Module 1 :

The equation of “continuity”

Lecture 6:

The Equation of Continuity for a Binary Mixture

The Equation of Continuity for a Binary Mixture

The molecular transport of one substance relative to another is known as diffusion (also known as *mass diffusion* or *concentration diffusion*). Let's assume that species 'A' is one component and species 'B', is another. Mass balance on component A over a fixed volume, $\Delta x\Delta y\Delta z$ is given as,

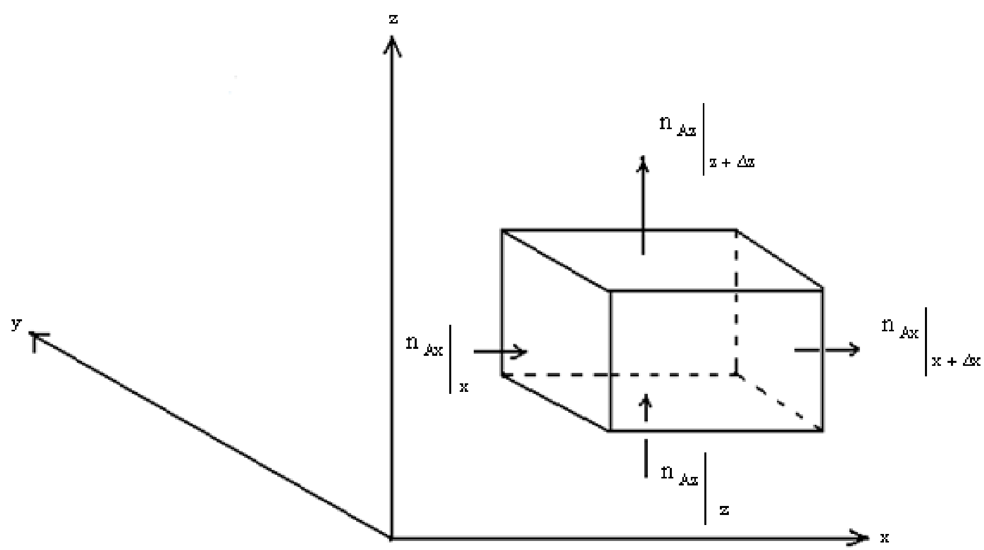


Fig.3.3 An arbitrary Control volume element

$$\begin{Bmatrix}\text{Total rate of change}\\ \text{of mass of A in}\\ \text{volume element}\end{Bmatrix} = \begin{Bmatrix}\text{Input of A across}\\ \text{the faces}\end{Bmatrix} - \begin{Bmatrix}\text{Output of A across}\\ \text{the faces}\end{Bmatrix} + \begin{Bmatrix}\text{Rate of production of A}\\ \text{by chemical reaction}\end{Bmatrix}$$

$$\Delta x\Delta y\Delta z\frac{\partial \rho_A}{\partial t} = \Big[\big((n_{Ax})_x - (n_{Ax})_{x+\Delta x}\big)\Delta y\Delta z + \big((n_{Ay})_y - (n_{Ay})_{y+\Delta y}\big)\Delta x\Delta z + \big((n_{Az})_z - (nAz)_{z+\Delta z}\big)\Delta x\Delta y\Big] + \\ + \ r_A\Delta x\Delta y\Delta z \tag{3.21}$$

where, r_A : Rate of reaction in mass/ (volume)(time)

Dividing by $\Delta x \Delta y \Delta z$ and taking the limit as $\Delta x, \Delta y$ and $\Delta z \to 0$ the above mass balance gives:

$$\frac{\partial \rho_A}{\partial t} = -\left(\frac{\partial n_{Ax}}{\partial x} + \frac{\partial n_{Ay}}{\partial y} + \frac{\partial n_{Az}}{\partial z}\right) + r_A \tag{3.22}$$

or

$$\boxed{\frac{\partial \rho_A}{\partial t} + \left(\nabla \bullet \underline{n}_A\right) = r_A} \tag{3.23}$$

Units of r_A : gm/cm^3-s

Equation (3.23) is the is the species balance equation in generalized vector-tensor notation for a component A in a binary system and is expressed in terms of mass concentration ρ_A and mass flux vector $\underline{n}_A$.

The mass flux vector is given

by $\underline{n}_A = \rho_A \underline{U}_A = w_A\left(\underline{n}_A + \underline{n}_B\right) - \rho D_{AB} \nabla w_A = w_A \rho \underline{U} - \rho D_{AB} \nabla w_A = \rho_A \underline{U} - \rho D_{AB} \nabla w_A$

(3.24)

Here w_A is the Mass fraction of component A, D_{AB} is the binary Diffusion Coefficient and $\underline{U}$ is the Mass average velocity.

Hence after inserting equation (3.24) in (3.23) we get

$$\boxed{\frac{\partial \rho_A}{\partial t} + \nabla \bullet \rho_A \underline{U} = \nabla \bullet \rho D_{AB} \nabla w_A + r_A} \tag{3.25}$$

Special case

Assume constant density ρ, then according to continuity equation

$$\therefore \nabla \bullet \underline{U} = 0$$

Also assume constant diffusivity D_{AB}. Hence equation (3.25) becomes:

$$\frac{\partial \rho_A}{\partial t} + \rho_A \left(\cancelto{0}{\nabla \bullet \underline{U}} \right) + \left(\underline{U} \bullet \nabla \rho_A \right) = D_{AB} \nabla^2 \rho_A + r_A \tag{3.26}$$

Dividing equation (3.26) by M_A we get the equation in molar concentration (see equation (3.1)) as

$$\boxed{\frac{\partial c_A}{\partial t} + \left(\underline{U} \bullet \nabla c_A \right) = D_{AB} \nabla^2 c_A + R_A} \qquad (3.27))$$

Equation (3.27) holds for a binary mixture, with ρ, D_{AB} constant. This equation is often used for dilute liquid solutions at constant T and P.

It can also be written as (according to the definition of substantial derivative)

$$\frac{Dc_A}{Dt} = D_{AB} \nabla^2 c_A + R_A \tag{3.28}$$

which is directly analogous to equation (see equation (2.23), discussed in derivation of Energy equation), if the latter is written as

$$\frac{DT}{Dt} = \frac{k}{\rho \hat{c}_p}\nabla^2 T + \frac{\dot{Q}}{\rho \hat{c}_p} \tag{3.29}$$

In molar units, the mass balance of A in the binary mixture can be written as

$$\frac{\partial c_A}{\partial t} + \left(\nabla \bullet \underline{N}_A\right) = R_A \tag{3.30}$$

As discussed in equation (3.15)-(3.16b)

$$\begin{aligned} \underline{N}_A &= x_A\left(\underline{N}_A + \underline{N}_B\right) - c\,D_{AB}\nabla x_A \\ &= x_A c\underline{U}^* - cD_{AB}\nabla x_A \\ &= c_A\underline{U}^* - c\,D_{AB}\nabla x_A \end{aligned} \tag{3.31}$$

where $c_A = x_A \times c$

Inserting equation (3.31) into equation (3.30) we get

$$\boxed{\frac{\partial c_A}{\partial t} + \nabla \bullet \left(\underline{U}^* \bullet c_A\right) = \nabla \bullet \left(cD_{AB}\nabla x_A\right) + R_A} \tag{3.32}$$

For Constant c and D_{AB}

Equation (3.32) can be written as

$$\boxed{\frac{\partial c_A}{\partial t} + c_A\left(\nabla \bullet \underline{U}^*\right) + \left(\underline{U}^* \bullet \nabla c_A\right) = \left(D_{AB}\nabla^2 c_A\right) + R_A} \tag{3.33}$$

If in addition A is in dilute concentration in solvent B, then $\underline{U}^* \approx \underline{U}$ and equation (3.32) becomes

$$\boxed{\frac{\partial c_A}{\partial t} + \nabla \bullet \left(\underline{U} \bullet c_A\right) = \nabla \bullet \left(cD_{AB} \nabla x_A\right) + R_A} \qquad (3.34)$$

Typical Boundary Conditions (B.C) on the Mass transport equation

In Mass Transfer studies we often encountered with problems that needs to be solved by assigning some boundary conditions. Some of these boundary conditions are discussed below.

I. **Initial Condition: At t=0** $\rightarrow \mathrm{c}\left(\mathrm{x},\mathrm{y},\mathrm{z},0\right) = \mathrm{c}_0\left(x, y, z\right)$

II. **Constant Surface Mass Flux:** Here dependant variable (c) and its normal derivative are specified. Figure shown below illustrates the surface condition. ***D* is the mass diffusivity.** It is also known as **Neumann B.C**.

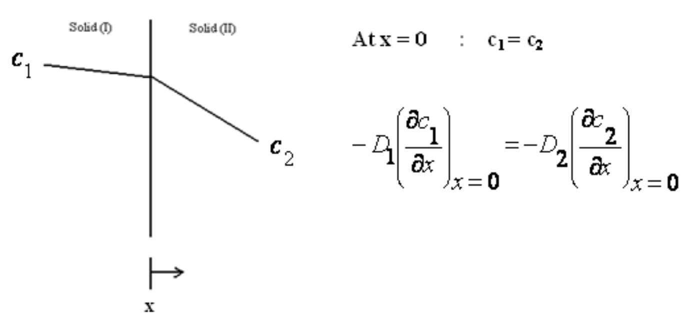
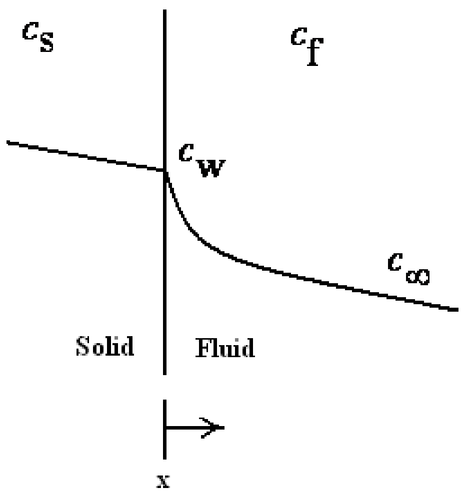


Fig.3.4 Mass transfer at the solid-solid interface

III. Here, Mass coefficient (K_c) is prescribed at the surface. In this, dependant variable (c) and its normal derivative are connected by an algebraic equation. This type of boundary condition is known as **Robin Mixed B.C.** This is an example of flux type B.C. In fluid-solid problems we need such type of B.Cs.



$$-D_{AB}\left(\frac{\partial c_s}{\partial x}\right)_{x=0} = K_c\left(c_w - c_\infty\right)$$

Fig.3.5 Mass transfer at the fluid-solid interface

IV. Given concentration (may be a function of time) or given flux at a surface. It can be given as

$$\frac{\partial c}{\partial t} = 0 \quad \textbf{(for steady state condition)}$$

V. Here normal derivative of the dependant variable is specified at the plane surface or at the wall

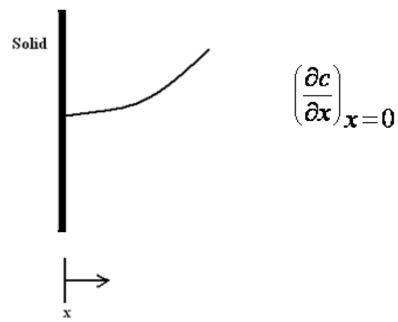


Fig.3.6 Mass transfer at the solid surface

VI. In this type, normal derivative of the dependant variable is defined for cylindrical or spherical geometry.

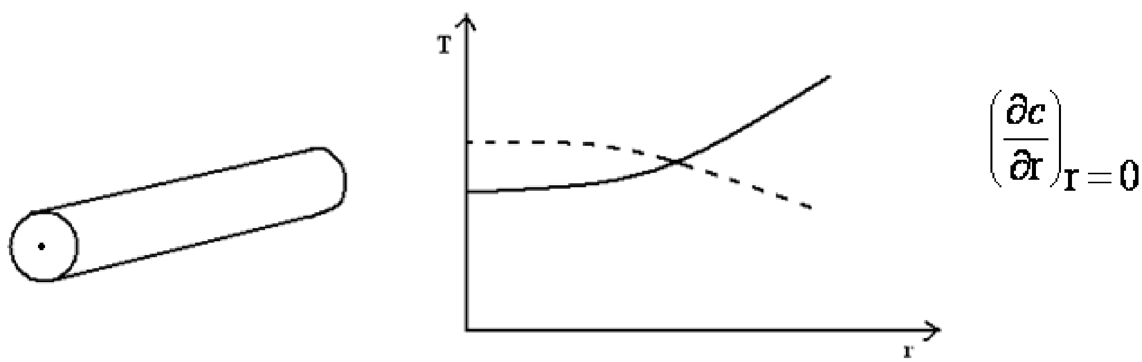


Fig.3.7 Mass transfer through walls of cylinder or sphere