefficient (convective) at the surface: $j_b = h_m.(C_{bs} - C_{ba})$ where $h_m$ = convective mass transfer coefficient, $C_{bs}$ = concentration in the fluid adjacent to the surface, and $C_{ba}$ = bulk concentration in the fluid stream.

## 14.5 Steady State Diffusion in Common Geometries

Now, we shall derive relations for concentration profiles and mass transfer rates in a few simple geometries such as a plain membrane, cylindrical shell and spherical shell.

### 14.5.1 Steady State Diffusion Through a Plain Membrane

Consider a plain membrane whose thickness $L$ is small compared to its other dimensions, i.e. mass diffusion through this membrane can be considered as one-dimensional. See Fig. 14.3.

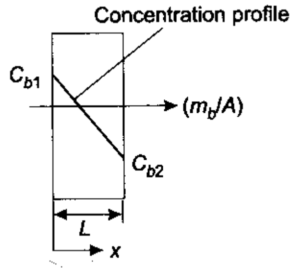


**FIGURE 14.3** Diffusion through a plain membrane

Then, for steady state (i.e. $(\partial C_b/\partial \tau) = 0$) and one-dimensional diffusion, differential equation 14.29 reduces to:

$$\frac{d^2 C_b}{dx^2} = 0$$

Integrating, $$\frac{dC_b}{dx} = C_1$$

Integrating again, $$C_b = C_1 \cdot x + C_2 \qquad \text{...(a)}$$

BCs: $C_b = C_{b1}$ at $x = 0$, and $C_b = C_{b2}$ at $x = L$

Therefore, $C_2 = C_{b1}$ and, $$C_1 = \frac{C_{b2} - C_{b1}}{L}$$

Subst. in Eq. a:

$$C_b = (C_{b2} - C_{b1}) \cdot \frac{x}{L} + C_{b1} \qquad \text{...(14.30)}$$

Eq. 14.30 gives the concentration profile, which is a straight line as shown in Fig. 14.3.

Now, mass transfer rate is obtained by applying the Fick's law, i.e.

$$\frac{m_b}{A} = -D_b \cdot \frac{dC_b}{dx}$$

i.e.
$$\frac{m_b}{A} = -D_b \cdot \frac{d}{dx}\left[(C_{b2} - C_{b1}) \cdot \frac{x}{L} + C_{b1}\right]$$

i.e.
$$\frac{m_b}{A} = -D_b \cdot \left(\frac{C_{b2} - C_{b1}}{L}\right)$$

i.e.
$$\frac{m_b}{A} = +\frac{D_b}{L} \cdot (C_{b1} - C_{b2}) \qquad \text{...(14.31)}$$

Eq. 14.31 gives the mass flux through the membrane.

**Alternatively:**

Since $D_b$ is constant, we can directly integrate the Fick's law equation between $x = 0$ and $x = L$, after separating the variables:

We have, from Fick's law:

$$\frac{m_b}{A} = -D_b \cdot \frac{dC_b}{dx}$$

Separating the variables and integrating,

$$\frac{m_b}{A} \cdot \int_0^L dx = -D_b \cdot \int_{C_{b1}}^{C_{b2}} dC_b \qquad \textit{(assuming } D_b = \textit{constant)}$$

i.e.
$$\frac{m_b}{A} = \frac{D_b}{L} \cdot (C_{b1} - C_{b2}) \qquad \textit{(same as Eq. 14.31)}$$

i.e.
$$m_b = \frac{C_{b1} - C_{b2}}{\frac{L}{D_b \cdot A}} = \frac{\text{Concentration potential}}{\text{Diffusion resistance}}$$

Note that the above equation gives diffusion mass flow rate (kg/s), which can be expressed in a form analogous to Ohm's law, i.e. as a ratio of concentration potential to the diffusion resistance.

Therefore, diffusion resistance for a plane membrane is given by:

$$R_{\text{membrane}} = \frac{L}{D_b \cdot A} \text{ s/m}^3 \qquad \text{...(14.32)}$$

Concentration profile is obtained by using the fact that in steady state, the mass diffusion rate through any section in the membrane must be constant. Let at any $x$, the concentration be $C_b$. Then, from Eq. 14.31,

$$\frac{m_b}{A} = \frac{D_b}{x} \cdot (C_{b1} - C_b)$$

Equating this with Eq. 14.31,

$$\frac{m_b}{A} = \frac{D_b}{x} \cdot (C_{b1} - C_b) = \frac{D_b}{L} \cdot (C_{b1} - C_{b2})$$

i.e.
$$\frac{(C_{b1} - C_b)}{x} = \frac{(C_{b1} - C_{b2})}{L}$$

i.e.
$$C_b = (C_{b2} - C_{b1}) \cdot \frac{x}{L} + C_{b1} \qquad \textit{(same as Eq. (14.30))}$$

Note that diffusion mass transfer and conduction heat transfer are analogous.

### 14.5.2 Steady State Diffusion through a Cylindrical Shell

Consider a cylindrical shell of length $L$ and inner and outer radii equal to $r_1$ and $r_2$, respectively, as shown in Fig. 14.4. Let the corresponding concentrations of species B at these radii be $C_{b1}$ and $C_{b2}$.

**Assumptions:**

1. Steady state, one-dimensional diffusion in the $r$ direction only
2. Constant $D$
3. No internal mass generation

Now, consider an elemental cylindrical shell at any radius $r$, with a thickness $dr$.

We have, from Fick's law:

$$\frac{m_b}{A} = -D_b \cdot \frac{dC_b}{dx}$$

For this system we write:

$$\frac{m_b}{2 \cdot \pi \cdot r \cdot L} = -D_b \cdot \frac{dC_b}{dr}$$

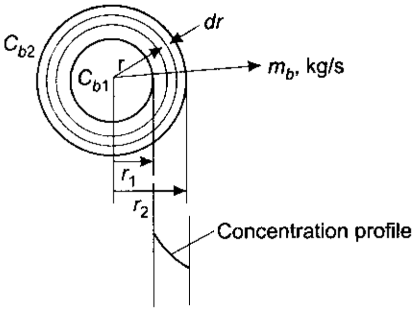


**FIGURE 14.4** Diffusion through a cylindrical shell

Separating the variables, and integrating from $r_1$ to $r_2$:

$$m_b \cdot \int_{r_1}^{r_2} \left(\frac{1}{r}\right) dr = -D_b \cdot 2 \cdot \pi \cdot L \cdot \int_{C_{b1}}^{C_{b2}} dC_b \qquad (assuming\ D_b = constant)$$

i.e.

$$m_b \cdot \ln\left(\frac{r_2}{r_1}\right) = 2 \cdot \pi \cdot D_b \cdot L \cdot (C_{b1} - C_{b2})$$

i.e.

$$m_b = \frac{C_{b1} - C_{b2}}{\dfrac{\ln\left(\dfrac{r_2}{r_1}\right)}{2 \cdot \pi \cdot D_b \cdot L}} \text{ kg/s} \qquad \text{...(14.33)}$$

i.e.

$$m_b = \frac{C_{b1} - C_{b2}}{R_{\text{diff\_cyl}}} \text{ kg/s} \qquad \text{...(14.34)}$$

where,

$$R_{\text{diff\_cyl}} = \frac{\ln\left(\dfrac{r_2}{r_1}\right)}{2 \cdot \pi \cdot D_b \cdot L} \text{ s/m}^3 = \text{diffusion resistance of cylindrical shell}$$

To get concentration distribution with radius:

Integrating from $r_1$ to $r$, (and concentration from $C_{b1}$ to $C_b$), Eq. 14.33 becomes:

$$m_b = \frac{C_{b1} - C_b}{\dfrac{\ln\left(\dfrac{r}{r_1}\right)}{2 \cdot \pi \cdot D_b \cdot L}} \text{ kg/s} \qquad \text{...(14.35)}$$

But, in steady state, since mass flow rate is same through each section of the cylindrical shell, equating Eqs. 14.33 and 14.35, we get:

$$\frac{C_{b1} - C_{b2}}{\dfrac{\ln\left(\dfrac{r_2}{r_1}\right)}{2 \cdot \pi \cdot D_b \cdot L}} = \frac{C_{b1} - C_b}{\dfrac{\ln\left(\dfrac{r}{r_1}\right)}{2 \cdot \pi \cdot D_b \cdot L}}$$

i.e.

$$\frac{C_b - C_{b1}}{C_{b2} - C_{b1}} = \frac{\ln\left(\dfrac{r}{r_1}\right)}{\ln\left(\dfrac{r_2}{r_1}\right)} \qquad \text{...(14.36)}$$

Eq. 14.36 gives the concentration distribution in the cylindrical shell as a function of radius, $r$. Note that the concentration distribution is logarithmic. This profile is also shown in Fig. 14.4.

Now, bringing in the concept of 'log mean area' for a cylindrical system, just as we did in the case of one-dimensional conduction through a cylindrical shell (see Chapter 4), we can write:

$$m_b = \frac{D_b \cdot (C_{b1} - C_{b2})}{\Delta x} \cdot A_m \qquad \text{...(14.37)}$$

where, $\Delta x = (r_2 - r_1)$ and, $A_m = \dfrac{2 \cdot \pi \cdot L \cdot (r_2 - r_1)}{\ln\left(\dfrac{r_2}{r_1}\right)}$ = log mean area.

### 14.5.3 *Steady State Diffusion through a Spherical Shell*

Consider a spherical shell of inner and outer radii equal to $r_1$ and $r_2$, respectively, as shown in Fig. 14.4. Let the corresponding concentrations of species B at these radii be $C_{b1}$ and $C_{b2}$.

**Assumptions:**

1. Steady state, one-dimensional diffusion in the $r$ direction only
2. Constant $D$
3. No internal mass generation

Now, consider an elemental spherical shell at any radius $r$, with a thickness $dr$.

We have, from Fick's law:

$$\frac{m_b}{A} = -D_b \cdot \frac{dC_b}{dx}$$

For this system:

$$\frac{m_b}{4 \cdot \pi \cdot r^2} = -D_b \cdot \frac{dC_b}{dr}$$

Separating the variables and integrating from $r_1$ to $r_2$:

$$m_b \cdot \int_{r_1}^{r_2} \left(\frac{1}{r^2}\right) dr = -D_b \cdot 4 \cdot \pi \cdot \int_{C_{b1}}^{C_{b2}} dC_b \qquad \textit{(assuming } D_b = \textit{constant)}$$

i.e.

$$m_b \cdot \left(\frac{1}{r_1} - \frac{1}{r_2}\right) = 4 \cdot \pi \cdot D_b \cdot (C_{b1} - C_{b2})$$

i.e.

$$m_b = \frac{C_{b1} - C_{b2}}{\dfrac{\left(\dfrac{1}{r_1} - \dfrac{1}{r_2}\right)}{4 \cdot \pi \cdot D_b}} \text{ kg/s} \qquad \text{...(14.38)}$$

i.e.

$$m_b = \frac{C_{b1} - C_{b2}}{R_{\text{diff\_sph}}} \qquad \text{...(14.39)}$$

where, $R_{\text{diff\_sph}} = \dfrac{\left(\dfrac{1}{r_1} - \dfrac{1}{r_2}\right)}{4 \cdot \pi \cdot D_b}$ s/m³ = diffusion resistance of spherical shell

To get concentration distribution with radius:

Integrating from $r_1$ to $r$, (and concentration from $C_{b1}$ to $C_b$), Eq. 14.38 becomes:

$$m_b = \frac{C_{b1} - C_b}{\dfrac{\left(\dfrac{1}{r_1} - \dfrac{1}{r}\right)}{4 \cdot \pi \cdot D_b}} \text{ kg/s} \qquad \text{...(14.40)}$$

But, in steady state, since mass flow rate is same through each section of the cylindrical shell, equating Eqs. 14.38 and 14.40, we get:

$$\frac{C_{b1}-C_{b2}}{\dfrac{\left(\dfrac{1}{r_1}-\dfrac{1}{r_2}\right)}{4\cdot\pi\cdot D_b}}=\frac{C_{b1}-C_b}{\dfrac{\left(\dfrac{1}{r_1}-\dfrac{1}{r}\right)}{4\cdot\pi\cdot D_b}}$$

i.e.

$$\frac{C_b-C_{b1}}{C_{b2}-C_{b1}}=\frac{\dfrac{1}{r}-\dfrac{1}{r_1}}{\dfrac{1}{r_2}-\dfrac{1}{r_1}} \qquad \text{...(14.41)}$$

Eq. 14.41 gives the concentration distribution in the spherical shell as a function of radius, $r$. Note that the concentration distribution is hyperbolic.

Now, bringing in the concept of 'mean area' for a spherical system, just as we did in the case of one-dimensional conduction through a spherical shell (see Chapter 4), we can write:

$$m_b=\frac{D_b\cdot(C_{b1}-C_{b2})}{\Delta x}\cdot A_m \qquad \text{...(14.42)}$$

where, $\Delta x=(r_2-r_1)$ and, $A_m=4\cdot\pi\cdot r_1\cdot r_2$ = mean area.

**Solubility factor $S$:**

Species concentration at the gas–solid interface is generally stated in terms of partial pressure of gas adjoining the interface and a 'solubility factor, $S$'. Then,

$$C_b=S\cdot p_a \qquad \text{...(14.43)}$$

where, $p_a$ = partial pressure, and, $S$ = solubility.

Solubility data for selected gas solid combinations are given in Tabl 14.6.

**TABLE 14.6** Solubility of selected gases and solids (For gas $i$, $S = C_{i,\text{ solid side}}/P_{i,\text{ gas side}}$)

| Gas | Solid | T, (K) | S, (kmol/m³bar) |
|---|---|---|---|
| $O_2$ | Rubber | 298 | 0.00312 |
| $N_2$ | Rubber | 298 | 0.00156 |
| $CO_2$ | Rubber | 298 | 0.04015 |
| He | $SiO_2$ | 293 | 0.00045 |
| $H_2$ | Ni | 358 | 0.00901 |

(*Note:* Permeability, $P = S\cdot D_{AB}$ where $D_{AB}$ = diffusivity of gas in solid.)

**Summary Table** Formulas for one-dimensional, steady state diffusion in simple geometries are summarised in Table 14.7 below:

**Example 14.1.** Air is contained in a vessel at a temperature of 20°C and pressure of 2 bar. Assuming the partial pressures of $O_2$ and $N_2$ to be in ratios of 0.21 and 0.79, respectively, calculate: (i) Molar concentrations (ii) Mass concentrations (i.e. densities), (iii) Mass fractions, and (iv) Molar fractions.

**Solution.**

**Data:**

$$T:=20+273\text{ K} \qquad p:=2\cdot10^5\text{ Pa} \qquad \frac{p_{O_2}}{p_{N_2}}:=\frac{0.21}{0.79} \qquad R_u:=8314\text{ J/kg mole K} \qquad M_{O_2}:=32 \qquad M_{N_2}:=28$$

(i) **Molar concentrations**

$$n_{O_2}=\frac{p_{O_2}}{R_u\cdot T}$$

i.e.

$$n_{O_2}:=\frac{0.21\cdot p}{R_u\cdot T}$$

**TABLE 14.7** One-dimensional, steady state diffusion in simple geometries

| Geometry | Mass flow rate (kg/s) | $R_{diffusion}$ (s/m³) | Concentration distribution |
|---|---|---|---|
| Plane membrane | $m_b = \dfrac{C_{b1} - C_{b2}}{\dfrac{L}{D_b \cdot A}}$ | $\dfrac{L}{D_b \cdot A}$ | $\dfrac{C_b - C_{b1}}{C_{b2} - C_{b1}} = \dfrac{x}{L}$ |
| Cylindrical shell | $m_b = \dfrac{C_{b1} - C_{b2}}{\dfrac{\ln\left(\frac{r_2}{r_1}\right)}{2 \cdot \pi \cdot D_b \cdot L}}$ | $\dfrac{\ln\left(\frac{r_2}{r_1}\right)}{2 \cdot \pi \cdot D_b \cdot L}$ | $\dfrac{C_b - C_{b1}}{C_{b2} - C_{b1}} = \dfrac{\ln\left(\frac{r}{r_1}\right)}{\ln\left(\frac{r_2}{r_1}\right)}$ |
| Spherical shell | $m_b = \dfrac{C_{b1} - C_{b2}}{\dfrac{\left(\frac{1}{r_1} - \frac{1}{r_2}\right)}{4 \cdot \pi \cdot D_b}}$ | $\dfrac{\left(\frac{1}{r_1} - \frac{1}{r_2}\right)}{4 \cdot \pi \cdot D_b}$ | $\dfrac{C_b - C_{b1}}{C_{b2} - C_{b1}} = \dfrac{\frac{1}{r} - \frac{1}{r_1}}{\frac{1}{r_2} - \frac{1}{r_1}}$ |

i.e. $n_{O_2} = 0.017$ **kg mole/m³** *(molar concentration of Oxygen.)*

Similarly,

$$n_{N_2} = \frac{p_{N_2}}{R_u \cdot T}$$

i.e.

$$n_{N_2} := \frac{79 \cdot p}{R_u \cdot T}$$

i.e. $n_{N_2} = 0.065$ **kg mole/m³** *(molar concentration of Nitrogen.)*

(ii) **Mass densities**

We have the relation between molar and mass densities:

$$n_A = \frac{\rho_A}{M_A} \qquad \text{...(14.1)}$$

Therefore,

$$\rho_{O_2} := M_{O_2} \cdot n_{O_2}$$

i.e. $\rho_{O_2} = 0.552$ **kg/m³** *(mass density of Oxtygen.)*

Similarly,

$$\rho_{N_2} := M_{N_2} \cdot n_{N_2}$$

i.e. $\rho_{N_2} = 1.816$ **kg/m³** *(mass density of Nitrogen.)*

(iii) **Mass fractions**

Total mass density,

$$\rho := \rho_{O_2} + \rho_{N_2}$$

i.e. $\rho = 2.368\ \text{kg/m}^3$

Therefore,

$$w_{O_2} := \frac{\rho_{O_2}}{\rho}$$

i.e. $w_{O_2} = 0.233$ *(mass fraction of Oxygen.)*

and,

$$w_{N_2} := \frac{\rho_{N_2}}{\rho}$$

i.e. $w_{N_2} = 0.767$ *(mass fraction of Nitrogen.)*

(iv) **Molar fractions**

Total molar concentration, $n := n_{O_2} + n_{N_2}$

i.e. $n = 0.082$ kg mole/m$^3$

Therefore,

$$y_{O_2} := \frac{n_{O_2}}{n}$$

i.e. $y_{O_2} = 0.21$ *(mole fraction of Oxygen.)*

and,

$$y_{N_2} := \frac{n_{N_2}}{n}$$

i.e. $y_{N_2} = 0.79$ *(mole fraction of Nitrogen.)*

Note that mole fractions should be equal to partial pressure fractions.

**Example 14.2.** Calculate the diffusion coefficient of ammonia ($NH_3$) in air at 20°C and 1 atm. pressure. Then, calculate the value of $D$ for a pressure of 3 atm. and temperature of 57°C.

**Solution.** We shall use the empirical relation given by Eq. 14.22:

$$D = 0.0043 \cdot \frac{T^{\frac{3}{2}}}{p_t \cdot \left(V_b^{\frac{1}{3}} + V_c^{\frac{1}{3}}\right)^2} \cdot \left(\frac{1}{M_B} + \frac{1}{M_C}\right)^{\frac{1}{2}} \text{ cm}^2/\text{s} \qquad \text{...(14.22)}$$

where, $p_t$ = total pressure (atm.)
$T$ = absolute temperature (K)
$M_B, M_C$ = molecular weights of gas species
$V_b, V_c$ = molecular volumes of B and C at normal boiling points, cm$^3$/gm mole.

Let us denote B for $NH_3$ and C for air. Getting the data for molecular weight and molecular volumes from Table 14.1, we have:

**Data:**

$P_t := 1$ atm. $M_B := 17$ $V_b := 25.81$ cm$^3$/gm $M_c := 29$ $V_c := 29.89$ cm$^3$/gm $T := 20 + 273$ K

Then,

$$D := 0.0043 \frac{T^{\frac{3}{2}}}{p_t \cdot \left(V_b^{\frac{1}{3}} + V_c^{\frac{1}{3}}\right)^2} \cdot \left(\frac{1}{M_B} + \frac{1}{M_C}\right)^{\frac{1}{2}}$$

i.e. $D = 0.179$ **cm²/s** *(Diffusiviy of* $NH_3$ *in air at 1 atm and 20°C.)*

(ii) **At 3 atm. And 57°C**

We have the relation:

$$\frac{D_1}{D_2} = \left(\frac{T_1}{T_2}\right)^{\frac{3}{2}} \cdot \left(\frac{P_1}{P_2}\right) \qquad \text{...(14.23)}$$

Here,
$D_1 := 0.179$ m$^2$/s
$T_1 := 20 + 273$ K
$P_1 := 1$ atm
$P_2 := 3$ atm
$T_2 := 57 + 273$ K

Therefore,

$$D_2 := \frac{D_1}{\left[\left(\frac{T_1}{T_2}\right)^{\frac{3}{2}} \cdot \left(\frac{P_1}{P_2}\right)\right]}$$

i.e. $D_2 = 0.642$ **cm²/s** *(Diffusiviy of* $NH_3$ *in air at 3 atm and 57°C.)*

**ple 14.3.** A steel, rectangular container having walls 15 mm thick, is used to store gaseous hydrogen at elevated essure. The molar concentrations of hydrogen in steel at the inside and outside surfaces are 1 kg mole/m$^3$ and zero, espectively. Assuming the diffusion coefficient for hydrogen in steel to be $0.25 \times 10^{-12}$ m$^2$/s, calculate the molar diffusion flux for hydrogen through steel. (M.U. 1999)

**Solution.**

**Data:**

$L := 0.015$ m $\quad D_b := 0.25 \cdot 10^{-12}$ m$^2$/s $\quad C_{b1} := 1$ kg mole/m$^3$ $\quad C_{b2} := 0.0$ kg mole/m$^3$

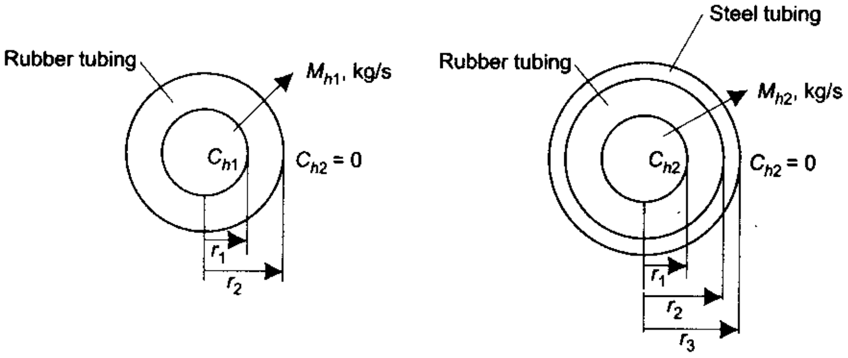
We have, for molar flux through a plane membrane:

$$J_b := \frac{D_b}{L} \cdot (C_{b1} - C_{b2}) \text{ kg mole/(m}^2\text{s)}$$

i.e. $\quad J_b = 16.667 \cdot 10^{-12}$ kg mole/m$^2$s $\qquad$ *(Molal flux of $H_2$ through steel.)*

**Example 14.4.** Hydrogen gas at 2 bar, 25°C is flowing through a vulcanised rubber tube, 30 mm ID, 50 mm OD. Solubility of $H_2$ in rubber is 0.053 m$^3$ of $H_2$ per atm. per m$^3$ of rubber at 25°C. Diffusivity of $H_2$ through rubber is $18 \times 10^{-11}$ m$^2$/s. Density of $H_2$ is 0.0899 kg/m$^3$ at 1 bar pres-sure and 0°C. Calculate percentage reduction in hydrogen loss if the rubber pipe is covered by 2.5 mm thick steel tubing. Assume diffusivity of $H_2$ through steel as $1.0 \times 10^{-12}$ m$^2$/s at 25°C. (M.U.)

**Solution.** See Fig. Ex. 14.4.



(a) only rubber tubing

(b) with steel tubing over the rubber tubing

**FIGURE** Example 14.4 Diffusion through a cylindrical shell

**Data:**

$P_1 := 2 \times 10^5$ Pa $\quad L := 1$ m $\quad r_1 := 15 \cdot 10^{-3}$ m $\quad r_2 := 25 \cdot 10^{-3}$ m $\quad r_3 := r_2 + 2.5 \cdot 10^{-3}$ m $\quad T_1 := 25 + 273$ K

$D_{H_2\_rubber} := 18 \cdot 10^{-11}$ m$^2$/s $\quad D_{H_2\_rubber} = 1 \cdot 10^{-12}$ m$^2$/s

Solubility of hydrogen in rubber at 1 bar = 0.053 m$^3$/bar/m$^3$ of rubber

Therefore, solubility at 2 bar pressure: S = $2 \cdot 0.053$ m$^3$/m$^3$ of rubber

i.e. $\quad$ S := 0.106 m$^3$/m$^3$ of rubber

Gas constant $R$ for Hydrogen:

Given that at 1 bar, 0°C, density is 0.0899 kg/m$^3$

Therefore, $R_{H_2} = \dfrac{p}{\rho \cdot T}$

i.e. $$R_{H_2} := \frac{1.0 \times 10^5}{0.0899 \times 273}$$

i.e. $$R_{H_2} = 4.075 \cdot 10^3 \text{ J/kgK}$$

Diffusion through rubber wall:

$$C_{h1} = \rho_1 = \frac{S \cdot P_1}{R_{H_2} \cdot T_1} \text{ kg/m}^3 \text{ of rubber}$$ *(concentration on the inside surface)*

i.e. $\quad C_{h1} := 0.01746$ kg/m$^3$ of rubber

and, $\quad C_{h2} := 0$ kg/m$^3$ of rubber $\qquad$ *(concentration on the outside surface)*

Therefore, resistance to diffusion through rubber:

$$R_{diff\_rubber} := \frac{\ln\left(\frac{r_2}{r_1}\right)}{2\cdot\pi\cdot D_{H_2\_rubber}\cdot L} \text{ s/m}^3 \qquad \textit{(for cylindrical shell)}$$

i.e. $R_{diff\_rubber} = 4.517\cdot 10^8 \text{ s/m}^3$.

**Case (i): Only rubber tubing:**

Mass diffusion rate: $m_{h1} := \frac{C_{h1}-C_{h2}}{R_{diff\_rubber}}$

i.e. $m_{h1} = 3.866\cdot 10^{-11}$ kg/s.

**Case (ii): With steel casing over rubber tubing:**

Now, resistance to diffususion through steel:

$$R_{diff\_steel} := \frac{\ln\left(\frac{r_3}{r_2}\right)}{2\cdot\pi\cdot D_{H_2\_steel}\cdot L} \text{ s/m}^3 \qquad \textit{(for cylindrical shell)}$$

i.e. $R_{diff\_steel} = 1.517 \times 10^{10} \text{ s/m}^3$

Therefore,

$R_{total} := R_{diff\_rubber} + R_{diff\_steel}$

i.e. $R_{total} = 1.562\cdot 10^{10} \text{ s/m}^3$

And, $m_{h2} := \frac{C_{h1}-C_{h2}}{R_{total}}$

i.e. $m_{h2} = 1.118\cdot 10^{-12}$ **kg/s** ***(mass dffusion rate of $H_2$ with steel tubing over the rubber turbing.)***

Therefore, percentage reduction in mass diffusion because of steel turbing:

$$\text{Reduction} := \frac{m_{h1}-m_{h2}}{m_{h1}}\cdot 100$$

i.e. Reduction = 97.109% ***(percentage reduction as a result of putting steel tubing over rubber tubing.)***

**Example 14.5.** Hydrogen gas is stored at 358 K in a 4.0 m ID, 5 cm thick spherical container made of Nickel. Molar concentration of hydrogen in Ni at the inner surface is 0.09 kg mole/m$^3$ and is equal to zero at the outer surface. Determine the mass diffusion rate of hydrogen through the walls of the container.

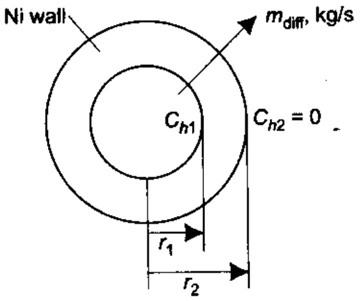


**FIGURE** Example 14.5 Diffusion through a spherical shell

**Solution.** From Table 14.5, we have, for $H_2$–$N_i$ at 358 K:

$D_{H_2\_Nickel} = 1.2\cdot 10^{-12} \text{ m}^2\text{/s}$

$r_1 := 2$ m $\quad r_2 := 2.05$ m $\quad T_1 := 358$ K $\quad C_{b1} := 0.09$ kg mole/m$^3$

$C_{b2} := 0$ kg mole/m$^3$ $\quad M_{H_2} := 2$

We have, the molar diffusion rate for a spherical shell:

$$N_b := \frac{C_{b1}-C_{b2}}{\frac{\left(\frac{1}{r_1}-\frac{1}{r_2}\right)}{4\cdot\pi\cdot D_{H_2\_Nickel}}} \text{ kg mole/s}$$

i.e. $N_b = 1.113\cdot 10^{-10}$ kg mole/s

Therefore, mass diffusion rate:

$m_b := N_b\cdot M_{H_2}$

i.e. $m_b = 2.226\cdot 10^{-10}$ kg/s ***(mass diffusion rate of hydrogen through Ni wall of spherical container.)***

**Example 14.6.** Helium gas is stored at a pressure of 6 bar and 293 K in a 0.4 m ID, 3 mm thick spherical container made of fused silica. Determine the rate of pressure drop due to diffusion. Given: $D = 0.04 \times 10^{-12}$ m$^2$/s, and solubility of gas at the solid surface on the inside is $18 \times 10^{-9}$ kg/(m$^3$Pa).

**Solution.** Since the wall thickness is small as compared to the radius, we can approximate the shell as a flat plate.

$p := 6 \cdot 10^5$ Pa $\quad r := 0.2$ m $\quad L := 0.003$ m $\quad T := 293$ K $\quad R_{He} := \frac{8314}{4}$ J(kgK) i.e. $R_{He} = 2.079 \cdot 10^3$ J/kgK)

$S := 18 \cdot 10^{-9}$ kg/(m$^3$Pa) $\quad D_{bc} := 0.04 \cdot 10^{-12}$ m$^2$/s

Mass of gas in the container: $m = \frac{p \cdot V}{R_{He} \cdot T}$

Since pressure drop due to diffusion is very slow, temperature $T$ can be considered as constant. Also, since the tank is rigid, volume $V$ can be considered as constant.

Therefore,

$$\frac{dm}{d\tau} = \frac{V}{R_{He} \cdot T} \cdot \frac{dp}{d\tau} \qquad \text{...(a)}$$

But, $dm/d\tau$ must also be equal to the diffusion rate, i.e.

$$\frac{dm}{d\tau} = A \cdot D_{bc} \cdot \frac{\rho_{b1} - \rho_{b2}}{L} \qquad \textit{(for a flat plate (membrane)...(b))}$$

where, $A$ = area of cross section, $\rho_{b2} = 0$ at the outer surface

Therefore, equating Eqs. a and b,

$$\frac{V}{R_{He} \cdot T} \cdot \frac{dp}{d\tau} = \frac{A \cdot D_{bc} \cdot \rho_{b1}}{L}$$

i.e.

$$\frac{dp}{d\tau} = \frac{R_{He} \cdot T \cdot A \cdot D_{bc} \cdot \rho_{b1}}{V \cdot L} \qquad \text{...(c)}$$

Now, for a sphere:

$$A := 4 \cdot \pi \cdot r^2$$

$$V := \frac{4}{3} \cdot \pi \cdot r^3$$

and,

$$\frac{A}{V} = 15$$

Now, $\quad \rho_{b1}$ = solubility x pressure

i.e. $\quad \rho_{b1} := S \cdot p$

Then, substituting in Eq. c, we get:

$$\frac{dp}{d\tau} = 1.315 \times 10^{-6} \text{ Pa/s} \qquad \textit{(rate of pressure drop.)}$$

**Note:** This is the initial rate of pressure drop. With time, pressure inside the container will fall; then, the rate of pressure drop will also decrease.

## 14.6 Equimolal Counter-diffusion in Gases

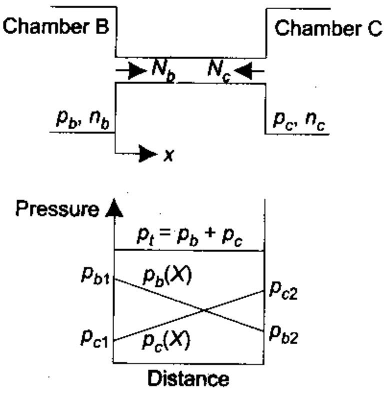


**FIGURE 14.5** Equimolal counter-diffusion in a binary gas mixture

Consider a binary mixture of species B and C. 'Equimolal counter-diffusion' implies that in the diffusion process, each molecule of component B is replaced by each molecule of component C and vice-versa. Refer to Fig. 14.5, which shows two chambers B and C, both containing mixtures of B and C, but at different concentrations, connected to each other by a passage; component B diffuses from higher concentration to the lower concentration and equimolal counter-diffusion occurs between B and C and each molecule of B is replaced by each molecule of C and vice-versa. Total pressure, $p_t$ of the system remains constant, and, $p_t = p_b + p_c$.

Distillation columns are good examples for equimolal counter-diffusion. Venting of a gas to, say, atmosphere, also involves equimolal counter-diffusion.

From Fick's law, we have molar diffusion rates of species B and C: (See eqn. 14.20)

$$N_b = \frac{m_b}{M_b} = -D_{bc} \cdot \frac{A}{R_u \cdot T} \cdot \frac{dp_b}{dx} \text{ kg mole/s} \qquad \text{...(14.44a)}$$

and, $$N_c = \frac{m_c}{M_c} = -D_{cb}\cdot\frac{A}{R_u\cdot T}\cdot\frac{dp_c}{dx} \text{ kg mole/s} \qquad \text{...(14.44b)}$$

where, $p_b$ and $p_c$ are partial pressures of species B and C, respectively.

Note from the Fig. 14.5 that each of the components diffuses in the direction of its drop in concentration.

Now, from Dalton's law, total pressure of the system is equal to the sum of the partial pressures of the components of the mixture, i.e.

$$P_t = p_b + p_c$$

Differentiating w.r.t. $x$,

$$\frac{dp_t}{dx} = \frac{dp_b}{dx} + \frac{dp_c}{dx}$$

However, under steady state conditions, total pressure of the system is constant, i.e.

$$\frac{dp_t}{dx} = 0 \text{ and, } \frac{dp_b}{dx} = \frac{-dp_c}{dx}$$

Also, $N_b$ and $N_c$ are numerically equal, since both the species are diffusing in opposite directions but at a constant rate, i.e.

$$N_b = -N_c$$

i.e. $$-D_{bc}\cdot\frac{A}{R_u\cdot T}\cdot\frac{dp_b}{dx} = D_{cb}\cdot\frac{A}{R_u\cdot T}\cdot\frac{dp_c}{dx}$$

Substituting for $dp_c/dx$:

$$-D_{bc}\cdot\frac{A}{R_u\cdot T}\cdot\frac{dp_b}{dx} = -D_{cb}\cdot\frac{A}{R_u\cdot T}\cdot\frac{dp_b}{dx}$$

or, $$D_{bc} = D_{cb} = D. \qquad \text{...(14.45)}$$

Note the important fact from Eq. 14.45 that in equimolal counter-diffusion, the diffusion coefficient of component B in component C is equal to the diffusion coefficient of component C in component B. Value of $D$ in a binary mixture is calculated using the empirical Eq. 14.22, as already described.

For constant $D_{bc}$, Eq. 14.44 may be integrated between any two planes, to give:

$$N_b = \frac{m_b}{M_b} = -D\cdot\frac{A}{R_u\cdot T}\cdot\frac{(p_{b2} - p_{b1})}{(x_2 - x_1)}$$

i.e. $$N_b = \frac{m_b}{M_b} = D\cdot\frac{A}{R_u\cdot T}\cdot\frac{(p_{b1} - p_{b2})}{(x_2 - x_1)} \text{ kg mole/s} \qquad \text{...(14.46)}$$

In Eq. 14.46, $p_{b1}$ and $p_{b2}$ are the partial pressures of component B at locations $x_1$ and $x_2$, respectively.

**Example 14.7.** A distillation column containing a mixture of Benzene and Toluene is at 101 kN/m$^2$ pressure and temperature = 100°C. The liquid and vapour phase contain 30 mol% and 45 mol% of Benzene. At 100°C, the vapour pressure of Toluene is 70 kN/m$^2$ and diffusivity is $5 \times 10^{-6}$ m$^2$/s. Work out the rate of interchange of Benzene and Toluene between the liquid and vapour phases if resistance to mass transfer lies in a film 0.25 mm thick. Universal gas constant = 8.314 kJ/kg mole K. (M.U. Dec. 1998)

**Solution.** This is the case of a distillation column, and equimolar counter-diffusion occurs in the column. Let subscripts: t → for Toluene and, b → for Benzene.

**Data:**

$p_{tot} := 1.01\cdot10^5$ N/m$^2$ $\quad p_{vap\_toluene} := 7.0\cdot10^4$ N/m$^2$ $\quad y_{b\_liq} := 0.3 \quad y_{b\_vap} := 0.45 \quad A := 1$ m$^2$ (assumed)

$T := 373$ K $\quad D := 5\cdot10^{-6}$ m$^2$/s $\quad R_u := 8314$ J/kg mole K

$\Delta x := 0.00025$ m; *(Note that $\Delta x = (x_2 - x_1)$, distance through which diffusion occurs)*

Now, we have for Toluene, mass diffusion rate:

$$m_t = \frac{D\cdot A\cdot M_t}{R_u\cdot T}\cdot\frac{(p_{t1} - p_{t2})}{(x_2 - x_1)} \text{ kg/s} \qquad \text{(from Eq. (14.46))}$$

And, molal flux:

$$\frac{N_t}{A} = \frac{m_t}{M_t\cdot A} = \frac{D}{R_u\cdot T}\cdot\frac{(p_{t1} - p_{t2})}{(x_2 - x_1)} \text{ kg mole/(sm}^2\text{)}$$

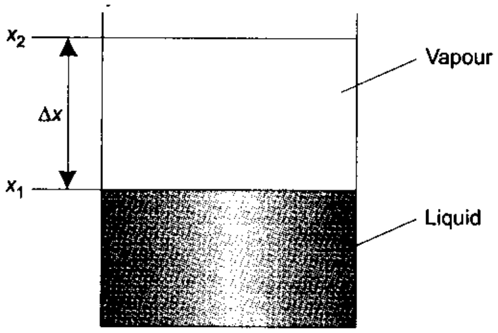


**FIGURE** Example 14.7 Equimolal counter-diffusion

Now, $p_{t1}$ = partial pressure of Toluene at $x_1$, i.e. in liquid phase:

$p_{t1} := (p_{\text{vap\_toluene}}) \cdot (1 - y_{\text{b\_liq}})$ ...*By Raqult's law*

i.e. $p_{t1} = 4.9 \times 10^4\ \text{N/m}^2$

And, $p_{t2}$ = partial pressure of Toluene at $x_2$, i.e. in vapour phase:

$p_{t2} := (p_{\text{tot}}) \cdot (1 - y_{\text{b\_vap}})$ ...*By Dalton's law*

i.e. $p_{t2} = 5.555 \times 10^4\ \text{N/m}^2$

Therefore, molal flux for Toluene:

$$\frac{N_t}{A} = \frac{D}{R_u \cdot T} \cdot \frac{(p_{t1} - p_{t2})}{(x_2 - x_1)} = \frac{D}{R_u \cdot T} \cdot \frac{(p_{t1} - p_{t2})}{\Delta x}$$

i.e. $\frac{N_t}{A} = -4.224 \times 10^{-5}$ **kg mole/(sm²).**

Negative sign indicates that Toluene diffuses from $x_2$ to $x_1$, i.e. from vapour to liquid. Benzene will diffuse at the same rate but in opposite direction. i.e. $N_t = -N_b$.

**Example 14.8.** A tank contains a mixture of $CO_2$ and $N_2$, in the mole proportions of 0.2 and 0.8 at 1 bar and 290 K. It is connected by a duct of cross-sectional area 0.1 m² to another tank containing a mixture of $CO_2$ and $N_2$ in the molal proportions of 0.8 and 0.2. The duct is 0.5 m long. Determine the diffusion rates of $CO_2$ and $N_2$ in kg/s. Given: $D = 0.16 \times 10^{-4}\ \text{m}^2/\text{s}$ for $CO_2/N_2$...at 293 K...from tables. (M.U. Dec. 1998)

**Solution.** This is the case of equimolar counter-diffusion between $CO_2$ and $N_2$.

**Data:**

$P_{\text{tot}} := 1.00 \cdot 10^5\ \text{Pa}$ $\quad p1_{CO_2} := 0.2 \cdot 10^5\ \text{Pa}$ $\quad p1_{N_2} := 0.8 \times 10^5\ \text{Pa}$ $\quad p2_{CO_2} := 0.8 \cdot 10^5\ \text{Pa}$

$p2_{N_2} := 0.2 \cdot 10^5\ \text{Pa}$ $\quad T := 290\ \text{K}$ $\quad \Delta x := 0.5\ \text{m}$ $\quad A := 0.1\ \text{m}^2$ $\quad D := 16 \cdot 10^{-6}\ \text{m}^2/\text{s}$

$R_u := 8314\ \text{J/(kg mole K)}$

For equimolar counter-diffusion, we have:

Molar flow rate, from Eq. 14.46:

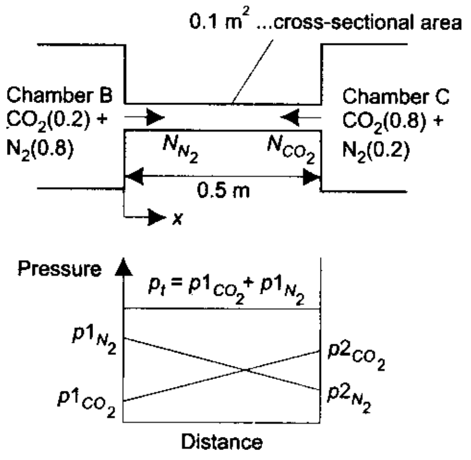


**FIGURE** Example 14.8 Equimolal counter-diffusion in a binary gas mixture

$$N_b = \frac{m_b}{M_b} = D \cdot \frac{A}{R_u \cdot T} \cdot \frac{(p_{b1} - p_{b2})}{(x_2 - x_1)}\ \text{kg mole/s} \qquad \text{...(14.46)}$$

For Nitrogen, in this case, we can write:

$$N_{\text{nitrogen}} := D \cdot \frac{A}{R_u \cdot T} \cdot \frac{(p1_{N_2} - p2_{N_2})}{\Delta x}$$

i.e. $N_{\text{nitrogen}} = 7.963 \times 10^{-8}$ **kg mole/s** (***molar flow rate of*** $N_2$)

and, mass flow rate of Nitrogen: = $N_{\text{nitrogen}} \times$ (Mol. wt. of Nitrogen)

i.e. $N_{\text{nitrogen}} \cdot 28 = 2.23 \cdot 10^{-6}$ **kg/s** (***mass flow rate of*** $N_2$.)

For $CO_2$, we can write:

$$N_{CO_2} := D \cdot \frac{A}{R_u \cdot T} \cdot \frac{(p1_{CO_2} - p2_{CO_2})}{\Delta x}$$

i.e. $N_{CO_2} = -7.963 \times 10^{-8}$ kg mole/s (*molar flow rate of* $CO_2$.)

**Note:** Molar flow rate of $CO_2$ is equal to that of $N_2$, but in opposite direction, as indicated by negative sign.

And, mass flow rate of $CO_2$: = $N_{CO_2} \cdot$ (Mol. wt. of $CO_2$)

i.e. $N_{CO_2} \cdot 44 = -3.504 \cdot 10^{-6}$ kg/s (*mass flow rate of* $CO_2$.)

**Example 14.9.** A spherical ball of ice, 1 cm diameter is suspended in still dry air at 1.013 bar. Calculate the initial rate of evaporation at the surface.

Take $D = 0.256 \times 10^{-4}\ \text{m}^2/\text{s}$. At 0 deg.C, saturated vapour pressure = 0.0061 bar.

**Solution.**

**Data:** $T := 273\ \text{K}$ $\quad D := 0.256 \cdot 10^{-4}\ \text{m}^2/\text{s}$ $\quad P_t := 1.013 \cdot 10^5\ \text{Pa}$ $\quad r_1 := 0.5 \times 10^{-2}\ \text{m}$

$r_2 := \infty$ m   $R_u := 8314$ J/kg mole K

At 0 deg. C: $p_{v1} := 0.006\cdot 10^5$ N.m$^2$ *(vapour pressure of water vapour)*

Therefore, $p_{a1} := p_t - p_{v1}$

i.e. $p_{a1} := 1.007\cdot 10^5$ N/m$^2$ *(partial pressure of air)*

At $r$ = infinity: $p_{v2} := 0$ *(vapour pressure of water vapour)*

Therefore, $p_{a2} := p_t - p_{v2}$

i.e. $p_{a2} := 1.013\cdot 10^5$ N/m$^2$ *(partial pressure of air)*

For equimolar counter-diffusion in spherical coordinates

$$\frac{N_b}{A} = \frac{-D}{R_u\cdot T}\cdot\frac{dp_b}{dx} \text{ kg mole/s m}^2 \qquad \textit{(molar flux)}$$

i.e.

$$\frac{N_b}{4\cdot\pi\cdot r^2} = \frac{-D}{R_u\cdot T}\cdot\frac{dp_b}{dx}$$

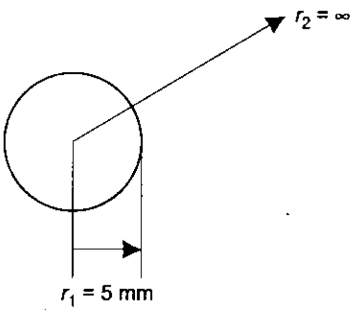


**FIGURE** Example 14.9
Equimolal counter-diffusion from a sphere to surroundings

Separating the variables and integrating,

$$\int_1^2 dp_v = -\frac{-N_b\cdot R_u\cdot T}{4\cdot\pi\cdot D}\cdot\int_1^2\left(\frac{1}{r^2}\right)dr$$

i.e.

$$(p_{v1}-p_{v2}) = \frac{-N_b\cdot R_u\cdot T}{4\cdot\pi\cdot D}\cdot\left(\frac{1}{r_1}-\frac{1}{r_2}\right)$$

But, $r_2 = \infty$ and, $p_{v2} = 0$

Therefore,

$$N_{\text{water}} := \frac{4\cdot\pi\cdot D\cdot p_v\cdot r_1}{R_u\cdot T}$$

i.e. $N_{\text{water}} = 4.323\cdot 10^{-10}$ kg.mole/s *(initial rate of evaporation of water)*

We can also write:

$N_{\text{water}}\cdot 18 = 7.781\cdot 10^{-9}$ kg/s. (since mol. wt. of water vap. = 18)

**Example 14.10.** A pipe carrying ammonia at 1 atm. is maintained at that pressure by venting ammonia to atmosphere through a 5 mm ID, 5 m long tube. Assuming both ammonia and atmospheric air to be at 25 deg.C, determine: (a) mass flow rate of ammonia diffusing into the atmosphere, and (b) mass flow rate of air that diffuses into the pipe line. Take the diffusion coefficient of ammonia in air (or, air in ammonia) as: $D = 0.26\times 10^{-4}$ m$^2$/s.

**Solution.** This is a case of equimolal counter-diffusion, where two large reservoirs containing mixture of ideal gases at different concentrations, are connected to each other by a pipe.

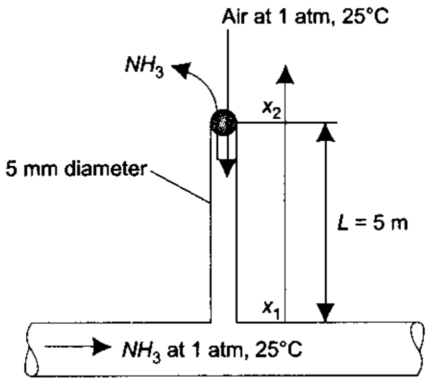


**FIGURE** Example 14.10 Equimolal counter-diffusion of $NH_3$ and Air

**Data:**

$P_{1\_NH_3} := 1.013\cdot 10^5$ Pa *(partial pressure of ammonia at section-1)*

$P_{2\_NH_3} := 0$ Pa *(partial pressure of ammonia at section-2, i.e. at atmosphere)*

$x_1 := 0$ m   $x_2 := 5$ m   $d := 0.005$ m   $L := 5$ m   $T := 298$ K

$D := 0.26\times 10^{-4}$ m$^2$/s   $R_u := 8314$ J/kg moleK

$A := \frac{\pi\cdot d^2}{4}$ i.e. $A = 1.963\cdot 10^{-5}$ m$^2$ *(cross-sectional area of vent pipe)*

Note that the pressure of ammonia at the bottom of vent pipe ($x = 0$) is 1 atm. and is equal to zero at the top ($x = L$)

For equi-molal diffusion, we have:

$$N_b := \frac{m_b}{M_b} = D\cdot\frac{A}{R_u\cdot T}\cdot\frac{(p_{b1}-p_{b2})}{(x_2-x_1)} \text{ kg mole/s.} \qquad \text{...(14.46)}$$

With the notations used above, we get:

$$N_{NH_3} := D\cdot\frac{A}{R_u\cdot T}\cdot\frac{(p_{1\_NH_3}-p_{2\_NH_3})}{(x_2-x_1)} \text{ kg mole/s.}$$

i.e. $$N_{NH_3} = 4.175 \cdot 10^{-12} \text{ kg mole/s.}$$

Therefore, mass diffusion rate of ammonia into air:

$$M_{NH_3} := 17 \qquad \textit{(molecular wt. of } NH_3\textit{)}$$

and, $$m_{NH_3} := N_{NH_3} \cdot M_{NH_3}$$

i.e. $$m_{NH_3} = 7.097 \cdot 10^{-11} \textbf{ kg/s} \qquad \textbf{\textit{(mass diffusion rate of ammonia into atmosphere.)}}$$

And, mass diffusion rate of air into ammonia:

For equimolal diffusion, we have the molal diffusion rate of ammonia into air is *equal* to the molal diffusion rate of air into ammonia.

i.e. $$N_{Air} = N_{NH_3} = (4.175 \cdot 10^{-12}) \text{ kg mole/s}$$

Therefore, mass diffusion rate of air into ammonia:

$$M_{air} := 29 \qquad \textit{(Molecular weight of air)}$$

and, $$m_{Air} = N_{air} \cdot M_{air}$$

i.e. $$m_{Air} = -1.211 \cdot 10^{-10} \textbf{ kg/s} \qquad \textbf{\textit{(mass diffusion rate of air into ammonia.)}}$$

**Note:** negative sign simply indicates that mass diffusion of air is in the opposite direction, i.e. from atmosphere to ammonia in the pipe.

## 14.7 Steady State Uni-directional Diffusion—Diffusion of Water Vapour through Air

Let us consider a binary gas mixture wherein one gas diffuses through another gas which remains as a stagnant layer; familiar examples of uni-directional diffusion through a stagnant gas layer are: absorption, humidification and, the diffusion of water vapour through a layer of air, when evaporation of water occurs, say in a well or a test tube.

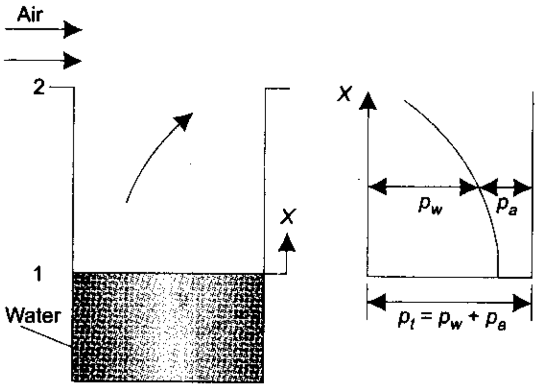


**FIGURE 14.6** Diffusion of water vapour through air

Consider the evaporation of water contained in a well and the subsequent diffusion of this water vapour through the stagnant gas layer above the water. See Fig. 14.6.

**Assumptions:**

(i) steady state and isothermal conditions exist
(ii) total pressure is constant
(iii) both air and water vapour behave like perfect gases
(iv) air has negligible solubility in waer, and
(v) air movement at the top is very slow, i.e. movement of air is just sufficient to carry away the evaporated water, but not large enough to cause any change in the concentration profile of air.

Water which evaporates at surface 1 (see the Fig. 14.6) diffuses through air standing above it; and, in steady state, this upward movement of water vapour must be balanced by a downward diffusion of air so that concentration at any location $x$, remains a constant.

Downward diffusion of air:

$$m_a = -D \cdot \frac{A \cdot M_a}{R_u \cdot T} \cdot \frac{dp_a}{dx} \qquad \text{...(14.47)}$$

Since air is not soluble in water, this downward movement of air will cause a bulk mass movement upward, with a velocity just large enough to compensate for the diffusion of air downward.

Bulk mass transfer of air is equal to:

$$m_a = -\rho_a \cdot A \cdot u = -p_a \cdot \frac{M_a}{R_u \cdot T} \cdot A \cdot u \qquad \text{...(14.48)}$$

where, $u$ = bulk velocity upward

Equating Eqs. 14.47 and 14.48, we get:

$$D\cdot\frac{A\cdot M_a}{R_u\cdot T}\cdot\frac{dp_a}{dx} = p_a\cdot\frac{M_a}{R_u\cdot T}\cdot A\cdot u$$

i.e.
$$u = \frac{D}{p_a}\cdot\frac{dp_a}{dx} \qquad \text{...(14.49)}$$

Now, the total mass transfer of water is equal to the upward mass diffusion of water *plus* water vapours carried upward by bulk movement of air.

i.e.
$$m_{w_{\text{tot}}} = -D\cdot\frac{A\cdot M_w}{R_u\cdot T}\cdot\frac{dp_w}{dx} + \rho_w\cdot A\cdot u \qquad \text{...(14.50)}$$

i.e.
$$m_{w_{\text{tot}}} = -D\cdot\frac{A\cdot M_w}{R_u\cdot T}\cdot\frac{dp_w}{dx} + \frac{p_w\cdot M_w\cdot A}{R_u\cdot T}\cdot\frac{D}{p_a}\cdot\frac{dp_a}{dx} \qquad \text{...(14.51), } \textit{using Eq. (14.49)}$$

In the above equations, $p_a$ = partial pressure of air and, $p_w$ = partial pressure of water vapour. Now, from Dalton's law of partial pressures, we have, the total pressure:

$$p_t = p_a + p_w$$

Therefore,
$$\frac{dp_t}{dx} = \frac{dp_a}{dx} + \frac{dp_w}{dx}$$

But, the total pressure of the system is constant; so,

$$\frac{dp_t}{dx} = 0$$

Therefore,
$$\frac{dp_a}{dx} = \frac{-dp_w}{dx}$$

Then, substituting in Eq. 14.51,

$$m_{w_{\text{tot}}} = -D\cdot\frac{A\cdot M_w}{R_u\cdot T}\cdot\frac{dp_w}{dx} - \frac{p_w\cdot M_w\cdot A}{R_u\cdot T}\cdot\frac{D}{p_a}\cdot\frac{dp_w}{dx}$$

i.e.
$$m_{w_{\text{tot}}} = -D\cdot\frac{A\cdot M_w}{R_u\cdot T}\cdot\frac{dp_w}{dx}\cdot\left(1+\frac{p_w}{p_a}\right)$$

i.e.
$$m_{w_{\text{tot}}} = -D\cdot\frac{A\cdot M_w}{R_u\cdot T}\cdot\frac{dp_w}{dx}\cdot\left(\frac{p_a+p_w}{p_a}\right)$$

i.e.
$$m_{w_{\text{tot}}} = -D\cdot\frac{A\cdot M_w}{R_u\cdot T}\cdot\frac{dp_w}{dx}\cdot\left(\frac{p_t}{p_t-p_w}\right), \qquad \text{...(14.52)}$$

Eq. 14.52 is known as '**Stefan's law**' for an ideal gas diffusing through another, stationary, ideal gas component in a binary gas mixture.

Integrating Stefan's equation between planes $x_1$ and $x_2$,

$$m_{w_{\text{tot}}}\cdot\int_{x_1}^{x_2} dx = \frac{-D\cdot A}{R_u\cdot T}\cdot M_w\cdot p_t\cdot\int_{p_{w1}}^{p_{w2}}\frac{1}{(p_t-p_w)}dp_w$$

i.e.
$$m_{w_{\text{tot}}}\cdot(x_2-x_1) = \frac{D\cdot A}{R_u\cdot T}\cdot M_w\cdot p_t\cdot\int_{p_{w1}}^{p_{w2}}\frac{1}{(p_w-p_t)}dp_w$$

i.e.
$$m_{w_{\text{tot}}}\cdot(x_2-x_1) = \frac{D\cdot A}{R_u\cdot T}\cdot M_w\cdot p_t\cdot\ln\left(\frac{p_{w2}-p_t}{p_{w1}-p_t}\right)$$

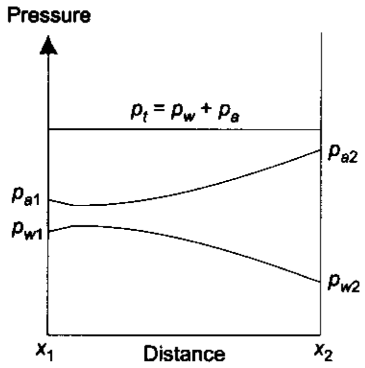


**FIGURE 14.7** Uni-directional diffusion of water vapour in a stationary gas (i.e. air)

i.e. $$m_{w_{tot}} \cdot (x_2 - x_1) = \frac{D \cdot A}{R_u \cdot T} \cdot M_w \cdot p_t \cdot \ln\left(\frac{p_t - p_{w2}}{p_t - p_{w1}}\right)$$

i.e. $$m_{w_{tot}} \cdot (x_2 - x_1) = \frac{D \cdot A}{R_u \cdot T} \cdot M_w \cdot p_t \cdot \ln\left(\frac{p_{a2}}{p_{a1}}\right)$$

Therefore,

$$m_{w_{tot}} = \frac{D \cdot A}{R_u \cdot T} \cdot \frac{M_w \cdot p_t}{(x_2 - x_1)} \cdot \ln\left(\frac{p_{a2}}{p_{a1}}\right) \text{ ...kg/s} \quad \text{...(14.53)}$$

Now, let us define 'Log Mean Partial pressure of Air (LMPA)' as:

$$\text{LMPA} = \frac{p_{a2} - p_{a1}}{\ln\left(\frac{p_{a2}}{p_{a1}}\right)}$$

i.e. $$\ln\left(\frac{p_{a2}}{p_{a1}}\right) = \frac{p_{a2} - p_{a1}}{\text{LMPA}}$$

Then, Eq. 14.53 can be written as:

$$m_{w_{tot}} = \frac{D \cdot A}{R_u \cdot T} \cdot \frac{M_w \cdot p_t}{(x_2 - x_1)} \cdot \frac{(p_{a2} - p_{a1})}{\text{LMPA}}$$

i.e. $$m_{w_{tot}} = \frac{D \cdot A}{R_u \cdot T} \cdot \frac{M_w \cdot p_t}{(x_2 - x_1)} \cdot \frac{(p_{w1} - p_{w2})}{\text{LMPA}} \text{ kg/s.} \quad \text{...(14.54)}$$

Note that, in Eq. 14.54, instead of LMPA we can use arithmetic mean pressure, [i.e. $(p_{a1} + p_{a2})/2$], if the partial pressure of water vapour does not change much as compared to the total pressure of the mixture.

Let the partial pressure of water be $p_w$ at any plane $x$; then, integrating the Stefan's equation between planes $x_1$ and $x$, we get:

$$m_w \cdot (x - x_1) = \frac{D \cdot A}{R_u \cdot T} \cdot M_w \cdot p_t \cdot \ln\left(\frac{p_t - p_w}{p_t - p_{w1}}\right)$$

i.e. $$p_w = p_t - (p_t - p_{w1}) \cdot \exp\left[\frac{m_w}{p_t \cdot M_w} \cdot (x - x_1) \cdot \frac{R_u \cdot T}{D \cdot A}\right] \quad \text{...(14.55)}$$

Eq. 14.55 gives the variation of partial pressure of water vapour with distance $x$ along the tube.

And, for the stagnant gas, i.e. air:

$$p_a = p_t - p_w$$

i.e. $$p_a = (p_t - p_{w1}) \cdot \exp\left[\frac{m_w}{p_t \cdot M_w} \cdot (x - x_1) \cdot \frac{R_u \cdot T}{D \cdot A}\right] \quad \text{...(14.56)}$$

Variation of $p_w$ and $p_a$ with $x$, are shown graphically in Fig. 14.7:

**Example 14.11.** Calculate the hourly loss of water from a well 6 m deep and cross-sectional area 5 m$^2$. Temperature is 30 deg.C and pressure is 1.013 bar. Given: $D = 0.256$ cm$^2$/s. Also, saturated pressure of water at 30°C = 0.042 bar.

**Solution.** This is a case of uni-directional diffusion of water vapour through a column of air. Therefore, Eq. 14.53 is applicable. Refer Fig. 14.6.

**Data:**

$P_{w1} := 0.042 \times 10^5$ Pa $\quad P_t = 1.013 \times 10^5$ Pa $\quad x_1 := 0$ m $\quad x_2 := 6$ m $\quad A := 5$ m$^2$ $\quad T := 30 + 273$ K

$D := 0.256 \times 10^{-4}$ m$^2$/s $\quad R_u := 8314$ J/kg moleK $\quad M_w := 18$

Then, from Eq. 14.53, we have:

$$m_w = \frac{D \cdot A}{R_u \cdot T} \cdot \frac{M_w \cdot p_t}{(x_2 - x_1)} \cdot \ln\left(\frac{p_{a2}}{p_{a1}}\right) \qquad ...(14.53)$$

where, $p_{a2}$ and $p_{a1}$ are partial pressures of **non-diffusing gas**, i.e. air.

Now, $p_{a1} := p_t - p_{w1}$

i.e. $p_{a1} = 9.71 \times 10^4$ Pa *(partial pressure of air at bottom of well)*

and, $p_{a2} := p_t - 0$

i.e. $p_{a2} = 1.013 \times 10^5$ Pa *(partial pressure of air at top of well)*

Therefore,

Diffusion rate of water vapour is given by:

$$m_w := \frac{D \cdot A}{R_u \cdot T} \cdot \frac{M_w \cdot p_t}{(x_2 - x_1)} \cdot \ln\left(\frac{p_{a2}}{p_{a1}}\right)$$

i.e. $m_w = 6539 \times 10^{-7}$ kg/s

and, $m_w \cdot 3600 = 2.354 \times 10^{-3}$ **kg/hr** ***(hourly loss of water.)***

**Example 14.12.** In a Stefan tube experiment with carbon tetrachloride ($CCl_4$), following data are noted: Diameter of tube = 1 cm. Length of tube above liquid surface = 12 cm. Temperature maintained = 0°C. Pressure maintained = 76 cmHg. Vapour pressure of $CCl_4$ at 0°C = 33 mmHg. Evaporation of $CCl_4$ = 0.037 g. Time of evaporation = 10 h. Estimate the diffusion coefficient of $CCl_4$ into air.

**Solution.** Stefan tube experiment is conducted to determine the diffusion coefficient of diffusing gas in a column of non-diffusing gas, i.e. $CCl_4$ in air, in this case.

**Data:**

$d := 0.01$ m $\quad \Delta x := 0.12$ m $\quad T := 273$ K $\quad p_t := 760$ mmHg $\quad p_{w1} := 33$ mmHg $\quad P_{a1} := p_t - p_{w1}$ mmHg

i.e. $p_{a1} := 727$ mmHg $\quad p_{a2} := p_t - 0$ mmHg i.e. $p_{a2} = 760$ mmHg $\quad R_u := 8314$ J/kg moleK

$m_w = \dfrac{0.037 \times 10^{-3}}{10 \times 3600}$ kg/s i.e. $m_w = 1.028 \times 10^{-9}$ kg/s (evap. rate of $CCl_4$) $\quad p := 1.013 \times 10^5$ Pa (total pressure)

$M_w := 154$ (mol. wt. of $CCl_4$)

$$A := \frac{\pi \cdot d^2}{4} \text{ m}^2$$

i.e. $A = 7.854 \times 10^{-5}$ m *(cross-sectional area of tube)*

Now, we have for uni-directional gas diffusion:

$$m_w = \frac{D \cdot A \cdot M_w \cdot p \cdot \ln\left(\frac{p_{a2}}{p_{a1}}\right)}{R_u \cdot T \cdot \Delta x}$$

Therefore,

$$D := \frac{m_w \cdot R_u \cdot T \cdot \Delta x}{A \cdot M_w \cdot p \cdot \ln\left(\frac{p_{a2}}{p_{a1}}\right)} \text{ m}^2/\text{s}$$ *(diffusivity of $CCl_4$ in air)*

i.e. $D = 5.147 \times 10^{-6}$ **m²/s** ***(diffusivity of $CCl_4$ in air.)***

## 14.8 Steady-state Diffusion in Liquids

Now, let us study steady state equimolal counter-diffusion and uni-directional diffusion in a binary mixture of liquids. While dealing with liquids, we generally write the equations in terms of molar concentrations.

### 14.8.1 Steady-state Equimolal Counter-diffusion in Liquids

Writing in terms of molar concentrations, the molar flux of component B is given by:

$$J_b = -D \cdot \frac{dC_b}{dx} \qquad ...(14.57)$$

Integrating between $x = x_1$ and $x = x_2$ (with $C_b$ varying from $C_{b1}$ to $C_{b2}$):

$$J_b = D \cdot \frac{C_{b1} - C_{b2}}{x_2 - x_1} \qquad ...(14.58)$$

where,

$C_{b1}, C_{b2}$ = molal concentrations at $x_1$ and $x_2$, in kg mole/m$^3$,
$D$ = mass diffusivity for liquid-to-liquid in binary liquid mixture, m$^2$/s.
$J_b$ = mass flux of species B, kg mole/(m$^2$s), and
$x$ = distance, m.

In case of liquids, mole fraction is defined as:

$$x_i = \frac{C_i}{C} = \text{mole fraction of component } i, \text{ where } i = \text{B or C}$$

and, $C_b + C_c = C$ = total molal concentration of the mixture, kg mole/m$^3$

Then, in terms of mole fraction, Eq. 14.58 is expressed as:

$$J_b = D \cdot C\,\frac{x_{b1} - x_{b2}}{x_2 - x_1}\ \text{kg mole/(m}^2\text{s).} \qquad \text{...(14.59)}$$

### 14.8.2 Steady-state Uni-directional Diffusion in Liquids

This analysis is similar to that done in case of gases. However, now, Eq. 14.54 is written as a molal flux and, instead of partial pressures used in case of gases, now molal concentrations are used for liquids.

Eq. 14.54 for gases may be re-written as:

$$\frac{m_{w_{tot}}}{A \cdot M_w} = \frac{D}{R_u \cdot T} \cdot \frac{p_t}{(x_2 - x_1)} \cdot \frac{(p_{w1} - p_{w2})}{LMPA}\ \text{kg mole/(m}^2\text{s)}$$

In an analogous manner, for liquids, we write: (liquid B diffusing in stationary liquid C)

$$J_b = D \cdot \frac{C}{(x_2 - x_1)} \cdot \frac{C_{b1} - C_{b2}}{C_{c,\ln}} = D \cdot \frac{C}{(x_2 - x_1)} \cdot \frac{C_{C2} - C_{c1}}{C_{c,\ln}}\ \text{kg mole/(m}^2\text{s)} \qquad \text{...(14.60)}$$

where, $C_{c,\ln}$ = logarithmic mean concentration of component C, defined as:

$$C_{c,\ln} = \frac{C_{c2} - C_{c1}}{\ln\left(\frac{C_{c2}}{C_{c1}}\right)} \qquad \text{...(14.61)}$$

and, note that $C = C_b + C_c$ and $C_{b2} - C_{b1} = C_{c1} - C_{c2}$

In terms of mole fractions, Eqs. 14.60 and 14.61 can be written as:

$$J_b = D \cdot \frac{C}{(x_2 - x_1)} \cdot \frac{X_{c2} - X_{c1}}{X_{c,\ln}} = D \cdot \frac{C}{(x_2 - x_1)} \cdot \frac{X_{b1} - X_{b2}}{X_{b,\ln}}\ \text{kg mole/(m}^2\text{s)} \qquad \text{...(14.62)}$$

where, $X_{c,\ln}$ = logarithmic mean mole fraction of component C, defined as:

$$X_{c,\ln} = \frac{X_{c2} - X_{c1}}{\ln\left(\frac{X_{c2}}{X_{c1}}\right)} \qquad \text{...(14.63)}$$

In the above equations,

$C$ = total molal concentration of mixture, kg mole/m$^3$,
$X_i = C_i/C$ = mole fraction
$D$ = mass diffusivity , m$^2$/s,
$J_b$ = mass flux of species B, kg mole/(m$^2$s),
$x$ = distance, m.

## 14.9 Transient Mass Diffusion in Semi-infinite, Stationary Medium

Now, consider a semi-infinite medium in which the component B is initially at a uniform concentration $C_{bi}$ throughout. Then, suddenly the surface at $x = 0$ is exposed to a concentration of B equal to $C_{bs}$ and maintained at that value for all $\tau$. We are interested to know the value of $C_b$ at a given distance $x$ from the surface at a given time $\tau$.

We have already derived the general differential eqn. for mass diffusion, viz.

$$\nabla^2 C_b = (1/D).(\partial C_b/\partial \tau) \qquad \text{.... (14.29)}$$

Then, transient, uni-directional mass diffusion equation can be written as:

$$\frac{dC_b}{d\tau} = D\cdot\frac{d^2C_b}{dx^2} \qquad \text{...(14.64)}$$

This equation has to be solved with the following boundary conditions:

(i) $C_b = C_{bi}$ at $\tau = 0$, for all $x$

(ii) $C_b = C_{bs}$ at $x = 0$, for all $\tau$

(iii) $C_b = C_{bi}$ at $x = \infty$, for all $\tau$

Note immediately that Eq. 14.64 and the set of boundary conditions are similar to the case of transient one-dimensional heat conduction encountered in Chapter 7. By analogy, now, we can write the solution for Eq. 14.64 also, looking at the solution in the case of heat conduction, i.e.

$$\frac{T(x,\tau)-T_0}{T_i-T_0} = \text{erf}\left(\frac{x}{2\cdot\sqrt{\alpha\cdot\tau}}\right) \qquad \text{...(7.29)}$$

where $T_i$ = initial uniform temp. and $T_o$ = temp. to which the suddenly exposed and then maintained for all times.

So, we have for solution of Eq. 14.64:

$$\frac{C_b-C_{bs}}{C_{bi}-C_{bs}} = \frac{C_{bs}-C_b}{C_{bs}-C_{bi}} = \text{erf}\left(\frac{x}{2\cdot\sqrt{D\cdot\tau}}\right) = \text{erf}(u) \qquad \text{...(14.65)}$$

where, $u = \dfrac{x}{2\cdot\sqrt{D\cdot\tau}}$

**Mass flow rate through the boundary** is given by:

$$\frac{m_b}{A} = -D\cdot\frac{dC_b}{dx} = \frac{-D\cdot(C_{bi}-C_{bs})}{\sqrt{\pi\cdot D\cdot\tau}}\cdot e^{-u^2} \qquad \text{...(14.66)}$$

and,

$$\left(\frac{m_b}{A}\right)_{x=0} = \frac{-D\cdot(C_{bi}-C_{bs})}{\sqrt{\pi\cdot D\cdot\tau}} \qquad \text{...(14.67)}$$

This solution is applicable, typically, in case of solid state diffusion in case-hardening of mild steel in a carburising atmosphere.

Another quantity of interest in solid diffusion process is the 'penetration depth' ($\delta_{\text{diff}}$), defined as the location $x$ where the tangent to the concentration profile at the surface ($x = 0$) intercepts the $C_b = C_{bi}$ line (See Fig.14.8).

Then, penetration depth is obtained as:

$$\delta_{\text{diff}} = \frac{C_{bs}-C_{bi}}{\left[-\left(\dfrac{dC_b}{dx}\right)\right]_{x=0}} = \frac{C_{bs}-C_{bi}}{\dfrac{(C_{bs}-C_{bi})}{\sqrt{\pi\cdot D\cdot\tau}}} \qquad \textit{(differentiating Eq. 14.65)}$$

i.e.

$$\delta_{\text{diff}} = \sqrt{\pi\cdot D\cdot\tau} \qquad \text{...(14.68)}$$

**Example 14.13.** A mild steel piece has uniform, initial carbon concentration of 0.2 % by mass. It is exposed to a carburising atmosphere in a furnace, where the surface concentration is maintained at 1.3 %. Determine how long the piece must be kept in the furnace for the concentration of carbon at a location 0.4 mm below the surface to reach 1 %. Take $D = 5 \times 10^{-10}$ m²/s.

**Solution.** This problem is of transient mass diffusion in a semi-infinite medium.

**Data:**

$C_{bi} := 0.002$ *(initial concentration of carbon)*

$C_{bs} := 0.013$ *(surface concentration of carbon)*

$C_b := 0.01$ *(desired concentration at $x$ = 0.4 mm)*

$x := 0.4 \times 10^{-3}$ m *(depth of penetration)*

$D := 5 \times 10^{-10}$ m²/s *(diffusion coefficient)*

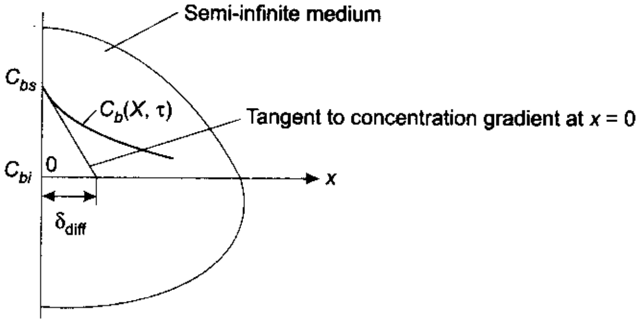


**FIGURE 14.8** Transient diffusion in a semi-infinite medium-penetration depth

Then, for diffusion in a semi-infinite medium, we have:

$$\frac{C_{bs}-C_b}{C_{bs}-C_{bi}} = \operatorname{erf}\left(\frac{x}{2\cdot\sqrt{D\cdot\tau}}\right) \qquad \text{...(14.65)}$$

i.e.
$$\frac{C_{bs}-C_b}{C_{bs}-C_{bi}} = \frac{w_{bs}-w_b}{w_{bs}-w_{bi}} = \operatorname{erf}\left(\frac{x}{2\cdot\sqrt{D\cdot\tau}}\right) \qquad \text{(A)}$$

Now, from data:

$$\frac{C_{bs}-C_b}{C_{bs}-C_{bi}} = 0.273$$

Then, from table of error functions, we read

$$\operatorname{erf}(0.247) = 0.273$$

Then, from Eq. A:

$$\frac{x}{2\cdot\sqrt{D\cdot\tau}} = 0.247$$

and,
$$\tau := \frac{\left(\frac{x}{2\cdot 0.247}\right)^2}{D}$$

i.e. $\tau := 1.311\cdot 10^3$ s *(time required)*

i.e. $\tau := 0.364$ h *(time required.)*

**Alternatively:**

If we do not have the table of error functions, still the problem can be easily solved with the solve block of Mathcad; Mathcad has built-in-error functions available.

We start with a guess value for $\tau$ and write the constraint under 'Given', then, command 'Find' gives the value of $\tau$, as shown below:

$\tau := 100$ s *(guess value)*

Given

$$\frac{C_{bs}-C_b}{C_{bs}-C_{bi}} = \operatorname{erf}\left(\frac{x}{2\cdot\sqrt{D\cdot\tau}}\right)$$

$\text{Find}(\tau) = 1.315\cdot 10^3$

i.e. $\tau = 1315$ s *(time of exposure required in the furnace)*

i.e. $\frac{\tau}{3600} = 0.365$ h *(time of exposure required in the furnace.)*

**Note:** Values of $\tau$ obtained are practically the same, by both the methods.

## 14.10 Transient Mass Diffusion in Common Geometries

Transient mass diffusion analysis is important in hardening of mild steel by carburising, where the steel component is packed in a carbonaceous material and kept in a furnace at high temperature for a desired length of time. We have worked out an example of this type already. Transient analysis is also required in gem industry (to get desired colour for valuable stones), in 'doping' of n-or p-type of semiconductor materials, in drying of coal, timber, food, textiles, etc.

Transient mass diffusion and transient heat conduction are analogous if the solution is dilute. One-dimensional transient heat conduction in plane walls, cylinders and spheres was discussed in Chapter 7 and Tabular and Chart solutions were presented. These solutions are applicable to transient mass diffusion problems, too, if:

(i) the diffusion coefficient ($D$) is constant (corresponding to constant thermal diffusivity, in transient heat conduction)
(ii) there are no homogeneous reactions occurring (corresponding to no heat generation), and
(iii) initial concentration of species B is constant throughout the medium (corresponding to uniform initial temperature).

Quantities which are analogous in heat and mass transfer are tabulated in Table 14.8.

Then, for example, for a plane wall, we have the temperature distribution given by:

Plane wall: $$\theta(x, \tau) = \frac{T(x, \tau) - T_a}{T_i - T_a} = A_1 \cdot e^{-\lambda_1^2 \cdot Fo} \cdot \cos\left(\frac{\lambda_1 \cdot x}{L}\right) \quad (Fo > 0.2 \ldots(7.24a))$$

Now, the corresponding equation can be written for transient mass diffusion in a plane wall and the values of constants $A_1$ and $\lambda_1$ (as a function of $B_i$) can be taken from the Table 7.1 given in Chapter 7. Similarly the chart solutions given by Heisler's charts can be applied for transient, one-dimensional mass diffusion problems.

## 14.11 Mass Transfer Coefficient

Mass transfer coefficient is defined in a manner analogous to convective heat transfer coefficient.

Remember that convective heat transfer coefficient '$h$' is obtained from Newton's law:

$$Q = h \cdot A \cdot \Delta T, \text{ W} \quad \ldots(14.69)$$

**(a) Steady state diffusion of a fluid across a solid layer of thickness ($x_2 - x_1$):**

Mass diffusion rate for diffusion through a solid layer is given by: (see Eq. 14.31)

$$m_b = \frac{D \cdot A \cdot (C_{b1} - C_{b2})}{x_2 - x_1} \text{ kg/s} \quad \ldots(14.70)$$

Writing this in a manner analogous to Eq. 14.69:

$$m_b = \frac{D \cdot A \cdot (C_{b1} - C_{b2})}{x_2 - x_1} = h_{mc} \cdot A \cdot (C_{b1} - C_{b2})$$

Therefore, $h_{mc}$, the mass transfer coefficient based on concentration differences, can be written as:

**TABLE 14.8** Analogous quantities in heat conduction and mass diffusion

| Heat conduction | Mass diffusion |
|---|---|
| $T$ | $C$, $y$, $\rho$ or w |
| $\alpha$ | $D_{bc}$ |
| $\theta(x, \tau) = \frac{T(x, \tau) - T_a}{T_i - T_a}$ | $\theta_{\text{mass}} = \frac{w_b(x, \tau) - w_{ba}}{w_{bi} - w_{ba}}$ |
| $\zeta = \frac{x}{2 \cdot \sqrt{\alpha \cdot \tau}}$ | $\zeta_{\text{mass}} = \frac{x}{2 \cdot \sqrt{D_{bc} \cdot \tau}}$ |
| $B_i = \frac{h \cdot L}{k}$ | $B_{i_{\text{mass}}} = \frac{h_{\text{mass}} \cdot L}{D_{bc}}$ |
| $Fo = \frac{\alpha \cdot \tau}{L^2}$ | $Fo_{\text{mass}} = \frac{D_{bc} \cdot \tau}{L^2}$ |

$$h_{mc} = \frac{D}{(x_2 - x_1)} \text{ m/s} \qquad \text{...(14.71)}$$

Note the units of mass transfer coefficient: m/s.

**(b) Steady state equimolal counter-diffusion:**

In this case, from Eq. 14.46, we can write the mass diffusion rate as:

$$m_b = D \cdot A \cdot \frac{M_b}{R_u \cdot T} \cdot \frac{(p_{b1} - p_{b2})}{(x_2 - x_1)}$$

i.e.

$$m_b = \frac{D}{(x_2 - x_1)} \cdot \frac{M_b}{R_u \cdot T} \cdot A \cdot (p_{b1} - p_{b2})$$

i.e.

$$m_b = h_{mc} \cdot \frac{M_b}{R_u \cdot T} \cdot A \cdot (p_{b1} - p_{b2}) \text{ kg/s} \qquad \text{...(14.72)}$$

Now, if we define a mass transfer coefficient $h_{mp}$, based on partial pressure differences, we rewrite Eq. 14.72 as:

$$m_b = h_{mc} \cdot \frac{M_b}{R_u \cdot T} \cdot A \cdot (p_{b1} - p_{b2}) = h_{mp} \cdot A \cdot (p_{b1} - p_{b2})$$

And, it is clear that:

$$h_{mp} = h_{mc} \cdot \frac{M_b}{R_u \cdot T}$$

i.e.

$$h_{mp} = \frac{h_{mc}}{R \cdot T} \qquad \text{...(14.73)}$$

i.e. mass transfer coefficient based on pressure difference is obtained by simply dividing the mass transfer coefficient based on concentration differences by $(R.T)$ where $R$ = particular gas constant, and, $T$ = temperature in Kelvin.

**(c) Diffusion of water vapour through a layer of stagnant air:**

In this case, we have seen that the mass diffusion rate of water vapour is given by:

$$m_w = \frac{D \cdot A}{R_u \cdot T} \cdot \frac{M_w \cdot p_t}{(x_2 - x_1)} \cdot \ln\left(\frac{p_{a2}}{p_{a1}}\right) \qquad \text{...(14.53)}$$

i.e.

$$m_w = \frac{D \cdot A}{R_u \cdot T} \cdot \frac{M_w \cdot p_t}{(x_2 - x_1)} \cdot \ln\left(\frac{p_t - p_{w2}}{p_t - p_{w1}}\right) = h_{mp} \cdot A \cdot (p_{w1} - p_{w2}) \qquad \text{...say}$$

Then, for this case, the mass transfer coefficient based on pressure difference can be written as:

$$h_{mp} = \frac{D \cdot p_t}{(x_2 - x_1) \cdot (p_{w1} - p_{w2})} \cdot \frac{M_w}{R_u \cdot T} \cdot \ln\left(\frac{p_t - p_{w2}}{p_t - p_{w1}}\right) \qquad \text{...(14.74)}$$

And, for this case, the mass transfer coefficient based on concentration difference would be:

$$h_{mc} = h_{mp} \cdot (R \cdot T) = \frac{D \cdot p_t}{(x_2 - x_1) \cdot (p_{w1} - p_{w2})} \cdot \ln\left(\frac{p_t - p_{w2}}{p_t - p_{w1}}\right) \qquad \text{...(14.75)}$$

## 14.12 Convective Mass Transfer

So far, we considered molecular diffusion of a fluid through a solid, or between two fluids. In these cases, the bulk velocities of the species were insignificant and only the diffusion velocities were of significance.

However, when the bulk velocities of species diffusing are significant, we have the convective mass transfer. This is analogous to convective heat transfer, just as the molecular diffusion is analogous to conduction heat transfer.

Convective mass transfer involves the transportation of material across the boundary. Again, just as in the case of convective heat transfer, convective mass transfer is of two types: (a) 'Free (or natural) convective mass transfer, and (b) 'Forced' convective mass transfer. In free convective mass transfer, buoyancy forces cause the circulation due to density differences, whereas in forced convective mass transfer, an external agency such as a fan or pump causes the circulation. Further, forced convective mass transfer may be of laminar or turbulent types, depending on the Reynolds number.

Recall that for convective mass transfer, we have the Newton's equation for heat flux:

$$\frac{Q}{A} = h \cdot \Delta T$$

Similarly, the equation for mass flux in the case of convective mass transfer is:

$$\frac{m_b}{A} = h_m \cdot \Delta C_b \qquad \text{...(14.76)}$$

where, $h_m$ = convective mass transfer coefficient, and $\Delta C_b$ = concentration difference of species B.

Just as in the case of convective heat transfer, analytical treatment of convective mass transfer is complicated, because of the effects of flow velocity, surface geometry, flow regime, flow type (i.e. external or internal flow), composition and variation of fluid properties. Therefore, generally, empirical relations, obtained as a result of experimentation, are resorted to.

For flow over a flat plate, we saw earlier that a velocity boundary layer develops; similarly, a concentration boundary layer also develops and the equations for conservation of momentum, energy and concentration may be written as follows:

Momentum: $u.(\partial u/\partial x) + v.(\partial u/\partial y) = \nu.(\partial^2 u/\partial y^2)$
Energy : $u.(\partial T/\partial x) + v.(\partial T/\partial y) = \alpha.(\partial^2 T/\partial y^2)$ , and
Concentration : $u.(\partial C/\partial x) + v.(\partial C/\partial y) = D.(\partial^2 C/\partial y^2)$,

where, $C$ = concentration of component diffusing throug2h the boundary layer.

With reference to the velocity, temperature and concentration boundary layers, we have the following non-dimensional numbers appearing in the empirical correlations:

**Prandtl number (*Pr*)** *Pr* is defined as: $Pr = \nu/\alpha$, and is the connecting link between the velocity and temperature profiles. $Pr = 1$ indicates that these profiles are identical.

**Schmidt number (*Sc*)** *Sc* is defined as: $Sc = \nu/D$, and is the connecting link between the velocity and concentration profiles. $Sc = 1$ indicates that these profiles are identical.

**Lewis number (*Le*)** *Le* is defined as: $Le = \alpha/D$, and is the connecting link between the temperature and concentration profiles. $Le = 1$ indicates that these profiles are identical.

All the three boundary layers will coincide if $Pr = Sc = Le$.

Noting that the governing equations for momentum, energy and mass transfer are similar, it is reasonable to guess that the empirical correlations for mass transfer coefficient will also be similar to the correlations for the convective heat transfer, studied earlier. For heat transfer coefficient, we had the general correlation of the type:

$$Nu = \frac{h \cdot L}{k} = f\,(Re, Pr)$$

In an analogous manner, for mass transfer coefficient in convective mass transfer, we have:

$$Sh = \frac{h_m \cdot L}{D} = f(Re, Sc) \qquad \text{...(14.77)}$$

where, *Sh* is the 'Sherwood number', which represents a non-dimensional mass transfer coefficient.

Table 14.9 gives the Sherwood number relations for a few convective mass transfer situations, written by analogy with Nusselt number relations for similar convective heat transfer situations.

Note that in Table 14.9, for mass transfer, Grashoff number is defined as follows:

$$Gr = \frac{g \cdot (\rho_a - \rho_s) \cdot L^3}{\rho \cdot \nu^2} = \frac{g \cdot \left(\frac{\Delta \rho}{\rho}\right) \cdot L^3}{\nu^2}$$

TABLE 14.9 Sherwood number relations for convective mass transfer

| Convective heat transfer | Convective mass transfer |
|---|---|
| **1. Forced convection over a flat plate:** | |
| Local heat transfer coefficient: | Local mass transfer coefficient: |
| $Nu_x = 0.332 \cdot \sqrt{Re_x} \cdot Pr^{0.333}$ ...laminar flow ($Re < 5 \times 10^5$) | $Sh_x = \frac{h_m \cdot x}{D} = 0.332 \cdot \sqrt{Re_x} \cdot Sc^{0.333}$ |
| $Nu_x = 0.0298 \cdot Re_x^{0.8} \cdot Pr^{0.333}$ ...turbulent flow ($Re > 5 \times 10^5$) | $Sh_x = \frac{h_m \cdot x}{D} = 0.0298 \cdot Re_x^{0.8} \cdot Sc^{0.333}$ |
| Average heat transfer coefficient: | Average mass transfer coefficient: |
| $Nu_a = 0.664 \cdot \sqrt{Re_L} \cdot Pr^{0.333}$ ...laminar flow | $Sh_a = \frac{h_m \cdot L}{D} = 0.664 \cdot Re_L^{0.5} \cdot Sc^{\frac{1}{3}}$, $Sc > 0.5$ |
| $Nu_a = 0.037 \cdot Re_L^{0.8} \cdot Pr^{0.333}$ ...turbulent flow | $Sh_a = \frac{h_m \cdot L}{D} = 0.037 \cdot Re_L^{0.8} \cdot Sc^{\frac{1}{3}}$, $Sc > 0.5$ |
| For mixed b.l. conditions with $Re_c = 5 \times 10^5$:<br>$Nu_a = (0.037 \cdot Re_L^{0.8} - 870) \cdot Pr^{0.33}$ | For mixed b.l. conditions with $Re_c = 5 \times 10^5$:<br>$Sh_a = (0.037 \cdot Re_L^{0.8} - 870) \cdot Sc^{0.33}$ |
| **2. Fully developed flow in smooth, circular pipes:**<br>Laminar flow ($Re < 2300$):<br>$Nu = 3.66$ ...for uniform wall temperature<br>$Nu = 4.36$ ...for uniform wall heat flux<br>Turbulent flow ($Re > 10000$):<br>$Nu = 0.023 \cdot Re^{0.8} \cdot Pr^{0.4}$ $0.7 < Pr < 160$ | $Sh = 3.66$ ...(for uniform wall mass concentration), and $Sh = 4.36$ for constant wall mass flux. Turbulent flow ($2000 < Re < 35000$):<br>Gilliand's relation:<br>$Sh = 0.023 \cdot Re^{0.83} \cdot Sc^{0.44}$, $0.6 < Sc < 2.5$ |
| **3. Natural convection over surfaces:**<br>(a) Vertical plate: | |
| $Nu = 0.59 \cdot (Gr \cdot Pr)^{\frac{1}{4}}$ $10^5 < Gr \cdot Pr < 10^9$ | $Sh = 0.59 \cdot (Gr \cdot Sc)^{\frac{1}{4}}$ $10^5 < Gr \cdot Sc < 10^9$ |
| $Nu = 0.1 \cdot (Gr \cdot Pr)^{\frac{1}{3}}$ $10^9 < Gr \cdot Pr < 10^{13}$ | $Sh = 0.1 \cdot (Gr \cdot Sc)^{\frac{1}{3}}$ $10^9 < Gr \cdot Sc < 10^{13}$ |
| (b) Upper surface of horizontal plate,<br>(surface is hot, $T_s > T_a$): | Fluid near the surface is light,<br>($\rho_s < \rho_a$): |
| $Nu = 0.54 \cdot (Gr \cdot Pr)^{\frac{1}{4}}$ $10^4 < Gr \cdot Pr < 10^7$ | $Sh = 0.54 \cdot (Gr \cdot Sc)^{\frac{1}{4}}$ $10^4 < Gr \cdot Pr < 10^7$ |
| $Nu = 0.15\ (Gr \cdot Pr)^{\frac{1}{3}}$ $10^7 < Gr \cdot Pr < 10^{11}$ | $Sh = 0.15 \cdot (Gr \cdot Sc)^{\frac{1}{3}}$ $10^7 < Gr \cdot Pr < 10^{11}$ |
| (c) Lower surface of horizontal plate,<br>(surface is hot, $T_s > T_a$): | Fluid near the surface is light,<br>($\rho_s < \rho_a$): |
| $Nu = 0.27 \cdot (Gr \cdot Pr)^{\frac{1}{4}}$ $10^5 < Gr \cdot Pr < 10^{11}$ | $Sh = 0.27 \cdot (Gr \cdot Sc)^{\frac{1}{4}}$ $10^5 < Gr \cdot Sc < 10^{11}$ |
| **4. For natural convection through a tube:**<br>Steinberger and Treybol relation for mass transfer is given by: | |
| $Sh = 2 + 0.57 \cdot (Gr \cdot Sc)^{0.25}$ | ...for $Gr \cdot Sc < 10^8$ |
| and, $Sh = 2 + 0.025 \cdot (Gr \cdot Sc)^{0.33} \cdot Sc^{0.245}$ | ...for $Gr \cdot Sc > 10^8$ |

## 14.13 Reynolds and Colburn Analogies for Mass Transfer

Reynolds and Colburn analogies for heat transfer can be extended to the case of mass transfer, to get a relation between the mass transfer coefficient and the friction factor. **Reynolds analogy** for heat transfer in a of pipe flow is written as:

$$\frac{Nu}{Re \cdot Pr} = St = \frac{h}{\rho \cdot C_p \cdot V} = \frac{C_f}{2} \qquad ...(14.78)$$

Similarly, for mass transfer, we write:

$$\frac{Sh}{Re\cdot Sc} = St_m = \frac{h_m}{V} = \frac{C_f}{2} \quad \text{...(14.79)}$$

where, $St_m = h_m/V$ is the Stanton number for mass transfer.

Remember that Reynolds analogy is valid only when $Pr = Sc = 1$.

When $Pr$ (or, $Sc$) is different from unity, we have the **Colburn analogy:**

$$j_H = St\cdot(Pr)^{\frac{2}{3}} = \frac{C_f}{2} \quad (0.5 < Pr < 50\text{...}\textit{for heat transfer}\text{...(14.80)})$$

and,

$$j_M = St_m\cdot(Sc)^{\frac{2}{3}} = \frac{C_f}{2} \quad (0.6 < Sc < 3000\text{...}\textit{for mass transfer}\text{...(14.81)})$$

where, $j_M$ is the Colburn factor for mass transfer.

Relations for $C_f$ (= friction factor) are already given in Chapter on Forced Convection.

From Eqs. 14.80 and 14.81, we can write:

$$\frac{St}{St_m} = \left(\frac{Sc}{Pr}\right)^{\frac{2}{3}}$$

i.e.

$$\frac{h}{h_m} = \rho\cdot C_p\cdot\left(\frac{Sc}{Pr}\right)^{\frac{2}{3}} = \rho\cdot C_p\cdot\left(\frac{\alpha}{D}\right)^{\frac{2}{3}} \quad \text{...(14.82)}$$

Now, non-dimensional number $(\alpha/D) = Le$ is known as '**Lewis number**'.

Therefore, we have:

$$\frac{h}{h_m} = \rho\cdot C_p\cdot Le^{\frac{2}{3}} \quad \text{...(14.83)}$$

Above relation is useful in cases of simultaneous heat and mass transfer.

Air–water vapour mixtures are of special interest in air conditioning applications. For air–water vapour mixtures, $Le = 0.872$ and $Le^{2/3}$ is nearly equal to unity. Therefore, for air–water vapour mixtures, the relation between heat and mass transfer coefficients is conveniently expressed as:

$$h = \rho\cdot C_p\cdot h_m \quad (\textit{for air–water vapour mixture}\text{...(14.84)})$$

Eq. 14.84 is known as **Lewis relation** and is normally used in air-conditioning applications.

**Note:** It should be remembered that the analogy between convection heat and mass transfer is valid only for low mass flux conditions.

**Example 14.14.** Air at a temperature of 20°C, and RH of 40% flows over a water surface at a velocity of 1.5 m/s. Length parallel to flow is 18 cm. Average surface temperature is 16°C. Estimate the amount of water evaporated per hr/m2 of surface area. Partial pressure of water vapour at 20°C and 40% RH is 0.011 bar and at 16°C and saturated, the vapour pressure is 0.017 bar. Viscosity and density of air are: $18.38 \times 10^{-6}$ kg/ms and 1.22 kg/m$^3$, respectively. Assume $D = 0.256$ cm$^2$/s.

**Solution.** See Fig. Ex. 14.14.

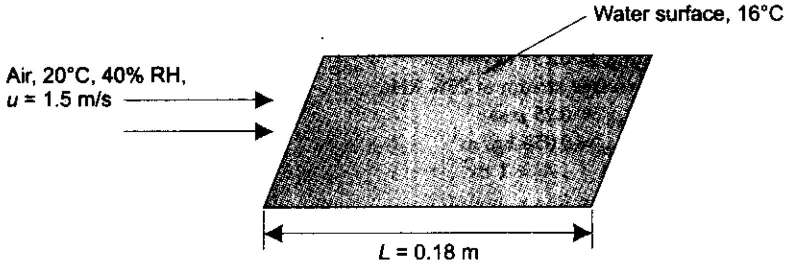


**FIGURE** Example 14.14 Convective mass transfer from surface of water

**Data:**

$u := 1.5\ \text{m/s}$ $L := 0.18\ \text{m}$ $\mu := 18.38 \cdot 10^{-6}\ \text{kg/(ms)}$ $\rho := 1.22\ \text{kg/m}^3$ $\nu := \dfrac{\mu}{\rho}$ i.e. $\nu = 1.507 \cdot 10^{-5}\ \text{m}^2\text{/s}$

$D := 0.256 \times 10^{-4}\ \text{m}^2\text{/s}$ $R_u := 8314\ \text{J/kg mole K}$ $R_{H_2O} := \dfrac{R_u}{18}$ i.e. $R_{H_2O} = 461.889\ \text{J/kgK}$ $T_1 := 16 + 273\ \text{K}$

$T_2 := 20 + 273\ \text{K}$ $A := 1\ \text{m}^2$ $p_{w1} := 0.017 \cdot 10^5\ \text{Pa}$ $p_{w2} := 0.011 \cdot 10^5\ \text{Pa}$

Reynolds number:

$$Re := \frac{u \cdot L}{\nu}$$

i.e. $Re = 1.792 \times 10^4$ *(Less than $5 \times 10^5$...so, laminar)*

Mass transfer coefficient:

For laminar flow over a surface, we have:

$$Sh = \frac{h_{mc} \cdot L}{D} = 0.664 \cdot Re^{0.5} \cdot Sc^{0.33}$$ *(Sherwood number)*

Now, $$Sc := \frac{\nu}{D}$$

i.e. $Sc = 0.588$

Therefore,

$$Sh := 0.664 \cdot Re^{0.5} \cdot Sc^{0.33}$$

i.e. $Sh = 74.623$ *(Sherwood number)*

and, $$h_{mc} := \frac{Sh \cdot D}{L}\ \text{m/s}$$ *(mass transfer coefficient based on concentration)*

i.e. $h_{mc} = 0.011\ \text{m/s}$

Concentrations (i.e. densities):

$$C_{w1} := \frac{p_{w1}}{R_{H_2O} \cdot T_1}$$

i.e. $C_{w1} = 0.013\ \text{kg/m}^3$ *(concentration (density) at temperature $T_1$)*

and, $$Cw_2 := \frac{p_{w2}}{R_{H_2O} \cdot T_2}$$

i.e. $C_{w2} = 8.128 \times 10^{-3}\ \text{kg/m}^3$ *(concentration (density) at temperature $T_2$)*

Therefore, mass diffusion of water is given by:

$$m_w := h_{mc} \cdot A \cdot (C_{w1} - C_{w2})$$

i.e. $m_w = 4.89 \times 10^{-5}\ \text{kg/s per m}^2\ \text{area}$

i.e. $m_w = 3600 = 0.176\ \text{kg/hr per m}^2$.

**Example 14.15.** Air at a temperature of 25°C, and RH of 20% flows through a pipe of 20 mm ID with a velocity of 5 m/s. The inside surface of the tube is constantly wetted with water such that a thin water film is maintained on the surface. Determine the amount of water evaporated per m$^2$ of surface area.

Given: $\nu = 15.7 \times 10^{-6}\ \text{m}^2\text{/s}$, $Sc = 0.6$, and $D = 0.26 \times 10^{-4}\ \text{m}^2\text{/s}$.

**Solution.** This is a case of convective mass transfer.

**Data:**

$\mu := 5.0\ \text{m/s}$ $d := 0.02\ \text{m}$ $\nu := 15.7 \cdot 10^{-6}\ \text{m}^2\text{/s}$

$\rho_{sat} := 0.231\ \text{kg/m}^3$ *(density of water vapour at saturation at 25 deg.C)*

Therefore, density of vapour in free stream at 25% RH:

$$\rho_{\text{free\_stream}} := 0.25\ \rho\ \text{sat}$$

i.e. $\rho_{\text{free\_stream}} = 0.058\ \text{kg/m}^3$ *(density of water vapour at free stream conditions)*

$D := 0.26 \cdot 10^{-4}\ \text{m}^2\text{/s}$ $Sc := 0.6$ $A := 1\ \text{m}^2$

Reynolds number:

$$Re := \frac{u \cdot d}{\nu}$$ (Reynolds number)

i.e. $Re = 6.369 \cdot 10^3 > 2300$ *(therefore, turbulent flow)*

Then, Sherwood number relation is:

$$Sh := 0.023 \cdot Re^{0.83} \cdot Sc^{0.44}$$

i.e. $$Sh = 27.873$$

But, $$Sh = \frac{h_{mc} \cdot d}{D}$$

where, $h_{mc}$ = mass transfer coefficient based on concentration (i.e. density) difference.

Therefore,

$$h_{mc} := \frac{Sh \cdot D}{d}$$

i.e. $$h_{mc} = 0.036 \text{ m/s}$$

Then, mass evaporaion rate:

$$m := h_{mc} \cdot A \cdot (\rho_{\text{sat}} - \rho_{\text{free\_stream}}) \text{ kg/(sm}^2\text{)}$$

i.e. $$m = 6.278 \times 10^{-3} \text{ kg/(sm}^2\text{)}$$ *(mass evaporation rate per $m^2$ surface area.)*

**Note:** One sq. m of surface area of the pipe is equivalent to a length of: $\frac{1}{\pi \cdot d} = 15.915$ metres.

i.e. Mass evaporation rate per metre length of pipe is given by:

$$\frac{m}{15.915} = 3.944 \times 10^{-4} \text{ kg/s per metre length.}$$

**Example 14.16.** In an experiment, when atmospheric air at $T_a$ = 30 deg.C was blown past a wet bulb thermometer, the wet bulb reading obtained was $T_w$ = 20°C. What is the value of concentration of water vapour $C_a$ in the free stream? Also, determine the relative humidity (RH) of the free stream. (Note: RH is equal to the ratio of concentration $C_a$ of water vapour in free stream to the saturation concentration at the free stream temperature of 30°C, $C_{\text{sat}}$. $C_{\text{sat}}$ is obtained from Steam Tables.)

**Solution.** This problem involves simultaneous heat and mass transfer.

**Data:**

$$T_a := 30°\text{C}$$ *(temperature of atmospheric air)*

$$T_w := 20°\text{C}$$ *(wet bulb temperature)*

In steady state, we can state the energy balance as:

heat transfer from air stream to wet cloth = latent heat of evaporation of water

i.e. $$h \cdot A \cdot (T_a - T_w) = h_m \cdot A \cdot (\rho_w - \rho_a) \cdot h_{fg} \qquad \text{...(a)}$$

Remember $$C_w = \rho_w$$

i.e. $$\frac{h}{h_m} \cdot (T_a - T_w) = (\rho_w - \rho_a) \cdot h_{fg} \qquad \text{...(b)}$$

But, the ratio, $h/h_m$ is given from Lewis relation, as:

$$\frac{h}{h_m} = \rho \cdot C_p \cdot Le^{\frac{2}{3}} = \rho \cdot C_p \cdot \left(\frac{\alpha}{D}\right)^{\frac{2}{3}}$$

Then, Eq. b becomes:

$$\rho \cdot C_p \cdot \left(\frac{\alpha}{D}\right)^{\frac{2}{3}} \cdot (T_a - T_w) = (\rho_w - \rho_a) \cdot h_{fg} \qquad \text{...(c)}$$

Now, properties of air are evaluated at the film temperature $T_f = \frac{30 + 20}{2}$

i.e. properties at: $T_f := 25°\text{C}$

Air: $\rho := 1.186 \text{ kg/m}^3$ $\quad C_p := 1005 \text{ J/(kgC)}$ $\quad \alpha := 2.18 \cdot 10^{-5} \text{ m}^2\text{/s}$

$D := 0.26 \cdot 10^{-4} \text{ m}^2\text{/s}$ (from Tables) $\quad \frac{\alpha}{D} = 0.838$ = Le = Lewis number

Water:

$$h_{fg} := 2454.1 \cdot 10^3 \text{ J/kg at } 20°\text{C}$$

Saturated concentration of water vapour at $T_w$ = 20°C is determined from:

$$\rho_w = \frac{p_w \cdot M_w}{R_u \cdot T_w} = \frac{2339 \cdot 18}{8314 \cdot 293} = 0.01728$$

Note that in the above, $p_w$ = saturation pressure = 2339 Pa, corresponding to $T_w$ = 20°C, from Steam Tables.

i.e. $\rho_w = 0.01728\ \text{kg/m}^3 = C_{\text{sat}} =$ saturation concentration (density) of water vapour at wet bulb temperature of 20°C

Then, from Eq. c:

$$\rho \cdot C_p \cdot \left(\frac{\alpha}{D}\right)^{\frac{2}{3}} \cdot (T_a - T_w) = (\rho_w - \rho_a) \cdot h_{fg} \qquad \text{...(c)}$$

i.e.

$$\rho_a := \rho_w - \frac{\rho \cdot C_p \cdot \left(\frac{\alpha}{D}\right)^{\frac{2}{3}} \cdot (T_a - T_w)}{h_{fg}}$$

i.e. $\rho_a = 0.013\ \text{kg/m}^3$ *(concentration of water vapour in free stream)*

Relative humidity:

Saturation concentration at $T_a = 30°\text{C}$: $\rho_{\text{sat}} := 0.0304\ \text{kg/m}^3$ *(from Steam Tables)*

Therefore,

$$\text{RH} := \frac{\rho_a}{\rho_{\text{sat}}}$$

i.e. RH = 0.426 = 42.6% *(relative humidity of free stream.)*

## 14.14 Summary

Mass transfer is an important phenomenon with vast industrial applications.

Diffusion mass transfer occurs due to concentration difference and is similar to heat conduction. The governing law is the Fick's law of diffusion, analogous to the Fourier's law of conduction, i.e.

$$j_B = \frac{m_B}{A} = -D_{BC} \cdot \frac{dC_B}{dx}\ \text{kg/(sm}^2\text{)} \qquad \text{...(14.18)}$$

$D_{BC}$ is the diffusion coefficient for species B in a mixture of B and C. Values of diffusion coefficients for gases, liquids and solids was discussed.

Equimolal diffusion of gases in a binary mixture was studied. This is important in distillation process, and in venting a gas from a pipe line to atmosphere.

Next, the diffusion of a gas in a stationary gas column was explained. This phenomenon has applications in absorption and humidification. Evaporation of water vapour in a stationary column of air was studied, as an example.

Transient diffusion was explained briefly. Equations for transient diffusion are written by analogy with transient conduction.

Convective mass transfer involves transport of mass across the boundary and is affected by the flow field. Analogous to 'heat transfer coefficient', a 'mass transfer coefficient' is also defined and the governing law is similar to the Newton's law of cooling.

Analogy between heat and mass transfer was explained and relations for convective mass transfer were written for various geometries and flow conditions, by analogy with heat transfer relations under similar situations.

Finally, topic of simultaneous heat and mass transfer, which has important applications in the field of air conditioning, was discussed.

## Questions

1. State Fick's law of mass transfer by diffusion and explain its analogy with Fourier's law of conduction. [M.U.]
2. Define: (a) diffusion coefficient, (b) mass transfer coefficient.
3. Write a short note on diffusion coefficient in a binary mixture of: (a) gases (b) liquids, and (c) solids.
4. How does $D$ depend on pressure and temperature in a binary gas mixture?
5. Derive a mass diffusion equation in general form in cartesian coordinates for mass diffusion in stationary medium in the same lines as that of general heat conduction equation, in differential form.

   Using the above general equation show that the governing differential equation for steady state diffusion through a plane membrane reduces to the form:

$$\frac{d^2C_A}{dx^2} = 0$$

where, $C_A$ is the concentration of species A. [M.U.]

6. Define: Sherwood number, Schmidt number and Lewis number. [M.U.]
7. Derive a basic differential equation for equimolal counter-diffusion in gases and solve the same for constant pressure situation to get the mass flux of species A as:

$$\text{Mass flux} = \frac{-D\cdot M_A}{R_u\cdot T}\cdot\frac{(P_{a2}-P_{a1})}{\Delta x}$$

   where, $P_{a1}$ and $P_{a2}$ are partial pressures of species A at $x$ and $(x + \Delta x)$ locations, $M_A$ is the molecular mass of species A, $T$ is the temperature of gases in Kelvin, and $R_u$ is the Universal gas constant. [M.U.]
8. Prove that during isothermal evaporation, rate of mass transfer of water vapour into atmospheric air is given by:

$$N_A = \frac{D\cdot P\cdot(P_{a1}-P_{a2})}{R_u\cdot T\cdot\Delta x\cdot P_{\ln}}\ \text{kg mole/(s m}^2)$$

   Notations in the above equation are as defined earlier. [M.U.]
9. Write a short note on the analogy between momentum, heat and mass transfer. [M.U.]
10. Explain in brief two main methods of mass transfer and bring out their differences. [M.U.]
11. Show that kinematic viscosity, thermal diffusivity and diffusion coefficient have the same units. [M.U.]
12. For convective mass transfer, name the non-dimensional number that plays the same role in mass transfer as that of Prandtl number in heat transfer and write down an expression for the same. [M.U.]
13. Derive Stefan's law (isothermal evaporation of water). [M.U.]
14. Derive an equation to determine the amount of mass transferred through a composite plane wall with one layer of diffusivity $D_{ab}$ and another with diffusivity $D_{ac}$, with concentrations $C_{a1}$ and $C_{a2}$ on either side of wall, wall thicknesses $\Delta x_1$ and $\Delta x_2$. [M.U.]

## Problems

1. Air is contained in a vessel at a temperature of 20°C and pressure of 3 bar. Assuming the partial pressures of $O_2$ and $N_2$ to be in ratios of 0.21 and 0.79, respectively, calculate: (i) Molar concentrations (ii) Mass concentrations (i.e. densities), (iii) Mass fractions, and (iv) Molar fractions.
2. Calculate the diffusion coefficient of $CO_2$ in air at 20°C and 1 atm. pressure. Then, calculate the value of $D$ for a pressure of 3 atm. and temperature of 57°C.
3. A steel, rectangular container having walls 10 mm thick, is used to store gaseous hydrogen at elevated pressure. The molar concentrations of hydrogen in steel at the inside and outside surfaces are 1.1 kg.mole/m$^3$ and zero, respectively. Assuming the diffusion coefficient for hydrogen in steel to be $0.25 \times 10^{-12}$ m$^2$/s, calculate the molar diffusion flux for hydrogen through steel.
4. Hydrogen gas at 2 atm., 25°C is flowing through a rubber pipe, 25 mm ID, 50 mm OD. Solubility of $H_2$ in rubber is 0.053 cm$^3$ of $H_2$ per cm$^3$ of rubber at 1 atm. pressure. Diffusivity of $H_2$ through rubber is $0.7 \times 10^{-4}$ m$^2$/h. Find the loss of hydrogen per metre length of pipe. [M.U.]
5. Hydrogen gas is stored at 358 K in a 3.0 m ID, 5 cm thick spherical container made of Nickel. Molar concentration of hydrogen in Ni at the inner surface is 0.12 kg.mole/m$^3$ and is equal to zero at the outer surface. Determine the mass diffusion rate of hydrogen through the walls of the container. (Take $D = 1.2 \times 10^{-12}$ m$^2$/s)
6. Helium gas is stored at a pressure of 4 bar and 293 K in a 0.3 m ID, 3 mm thick spherical container made of fused silica. Determine the rate of pressure drop due to diffusion. Given: $D = 0.04 \times 10^{-12}$ m$^2$/s, and solubility of gas at the solid surface on the inside is $18 \times 10^{-9}$ kg/(m$^3$Pa).
7. In problem 6, if the container is a long cylinder of diameter 0.3 m, calculate mass of helium lost by diffusion per metre length. Rest of the data are same.
8. A gas mixture consists of oxygen and nitrogen at 1 bar and 27°C. The oxygen content, by volume, at two planes 3 mm apart are 15 % and 30%, respectively. Calculate the rate of diffusion in kg mole/(sm$^2$), if:
   (i) nitrogen is non-diffusing
   (ii) there is equimolar counter-diffusion of the two gases.
   Take $D = 0.181$ cm$^2$/s. [M.U.]
9. A tank contains a mixture of $CO_2$ and $N_2$, in the mole proportions of 0.3 and 0.7 at 1 bar and 290 K. It is connected by a duct of cross-sectional area 0.1 m$^2$ to another tank containing a mixture of $CO_2$ and $N_2$ in the molal proportions of 0.7 and 0.3. The duct is 0.75 m long. Determine the diffusion rates of $CO_2$ and $N_2$ in kg/s. Given: $D = 0.16 \times 10^{-4}$ m$^2$/s for $CO_2/N_2$ at 293 K from tables.

10. A spherical ball of ice, 1.5 cm diameter is suspended in still dry air at 1.013 bar. Calculate the initial rate of evaporation at the surface.
Take $D = 0.256 \times 10^{-4}$ m$^2$/s. At 0 deg.C, saturated vapour pressure = 0.0061 bar.
11. Each of two large vessels contains uniform mixture of nitrogen and carbon dioxide at 1 bar and 288.9 K. Vessel 1 contains 90 mole % of $N_2$ and 10 mole % $CO_2$, whereas vessel 2 contains 20 mole % $N_2$ and 80 mole % $CO_2$. The two vessels are connected by a duct of 0.15 m ID and 1.22 m long. Determine the rate of transfer of $N_2$ between the two vessels in kg/s, assuming steady state transfer. Mass diffusivity for $N_2$–$CO_2$ mixture at 1 bar and 288.9 K may be taken as:
$D = 0.16 \times 10^{-4}$ m$^2$/sec. [M.U.]
12. Estimate the evaporation rate of water, which is available at the bottom of a well 2.5 m diameter and 5 m deep, into dry atmospheric air at 25°C. The diffusion coefficient is 0.0925 m$^2$/h and the atmospheric pressure is 1 bar. The partial pressure of water at the water surface is 0.0312 bar. [M.U.]
13. A pan 20 mm diameter 20 mm deep, is filled with water to a level of 10 mm and is exposed to dry air at 40°C. Calculate the time required for all water to evaporate. What will be the change in time required if the temp of air is 30°C? $D = 0.256$ cm$^2$/s? [M.U.]
14. Estimate the diffusion rate of water at 27°C in a test tube 20 mm diameter 5 cm deep, into dry air at same temperature. Take $D = 0.26$ cm$^2$/s. Saturated vapour pressure of water at 27°C = 0.035 bar. [M.U.]
15. Water at 20°C is spilled in a room. Thickness of water layer is 1 mm. Absolute humidity of air is 3 g of vapour per kg of dry air. Calculate time required for complete evaporation of water spilled, if evaporation is by molecular diffusion through an air film of 5 mm thickness.
Atmospheric temperature and pressure are 1 bar and 20°C, respectively. Assume surface area of floor as 1 m$^2$. Take $D = 0.26 \times 10^{-4}$ m$^2$/s. [M.U.]
[Hint: Remember:

$$\frac{p_{w2}}{p_{a2}} = \frac{m_w}{m_a} \cdot \frac{M_a}{M_w}$$

and, $p_{w2} + p_{a2} = 1$, where $m_w$ = mass of water vapour $m_a$ = mass of dry air, $M_a$ and $M_w$ are the molecular weighs of air and water vapour, respectively.]
16. A mild steel piece has uniform, initial carbon concentration of 0.15% by mass. It is exposed to a carburising atmosphere in a furnace, where the surface concentration is maintained at 1.2%. Determine how long the piece must be kept in the furnace for the concentration of carbon at a location 0.4 mm below the surface to reach 1%. Take $D = 5 \times 10^{-10}$ m$^2$/s.
17. Air at 1 atm. and 25°C, containing small quantities of iodine, flows with a velocity of 4.5 m/s inside a 5 cm diameter tube. Determine the mass transfer coefficient for iodine transfer from the air stream to the surface. Assume: $D = 0.82 \times 10^{-5}$ m$^2$/s; $\nu = 15.5 \times 10^{-6}$ m$^2$/s.
18. Air at a temperature of 21°C, and RH of 40% flows over a water surface at a velocity of 1.2 m/s. Length parallel to flow is 15 cm. Average surface temperature is 15°C. Estimate the amount of water evaporated per hr/m$^2$. of surface area. Partial pressure of water vapour at 21°C and 40% RH is 0.011 bar and at 15°C and saturated, the vapour pressure is 0.017 bar. Viscosity and density of air are: 18.38 x $10^{-6}$ kg/m.s and 1.22 kg/m$^3$, respectively. Assume $D = 0.256 \times 10^{-4}$ m$^2$/s, $p_o = 1.013$ bar, and

$$Sh = 0.023 \cdot Re^{0.8} \cdot Sc^{\frac{1}{3}}$$ [M.U.]
19. Air at a temperature of 30°C, and RH of 15% flows through a pipe of 15 mm ID with a velocity of 5 m/s. The inside surface of the tube is constantly wetted with water such that a thin water film is maintained on the surface. Determine the amount of water evaporated per sq.m of surface area.
Given: $\nu = 16 \times 10^{-6}$ m$^2$/s, $Sc = 0.6$, and $D = 0.26 \times 10^{-4}$ m$^2$/s.
20. Atmospheric air at $T_a = 50$ deg.C was blown past a wet bulb thermometer, the wet bulb reading obtained was $T_w = 30$°C. What is the value of concentration of water vapour $C_a$ in the free stream? Also, determine the relative humidity (RH) of the free stream. (Note: RH is equal to the ratio of concentration $C_a$ of water vapour in free stream to the saturation concentration at the free stream temperature of 50°C, $C_{sat}$. $C_{sat}$ is obtained from Steam Tables.)

# Appendix

**TABLE A-1** Conversion factors

| *Quantity* | *Multiply* | *by* | *to get* |
|---|---|---|---|
| Length | m | 3.2808 | ft |
| | ft | 0.304804 | m |
| Area | m$^2$ | 0.764 | ft$^2$ |
| | ft$^2$ | 1.308901 | m$^2$ |
| Volume | m$^3$ | 35.34 | ft$^3$ |
| | ft$^3$ | 0.028297 | m$^3$ |
| Mass | kg | 2.3046 | lb |
| | lb | 0.433915 | kg |
| Density | kg/m$^3$ | 0.062428 | lb/ft$^3$ |
| | lb/ft$^3$ | 16.01845 | kg/m$^3$ |
| Temperature | K | 0.555556 | R |
| | R | 1.8 | K |
| Mass transfer coefficient | m/s | 11811 | ft/h |
| | ft/h | 8.47E-05 | m/s |
| Volume flow rate | m$^3$/s | 127130 | ft$^3$/h |
| | ft$^3$/h | 7.87E-06 | m$^3$/s |
| Acceleration | m/s$^2$ | 42520000 | ft/h$^2$ |
| | ft/h$^2$ | 2.35E-08 | m/s$^2$ |
| Energy | J | 0.000948 | Btu |
| | Btu | 1054.997 | J |
| Force | N | 0.22481 | lb$_f$ |
| | lb$_f$ | 4.448201 | N |
| Heat transfer rate | W | 3.4123 | Btu/h |
| | Btu/h | 0.293057 | W |
| Heat flux | W/m$^2$ | 0.3171 | Btu/h ft$^2$ |
| | Btu/h ft$^2$ | 3.153579 | W/m$^2$ |
| Heat generation rate | W/m$^3$ | 0.09665 | Btu/h ft$^3$ |
| | Btu/h ft$^3$ | 10.34661 | W/m$^3$ |
| Heat transfer coefficient | W/m$^2$K | 0.17612 | Btu/h ft$^2$ F |
| | Btu/h ft$^2$ F | 5.677947 | W/m$^2$K |
| Kinetic viscosity & diffusivity | m$^2$/s | 38750 | ft$^2$/h |
| | ft$^2$/h | 2.58E-05 | m$^2$/s |
| Latent heat | J/kg | 0.00043 | Btu/lb$_m$ |
| | Btu/lb$_m$ | 2325.852 | J/kg |

*Contd.*

*Contd.*

| | | | |
|---|---|---|---|
| Mass flow rate | kg/s | 7936.6 | $lb_m/h$ |
| | $lb_m/h$ | 0.000126 | kg/s |
| Pressure and stress | $N/m^2$ | 0.020886 | $lb_f/ft^2$ |
| | $lb_f/ft^2$ | 47.87896 | $N/m^2$ |
| Specific heat | J/kgK | 0.000239 | $Btu/lb_mF$ |
| | $Btu/lb_mF$ | 4186.553 | J/kgK |
| Thermal conductivity | W/mK | 0.57782 | Btu/h ft F |
| | Btu/h ft F | 1.730643 | W/mK |
| Thermal resistance | K/W | 0.5275 | F/hBtu |
| | F/h.Btu | 1.895735 | K/W |
| Dynamic viscosity | kg/ms | 2419.1 | $lb_m/fth$ |
| | $lb_m/fth$ | 0.000413 | kg/ms |

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