Abdelhafid Boussouf University

Faculty of Sciences and Technology

Department of Mechanical and Electromechanical Engineering

Pr. SAOULI SALAH

ADVANCED HEAT AND MASS TRANSFER

2026-2027

Conduction

1. Fourier's Law

For a homogeneous and isotropic solid (thermal conductivity does not depend on direction), Fourier's law is

$$\vec{q}(M,t) = -\lambda \vec{\nabla} T(M,t)$$

where the temperature gradient is a vector normal to the isothermal surface, the heat flux vector $\vec{q}(\vec{r},t)$ represents the quantity of heat per unit time and per unit area of the isothermal surface in the direction of decreasing temperatures. The coefficient λ is the thermal conductivity of the medium, which is a positive scalar.

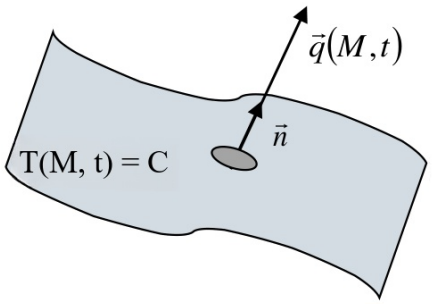


Figure II. 1. Fourier's Law.

In Cartesian coordinates, Fourier's law is written

$$\vec{q}(x,y,z,t) = -\lambda \frac{\partial T(x,y,z,t)}{\partial x}\vec{i} - \lambda \frac{\partial T(x,y,z,t)}{\partial y}\vec{j} - \lambda \frac{\partial T(x,y,z,t)}{\partial z}\vec{k}$$

therefore, the heat flux vector has the components

$$q_x(x,y,z,t) = -\lambda \frac{\partial T(x,y,z,t)}{\partial x}$$

$$q_y(x,y,z,t) = -\lambda \frac{\partial T(x,y,z,t)}{\partial y}$$

$$q_z(x,y,z,t) = -\lambda \frac{\partial T(x,y,z,t)}{\partial z}$$

2. Generalized Fourier Law

In the previous case, we assumed that the solid is isotropic, meaning that the thermal conductivity λ does not depend on direction. However, there are materials, whether natural or synthetic, that have thermal conductivities varying with direction. In the case of orthotropic solids, the thermal conductivity λ has different components in the three directions, namely λ_x, λ_y, and λ_z. In this case, the heat flux vector is written

$$\vec{q}(x,y,z,t) = -\lambda_x \frac{\partial T}{\partial x}\vec{i} - \lambda_y \frac{\partial T}{\partial y}\vec{j} - \lambda_z \frac{\partial T}{\partial z}\vec{k}$$

and the components of the heat flux vector become

$$q_x(x,y,z,t) = -\lambda_x \frac{\partial T}{\partial x}$$

$$q_y(x,y,z,t) = -\lambda_y \frac{\partial T}{\partial y}$$

$$q_z(x,y,z,t) = -\lambda_z \frac{\partial T}{\partial z}$$

For an anisotropic solid, the heat flux component, for example q_1, in the direction Ox_1 is a linear combination of the temperature gradients in the directions Ox_1, Ox_2, and Ox_3.

The components of the heat flux vector in the directions Ox_1, Ox_2 and Ox_3 are given by

$$q_1(x_1, x_2, x_3, t) = -\lambda_{11}\frac{\partial T}{\partial x_1} - \lambda_{12}\frac{\partial T}{\partial x_2} - \lambda_{13}\frac{\partial T}{\partial x_3}$$

$$q_2(x_1, x_2, x_3, t) = -\lambda_{21}\frac{\partial T}{\partial x_1} - \lambda_{22}\frac{\partial T}{\partial x_2} - \lambda_{23}\frac{\partial T}{\partial x_3}$$

$$q_3(x_1, x_2, x_3, t) = -\lambda_{31}\frac{\partial T}{\partial x_1} - \lambda_{32}\frac{\partial T}{\partial x_2} - \lambda_{33}\frac{\partial T}{\partial x_3}$$

or in compact form

$$q_i(x_j, t) = -\lambda_{ij}\frac{\partial T}{\partial x_j}$$

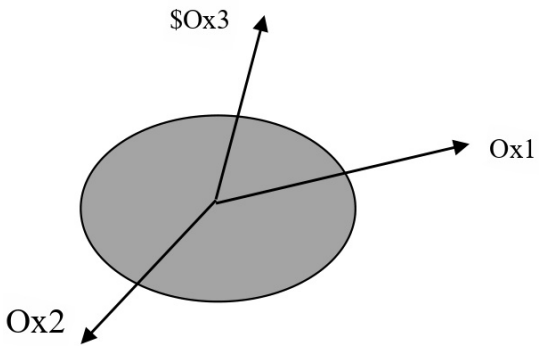


Figure II.2. Anisotropic solid.

Consequently, in an anisotropic solid, the heat flux vector is not necessarily perpendicular to the isothermal surface. The thermal conductivity of an anisotropic solid possesses nine components λ_{ij} called coefficients of thermal conductivity. These relations can be written in matrix form, namely

$$\begin{pmatrix} -q_1 \\ -q_2 \\ -q_3 \end{pmatrix} = \begin{pmatrix} \lambda_{11} & \lambda_{12} & \lambda_{13} \\ \lambda_{21} & \lambda_{22} & \lambda_{23} \\ \lambda_{31} & \lambda_{32} & \lambda_{33} \end{pmatrix} \begin{pmatrix} \frac{\partial T}{\partial x_1} \\ \frac{\partial T}{\partial x_2} \\ \frac{\partial T}{\partial x_3} \end{pmatrix}$$

According to Onsager's theory of thermodynamics of irreversible phenomena, when the fluxes (q_i) and the forces ($\frac{\partial T}{\partial x_j}$) are linked to the forces by linear relations as in our case, the phenomenological coefficients must necessarily satisfy the relations

$$\lambda_{ij} = \lambda_{ji}\,,\ \lambda_{ii} \succ 0\,,\ \lambda_{ii}\lambda_{jj} \succ \lambda_{ij}^2$$

3. Derivation of the Heat Equation

Let us write an energy balance for a volume element v enclosed by a surface S.

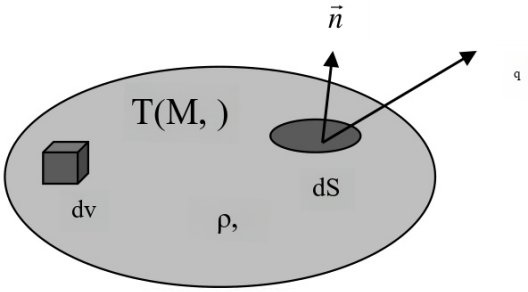


Figure II. 3. Control volume in a heat transfer field.

The variation of the internal energy U is equal to the sum of the heating power and the internal heat generated by an internal source of volumetric density q_s

$$\frac{dU}{dt} = -\int_s \vec{q} \bullet \vec{n} dS + \int_v q_s dv \qquad \text{(II.1)}$$

At the same time, the variation in internal energy, knowing that the latter depends only on temperature, is written as

$$\frac{dU}{dt} = \int_v \rho C_P \frac{\partial T(M,t)}{\partial t} dv \qquad \text{(II.2)}$$

where ρ and C_P are respectively the volumetric mass and the constant-pressure heat capacity of the medium. By inserting these terms into the energy balance, we obtain

$$\int_v \rho C_P \frac{\partial T(M,t)}{\partial t} dv = -\int_v \vec{\nabla} \bullet \vec{q} dv + \int_v q_s dv \qquad \text{(II.3)}$$

with Fourier's law

$$\vec{q} = -\lambda \vec{\nabla} T(M,t) \qquad \text{(II.4)}$$

we arrive at

$$\int_v \rho C_P \frac{\partial T(M,t)}{\partial t} dv = \int_v \vec{\nabla} \bullet \left(\lambda \vec{\nabla} T(M,t)\right) dv + \int_v q_s(M,t) dv \qquad \text{(II.5)}$$

by placing all terms under the integration sign, we obtain

$$\int_v \left[\rho C_P \frac{\partial T(M,t)}{\partial t} - \vec{\nabla} \bullet \left(\lambda \vec{\nabla} T(M,t)\right) - q_s(M,t) \right] dv = 0 \qquad \text{(II.6)}$$

This integral can be zero only if the function under the integral sign is zero, from which follows the relation

$$\rho C_P \frac{\partial T(M,t)}{\partial t} = \vec{\nabla} \bullet \left(\lambda \vec{\nabla} T(M,t)\right) + q_s(M,t) \qquad \text{(II.7)}$$

This is the heat equation in its general form within a stationary solid in the presence of internal heat sources.

Generally, the thermal conductivity λ can be considered constant, and consequently, the heat equation takes the form

$$\rho C_P \frac{\partial T(M,t)}{\partial t} = \lambda \, \Delta T(M,z) + q_s(M,t) \qquad \text{(II.8)}$$

where Δ is the Laplacian operator.

Divide both sides of this equation by the term ρC_p, to obtain

$$\frac{\partial T(M,t)}{\partial t} = a \, \Delta T(M,z) + \frac{q_s(M,t)}{\rho C_P} \qquad \text{(II.9)}$$

The coefficient $a = \frac{\lambda}{\rho C_P}$ is called the thermal diffusion coefficient.

4. Heat Equation in an Anisotropic Solid

In an anisotropic solid, the components of the heat flux vector are given by

$$q_x(M,t) = -\lambda_{11} \frac{\partial T(M,t)}{\partial x} - \lambda_{12} \frac{\partial T(M,t)}{\partial y} - \lambda_{13} \frac{\partial T(M,t)}{\partial z}$$

$$q_y(M,t) = -\lambda_{21} \frac{\partial T(M,t)}{\partial x} - \lambda_{22} \frac{\partial T(M,t)}{\partial y} - \lambda_{23} \frac{\partial T(M,t)}{\partial z}$$

$$q_z(M,t) = -\lambda_{31} \frac{\partial T(M,t)}{\partial x} - \lambda_{32} \frac{\partial T(M,t)}{\partial y} - \lambda_{33} \frac{\partial T(M,t)}{\partial z}$$

Substituting these relations into the heat equation

$$\rho C_P \frac{\partial T(M,t)}{\partial t} = -\vec{\nabla} \bullet \vec{q} + q_s(M,t)$$

let

$$\rho C_P \frac{\partial T(M,t)}{\partial t} = -\frac{\partial q_x(M,t)}{\partial x} - \frac{\partial q_y(M,t)}{\partial y} - \frac{\partial q_z(M,t)}{\partial z} + q_s(M,t)$$

We obtain the heat equation in Cartesian coordinates in an anisotropic medium in the form

$$\rho C_P \frac{\partial T(M,t)}{\partial t} =$$
$$\lambda_{11} \frac{\partial^2 T(M,t)}{\partial x^2} + \lambda_{22} \frac{\partial^2 T(M,t)}{\partial y^2} + \lambda_{33} \frac{\partial^2 T(M,t)}{\partial z^2}$$
$$+ (\lambda_{12} + \lambda_{21}) \frac{\partial^2 T(M,t)}{\partial x \partial y} + (\lambda_{13} + \lambda_{31}) \frac{\partial^2 T(M,t)}{\partial x \partial z}$$
$$+ (\lambda_{23} + \lambda_{32}) \frac{\partial^2 T(M,t)}{\partial y \partial z} + q_s(M,t)$$

5. Nonlinear Boundary Conditions

Consider a surface element of the solid with a unit normal vector $\vec{n}$ subject to convective heat transfer q_{conv}, radiative heat transfer q_{ray}, and an external heat source q_a, as shown in Figure I. 4.

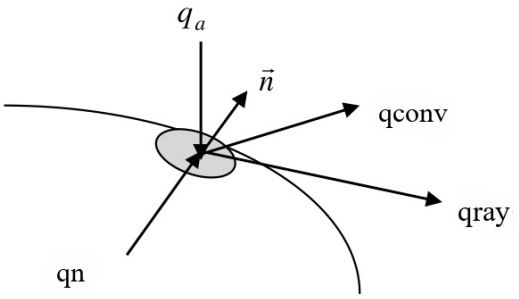


Figure II.4. Boundary Conditions.

The heat flux exchanged by convection q_{conv}, according to Newton's law, is

$$q_{conv} = h\left(T - T_{\infty}\right)$$

The heat flux, quantity of heat exchanged by radiation q_{ray}, according to the Stefan-Boltzmann law, is

$$q_{ray} = \varepsilon\sigma\left(T^4 - T_r^4\right)$$

The heat flux in the direction normal to the surface is

$$q_n = -\lambda\,\vec{\nabla}T \bullet \vec{n}$$

In Cartesian coordinates, we have

$$\vec{q} = -\lambda\frac{\partial T}{\partial x}\vec{i} - \lambda\frac{\partial T}{\partial y}\vec{j} - \lambda\frac{\partial T}{\partial z}\vec{k}$$

$$\vec{n} = l_x\,\vec{i} + l_y\,\vec{j} + l_z\,\vec{k}$$

Substituting these relations into relation I.23, we obtain

$$q_n = -\lambda\left(l_x\frac{\partial T}{\partial x} + l_y\frac{\partial T}{\partial y} + l_z\frac{\partial T}{\partial z}\right) = -\lambda\frac{\partial T}{\partial n}$$

$$q_n + q_a = q_{conv} + q_{ray}$$

By substituting relations I.21, I.22, and I.23 into the relation above, we obtain

$$-\lambda\frac{\partial T}{\partial n} + q_a = h\left(T - T_{\infty}\right) + \varepsilon\sigma\left(T^4 - T_r^4\right)$$

Relation that can also be written in the form

$$\lambda\frac{\partial T}{\partial n} + hT + \varepsilon\sigma T^4 = q_a + hT_{\infty} + \varepsilon\sigma T_r^4$$

In this equation, all quantities on the right-hand side are known and the surface temperature T is unknown.

The general boundary condition is nonlinear because it contains the fourth power of the unknown, which is the temperature.

In the case where $\frac{|T-T_r|}{T_r} \ll 1$, it is possible to linearize Equation I.29. Indeed, let us assume that

$$\frac{T-T_r}{T_r} = \alpha \,,\ (\alpha \prec\prec 1)$$

hence

$$T = (\alpha + 1)T_r$$

The term $T^4 - T_r^4$ can be written in the form

$$T^4 - T_r^4 = (T - T_r)(T^3 + TT_r^2 + T^2T_r + T_r^3)$$

Substituting T with its expression, we obtain

$$T^4 - T_r^4 = (T - T_r)(\alpha^3 + 4\alpha^2 + 6\alpha + 4)T_r^3$$

Since α is very small compared to unity, we can write this relation in the form

$$T^4 - T_r^4 = 4T_r^3(T - T_r)$$

Consequently, the equation becomes

$$-\lambda \frac{\partial T}{\partial n} + q_a = h(T - T_\infty) + h_r(T - T_r)$$

where h_r is the exchange coefficient for radiation given by the relation

$$h_r = 4\varepsilon\sigma T_r^3$$

6. Linear Boundary Conditions

If we examine the heat equation closely, we observe that it contains a first-order derivative with respect to time and second-order derivatives with respect to space; this necessarily implies three boundary conditions. There is one initial condition with respect to time and two boundary conditions with respect to space, which we will detail in the following.

6.1. Initial Condition

If the temperature distribution at time $t = t_0$ is a certain function $f(M, t_0)$, the initial condition is

$$T(M,t) = f(M,t_0) \tag{II.10}$$

6.2. Boundary Conditions

The boundary conditions imposed on the temperature $T(M, t)$ depend on the physical scenarios considered.

a) Surface at constant temperature (Dirichlet condition)

If for a spatial position M_0, the temperature is constant, then the boundary condition in this case is

$$T(M,t) = g(M_0,t) \tag{II.11}$$

This condition is also called a first-type condition. In practice, this boundary condition occurs in cases where the surface is in contact with a melting solid or a boiling liquid (phase change). In these two cases, there is heat transfer across the surface while the temperature remains constant during this phase change.

b) Surface subjected to a heat flux (Neumann condition)

If, for the spatial position M_0, a heat flux q is imposed, the boundary condition in this case becomes

$$-\lambda \frac{\partial T(M_0,t)}{\partial M} = q \qquad \text{(II.12)}$$

This boundary condition, also known as the second-type boundary condition, arises during surface heating by a heat flux, such as with an electrical resistance.

If the spatial position M_0 is adiabatic, i.e., isolated, the boundary condition is then

$$\frac{\partial T(M_0,t)}{\partial M} = 0 \qquad \text{(II.13)}$$

c) Surface in contact with a fluid (third-type boundary condition)

Finally, for the spatial position M_0, heat exchange may occur by convection; in this case, the boundary condition is written as

$$-\lambda \frac{\partial T(M_0,t)}{\partial M} = h\left(T(M_0,t) - T_\infty\right) \qquad \text{(II.14)}$$

7. Another way to derive the heat equation

7.1. Cartesian Coordinates

Consider a elementary cube with sides dx, dy, and dz surrounding a stationary medium at temperature $T(x,y,z,t)$. The quantities of heat per condition perpendicular to each surface of the cube at points x, y, and z are

$$Q_x = -\lambda \frac{\partial T}{\partial x} dydz, \quad Q_y = -\lambda \frac{\partial T}{\partial y} dxdz, \quad Q_z = -\lambda \frac{\partial T}{\partial z} dxdy \qquad \text{(II.15)}$$

The quantities of heat conducted through the surfaces opposite to the previous surfaces are obtained by a first-order Taylor expansion, namely

$$Q_{x+dx} = Q_x + \frac{\partial Q_x}{\partial x} dx \qquad \text{(II.16)}$$

$$Q_{y+dy} = Q_y + \frac{\partial Q_y}{\partial y} dy \qquad \text{(II.17)}$$

$$Q_{z+dz} = Q_z + \frac{\partial Q_z}{\partial z} dz \qquad \text{(II.18)}$$

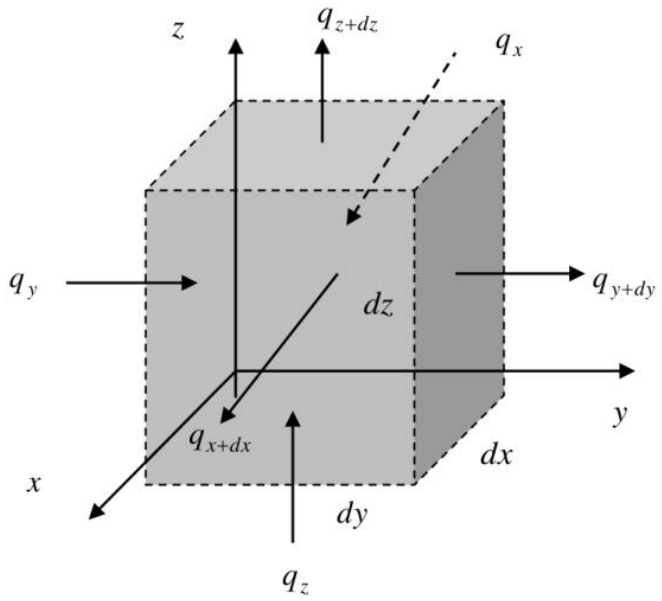


Figure II. 5. Volume element $dv = dxdydz$ in Cartesian coordinates.

If a volumetric heat source q_s exists in the medium, the generated energy E_g within the cube's volume is then

$$dE_g = q_s dxdydz \tag{II.19}$$

The stored energy E_{st} in the volume of the cube is

$$dE_{St} = \rho C_P \frac{\partial T}{\partial t} dxdydz \tag{II.20}$$

The energy balance over the volume of the cube, in accordance with the principle of conservation of energy, is

$$dE_{St} = dE_e + dE_g - dE_s \tag{II.21}$$

let

$$\rho C_P \frac{\partial T}{\partial t} dxdydz = Q_x + Q_y + Q_z + q_s dxdydz - Q_{x+dx} - Q_{y+dy} - Q_{z+dz}$$

$$\rho C_P \frac{\partial T}{\partial t} dxdydz = \frac{\partial Q_x}{\partial x} dx - \frac{\partial Q_y}{\partial y} dy - \frac{\partial Q_z}{\partial z} dz + q_s dxdydz \tag{II.22}$$

and by substituting relations II.15, we find

$$\rho C_P \frac{\partial T(x,y,z,t)}{\partial t} dxdydz = \frac{\partial}{\partial x}\left(\lambda \frac{\partial T}{\partial x}\right) dxdydz + \frac{\partial}{\partial y}\left(\lambda \frac{\partial T}{\partial y}\right) dxdydz + \frac{\partial}{\partial z}\left(\lambda \frac{\partial T}{\partial z}\right) dxdydz + q_s dxdydzz \tag{II.23}$$

By simplifying by the volume element $dx\,dy\,dz$, we arrive at the heat equation in Cartesian coordinates in its most general form

$$\rho C_P \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\lambda \frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial y}\left(\lambda \frac{\partial T}{\partial y}\right) + \frac{\partial}{\partial z}\left(\lambda \frac{\partial T}{\partial z}\right) + q_s \tag{II.24}$$

If the thermal conductivity λ is constant, we recover Equation II.9, namely

$$\frac{\partial T}{\partial t} = a\left[\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right] + \frac{q_s}{\rho C_P} \qquad \text{(II.25)}$$

7.2. Cylindrical Coordinates

When the nabla operator ∇ is expressed in cylindrical coordinates, Fourier's law is written

$$\vec{q} = -\lambda\left(\frac{\partial T(r,\varphi,z)}{\partial r}\vec{e}_r + \frac{1}{r}\frac{\partial T(r,\varphi,z)}{\partial \varphi}\vec{e}_\theta + \frac{\partial T(r,\varphi,z)}{\partial z}\vec{e}_z\right) \qquad \text{(II.26)}$$

heat fluxes

$$q_r = -\lambda\frac{\partial T}{\partial r},\ q_\varphi = -\frac{\lambda}{r}\frac{\partial T}{\partial \varphi},\ q_z = -\lambda\frac{\partial T}{\partial z} \qquad \text{(II.27)}$$

are respectively the components of the heat flux in the radial, circumferential, and axial directions.

By applying the principle of energy conservation to the volume element $rdrd\varphi dz$, the heat equation is written as

$$\rho C_P\frac{\partial T}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(\lambda r\frac{\partial T}{\partial r}\right) + \frac{1}{r^2}\frac{\partial}{\partial \varphi}\left(\lambda\frac{\partial T}{\partial \varphi}\right) + \frac{\partial}{\partial z}\left(\lambda\frac{\partial T}{\partial z}\right) + q_S \qquad \text{(II.28)}$$

If the thermal conductivity λ is constant, this equation becomes

$$\frac{\partial T}{\partial t} = a\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 T}{\partial \varphi^2} + \frac{\partial^2 T}{\partial z^2}\right] + \frac{q_S}{\rho C_P} \qquad \text{(II.29)}$$

7.3. Spherical Coordinates

By expressing the nabla operator ∇ in spherical coordinates, Fourier's law is written as

$$\vec{q} = -\lambda\left[\frac{\partial T(r,\varphi,\theta)}{\partial r}\vec{e}_r + \frac{1}{r}\frac{\partial T(r,\varphi,\theta)}{\partial \theta}\vec{e}_\theta + \frac{1}{r\sin\theta}\frac{\partial T(r,\varphi,\theta)}{\partial \varphi}\vec{e}_\varphi\right] \tag{II.30}$$

heat fluxes

$$q_r = -\lambda\frac{\partial T}{\partial r},\ q_\theta = -\frac{\lambda}{r}\frac{\partial T}{\partial \theta},\ q_\varphi = -\frac{\lambda}{r\sin\theta}\frac{\partial T}{\partial \varphi} \tag{II.31}$$

are respectively the components of the heat flux in the radial, polar, and azimuthal directions. By applying the principle of energy conservation to the volume element $r^2\sin\theta\, dr\, d\theta\, d\varphi$, the heat equation is written

$$\rho C_P\frac{\partial T}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(\lambda r^2\frac{\partial T}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial \varphi}\left(\lambda\frac{\partial T}{\partial \varphi}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\lambda\sin\theta\frac{\partial T}{\partial \theta}\right) + q_S \tag{II.32}$$

If the thermal conductivity λ is constant, the equation becomes

$$\frac{\partial T}{\partial t} = \frac{\alpha}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right) + \frac{\alpha}{r^2\sin^2\theta}\frac{\partial}{\partial \varphi}\left(\frac{\partial T}{\partial \varphi}\right) + \frac{\alpha}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial T}{\partial \theta}\right) + \frac{q_S}{\rho C_P} \tag{II.33}$$

8. Special Forms of the Heat Equation

We return to the heat equation in its general form for the case where thermal conductivity is constant, namely

$$\frac{\partial T(M,t)}{\partial t} = a\Delta T(M,z) + \frac{q_s(M,t)}{\rho C_P} \tag{II.34}$$

and let us consider the different particular cases.

8.1. Fourier's Equation

In the absence of internal heat sources ($q_S(M,t)=0$), the heat equation becomes

$$\frac{\partial T(M,t)}{\partial t} = a\Delta T(M,z) \qquad \text{(II.35)}$$

this equation is called the Fourier equation.

8.2. Poisson Equation

In steady state, the temperature does not depend on time ($\frac{\partial T(M,t)}{\partial t}=0$), the heat equation is known under the name of the Poisson equation and it is written as

$$\Delta T(M)+\frac{q_s(M)}{\lambda}=0 \qquad \text{(II.36)}$$

8.3. Laplace Equation

The Laplace equation is obtained in the case of steady-state regime and in the absence of internal heat sources ($q_S(M,t)=0$), i.e.,

$$\Delta T(M)=0 \qquad \text{(II.37)}$$

Conduction in Transient Regime

1. Case of negligible internal resistance

Consider the case of cooling a solid body of density ρ, specific heat capacity C, volume V, and surface area S, initially at temperature T and rapidly immersed in a fluid at temperature T_∞ (assumed constant). The body is assumed to be of small dimensions such that any internal temperature gradient is neglected (negligible internal resistance). If h is the convective heat transfer coefficient, the change in internal energy is equal to the quantity of heat exchanged by convection between the solid body and the fluid.

$$-\rho CV\frac{dT(t)}{dt}=hS(T(t)-T_{\infty}) \qquad \text{(IV.1)}$$

with the boundary condition

$$t=0\ ,T=T_0 \qquad \text{(IV.2)}$$

Since T_{∞} is assumed to be constant, the solution to Equation IV. 1 is

$$\frac{T(t)-T_{\infty}}{T_0-T_{\infty}}=e^{-\frac{hS}{\rho CV}t} \qquad \text{(IV.3)}$$

The term $\frac{hS}{\rho CV}t$ can be written in the form

$$\frac{hS}{\rho CV}t=\frac{hL}{\lambda}\frac{at}{L^2} \qquad \text{(IV.4)}$$

where $a=\frac{\lambda}{\rho C}$ is the thermal diffusivity and $L=\frac{V}{S}$ is the characteristic length of the solid body. The ratio $\frac{hL}{\lambda}$ is a dimensionless number called the Biot number, and the ratio $\frac{at}{L^2}$ is also a dimensionless number called the Fourier number, such that

$$Bi=\frac{hL}{\lambda},\ Fo=\frac{at}{L^2} \qquad \text{(IV.5)}$$

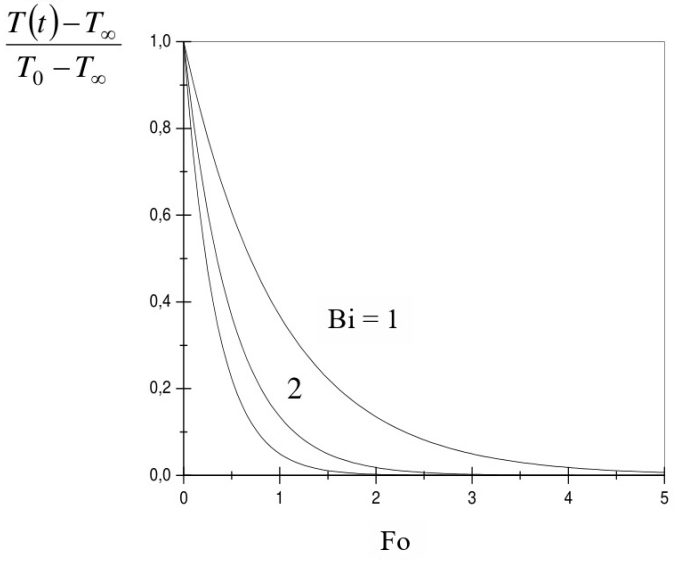


Figure IV. 1. Temperature profile $\frac{T(t)-T_\infty}{T_0-T_\infty}$ as a function of

Fourier number for different values of the Biot number.

Consequently, the temperature of the solid body can be written in the form

$$\frac{T(t)-T_\infty}{T_0-T_\infty} = e^{-BiFo} \qquad \text{(IV.6)}$$

2. Case of a semi-infinite solid

Consider heat conduction in the transient regime within a semi-infinite solid of width L. The temperature distribution $T(x,t)$ is obtained by solving the Fourier equation

$$\frac{1}{a}\frac{\partial T(x,t)}{\partial t}=\frac{\partial^2 T(x,t)}{\partial x^2} \qquad \text{(IV.7)}$$

with the boundary conditions

$$\frac{\partial T(0,t)}{\partial x}=0,\ T(x,L)=T_0,\ T(x,0)=f(x) \qquad \text{(IV.8)}$$

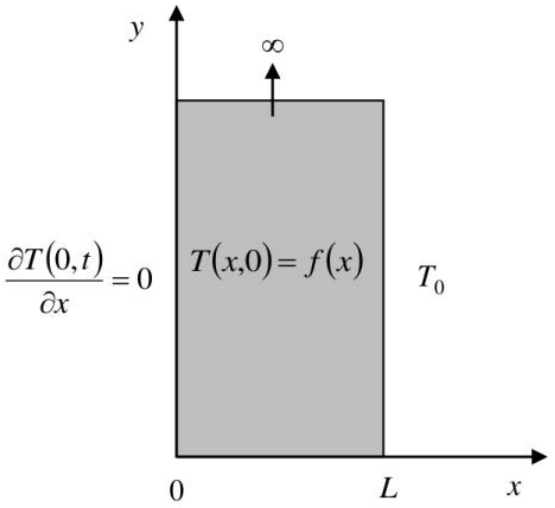


Figure IV.2. Semi-infinite solid.

Let us use the method of separation of variables and seek the solution in the form

$$T(x,t)=X(x)\Theta(t) \qquad \text{(IV.9)}$$

By replacing the second derivative with respect to the coordinate x ($\frac{\partial^2 T(x,t)}{\partial x^2}=X''(x)\Theta(t)$) and the first derivative with respect to time

$t(\frac{\partial T(x,t)}{\partial t} = X(x)\dot{\Theta}(t))$ in the Fourier equation, we obtain two independent ordinary differential equations

$$X''(x) + k^2 X(x) = 0 \qquad \text{(IV.10)}$$

$$\dot{\Theta}(t) + ak^2 \Theta(t) = 0 \qquad \text{(IV.11)}$$

where k is a positive real constant. The solutions to these differential equations are

$$X(x) = C_1 \cos kx + C_2 \sin kx \qquad \text{(IV.12)}$$

$$\Theta(t) = C_3 e^{-ak^2 t} \qquad \text{(IV.13)}$$

therefore, the temperature $T(x,t)$ is

$$T(x,t) = C_3 e^{-ak^2 t}\left(C_1 \cos kx + C_2 \sin kx\right)$$

and since T_0 is constant, we can write this temperature in the form

$$T(x,t) - T_0 = C_3 e^{-ak^2 t}\left(C_1 \cos kx + C_2 \sin kx\right) \qquad \text{(IV.14)}$$

with the boundary conditions

$$\frac{\partial T(0,t) - T_0}{\partial x} = 0,\ T(x,L) - T_0 = 0,\ T(x,0) - T_0 = f(x) \qquad \text{(IV.15)}$$

Applying these conditions to the limits, we obtain

$$T(x,t) - T_0 = \sum_{n=0}^{n=\infty} C_n e^{-a k_n^2 t} \cos k_n x \qquad \text{(IV.16)}$$

where the coefficient k_n is

$$k_n = \left(n + \frac{1}{2}\right)\frac{\pi}{L} \qquad \text{(IV.17)}$$

the coefficient C_n is calculated using the formula

$$C_n = \frac{2}{L}\int_0^L f(x)\cos k_n x dx \qquad \text{(IV.18)}$$

3. Two-dimensional case in Cartesian coordinates

Let us now consider conduction in the transient regime within a rectangular plate with sides L_1 and L_2.

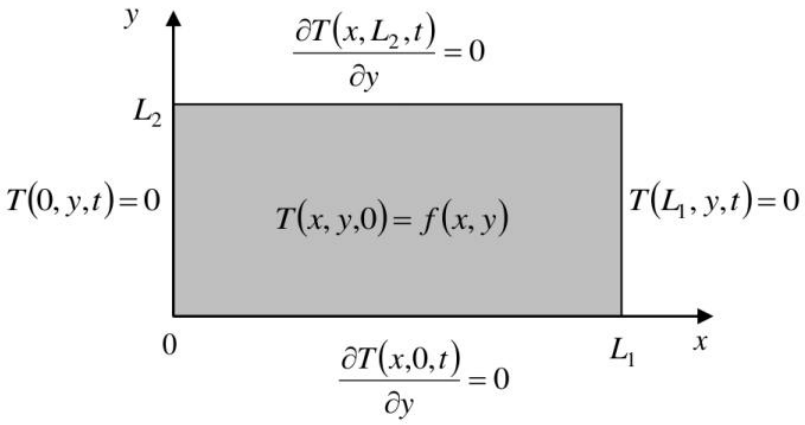


Figure IV. 3. Transient two-dimensional conduction in a rectangular plate.

The two-dimensional Fourier equation in this case is

$$\frac{1}{a}\frac{\partial T(x,y,t)}{\partial t} = \frac{\partial^2 T(x,y,t)}{\partial x^2} + \frac{\partial^2 T(x,y,t)}{\partial y^2} \qquad \text{(IV.19)}$$

The boundary conditions for this problem are

$$T(x,y,0) = f(x,y),\ T(0,y,t) = 0,\ T(L_1,y,t) = 0 \qquad \text{(IV.20)}$$

$$\frac{\partial T(x,0,t)}{\partial y}=0\,,\ \frac{\partial T(x,L_2,t)}{\partial y}=0 \qquad \text{(IV.21)}$$

Let us seek the solution to the Fourier equation in the form

$$T(x,y,t)=X(x)Y(y)\Theta(t) \qquad \text{(IV.22)}$$

By differentiating this function twice with respect to the spatial variables x and y, and once with respect to time t, we obtain

$$\frac{X''(x)}{X(x)}=\frac{1}{a}\frac{\dot{\Theta}(t)}{\Theta(t)}-\frac{Y''(y)}{Y(y)}=-k^2 \qquad \text{(IV.23)}$$

relation from which we deduce the first ordinary differential equation for the function $X(x)$, which is

$$X''(x)+k^2X(x)=0 \qquad \text{(IV.24)}$$

whose solution is

$$X_m(x)=C_1\sin\frac{m\pi x}{L_1} \qquad \text{(IV.25)}$$

Substituting the value of the coefficient k, where $k=\frac{m\pi}{L_1}$, into Equation IV.23, we obtain

$$\frac{Y''(y)}{Y(y)}=\frac{1}{a}\frac{\dot{\Theta}(t)}{\Theta(t)}+\frac{m^2\pi^2}{L_1^2}=-\mu^2 \qquad \text{(IV.26)}$$

equation from which we deduce the second ordinary differential equation for the function $Y(y)$ and which is

$$Y''(y)+\mu^2Y(y) \qquad \text{(IV.27)}$$

whose solution is

$$Y_n(y)=C_2\cos\frac{n\pi y}{L_2} \qquad \text{(IV.28)}$$

By substituting the value of the coefficient μ, which is $\mu = \frac{n\pi}{L_2}$, into equation IV. 23, we obtain

$$\frac{1}{a}\frac{\dot{\Theta}(t)}{\Theta(t)} + \frac{m^2\pi^2}{L_1^2} + \frac{n^2\pi^2}{L_2^2} = 0 \qquad \text{(IV.29)}$$

$$\dot{\Theta}(t) + a\pi^2\left(\frac{m^2}{L_1^2} + \frac{n^2}{L_2^2}\right)\Theta(t) = 0 \qquad \text{(IV.30)}$$

$$\Theta_{mn}(t) = C_{mn}\exp\left(-a\pi^2\left(\frac{m^2}{L_1^2} + \frac{n^2}{L_2^2}\right)t\right) \qquad \text{(IV.31)}$$

Consequently, the temperature $T_{mn}(x, y, t)$ is given by

$$T(x, y, t) = \sum_{m=1}^{m=\infty}\sum_{n=1}^{n=\infty} A_{mn}\exp\left(-a\pi^2\left(\frac{m^2}{L_1^2} + \frac{n^2}{L_2^2}\right)t\right)\sin\frac{m\pi x}{L_1}\cos\frac{n\pi y}{L_2} \qquad \text{(IV.46)}$$

The application of the initial condition yields the relation

$$f(x, y) = \sum_{m=1}^{m=\infty}\sum_{n=1}^{n=\infty} A_{mn}\sin\frac{m\pi x}{L_1}\cos\frac{n\pi y}{L_2} \qquad \text{(IV.47)}$$

Consequently, the coefficients A_{mn} are calculated from the formula

$$A_{mn} = \frac{4}{L_1 L_2}\int_0^{L_1}\int_0^{L_2} f(x, y)\sin\frac{m\pi x}{L_1}\cos\frac{n\pi y}{L_2}\,dxdy \qquad \text{(IV.48)}$$

4. Case of a Sphere

Consider a sphere of radius R that exchanges heat by convection with the external medium at temperature T_∞. We will assume that the initial temperature of the sphere is a certain function $f(r)$; furthermore, we assume that the temperature of the sphere depends only on the radius r. The Fourier equation in this case is written as

$$\frac{\partial T(r,t)}{\partial t} = a\,\Delta T(r,t) \qquad \text{(IV.49)}$$

with the boundary conditions

$$T(r,0) = f(r),\ -\lambda\frac{\partial T(R,t)}{\partial r} = h(T(R,t) - T_\infty) \qquad \text{(IV.50)}$$

Since T_∞ is constant, let us seek the solution to the Fourier equation in the form

$$T(r,t) - T_\infty = AV(r)e^{-\omega t} \qquad \text{(IV.51)}$$

Substituting this expression into the Fourier equation, we obtain

$$\Delta V(r) + \frac{\omega}{a}V(r) = 0 \qquad \text{(IV.52)}$$

or even

$$\frac{d^2V(r)}{dr^2} + \frac{2}{r}\frac{dV(r)}{dr} + \frac{\omega}{a}V(r) = 0 \qquad \text{(IV.53)}$$

If we use the function $U(r) = rV(r)$, the previous equation becomes

$$\frac{d^2U(r)}{dr^2} + \alpha^2 U(r) = 0 \qquad \text{(IV.54)}$$

where $\alpha^2 = \frac{\omega}{a}$. The solution to this differential equation is

$$U(r) = C_1 \cos\alpha\, r + C_2 \sin\alpha\, r$$

from which we obtain for the function $V(r)$ the equation

$$V(r) = C_1 \frac{\cos\alpha\, r}{r} + C_2 \frac{\sin\alpha\, r}{r} \qquad \text{(IV.55)}$$

Let us note that for $r = 0$, the function $V(r)$ will be indeterminate; therefore, we must set $C_1 = 0$, from which

$$V(r) = C_2 \frac{\sin\alpha\, r}{r} \qquad \text{(IV.55)}$$

therefore, the temperature $T(r) - T_\infty$ is given by

$$T(r,t) - T_\infty = A \frac{\sin\alpha\, r}{r} e^{-\omega t} \qquad \text{(IV.56)}$$

Application of the boundary condition

$$-\lambda \frac{\partial\left(T(R,t) - T_\infty\right)}{\partial r} = h\left(T(R,t) - T_\infty\right)$$

$$A \frac{\alpha R \cos\alpha R - \sin\alpha R}{R^2} e^{-\omega t} = -\frac{h}{\lambda} A \frac{\sin\alpha\, R}{R} e^{-\omega t}$$

relation, which after rearrangement becomes

$$\alpha_n R \cot g\, \alpha_n R = 1 - \frac{h}{\lambda} R \qquad \text{(IV.57)}$$

The possible values of the coefficient α_n are solutions to this equation; consequently, the temperature $T(r) - T_\infty$ can be represented by the series

$$T(r,t) - T_\infty = \sum_{n=1}^{n=\infty} A_n e^{-a\alpha_n^2 t} \frac{\sin\alpha_n r}{r} \qquad \text{(IV.58)}$$

From the initial condition, we have

$$rf(r)=\sum_{n=1}^{n=\infty} A_n \sin\alpha_n r \qquad \text{(IV.59)}$$

Since the functions $\sin(\alpha_n r)$ are orthogonal in the interval $[0, R]$, the coefficients A_n are determined from the formula

$$A_n = \frac{\int_0^R rf(r)\sin\alpha_n r dr}{\int_0^R \sin^2\alpha_n r dr} \qquad \text{(IV.60)}$$

5. Semi-infinite plate subjected to a periodic temperature

Consider a semi-infinite solid whose one side is subjected to a periodic temperature of the form $T(0,t)=T_0\cos(\omega t)$ as shown in Figure IV.4.

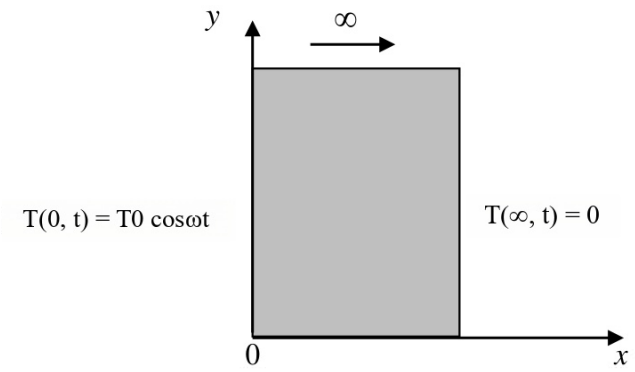


Figure IV.4. Semi-infinite solid subjected to a periodic temperature.

The Fourier equation is

$$\frac{1}{a}\frac{\partial T}{\partial t}=\frac{\partial^2 T}{\partial x^2} \qquad \text{(IV.61)}$$

with the boundary conditions

$$T(0,t)=T_0\cos\omega t\ ,\ T(\infty,t)=0 \qquad \text{(IV.62)}$$

Let us seek the solution in the form $T(x,t)=X(x)e^{i\omega t}$; indeed, if we substitute this solution into the Fourier equation, we obtain the following differential equation for the function $X(x)$

$$\frac{d^2X(x)}{dx^2}-\frac{i\omega}{a}X(x)=0 \qquad \text{(IV.63)}$$

whose solution is

$$X(x)=C_1e^{x\sqrt{\frac{i\omega}{a}}}+C_2e^{-x\sqrt{\frac{i\omega}{a}}} \qquad \text{(IV.64)}$$

However, in accordance with the second boundary condition, the temperature must be finite for $x=\infty$. To satisfy this constraint, we must eliminate the divergent term in the solution by setting $C_1=0$. Consequently, the solution selected in this case is

$$X(x)=C_2e^{-x\sqrt{\frac{i\omega}{a}}} \qquad \text{(IV.64)}$$

Given that $\sqrt{i\omega}=\sqrt{\frac{\omega}{2}}+i\sqrt{\frac{\omega}{2}}$, we can write that

$$T(x,t)=C_2e^{-x\sqrt{\frac{\omega}{2a}}}e^{i\left(\omega t-x\sqrt{\frac{\omega}{2a}}\right)} \qquad \text{(IV.65)}$$

The real part of this solution is

$$T(x,t)=C_2e^{-x\sqrt{\frac{\omega}{2a}}}\cos\left(\omega t-x\sqrt{\frac{\omega}{2a}}\right) \qquad \text{(IV.66)}$$

From the first boundary condition, we obtain

$$C_2 = T_0$$

and consequently, the temperature $T(x,t)$ becomes

$$T(x,t) = T_0 e^{-x\sqrt{\frac{\omega}{2a}}} \cos\left(\omega t - x\sqrt{\frac{\omega}{2a}}\right) \qquad \text{(IV.67)}$$

We observe that the amplitude of the temperature $T(x,t)$ decreases with the abscissa x, and furthermore there is a phase shift between the temperature $T(x,t)$ and the temperature $T(0,t)$ equal to $x\sqrt{\frac{\omega}{2a}}$.

Thermal radiation

1. Introduction

Heat transfer occurs via three distinct modes: conduction, convection, and thermal radiation. When a temperature gradient exists within a stationary medium—whether solid or fluid—we use the term conduction to describe heat transfer occurring through that medium. The term convection refers to the mode of heat transfer between a solid surface and a moving fluid, or between two fluids in motion, when a temperature gradient is present. The third mode of heat transfer involves thermal radiation. Any solid or fluid surface emits thermal radiation in the form of electromagnetic waves (light) that propagate through the surrounding space without a material medium.

Conduction is the process by which heat is transmitted within a solid system from its hot region to its cold region or between two systems in contact (one hot and the other cold). This energy transfer occurs through the vibrations of the system's molecules around their equilibrium positions. According to kinetic theory, the energy or speed of the molecules is proportional to the temperature. Therefore, as they move toward regions of lower temperature, molecules transfer part of their energy through elastic collisions or by electron diffusion (in the case of metals).

Conduction attempts to balance the temperature within the system, but the process continues as long as a temperature difference is maintained

$$\vec{q} = -\lambda S \vec{\nabla} T(M,t) \qquad \text{(VI.1)}$$

During heat transfer between a fluid and a solid or between two fluids, the amount of heat exchanged is given by Newton's formula

$$Q = \bar{h}S\left(T_P - T_\infty\right) \tag{VI.2}$$

where $\bar{h}$ is the average convective heat transfer coefficient, T_p and T_∞ are respectively the surface and fluid temperatures, and S is the exchange surface. Any surface at temperature T_p emits radiation known as thermal radiation, provided that this temperature differs from absolute zero. This quantity of heat is calculated using the formula

$$Q \propto T^4 \tag{VI.3}$$

If the surface at temperature T_P is surrounded by an infinite medium at temperature T_∞, the net heat exchanged is

$$Q \propto \left(T_0^4 - T_\infty^4\right) \tag{VI.4}$$

2. Nature of Thermal Radiation

The energy of thermal radiation consists of electromagnetic waves or massless particles called photons. In nature, no single descriptive model of radiation energy is capable of describing all observed phenomena on its own. Electromagnetic waves and photons propagate through any medium at the speed c, known as the speed of light. The speed of light depends on the medium in which it propagates; it is related to the speed in a vacuum c_0 by the formula

$$c = \frac{c_0}{n} \tag{VI.5}$$

where n is the refractive index of the medium and $c_0 = 2.998 \times 10^8$ ms $^{-1}$. By definition, the refractive index of a vacuum is $n = 1$. For gases

At ambient temperature, the refractive index is close to unity; for air, its value is $n = 1.00029$ for visible light. Light propagates more slowly in dielectrics, which have a refractive index between 1.4 and 4 and do not penetrate conductors. Any electromagnetic wave is characterized either by its frequency ν, its angular frequency ω, its wavelength λ, or its wavenumber η. These different quantities are related by the expression

$$\nu = \frac{\omega}{2\pi} = \frac{c}{\lambda} = c\eta \qquad \text{(VI.6)}$$

If we consider the corpuscular aspect of light, each photon carries an energy ε given by the relation

$$\varepsilon = h\nu = \frac{hc}{\lambda} \qquad \text{(VI.7)}$$

where h is Planck's constant whose value is

$$h = 6{,}626.10^{-34}\ J.s \qquad \text{(VI.8)}$$

The frequency of an electromagnetic wave does not change when it passes from one medium to another, since the photon's energy must be conserved; however, its wavelength changes because the refractive index varies from one medium to another. The following figure shows the electromagnetic spectrum. Note that thermal radiation lies between $\lambda = 0.1\,\mu\text{m}$ and $\lambda = 100\,\mu\text{m}$, thus covering the visible portion of the electromagnetic spectrum.

When an electromagnetic wave strikes a solid or liquid surface, the wave may be partially or totally reflected, and the non-reflected portion penetrates the medium. As it traverses the medium, the wave continues to be attenuated. If the wave is completely absorbed, the medium is said to be opaque. If the wave traverses the medium without attenuation, the medium is considered transparent; if the attenuation is partial, it is considered semi-transparent.

A completely opaque surface that does not reflect any wave is called a perfect absorbing surface or a black surface. A surface that does not reflect any radiation cannot be seen; it appears black to our eyes and, consequently, absorbs the maximum amount of radiation falling upon it.

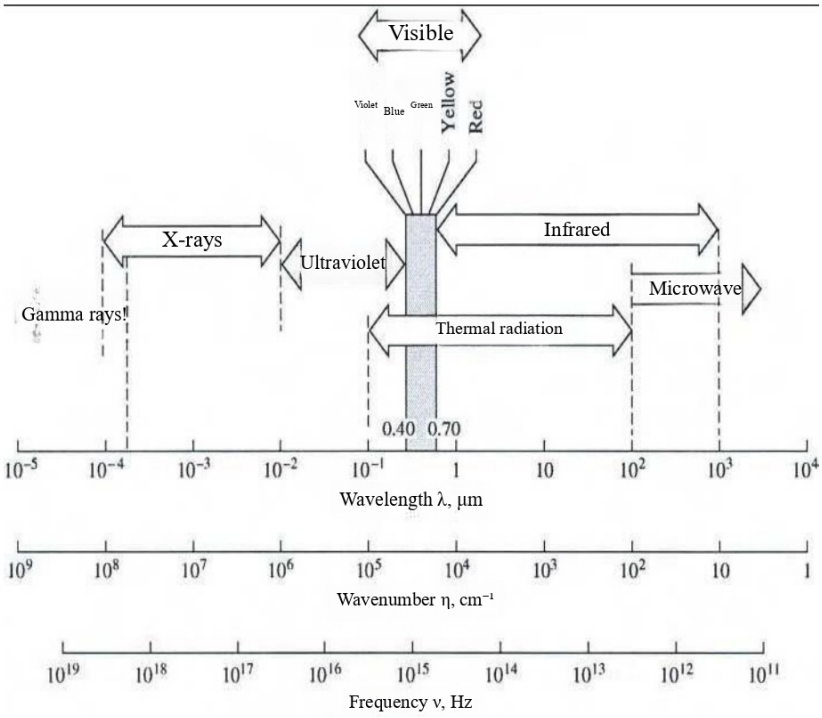


Figure VI. 1. Spectrum of electromagnetic waves.

Consider a cavity whose inner wall is black, thermally insulated on the outside, and containing a small black object. Over time, in accordance with the second principle of thermodynamics, the cavity and the small object reach the same equilibrium temperature. This means that each surface that this

emit as much radiation from the cavity or the small emitting body as they absorb. However, since their surfaces are black, they absorb the maximum amount of radiation and consequently also emit the maximum amount of radiation.

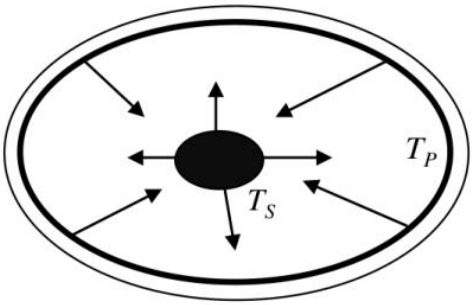


Figure VI. 2. Enclosure in equilibrium with a body.

When studying the interactions between radiation and matter, we always invoke the concept of a black body. Thus, a black body is a surface that absorbs and emits the maximum amount of radiation in all directions.

3. Fundamental Laws of Thermal Radiation

3.1. Definitions

3.1.1. Solid angle

By analogy with the angle formed by two lines in a plane, which we measure in radians by the length of the arc intercepted on the unit circle. We measure a solid angle Ω in steradians by the area of the surface intercepted by a cone of unit radius. A solid angle Ω is therefore measured in steradians by the ratio $\frac{S}{R^2}$ of the surface intercepted on a sphere of radius R to square of this radius. Indeed, the solid angle Ω around a point P located on a plane is

$$\Omega = \frac{S}{R^2} = \frac{4\pi R^2}{R^2} = 4\pi \qquad \text{(VI.9)}$$

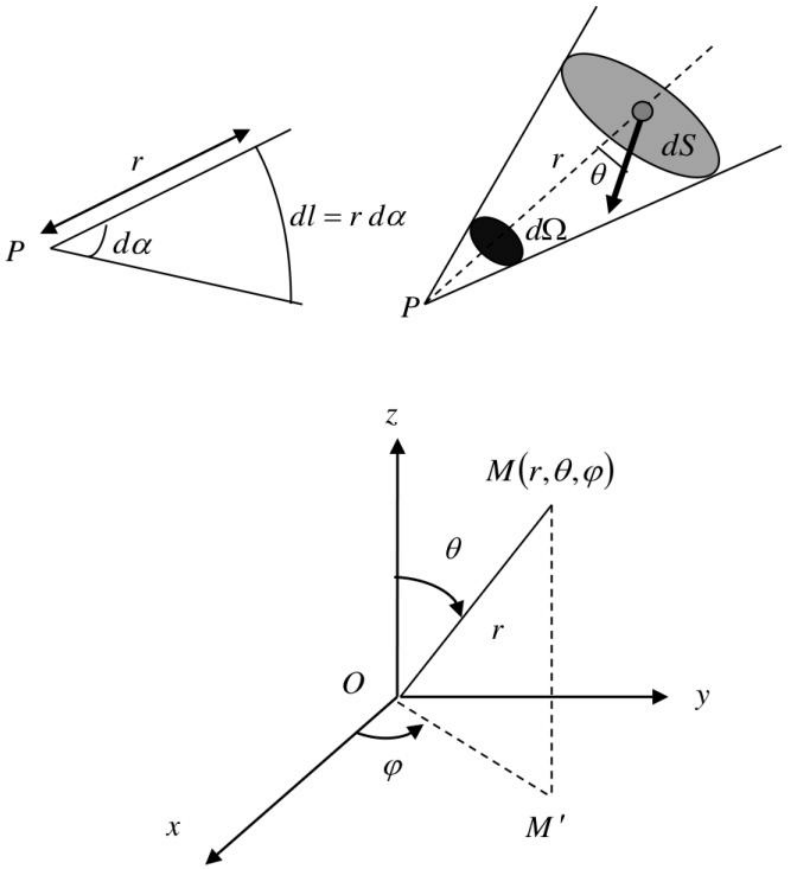


Figure VI. 3. Definitions of the planar angle, the solid angle, and spherical coordinates.

A surface element dS sufficiently small to be considered planar, and any point located at a distance r from a point P, is seen from point P under a solid angle $d\Omega$ such that

$$d\Omega = \frac{dS\cos\alpha}{r^2} \qquad \text{(VI.10)}$$

Here α is the angle between the normal vector to the surface element dS and the direction connecting point P to the center of the surface element dS. Indeed, if we denote by dS_P the projection of the surface dS onto the sphere centered at P, we can write

$$d\Omega = \frac{dS_P}{r^2} = \frac{dS\cos\alpha}{r^2} \qquad \text{(VI.11)}$$

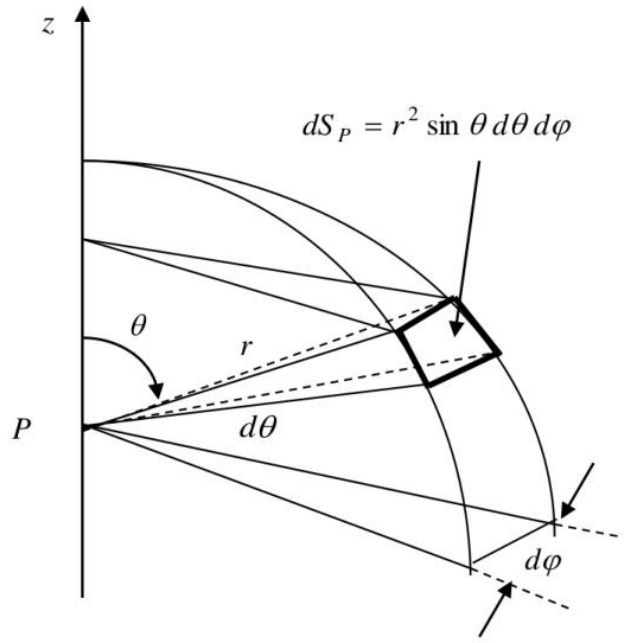


Figure VI.4. Solid angle in spherical coordinates.

If we substitute the expression for the surface element dS_P into the definition of the solid angle $d\Omega$, we obtain

$$d\Omega = \frac{r^2 \sin\theta \, d\theta \, d\varphi}{r^2} = \sin\theta \, d\theta \, d\varphi \qquad \text{(VI.12)}$$

The solid angle under which a hemisphere is viewed is

$$\Omega = \int_0^{\frac{\pi}{2}} \int_0^{2\pi} \sin\theta \, d\theta \, d\varphi = 2\pi \int_0^{\frac{\pi}{2}} \sin\theta \, d\theta = 2\pi \qquad \text{(VI.13)}$$

3.1.2. Relationship between radiative intensity and radiation emission

Consider an emission in a particular direction from an elementary surface dS_0 as shown in the figure below.

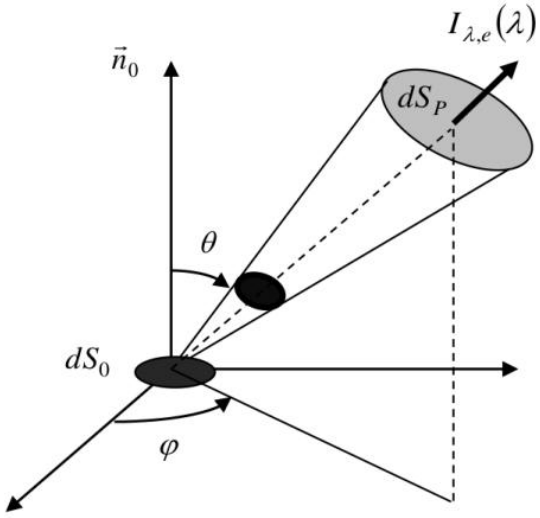


Figure VI. 5. Emission of radiation into the solid angle $d\Omega$

Let us find the rate at which emission from the surface dS_0 passes through the surface dS_P. This quantity can be expressed in terms of the spectral intensity $I_{\lambda,e}$ of the emitted radiation. Formally, we define the spectral intensity $I_{\lambda,e}$ as the

rate at which radiant energy is emitted at wavelength λ in the direction (φ, θ) per unit area of the emitting surface normal to this direction, per unit solid angle around this direction, and per unit wavelength interval $d\lambda$ around the wavelength λ.

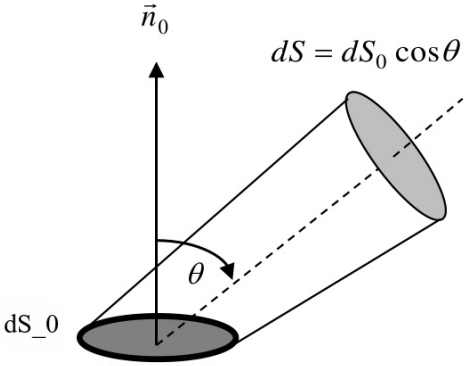


Figure VI. 6. Projection of the surface dS_0 in the direction θ. Mathematically, the intensity $I_{\lambda,\varepsilon}$ is

$$I_{\lambda,e}(\lambda,\theta,\varphi) = \frac{dq}{dS_0 \cos\theta \, d\Omega \, d\lambda} \qquad \text{(VI.14)}$$

where $dq_\lambda = \frac{dq}{d\lambda}$ is the rate at which radiation at wavelength λ leaves the surface dS_0 and passes through the surface dS. Note that the unit of spectral intensity $I_{\lambda,e}$ is W/m^2·sr·μm. Equation VI. 14 can be rewritten in the form

$$dq_\lambda = I_{\lambda,e}(\lambda,\theta,\varphi) dS_0 \cos\theta \, d\Omega \qquad \text{(VI.15)}$$

This relation allows us to calculate the rate at which radiation emitted by a surface propagates through a region of

the space defined by the solid angle $d\Omega$ around the direction (θ, φ). However, to calculate this rate, one must know the spectral intensity $I_{\lambda,e}(\lambda, \theta, \varphi)$ of the emitted radiation. Let us introduce a new quantity dq'_{λ} defined as the spectral flux of the radiation associated with the emitting surface dS_0; indeed, we can write

$$dq'_{\lambda} = \frac{dq_{\lambda}}{dS_0} \qquad \text{(VI.16)}$$

from relation VI. 15, we have

$$dq'_{\lambda} = I_{\lambda,e}(\lambda, \theta, \varphi)\cos\theta\, d\Omega \qquad \text{(VI.17)}$$

by using relation VI. 12, we obtain

$$dq'_{\lambda} = I_{\lambda,e}(\lambda, \theta, \varphi)\cos\theta \sin\theta\, d\theta\, d\varphi \qquad \text{(VI.18)}$$

3.1.3. Issuing Power

The hemispherical emissive power E_{λ} is defined as the rate at which radiation of wavelength λ is emitted in all directions from a surface per unit wavelength interval around λ and per unit surface area. Consequently, the hemispherical emissive power E_{λ} is the spectral heat flux associated with emission into a hypothetical hemisphere surrounding the surface dS_0. This hemispherical emissive power is given by the relation

$$E_{\lambda}(\lambda) = q'_{\lambda}(\lambda) = \int_0^{\frac{\pi}{2}} \int_0^{2\pi} I_{\lambda,e}(\lambda, \theta, \varphi)\cos\theta \sin\theta\, d\theta\, d\varphi \qquad \text{(VI.19)}$$

Let us note that the hemispherical emissive power E_{λ} is associated with the surface dS_0, whereas the intensity $I_{\lambda,e}(\lambda, \theta, \varphi)$ is associated with the projected surface $dS = dS_0 \cos\theta$. The hemispherical emissive power

total E is the rate at which radiation is emitted per unit surface area in all directions and across all possible wavelengths. Therefore, we must have

$$E = \int_0^{\infty} E_\lambda(\lambda) d\lambda \qquad \text{(VI.20)}$$

or else

$$E = \int_0^{\infty} \int_0^{\frac{\pi}{2}} \int_0^{2\pi} I_{\lambda,e}(\lambda,\theta,\varphi) \cos\theta \sin\theta \, d\theta \, d\varphi \, d\lambda \qquad \text{(VI.21)}$$

The term emissive power implies that the emission of radiation is in all directions; in this case, it is possible to omit the word hemispherical. Henceforth, we use simply the terms spectral emissive power and total emissive power. Generally, the directional distribution of radiation emission depends on the nature of the emitting surface, but there exists a special case, which is that of an emitting surface known as diffuse. Thus, for a diffuse emitting surface, the intensity of emitted radiation $I_{\lambda,e}(\lambda,\theta,\varphi)$ does not depend on the direction, i.e., $I_{\lambda,e}(\lambda,\theta,\varphi) = I_{\lambda,e}(\lambda)$. In this case, Equation VI. 21 is written

$$E_\lambda(\lambda) = I_{\lambda,e}(\lambda) \int_0^{\frac{\pi}{2}} \int_0^{2\pi} \cos\theta \sin\theta \, d\theta \, d\varphi = \pi I_{\lambda,e}(\lambda) \qquad \text{(VI.22)}$$

The same holds for the total emissive power; from Equation VI.20, we also obtain

$$E = \pi I_e \qquad \text{(VI.23)}$$

3.1.4. Irradiation

Having considered the radiation emitted by a surface, let us now turn to the radiation incident on an arbitrary surface. This incident radiation may originate from emission and reflection of other surfaces and will have a spectral and directional distribution determined by the spectral intensity $I_{\lambda,i}(\lambda,\theta,\varphi)$. This quantity is defined as the rate at which radiant energy of a given wavelength falls in the direction (θ,φ) per unit of receiving surface area normal to that direction, per unit solid angle $d\Omega$ around this direction, and per unit wavelength interval $d\lambda$ around the wavelength λ.

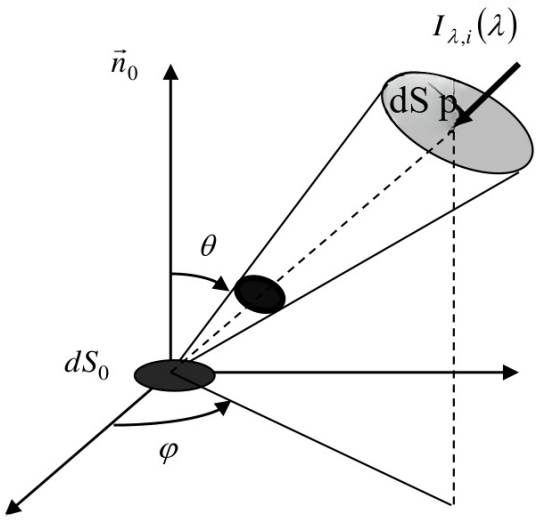


Figure VI. 7. Direction of the incident radiation.

The spectral intensity of the incident radiation $I_{\lambda,i}(\lambda,\theta,\varphi)$ can be related to a new radiative flux called irradiation, which encompasses all incident radiation from all directions. The spectral irradiation $G_\lambda(\lambda,\theta,\varphi)$ defines the rate of radiation with wavelength

of wavelength λ incident on the unit surface area per unit wavelength interval $d\lambda$ around the wavelength λ. Consequently, the irradiance $G_\lambda(\lambda,\theta,\varphi)$ is defined by the relation

$$G_\lambda(\lambda)=\int_0^{\frac{\pi}{2}}\int_0^{2\pi} I_{\lambda,i}(\lambda,\theta,\varphi)\cos\theta\sin\theta\,d\theta\,d\varphi \qquad \text{(VI.24)}$$

If we consider the total irradiation G, which is the rate of incident radiation on a surface, coming from all directions and encompassing all wavelengths, we can then write

$$G=\int_0^{\infty} G_\lambda(\lambda)d\lambda \qquad \text{(VI.25)}$$

Taking into account relation VI. 24, we obtain

$$G=\int_0^{\infty}\int_0^{\frac{\pi}{2}}\int_0^{2\pi} I_{\lambda,e}(\lambda,\theta,\varphi)\cos\theta\sin\theta\,d\theta\,d\varphi\,d\lambda \qquad \text{(VI.26)}$$

If the incident radiation is diffuse, the intensity $I_{\lambda,i}(\lambda,\theta,\varphi)$ will be independent of direction and consequently, we obtain

$$G_\lambda(\lambda)=\pi I_{\lambda,i}(\lambda) \qquad \text{(VI.27)}$$

et

$$G=\pi I_i \qquad \text{(VI.28)}$$

3.1.5. Radiosity

Radiosity encompasses all radiation emitted by a surface. This radiation accounts for the radiation reflected by the

surface in addition to the radiation directly emitted by that same surface.

The spectral radiance $J_\lambda(\lambda,\theta,\varphi)$ represents the rate at which radiant energy of a given wavelength leaves, in the direction (θ,φ), a unit surface per unit wavelength interval $d\lambda$ around the wavelength λ.

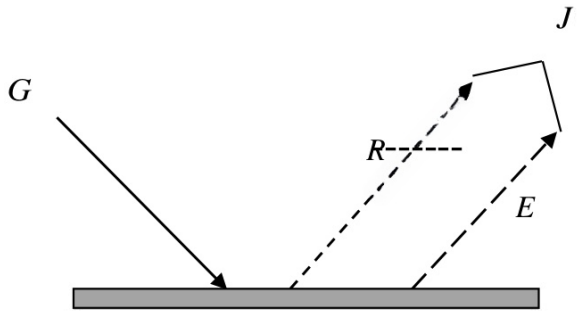


Figure VI. 8. Radiosity of a surface.

If we denote by $I_{\lambda,e+r}(\lambda,\theta,\varphi)$ the spectral intensity of the emitted radiation plus the reflected radiation from the surface, we can then write

$$J_\lambda(\lambda)=\int_0^{\frac{\pi}{2}}\int_0^{2\pi} I_{\lambda,e+r}(\lambda,\theta,\varphi)\cos\theta\sin\theta\,d\theta\,d\varphi \qquad \text{(VI.29)}$$

the total radiosity J is

$$J=\int_0^{\infty}\int_0^{\frac{\pi}{2}}\int_0^{2\pi} I_{\lambda,e+r}(\lambda,\theta,\varphi)\cos\theta\sin\theta\,d\theta\,d\varphi\,d\lambda \qquad \text{(VI.30)}$$

If the surface is a diffuse emitter and a diffuse reflector, we can write that

$$J_\lambda(\lambda) = \pi I_{\lambda,e+r}(\lambda) \qquad \text{(VI.31)}$$

et

$$J = \pi I_{e+r} \qquad \text{(VI.32)}$$

4. Maxwell's Equations and Electromagnetic Waves

4.1. Maxwell's Equations

The Maxwell equations are derived from the following four laws

a) Gauss's law: the electric field flux through a closed surface is equal to the total enclosed electric charge divided by the permittivity of free space.

b) The absence of magnetic monopoles implies that the magnetic flux through any closed surface is zero.

c) Faraday-Henry Law: the electromotive force generated around a closed circuit is equal to the negative time derivative of the magnetic flux through the closed circuit.

d) Ampère-Maxwell Law: the circulation of the magnetic field around a closed circuit is proportional to the sum of all currents passing through the circuit.

Consider two electric charges q_1 and q_2 located in space at points P_1 and P_2. By virtue of Coulomb's law, the force F_{12} acting on the electric charge q_2 is

$$\vec{F}_{12} = \frac{q_1 q_2}{4\pi\varepsilon_0} \frac{\vec{r}_2 - \vec{r}_1}{\left|\vec{r}_2 - \vec{r}_1\right|^3} \qquad \text{(VI.33)}$$

where $\vec{r}_1$ and $\vec{r}_2$ are the position vectors of points P_1 and P_2 with respect to a Cartesian coordinate system in space, and ε_0 is the permittivity of free space.

If we consider N electric charges $q_1, \ldots, q_N$ located in space at points $P_1, \ldots P_N$ with position vectors $\vec{r}_1, \ldots \vec{r}_N$, the force $\vec{F}$ acting on a test charge q with position vector $\vec{r}$ is

$$\vec{F} = q\sum_{i=1}^{i=N} \frac{q_i}{4\pi\varepsilon_0} \frac{\vec{r} - \vec{r}_i}{\left|\vec{r} - \vec{r}_i\right|^3} \qquad \text{(VI.34)}$$

Let us introduce a vector field $\vec{E}(\vec{r})$ called the electric field, such that the force acting on the test electric charge q is given by

$$\vec{F} = q\vec{E}(\vec{r}) \qquad \text{(VI.35)}$$

In this case, the electric field $\vec{E}(\vec{r})$ is written

$$\vec{E}(\vec{r}) = \sum_{i=1}^{i=N} \frac{q_i}{4\pi\varepsilon_0} \frac{\vec{r} - \vec{r}_i}{\left|\vec{r} - \vec{r}_i\right|^3} \qquad \text{(VI.36)}$$

For a singular electric charge, the electric field is

$$\vec{E}(\vec{r}) = \frac{q}{4\pi\varepsilon_0} \frac{\vec{r}}{\left|\vec{r}\right|^3} \qquad \text{(VI.37)}$$

Now suppose that instead of discrete electric charges, we have a continuous charge distribution represented by the volume charge density $\rho(\vec{r})$. The electric charge at a point P with position vector $\vec{r}$ is $\rho(\vec{r})dV$, where dV is the volume element around point P. The electric field created by this charge distribution is given by

$$\vec{E}(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\int_v \rho(\vec{r}')\frac{\vec{r}-\vec{r}'}{\left|\vec{r}-\vec{r}'\right|^3}dV \qquad \text{(VI.38)}$$

Consider an electric charge q placed at the origin. The electric field generated by this charge is radial and possesses spherical symmetry about the origin. If we take a sphere of radius r centered on the electric charge, the flux of the electric field $\vec{E}(\vec{r})$ through the surface of the sphere is

$$\int_S \vec{E}(\vec{r}) \bullet d\vec{S} = \int_S E_r dS = E_r 4\pi r^2 = \frac{q}{4\pi\varepsilon_0 r^2} 4\pi r^2 = \frac{q}{\varepsilon_0} \text{(VI.39)}$$

From Ostrogradsky's theorem, we have

$$\int_S \vec{E}(\vec{r}) \bullet d\vec{S} = \int_V \vec{\nabla} \bullet \vec{E}(\vec{r}) dV \qquad \text{(VI.40)}$$

hence

$$\int_V \vec{\nabla} \bullet \vec{E}(\vec{r}) dV = \frac{q}{\varepsilon_0} \qquad \text{(VI.41)}$$

where $\vec{\nabla}$ is the nabla operator. If, instead of having an electric charge q, we have a volume charge density $\rho(\vec{r})$, formula VI. 41 becomes

$$\int_V \vec{\nabla} \bullet \vec{E}(\vec{r}) dV = \frac{1}{\varepsilon_0}\int_V \rho(\vec{r}) dV \qquad \text{(VI.42)}$$

let

$$\vec{\nabla} \bullet \vec{E}(\vec{r},t) = \frac{\rho(\vec{r},t)}{\varepsilon_0} \qquad \text{(VI.43)}$$

The magnetic field lines $\mathbf{B}(\vec{r},t)$ are always closed loops due to the absence of magnetic monopoles. Consequently, the magnetic flux through any

the surface traversed by the magnetic field lines is zero, hence

$$\int_S \vec{B}(\vec{r},t)\bullet d\vec{S} = -\int_S \vec{B}(\vec{r},t)\bullet \vec{n}_1 dS + \int_S \vec{B}(\vec{r},t)\bullet \vec{n}_1 dS = 0 \quad \text{(VI.44)}$$

Using Ostrogradsky's theorem, we have

$$\int_S \vec{B}(\vec{r},t)\bullet d\vec{S} = \int_V \vec{\nabla}\bullet \vec{B}(\vec{r},t)dV \quad \text{(VI.45)}$$

wherefrom

$$\vec{\nabla}\bullet \vec{B}(\vec{r},t) = 0 \quad \text{(VI.46)}$$

According to the Faraday-Henry law, the electromotive force $V(t)$ is

$$V(t) = -\frac{d}{dt}\int_S \vec{B}(\vec{r},t)\bullet d\vec{S} \quad \text{(VI.47)}$$

However, we know that the electromotive force generated around a closed circuit is the circulation of the electric field around this circuit.

$$V(t) = \int_C \vec{E}(\vec{r},t)\bullet d\vec{l} \quad \text{(VI.48)}$$

By eliminating the electromotive force between relations VI. 47 and VI. 48, we obtain

$$\int_C \vec{E}(\vec{r},t)\bullet d\vec{l} = -\frac{d}{dt}\int_S \vec{B}(\vec{r},t)\bullet d\vec{S} \quad \text{(VI.49)}$$

If we use Stokes' theorem

$$\int_C \vec{E}(\vec{r},t)\bullet d\vec{l} = \int_S \vec{\nabla}\times \vec{E}(\vec{r},t)\bullet d\vec{S} \quad \text{(VI.50)}$$

Equation VI. 49 is written as

$$\int_S \vec{\nabla} \times \vec{E}(\vec{r},t) \bullet d\vec{S} = -\frac{d}{dt}\int_S \vec{B}(\vec{r},t) \bullet d\vec{S} \qquad \text{(VI.51)}$$

from which

$$\vec{\nabla} \times \vec{E}(\vec{r},t) = -\frac{\partial \vec{B}(\vec{r},t)}{\partial t} \qquad \text{(VI.52)}$$

According to the Ampère-Maxwell law, the circulation of the magnetic field is

$$\int_C \vec{B}(\vec{r},t) \bullet d\vec{l} = \mu_0 I(t) \qquad \text{(VI.53)}$$

where μ_0 is the permeability of free space and $I(t)$ is the sum of all currents flowing through the circuit. The electric current I can be written in the form

$$I(t) = \int_S \vec{j} \bullet d\vec{S} + \varepsilon_0 \int_S \frac{\partial \vec{E}(\vec{r},t)}{\partial t} \bullet d\vec{S} \qquad \text{(VI.54)}$$

By combining these two equations, we obtain

$$\int_C \vec{B}(\vec{r},t) \bullet d\vec{l} = \mu_0 \int_S \vec{j} \bullet d\vec{S} + \varepsilon_0 \mu_0 \int_S \frac{\partial \vec{E}(\vec{r},t)}{\partial t} \bullet d\vec{S} \qquad \text{(VI.55)}$$

with Stokes' theorem, this relation is written

$$\vec{\nabla} \times \vec{B}(\vec{r},t) = \mu_0 \vec{j} + \varepsilon_0 \mu_0 \frac{\partial \vec{E}(\vec{r},t)}{\partial t} \qquad \text{(VI.56)}$$

Now, let us summarize Maxwell's equations

$$\vec{\nabla} \bullet \vec{E}(\vec{r},t) = \frac{\rho(\vec{r},t)}{\varepsilon_0} \qquad \text{(VI.57)}$$

$$\vec{\nabla} \bullet \vec{B}(\vec{r},t) = 0 \qquad \text{(VI.58)}$$

$$\vec{\nabla} \times \vec{E}(\vec{r},t) = -\frac{\partial \vec{B}(\vec{r},t)}{\partial t} \qquad \text{(VI.59)}$$

$$\vec{\nabla} \times \vec{B}(\vec{r},t) = \mu_0 \vec{j} + \varepsilon_0 \mu_0 \frac{\partial \vec{E}(\vec{r},t)}{\partial t} \qquad \text{(VI.60)}$$

If we consider the regions where $\rho(\vec{r},t) = 0$ and $\vec{j} = 0$, Maxwell's equations become

$$\vec{\nabla} \bullet \vec{E}(\vec{r},t) = 0 \qquad \text{(VI.61)}$$

$$\vec{\nabla} \bullet \vec{B}(\vec{r},t) = 0 \qquad \text{(VI.62)}$$

$$\vec{\nabla} \times \vec{E}(\vec{r},t) = -\frac{\partial \vec{B}(\vec{r},t)}{\partial t} \qquad \text{(VI.63)}$$

$$\vec{\nabla} \times \vec{B}(\vec{r},t) = \varepsilon_0 \mu_0 \frac{\partial \vec{E}(\vec{r},t)}{\partial t} \qquad \text{(VI.64)}$$

If we take the vector product of the nabla operator ∇ with Equation VI.63, we obtain

$$\vec{\nabla} \times \left(\vec{\nabla} \times \vec{E}(\vec{r},t)\right) = -\frac{\partial\left(\vec{\nabla} \times \vec{B}(\vec{r},t)\right)}{\partial t} \qquad \text{(VI.65)}$$

From the vector identity

$$\vec{\nabla} \times \left(\vec{\nabla} \times \vec{E}(\vec{r},t)\right) = \vec{\nabla}\left(\vec{\nabla} \bullet \vec{E}(\vec{r},t)\right) - \Delta\vec{E}(\vec{r},t) \qquad \text{(VI.66)}$$

Equation VI. 65 is written as

$$\vec{\nabla}\left(\vec{\nabla} \bullet \vec{E}(\vec{r},t)\right) - \Delta\vec{E}(\vec{r},t) = -\frac{\partial\left(\vec{\nabla} \times \vec{B}(\vec{r},t)\right)}{\partial t} \qquad \text{(VI.67)}$$

but since $\nabla \cdot \vec{E}(\vec{r},t) = 0$, we obtain

$$\Delta\vec{E}(\vec{r},t) = \frac{\partial\left(\vec{\nabla} \times \vec{B}(\vec{r},t)\right)}{\partial t} \qquad \text{(VI.68)}$$

and by applying relation VI. 64, it follows

$$\Delta\vec{E}(\vec{r},t)=\varepsilon_0\mu_0\frac{\partial^2\vec{E}(\vec{r},t)}{\partial t^2} \qquad \text{(VI.69)}$$

Using the same procedure, we obtain a similar equation for the magnetic field

$$\Delta\vec{B}(\vec{r},t)=\varepsilon_0\mu_0\frac{\partial^2\vec{B}(\vec{r},t)}{\partial t^2} \qquad \text{(VI.70)}$$

If we write equation VI. 69 in the form

$$\Delta\vec{E}(\vec{r},t)=\frac{1}{\frac{1}{\varepsilon_0\mu_0}}\frac{\partial^2\vec{E}(\vec{r},t)}{\partial t^2} \qquad \text{(VI.71)}$$

Equation having the form of a wave equation

$$\Delta f(\vec{r},t)=\frac{1}{C^2}\frac{\partial^2 f(\vec{r},t)}{\partial t^2} \qquad \text{(VI.72)}$$

differential equation describing the propagation of the quantity $f(\vec{r},t)$ as a wave with speed C. Thus, the electric and magnetic fields obeying equations VI. 69 and VI. 70 propagate as waves with the speed

$$c_0=\sqrt{\frac{1}{\varepsilon_0\mu_0}} \qquad \text{(VI.73)}$$

If we take the numerical values of $\varepsilon_0=8.8542\times10^{-12}\,C^2N^{-1}m^{-2}$ and $\mu_0=4\pi\times10^{-7}\,NA^{-2}$, we obtain for the speed c_0 the value

$$c_0=\sqrt{\frac{1}{\varepsilon_0\mu_0}}=2{,}998.10^8\,ms^{-1} \qquad \text{(VI.74)}$$

which is nothing other than the speed of light in a vacuum. This analogy led Maxwell to suppose that light is the propagation of two waves formed, one by an electric field and the other by a magnetic field; this is what we call an electromagnetic wave.

$$\Delta\vec{E}(\vec{r},t)=\frac{1}{c_0^2}\frac{\partial^2\vec{E}(\vec{r},t)}{\partial t^2} \qquad \text{(VI.75)}$$

$$\Delta\vec{B}(\vec{r},t)=\frac{1}{c_0^2}\frac{\partial^2\vec{B}(\vec{r},t)}{\partial t^2} \qquad \text{(VI.76)}$$

The so-called monochromatic plane electromagnetic waves are described by the following expressions

$$\vec{E}(\vec{r},t)=\vec{M}e^{i\left(\vec{k}\cdot\vec{r}-\omega t\right)} \qquad \text{(VI.77)}$$

$$\vec{B}(\vec{r},t)=\vec{N}e^{i\left(\vec{k}\cdot\vec{r}-\omega t\right)} \qquad \text{(VI.78)}$$

where $\omega=2\pi\nu$ and $|\vec{k}|=\frac{\omega}{c}=\frac{2\pi}{\lambda}$ are respectively the frequency

angular and the modulus of the wave vector $\vec{k}$. Let us write these equations in the form

$$\vec{E}(\vec{r},t)=\vec{M}e^{i\vec{k}\cdot\vec{r}}e^{-i\omega t} \qquad \text{(VI.79)}$$

$$\vec{B}(\vec{r},t)=\vec{N}e^{i\vec{k}\cdot\vec{r}}e^{-i\omega t} \qquad \text{(VI.80)}$$

Let us assume that $\vec{E}_0(\vec{r})=\vec{M}e^{i\vec{k}\cdot\vec{r}}$ and $\vec{B}_0(\vec{r})=\vec{N}e^{i\vec{k}\cdot\vec{r}}$. We can then describe a monochromatic plane electromagnetic wave via the relations

$$\vec{E}(\vec{r},t)=\vec{E}_0(\vec{r})e^{-i\omega t} \qquad \text{(VI.81)}$$

$$\vec{B}(\vec{r},t)=\vec{B}_0(\vec{r})e^{-i\omega t} \qquad \text{(VI.82)}$$

Substituting these expressions into Equations VI.69 and VI.70, we obtain

$$\Delta\left(\vec{E}_0(\vec{r})e^{-i\omega t}\right)=\frac{1}{c_0^2}\frac{\partial^2\left(\vec{E}_0(\vec{r})e^{-i\omega t}\right)}{\partial t^2} \qquad \text{(VI.83)}$$

$$\Delta\left(\vec{B}_0(\vec{r})e^{-i\omega t}\right)=\frac{1}{c_0^2}\frac{\partial^2\left(\vec{B}_0(\vec{r})e^{-i\omega t}\right)}{\partial t^2} \qquad \text{(VI.84)}$$

soient

$$\Delta\vec{E}_0(\vec{r})e^{-i\omega t}=-\frac{\omega^2}{c_0^2}\vec{E}_0(\vec{r})e^{-i\omega t} \qquad \text{(VI.85)}$$

$$\Delta\vec{B}_0(\vec{r})e^{-i\omega t}=-\frac{\omega^2}{c_0^2}\vec{B}_0(\vec{r})e^{-i\omega t} \qquad \text{(VI.86)}$$

and by simplifying with $e^{-\omega t}$, we arrive at the equations

$$\Delta\vec{E}_0(\vec{r})+\frac{\omega^2}{c_0^2}\vec{E}_0(\vec{r})=0 \qquad \text{(VI.87)}$$

$$\Delta\vec{B}_0(\vec{r})+\frac{\omega^2}{c_0^2}\vec{B}_0(\vec{r})=0 \qquad \text{(VI.88)}$$

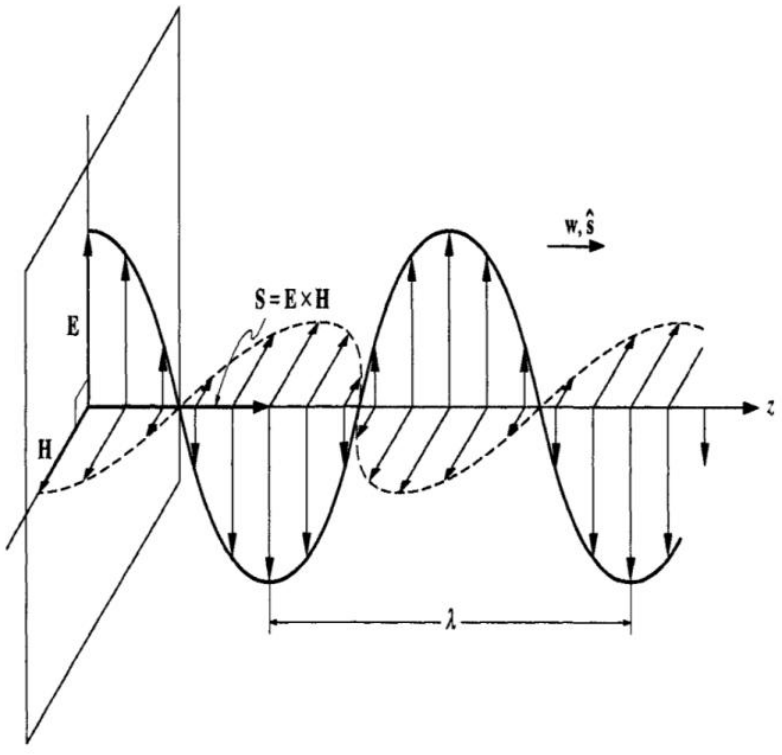


Figure VI.9. Plane electromagnetic wave.

Let us take the equation $\vec{E}(\vec{r},t)=\vec{M}e^{i(\vec{k}\cdot\vec{r}-\omega t)}$ and, by calculating $\vec{\nabla}\bullet\vec{E}(\vec{r},t)$, we obtain

$$\vec{\nabla}\bullet\left(\vec{M}e^{i\left(\vec{k}\cdot\vec{r}-\omega t\right)}\right)=i\vec{k}\bullet\vec{E}(\vec{r},t) \qquad \text{(VI.89)}$$

also for $\nabla\cdot\vec{B}(\vec{r},t)$

$$\vec{\nabla}\bullet\left(\vec{N}e^{i\left(\vec{k}\cdot\vec{r}-\omega t\right)}\right)=i\vec{k}\bullet\vec{B}(\vec{r},t) \qquad \text{(VI.90)}$$

From the first two Maxwell equations, $\nabla\cdot\mathbf{E}(\mathbf{r},t)=0$ and $\nabla\cdot\mathbf{B}(\mathbf{r},t)=0$, we deduce that

$$\vec{k}\bullet\vec{E}(\vec{r},t)=0 \qquad \text{(VI.91)}$$

$$\vec{k}\bullet\vec{B}(\vec{r},t)=0 \qquad \text{(VI.92)}$$

These two relations show that the wave vector $\vec{k}$ is perpendicular to the electric field vector $\vec{E}(\vec{r},t)$ and to the magnetic field vector $\vec{B}(\vec{r},t)$, and consequently, the electric field $\vec{E}(\vec{r},t)$ and magnetic field $\vec{B}(\vec{r},t)$ are also perpendicular to each other.

4.2. Stationary Electromagnetic Waves in a Cavity

Consider a metallic cavity with sides L_1, L_2 and L_3 at temperature T. Each wall emits electromagnetic radiation (thermal radiation) which is reflected off the other walls and forms a set of standing electromagnetic waves. The electric fields of the standing electromagnetic waves in this cavity in the directions Ox, Oy and Oz are

$$E_x(x,y,z,t)=E_{0x}\cos k_x x\sin k_y y\sin k_z z\sin 2\pi\nu t \qquad \text{(VI.93)}$$

E_y(x, y, z, t) = E_{0y} $\sin(k_x x)\cos(k_y y)\sin(k_z z)\sin(2\pi\nu t)$ (VI.94)

$$E_z(x, y, z, t) = E_{0z} \sin k_x x \sin k_y y \cos k_z z \sin 2\pi\nu t \quad \text{(VI.95)}$$

where E_{0x}, E_{0y} and E_{0z} are the amplitudes of the electric field in the directions Ox, Oy and Oz, and k_x, k_y and k_z are the projections of the wave vector $\vec{k}$.

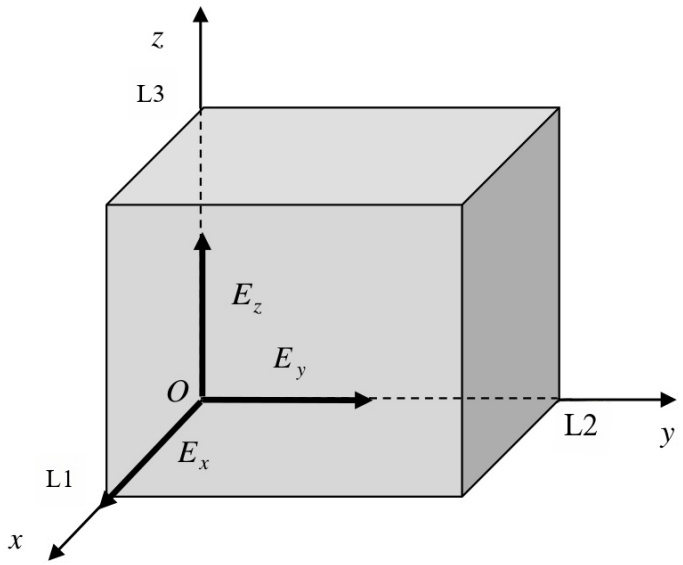


Figure VI. 10. Cavity containing electromagnetic waves.

If we consider the wave along the Ox axis, for example, we note that the wave has a sinusoidal amplitude $E_{0x}\sin(k_x x)$ which oscillates in time like a harmonic oscillator with a frequency ν. On the walls of the cavity, the boundary conditions are such that the tangential components of the field vanish at the walls.

For the walls perpendicular to the Ox axis, the tangential components of the electric field are $E_y(x,y,z,t)$ and $E_z(x,y,z,t)$. Indeed, we can write

$$E_y(0,y,z,t) = E_{0y} \sin k_x 0 \cos k_y y \sin k_z z \sin 2\pi\nu t = 0 \quad \text{(VI.96)}$$

$$E_y(L_1,y,z,t) = E_{0y} \sin k_x L_1 \cos k_y y \sin k_z z \sin 2\pi\nu t = 0 \quad \text{(VI.97)}$$

$$E_z(0,y,z,t) = E_{0z} \sin k_x 0 \sin k_y y \cos k_z z \sin 2\pi\nu t = 0 \quad \text{(VI.98)}$$

$$E_z(L_1,y,z,t) = E_{0z} \sin k_x L_1 \sin k_y y \cos k_z z \sin 2\pi\nu t = 0 \quad \text{(VI.99)}$$

We note that for $x=0$, the fields $E_y(x,y,z,t)$ and $E_z(x,y,z,t)$ vanish; this is the first node. A second node also exists for $x=L_1$ if the following condition is satisfied

$$k_x L_1 = n_x \pi \quad \text{(VI.100)}$$

We can write the same conditions for the two faces perpendicular to the Oy axis, namely

$$E_x(x,0,z,t) = E_{0x} \cos k_x x \sin k_y 0 \sin k_z z \sin 2\pi\nu t = 0 \quad \text{(VI.101)}$$

$$E_x(x,L_2,z,t) = E_{0x} \cos k_x x \sin k_y L_2 \sin k_z z \sin 2\pi\nu t = 0 \quad \text{(VI.102)}$$

$$E_z(x,0,z,t) = E_{0z} \sin k_x x \sin k_y 0 \cos k_z z \sin 2\pi\nu t = 0 \quad \text{(VI.103)}$$

$$E_z(x,L_2,z,t) = E_{0z} \sin k_x x \sin k_y L_2 \cos k_z z \sin 2\pi\nu t = 0 \quad \text{(VI.104)}$$

We deduce the second node from the condition

$$k_y L_2 = n_y \pi \quad \text{(VI.105)}$$

For the faces perpendicular to the axis Oz, we write

$$E_x(x,y,0,t) = E_{0x} \cos k_x x \sin k_y y \sin k_z 0 \sin 2\pi\nu t = 0 \quad \text{(VI.106)}$$

$$E_x(x,y,L_3,t) = E_{0x} \cos k_x x \sin k_y y \sin k_z L_3 \sin 2\pi\nu t = 0 \quad \text{(VI.107)}$$

$$E_y(x, y, 0, t) = E_{0y} \sin k_x x \cos k_y y \sin k_z 0 \sin 2\pi\nu t = 0 \quad \text{(VI.108)}$$

$$E_y(x, y, L_3, t) = E_{0y} \sin k_x x \cos k_y y \sin k_z L_3 \sin 2\pi\nu t = 0 \quad \text{(VI.109)}$$

We deduce the second node from the condition

$$k_z L_3 = n_z \pi \quad \text{(VI.110)}$$

In summary, we have obtained three conditions for obtaining standing electromagnetic waves in a cavity; these conditions are

$$k_x = \frac{n_x \pi}{L_1}, \; k_y = \frac{n_y \pi}{L_2}, \; k_z = \frac{n_z \pi}{L_3} \quad \text{(VI.111)}$$

where n_x, n_y, and n_z are positive integers ranging from zero to infinity. If we consider the component $E_x(x, y, z, t)$ of the electric field, it must necessarily satisfy the equation

$$\frac{\partial^2 E_x(x, y, z, t)}{\partial x^2} + \frac{\partial^2 E_x(x, y, z, t)}{\partial y^2} + \frac{\partial^2 E_x(x, y, z, t)}{\partial z^2} = \frac{1}{c_0^2} \frac{\partial^2 E_x(x, y, z, t)}{\partial t^2} \quad \text{(VI.112)}$$

by substituting equation VI. 93, we obtain

$$k_x^2 + k_y^2 + k_z^2 = \frac{\omega^2}{c_0^2} \quad \text{(VI.113)}$$

From relations VI. 111, we arrive at

$$\left(\frac{n_x \pi}{L_1}\right)^2 + \left(\frac{n_y \pi}{L_2}\right)^2 + \left(\frac{n_z \pi}{L_3}\right)^2 = \frac{\omega^2}{c_0^2} \quad \text{(VI.114)}$$

Let the cavity be cubic with side length L, and replacing the angular frequency ω by the frequency ν, Equation VI. 114 becomes

$$n_x^2 + n_x^2 + n_x^2 = \frac{4L^2\nu^2}{c_0^2} \qquad \text{(VI.115)}$$

Since the numbers n_x, n_y, and n_z take values ranging from zero to infinity, they define an infinity of standing waves within the cavity. Let us note that if we consider a coordinate system defined by the numbers n_x, n_y, and n_z, Equation VI. 115 is the equation of a sphere with radius $\frac{2L\nu}{c_0}$. We can consider that the variations in the numbers n_x, n_y, and n_z are continuous, and in this case, the number of oscillation modes N_ν will be defined by the relation

$$N_\nu = \frac{1}{8}\frac{4\pi}{3}\left(\frac{2L\nu}{c_0}\right)^3 \qquad \text{(VI.116)}$$

The number of oscillation modes n_ν per unit volume and per frequency interval is

$$n_\nu = \frac{1}{V}\frac{dN_\nu}{d\nu} \qquad \text{(VI.117)}$$

If we use the relation $N_\nu = \frac{4\pi L^3\nu^3}{3c_0^3}$, we obtain

$$n_\nu = \frac{1}{L^3}\frac{d\left(\frac{4\pi L^3\nu^3}{3c_0^3}\right)}{d\nu} = \frac{4\pi\nu^2}{c_0^3} \qquad \text{(VI.118)}$$

The electromagnetic energy density u_ν contained in the cavity volume is

$$u_\nu = 2n_\nu \overline{E} \qquad \text{(VI.119)}$$

where $\overline{E}$ is the average energy of each oscillator contained in the cavity, the factor 2 arises from the polarization of the electric field. Substituting the relation into Equation VI.118, we then obtain

$$u_\nu = \frac{8\pi\nu^2}{c_0^3}\overline{E} \qquad \text{(VI.120)}$$

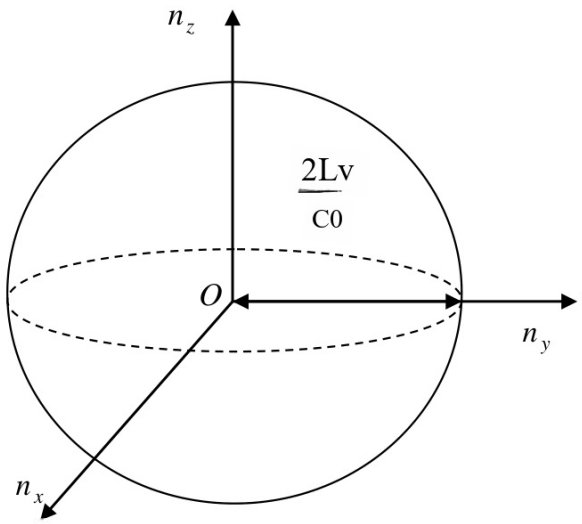


Figure VI. 11. Coordinate system n_x, n_y and n_z.

5. Blackbody radiation, Planck's law

5.1. Concept of Black Body

A black body has the following characteristics:

a) It absorbs all incident radiation regardless of wavelength and direction of propagation.

b) For a given temperature and wavelength, no body can emit radiant energy greater than that emitted by a black body.

c) Although the radiation emitted by a black body depends on temperature and wavelength, it is independent of direction. Thus, the black body is a diffuse emitter.

As a perfect emitter and absorber, the black body serves as a standard reference for comparing the radiative properties of surfaces under study.

Although it is common to admit that certain surfaces approach a body, no surface possesses its specific properties. The most admissible approach to a black body is a cavity whose inner surface is maintained at a uniform temperature. If radiation enters the cavity through a small opening, it will undergo a multitude of reflections on the inner surface before exiting through the same opening; in this case, the radiation is almost totally absorbed, and we realize a black body. From a thermodynamic point of view, it is possible to admit that the radiation leaving the cavity will depend only on the temperature of the inner wall and corresponds to the radiation of a black body.

Since the emission of radiation from a black body is diffuse, the spectral intensity $I_{\lambda,b}$ emitted is certainly independent of direction. The radiation accumulated in the cavity results from the emissions and reflections of the inner wall of the cavity; it must be of the same nature as the radiation exiting through the opening and, consequently, the radiation within the cavity is also a black body radiation. Thus, for any portion of the inner wall of the cavity, we always have $G_\lambda(\lambda, T) = E_{\lambda,b}(\lambda, T)$.

5.2. Planck's Law

We have obtained the energy density contained within the volume of a cavity containing electromagnetic radiation; this energy density is given by the formula

$$u_\nu = \frac{8\pi\nu^2}{c_0^3}\overline{E} \qquad \text{(VI.121)}$$

From statistical thermodynamics, we know that the probability of finding a system N_i in an energy state E_i is given by the [expression] that we call the Boltzmann distribution

$$P = Ae^{-\frac{E_i}{kT}} \qquad \text{(VI.122)}$$

where k is the Boltzmann constant and E_i is the absolute temperature of the system. Consequently, the average energy $\overline{E}$ of such a system is

$$\overline{E_i} = \frac{\int_0^\infty E_i e^{-\frac{E_i}{kT}} dE_i}{\int_0^\infty e^{-\frac{E_i}{kT}} dE_i} \qquad \text{(VI.123)}$$

Planck's hypothesis is that the energy exchanged between the oscillators on the wall of the cavity of a black body and the standing electromagnetic waves found therein occurs in discrete packets of energy called quanta, given by the formula

$$E_n = nh\nu \qquad \text{(VI.124)}$$

where n is an integer.

Let us now calculate the average energy $\overline{E}$ of the oscillators located on the cavity wall that constitutes the black body. This average energy $\overline{E}$ is given by the formula in which we have replaced the integral by a summation, since the energies E_n are exchanged in discrete packets $E_n = nh\nu$

$$\overline{E} = \frac{\sum_{n=0}^{n=\infty} nh\nu\, e^{-\frac{nh\nu}{kT}}}{\sum_{n=0}^{n=\infty} e^{-\frac{nh\nu}{kT}}} \qquad \text{(VI.125)}$$

If we let $x = \frac{h\nu}{kT}$, the previous formula can then be written in the form

$$\overline{E} = kT \frac{\sum_{n=0}^{n=\infty} nx e^{-nx}}{\sum_{n=0}^{n=\infty} e^{-nx}} = kT \frac{N(x)}{D(x)} \qquad \text{(VI.126)}$$

where the functions $N(x)$ and $D(x)$ are defined by the following expressions

$$N(x) = \sum_{n=0}^{n=\infty} nx e^{-nx} \qquad \text{(VI.127)}$$

$$D(x) = \sum_{n=0}^{n=\infty} e^{-nx} \qquad \text{(VI.128)}$$

If we explicitly define the function $D(x)$

$$D(x) = 1 + e^{-x} + e^{-2x} + e^{-3x} + \cdots e^{-nx} \qquad \text{(VI.129)}$$

we note that it represents a geometric sequence with ratio e^{-x} ; consequently, we can write the function $D(x)$ in the form

$$D(x) = \frac{1}{1 - e^{-x}} \qquad \text{(VI.130)}$$

Explicitly, the function $N(x)$ is written as

$$N(x) = xe^{-x} + 2xe^{-2x} + 3xe^{-3x} + \cdots + nxe^{-nx} \quad \text{(VI.131)}$$

or even

$$N(x) = x\left(e^{-x} + 2e^{-2x} + 3e^{-3x} + \cdots + ne^{-nx}\right) \quad \text{(VI.132)}$$

this way, the function $N(x)$ can also be rewritten as

$$N(x) = -x\frac{d}{dx}\left(1 + e^{-x} + e^{-2x} + e^{-3x} + \cdots + e^{-nx}\right) = -x\frac{d}{dx}\left(\frac{1}{1-e^{-x}}\right) \quad \text{(VI.133)}$$

let

$$N(x) = \frac{xe^{-x}}{\left(1-e^{-x}\right)^2} \quad \text{(VI.134)}$$

By substituting the expressions for the functions $N(x)$ and $D(x)$ into Equation VI. 126, we obtain for the average energy the relation

$$\overline{E} = kT\frac{xe^{-x}\left(1-e^{-x}\right)}{\left(1-e^{-x}\right)^2} = kT\frac{h\nu}{kT}\frac{e^{-x}}{\left(1-e^{-x}\right)} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \quad \text{(VI.135)}$$

Consequently, the energy density u_ν contained within the volume of a cavity containing electromagnetic radiation is

$$u_\nu = \frac{8\pi h}{c_0^3}\frac{\nu^3}{e^{\frac{h\nu}{kT}} - 1} \quad \text{(VI.136)}$$

Let us now find the relationship between the energy density u_ν and the spectral emissive power E_ν.

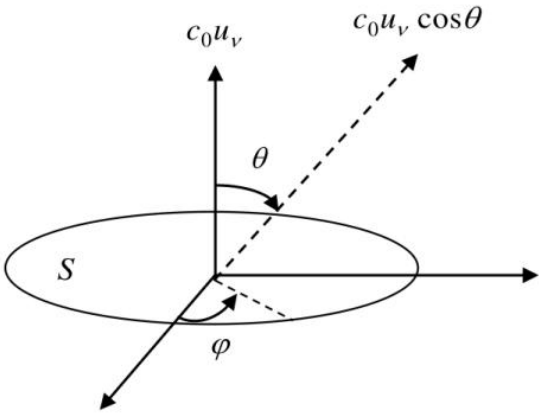


Figure VI. 12. Radiated power in the direction θ.

If we denote dP as the power radiated by the surface element dS, the energy $dPdt$ radiated during the time interval dt is equal to the electromagnetic energy contained within the volume dSc_0dt; we then obtain

$$\frac{dP}{dS} = \frac{1}{2} u_\nu c_0 \cos\theta \qquad \text{(VI.137)}$$

The radiated power per unit area is distributed over all possible directions, proportionally to the solid angle $d\Omega$, which allows one to write

$$E_{\nu,b} = \frac{\int_\Omega \frac{dP}{dS} d\Omega}{\int_\Omega d\Omega} \qquad \text{(VI.138)}$$

and substituting the expressions for the solid angle $d\Omega = \sin\theta\, d\theta\, d\varphi$ and the power radiated per unit surface $\frac{dP}{dS} = \frac{1}{2} u_\nu c_0 \cos\theta$, this relation becomes

$$E_{\nu,b} = \frac{1}{2} u_\nu c_0 \frac{\int_0^{\frac{\pi}{2}} \int_0^{2\pi} \cos\theta \sin\theta \, d\theta \, d\varphi}{\int_0^{\frac{\pi}{2}} \int_0^{2\pi} \sin\theta \, d\theta \, d\varphi} \qquad \text{(VI .139)}$$

by calculating the integrals, we arrive at the relation

$$E_{\nu,b} = \frac{c_0}{4} u_\nu \qquad \text{(VI .140)}$$

If we substitute the energy density u_ν with its expression, the spectral emissive power of the black body becomes

$$E_{\nu,b} = \frac{2\pi h}{c_0^2} \frac{\nu^3}{e^{\frac{h\nu}{kT}} - 1} \qquad \text{(VI.141)}$$

Generally, we use the wavelength λ instead of the frequency ν; for this, we write the expression of the spectral emissive power as a function of the wavelength λ, using the relation

$$E_{\lambda,b} = -E_{\nu,b} \frac{d\nu}{d\lambda} \qquad \text{(VI.142)}$$

from which

$$E_{\lambda,b} = -\frac{2\pi h}{c_0^2} \frac{\nu^3}{e^{\frac{h\nu}{kT}} - 1} \frac{d\nu}{d\lambda} \qquad \text{(VI.143)}$$

from the relation $\nu = \frac{c_0}{\lambda}$, we have

$$\frac{d\nu}{d\lambda} = -\frac{c_0}{\lambda^2} \qquad \text{(VI.144)}$$

Now, by substituting $\frac{d\nu}{d\lambda} = -\frac{c_0}{\lambda^2}$ and $\nu = \frac{c_0}{\lambda}$ into equation VI. 141, we obtain

$$E_{\lambda,b} = \frac{2\pi h}{c_0^2} \frac{\left(\frac{c_0}{\lambda}\right)^3}{e^{\frac{hc_0}{\lambda kT}} - 1} \frac{c_0}{\lambda^2} \qquad \text{(VI.145)}$$

let

$$E_{\lambda,b}(\lambda,T) = \frac{2\pi h c_0^2}{\lambda^5 \left(e^{\frac{hc_0}{\lambda kT}} - 1 \right)} \qquad \text{(VI.146)}$$

The spectral intensity $I_{\lambda,b}(\lambda, T)$ for a black body is consequently equal to

$$I_{\lambda,b}(\lambda,T) = \frac{2 h c_0^2}{\lambda^5 \left(e^{\frac{hc_0}{\lambda kT}} - 1 \right)} \qquad \text{(VI.147)}$$

If we introduce the constants $C_1 = 2\pi h c_0^2$ and $C_2 = \frac{hc_0}{k}$, the spectral emissive power can be written in the form

$$E_{\lambda,b}(\lambda,T) = \frac{C_1}{\lambda^5 \left(e^{\frac{C_2}{\lambda T}} - 1 \right)} \qquad \text{(VI.148)}$$

This formula is known as Planck's law for blackbody radiation, given the values of $c_0 = 2.998 \times 10^8$ m s^{-1}, $h = 6.626 \times 10^{-34}$ J s, and $k = 1.381 \times 10^{-23}$ J K^{-1}, which correspond respectively to the speed of the

speed of light in vacuum, the Planck constant, and the Boltzmann constant, we obtain, for the constants C_1 and C_2, the values

$$C_1 = 2\pi h c_0^2 = 3{,}742.10^8\ W\mu m^4 m^{-2} \qquad \text{(VI.149)}$$

$$C_2 = \frac{hc_0}{k} = 1{,}439.10^4\ \mu mK \qquad \text{(VI.150)}$$

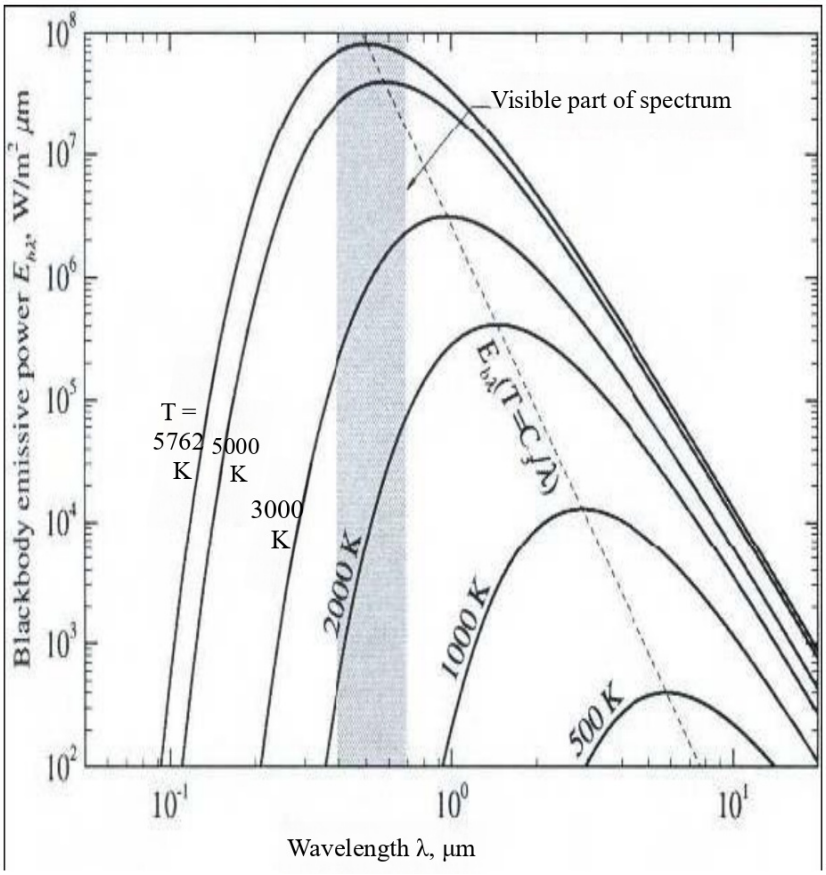


Figure VI. 13. Emissive power of a black body as a function of wavelength.

5.3. Wien's Displacement Law

We note that the spectral emissive power distribution $E_{\lambda,b}(\lambda,T)$ of a black body has a maximum at λ_{max} which depends on the temperature T. To find this maximum, let us calculate

$$\frac{dE_{\lambda,b}(\lambda,T)}{d\lambda}=0 \qquad \text{(VI.151)}$$

by differentiating relation VI. 148 with respect to the wavelength λ, we obtain

$$\frac{dE_{\lambda,b}(\lambda,T)}{d\lambda}=\frac{-5C_1\lambda^4\left(e^{\frac{C_2}{\lambda T}}-1\right)+C_1C_2\frac{\lambda^3}{T}e^{\frac{C_2}{\lambda T}}}{\left(\lambda^5\left(e^{\frac{C_2}{\lambda T}}-1\right)\right)^2}=0 \qquad \text{(VI.152)}$$

from which

$$-5C_1\lambda^4\left(e^{\frac{C_2}{\lambda T}}-1\right)+C_1C_2\frac{\lambda^3}{T}e^{\frac{C_2}{\lambda T}}=0 \qquad \text{(VI.153)}$$

by simplifying and rearranging, we obtain

$$\lambda T\left(e^{\frac{C_2}{\lambda T}}-1\right)=\frac{C_2}{5}e^{\frac{C_2}{\lambda T}} \qquad \text{(VI .154)}$$

If we denote by $x=\frac{C_2}{\lambda T}$, this relation can then be written in the form

$$\frac{e^x-1}{e^x}=\frac{x}{5} \qquad \text{(VI.155)}$$

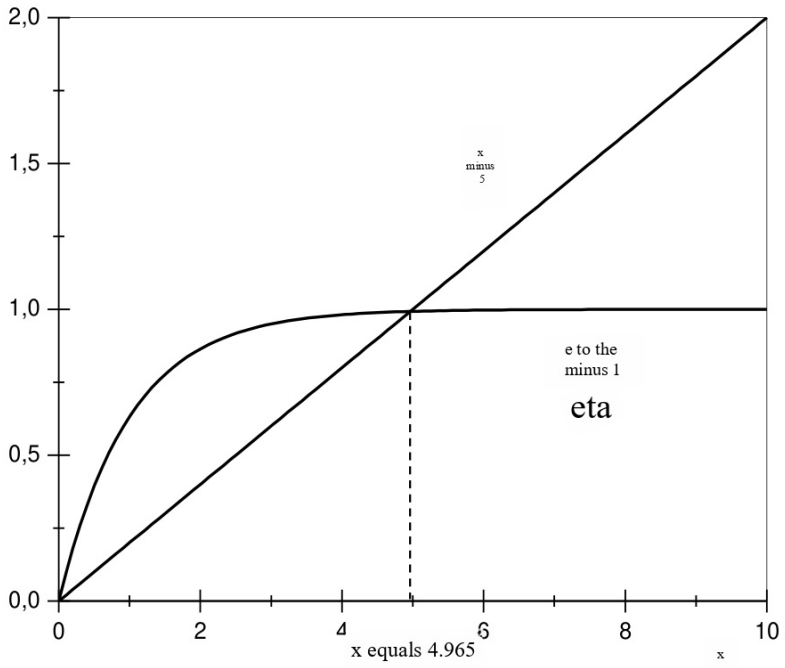


Figure VI. 14. Functions $\frac{e^x-1}{e^x}$ and $\frac{x}{5}$.

In Figure VI.14, we have plotted the functions $\frac{e^x-1}{e^x}$ and $\frac{x}{5}$. Their intersection point is the solution to the equation $\frac{e^x-1}{e^x}=\frac{x}{5}$. The value x corresponding to the solution is $x=4.965$. Knowing that $x=\frac{C_2}{\lambda T}$, we can then write

$$\frac{C_2}{\lambda_{\max} T} = 4{,}965 \qquad \text{(VI.156)}$$

by substituting the numerical value of the constant C_2, we obtain

$$\lambda_{\max} T = 2898 \mu m K \qquad \text{(VI.157)}$$

This relation is known as Wien's displacement law. This law shows that the wavelength corresponding to the maximum value of the spectral emissive power is inversely proportional to the absolute temperature of the black body. The maximum spectral emissive power $E_{\lambda_{\max}}(T)$, which corresponds to the maximum wavelength $\lambda_{\max}$, is obtained by substituting relation VI. 157 into equation VI. 148, namely

$$E_b(\lambda_{\max}, T) = C_3 T^5 \qquad \text{(VI.158)}$$

This relationship shows that the maximum spectral emissive power $E_{\lambda_{\max}}(T)$ depends on the fifth power of the absolute temperature of the black body.

5.4. Limiting Cases of Planck's Law

Now, let us examine the limiting cases of Planck's law. Consider the case where the term $\frac{C_2}{\lambda T}$ is very small compared to unity,

we can then expand the term $e^{\frac{c_2}{\lambda T}}$ to first order, namely

$$e^{\frac{C_2}{\lambda T}} = 1 + \frac{C_2}{\lambda T} \qquad \text{(VI.159)}$$

by substituting into equation VI. 148, we obtain

$$E_{\lambda,b}(\lambda,T)=\frac{C_1}{\lambda^5\left(1+\frac{C_2}{\lambda T}-1\right)}=\frac{C_1}{C_2}\frac{T}{\lambda^4} \qquad \text{(VI.160)}$$

This law is called the Rayleigh-Jeans law.

If now, we consider the case where the term $\frac{C_2}{\lambda T}$ is very large compared to unity, we can then write that

$$E_{\lambda,b}(\lambda,T)=\frac{C_1}{\lambda^5}e^{-\frac{C_2}{\lambda T}} \qquad \text{(VI.161)}$$

this law is called Wien's law.

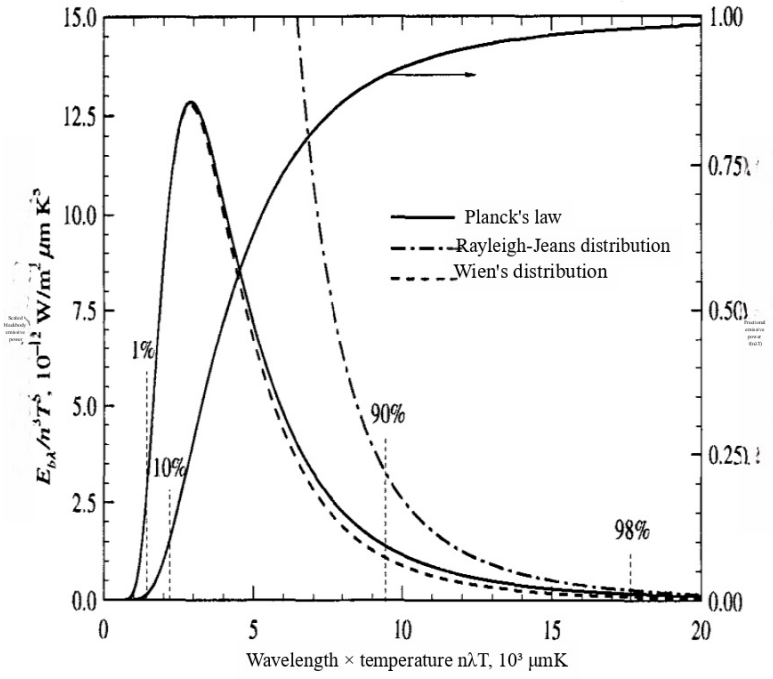


Figure VI. 15. Limiting cases of Planck's law.

5.5. Stefan-Boltzmann Law

The total emissive power of a black body $E_b(T)$, obtained by integrating the spectral emissive power $E_{\lambda,b}(\lambda, T)$ over all possible wavelengths λ, i.e.,

$$E_b(T) = \int_0^\infty E_{\lambda,b}(\lambda, T) d\lambda \qquad \text{(VI.162)}$$

Using Equation VI. 148, we can rewrite this relation in the form

$$E_b(T) = \int_0^\infty \frac{C_1 d\lambda}{\lambda^5 \left(e^{\frac{C_2}{\lambda T}} - 1 \right)} \qquad \text{(VI.163)}$$

To calculate this integral, let us perform a change of variable by setting $x = \frac{C_2}{\lambda T}$, from which

$$d\lambda = -\frac{C_2}{T} \frac{dx}{x^2} \qquad \text{(VI.164)}$$

and thus, the integral is written

$$E_b(T) = \frac{C_1}{C_2^4} T^4 \int_0^\infty \frac{x^3 dx}{e^x - 1} \qquad \text{(VI.165)}$$

Knowing that the integral $\int_0^\infty \frac{x^3 dx}{e^x - 1}$ is equal to $\frac{\pi^4}{15}$, we obtain

$$E_b(T) = \frac{\pi^4}{15} \frac{C_1}{C_2^4} T^4 \qquad \text{(VI.166)}$$

If we denote the constant term $\frac{\pi^4}{15}\frac{C_1}{C_2^4}$ by σ, the power

total emissivity of a black body, is given by

$$E_b(T) = \sigma T^4 \qquad \text{(VI.167)}$$

the constant σ is called the Stefan-Boltzmann constant and it is equal to

$$\sigma = 5{,}670.10^{-8}\ Wm^{-2}K^{-4} \qquad \text{(VI.168)}$$

Equation VI. 167 is the Stefan-Boltzmann law; it enables us to calculate the quantity of radiation emitted in all directions across the entire spectrum by a black body, simply by knowing its temperature.

5.6. Emission Bands

Sometimes, it is necessary to know the fraction of the total emissive power emitted by a black body within a certain wavelength interval $[0, \lambda]$. For a given temperature and a given wavelength interval $[0, \lambda]$, this fraction is determined from the relation

$$f_{0-\lambda} = \frac{\int_0^{\lambda} E_{\lambda,b}(\lambda, T)d\lambda}{\int_0^{\infty} E_{\lambda,b}(\lambda, T)d\lambda} \qquad \text{(VI.169)}$$

and if we introduce the expression for the spectral emissive power $E_{\lambda,b}(\lambda, T)$, this relation becomes

$$f_{0-\lambda} == \frac{\int_0^{\lambda} \frac{C_1 d\lambda}{\lambda^5\left(e^{\frac{C_2}{\lambda T}}-1\right)}}{\int_0^{\infty} \frac{C_1 d\lambda}{\lambda^5\left(e^{\frac{C_2}{\lambda T}}-1\right)}} = \frac{1}{\sigma T^4}\int_0^{\lambda} \frac{C_1 d\lambda}{\lambda^5\left(e^{\frac{C_2}{\lambda T}}-1\right)} \quad \text{(VI.170)}$$

The fraction of spectral emissive power emitted within the wavelength interval $[\lambda_1, \lambda_2]$ is

$$f_{\lambda_1-\lambda_2} = \frac{\int_0^{\lambda_2} E_{\lambda,b}(\lambda,T)d\lambda - \int_0^{\lambda_1} E_{\lambda,b}(\lambda,T)d\lambda}{\int_0^{\infty} E_{\lambda,b}(\lambda,T)d\lambda} = f_{0-\lambda_2} - f_{0-\lambda_1} \quad \text{(VI.171)}$$

If we make the variable change $x = \lambda T$, the fraction of emissive power $f_{\lambda_1-\lambda_2}$ in the interval $[\lambda_1, \lambda_2]$ can be rewritten in the form

$$f_{x_1-x_2} = \frac{C_1}{\sigma}\int_{x_1}^{x_2} \frac{dx}{x^5\left(e^{\frac{C_2}{x}}-1\right)} \quad \text{(VI.172)}$$

let

$$f_{x_1-x_2} = f_{0-x_2} - f_{0-x_1} \quad \text{(VI.173)}$$

5.7. Stefan-Boltzmann Law from Classical Thermodynamics

Consider a cavity of volume V at temperature T containing electromagnetic waves with energy density u. From the electromagnetic theory of light, the radiation pressure P in the cavity is

$$P = \frac{u}{3} \tag{VI.174}$$

If U is the internal energy of the cavity, we can then write

$$U = uV \tag{VI.175}$$

Based on the first principle of thermodynamics, we have

$$dU = -PdV + TdS \tag{VI.176}$$

or even

$$TdS = dU + PdV \tag{VI.177}$$

If we substitute the expressions for the internal energy U and the pressure P, it follows that

$$TdS = d(uV) + \frac{u}{3}dV = Vdu + udV + \frac{u}{3}dV \tag{VI.178}$$

or else

$$TdS = Vdu + \frac{4}{3}udV \tag{VI.179}$$

where the expression for entropy dS

$$dS = \frac{V}{T}du + \frac{4}{3T}udV \tag{VI.180}$$

Since the energy density u of electromagnetic waves in the cavity depends only on the temperature T, we can then write

$$du = \frac{du}{dT} dT \qquad \text{(VI.181)}$$

and in this case, Equation VI. 180 becomes

$$dS = \frac{V}{T} \frac{du}{dT} dT + \frac{4}{3T} u dV \qquad \text{(VI.182)}$$

Since the entropy S is a function of the temperature T and the volume V, its total differential is

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV \qquad \text{(VI.183)}$$

By comparing equations VI. 182 and VI. 183, we obtain

$$\left(\frac{\partial S}{\partial T} \right)_V = \frac{V}{T} \frac{du}{dT} \qquad \text{(VI.184)}$$

$$\left(\frac{\partial S}{\partial V} \right)_T = \frac{4}{3T} u \qquad \text{(VI.185)}$$

Since entropy S is a state function, it must necessarily satisfy the condition

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial^2 S}{\partial V \partial T} \qquad \text{(VI.186)}$$

If we calculate the functions $\frac{\partial^2 S}{\partial T \partial V}$ and $\frac{\partial^2 S}{\partial V \partial T}$ using the

relations VI. 184, VI. 185, we obtain

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial}{\partial V} \left(\frac{\partial S}{\partial T} \right) = \frac{\partial}{\partial V} \left(\frac{V}{T} \frac{du}{dT} \right) = \frac{1}{T} \frac{du}{dT} \qquad \text{(VI.187)}$$

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial}{\partial T} \left(\frac{\partial S}{\partial V} \right) = \frac{\partial}{\partial T} \left(\frac{4}{3T} u \right) = \frac{4}{3} \left(\frac{1}{T} \frac{du}{dT} - \frac{u}{T^2} \right) \qquad \text{(VI.188)}$$

If we substitute these expressions into Equation VI. 186, we obtain

$$\frac{1}{T}\frac{du}{dT} = \frac{4}{3}\left(\frac{1}{T}\frac{du}{dT} - \frac{u}{T^2}\right) \qquad \text{(VI.189)}$$

equation, which after simplification becomes

$$\frac{4u}{T} = \frac{du}{dT} \qquad \text{(VI.190)}$$

$$\frac{du}{u} = 4\frac{dT}{T} \qquad \text{(VI.191)}$$

The solution to this separable differential equation is

$$\ln u = \ln C + 4\ln T \qquad \text{(VI.192)}$$

or by eliminating the logarithmic function

$$u(T) = CT^4 \qquad \text{(VI.193)}$$

The energy density u is related to the emissive power E_b by the relation

$$E_b = \frac{c_0}{4}u \qquad \text{(VI.194)}$$

or else

$$E_b = \frac{c_0 C}{4}T^4 = AT^4 \qquad \text{(VI.195)}$$

This is the Stefan-Boltzmann law derived from classical thermodynamics.

6. Emission of Radiation by Real Surfaces

Having developed the concept of a black body to describe ideal emitting surfaces, we now consider the behavior of real surfaces. Recall that a black body is an ideal emitter and that no surface can emit more radiation than a black body at the same temperature. Consequently, the black body serves as a reference in describing the radiation emitted by a real surface. A property of radiation from a real surface, known as emissivity, can be defined as the ratio of the radiation emitted by any real surface to the radiation emitted by a black body at the same temperature. In general, the radiation emitted by a real surface differs from the radiation described by Planck's law. Similarly, the directional distribution differs from that of diffuse emission. We can now define the spectral directional emissivity $\varepsilon_{\lambda,\theta}(\lambda,\theta,\varphi,T)$ of a real surface at temperature T as the ratio of the radiation intensity emitted at wavelength λ in the direction (θ,φ) to the intensity of the radiation emitted by a black body at the same temperature and the same wavelength. Consequently

$$\varepsilon_{\lambda,\theta}(\lambda,\theta,\varphi,T)=\frac{I_{\lambda,e}(\lambda,\theta,\varphi,T)}{I_{\lambda,b}(\lambda,T)} \qquad \text{(VI.196)}$$

The absence of directional variables (θ,φ) in the denominator implies that the radiation intensity is independent of direction, which is a characteristic of blackbody radiation. The total directional emissivity $\varepsilon_{\theta}(\theta,\varphi,T)$, which is the average of the spectral directional emissivity $\varepsilon_{\lambda,\theta}(\lambda,\theta,\varphi,T)$, is defined by the relation

$$\varepsilon_{\theta}(\theta,\varphi,T)=\frac{I_{e}(\theta,\varphi,T)}{I_{b}(T)} \qquad \text{(VI.197)}$$

The hemispherical spectral emissivity $\varepsilon_\lambda(\lambda, T)$ is defined by

$$\varepsilon_\lambda(\lambda,T) = \frac{E_\lambda(\lambda,T)}{E_{\lambda,b}(\lambda,T)} \qquad \text{(VI.198)}$$

If we use the expression for spectral emissive power, we obtain

$$\varepsilon_\lambda(\lambda,T) = \frac{\int_0^{\frac{\pi}{2}}\int_0^{2\pi} I_{\lambda,e}(\lambda,\theta,\varphi,T)\cos\theta\sin\theta\, d\theta\, d\varphi}{\int_0^{\frac{\pi}{2}}\int_0^{2\pi} I_{\lambda,b}(\lambda,T)\cos\theta\sin\theta\, d\theta\, d\varphi} \qquad \text{(VI.199)}$$

Given that the spectral intensity $I_{\lambda,b}(\lambda, T)$ of a black body is independent of the direction (θ, φ), and utilizing relation VI.196, we can rewrite the relation in the form

$$\varepsilon_\lambda(\lambda,T) = \frac{I_{\lambda,b}(\lambda,T)\int_0^{\frac{\pi}{2}}\int_0^{2\pi} \varepsilon_{\lambda,\theta}(\lambda,\theta,\varphi,T)\cos\theta\sin\theta\, d\theta\, d\varphi}{I_{\lambda,b}(\lambda,T)\int_0^{\frac{\pi}{2}}\int_0^{2\pi} \cos\theta\sin\theta\, d\theta\, d\varphi} \qquad \text{(VI.200)}$$

let

$$\varepsilon_\lambda(\lambda,T)=\frac{\int_0^{\frac{\pi}{2}}\int_0^{2\pi}\varepsilon_{\lambda,\theta}(\lambda,\theta,\varphi,T)\cos\theta\sin\theta\,d\theta\,d\varphi}{\int_0^{\frac{\pi}{2}}\int_0^{2\pi}\cos\theta\sin\theta\,d\theta\,d\varphi} \quad \text{(VI.201)}$$

For the majority of surfaces, $\varepsilon_{\lambda,\theta}$ is independent of the angle φ, so by calculating the integral in the denominator, we obtain

$$\varepsilon_\lambda(\lambda,T)=2\int_0^{\frac{\pi}{2}}\int_0^{2\pi}\varepsilon_{\lambda,\theta}(\lambda,\theta,T)\cos\theta\sin\theta\,d\theta\,d\varphi \quad \text{(VI.202)}$$

The total hemispherical emissivity, which is the average over all possible directions and the full range of wavelengths, is

$$\varepsilon(T)=\frac{E(T)}{E_b(T)} \quad \text{(VI.203)}$$

Using the relations $E=\int_0^\infty E_\lambda(\lambda)d\lambda$ and $\varepsilon_\lambda(\lambda,T)=\frac{E_\lambda(\lambda,T)}{E_{\lambda,b}(\lambda,T)}$, we find

$$\varepsilon(T)=\frac{\int_0^\infty \varepsilon_\lambda(\lambda,T)E_{\lambda,b}(\lambda,T)d\lambda}{E_b(T)} \quad \text{(VI.204)}$$

7. Absorption, reflection and transmission of radiation by real surfaces

We have already defined the irradiance $G_\lambda(\lambda,\theta,\varphi)$ as the rate of wavelength-λ radiation incident per unit surface area

per unit wavelength interval $d\lambda$ around the wavelength λ.

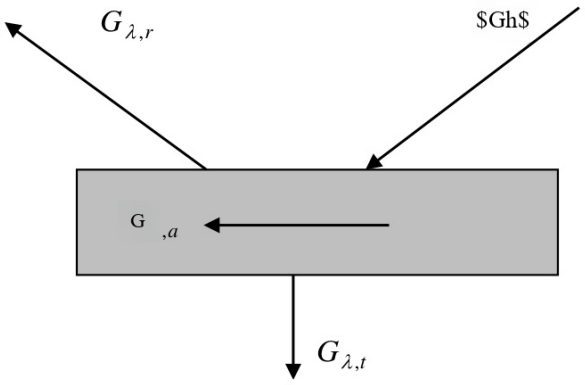


Figure VI. 16. Surface semi-transparent.

Generally, irradiation interacts with semi-transparent media; consequently, a portion of this radiation may be absorbed, reflected, or transmitted. By means of a simple balance, we can assert that

$$G_\lambda = G_{\lambda,r} + G_{\lambda,a} + G_{\lambda,t} \qquad \text{(VI.205)}$$

7. 1. Absorptivity

Absorptivity determines the fraction of irradiation absorbed by the surface. Like emissivity, it depends on the direction (θ,φ) and on the wavelength λ. The directional spectral absorptivity $\alpha_\lambda(\lambda,\theta,\varphi)$ is defined as the fraction of the incident spectral intensity in the direction (θ,φ) that is absorbed by the surface. Consequently

$$\alpha_{\lambda,\theta}(\lambda,\theta,\varphi) = \frac{I_{\lambda,a}(\lambda,\theta,\varphi)}{I_{\lambda,i}(\lambda,\theta,\varphi)} \qquad \text{(VI.206)}$$

The hemispherical spectral absorptivity $\alpha_\lambda(\lambda)$ is defined by

$$\alpha_\lambda(\lambda) = \frac{G_{\lambda,a}(\lambda)}{G_\lambda(\lambda)} \tag{VI.207}$$

relation that can also be written in the form

$$\alpha_\lambda(\lambda) = \frac{\int_0^{\frac{\pi}{2}} \int_0^{2\pi} \alpha_{\lambda,\theta}(\lambda,\theta,\varphi) I_{\lambda,i}(\lambda,\theta,\varphi) \cos\theta \sin\theta \, d\theta \, d\varphi}{\int_0^{\frac{\pi}{2}} \int_0^{2\pi} I_{\lambda,i}(\lambda,\theta,\varphi) \cos\theta \sin\theta \, d\theta \, d\varphi} \tag{VI.208}$$

If the incident radiation intensity is diffuse and $\alpha_{\lambda,\theta}$ is independent of the angle φ, Equation VI. 208 becomes

$$\alpha_\lambda(\lambda) = 2\int_0^{\frac{\pi}{2}} \alpha_{\lambda,\theta}(\lambda) \cos\theta \sin\theta \, d\theta \tag{VI.209}$$

The total hemispherical absorptivity α, representing the average over all directions and wavelengths, is defined by the fraction of the total irradiation absorbed by the surface, namely

$$\alpha = \frac{G_a}{G} \tag{VI.210}$$

relation that we can also write in the form

$$\alpha = \frac{\int_0^{\infty} \alpha_\lambda(\lambda) G_\lambda(\lambda) d\lambda}{\int_0^{\infty} G_\lambda(\lambda) d\lambda} \tag{VI.211}$$

7.2. Reflectivity

Reflectance determines the fraction of incident radiation reflected by the surface. Its definition is more complicated due to the fact that, in addition to its dependence on the direction (θ,φ) of the incident radiation, it also depends on the direction of the reflected radiation. The directional spectral reflectance $\rho_{\lambda,\theta}(\lambda,\theta,\varphi)$ of a surface is defined as the fraction of the incident spectral intensity in the direction (θ,φ) that is reflected by the surface. Mathematically, it is equal to

$$\rho_{\lambda,\theta}(\lambda,\theta,\varphi)=\frac{I_{\lambda,r}(\lambda,\theta,\varphi)}{I_{\lambda,i}(\lambda,\theta,\varphi)} \qquad \text{(VI.212)}$$

The hemispherical spectral reflectance $\rho_\lambda(\lambda)$ is defined as the fraction of irradiation reflected by the surface, namely

$$\rho_\lambda(\lambda)=\frac{G_{\lambda,r}(\lambda)}{G_\lambda(\lambda)} \qquad \text{(VI.213)}$$

relation that can be written in the form

$$\rho_\lambda(\lambda)=\frac{\int_0^{\frac{\pi}{2}}\int_0^{2\pi}\rho_{\lambda,\theta}(\lambda,\theta,\varphi)I_{\lambda,i}(\lambda,\theta,\varphi)\cos\theta\sin\theta\,d\theta\,d\varphi}{\int_0^{\frac{\pi}{2}}\int_0^{2\pi}I_{\lambda,i}(\lambda,\theta,\varphi)\cos\theta\sin\theta\,d\theta\,d\varphi} \qquad \text{(VI.214)}$$

The total hemispherical reflectivity ρ is

$$\rho=\frac{G_r}{G} \qquad \text{(VI.215)}$$

or in other terms

$$\rho = \frac{\int_0^\infty \rho_\lambda(\lambda) G_\lambda(\lambda) d\lambda}{\int_0^\infty G_\lambda(\lambda) d\lambda} \qquad \text{(VI.216)}$$

7.3. Transmissivity

The hemispherical spectral transmittance $\tau_\lambda(\lambda)$ is defined as the fraction of irradiation transmitted through the surface, namely

$$\tau_\lambda(\lambda) = \frac{G_{\lambda,t}(\lambda)}{G_\lambda(\lambda)} \qquad \text{(VI.217)}$$

$$\tau = \frac{G_t}{G} \qquad \text{(VI.218)}$$

$$\tau = \frac{\int_0^\infty \tau_\lambda(\lambda) G_\lambda(\lambda) d\lambda}{\int_0^\infty G_\lambda(\lambda) d\lambda} \qquad \text{(VI.219)}$$

$$G_\lambda = G_{\lambda,r} + G_{\lambda,a} + G_{\lambda,t} \qquad \text{(VI.220)}$$

$$\rho_\lambda(\lambda) G_\lambda + \alpha_\lambda(\lambda) G_\lambda + \tau_\lambda(\lambda) G_\lambda = G_\lambda \qquad \text{(VI.221)}$$

by simplifying with G_λ, we obtain a relationship linking the spectral reflectance, spectral absorptance, and spectral transmittance of a semi-transparent medium

$$\rho_\lambda(\lambda)+\alpha_\lambda(\lambda)+\tau_\lambda(\lambda)=1 \qquad \text{(VI.222)}$$

If we consider the average values over all wavelengths, we can also write that

$$\rho+\alpha+\tau=1 \qquad \text{(VI.223)}$$

For an opaque medium, there is no transmission of radiation; in this case, the previous relations are written as

$$\rho_\lambda(\lambda)+\alpha_\lambda(\lambda)=1 \qquad \text{(VI.224)}$$

$$\rho+\alpha=1 \qquad \text{(VI.225)}$$

8. Kirchhoff's Law

Consider an isothermal cavity with internal temperature T_p containing several bodies $C_i(1 \leq i \leq n)$ of surface area S_i and dimensions much smaller than those of the cavity, so that their presence does not affect the established radiation resulting from successive emissions and reflections by the inner wall of the cavity; thus, this wall constitutes a black body.

Regardless of their orientations, the irradiation received by each body is diffuse and originates from the emission of the cavity wall, which is a black body at temperature T_P. Consequently, we have

$$G = E_b(T_P) \qquad \text{(VI.226)}$$

In the steady state, a thermal equilibrium is established between the different bodies C_i and the cavity; consequently, we must have the condition of equality of the various temperatures, namely

$$T_1 = T_2 = T_3 = \cdots = T_n = T_P \qquad \text{(VI.227)}$$

This equality of temperatures implies the absence of net radiative heat transfer exchanged between the bodies.

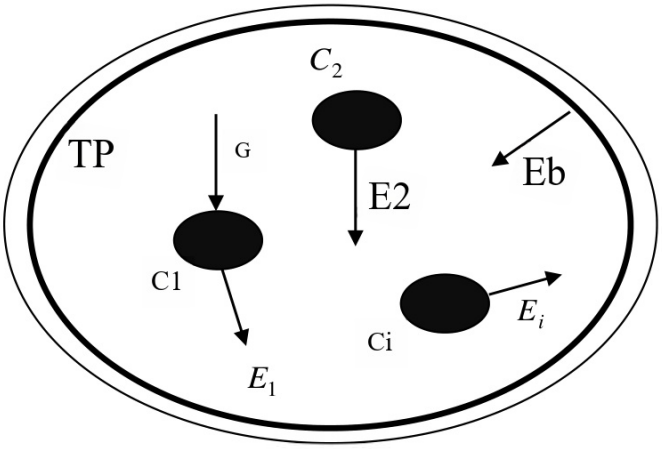


Figure VI. 17. Radiative exchange in an isothermal enclosure.

Consider a body C_1 in thermal equilibrium, which receives irradiation G and absorbs energy $\alpha_1 G S_1$. At the same time, it emits energy $E_1(T_1)$; consequently, we must have the equality

$$\alpha_1 G S_1 = E_1(T_P) S_1 \qquad \text{(VI.228)}$$

using relation VI. 226, we can also write

$$\alpha_1 E_b(T_P) S_1 = E_1(T_P) S_1 \qquad \text{(VI.229)}$$

let

$$E_b(T_P) = \frac{E_1(T_P)}{\alpha_1} \qquad \text{(VI.230)}$$

this result applies to each body C_i, we thus obtain the relation

$$\frac{E_1(T_P)}{\alpha_1} = \frac{E_2(T_P)}{\alpha_2} = \frac{E_3(T_P)}{\alpha_3} = \cdots = \frac{E_n(T_P)}{\alpha_n} = E_b(T_P) \quad \text{(VI.231)}$$

This relation is Kirchhoff's law. Since the absorptivities α_i are less than unity, we must always have $E_i(T_i) < E_b(T_P)$. Thus, no real surface has an emissive power greater than that of a black body at the same temperature. If
we use the relation $\varepsilon = \frac{E}{E_b}$, then the equation reads

$$\frac{\varepsilon_1}{\alpha_1} = \frac{\varepsilon_2}{\alpha_2} = \frac{\varepsilon_3}{\alpha_3} = \cdots = \frac{\varepsilon_n}{\alpha_n} = 1 \quad \text{(VI.232)}$$

This result shows that for any cavity, the total hemispherical emissivity is equal to the total hemispherical absorptivity, namely

$$\varepsilon = \alpha \quad \text{(VI.233)}$$

This relation can be generalized for spectral and directional quantities; thus, we must always have the equalities

$$\varepsilon_\lambda = \alpha_\lambda \quad \text{(VI.234)}$$

$$\varepsilon_{\lambda,\theta} = \alpha_{\lambda,\theta} \quad \text{(VI.235)}$$

9. Grey Surfaces

According to the definitions of hemispherical spectral properties, let us determine under what conditions the following equality holds

$$\varepsilon_\lambda(\lambda,T) = ?\alpha_\lambda(\lambda) \quad \text{(VI.236)}$$

let

$$\frac{\int_0^{\frac{\pi}{2}}\int_0^{2\pi}\varepsilon_{\lambda,\theta}(\lambda,\theta,\varphi,T)\cos\theta\sin\theta\,d\theta\,d\varphi}{\int_0^{\frac{\pi}{2}}\int_0^{2\pi}\cos\theta\sin\theta\,d\theta\,d\varphi} \tag{VI.237}$$

$$= \frac{\int_0^{\frac{\pi}{2}}\int_0^{2\pi}\alpha_{\lambda,\theta}(\lambda,\theta,\varphi)I_{\lambda,i}(\lambda,\theta,\varphi)\cos\theta\sin\theta\,d\theta\,d\varphi}{\int_0^{\frac{\pi}{2}}\int_0^{2\pi}I_{\lambda,i}(\lambda,\theta,\varphi)\cos\theta\sin\theta\,d\theta\,d\varphi}$$

As per Kirchhoff's law, we have $\varepsilon_\lambda(\lambda,T)=\alpha_\lambda(\lambda)$, $\varepsilon_{\lambda,\theta}=\alpha_{\lambda,\theta}$; this equality holds if and only if one of the following two conditions is satisfied:

a) The irradiation $I_{\lambda,i}$ is diffuse, i.e., it does not depend on the direction (θ,φ),

b) The surface is diffuse, meaning that $\varepsilon_{\lambda,\theta}$ and $\alpha_{\lambda,\theta}$ do not depend on the direction (θ,φ).

The first condition is satisfied in the majority of cases. The second condition is also satisfied for many surfaces, particularly non-conductive electrical surfaces.

Assuming that the irradiation and the surface are diffuse, let us determine under what conditions the equality $\varepsilon=\alpha$ is valid

$$\varepsilon = ?\,\alpha \tag{VI.238}$$

let

$$\frac{\int_0^\infty \varepsilon_\lambda(\lambda,T)E_{\lambda,b}(\lambda,T)d\lambda}{E_b(T)} = \frac{\int_0^\infty \alpha_\lambda(\lambda)G_\lambda(\lambda)d\lambda}{G} \qquad \text{(VI.239)}$$

Since $\varepsilon_\lambda = \alpha_\lambda$, the equality holds if and only if one of the following conditions is satisfied.

a) The irradiation corresponds to the emission of a black body having the temperature of the surface in question,

b) The surface is gray, meaning that ε_λ and α_λ are independent of the wavelength λ.

10. Shape Factor

10.1. Definition of the Shape Factor

Consider two arbitrary radiating surfaces S_i and S_j oriented arbitrarily in space. The surface elements dS_i and dS_j are separated by the distance $\vec{r}$, which makes angles θ_i and θ_j with the normal vectors to the surfaces $\vec{n}_i$ and $\vec{n}_j$. The factor F_{ij} is defined as the fraction of radiation leaving surface S_i and intercepted by surface S_j.

The quantity of radiation leaving the surface element dS_i and intercepted by the surface element dS_j is

$$dq_{ij} = I_{e+r,i}\cos\theta_i dS_i d\Omega_{ji} \qquad \text{(VI.240)}$$

where $I_{e+r,i}$ is the intensity of the radiation leaving the surface element dS_i by emission and reflection and $d\Omega_{ji}$ is the solid angle subtended by the surface element dS_j as seen from the surface element dS_i. This solid angle $d\Omega_{ji}$ is naturally given by the relation

$$d\Omega_{ji} = \frac{\cos\theta_j dS_j}{r^2} \qquad \text{(VI.241)}$$

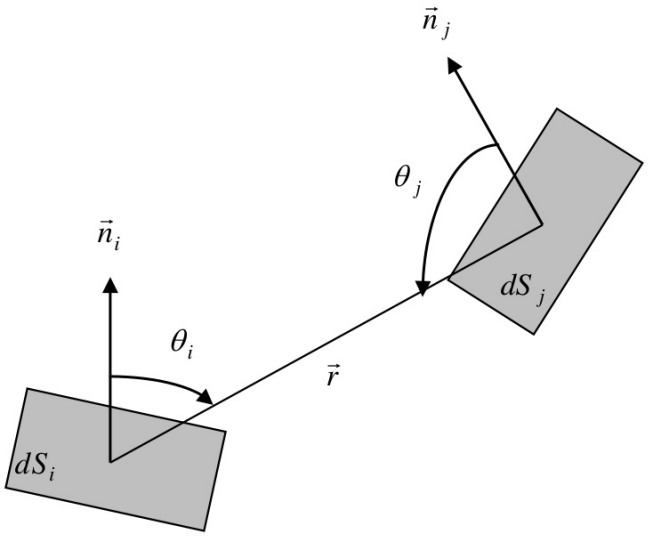


Figure VI. 18. Shape factor.

If we assume that the surface S_i emits and reflects in a diffuse manner, we can replace the intensity $I_{e+r,i}$ with the radiance ($J_i = \pi I_{e+r,i}$). By substituting the expression for the solid angle $d\Omega_{ji}$ and the intensity $I_{e+r,i}$ into the relation, we obtain

$$dq_{ij} = J_i \frac{\cos\theta_i \cos\theta_j dS_i dS_j}{\pi r^2} \qquad \text{(VI.242)}$$

The quantity of total radiation leaving surface S_i and intercepted by surface S_j is obtained by integrating over the entirety of surfaces S_i and S_j, namely

$$q_{ij} = J_i \int_{S_i} \int_{S_j} \frac{\cos\theta_i \cos\theta_j dS_i dS_j}{\pi r^2} \qquad \text{(VI.243)}$$

where the radiosity J_i is considered uniform over the entire surface S_i. The shape factor F_{ij}, as we have defined it, is then given by

$$F_{ij} = \frac{q_{ij}}{S_i J_i} \qquad \text{(VI.244)}$$

Using relation VI. 243, we obtain for the form factor F_{ij} the equation

$$F_{ij} = \frac{1}{S_i} \int_{S_i} \int_{S_j} \frac{\cos\theta_i \cos\theta_j dS_i dS_j}{\pi r^2} \qquad \text{(VI.245)}$$

In the same way, the shape factor F_{ji} is defined as the fraction of radiation leaving surface S_j and intercepted by surface S_i. By similar reasoning, we obtain the following relation for the shape factor F_{ji}, namely

$$F_{ji} = \frac{1}{S_j} \int_{S_i} \int_{S_j} \frac{\cos\theta_i \cos\theta_j dS_i dS_j}{\pi r^2} \qquad \text{(VI.246)}$$

10.2. Properties of the shape factor

From equations VI.245 and VI.246, we can write

$$\int_{S_i} \int_{S_j} \frac{\cos\theta_i \cos\theta_j dS_i dS_j}{\pi r^2} = F_{ij} S_i = F_{ji} S_j \qquad \text{(VI.247)}$$

hence the relationship

$$F_{ij} S_i = F_{ji} S_j \qquad \text{(VI.248)}$$

called the reciprocity relation.

For a closed enclosure, we also have the relation

$$\sum_{j=1}^{j=n} F_{ij} = 1 \qquad \text{(VI.249)}$$

Note that if a surface S_i is convex or planar, the shape factor $F_{ii} = 0$, and if it is concave, $F_{ii} \neq 0$.

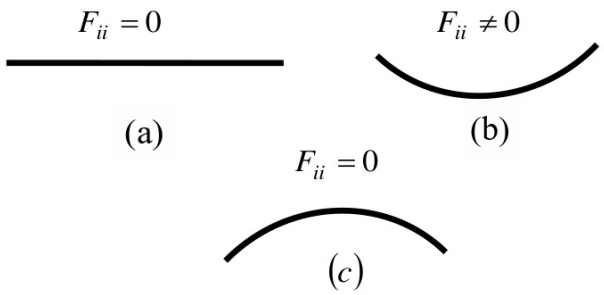


Figure VI. 19. Shape factor F_{ii}, (a): flat surface, (b): concave surface, (c): convex surface.

For an enclosure formed by n surfaces S_i, it is necessary to determine n^2 shape factors, which we can express in the form of a matrix

$$F = \begin{bmatrix} F_{11} & F_{12} & F_{13} & \vdots & F_{1n} \\ F_{21} & F_{22} & F_{23} & \vdots & F_{2n} \\ F_{31} & F_{32} & F_{33} & \vdots & F_{3n} \\ \vdots & \vdots & \vdots & \vdots & \\ F_{n1} & F_{n2} & F_{n3} & \vdots & F_{nn} \end{bmatrix} \qquad \text{(VI.250)}$$

However, it is not necessary to determine the n^2 individually. The n factor factors are determined from the summation rule applied to each surface. Furthermore

From this, $\frac{n(n-1)}{2}$ shape factors are obtained from the reciprocity relation; consequently, only $n^2 - n - \frac{n(n-1)}{2} = \frac{n(n-1)}{2}$ shape factors remain to be calculated directly. To illustrate what has been stated, consider an enclosure formed by three surfaces S_1, S_2, and S_3. For this enclosure, the matrix F is written

$$F = \begin{bmatrix} F_{11} & F_{12} & F_{13} \\ F_{21} & F_{22} & F_{23} \\ F_{31} & F_{32} & F_{33} \end{bmatrix} \qquad \text{(VI.251)}$$

There are therefore nine form factors, leaving only $\frac{3(3-1)}{2} = 3$ form factors to be determined directly, which are F_{12}, F_{13} and F_{23}. The other six form factors are obtained from the reciprocity and summation rules. By applying the reciprocity and summation rules, we can write the six relations necessary for the determination of the remaining six form factors; these relations are

$$F_{11} + F_{12} + F_{13} = 1 \qquad \text{(VI.252)}$$

$$F_{21} + F_{22} + F_{23} = 1 \qquad \text{(VI.253)}$$

$$F_{31} + F_{32} + F_{33} = 1 \qquad \text{(VI.254)}$$

$$F_{12}S_1 = F_{21}S_2 \qquad \text{(VI.255)}$$

$$F_{13}S_1 = F_{31}S_3 \qquad \text{(VI.256)}$$

$$F_{23}S_2 = F_{32}S_3 \qquad \text{(VI.257)}$$

11. Radiative exchanges between opaque, diffuse, and gray surfaces in an enclosure

To study the exchanges between surfaces within an enclosure, we must make certain assumptions. Each surface of the enclosure is assumed to be at a uniform temperature and characterized by uniform radiosity and irradiation. We will also assume that the surfaces are opaque, diffuse, and gray, and that the medium within the enclosure is considered non-participating. The radiative energy q_i leaving surface S_i is equal to the difference between the radiosity J_i emitted by this surface and the incident irradiation G_i it receives. Consequently, we must write that

$$q_i = S_i J_i - S_i G_i \qquad \text{(VI.258)}$$

From the definition of radiosity, we have

$$J_i = E_i + \rho_i G_i \qquad \text{(VI.259)}$$

Since the surface is opaque, we have the relation

$$\rho_i = 1 - \alpha_i \qquad \text{(VI.260)}$$

Relation VI. 259 can be written as

$$J_i = E_i + (1 - \alpha_i) G_i \qquad \text{(VI.261)}$$

Substituting this relation into equation VI. 258, we obtain

$$q_i = S_i \left(E_i + (1 - \alpha_i) G_i\right) - S_i G_i \qquad \text{(VI.262)}$$

let

$$q_i = S_i \left(E_i - \alpha_i G_i\right) \qquad \text{(VI.263)}$$

Knowing that the emissive power E_i of a surface can be expressed in terms of the emissive power of a black body at the same temperature $E_{b,i}$ via the relation $E_i = \varepsilon_i E_{b,i}$, and further, based on Kirchhoff's law, where $\alpha_i = \varepsilon_i$, we can now rewrite relations VI.261 and VI.263 in the form

$$J_i = \varepsilon_i E_{b,i} + (1-\varepsilon_i) G_i \qquad \text{(VI.264)}$$

$$q_i = S_i \varepsilon_i \left(E_{b,i} - G_i\right) \qquad \text{(VI.265)}$$

From equation VI. 264, the irradiation G_i is

$$G_i = \frac{J_i - \varepsilon_i E_{b,i}}{1-\varepsilon_i} \qquad \text{(VI.266)}$$

its substitution into relations VI. 265 leads us to the relation

$$q_i = S_i \left(J_i - \frac{J_i - \varepsilon_i E_{b,i}}{1-\varepsilon_i} \right) \qquad \text{(VI.267)}$$

let

$$q_i = \frac{\varepsilon_i S_i}{1-\varepsilon_i} \left(E_{b,i} - J_i\right) \qquad \text{(VI.268)}$$

This equation can be written in the form

$$q_i = \frac{E_{b,i} - J_i}{\frac{1-\varepsilon_i}{\varepsilon_i S_i}} \qquad \text{(VI.269)}$$

We conclude that this radiative transfer can be associated with the potential $E_{b,i} - J_i$ and with a radiative resistance of the surface $R_r = \frac{1-\varepsilon_i}{\varepsilon_i S_i}$.

11. 1. Radiative exchanges between surfaces

The irradiation G_i of the surface S_i from all radiosityes emitted by all surfaces of the enclosure, including the surface itself. We can then write

$$S_i G_i = \sum_{j=1}^{j=n} S_j F_{ji} J_j \qquad \text{(VI.270)}$$

Using the reciprocity relation $S_i F_{ij} = S_j F_{ji}$, this equation becomes

$$S_i G_i = \sum_{j=1}^{j=n} S_i F_{ij} J_j \qquad \text{(VI.271)}$$

By eliminating the surface S_i and substituting into Equation VI. 263, we obtain

$$q_i = S_i \left(J_i - \sum_{j=1}^{j=n} F_{ij} J_j \right) \qquad \text{(VI.272)}$$

11.1.1. Surface Isotherms

Suppose that the surfaces S_i of the enclosure are maintained at uniform temperatures T_i. By using the Stefan-Boltzmann law, relation VI. 268 can then be written in the form

$$q_i = \frac{\varepsilon_i S_i}{1-\varepsilon_i} \left(\sigma T_i^4 - J_i \right) \qquad \text{(VI.273)}$$

By combining equations VI. 272 and VI. 273, we obtain

$$J_i - \sum_{j=1}^{j=n} F_{ij} J_j = \frac{\varepsilon_i}{1-\varepsilon_i} \left(\sigma T_i^4 - J_i \right) \qquad \text{(VI.274)}$$

which after rearrangement becomes

$$J_i - (1-\varepsilon_i) \sum_{j=1}^{j=n} F_{ij} J_j = \varepsilon_i \sigma T_i^4 \qquad \text{(VI.275)}$$

If we introduce the Kronecker delta symbol δ_{ij}, we can then write

$$J_i = \delta_{ij} J_j \qquad \text{(VI.276)}$$

and thus, equation VI. 275 becomes

$$\delta_{ij} J_j - (1-\varepsilon_i) \sum_{j=1}^{j=n} F_{ij} J_j = \varepsilon_i \sigma T_i^4 \qquad \text{(VI.277)}$$

However, since the summation is over the index j, we are permitted to move the summation sign to the front of the entire left-hand side of the equation, yielding

$$\sum_{j=1}^{j=n} \left(\delta_{ij} - (1-\varepsilon_i) F_{ij}\right) J_j = \varepsilon_i \, \sigma \, T_i^4 \qquad \text{(VI.278)}$$

Since the indices i and j range from 1 to n, and the summation is over the index j, we can expand the equation to obtain a system of n equations for the radiosities J_i. This system of equations in matrix form is

$$\begin{bmatrix} 1-(1-\varepsilon_1)F_{11} & -(1-\varepsilon_1)F_{12} & \cdot & -(1-\varepsilon_1)F_{1n} \\ -(1-\varepsilon_2)F_{21} & 1-(1-\varepsilon_2)F_{22} & \cdot & -(1-\varepsilon_2)F_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ -(1-\varepsilon_n)F_{n1} & -(1-\varepsilon_n)F_{n2} & \cdot & 1-(1-\varepsilon_n)F_{nn} \end{bmatrix} \begin{bmatrix} J_1 \\ J_2 \\ \cdot \\ J_n \end{bmatrix} = \begin{bmatrix} \varepsilon_1 \sigma T_1^4 \\ \varepsilon_2 \sigma T_2^4 \\ \cdot \\ \varepsilon_n \sigma T_n^4 \end{bmatrix} \qquad \text{(VI.279)}$$

11.1.2. Surfaces Subject to a Wall Heat Flux

Suppose that the surfaces S_i of the enclosure are subjected to wall heat fluxes q_i. From relation VI. 272, we have

$$J_i - \sum_{j=1}^{j=n} F_{ij} J_j = \frac{q_i}{S_i} \qquad \text{(VI.280)}$$

If we introduce the Kronecker delta symbol δ_{ij}, we can then write

$$J_i = \delta_{ij} J_j \qquad \text{(VI.281)}$$

from which

$$\delta_{ij} J_j - \sum_{j=1}^{j=n} F_{ij} J_j = \frac{q_i}{S_i} \qquad \text{(VI.282)}$$

but since the summation is independent of the index i, we can transcribe this equation in the form

$$\sum_{j=1}^{j=n} \left(\delta_{ij} - F_{ij}\right) J_j = \frac{q_i}{S_i} \qquad \text{(VI.283)}$$

Since the indices i and j range from 1 to n, and the summation is over the index j, we can expand the equation to obtain a system of n equations for the radiosities J_i. This system of equations in matrix form is

$$\begin{bmatrix} 1-F_{11} & -F_{12} & \cdot & -F_{1n} \\ -F_{21} & 1-F_{22} & \cdot & -F_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ -F_{n1} & -F_{n2} & \cdot & 1-F_{nn} \end{bmatrix} \begin{bmatrix} J_1 \\ J_2 \\ \cdot \\ J_n \end{bmatrix} = \begin{bmatrix} \frac{q_1}{S_1} \\ \frac{q_2}{S_2} \\ \cdot \\ \frac{q_n}{S_n} \end{bmatrix} \qquad \text{(VI.284)}$$

12. Radiative exchanges between black surfaces

If the enclosure consists of black surfaces, the net radiation exchanged by the surface S_i is

$$q_i = S_i\left(E_{b,i} - G_i\right) \qquad \text{(VI.285)}$$

The irradiation falling on the surface S_i and originating from the other surfaces S_j is

$$S_i G_i = E_{b,1} S_1 F_{1i} + E_{b,2} S_2 F_{2i} + \cdots + E_{b,n} S_n F_{ni} = \sum_{j=1}^{j=n} E_{b,j} S_j F_{ji}$$

From the reciprocity relation

$$S_i F_{ij} = S_j F_{ji} \qquad \text{(VI.286)}$$

Relation VI. 285 is written as

$$q_i = S_i E_{b,i} - \sum_{j=1}^{j=n} E_{b,j} S_j F_{ji} = S_i E_{b,i} - \sum_{j=1}^{j=n} E_{b,j} S_i F_{ij} \qquad \text{(VI.287)}$$

let

$$q_i = S_i\left(E_{b,i} - \sum_{j=1}^{j=n} E_{b,j} F_{ij}\right) \qquad \text{(VI.288)}$$

or else

$$q_i = \sum_{j=1}^{j=n}\left(E_{b,i} - E_{b,j}\right) S_i F_{ij} \qquad \text{(VI.289)}$$

CHAPTER I

Mass Transfer Mechanisms

I. 1. Introduction

The movement of a chemical species from a region of high concentration to another of low concentration can be observed by placing a piece of blue paint in a glass of water. As soon as the paint begins to dissolve in the water, we observe that the water is dark blue near the piece of paint where the concentration is high. Due to the concentration gradient established in this medium, the blue color diffuses from the piece of paint over time as time passes. The progression of diffusion can be followed by observing the change in color of the water in the glass.

I. 2. Mass fraction and molar fraction

If ρ_α is the volumetric mass of species α, the total volumetric mass of the mixture will be

$$\rho = \sum_{\alpha=1}^{\alpha=N} \rho_\alpha \tag{I.1}$$

where N is the total number of constituent species in the mixture.

From this definition, we can define the following quantities:

1) The mass fraction of species α

$$\omega_\alpha = \frac{\rho_\alpha}{\sum_{\alpha=1}^{\alpha=N} \rho_\alpha} = \frac{\rho_\alpha}{\rho} \tag{I.2}$$

2) The molar concentration of species α

$$c_\alpha = \frac{\rho_\alpha}{M_\alpha} \tag{I.3}$$

where M_α is the molar mass of species α.

3) The mole fraction of species α

$$x_\alpha = \frac{c_\alpha}{\sum_{\alpha=1}^{\alpha=N} c_\alpha} = \frac{c_\alpha}{c} \qquad \text{(I.4)}$$

With these definitions, we can prove the following relations:

1) From the previous relation

$$x_\alpha = \frac{c_\alpha}{c}$$

we have

$$\sum_{\alpha=1}^{\alpha=N} x_\alpha = \frac{\sum_{\alpha=1}^{\alpha=N} c_\alpha}{c} = \frac{c}{c} = 1$$

$$\sum_{\alpha=1}^{\alpha=N} x_\alpha = 1 \qquad \text{(I.5)}$$

$$x_\alpha = \frac{c_\alpha}{c} = \frac{\frac{\rho_\alpha}{M_\alpha}}{c} = \frac{\rho_\alpha}{cM_\alpha}$$

ou

$$x_\alpha M_\alpha = \frac{\rho_\alpha}{c}$$

$$\sum_{\alpha=1}^{\alpha=N} x_\alpha M_\alpha = \frac{1}{c}\sum_{\alpha=1}^{\alpha=N} \rho_\alpha = \frac{\rho}{c} = M$$

let

$$\sum_{\alpha=1}^{\alpha=N} x_\alpha M_\alpha = M \qquad \text{(I.6)}$$

$$x_\alpha = \frac{c_\alpha}{c}$$

$$c_\alpha = \frac{\rho_\alpha}{M_\alpha} = \frac{\rho\rho_\alpha}{\rho M_\alpha} = \rho\frac{\omega_\alpha}{M_\alpha}$$

$$c = \sum_{\beta=1}^{\beta=N} c_\beta = \rho\sum_{\beta=1}^{\beta=N}\frac{\omega_\beta}{M_\beta}$$

it comes

$$x_\alpha = \frac{\rho\dfrac{\omega_\alpha}{M_\alpha}}{\rho\displaystyle\sum_{\beta=1}^{\beta=N}\frac{\omega_\beta}{M_\beta}}$$

hence

$$x_\alpha = \frac{\dfrac{\omega_\alpha}{M_\alpha}}{\displaystyle\sum_{\beta=1}^{\beta=N}\frac{\omega_\beta}{M_\beta}} \qquad \text{(I.7)}$$

4) From the definition of the mass fraction of species α

$$\omega_\alpha = \frac{\rho_\alpha}{\rho}$$

knowing that

$$\sum_{\alpha=1}^{\alpha=N} \omega_\alpha = \frac{\sum_{\alpha=1}^{\alpha=N} \rho_\alpha}{\rho} = \frac{\rho}{\rho}$$

we find

$$\sum_{\alpha=1}^{\alpha=N} \omega_\alpha = 1 \tag{I.8}$$

It is easy to find a relationship between the molar fraction x_α and the mass fraction ω_α, indeed

$$x_\alpha = \frac{c_\alpha}{c} = \frac{\rho_\alpha}{cM_\alpha} = \frac{\rho_\alpha}{\rho}\frac{\rho}{cM_\alpha} = \omega_\alpha \frac{M}{M_\alpha}$$

i.e.,

$$x_\alpha = \omega_\alpha \frac{M}{M_\alpha} \tag{I.9}$$

$$\frac{\omega_\alpha}{M_\alpha} = \frac{x_\alpha}{M}$$

it follows by summing over all species α

$$\sum_{\alpha=1}^{\alpha=N} \frac{\omega_\alpha}{M_\alpha} = \frac{1}{M} \sum_{\alpha=1}^{\alpha=N} x_\alpha = \frac{1}{M}$$

hence

$$\sum_{\alpha=1}^{\alpha=N} \frac{\omega_\alpha}{M_\alpha} = \frac{1}{M} \tag{I.10}$$

6) From the relation

$$\omega_\alpha = \frac{x_\alpha M_\alpha}{M}$$

taking into account the relationship

$$\sum_{\beta=1}^{\beta=N} x_\beta M_\beta = M$$

we find

$$\omega_\alpha = \frac{x_\alpha M_\alpha}{\sum_{\beta=1}^{\beta=N} x_\beta M_\beta} \qquad \text{(I.11)}$$

7) For a binary mixture, relation (I. 7) for the species A is written

$$x_A = \frac{\frac{\omega_A}{M_A}}{\frac{\omega_A}{M_A} + \frac{\omega_B}{M_B}}$$

where the gradient is

$$\vec{\nabla} x_A = \frac{\left(\frac{\omega_A}{M_A} + \frac{\omega_B}{M_B}\right)\vec{\nabla}\frac{\omega_A}{M_A} - \frac{\omega_A}{M_A}\left(\vec{\nabla}\frac{\omega_A}{M_A} + \vec{\nabla}\frac{\omega_B}{M_B}\right)}{\left(\frac{\omega_A}{M_A} + \frac{\omega_B}{M_B}\right)^2}$$

$$\vec{\nabla} x_A = \frac{\frac{\omega_B}{M_B}\vec{\nabla}\frac{\omega_A}{M_A} - \frac{\omega_A}{M_A}\vec{\nabla}\frac{\omega_B}{M_B}}{\left(\frac{\omega_A}{M_A} + \frac{\omega_B}{M_B}\right)^2}$$

and with the relation $\omega_B = 1 - \omega_A$, we obtain then

$$\vec{\nabla}x_A = \frac{\frac{(1-\omega_A)}{M_B}\vec{\nabla}\frac{\omega_A}{M_A} - \frac{\omega_A}{M_A}\vec{\nabla}\frac{(1-\omega_A)}{M_B}}{\left(\frac{\omega_A}{M_A}+\frac{\omega_B}{M_B}\right)^2}$$

thus

$$\vec{\nabla}x_A = \frac{\frac{\vec{\nabla}\omega_A}{M_A M_B}}{\left(\frac{\omega_A}{M_A}+\frac{\omega_B}{M_B}\right)^2} \qquad \text{(I.12)}$$

Certainly, for the species $\boldsymbol{B}$, this relation is written as

$$\vec{\nabla}x_B = \frac{\frac{\vec{\nabla}\omega_B}{M_A M_B}}{\left(\frac{\omega_A}{M_A}+\frac{\omega_B}{M_B}\right)^2} \qquad \text{(I.13)}$$

8) For a binary mixture, the relation (I. 11) for the species $\boldsymbol{A}$, is

$$\omega_A = \frac{x_A M_A}{x_A M_A + x_B M_B}$$

its gradient is

$$\vec{\nabla}\omega_A = \frac{\left(x_A M_A + x_B M_B\right)\vec{\nabla}x_A M_A - x_A M_A\left(\vec{\nabla}x_A M_A + \vec{\nabla}x_B M_B\right)}{\left(x_A M_A + x_B M_B\right)^2}$$

hence

$$\vec{\nabla}\omega_A = \frac{M_A M_B \vec{\nabla}x_A}{\left(x_A M_A + x_B M_B\right)^2} \qquad \text{(I.14)}$$

using the relation $\omega_B = 1 - \omega_A$, we obtain, for species $\boldsymbol{B}$

$$\vec{\nabla}\omega_B = \frac{M_A M_B \vec{\nabla} x_B}{\left(x_A M_A + x_B M_B\right)^2} \tag{I.15}$$

I. 3. Velocities

$$\vec{V} = \frac{\sum_{\alpha=1}^{\alpha=N} \rho_\alpha \vec{V}_\alpha}{\sum_{\alpha=1}^{\alpha=N} \rho_\alpha} = \frac{\sum_{\alpha=1}^{\alpha=N} \rho_\alpha \vec{V}_\alpha}{\rho} = \sum_{\alpha=1}^{\alpha=N} \frac{\rho_\alpha}{\rho} \vec{V}_\alpha$$

$$\vec{V} = \sum_{\alpha=1}^{\alpha=N} \omega_\alpha \vec{V}_\alpha \tag{I.16}$$

where $\vec{V}_\alpha$ is the average velocity of all molecules of species α. The term $\rho\vec{V}$ represents the mass passing, within the mixture, through a surface perpendicular to the velocity vector $\vec{V}$. Similarly, the mean molar velocity $\vec{V}^*$ is

$$\vec{V}^* = \frac{\sum_{\alpha=1}^{\alpha=N} c_\alpha \vec{V}_\alpha}{\sum_{\alpha=1}^{\alpha=N} c_\alpha} = \frac{\sum_{\alpha=1}^{\alpha=N} c_\alpha \vec{V}_\alpha}{c} = \sum_{\alpha=1}^{\alpha=N} \frac{c_\alpha}{c} \vec{V}_\alpha$$

$$\vec{V}^* = \sum_{\alpha=1}^{\alpha=N} x_\alpha \vec{V}_\alpha \tag{I.17}$$

where $\vec{V}_\alpha$ is the average velocity of all molecules of species α. The term $c\vec{V}^*$ represents the moles passing, within the mixture, through a surface perpendicular to the velocity vector $\vec{V}^*$.

From relations (I. 16) and (I. 17), and taking into account that $\sum_{\alpha=1}^{\alpha=N} \omega_\alpha = 1$ and $\sum_{\alpha=1}^{\alpha=N} x_\alpha = 1$, we obtain

$$\vec{V}-\vec{V}^{*}=\sum_{\alpha=1}^{\alpha=N}\omega_{\alpha}\vec{V}_{\alpha}-\vec{V}^{*}=$$

$$\sum_{\alpha=1}^{\alpha=N}\omega_{\alpha}\vec{V}_{\alpha}-\vec{V}^{*}\sum_{\alpha=1}^{\alpha=N}\omega_{\alpha}=\sum_{\alpha=1}^{\alpha=N}\omega_{\alpha}\vec{V}_{\alpha}-\sum_{\alpha=1}^{\alpha=N}\omega_{\alpha}\vec{V}^{*}$$

i.e.

$$\vec{V}-\vec{V}^{*}=\sum_{\alpha=1}^{\alpha=N}\omega_{\alpha}\left(\vec{V}_{\alpha}-\vec{V}^{*}\right) \qquad \text{(I.18)}$$

likewise

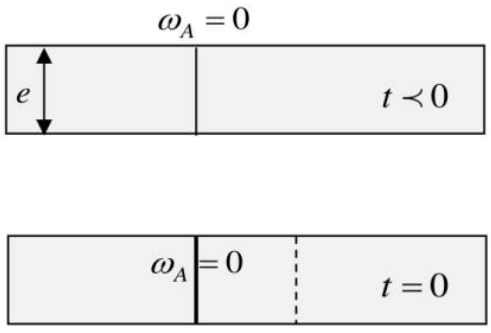
$$\vec{V}^{*}-\vec{V}=\sum_{\alpha=1}^{\alpha=N}x_{\alpha}\vec{V}_{\alpha}-\vec{V}=\sum_{\alpha=1}^{\alpha=N}x_{\alpha}\vec{V}_{\alpha}-\vec{V}\sum_{\alpha=1}^{\alpha=N}x_{\alpha}=\sum_{\alpha=1}^{\alpha=N}x_{\alpha}\vec{V}_{\alpha}-\vec{V}\sum_{\alpha=1}^{\alpha=N}x_{\alpha}\vec{V}$$

hence the relationship

$$\vec{V}^{*}-\vec{V}=\sum_{\alpha=1}^{\alpha=N}x_{\alpha}\left(\vec{V}_{\alpha}-\vec{V}\right) \qquad \text{(I.19)}$$

I. 4. Molecular Diffusion, Fick's Law

Consider a plane plate of silica glass with surface area S and thickness e. Suppose initially that the two faces of the plate are in contact with air, which is completely insoluble in silica glass. At a given instant, the air under the plate is suddenly replaced by helium, which is highly soluble in silica glass. Due to the porous structure of silica glass, helium atoms (monatomic gas whose atoms are the smallest in nature) gradually penetrate into the plate under the action of molecular movements and appear on the other side of the plate.



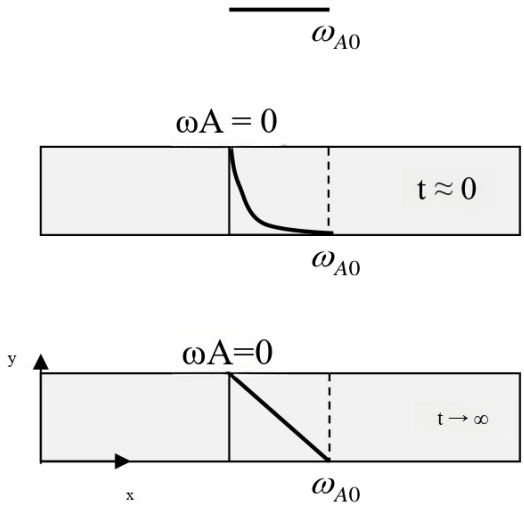


Figure I. 1. Development of the mass fraction profile of helium in the plate.

This phenomenon of molecular transport of one substance relative to another is known as diffusion. In this example, let us call helium species A and the silica glass species B. The concentrations will be given by the mass fractions ω_A and ω_B. The mass fraction ω_A is the mass of helium divided by the mass of helium plus the mass of the silica glass in a given microscopic volume. The same applies to the mass fraction ω_B.

At the beginning, the mass fraction of helium ω_A in the silica glass is zero everywhere. Immediately after, on the lower face of the plate, the mass fraction is equal to ω_{A0}, which is nothing other than the solubility of helium in silica glass. As time passes, the mass fraction of helium in the silica glass develops, with a mass fraction of zero on the upper face and ω_{A0} on the lower face. When the system reaches the

steady state, the mass fraction profile in the silica glass approaches a straight line such that

$$\frac{\omega_{Ay}}{S} = \rho D_{AB} \frac{\omega_{A0} - 0}{e - 0} = \rho D_{AB} \frac{\omega_{A0}}{e} \tag{I.20}$$

This shows that the mass flow rate (or mass flux) of helium per unit surface area is proportional to the difference in mass fractions divided by the thickness of the plate, ρ is the volumetric mass density of the helium-silica glass system and D_{AB} is a proportionality factor called the diffusion coefficient or diffusivity of the helium-silica glass system. For a differential element within the plate, Equation (I. 1) is written

$$j_{Ay} = -\rho\, D_{AB} \frac{d\omega_A}{dy} \tag{I.21}$$

The term $\frac{\omega_{Ay}}{S}$ has been replaced by j_{Ay}, the molecular mass flux of helium in the positive y-direction. This equation is the one-dimensional form of Fick's first law. It is valid for any solid, liquid, or gaseous binary solution, provided that the mass flux is defined relative to the mixing velocity. In general, for a binary mixture

$$V_y = \omega_A V_{Ay} + \omega_B V_{By} \tag{I.22}$$

the velocity $\vec{V}$ is an average in which the velocities of species A and B are weighted by their mass fractions. This velocity is called the mass-averaged velocity. The velocity of species A is not the instantaneous velocity of molecule A, but rather the arithmetic mean of all velocities of molecules A within a given volume.

The mass fluxes j_{Ay} and j_{By} of species A and B are defined by

$$j_{Ay} = \rho\omega_A \left(V_{Ay} - V_y\right) \tag{I.23}$$

$$j_{By} = \rho\omega_B \left(V_{By} - V_y\right) \tag{I.24}$$

locally, during the inter-diffusion of the two species A and B, there is a displacement of the center of mass in the direction y if the molecular weights of the two species are different. This means that the mass fluxes j_{Ay} and j_{By} are measured with respect to the movement of the center of mass. In vector form, the first Fick's law is written

$$\vec{j}_A = -\rho\, D_{AB} \vec{\nabla} \omega_A \tag{I.25}$$

$$\vec{j}_B = -\rho\, D_{BA} \vec{\nabla} \omega_B \tag{I.26}$$

These relations hold in isotropic fluids in which diffusion rates are independent of orientation. In certain solids or structured fluids, diffusion rates depend on spatial orientations; in such a case

$$\vec{j}_A = -\rho \left[D_{AB} \right] \vec{\nabla} \omega_A \tag{I.27}$$

where $[D_{AB}]$ is the symmetric diffusivity tensor. This equation shows that the mass flux is not necessarily parallel to the gradient of the mass fraction ω_A.

If we consider a binary mixture composed of two species A and B, from relation (I. 23), we have

$$\vec{j}_A = \rho \omega_A \left(\vec{V}_A - \vec{V} \right) \tag{I.28}$$

$$\vec{V} = \omega_A \vec{V}_A + \omega_B \vec{V}_B \tag{I.29}$$

it comes

$$\vec{j}_A = \rho \omega_A \left(\vec{V}_A - \left(\omega_A \vec{V}_A + \omega_B \vec{V}_B \right) \right) = \rho \omega_A \left(\left(1 - \omega_A \right) \vec{V}_A - \omega_B \vec{V}_B \right)$$

since $\omega_B = 1 - \omega_A$, we obtain

$$\vec{j}_A = \rho \omega_A \omega_B \left(\vec{V}_A - \vec{V}_B \right) \tag{I.30}$$

if we interchange the indices A and B, this relation is written

$$\vec{j}_A = \rho\omega_B\omega_A\left(-\left(\vec{V}_B - \vec{V}_A\right)\right) = -\rho\omega_A\omega_B\left(\vec{V}_B - \vec{V}_A\right) = -\vec{j}_B \quad \text{(I.31)}$$

thus

$$\vec{j}_A + \vec{j}_B = \vec{0} \quad \text{(I.32)}$$

now, let us use this relation to show that, in a binary mixture $D_{AB} = D_{BA}$, indeed

$$\vec{j}_A = -\rho\, D_{AB}\vec{\nabla}\omega_A = \rho\, D_{BA}\vec{\nabla}\omega_B = \rho\, D_{BA}\vec{\nabla}\left(1-\omega_A\right)$$

$$-\rho\, D_{AB}\vec{\nabla}\omega_A = -\rho\, D_{BA}\vec{\nabla}\omega_A$$

therefore

$$D_{AB} = D_{BA} \quad \text{(I.33)}$$

This result shows that in the case of a binary mixture, a single diffusivity is sufficient to describe diffusion.

In a binary mixture, for the mass fluxes, we have the relations

$$\vec{j}_A = \rho_A\left(\vec{V}_A - \vec{V}\right) = -\rho\, D_{AB}\vec{\nabla}\omega_A \quad \text{(I.34)}$$

$$\vec{j}_B = \rho_B\left(\vec{V}_B - \vec{V}\right) = -\rho\, D_{AB}\vec{\nabla}\omega_B \quad \text{(I.35)}$$

and for molar fluxes, the relations

$$\vec{j}_A^{\,*} = c_A\left(\vec{V}_A - \vec{V}^*\right) = -c\, D_{AB}\vec{\nabla}x_A \quad \text{(I.36)}$$

$$\vec{j}_B^{\,*} = c_B\left(\vec{V}_B - \vec{V}^*\right) = -c\, D_{AB}\vec{\nabla}x_B \quad \text{(I.37)}$$

The velocities $\vec{V}_\alpha - \vec{V}$ and $\vec{V}_\alpha - \vec{V}^*$ are respectively, the diffusion velocity of species α relative to the mean mass velocity $\vec{V}$ and the mean molar velocity $\vec{V}^*$.

I. 5. Mass Flux and Molar Flux

If $\vec{V}_\alpha$, $\vec{V}$ and $\vec{V}^*$ are respectively the velocities of species α with respect to a stationary coordinate system, the mass average velocity and the molar average velocity, the mass flux of species α is given by one of the formulas

$$\vec{n}_\alpha = \rho_\alpha \vec{V}_\alpha \tag{I.38}$$

$$\vec{j}_\alpha = \rho_\alpha \left(\vec{V}_\alpha - \vec{V}\right) \tag{I.39}$$

$$\vec{j}_\alpha^* = \rho_\alpha \left(\vec{V}_\alpha - \vec{V}^*\right) \tag{I.40}$$

as for the molar flux of species α, it is given by one of the formulas

$$\vec{N}_\alpha = c_\alpha \vec{V}_\alpha \tag{I.41}$$

$$\vec{J}_\alpha = c_\alpha \left(\vec{V}_\alpha - \vec{V}\right) \tag{I.42}$$

$$\vec{J}_\alpha^* = c_\alpha \left(\vec{V}_\alpha - \vec{V}^*\right) \tag{I.43}$$

The total mass flux is

$$\sum_{\alpha=1}^{\alpha=N} \vec{n}_\alpha = \rho \vec{V} \tag{I.44}$$

and the total molar flux is

$$\sum_{\alpha=1}^{\alpha=N} \vec{N}_\alpha = c \vec{V}^* \tag{I.45}$$

From relation (I. 39), we have

$$\sum_{\alpha=1}^{\alpha=N} \vec{j}_\alpha = \sum_{\alpha=1}^{\alpha=N} \rho_\alpha \vec{V}_\alpha - \vec{V} \sum_{\alpha=1}^{\alpha=N} \rho_\alpha = \rho \vec{V} - \rho \vec{V} = \vec{0}$$

therefore

$$\sum_{\alpha=1}^{\alpha=N} \vec{j}_\alpha = \vec{0} \tag{I.46}$$

from relation (I. 40), we have

$$\sum_{\alpha=1}^{\alpha=N} \vec{j}_\alpha^* = \sum_{\alpha=1}^{\alpha=N} \rho_\alpha \vec{V}_\alpha - \vec{V}^* \sum_{\alpha=1}^{\alpha=N} \rho_\alpha = \rho\vec{V} - \rho\vec{V}^*$$

wherefrom

$$\sum_{\alpha=1}^{\alpha=N} \vec{j}_\alpha^* = \rho\left(\vec{V} - \vec{V}^*\right) \tag{I.47}$$

Let us now consider the molar flux; in fact, starting from relation (I.42), we have

$$\sum_{\alpha=1}^{\alpha=N} \vec{J}_\alpha = \sum_{\alpha=1}^{\alpha=N} c_\alpha \vec{V}_\alpha - \vec{V} \sum_{\alpha=1}^{\alpha=N} c_\alpha = c\vec{V}^* - c\vec{V}$$

let

$$\sum_{\alpha=1}^{\alpha=N} \vec{J}_\alpha = c\left(\vec{V}^* - \vec{V}\right) \tag{I.48}$$

from relation (I. 43), it follows

$$\sum_{\alpha=1}^{\alpha=N} \vec{J}_\alpha^* = \sum_{\alpha=1}^{\alpha=N} c_\alpha \vec{V}_\alpha - \vec{V}^* \sum_{\alpha=1}^{\alpha=N} c_\alpha = c\vec{V}^* - c\vec{V}^*$$

hence

$$\sum_{\alpha=1}^{\alpha=N} \vec{J}_\alpha^* = \vec{0} \tag{I.49}$$

by eliminating the velocity vector $\vec{V}$ between relations (I. 38) and (I. 41),

$$\vec{n}_\alpha = \rho_\alpha \vec{V}$$

$$\vec{N}_\alpha = c_\alpha \vec{V}$$

we obtain

$$\vec{n}_\alpha = \frac{\rho_\alpha}{c_\alpha}\vec{N}_\alpha$$

but since $M_\alpha = \frac{\rho_\alpha}{c_\alpha}$, we find

$$\vec{n}_\alpha = M_\alpha \vec{N}_\alpha \qquad \text{(I.50)}$$

and we proceed in the same way with relations (I. 39) and (I. 42)

$$\vec{j}_\alpha = \rho_\alpha\left(\vec{V}_\alpha - \vec{V}\right)$$

$$\vec{J}_\alpha = c_\alpha\left(\vec{V}_\alpha - \vec{V}\right)$$

we arrive at the relation

$$\vec{j}_\alpha = M_\alpha \vec{J}_\alpha \qquad \text{(I.51)}$$

in the same way, with relations (I. 40) and (I. 43)

$$\vec{j}^*_\alpha = \rho_\alpha\left(\vec{V}_\alpha - \vec{V}^*\right)$$

$$\vec{J}^*_\alpha = c_\alpha\left(\vec{V}_\alpha - \vec{V}^*\right)$$

we obtain

$$\vec{j}^*_\alpha = M_\alpha \vec{J}^*_\alpha \qquad \text{(I.52)}$$

the total mass flux is the sum of the molecular mass flux and the mass flux due to convection

$$\vec{n}_\alpha = \vec{j}_\alpha + \rho_\alpha \vec{V} \qquad \text{(I.53)}$$

from this relation, we have

$$\vec{j}_\alpha = \vec{n}_\alpha - \rho_\alpha \vec{V}$$

with equation (I. 44), it follows that

$$\vec{j}_\alpha = \vec{n}_\alpha - \frac{\rho_\alpha}{\rho}\sum_{\beta=1}^{\beta=N}\vec{n}_\beta$$

let

$$\vec{j}_\alpha = \vec{n}_\alpha - \omega_\alpha \sum_{\beta=1}^{\beta=N}\vec{n}_\beta \qquad \text{(I.54)}$$

by substituting expressions (I.50) and (I.51), we find

$$M_\alpha \vec{J}_\alpha = M_\alpha \vec{N}_\alpha - \omega_\alpha \sum_{\beta=1}^{\beta=N} M_\beta \vec{N}_\beta$$

thus

$$\vec{J}_\alpha = \vec{N}_\alpha - \omega_\alpha \sum_{\beta=1}^{\beta=N} \frac{M_\beta}{M_\alpha}\vec{N}_\beta \qquad \text{(I.55)}$$

the total molar flux is the sum of the molecular molar flux and the molar flux due to convection

$$\vec{N}_\alpha = \vec{J}_\alpha^{*} + c_\alpha \vec{V}^{*} \qquad \text{(I.56)}$$

from there we have

$$\vec{J}_\alpha^{*} = \vec{N}_\alpha - c_\alpha \vec{V}^{*}$$

and by substituting relation (I. 45), we obtain

$$\vec{J}_\alpha^{*} = \vec{N}_\alpha - \frac{c_\alpha}{c}\sum_{\beta=1}^{\beta=N}\vec{N}_\beta$$

i.e.

$$\vec{J}_\alpha^{*} = \vec{N}_\alpha - x_\alpha \sum_{\beta=1}^{\beta=N}\vec{N}_\beta \qquad \text{(I.57)}$$

taking into account relations (I. 50) and (I. 52), this equation is written as

$$\frac{\vec{j}_\alpha^*}{M_\alpha} = \frac{\vec{n}_\alpha}{M_\alpha} - x_\alpha \sum_{\beta=1}^{\beta=N} \frac{\vec{n}_\beta}{M_\beta}$$

therefore

$$\vec{j}_\alpha^* = \vec{n}_\alpha - x_\alpha \sum_{\beta=1}^{\beta=N} \frac{M_\alpha}{M_\beta} \vec{n}_\beta \qquad \text{(I.58)}$$

I. 6. Mass flux and molar flux for a binary system

For a binary system consisting of two species $\boldsymbol{A}$ and $\boldsymbol{B}$, we have the relations

$$\vec{j}_A = -\rho D_{AB} \vec{\nabla} \omega_A \qquad \text{(I.59)}$$

$$\vec{j}_B = -\rho D_{BA} \vec{\nabla} \omega_B \qquad \text{(I.60)}$$

$$\vec{n}_A = -\rho D_{AB} \vec{\nabla} \omega_A + \omega_A \left(\vec{n}_A + \vec{n}_B\right) = -\rho D_{AB} \vec{\nabla} \omega_A + \rho_A \vec{V} \qquad \text{(I.61a)}$$

$$\vec{n}_B = -\rho D_{BA} \vec{\nabla} \omega_B + \omega_B \left(\vec{n}_A + \vec{n}_B\right) = -\rho D_{BA} \vec{\nabla} \omega_B + \rho_B \vec{V} \qquad \text{(I.61b)}$$

$$\vec{N}_A = -cD_{AB} \vec{\nabla} x_A + x_A \left(\vec{N}_A + \vec{N}_B\right) = -cD_{AB} \vec{\nabla} x_A + c_A \vec{V}^* \qquad \text{(I.62a)}$$

$$\vec{N}_B = -cD_{BA} \vec{\nabla} x_B + x_B \left(\vec{N}_B + \vec{N}_B\right) = -cD_{BA} \vec{\nabla} x_B + c_B \vec{V}^* \qquad \text{(I.62b)}$$

$$\rho\left(\vec{V}_A - \vec{V}_B\right) = -\frac{\rho D_{AB}}{\omega_A \omega_B} \vec{\nabla} \omega_A \qquad \text{(I.63a)}$$

$$c\left(\vec{V}_A - \vec{V}_B\right) = -\frac{cD_{AB}}{x_A x_B} \vec{\nabla} x_A \qquad \text{(I.63b)}$$

With relations (I. 63a) and (I. 63b), we have

$$\rho\left(\vec{V}_A - \vec{V}_B\right) = -\frac{\rho D_{AB}}{\omega_A \omega_B} \vec{\nabla} \omega_A$$

$$c\left(\vec{V}_A - \vec{V}_B\right) = -\frac{cD_{AB}}{x_A x_B} \vec{\nabla} x_A$$

if we use relations (I. 34) and (I. 36)

$$\vec{j}_A = -\rho\, D_{AB}\vec{\nabla}\omega_A$$

$$\vec{j}_A^{*} = -c\, D_{AB}\vec{\nabla}x_A$$

we can write

$$\rho\left(\vec{V}_A - \vec{V}_B\right) = \frac{\vec{j}_A}{\omega_A\omega_B}$$

$$c\left(\vec{V}_A - \vec{V}_B\right) = \frac{\vec{j}_A^{*}}{x_A x_B}$$

By eliminating the term $\left(\vec{V}_A - \vec{V}_B\right)$ between these two relations, we obtain

$$\frac{\vec{j}_A}{\rho\omega_A\omega_B} = \frac{\vec{j}_A^{*}}{c\, x_A x_B} \qquad \text{(I.63c)}$$

relation (I. 63b) is

$$\vec{V}_A - \vec{V}_B = -\frac{D_{AB}}{x_A x_B}\vec{\nabla}x_A$$

let us calculate $\vec{\nabla}\ln\frac{x_A}{x_B}$, indeed

$$\vec{\nabla}\ln\frac{x_A}{x_B} = \vec{\nabla}\left(\ln x_A - \ln x_B\right) = \vec{\nabla}\ln x_A - \vec{\nabla}\ln x_B$$

$$= \frac{\vec{\nabla}x_A}{x_A} - \frac{\vec{\nabla}x_B}{x_B} = \frac{\vec{\nabla}x_A}{x_A} - \frac{\vec{\nabla}\left(1 - x_A\right)}{x_B}$$

$$= \frac{\vec{\nabla}x_A}{x_A} + \frac{\vec{\nabla}x_A}{x_B} = \vec{\nabla}x_A\left(\frac{1}{x_A} + \frac{1}{x_B}\right) = \frac{x_A + x_B}{x_A x_B}\vec{\nabla}x_A$$

let

$$\vec{\nabla}x_A = x_A x_B\vec{\nabla}\ln\frac{x_A}{x_B}$$

therefore

$$\vec{V}_A - \vec{V}_B = -D_{AB}\vec{\nabla}\ln\frac{x_A}{x_B} \qquad \text{(I.63d)}$$

I. 7. Maxwell-Stefan Relations

Consider the mechanics of the elastic collision between a molecule of species A and a molecule of species B. The molecule of species A has velocity $\vec{V}_A$ and the molecule of species B has velocity $\vec{V}_B$.

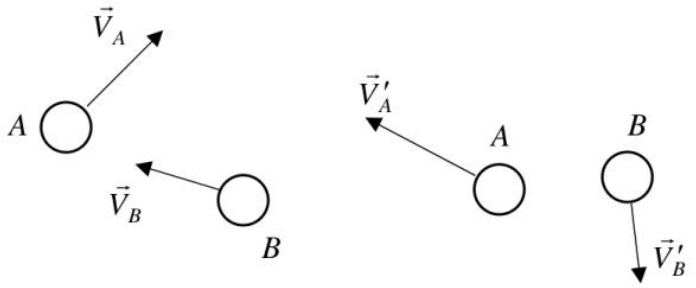


Figure I. 2. Elastic collision between the molecule of species A and the molecule of species B.

During an elastic collision, there is conservation of momentum and kinetic energy, namely

$$m_A\vec{V}_A + m_B\vec{V}_B = m_A\vec{V}'_A + m_B\vec{V}'_B$$

$$\frac{1}{2}m_A\vec{V}_A^2 + \frac{1}{2}m_B\vec{V}_B^2 = \frac{1}{2}m_A\vec{V}_A'^2 + \frac{1}{2}m_B\vec{V}_B'^2$$

relations, from which we obtain the velocities of molecules of species A and of species B after the collision

$$\vec{V}_A' = \frac{(m_A - m_B)\vec{V}_A + 2m_B\vec{V}_B}{m_A + m_B}$$

$$\vec{V}_B' = \frac{(m_B - m_A)\vec{V}_B + 2m_A\vec{V}_A}{m_A + m_B}$$

For the molecule of species A, the quantity of momentum exchanged during the elastic collision with the molecule of species B is

$$m_A\left(\vec{V}_A - \vec{V}_A'\right) = \frac{2m_A m_B}{m_A + m_B}\left(\vec{V}_A - \vec{V}_B\right) \qquad \text{(I.64)}$$

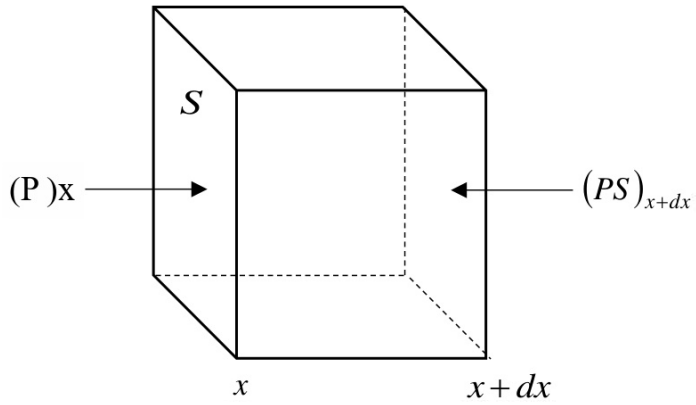


Figure I. 3. Control volume for deriving the Maxwell-Stefan relations.

When molecules of species A move through the mixture, they encounter other molecules that impede their motion. We observe that this situation closely resembles Poiseuille flow of a fluid in a tube. Consequently, we can apply Newton's second law, which states that the sum of forces acting on a system is equal to the variation of the momentum of that system.

In this control volume, molecules of species A may gain or lose momentum each time they collide with molecules of other species.

We assume that the only forces acting on the control volume are those due to pressure, which we assume to be constant throughout the system.

The collision rate between molecules of species A and molecules of species B depends on the number of molecules of species A per unit volume ($c_A = cx_A$) and the number of molecules of species B per unit volume ($c_B = cx_B$); thus, the number of $A-B$ collisions per unit volume and per unit time is proportional to $x_A x_B$.

The net force acting on the molecules of species A is equal to the difference between the pressure forces acting on the surfaces of the control volume, namely

$$F_{Sx} = (PS)_x - (PS)_{x+dx}$$

the partial pressure of species A is $P_A = x_A P$ and since the pressure is constant throughout the system, we can then write

$$F_{Sx} = (x_A PS)_x - (x_A PS)_{x+dx}$$

or even

$$F_{Sx} = (x_A PS)_x - (x_A PS)_x - \frac{d(x_A PS)_x}{dx}$$

$$F_{Sx} = -PS\frac{dx_A}{dx}$$

this net force is proportional to the collision rate and to the variation in the system's momentum, hence

$$-PS\frac{dx_A}{dx} \propto x_A x_B (V_{Ax} - V_{Bx})$$

Taking into account the other two forces F_{S_y} and F_{S_z} in the y and z directions, we obtain

$$-PS\,\vec{\nabla}x_A \propto x_A x_B\left(\vec{V}_A - \vec{V}_B\right)$$

To convert this proportionality into an equality, we introduce a coefficient f_{AB}, such that

$$-\vec{\nabla}x_A = \frac{f_{AB}}{PS}\,x_A x_B\left(\vec{V}_A - \vec{V}_B\right)$$

the term $\vec{\nabla}x_A$ is the force per unit volume of the mixture that attempts to pass the molecules of species A, with a relative velocity $(\vec{V}_A - \vec{V}_B)$, through the molecules of species A. The proportionality coefficient f_{AB} plays the role of a friction coefficient. Let us now introduce a new coefficient which we call the Maxwell-Stefan diffusivity D^*_{AB}, such that

$$D^*_{AB} = \frac{PS}{f_{AB}}$$

thus, for the species A

$$\vec{\nabla}x_A = -\frac{x_A x_B\left(\vec{V}_A - \vec{V}_B\right)}{D^*_{AB}} \qquad \text{(I.65)}$$

and for the species B

$$\vec{\nabla}x_B = -\frac{x_A x_B\left(\vec{V}_B - \vec{V}_A\right)}{D^*_{BA}} \qquad \text{(I.66)}$$

for a mixture containing N species, these relations are written

$$\vec{\nabla}x_\alpha = -\sum_{\beta=1}^{\beta=N}\frac{x_\alpha x_\beta\left(\vec{V}_\alpha - \vec{V}_\beta\right)}{D^*_{\alpha\beta}} \qquad \text{(I.67)}$$

and substituting the velocity vectors $\vec{V}_\alpha$ and $\vec{V}_\beta$ in terms of the molar fluxes $\vec{N}_\alpha$ and $\vec{N}_\beta$ using relation (I. 41)

$$\vec{N}_\alpha = c_\alpha \vec{V}_\alpha$$

$$\vec{\nabla} x_\alpha = -\sum_{\beta=1}^{\beta=N} \frac{\left(x_\alpha x_\beta \dfrac{\vec{N}_\beta}{c_\beta} - x_\alpha x_\beta \dfrac{\vec{N}_\alpha}{c_\alpha} \right)}{D^*_{\alpha\beta}}$$

$$\vec{\nabla} x_\alpha = -\sum_{\beta=1}^{\beta=N} \frac{\left(x_\alpha \vec{N}_\beta - x_\beta \vec{N}_\alpha \right)}{cD^*_{\alpha\beta}} \qquad \text{(I.68)}$$

and by substituting the relation

$$\vec{N}_\alpha = \vec{J}_\alpha + c_\alpha \vec{V}$$

$$\vec{\nabla} x_\alpha = -\sum_{\beta=1}^{\beta=N} \frac{\left(x_\alpha \left(\vec{J}_\beta + c_\beta \vec{V} \right) - x_\beta \left(\vec{J}_\alpha + c_\alpha \vec{V} \right) \right)}{cD^*_{\alpha\beta}}$$

$$\vec{\nabla} x_\alpha = -\sum_{\beta=1}^{\beta=N} \frac{\left(x_\alpha \vec{J}_\beta + x_\alpha c_\beta \vec{V} - x_\beta \vec{J}_\alpha - x_\beta c_\alpha \vec{V} \right)}{cD^*_{\alpha\beta}}$$

hence

$$\vec{\nabla} x_\alpha = -\sum_{\beta=1}^{\beta=N} \frac{\left(x_\alpha \vec{J}_\beta - x_\beta \vec{J}_\alpha \right)}{cD^*_{\alpha\beta}} \qquad \text{(I.69)}$$

Relations (I.68) and (I.69) are called the Maxwell-Stefan equations.

CHAPTER II

CONCENTRATION PROFILES IN STEADY STATE

In the z direction, equation (I. 62a)

$$\vec{N}_A = -cD_{AB}\vec{\nabla}x_A + x_A\left(\vec{N}_A + \vec{N}_B\right)$$

is written as

$$N_{Az} = -cD_{AB}\frac{dx_A}{dz} + x_A\left(N_{Az} + N_{Bz}\right)$$

or alternatively in terms of the mole fraction x_A of species A

$$\frac{dx_A}{dz} - \left(\frac{N_{Az} + N_{Bz}}{cD_{AB}}\right)x_A = -\frac{N_{Az}}{cD_{AB}} \qquad \text{(II.1)}$$

This is a first-order ordinary differential equation with a source term. The general solution to this differential equation without the source term is

$$x_{AG}\left(z\right) = C\, e^{\left(\frac{N_{Az}+N_{Bz}}{cD_{AB}}\right)z}$$

and the particular solution with the second member is

$$x_{AP}\left(z\right) = \frac{N_{Az}}{N_{Az} + N_{Bz}}$$

therefore, the global solution of the differential equation is

$$x_A\left(z\right) = x_{AG}\left(z\right) + x_{AP}\left(z\right) = C\, e^{\left(\frac{N_{Az}+N_{Bz}}{cD_{AB}}\right)z} + \frac{N_{Az}}{N_{Az} + N_{Bz}} \qquad \text{(II.2)}$$

where C is an integration constant. By assuming the boundary conditions

$$z = z_1,\ x_A\left(z_1\right) = x_{A1} \qquad \text{(II.3)}$$

we obtain

$$C = \left(x_{A1} - \frac{N_{Az}}{N_{Az} + N_{Bz}} \right) e^{-\left(\frac{N_{Az}+N_{Bz}}{cD_{AB}} \right) z_1}$$

by substituting this expression into Equation (II. 2) and after some algebraic manipulations, we obtain

$$N_{Az} + N_{Bz} = \frac{cD_{AB}}{z - z_1} \ln \frac{(N_{Az} + N_{Bz})\, x_A(z) - N_{Az}}{(N_{Az} + N_{Bz})\, x_{A1} - N_{Az}}$$

or even

$$N_{Az} = \frac{cD_{AB} N_{Az}}{(N_{Az} + N_{Bz})(z - z_1)} \ln \frac{(N_{Az} + N_{Bz})\, x_A(z) - N_{Az}}{(N_{Az} + N_{Bz})\, x_{A1} - N_{Az}} \qquad \text{(II.4)}$$

II. 1. Diffusion of a species A into a stationary species B

During the diffusion of species A into a stationary species B, the total molar flux of species B is zero

$$N_{Bz} = 0$$

Therefore, the total molar flux of species A, based on relation (II. 4), becomes

$$N_{Az} = \frac{cD_{AB}}{z - z_1} \ln \frac{N_{Az} x_A(z) - N_{Az}}{N_{Az} x_{A1} - N_{Az}} = \frac{cD_{AB}}{z - z_1} \ln \frac{1 - x_A(z)}{1 - x_{A1}}$$

$$N_{Az} = \frac{cD_{AB}}{z - z_1} \ln \frac{1 - x_A(z)}{1 - x_{A1}} \qquad \text{(II.5)}$$

at the distance $z = z_2$, this total molar flux is

$$N_{Az} = \frac{cD_{AB}}{z_2 - z_1} \ln \frac{1 - x_{A2}}{1 - x_{A1}} \qquad \text{(II.6)}$$

Since the system is in a steady state, the total molar flux remains constant; therefore, we can write

$$\frac{cD_{AB}}{z-z_1}\ln\frac{1-x_A(z)}{1-x_{A1}}=\frac{cD_{AB}}{z_2-z_1}\ln\frac{1-x_{A2}}{1-x_{A1}}$$

or else

$$\frac{1-x_A(z)}{1-x_{A1}}=\left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{\frac{z-z_1}{z_2-z_1}}$$

whereby the molar fraction profile $x_A(z)$ of species A

$$x_A(z)=1-(1-x_{A1})\left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{\frac{z-z_1}{z_2-z_1}} \qquad \text{(II.7)}$$

and based on the relation $x_B(z)=1-x_A(z)$, the profile of the molar fraction $x_B(z)$ of species B is

$$x_B(z)=x_{B1}\left(\frac{x_{B2}}{x_{B1}}\right)^{\frac{z-z_1}{z_2-z_1}} \qquad \text{(II.8)}$$

the average value of the mole fraction x_B of species B between positions z_1 and z_2 is

$$\overline{x_B}=\frac{1}{z_2-z_1}\int_{z_1}^{z_2}x_B(z)dz=\frac{1}{z_2-z_1}\int_{z_1}^{z_2}x_{B1}\left(\frac{x_{B2}}{x_{B1}}\right)^{\frac{z-z_1}{z_2-z_1}}dz$$

$$\eta=\frac{z-z_1}{z_2-z_1}$$

the mean value of the mole fraction $\overline{x_B}$ of species B becomes

$$\overline{x_B}=x_{B1}\int_0^1\left(\frac{x_{B2}}{x_{B1}}\right)^{\eta}d\eta$$

using the formula

$$\int a^{\eta} d\eta = \frac{a^{\eta}}{\ln a} + C$$

the mean value of the mole fraction x_B of species B is given by

$$\overline{x_B} = \frac{x_{B2} - x_{B1}}{\ln \frac{x_{B2}}{x_{B1}}} \qquad \text{(II.9)}$$

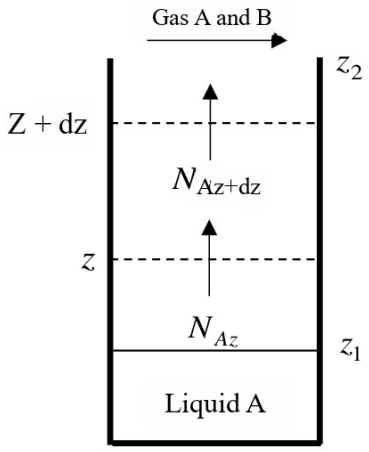


Figure II. 1. Diffusion of species A in a stationary gas containing species A and species B.

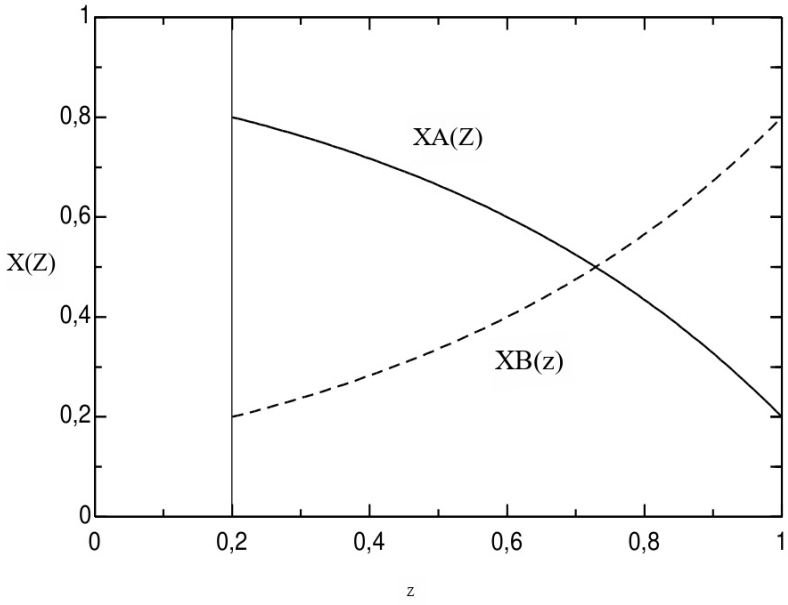


Figure II. 2. Molar concentration profiles of species A and of species B as a function of z.

We observe that the mean value of the mole fraction x_B of species B is nothing other than the logarithmic mean of the limiting mole fractions.

The total molar flux is

$$N_{Az} = \frac{cD_{AB}}{z_2 - z_1} \ln \frac{1 - x_{A2}}{1 - x_{A1}} = \frac{cD_{AB}}{z_2 - z_1} \ln \frac{x_{B2}}{x_{B1}}$$

and by substituting the mean value of the mole fraction $\overline{x_B}$, it follows

$$N_{Az} = \frac{cD_{AB}}{(z_2 - z_1)\overline{x_B}} (x_{B2} - x_{B1})$$

the term $x_{B2} - x_{B1}$ is nothing other than $x_{A1} - x_{A2}$, in fact

$$x_{B2} - x_{B1} = (1 - x_{A2}) - (1 - x_{A1}) = x_{A1} - x_{A2}$$

therefore

$$N_{Az} = \frac{cD_{AB}}{(z_2 - z_1)\overline{x_B}}(x_{A1} - x_{A2}) \qquad \text{(II.10)}$$

this relationship represents the evaporation rate as a function of the driving force $(x_{A1} - x_{A2})$.

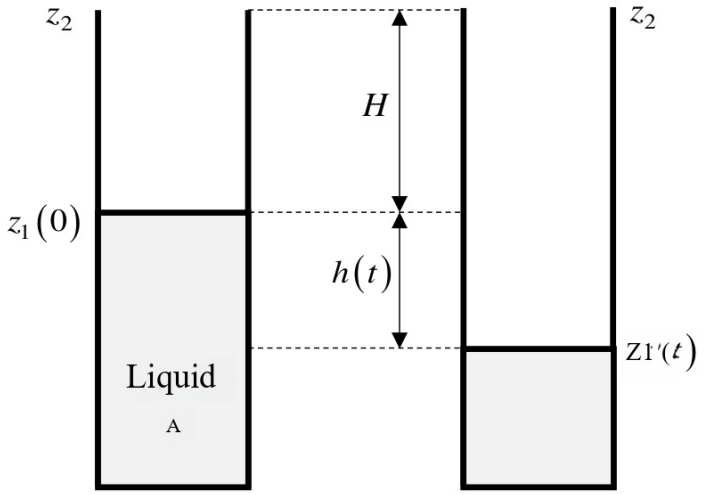


Figure II. 3. Evaporation of a liquid of species A in a gas containing species A.

Let us now study the variation of the height $z_1(t)$ of liquid A in a mixture of composition x_{A2}.

The evaporation rate of liquid A in the mixture is equal to the decrease in the mass of its column

$$-\frac{\rho_A S}{M_A}\frac{dz_1(t)}{dt}=\frac{cD_{AB}S}{(z_2-z_1(t))\overline{\overline{x_B}}}(x_{A1}-x_{A2})$$

where ρ_A and M_A are, respectively, the density and molar mass of the pure liquid, and S is the cross-sectional area of the tube containing the pure liquid A; after rearrangement, this relation becomes

$$(z_2-z_1(t))dz_1(t)=-\frac{cM_AD_{AB}(x_{A1}-x_{A2})}{\rho_A\overline{\overline{x_B}}}dt \qquad \text{(II.11)}$$

if we introduce the quantities

$$\Omega=\frac{cM_AD_{AB}(x_{A1}-x_{A2})}{\rho_A\overline{\overline{x_B}}},\ H=z_2-z_1(0),\ h(t)=z_1(0)-z_1(t)$$

et

$$H+h(t)=z_2-z_1(t),\ dh(t)=-dz_1(t)$$

Relation (II. 11) then reduces to the equation

$$(H+h(t))dh(t)=\Omega\,dt$$

by integrating the two sides separately

$$\int_0^{h(t)}(H+h(t))dh(t)=\int_0^{h(t)}\Omega\,dt$$

we obtain

$$Hh(t)+\frac{1}{2}h^2(t)=\Omega t$$

or even

$$h^2(t)+2Hh(t)-2\Omega t=0 \qquad \text{(II.12)}$$

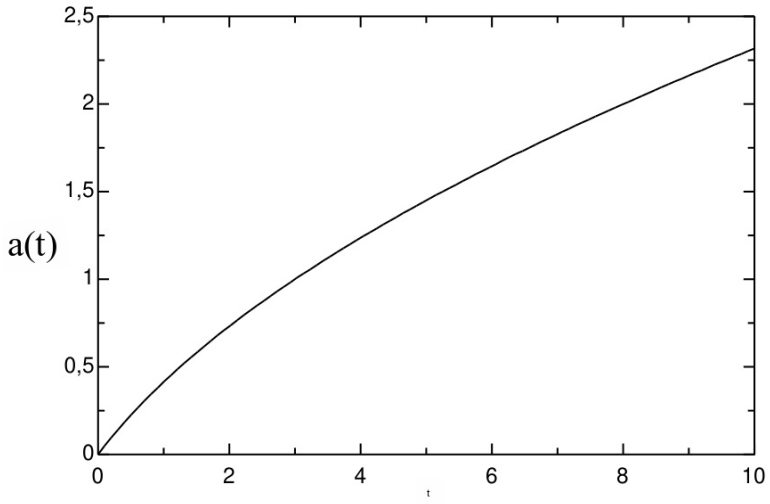


Figure II. 4. Variation of $z_a(t) = \frac{z_1(t) - z_1(0)}{z_1(0) - z_2}$ as a function of time.

The positive root of this quadratic algebraic equation is

$$h(t) = H\left[\sqrt{1 + \frac{2\Omega t}{H^2}} - 1\right]$$

if we substitute the expressions for $h(t)$, H, and Ω, we obtain

$$z_1(0) - z_1(t) = (z_2 - z_1(0))\left[\sqrt{1 + \frac{2cM_A D_{AB}(x_{A1} - x_{A2})t}{\rho_A \overline{x_B}(z_2 - z_1(0))^2}} - 1\right]$$

or in dimensionless form

$$\frac{z_1(t) - z_1(0)}{z_1(0) - z_2} = \left[\sqrt{1 + \frac{2cM_A D_{AB}(x_{A1} - x_{A2})\,t}{\rho_A \overline{x_B}(z_2 - z_1(0))^2}} - 1\right] \quad \text{(II.13)}$$

this relation can be used to determine the diffusion coefficient from the measurement of the liquid level in the tube as a function of time.

Consider diffusion in a stagnant gas film surrounding a liquid droplet using the balance method.

In steady state, the mass passing through a sphere of radius r is the same as that passing through a sphere of radius $r+dr$; mathematically, this is expressed by the equation

$$4\pi r^2 N_{Ar} = 4\pi (r+dr)^2 N_{Ar+dr} \qquad \text{(II.14)}$$

the total molar flux N_{Ar+dr} at radius $r+dr$ can be expanded using the Taylor formula and written in the form

$$N_{Ar+dr} = N_{Ar} + \frac{dN_{Ar}}{dr} dr$$

wherefrom

$$4\pi r^2 N_{Ar} = 4\pi \left(r^2 + 2rdr + dr^2\right)\left(N_{Ar} + \frac{dN_{Ar}}{dr} dr\right)$$

or even after simplification

$$r^2 \frac{dN_{Ar}}{dr} + 2rN_{Ar} = 0$$

it is easy to see that this relation can be written differently, namely

$$\frac{d}{dr}\left(r^2 N_{Ar}\right) = 0 \qquad \text{(II.15)}$$

since, according to Fick's law, the total molar flux N_{Ar} is

$$N_{Ar} = -\frac{cD_{AB}}{1-x_A(r)} \frac{dx_A(r)}{dr}$$

Equation (II. 15) becomes

$$\frac{d}{dr}\left(r^2\frac{cD_{AB}}{1-x_A(r)}\frac{dx_A(r)}{dr}\right)=0 \qquad \text{(II.16)}$$

suppose that the temperature across the gaseous film surrounding the liquid drop varies with the radius r according to the law

$$\frac{T(r)}{T_0}=\left(\frac{r}{r_1}\right)^n$$

where n is a real number. If we assume that the law of variation of the diffusion coefficient D_{AB} as a function of temperature $T(r)$ is

$$\frac{D_{AB}}{D_{AB,1}}=\left(\frac{T(r)}{T_1}\right)^{\frac{3}{2}}$$

then its variation as a function of the radius r is written

$$\frac{D_{AB}}{D_{AB,1}}=\left(\frac{r}{r_1}\right)^{\frac{3n}{2}}$$

by substituting this expression into Equation (II. 16) and since the concentration c is constant, we obtain the differential equation

$$\frac{d}{dr}\left(\frac{r^{\frac{3n+4}{2}}}{(1-x_A(r))}\frac{dx_A(r)}{dr}\right)=0 \qquad \text{(II.17)}$$

where the solution is

$$\frac{r^{\frac{3n+4}{2}}}{(1-x_A(r))}\frac{dx_A(r)}{dr}=C \qquad \text{(II.18)}$$

where C is a constant to be determined.

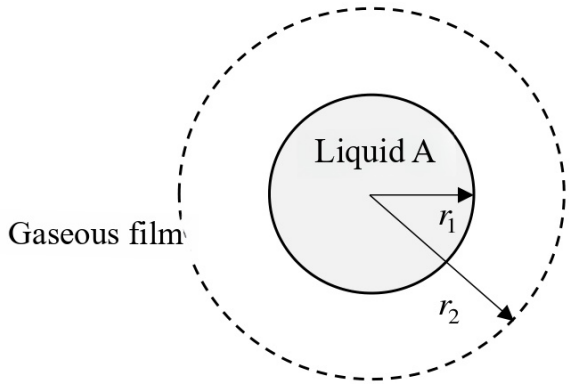


Figure II. 5. Evaporation of a liquid droplet of species A in a stagnant gas film.

The integration of this equation, after separation of variables, between x_{A1} and $x_A(r)$ for the mole fraction and between r_1 and r for the radius, is

$$\int_{x_{A1}}^{x_A(r)} \frac{dx_A(r)}{1-x_A(r)} = C\int_{r_1}^{r} r^{-\frac{3n+4}{2}}\,dr$$

this integral is easily calculated and yields the expression for the molar fraction $x_A(r)$ as a function of the radius r

$$\ln\frac{1-x_A(r)}{1-x_{A1}} = \frac{2C}{3n+2}\left(\frac{1}{r^{\frac{3n+2}{2}}} - \frac{1}{r_1^{\frac{3n+2}{2}}}\right) \qquad \text{(II.19)}$$

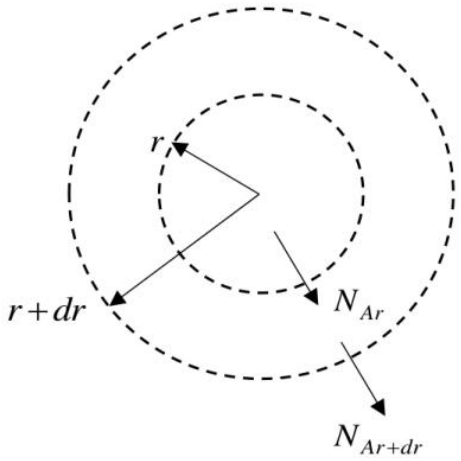


Figure II.6. Control surface for deriving the mass balance.

The integration of Equation (II. 18) this time, between x_{A1} and x_{A2} for the mole fraction and between r_1 and r_2 for the radius, is

$$\int_{x_{A1}}^{x_{A2}} \frac{dx_A(r)}{1-x_A(r)} = C\int_{r_1}^{r_2} r^{-\frac{3n+4}{2}}\,dr$$

hence

$$\ln\frac{1-x_{A2}}{1-x_{A1}} = \frac{2C}{3n+2}\left(\frac{1}{r_2^{\frac{3n+2}{2}}} - \frac{1}{r_1^{\frac{3n+2}{2}}}\right) \qquad \text{(II.20)}$$

Eliminating the constant C between relations (II.19) and (II.20), we arrive at the relation

$$\frac{\ln\dfrac{1-x_A(r)}{1-x_{A1}}}{\dfrac{1}{r^{\frac{3n+2}{2}}} - \dfrac{1}{r_1^{\frac{3n+2}{2}}}} = \frac{\ln\dfrac{1-x_{A2}}{1-x_{A1}}}{\dfrac{1}{r_2^{\frac{3n+2}{2}}} - \dfrac{1}{r_1^{\frac{3n+2}{2}}}}$$

which after simplification becomes

$$\frac{1-x_A(r)}{1-x_{A1}}=\left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{\frac{\alpha(r)}{\beta}} \qquad \text{(II.21)}$$

where $\alpha(r)$ and β are

$$\alpha(r)=\frac{1}{r^{\frac{3n+2}{2}}}-\frac{1}{r_1^{\frac{3n+2}{2}}},\ \beta=\frac{1}{r_2^{\frac{3n+2}{2}}}-\frac{1}{r_1^{\frac{3n+2}{2}}}$$

the total molar flux N_{Ar} through any sphere of radius r between r_1 and r_2 is

$$N_{Ar}(r_1)=\left[-\frac{cD_{AB,1}r^{\frac{3n}{2}}}{(1-x_A(r))r_1^{\frac{3n}{2}}}\frac{dx_A(r)}{dr}\right]_{r=r_1}$$

the substitution of the expression for the derivative of the mole fraction $\frac{dx_A(r)}{dr}$ calculated from relation (II. 21) for $r=r_1$, we obtain

$$N_{Ar}(r_1)=\frac{3n+2}{2}\frac{cD_{AB,1}}{r_1^{\frac{3n+4}{2}}\left(\frac{1}{r_1^{\frac{3n+2}{2}}}-\frac{1}{r_2^{\frac{3n+2}{2}}}\right)}\ln\frac{1-x_{A2}}{1-x_{A1}} \qquad \text{(II.21)}$$

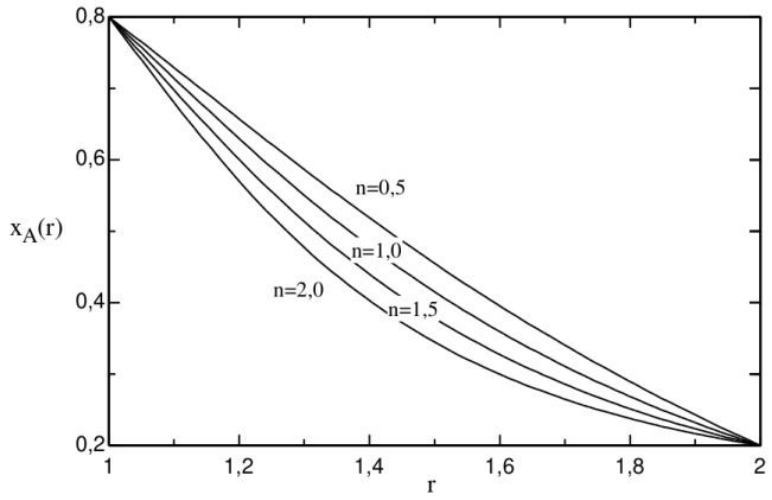


Figure II. 7. Molar fraction profiles $x_A(r)$ as a function of radius r for different values of n.

II. 2. Equimolar Counter-diffusion

In the case of equimolar diffusion, we have

$$N_{Az} = -N_{Bz}$$

It is clear that relation (II. 4) cannot be used because it contains an indeterminacy; for this reason, we must use the relation

$$N_{Az} = -cD_{AB}\frac{dx_A(z)}{dz}$$

which, after integration between the distances $z = z_1$ and $z = z$, leads to the expression

$$x_A(z) - x_{A1} = -\frac{N_{Az}}{cD_{AB}}(z - z_1) \qquad \text{(II.22)}$$

whereby the total molar flux of species A

$$N_{Az} = cD_{AB}\frac{x_{A1} - x_A(z)}{z - z_1}$$

at the distance $z = z_2$, this total molar flux is

$$N_{Az} = cD_{AB}\frac{x_{A1} - x_{A2}}{z_2 - z_1}$$

since the system is in a steady state, we always have the constancy of the total molar flux, and thus

$$cD_{AB}\frac{x_{A1} - x_A(z)}{z - z_1} = cD_{AB}\frac{x_{A1} - x_{A2}}{z_2 - z_1}$$

from this equality, the profile of the molar fraction $x_A(z)$ of species A as a function of distance z is given by

$$x_A(z) = x_{A1} + (x_{A2} - x_{A1})\frac{z - z_1}{z_2 - z_1} \qquad \text{(II.23)}$$

as for the molar fraction profile $x_B(z)$ of species B as a function of distance z, it is given by the expression

$$x_B(z) = x_{B1} + (x_{B2} - x_{B1})\frac{z - z_1}{z_2 - z_1} \qquad \text{(II.24)}$$

II. 3. Diffusion with Heterogeneous Chemical Reaction

Consider a catalytic reactor in which the homogeneous chemical reaction takes place

$$2A \rightarrow B$$

We will assume that each catalytic particle is surrounded by a stagnant gas containing species A, which instantaneously and irreversibly converts to species B according to the reaction $2A \rightarrow B$, after which these two species exit the reactor in a gaseous stream now containing both species A and B.

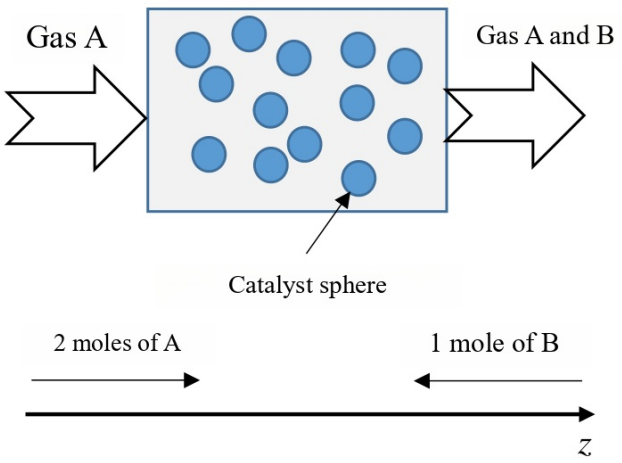


Figure II. 8. Schematic of the catalytic reactor and movement of species A and B.

In this situation, for every mole of species B moving in the negative z direction, there are two moles of species A moving in the positive z direction. Consequently, in the steady-state regime, we can write, between the total molar fluxes of species A and B, the relation

$$N_{Bz} = -\frac{1}{2} N_{Az} \tag{II.25}$$

the total molar flux of species A is

$$N_{Az} = -cD_{AB} \frac{dx_A(z)}{dz} + x_A(z)(N_{Az} + N_{Bz})$$

and substituting relation (II. 25), we obtain

$$N_{Az} = -cD_{AB} \frac{dx_A(z)}{dz} + x_A(z)\left(N_{Az} - \frac{1}{2} N_{Az}\right)$$

$$\frac{dx_A(z)}{1 - \frac{1}{2} x_A(z)} = -\frac{N_{Az}}{cD_{AB}} dz \tag{II.26}$$

the integration of this relation between the distances $z=0$ and $z=\delta$ is

$$\int_{x_{A0}}^{0} \frac{dx_A(z)}{1-\frac{1}{2}x_A(z)} = -\frac{N_{Az}}{cD_{AB}} \int_0^{\delta} dz$$

$$\left[-2\ln\left(1-\frac{1}{2}x_A(z)\right)\right]_{x_{A0}}^{0} = -\frac{N_{Az}}{cD_{AB}}[z]_0^{\delta}$$

let

$$2\ln\left(1-\frac{1}{2}x_{A0}\right) = -\frac{N_{Az}}{cD_{AB}}\delta \qquad \text{(II.27)}$$

by integrating again the relation (II.26) between the distances $z=0$ and $z=z$, we obtain

$$\left[-2\ln\left(1-\frac{1}{2}x_A(z)\right)\right]_{x_{A0}}^{x_A(z)} = -\frac{N_{Az}}{cD_{AB}}[z]_0^{z}$$

$$2\ln\left(1-\frac{1}{2}x_{A0}\right) - 2\ln\left(1-\frac{1}{2}x_A(z)\right) = -\frac{N_{Az}}{cD_{AB}}z \qquad \text{(II.28)}$$

since the ratio $\frac{N_{Az}}{cD_{AB}}$ is constant, we can write

$$\frac{\ln\left(1-\frac{1}{2}x_{A0}\right)}{\delta} = \frac{\ln\left(1-\frac{1}{2}x_{A0}\right) - \ln\left(1-\frac{1}{2}x_A(z)\right)}{z}$$

$$\ln\left(1-\frac{1}{2}x_{A0}\right)^{\frac{z}{\delta}} = \ln\frac{1-\frac{1}{2}x_{A0}}{1-\frac{1}{2}x_A(z)}$$

$$x_A(z) = 2 - 2\left(1 - \frac{1}{2}x_{A0}\right)^{1-\frac{z}{\delta}} \qquad \text{(II.29)}$$

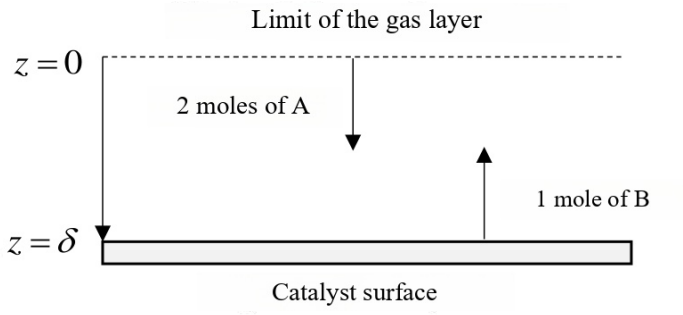


Figure II. 9. Schematic of the catalyst surface where the reaction $2A \rightarrow B$ takes place.

The total molar flux of species A is

$$N_{Az}(z=0) = -\frac{cD_{AB}}{1 - \frac{1}{2}x_A(0)}\left[\frac{dx_A(z)}{dz}\right]_{z=0}$$

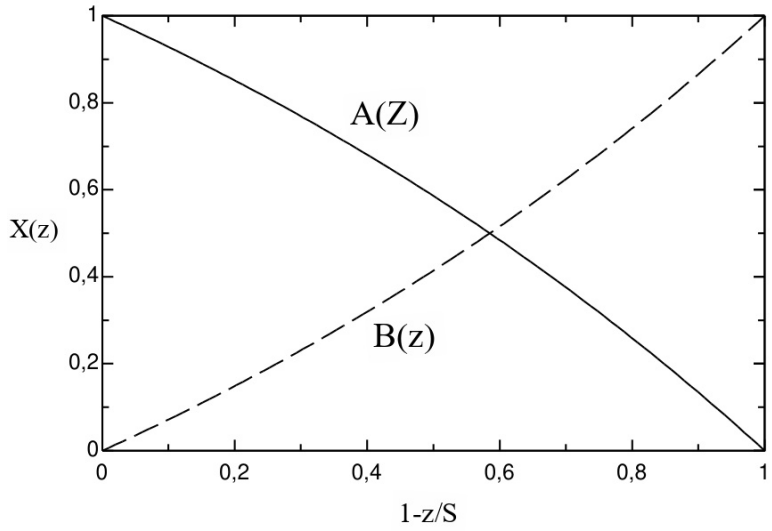


Figure II. 10. Mole fraction profiles $x_A(z)$ and $x_B(z)$ as a function of z for the reaction $2A \rightarrow B$.

the derivative of the molar fraction $x_A(z)$ with respect to the distance z is

$$\frac{dx_A(z)}{dz} = \frac{2\ln\left(1-\frac{1}{2}x_{A0}\right)}{\delta}\left(1-\frac{1}{2}x_{A0}\right)^{1-\frac{z}{\delta}}$$

substituting into the expression for the total molar flux at $z=0$ leads to

$$N_{Az}(z=0) = -\frac{cD_{AB}}{1-\frac{1}{2}x_{A0}}\frac{2\left(1-\frac{1}{2}x_{A0}\right)\ln\left(1-\frac{1}{2}x_{A0}\right)}{\delta}$$

or even

$$N_{Az}(z=0)=\frac{2cD_{AB}}{\delta}\left(-\ln\left(1-\frac{1}{2}x_{A0}\right)\right)$$

therefore, the total molar flux is

$$N_{Az}(z=0)=\frac{2cD_{AB}}{\delta}\ln\frac{1}{1-\frac{1}{2}x_{A0}} \qquad \text{(II.30)}$$

this quantity can be interpreted as the reaction rate per unit surface area of the catalyst.

Now, suppose that the reaction $2A \rightarrow B$ is not instantaneous on the catalyst surface. Assume, in this case, that the rate of disappearance of species A on the catalyst surface is proportional to the concentration of species A in the liquid near the interface

$$N_{Az}=k_1''cx_A \qquad \text{(II.31)}$$

where k_1'' is the first-order reaction constant.

Since the regime is steady, the molar flux of species A crossing the unit surface at position z is the same as that crossing the unit surface at position $z+dz$, from which the mass balance

$$N_{Az}S = N_{Az+dz}S$$

with the Taylor expansion applied to the molar flux N_{Az+dz}, we obtain

$$N_{Az}S=\left(N_{Az}+\frac{dN_{Az}}{dz}dz\right)S$$

i.e.

$$\frac{dN_{Az}}{dz}=0 \qquad \text{(II.32)}$$

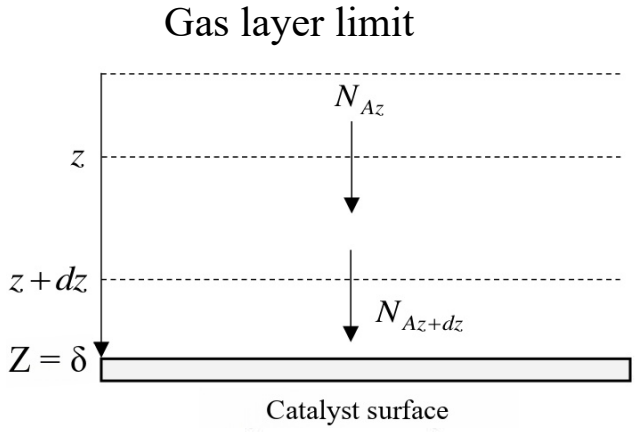


Figure II. 11. Schematic for deriving the mass balance of the reaction $2A \rightarrow B$.

the molar flux N_{Az} of species A, from equation (II.26), is

$$N_{Az} = -\frac{cD_{AB}}{1-\frac{1}{2}x_A(z)}\frac{dx_A(z)}{dz}$$

if we substitute this expression into equation (II.32), we obtain the ordinary differential equation

$$\frac{d}{dz}\left(\frac{1}{1-\frac{1}{2}x_A(z)}\frac{dx_A(z)}{dz}\right)=0$$

whose boundary conditions are

$$z=0,\ x_A(z)=x_{A0}$$

$$z=\delta,\ x_A(z)=\frac{N_{Az}}{k_1''c}$$

the solution to this ordinary differential equation is

$$-2\ln\left(1-\frac{1}{2}x_A(z)\right)=C_1 z+C_2$$

the integration constants C_1 and C_2 are obtained from the boundary conditions, and are

$$C_1=\frac{2\ln\left(1-\frac{1}{2}x_{A0}\right)-2\ln\left(1-\frac{1}{2}\frac{N_{Az}}{k_1''c}\right)}{\delta}$$

$$C_2=-2\ln\left(1-\frac{1}{2}x_{A0}\right)$$

therefore, the molar fraction $x_A(z)$ of species A is written

$$1-\frac{1}{2}x_A(z)=\left(1-\frac{1}{2}\frac{N_{Az}}{k_1''c}\right)^{\frac{z}{\delta}}\left(1-\frac{1}{2}x_{A0}\right)^{1-\frac{z}{\delta}} \qquad \text{(II.33)}$$

$$N_{Az}(z=0)=-\frac{cD_{AB}}{1-\frac{1}{2}x_A(0)}\left[\frac{dx_A(z)}{dz}\right]_{z=0}$$

the mole fraction $x_A(z)$ of species A, from relation (II.33), is given by

$$x_A(z)=2-2\left(1-\frac{1}{2}\frac{N_{Az}}{k_1''c}\right)^{\frac{z}{\delta}}\left(1-\frac{1}{2}x_{A0}\right)^{1-\frac{z}{\delta}}$$

and its derivative at $z=0$ is

$$\left[\frac{dx_A(z)}{dz}\right]_{z=0}=\frac{2}{\delta}\left(1-\frac{1}{2}x_{A0}\right)\left[\ln\left(1-\frac{1}{2}\frac{N_{Az}}{k_1''c}\right)-\ln\left(1-\frac{1}{2}x_{A0}\right)\right]$$

which gives the molar flux N_{Az} of species A the expression

$$N_{Az}(z=0)=\frac{2cD_{AB}}{\delta}\ln\frac{1-\frac{1}{2}\frac{N_{Az}}{k_1''c}}{1-\frac{1}{2}x_{A0}} \qquad \text{(II.34)}$$

For very large k_1'' (i.e., $\frac{1}{2}\frac{N_{Az}}{k_1''c}$ is very small), the Taylor expansion of the term $\ln\left(1-\frac{1}{2}\frac{N_{Az}}{k_1''c}\right)$ using the formula

$$\ln(1-x)=-x-\frac{x^2}{2}+\cdots$$

leads us to the relation

$$\ln\left(1-\frac{1}{2}\frac{N_{Az}}{k_1''c}\right)=-\frac{1}{2}\frac{N_{Az}}{k_1''c}$$

by substituting it into the expression for the molar flux N_{Az} of species A, we obtain

$$N_{Az}(z=0)=\frac{2cD_{AB}}{\delta}\left[-\frac{1}{2}\frac{N_{Az}}{k_1''c}-\ln\left(1-\frac{1}{2}x_{A0}\right)\right]$$

or again

$$N_{Az}(z=0)=\frac{2cD_{AB}}{\delta\left(1+\frac{D_{AB}}{k_1''\delta}\right)}\ln\frac{1}{1-\frac{1}{2}x_{A0}} \qquad \text{(II.35)}$$

The term $\frac{D_{AB}}{k_1''\delta}$ illustrates the effect of the surface reaction kinetics of the catalyst on the diffusion-reaction process.

The inverse of the term $\frac{D_{AB}}{k_1'' \delta}$ is called the second number of Damköhler Da_{II}

$$Da_{II} = \frac{k_1'' \delta}{D_{AB}}$$

II. 4. Diffusion with Homogeneous Chemical Reaction

Consider a container containing a liquid B in which a gas A dissolves and diffuses isothermally, undergoing a first-order homogeneous irreversible reaction such that

$$A + B \rightarrow AB$$

the mass balance, in steady state, of species A in the control volume $S\,dz$ is

$$N_{Az} S - k_1''' c_A S\, dz = N_{Az+dz} S$$

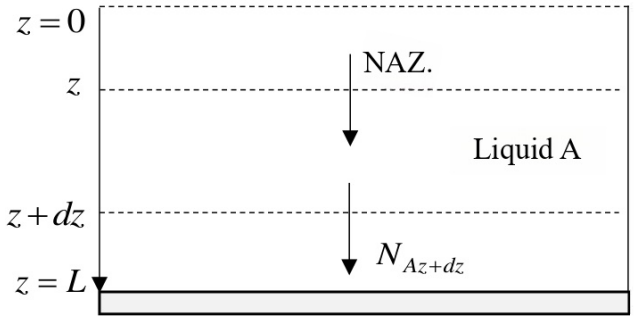


Figure II. 12. Schematic for deducing the mass balance of the reaction $A + B \rightarrow AB$.

Using a Taylor series expansion, for the molar flux N_{A_z+dz}, we obtain

$$N_{Az}S - k_1'''c_A S\,dz = \left(N_{Az} + \frac{dN_{Az}}{dz}dz\right)S$$

$$N_{Az}S - k_1'''c_A S\,dz = N_{Az}S + \frac{dN_{Az}}{dz}S\,dz$$

hence

$$\frac{dN_{Az}}{dz} + k_1'''c_A = 0$$

by substituting the molar flux N_{Az} derived from Fick's law

$$N_{Az} = -D_{AB}\frac{dc_A}{dz}$$

we obtain, for the concentration of species A, the ordinary differential equation

$$D_{AB}\frac{d^2c_A}{dz^2} - k_1'''c_A = 0 \qquad \text{(II.36)}$$

with the boundary conditions

$$z = 0,\ c_A(z) = c_{A0}$$

$$z = L,\ \frac{dc_A}{dz} = 0$$

if we introduce the dimensionless quantities

$$\xi = \frac{z}{L},\ \Gamma(\xi) = \frac{c_A}{c_{A0}}$$

in the ordinary differential equation (II. 36), we obtain

$$D_{AB}\frac{d^2\left(c_{A0}\Gamma(\xi)\right)}{d(L\xi)^2}-k_1'''\left(c_{A0}\Gamma(\xi)\right)=0$$

i.e.

$$\frac{d^2\Gamma(\xi)}{d\xi^2}-\Phi^2\Gamma(\xi)=0 \qquad \text{(II.37)}$$

where the constant parameter Φ is

$$\Phi^2=\frac{k_1'''L^2}{D_{AB}}$$

for the function $\Gamma(\xi)$, the boundary conditions are written as

$$\xi=0,\ \Gamma(\xi)=1$$

$$\xi=1,\ \frac{d\Gamma(\xi)}{d\xi}=0$$

the solution to the ordinary differential equation (II. 37) is

$$\Gamma(\xi)=C_1e^{\Phi\xi}+C_2e^{-\Phi\xi} \qquad \text{(II.38)}$$

the integration constants C_1 and C_2 are determined from the boundary conditions for the function $\Gamma(\xi)$ and are

$$C_1=\frac{e^{-\Phi\xi}}{2\cosh\Phi},\ C_2=\frac{e^{\Phi\xi}}{2\cosh\Phi}$$

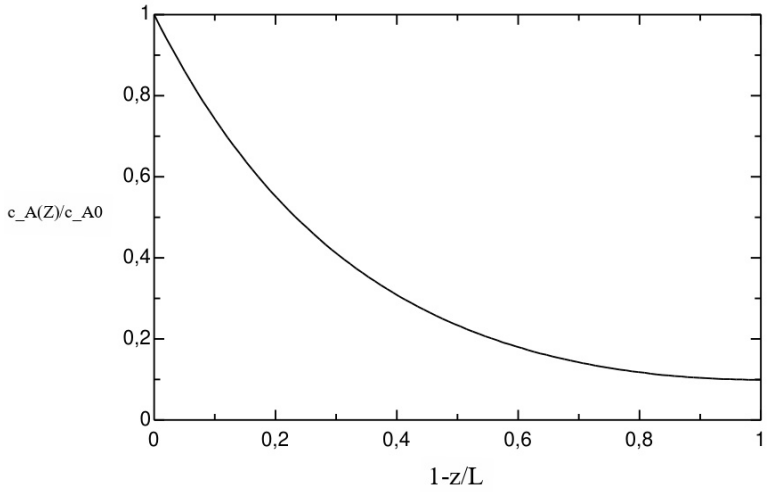


Figure II. 13. Molar concentration profile $\frac{c_A(z)}{c_{A0}}$ as a function of z.

after substituting these integration constants into the solution (II.38), we obtain for the function $\Gamma(\xi)$ the expression

$$\Gamma(\xi) = \frac{\cosh\Phi(1-\xi)}{\cosh\Phi}$$

which can be written in original variables in the form

$$\frac{c_A(z)}{c_{A0}} = \frac{\cosh\sqrt{\frac{k_1'''L^2}{D_{AB}}}\left(1-\frac{z}{L}\right)}{\cosh\sqrt{\frac{k_1'''L^2}{D_{AB}}}} \qquad \text{(II.39)}$$

the molar flux N_{Az} of species A is

$$N_{Az}(z=0) = -D_{AB}\left[\frac{dc_A(z)}{dz}\right]_{z=0}$$

using expression (II. 39), we find

$$N_{Az}(z=0) = \sqrt{D_{AB}k_1'''}\, c_{A0} \tanh\sqrt{\frac{k_1'''L^2}{D_{AB}}} \qquad \text{(II.40)}$$

II. 5. Absorption of a Gas by a Falling Liquid

Consider the absorption of a gas of species $\boldsymbol{A}$ in a liquid film $\boldsymbol{B}$ in laminar and two-dimensional flow over a vertical surface under the effect of gravity. Before beginning the calculations, let us adopt the following assumptions:

a) Gas diffusion in the liquid film does not affect its velocity profile,

b) The solubility of the gas in the liquid film is very low, so that the viscosity of the liquid does not change during the absorption process,

c) Gas diffusion in the liquid film is very slow, which leads us to assume that the penetration depth of the gas in the liquid film is very small compared to the thickness of the liquid film

The movement of the liquid film $\boldsymbol{B}$ on the vertical plane is governed by the continuity equation

$$\frac{\partial V_z(z,x)}{\partial z} + \frac{\partial V_x(z,x)}{\partial x} = 0 \qquad \text{(II.41)}$$

and the equation of motion

$$V_z(z,x)\frac{\partial V_z(z,x)}{\partial z} + V_x(z,x)\frac{\partial V_z(z,x)}{\partial x} = g + \nu\frac{\partial^2 V_z(z,x)}{\partial x^2} \qquad \text{(II.42)}$$

subject to boundary conditions

$$x=0,\ \frac{dV_z(x)}{dx} = 0 \qquad \text{(II.42a)}$$

$$x = \delta\,,\ V_z(x) = 0 \qquad \text{(II.42b)}$$

the velocity vector $\vec{V}(z,x)$ of the two-dimensional flow in the (z,x) plane is

$$\vec{V}(z,x) = V_z(z,x)\vec{k} + V_x(z,x)\vec{i}$$

but since the liquid film $\boldsymbol{B}$ is very thin, it is legitimate to assume that the component $V_x(z,x)$ of the velocity vector $\vec{V}(z,x)$ is zero, hence

$$V_x(z,x) = 0$$

this leads us, starting from the continuity equation (II. 41), to write

$$\frac{\partial V_z(z,x)}{\partial z} = 0$$

this relation shows that the $V_z(z,x)$ component of the velocity vector $\vec{V}(z,x)$ will depend only on the x coordinate

$$V_z(z,x) = V_z(x)$$

With these approximations, the equation of motion (II. 42) of the liquid film $\boldsymbol{B}$ reduces to the equation

$$\nu \frac{d^2 V_z(x)}{dx^2} + g = 0$$

whose solution is

$$V_z(x) = -\frac{g}{2\nu}x^2 + C_1 x + C_2$$

where C_1 and C_2 are integration constants to be determined from the boundary conditions (II. 42a) and (II. 42b), in this case

$$C_1 = 0\,,\ C_2 = \frac{g\delta^2}{2\nu}$$

Thus, we obtain for the velocity profile $V_z(x)$ the expression

$$V_z(x) = V_{\max}\left(1 - \left(\frac{x}{\delta}\right)^2\right) \qquad \text{(II.43)}$$

where the maximum speed $V_{\max}$ is

$$V_{\max} = \frac{g\delta^2}{2\nu}$$

Since the regime is steady-state, the mass balance for species A is written as

$$N_{Az}Wdx + N_{Ax}Wdz = N_{Az+dz}Wdx + N_{Ax+dx}Wdz$$

The use of a Taylor series expansion for the molar fluxes N_{Az+dz} and N_{Ax+dx} yields

$$N_{Az}Wdx + N_{Ax}Wdz = \left(N_{Az} + \frac{dN_{Az}}{dz}dz\right)Wdx + \left(N_{Ax} + \frac{dN_{Ax}}{dz}dx\right)Wdz,$$

relation, which after simplification becomes

$$\frac{\partial N_{Az}}{\partial z} + \frac{\partial N_{Ax}}{\partial x} = 0 \qquad \text{(II.44)}$$

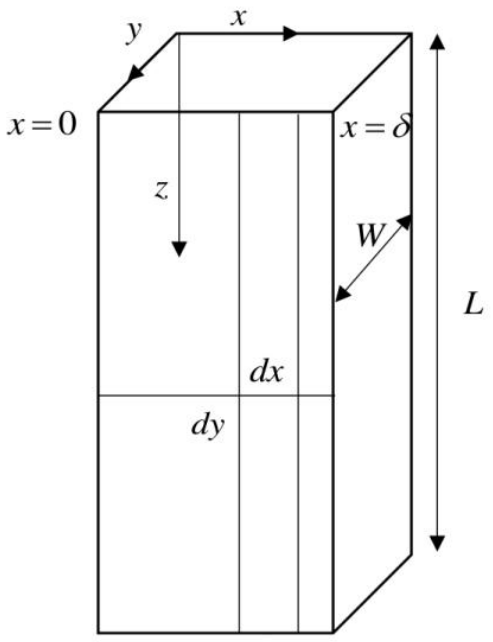


Figure II. 14. Absorption of gas A in a liquid film B.

under the assumption of a constant concentration c, the molar flux N_{Az} of species A in the z direction, in accordance with equation (I. 62a), is given by

$$N_{Az} = -D_{AB}\frac{\partial c_A(z,x)}{\partial z} + c_A(z,x)\,V_z^*(x)$$

since the transport of species A in the z direction occurs essentially by convection and that for dilute solutions $V_z^*(x) = V_z(x)$, this equation simplifies to

$$N_{Az} = c_A(z,x)\,V_z(x) \qquad \text{(II.45)}$$

As for the transfer of species A in the x direction, it occurs by diffusion, meaning that there is practically no convective transfer due to the low solubility of species A in liquid B. Consequently, the molar flux N_{Az} of species A in the x direction is given by

$$N_{Ax} = -D_{AB}\frac{\partial c_A(z,x)}{\partial x} \qquad \text{(II.46)}$$

by substituting relations (II. 43), (II. 45) and (II. 46) into equation (II. 44), we obtain the partial differential equation

$$V_{\max}\left(1-\left(\frac{x}{\delta}\right)^2\right)\frac{\partial c_A(z,x)}{\partial z} = D_{AB}\frac{\partial^2 c_A(z,x)}{\partial x^2} \qquad \text{(II.47)}$$

with the boundary conditions

$$z = 0,\ c_A(z,x) = 0 \qquad \text{(II.47a)}$$

$$x = 0,\ c_A(z,x) = c_{A0} \qquad \text{(II.47b)}$$

$$x = \delta,\ \frac{\partial c_A(z,x)}{\partial x} = 0 \qquad \text{(II.47c)}$$

The first boundary condition reflects the fact that liquid B is pure upon entering at the top of the vertical surface; the second boundary condition stipulates that at the liquid-gas interface, the concentration c_A of species A is determined by its solubility c_{A0} in liquid B; and the third boundary condition indicates that species A cannot cross the vertical surface.

According to the hypothesis of a short contact time, species A penetrates only over a short distance from the liquid-gas interface; consequently, species A will perceive the liquid as moving at speed $V_{\max}$ and the vertical surface as being located at an infinite distance. With these simplifying hypotheses, we can reformulate equations (II. 47), (II. 47a), (II. 47b) and (II. 47c) and write

$$V_{\max} \frac{\partial c_A(z,x)}{\partial z} = D_{AB} \frac{\partial^2 c_A(z,x)}{\partial x^2} \qquad \text{(II.48)}$$

$$z = 0,\ c_A(z,x) = 0 \qquad \text{(II.48a)}$$

$$x = 0,\ c_A(z,x) = c_{A0} \qquad \text{(II.48b)}$$

$$x = \infty,\ c_A(z,x) = 0 \qquad \text{(II.48c)}$$

if we introduce the dimensionless variable

$$\eta = \frac{x}{\sqrt{\frac{4D_{AB}z}{V_{\max}}}} \qquad \text{(II.49)}$$

and we calculate the partial derivatives $\frac{\partial c_A(z,x)}{\partial z}$ and $\frac{\partial^2 c_A(z,x)}{\partial x^2}$ as a function of this new dimensionless variable η, we obtain

$$\frac{\partial c_A(z,x)}{\partial z} = \frac{dc_A(z,x)}{d\eta}\frac{\partial \eta}{\partial z},\ \frac{\partial \eta}{\partial z} = \frac{\partial}{\partial z}\left(\frac{x}{\sqrt{\frac{4D_{AB}z}{V_{\max}}}}\right) = -\frac{1}{2}\frac{\eta}{z}$$

$$\frac{\partial c_A(z,x)}{\partial z} = -\frac{1}{2}\frac{\eta}{z}\frac{dc_A(z,x)}{d\eta} \qquad \text{(II.50)}$$

$$\frac{\partial c_A(z,x)}{\partial x} = \frac{dc_A(z,x)}{d\eta}\frac{\partial \eta}{\partial x},\ \frac{\partial \eta}{\partial x} = \frac{\partial}{\partial z}\left(\frac{x}{\sqrt{\frac{4D_{AB}z}{V_{\max}}}}\right) = \frac{1}{\sqrt{\frac{4D_{AB}z}{V_{\max}}}}$$

$$\frac{\partial c_A(z,x)}{\partial x} = \frac{1}{\sqrt{\frac{4D_{AB}z}{V_{\max}}}}\frac{dc_A(z,x)}{d\eta}$$

$$\frac{\partial^2 c_A(z,x)}{\partial x^2} = \frac{1}{\frac{4D_{AB}z}{V_{\max}}}\frac{d^2 c_A(z,x)}{d\eta^2} \qquad \text{(II.51)}$$

substituting relations (II. 50) and (II. 51) into equation (II. 48), we arrive at the equation

$$-\frac{1}{2}\frac{\eta}{z}\frac{dc_A(z,x)}{d\eta} = \frac{D_{AB}}{V_{\max}}\frac{1}{\frac{4D_{AB}z}{V_{\max}}}\frac{d^2 c_A(z,x)}{d\eta^2} \qquad \text{(II.52)}$$

with the dimensionless concentration $\Sigma(\eta)$ defined by

$$\Sigma(\eta) = \frac{c_A(z,x)}{c_{A0}}$$

the differential equation (II. 52) becomes

$$\frac{d^2\Sigma(\eta)}{d\eta^2} + 2\eta\frac{d\Sigma(\eta)}{d\eta} = 0 \qquad \text{(II.53)}$$

$$\eta = 0,\ \Sigma(\eta) = 1 \qquad \text{(II.53a)}$$

$$\eta = \infty,\ \Sigma(\eta) = 0 \qquad \text{(II.53b)}$$

to reduce the order of the ordinary differential equation (II. 53), we introduce the function $\overline{\Sigma}(\eta)$ such that

$$\overline{\Sigma}(\eta) = \frac{d\Sigma(\eta)}{d\eta} \qquad \text{(II.54)}$$

hence

$$\frac{d\overline{\Sigma}(\eta)}{d\eta} + 2\eta\overline{\Sigma}(\eta) = 0$$

where the solution is

$$\overline{\Sigma}(\eta) = C_1 e^{-\eta^2}$$

beyond

$$\frac{d\Sigma(\eta)}{d\eta} = C_1 e^{-\eta^2}$$

and thus

$$\Sigma(\eta) = C_1\int_0^{\eta} e^{-\eta^2}d\eta + C_2 \qquad \text{(II.55)}$$

where C_1 and C_2 are integration constants that we determine from the boundary conditions (II. 53a) and (II. 53b)

$$C_1\int_0^0 e^{-\eta^2}d\eta + C_2 = 1,\ C_1\int_0^\infty e^{-\eta^2}d\eta + C_2 = 0$$

from these relations, it follows

$$C_1 = -\frac{1}{\int_0^\infty e^{-\eta^2}d\eta},\ C_2 = 1$$

by substituting the expressions for these integration constants into equation (II. 55), we obtain

$$\Sigma(\eta) = 1 - \frac{\int_0^\eta e^{-\eta^2}d\eta}{\int_0^\infty e^{-\eta^2}d\eta} = 1 - \frac{2}{\sqrt{\pi}}\int_0^\eta e^{-\eta^2}d\eta \qquad \text{(II.56)}$$

from the definition of the error function $\mathrm{erf}(\eta)$

$$erf(\eta) = \frac{2}{\sqrt{\pi}}\int_0^\eta e^{-\eta^2}d\eta$$

Equation (II. 56) can be written as

$$\Sigma(\eta) = 1 - erf(\eta)$$

it follows that

$$\frac{c_A(z,x)}{c_{A0}} = 1 - erf\left(\frac{x}{\sqrt{\frac{4D_{AB}z}{V_{\max}}}}\right) \qquad \text{(II.57)}$$

the molar flux N_{Ax} of species A at the liquid-gas interface is

$$N_{Ax}(x=0) = -D_{AB}\left(\frac{\partial c_A(z,x)}{\partial x}\right)_{x=0}$$

with the derivative of the error function given by the formula

$$\frac{d(erf(\eta))}{d\alpha} = \frac{2}{\sqrt{\pi}} \frac{d\eta}{d\alpha} e^{-\eta^2}$$

we obtain for the concentration gradient $c_A(z,x)$ the expression

$$\frac{\partial c_A(z,x)}{\partial x} = -\frac{2c_{A0}}{\sqrt{\pi}} \frac{d\left(\frac{x}{\sqrt{\frac{4D_{AB}z}{V_{\max}}}} \right)}{dx} e^{-\frac{x^2}{\frac{4D_{AB}z}{V_{\max}}}}$$

$$\frac{\partial c_A(z,x)}{\partial x} = -\frac{2c_{A0}}{\sqrt{\pi}} \frac{e^{-\frac{x^2}{\frac{4D_{AB}z}{V_{\max}}}}}{\sqrt{\frac{4D_{AB}z}{V_{\max}}}}$$

which writes for $x=0$

$$\left(\frac{\partial c_A(z,x)}{\partial x} \right)_{x=0} = -\frac{2c_{A0}}{\sqrt{\pi}} \frac{1}{\sqrt{\frac{4D_{AB}z}{V_{\max}}}}$$

thus

$$N_{Ax}(x=0) = \frac{2c_{A0}D_{AB}}{\sqrt{\pi}} \frac{1}{\sqrt{\frac{4D_{AB}z}{V_{\max}}}}$$

be it finally

$$N_{Ax}(x=0) = c_{A0}\sqrt{\frac{D_{AB}V_{\max}}{\pi z}} \qquad \text{(II.58)}$$

the total mass of species A absorbed at the liquid-gas interface is

$$m_A = \int_0^W \int_0^L N_{Ax}(x=0)\,dz\,dy$$

by substituting expression (II. 58), it follows

$$m_A = \int_0^W \int_0^L c_{A0}\sqrt{\frac{D_{AB}V_{\max}}{\pi z}}\,dz\,dy$$

by integrating, we obtain

$$m_A = c_{A0}WL\sqrt{\frac{4D_{AB}V_{\max}}{\pi L}} \qquad \text{(II.59)}$$

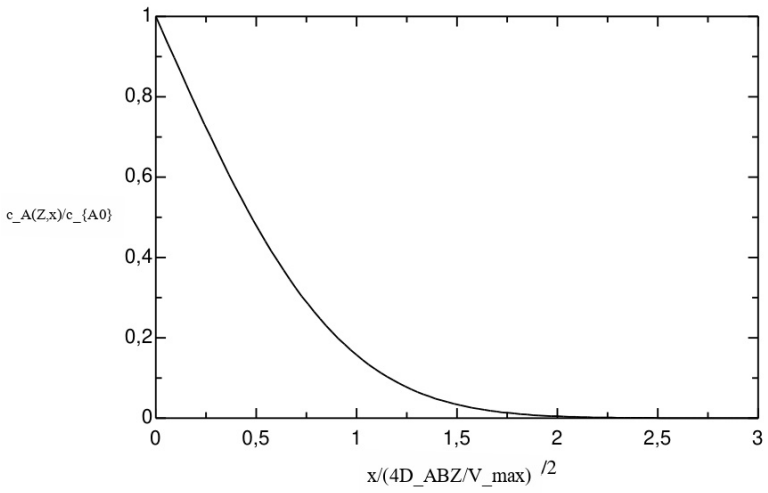


Figure II. 15. Molar concentration profile $\frac{c_A(z,x)}{c_{A0}}$ in fonction de $\frac{x}{\sqrt{\frac{4D_{AB}z}{V_{\max}}}}$.

II. 6. Dissolution of a solid in a flowing liquid

Consider the two-dimensional laminar flow of a liquid B of constant thickness δ over a vertical surface composed of a species A slightly soluble in this liquid. The motion of liquid B on the soluble surface is described by these two equations, which are the continuity equation and the equation of motion.

$$\frac{\partial V_z(z,x)}{\partial z} + \frac{\partial V_x(z,x)}{\partial x} = 0 \qquad \text{(II.60)}$$

$$V_z(z,x)\frac{\partial V_z(z,x)}{\partial z} + V_x(z,x)\frac{\partial V_z(z,x)}{\partial x} = g + \nu\frac{\partial^2 V_z(z,x)}{\partial x^2} \qquad \text{(II.61)}$$

Since the liquid film B is very thin, it is justified to assume that the x-component $V_x(z,x)$ of the velocity vector $\vec{V}(z,x)$ is zero, thereby

$$V_x(z,x) = 0$$

this leads us, starting from the continuity equation (II. 60), to write

$$\frac{\partial V_z(z,x)}{\partial z} = 0$$

this relation shows that the velocity component $V_z(z,x)$ of the velocity vector $\vec{V}(z,x)$ will depend only on the coordinate x

$$V_z(z,x) = V_z(x)$$

With these simplifications, the equation of motion becomes

$$\nu\frac{d^2 V_z(x)}{dx^2} + g = 0 \qquad \text{(II.62)}$$

with the boundary conditions

$$x = 0,\ V_z(x) = 0 \qquad \text{(II.62a)}$$

$$x = \delta,\ \frac{dV_z(x)}{dx} = 0 \qquad \text{(II.62b)}$$

the solution to equation (II. 62) is

$$V_z(x) = -\frac{g}{2\nu}x^2 + C_1 x + C_2$$

where the integration constants C_1 and C_2, determined from the boundary conditions, are

$$C_1 = \frac{g\delta}{\nu},\ C_2 = 0$$

and this leads to the velocity profile $V_z(x)$ of the liquid film B which we write in the form

$$V_z(x) = \frac{g\delta^2}{2\nu}\left(2\left(\frac{x}{\delta}\right) - \left(\frac{x}{\delta}\right)^2\right) \qquad \text{(II.63)}$$

the transfer of species A into the liquid film B is described by equation (II. 47) (where the velocity profile (II. 43) is replaced by the velocity profile (II. 63)), we therefore have

$$\frac{g\delta^2}{2\nu}\left(2\left(\frac{x}{\delta}\right) - \left(\frac{x}{\delta}\right)^2\right)\frac{\partial c_A(z,x)}{\partial z} = D_{AB}\frac{\partial^2 c_A(z,x)}{\partial x^2} \qquad \text{(II.64)}$$

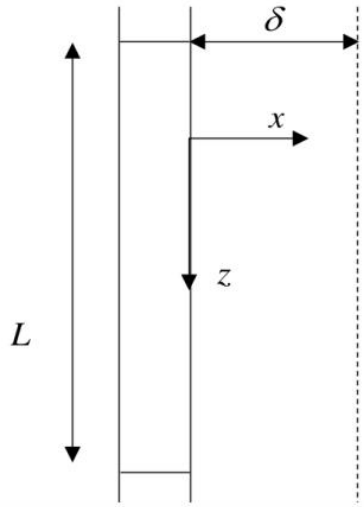


Figure II. 16. Dissolution of a solid surface composed of a species A in a liquid film B.

Since species A is sparingly soluble in liquid B, it is possible to consider that diffusion occurs over a very short distance relative to the thickness δ of liquid film B. In this case, we can therefore write

$$\left(\frac{x}{\delta}\right) \succ\succ \left(\frac{x}{\delta}\right)^2$$

and the velocity profile $V_z(x)$ of the liquid film $\boldsymbol{B}$ becomes

$$V_z(x) = \frac{g\delta^2}{2\nu}\left(2\left(\frac{x}{\delta}\right)\right)$$

let

$$V_z(x) = \frac{g\delta}{\nu}x$$

with this approximation, equation (II. 64) reduces to

$$x\frac{\partial c_A(z,x)}{\partial z} = \frac{D_{AB}\,\nu}{g\delta}\frac{\partial^2 c_A(z,x)}{\partial x^2} \qquad \text{(II.65)}$$

with the boundary conditions

$$z = 0,\ c_A(z,x) = 0 \qquad \text{(II.65a)}$$

$$x = 0,\ c_A(z,x) = c_{A0} \qquad \text{(II.65b)}$$

$$x = \infty,\ c_A(z,x) = 0 \qquad \text{(II.65c)}$$

The first boundary condition reflects the fact that liquid $\boldsymbol{B}$ is pure upon entering at the top of the vertical surface, the second boundary condition stipulates that at the liquid-gas interface, the concentration c_A of species $\boldsymbol{A}$ is determined by its solubility c_{A0} in liquid $\boldsymbol{B}$, and the third boundary condition arises from the fact that species $\boldsymbol{A}$ is negligible far from the vertical surface.

with the dimensionless variable η and the dimensionless molar concentration $\Sigma(\eta)$

$$\eta = x\left(\frac{g\delta}{9D_{AB}\nu z}\right)^{\frac{1}{3}},\ \Sigma(\eta) = \frac{c_A(z,x)}{c_{A0}}$$

Equation (II. 65) reduces to the ordinary differential equation

$$\frac{d^2\Sigma(\eta)}{d\eta^2} + 3\eta^2\frac{d\Sigma(\eta)}{d\eta} = 0 \qquad \text{(II.66)}$$

with the boundary conditions

$$\eta = 0,\ \Sigma(\eta) = 1 \qquad \text{(II.66a)}$$

$$\eta = \infty,\ \Sigma(\eta) = 0 \qquad \text{(II.66b)}$$

to solve this differential equation, we reduce its order by setting

$$\overline{\Sigma}(\eta) = \frac{d\Sigma(\eta)}{d\eta}$$

from which the new differential equation

$$\frac{d\overline{\Sigma}(\eta)}{d\eta} + 3\eta^2\overline{\Sigma}(\eta) = 0$$

whose solution is

$$\overline{\Sigma}(\eta) = C_1 e^{-\eta^3}$$

it follows, then

$$\frac{d\Sigma(\eta)}{d\eta} = C_1 e^{-\eta^3}$$

the integration of this relation yields the profile of the dimensionless concentration, namely

$$\Sigma(\eta) = C_1\int_0^{\eta} e^{-\eta^3}\,d\eta + C_2$$

where C_1 and C_2 are integration constants derived from the boundary conditions (II. 66a) and (II. 66b)

$$C_1\int_0^0 e^{-\eta^3}d\eta + C_2 = 1,\ C_1\int_0^\infty e^{-\eta^3}d\eta + C_2 = 0$$

solvent

$$C_1 = -\frac{1}{\int_0^\infty e^{-\eta^3}d\eta},\ C_2 = 1$$

after substituting these constants into the dimensionless concentration profile, we obtain

$$\Sigma(\eta) = 1 - \frac{\int_0^\eta e^{-\eta^3}d\eta}{\int_0^\infty e^{-\eta^3}d\eta} = \frac{\int_0^\infty e^{-\eta^3}d\eta - \int_0^\eta e^{-\eta^3}d\eta}{\int_0^\infty e^{-\eta^3}d\eta}$$

relation which takes the form

$$\Sigma(\eta) = \frac{\int_0^\infty e^{-\eta^3}d\eta + \int_\eta^0 e^{-\eta^3}d\eta}{\int_0^\infty e^{-\eta^3}d\eta}$$

$$\Sigma(\eta) = \frac{\int_\eta^\infty e^{-\eta^3}d\eta}{\int_0^\infty e^{-\eta^3}d\eta} \qquad \text{(II.67)}$$

Let us introduce the gamma function $\Gamma(n)$, which is defined by the integral

$$\Gamma(n)=\int_0^{\infty}\beta^{n-1}e^{-\beta}d\beta$$

if we assume that

$$\beta=\eta^3,\ d\beta=3\eta^2 d\eta$$

The integral $\int_0^{\infty}e^{-\eta^3}d\eta$ is written as

$$\int_0^{\infty}e^{-\eta^3}d\eta=\int_0^{\infty}e^{-\beta}\frac{d\beta}{3\beta^{\frac{2}{3}}}=\frac{1}{3}\int_0^{\infty}\beta^{-\frac{2}{3}}e^{-\beta}d\beta$$

by comparing this relation with the definition of the gamma function, we note that

$$n-1=-\frac{2}{3}$$

hence

$$n=\frac{1}{3}$$

and beyond, it comes

$$\int_0^{\infty}e^{-\eta^3}d\eta=\frac{1}{3}\Gamma\left(\frac{1}{3}\right)=\Gamma\left(\frac{1}{3}+1\right)=\Gamma\left(\frac{4}{3}\right)$$

With these manipulations, we obtain the following formula for the molar concentration $c_A(z,x)$ of species A:

$$\frac{c_A(z,x)}{c_{A0}}=\frac{\int_{\eta}^{\infty}e^{-\eta^3}d\eta}{\Gamma\left(\frac{4}{3}\right)} \qquad \text{(II.68)}$$

the molar flux N_{Ax} of species A at the soluble-liquid surface interface B is

$$N_{Ax}(x=0) = -D_{AB}\left(\frac{\partial c_A(z,x)}{\partial x}\right)_{x=0}$$
$$= -D_{AB}c_{A0}\left(\frac{\partial \eta}{\partial x}\frac{d}{d\eta}\left(\frac{c_A(z,x)}{c_{A0}}\right)\right)_{x=0}$$

knowing that

$$\frac{\partial \eta}{\partial x} = \frac{\partial}{\partial x}\left(x\left(\frac{g\delta}{9D_{AB}\nu z}\right)^{\frac{1}{3}}\right) = \left(\frac{g\delta}{9D_{AB}\nu z}\right)^{\frac{1}{3}}$$

he comes

$$N_{Ax}(x=0) = -D_{AB}c_{A0}\left(-\left(\frac{g\delta}{9D_{AB}\nu z}\right)^{\frac{1}{3}}\frac{e^{-\eta^3}}{\Gamma\left(\frac{4}{3}\right)}\right)_{x=0}$$

relation, which after simplification, is written as

$$N_{Ax}(x=0) = \frac{c_{A0}}{\Gamma\left(\frac{4}{3}\right)}\left(\frac{gD_{AB}^2\delta}{9\nu z}\right)^{\frac{1}{3}} \qquad \text{(II.69)}$$

the total mass of species A dissolved in liquid B is

$$m_A = \int_0^W\int_0^L N_{Ax}(x=0)dzdy$$

and by substituting relation (II. 69)

$$m_A = \int_0^W \int_0^L \frac{c_{A0}}{\Gamma\left(\frac{4}{3}\right)} \left(\frac{g D_{AB}^2 \delta}{9 \nu z} \right)^{\frac{1}{3}} dz dy$$

and by integrating, we obtain

$$m_A = \frac{2 D_{AB} c_{A0} W L}{\Gamma\left(\frac{7}{3}\right)} \left(\frac{g \delta}{9 D_{AB} \nu L} \right)^{\frac{1}{3}} \qquad \text{(II.70)}$$

II. 7. Diffusion with Chemical Reaction in a Porous Catalytic Medium

Consider the diffusion of a gas containing species A as reactant and species B as product, with a molar production rate per unit volume Ω, through a catalytic porous reactor composed of spherical particles of radius R.

Let us perform a mass balance of species A within a spherical shell of thickness dr. In a steady state, the sum of the mass $4\pi r^2 N_{Ar}$ of species A crossing the sphere of radius r and the production rate $\Omega 4\pi r^2 dr$ is equal to the mass $4\pi(r+dr)^2 N_{Ar+dr}$ of species A leaving the sphere of radius $r+dr$. Mathematically, this is expressed by the equation

$$4\pi r^2 N_{Ar} + 4\pi r^2 dr \Omega = 4\pi (r+dr)^2 N_{Ar+dr} \qquad \text{(II.71)}$$

the total molar flux N_{Ar+dr} at the radius $r+dr$ can be developed using the Taylor formula and written in the form

$$N_{Ar+dr} = N_{Ar} + \frac{dN_{Ar}}{dr} dr$$

hence

$$4\pi r^2 N_{Ar} + 4\pi r^2 dr \Omega = 4\pi \left(r^2 + 2rdr + dr^2 \right) \left(N_{Ar} + \frac{dN_{Ar}}{dr} dr \right)$$

$$r^2 \frac{dN_{Ar}}{dr} + 2rN_{Ar} + r^2\Omega = 0$$

$$\frac{d}{dr}\left(r^2 N_{Ar}\right) + r^2\Omega = 0 \qquad \text{(II.72)}$$

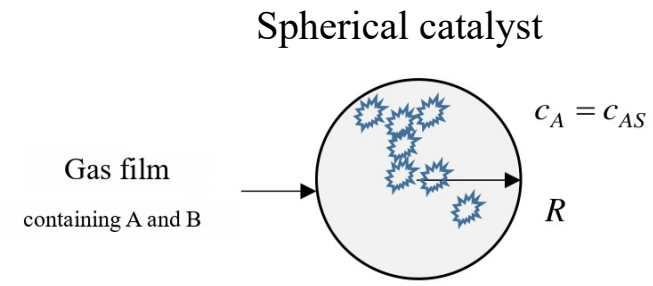


Figure II. 17. Porous catalyst particle in which the reaction $A \rightarrow B$ takes place.

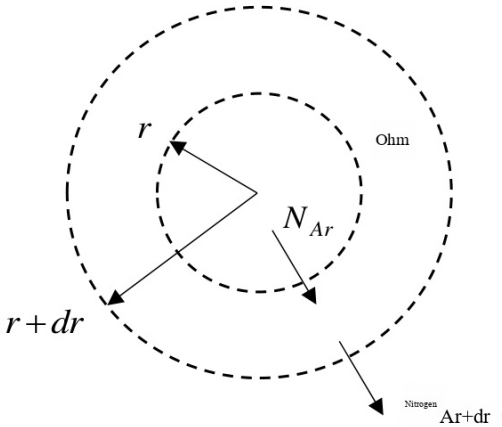


Figure II.18. Control volume for deriving the mass balance.

Without considering the microscopic mechanisms of diffusion at the pore scale, it is possible to define the diffusion of species A in these porous catalytic particles via the relationship

$$N_{Ar} = -D_A \frac{dc_A(r)}{dr}$$

the molar production rate Ω per unit volume is

$$\Omega = k_1'' S c_A$$

where S and k_1'' are, respectively, the available surface area per unit volume of the catalyst and the first-order reaction rate constant. Substituting these two expressions into Equation (II. 72) leads to

$$\frac{d}{dr}\left(-r^2 D_A \frac{dc_A(r)}{dr}\right) + r^2 k_1'' S c_A = 0$$

$$\frac{D_A}{r^2}\frac{d}{dr}\left(r^2 \frac{dc_A(r)}{dr}\right) - k_1'' S c_A = 0 \qquad \text{(II.73)}$$

with the boundary conditions

$$r = 0,\ c_A(r) = finie \qquad \text{(II.73a)}$$

$$r = R,\ c_A(r) = c_{AS} \qquad \text{(II.73b)}$$

if we introduce the function $\Sigma(r)$, such that

$$\frac{c_A(r)}{c_{AS}} = \frac{\Sigma(r)}{r}$$

the derivative $\frac{dc_A(r)}{dr}$ is written as

$$\frac{dc_A(r)}{dr} = c_{AS}\frac{d}{dr}\left(\frac{\Sigma(r)}{r}\right) = c_{AS}\left(\frac{1}{r}\frac{d\Sigma(r)}{dr} - \frac{\Sigma(r)}{r^2}\right)$$

by substituting it into equation (II. 73), we obtain the ordinary differential equation

$$\frac{d^2\Sigma(r)}{dr^2} - \frac{k_1'' S}{D_A}\Sigma(r) = 0$$

whose solution is

$$\Sigma(r) = C_1 \cosh\sqrt{\frac{k_1'' S}{D_A}}\, r + C_2 \sinh\sqrt{\frac{k_1'' S}{D_A}}\, r$$

which, in terms of the concentration $c_A(r)$, can be written

$$\frac{c_A(r)}{c_{AS}} = \frac{C_1}{r}\cosh\sqrt{\frac{k_1'' S}{D_A}}\, r + \frac{C_2}{r}\sinh\sqrt{\frac{k_1'' S}{D_A}}\, r \qquad \text{(II.74)}$$

The integration constants C_1 and C_2, determined from the boundary conditions (II. 73a) and (II. 73a), are

$$C_1 = 0\,,\; C_2 = \frac{R}{\sinh\sqrt{\frac{k_1'' S}{D_A}}\, R}$$

by substituting them into the solution (II. 74), we obtain, finally, for the concentration $c_A(r)$, the expression

$$\frac{c_A(r)}{c_{AS}} = \frac{R}{r}\frac{\sinh\sqrt{\frac{k_1'' S}{D_A}}\, r}{\sinh\sqrt{\frac{k_1'' S}{D_A}}\, R} \qquad \text{(II.75)}$$

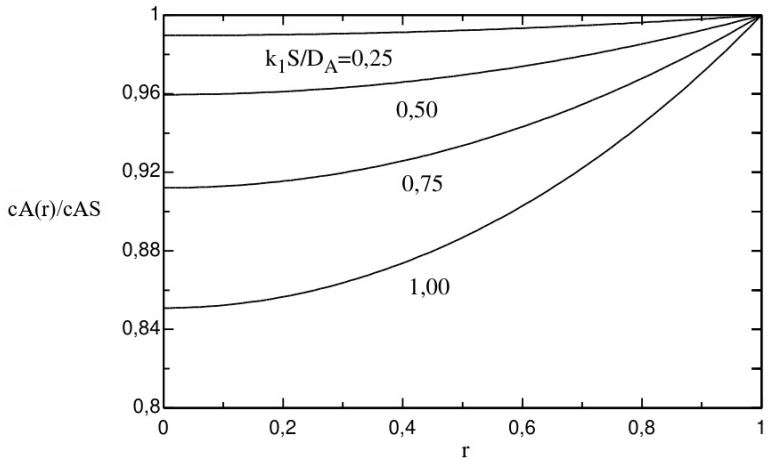


Figure II. 19. Profile of the molar concentration $\frac{c_A(r)}{c_{AS}}$ as a function of radius r.

the molar flux N_{Ar} of species A on the surface of the catalyst particles is

$$N_{Ar}(r=R) = -D_A\left[\frac{dc_A(r)}{dr}\right]_{r=R}$$

the derivative of the concentration $c_A(r)$, from equation (II. 75), is

$$\frac{dc_A(r)}{dr} = -\frac{c_{AS}R}{r^2}\frac{\sinh\sqrt{\frac{k_1''S}{D_A}}\,r}{\sinh\sqrt{\frac{k_1''S}{D_A}}\,R} + \frac{c_{AS}R}{r}\sqrt{\frac{k_1''S}{D_{AB}}}\frac{\cosh\sqrt{\frac{k_1''S}{D_A}}\,r}{\sinh\sqrt{\frac{k_1''S}{D_A}}\,R}$$

which, for $r=R$, takes the form

$$\left[\frac{dc_A(r)}{dr}\right]_{r=R} = c_{AS}\left(-\frac{1}{R} + \sqrt{\frac{k_1''S}{D_A}}\coth\sqrt{\frac{k_1''S}{D_A}}\,R\right)$$

its substitution into the molar flux expression yields

$$N_{Ar}(r=R) = D_{AB}c_{AS}\left(\frac{1}{R} - \sqrt{\frac{k_1''S}{D_A}}\coth\sqrt{\frac{k_1''S}{D_A}}\,R\right) \quad \text{(II.76)}$$

the molar flow rate of species A is

$$m_A = 4\pi R^2 N_{Ar}(r=R)$$

let

$$m_A = 4\pi R D_A c_{AS}\left(1 - R\sqrt{\frac{k_1''S}{D_A}}\coth\sqrt{\frac{k_1''S}{D_A}}\,R\right) \quad \text{(II.77)}$$

II. 8. Non-equimolar counter-diffusion

When the molar fluxes of the two species A and B are opposite and unequal, the diffusion is referred to as non-equimolar counter-diffusion. This type of process occurs in the presence of chemical reactions. In this case, we have

$$N_{Bz} = -nN_{Az} \quad (n \neq 1)$$

by substituting this relation into equation (II. 4), it follows

$$N_{Az} = \frac{cD_{AB}N_{Az}}{(N_{Az} - nN_{Az})(z - z_1)} \ln \frac{(N_{Az} - nN_{Az})\, x_A(z) - N_{Az}}{(N_{Az} - nN_{Az})\, x_{A1} - N_{Az}}$$

from which

$$N_{Az} = \frac{cD_{AB}}{(1-n)(z - z_1)} \ln \frac{(1-n)\, x_A(z) - 1}{(1-n)\, x_{A1} - 1} \qquad \text{(II.78)}$$

at the distance $z = z_2$, this total molar flux is

$$N_{Az} = \frac{cD_{AB}}{(1-n)(z_2 - z_1)} \ln \frac{(1-n)\, x_{A2} - 1}{(1-n)\, x_{A1} - 1}$$

since the system is in a steady state, we always have the constancy of the total molar flux, and thus

$$\frac{cD_{AB}}{(1-n)(z - z_1)} \ln \frac{(1-n)\, x_A(z) - 1}{(1-n)\, x_{A1} - 1} = \frac{cD_{AB}}{(1-n)(z_2 - z_1)} \ln \frac{(1-n)\, x_{A2} - 1}{(1-n)\, x_{A1} - 1}$$

$$\frac{(1-n)\, x_A(z) - 1}{(1-n)\, x_{A1} - 1} = \left[\frac{(1-n)\, x_{A2} - 1}{(1-n)\, x_{A1} - 1} \right]^{\frac{z - z_1}{z_2 - z_1}}$$

from this relation, the molar fraction profiles $x_A(z)$ of species A and $x_B(z)$ of species B are given by

$$x_A(z) = \frac{1}{1-n} + \left(x_{A1} - \frac{1}{1-n} \right) \left[\frac{(1-n)\, x_{A2} - 1}{(1-n)\, x_{A1} - 1} \right]^{\frac{z - z_1}{z_2 - z_1}} \qquad \text{(II.79)}$$

$$x_B(z) = \frac{n}{n-1} - \left(x_{A1} - \frac{1}{1-n} \right) \left[\frac{(1-n)\, x_{A2} - 1}{(1-n)\, x_{A1} - 1} \right]^{\frac{z - z_1}{z_2 - z_1}} \qquad \text{(II.80)}$$

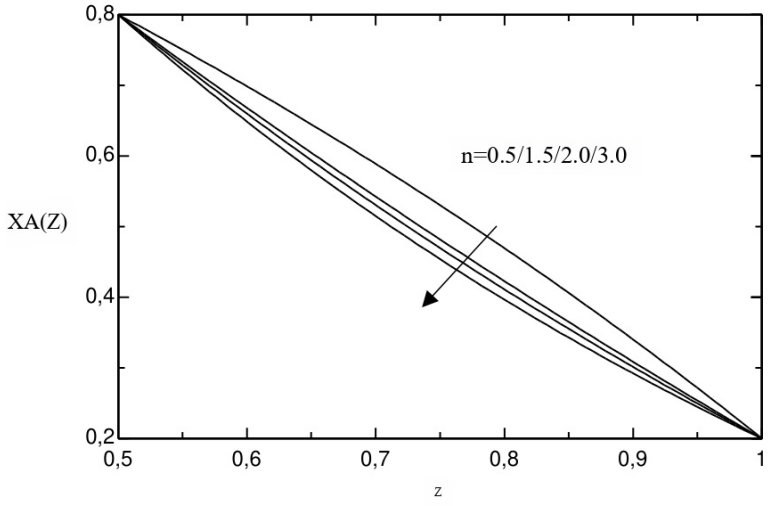


Figure II. 20. Profiles of the mole fraction $x_A(z)$ as a function of z for different values of n.