# King Mongkut's University of Technology Thonburi

## FDE618: Transport Phenomena in Food Processing
## ChE610: Fundamentals of Transport Phenomena

## Chapter 4
## Transport Processes in a Multi-Component System

When more than one species (components) are presented in the system analyzed, i.e., there are composition variations within the system, a modified form of the governing conservation equations as well as initial and boundary conditions is needed.

### 4.1 Governing Equations for a Multi-Component System

Prior to deriving the set of governing conservation equations as well as boundary conditions needed to analyze a multi-component system, the following symbols are first defined:

| | |
|---|---|
| $\vec{n}_i$ | mass flux of *i* relative to stationary coordinates $\left(\equiv \rho_i \vec{v}_i\right)$ |
| $\vec{N}_i \left(= \vec{n}_i / M_i\right)$ | molar flux of *i* relative to stationary coordinates |
| $\vec{v}_i$ | velocity of *i* relative to stationary coordinates |
| $\rho_i$ | mass concentration of *i* (kg m$^{-3}$) |
| $c_i$ | molar concentration of *i* (mol m$^{-3}$) |
| $\omega_i$ | mass fraction of *i* $\left(= \rho_i / \rho\right)$ |
| $x_i$ | molar fraction of *i* $\left(c_i / c\right)$; $c$ = total molar density $\left(= \rho / M = \sum c_i\right)$ |
| $M$ | molecular weight of mixture = $\sum x_i M_i$ |

It is possible to further decompose $\vec{n}_i$ into two parts:

$$\vec{n}_i = \rho_i \vec{v} + \vec{j}_i \equiv \rho_i \vec{v}_i \qquad (4.1A)^1$$

where,

$$\vec{v} = \frac{\sum \rho_i \vec{v}_i}{\sum \rho_i} \qquad (4.1B)^2$$

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[1] See also Tables 16.1-1 and 16.1-2 (Bird et al., 1960, p. 498) or Tables 17.7-1 and 17.7-2 (Bird et al., 2002, pp. 534-535); Table 16.1-3 (Bird et al., 1960, p. 499) or Table 17.8-1 (Bird et al., 2002, p. 537); and Table 16.2-1 (Bird et al., 1960, p. 502) or Table 17.8-2 (Bird et al., 2002, p. 537).

[2] This velocity is sometimes called "mass average velocity."

and,

$$\sum \vec{n}_i \;=\; \sum \rho_i \vec{v} + \sum \vec{j}_i \tag{4.1C}$$

since

$$\sum \vec{n}_i \;=\; \vec{v} \sum \rho_i + \sum \vec{j}_i \;\; (\text{or } \rho\vec{v} + \sum \vec{j}_i\,) \tag{4.1D}$$

therefore,

$$\sum \vec{j}_i = 0 \tag{4.1E}$$

So, for a two-component system (say, components *A* and *B*), $j_A = j_B$.

When there are *i* species in the system, *i*-1 species balances and one overall balance are normally written.

To derive the governing equations for multi-component systems, consider the system shown in Figure 4.1,

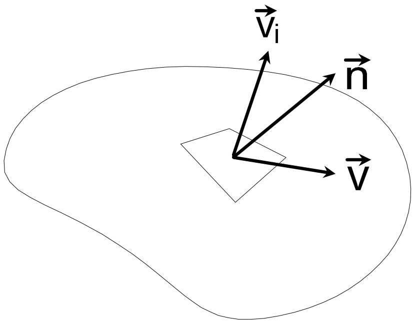

**Figure 4.1. A Multi-component system**

in this figure, $\vec{n} \cdot \rho_i (\vec{v}_i - \vec{v}) = \vec{n} \cdot \vec{j}_i$.

A species balance equation can be written as:

{Rate of change of mass of *i*} + {Net rate of efflux of *i*} =
{Net rate of production of *i*} (4.1F)[3]

in mathematical terms:

$$\frac{D}{Dt}\int_V \rho\omega_i \, dV \;+\; \int_A \vec{n} \cdot \vec{j}_i \, dA \;=\; \int_V r_i''' \, dV \tag{4.1G}$$

$$\int_V \rho \frac{D\omega_i}{Dt} dV \;+\; \int_V \nabla \cdot \vec{j}_i \, dV = \int_V r_i''' \, dV \tag{4.1H}$$

or,

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[3] For an overall mass balance, the term on the right of this equation is zero.

$$\rho\frac{D\omega_i}{Dt}+\nabla\cdot\vec{j}_i \quad = \quad r_i''' \tag{4.1I}$$

This equation is similar to equation (18.3-1) in Bird et al. (1960) or equation (19.1-7a) in Bird et al. (2002, p. 588).

Summation of equation (4.1I) gives an overall mass balance:

$$\sum\rho\frac{D\omega_i}{Dt}+\sum\nabla\cdot\vec{j}_i=\sum r_i''' \rightarrow \rho\frac{D}{Dt}\sum\omega_i+\nabla\cdot\sum\vec{j}_i=\sum r_i''' \tag{4.1J}$$

Since $\sum\vec{j}_i=0$ and $\sum r_i'''=0$, equation (4.1J) simplifies to equation (2.1C).

An alternate form of equation (4.1I) can be written as:

$$\frac{\partial\rho_i}{\partial t}+\nabla\cdot\vec{n}_i=r_i''' \tag{4.1K}$$

Equation (4.1K) is indeed similar to equation (18.1-6) in Bird et al. (1960) or equation (19.1-6) in Bird et al. (2002).

For the momentum equation, a momentum balance is first written as:

{Rate of change of momentum} + {Net rate of efflux of momentum} =
{Sum of external forces} (4.1L)

or, in mathematical terms,

$$\frac{D}{Dt}\int_V\rho\,\vec{v}(or\sum\rho_p\,\vec{v}_i\,)dV+\int_A\sum(\vec{n}\cdot\vec{j}_i\,)\vec{v}_i\,dA=\int_V\sum\rho_i\,\vec{G}_i\,dV+\int_A(\vec{n}\cdot\underline{\sigma})dA \tag{4.1M}$$

or,

$$\rho\frac{D\vec{v}}{Dt}+\sum\nabla\cdot\vec{j}_i\,\vec{v}_i=\sum\rho_i\,\vec{G}_i+\nabla\cdot\underline{\sigma} \tag{4.1N}$$

where $\vec{G}_i$ is the body force per unit mass for species *i*. The second term on the left of (4.1N) is called momentum of diffusion and is normally neglected. In terms of viscous stress (see section 2.2), this equation can be written as:

$$\rho\frac{D\vec{v}}{Dt}=\sum\rho_i\,\vec{G}_i-\nabla p+\nabla\cdot\underline{\tau} \tag{4.1O}$$

This equation is similar to equation (18.3-2) in Bird et al. (1960) or equation (C) of Table 19.2-3 of Bird et al. (2002, p. 588).

To derive an energy equation, an energy balance is first written as:

{Rate of change of total energy} = {Net rate of heat addition} –
{Rate at which work is done by the system} –
{Net rate of efflux of total energy} (4.1P)

The term on the left of the balance can be expressed mathematically (where potential energy is neglected) as:

$$\frac{D}{Dt}\int_V \left( \sum \rho_i \vec{u}_i + \sum \frac{\rho_i \vec{v}_i^{\,2}}{2} \right) dV \tag{4.1Q}$$

The first term on the right is:

$$\int_V \nabla \cdot \left( -\vec{q} \right) dV \tag{4.1R}$$

The second term on the right can be written as:

$$\int_V \sum \rho_i G_i \vec{v}_i \, dV \text{ - } \int_A \left( \vec{n} \cdot \underline{\sigma} \right) \cdot \vec{v} \, dA \tag{4.1S}$$

where the work done by the body forces can be expressed as:

$$\sum \rho_i \vec{G}_i \cdot \left( \vec{v} + \frac{\vec{j}_i}{\rho_i} \right) dV = (\sum \rho_i \vec{v} \cdot \vec{G}_i + \sum \vec{G}_i \cdot \vec{j}_i )dV \tag{4.1T}$$

The last term of the balance can be expressed as:

$$\int_V \sum \nabla \cdot \left( \bar{h}_i + \frac{\vec{v}_i^{\,2}}{2} \right) \vec{j}_i \, dV \tag{4.1U}$$

in which the kinetic energy term is normally neglected.

After some manipulation the energy equation becomes:

$$\rho \frac{D}{Dt}\left[ \sum \omega_i \vec{u}_i + \frac{\vec{v}_i^{\,2}}{2} \right] = -\nabla \cdot \vec{q} + \underline{\sigma} : \nabla \vec{v} + \vec{v} \cdot \nabla \cdot \underline{\sigma} + \vec{v} \cdot \sum \rho_i \vec{G}_i + \sum \vec{j}_i \vec{G}_i - \sum \nabla \cdot \vec{j}_i \bar{h}_i \tag{4.1V}$$

If one takes the dot product of the momentum equation with $\vec{v}$ and subtracts the resulted product from equation (4.1V), one will have (see section 2.3):

$$\rho\frac{Du}{Dt} = -\nabla\cdot\left(\vec{q}+\sum\vec{j}_i\,\bar{h}_i\right) - p\nabla\cdot\vec{v} + \underline{\tau}:\nabla\vec{v} + \sum\vec{j}_i\cdot\vec{G}_i \tag{4.1W}$$

with two extra terms as compared with equation (2.3E). Equation (4.1W) is the energy equation for multi-component systems in terms of the internal energy *u*. In terms of the enthalpy *h*:

$$\rho\frac{Dh}{Dt} = -\nabla\cdot\left(\vec{q}+\sum\vec{j}_i\,\bar{h}_i\right) + \frac{Dp}{Dt} + \underline{\tau}:\nabla\vec{v} + \sum\vec{j}_i\cdot\vec{G}_i \tag{4.1X}$$

or,

$$\rho\frac{Dh}{Dt} = \rho c_p\frac{DT}{Dt} + (1-T\beta)\frac{Dp}{Dt} + \sum\bar{h}_i\,\rho\frac{D\omega_i}{Dt} \tag{4.1Y}$$

Since $\sum\bar{h}_i\,\rho\frac{D\omega_i}{Dt} = \sum\bar{h}_i\left(r_i''' - \nabla\cdot\vec{j}_i\right)$,

$$\rho c_p\frac{DT}{Dt} = -\nabla\cdot\vec{q} - \sum\vec{j}_i\cdot\nabla\bar{h}_i - \sum\bar{h}_i r_i''' + \underline{\tau}:\nabla\vec{v} + T\beta\frac{Dp}{Dt} + \sum\vec{j}_i\cdot\vec{G}_i \tag{4.1Z}$$

Equation (4.1Z) is the energy equation in terms of the temperature *T*. This equation is similar to equation (F) of Table 19.2-4 of Bird et al. (2002).

With the assumptions that the fluid density is constant, all $\vec{G}_i$ and heat capacities are identical and that the solution is ideal, equation (4.1Z) can be simplified to:

$$\rho c_p\frac{DT}{Dt} = -\nabla\cdot\vec{q} - \sum h_i r_i''' + \underline{\tau}:\nabla\vec{v} \tag{4.1AA}$$

where the second term on the right represents the heat of reactions. This equation is similar to equation (F) in Table 18.3-1 of Bird et al. (1960).

In such cases where thermal and pressure diffusion is neglected and the solution under consideration is assumed to be ideal, it is possible to express the mass flux as:

$$\vec{j}_i \;=\; -\rho D_i\nabla\omega_i \tag{4.1AB}$$

or,

$$\vec{J}_i \;=\; -cD_i\nabla x_i \tag{4.1AC}$$ [4]

Equations (4.1AB) and (4.1AC) are just different forms of Fick's first law of diffusion (written in terms of mass and molar diffusion fluxes, respectively). Other forms are also

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[4] Equation (4.1AC) is the most frequently used form of Fick's first law of diffusion.

available (see, for example, Table 16.2-1 in Bird et al., 1960; or Table 17.8-2 in Bird et al., 2002). From equation (4.1I) it is therefore possible to write other forms of species balance equation as:

$$\rho\frac{D\omega_i}{Dt} - \rho D_i \nabla^2 \omega_i = r_i''' \tag{4.1AD}$$

$$\frac{D\rho_i}{Dt} - D_i \nabla^2 \rho_i = r_i''' \tag{4.1AE}$$

$$\frac{Dc_i}{Dt} - D_i \nabla^2 c_i = R_i''' \tag{4.1AF}$$

Our next task is to derive the interface boundary conditions for a multi-component system.

## 4.2 Interface Boundary Conditions for a Multi-Component System

Consider first the pillbox control volume in Figure 4.2.

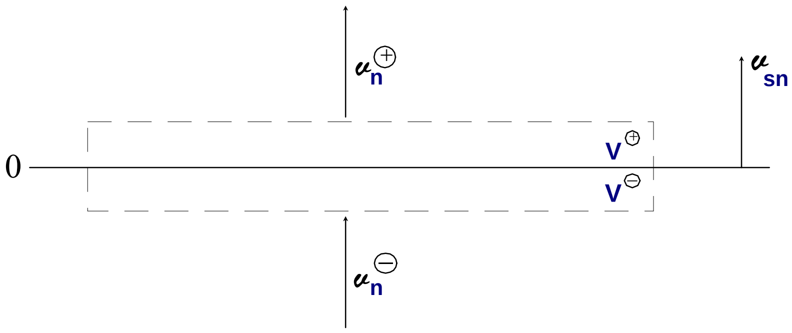

**Figure 4.2. Pillbox control volume for a multi-component system**

If a chemical reaction is allowed to take place at the interface it is possible to write a species balance (for component *i*) as:

$$\rho_i^{(+)}\left(v_{ni}^{(+)} - v_s\right) - \rho_i^{(-)}\left(v_{ni}^{(-)} - v_s\right) = r_i''' \tag{4.2A}$$

where $r_i'''$ is the rate of reaction (rate of production of *i*) per unit surface area. Using a jump operator, equation (4.2A) can be written as:

$$\left\|\dot{m}_i\right\| = r_i''' \tag{4.2B}$$

If there is no chemical reaction, the jump balance in equation (4.2B) equals to zero and the species balance reduces to:

$$\left\|\rho_i\left(v_{ni} - v_s\right)\right\| = 0 \tag{4.2C}$$

Since $\overset{\bullet}{m}_i = \rho_i v_{ni} - \rho_i v_s$ or $\dot{m}_i = n_i - \rho_i v_s$,

$$n_i^{(+)} - n_i^{(-)} = \left(\rho_i^{(+)} - \rho_i^{(-)}\right) v_s + r_i''' \tag{4.2D}$$

Dividing both sides of equation (4.2D) by $M_i$ yields:

$$N_i^{(+)} - N_i^{(-)} = \left(c_i^{(+)} - c_i^{(-)}\right) v_s + R_i''' \tag{4.2E}$$

For jump energy balance, recalling first the simplified jump energy balance (see section 3.3, p. 38):

$$\left\| \dot{m}\, h + q_n \right\| = 0 \tag{4.2F}$$

modifying equation (4.2F) to serve a system with multi components yields:

$$\left\| \sum \dot{m}_i \bar{h}_i + q_n \right\| = 0 \tag{4.2G}$$

where $\bar{h}_i$ is the partial mass enthalpy of *i*. Since $\dot{m}_i = n_i - \rho_i v_s$, equation (4.2G) can be rewritten as:

$$\sum \left(n_i^{(+)} - \rho_i^{(+)} v_s\right) \bar{h}_i^{(+)} - \sum \left(n_i^{(-)} - \rho_i^{(-)} v_s\right) \bar{h}_i^{(-)} = k^{(+)} \frac{\partial T^{(+)}}{\partial n} - k^{(-)} \frac{\partial T^{(-)}}{\partial n} \tag{4.2H}$$

or in terms of molar fluxes:

$$\sum \left(N_i^{(+)} - c_i^{(+)} v_s\right) \bar{H}_i^{(+)} - \sum \left(N_i^{(-)} - c_i^{(-)} v_s\right) \bar{H}_i^{(-)} = k^{(+)} \frac{\partial T^{(+)}}{\partial n} - k^{(-)} \frac{\partial T^{(-)}}{\partial n} \tag{4.2I}$$

Thermodynamic equilibrium at the interface can also be written for a multi-component system:

$$\mu_i^{(+)} = \mu_i^{(-)} \tag{4.2J}$$

or in terms of the so-called distribution coefficient $K_i$, which is a function of temperature, pressure and compositions:

$$\rho_i^{(+)} = K_i \rho_i^{(-)} \tag{4.2K}$$

For a system with chemical reactions, it is more convenient to use equations (4.2E) and (4.2I) than their respective mass fluxes forms.

If it is desirable to make the species balance equation (4.1AD) dimensionless, it is necessary to define dimensionless variables (in addition to those defined in Chapter 2) as:

$v^* = \frac{v}{U}$, $\omega_i^* = \frac{\omega_i - \omega_R}{\Delta\omega}$ and $R_i^* = \frac{r_i'''}{r_o'''}$, where $U$, $\omega_R$, $\Delta\omega$ and $r_0'''$ are characteristics velocity, mass fraction, mass fraction difference and reaction rate, respectively. Using these newly defined dimensionless variables, the dimensionless species balance can be written as:

$$\frac{D\omega^*}{Dt} = \frac{1}{\mathrm{Re\,Sc}}\left[\nabla^{*2}\omega_i^* + \left(\frac{r_{io}'''L^2}{\rho D_i \Delta\omega}\right)R_i'''\right] \tag{4.2L}$$

where Sc = $\frac{\mu}{\rho D_i}$ is the Schmidt number and $\frac{r_{io}'''L^2}{\rho D_i \Delta\omega}$ is the so-called Damköhler Group II for homogeneous reaction.

In summary, for constant physical properties (in each phase) fluids with no thermal and pressure diffusion, a complete set of governing conservation equations is:

**Overall continuity**: $\nabla \cdot \vec{v} = 0$

**Species continuity:** $\rho\frac{D\omega_i}{Dt} = D_i\nabla^2\rho_i + r_i'''$

**Momentum equation:** $\frac{D\vec{v}}{Dt} = \vec{G} - \frac{1}{\rho}\nabla p + \nu\nabla^2\vec{v}$

**Energy equation:** $\frac{DT}{Dt} = \alpha\nabla^2 T - \frac{1}{\rho c_p}\sum h_i r_i''' + \frac{\nu}{c_p}\Phi_v$

Interface boundary conditions (jump balances) are:

**Species mass balance:** $\| \rho_i(v_{ni} - v_s) \| = r_i'''$

$\| n_i - \rho_i v_s \| = r_i'''$

$\| N_i - c_i v_s \| = R_i'''$

**Simplified energy balance:** $\| \sum \dot{m}_i \bar{h}_i + q_n \| = 0$

where $\dot{m}_i = \rho_i(v_{ni} - v_s)$

**Thermodynamic equilibrium:** $\| \mu_i \| = 0$

Example 1 Methyl alcohol is contained in a cylindrical container of cross sectional area *A*, fitted with a movable, frictionless piston of mass *M*. The cylinder and piston are perfectly insulated. Above the liquid is a gas phase, which is initially pure oxygen at a temperature of 150°C. The pressure above the piston is constant at one atmosphere. Methyl alcohol is originally at a uniform temperature corresponding to saturation at the prevailing temperature (roughly 65°C). At time $t = 0$, heat transfer and vaporization begin. The initial liquid height is $\Delta_0$ and the initial height of the piston is $\xi_0$. It is also assumed that:

- Oxygen is insoluble in the liquid
- The properties are constant in each phase (but not equal)

- Only concentration diffusion occurs
- The simplified jump balances apply

Set up the differential equations, initial and boundary conditions, which describe this situation and which allow the calculation of the final positions of $\mathit{\Delta}$ and $\xi$.

Solution Based on the aforementioned statements and assumptions the simplified governing conservation equations for both phases (liquid and gas) can be written as:

**Liquid phase (prime phase)**

Continuity $$\frac{\partial v_z'}{\partial z} = 0 \tag{E41A}$$

Momentum $$\frac{\partial p'}{\partial z} = -\rho' g \tag{E41B}$$

Energy $$\rho' c_p' \frac{\partial T'}{\partial t} = k' \frac{\partial^2 T'}{\partial z^2} \tag{E41C}$$

**Gas phase**

Overall continuity $$\frac{\partial v_z}{\partial z} = 0 \tag{E41D}$$

Methanol balance $$\frac{\partial \omega_m}{\partial t} + v_z \frac{\partial \omega_m}{\partial z} = D \frac{\partial^2 \omega_m}{\partial z^2} \tag{E41E}$$

Momentum $$\rho \frac{\partial v_z}{\partial t} = -\frac{\partial p}{\partial z} - \rho g \tag{E41F}$$

Energy $$\rho c_p \left( \frac{\partial T}{\partial t} + v_z \frac{\partial T}{\partial z} \right) = k \frac{\partial^2 T}{\partial z^2} \tag{E41G}$$

A total of 4 initial conditions and 9 boundary conditions are needed to solve the above two sets of equations. The initial conditions are: at $t = 0$, $v_z = 0$, $T' = 65^{o}$C, $T = 150^{o}$C, and $\omega_m = 0$. The boundary conditions are derived by performing the following balances at the interface ($z = \mathit{\Delta}$):

Overall mass balance:

$$\left\| \rho (v_n - v_s) \right\| = 0$$

or,

$$\rho (v_z - v_s) = \rho' (v_z - v_s), \text{ where } v_s = \frac{d\Delta}{dt}; \text{ at } t = 0,\ \mathit{\Delta} = \mathit{\Delta}_0$$

Hence at $z = \mathit{\Delta}$, $$v_z = \left( 1 - \frac{\rho'}{\rho} \right) \frac{d\mathit{\Delta}}{dt} \tag{E41H}$$

Species (methanol) balance:

$$\left\| n_m - \rho_m v_s \right\| = 0$$

or, after simplification,

$$n_m = \left(\rho_m - \rho'_m\right) v_s \text{ where } \rho_m = \omega_m \rho$$

Hence at $z = \mathit{\Delta}$,

$$-\rho D \frac{\partial \omega_m}{\partial z} = -\rho'\left(1 - \omega_m\right) \frac{d\mathit{\Delta}}{dt} \tag{E41I}$$

Jump momentum balance:

$$\left\| p \right\| = 0 \text{ or } p = p' \tag{E41J}$$

Jump energy balance:

$$\left\| \sum \dot{m}_i \bar{h}_i + q_n \right\| = 0$$

or,

$$\dot{m}_A \bar{h}_A + \dot{m}_B \bar{h}_B + q_n = \dot{m}'_A \bar{h}_A + \dot{m}'_B \bar{h}'_B + q'_n \quad (A = \text{methanol; } B = \text{oxygen})$$

or, after simplification,

$$\dot{m}_A \Delta h_A = k \frac{\partial T}{\partial z} - k' \frac{\partial T'}{\partial z}$$

Since from an interface mass balance:

$$\dot{m}_A = -\rho'_A v_s \text{ and } v_s = \frac{d\mathit{\Delta}}{dt}$$

Thus, at $z = \mathit{\Delta}$,

$$\rho_A \mathit{\Delta} h_A \frac{d\mathit{\Delta}}{dt} = k' \frac{\partial T'}{\partial z} - k \frac{\partial T}{\partial z} \tag{E41K}$$

Thermodynamic equilibrium states that, at the interface:

$$\left\| T \right\| = 0 \text{ or } T = T' \tag{E41L}$$

and,

$$\left\| \mu_m \right\| = 0 \text{ or } \mu_m = \mu'_m \tag{E41M}$$

Other boundary conditions include: at $z = 0$, $\frac{\partial T'}{\partial z} = 0$; at z = $\xi$, $\frac{\partial T}{\partial z} = 0$ and $\frac{\partial \omega_m}{\partial z} = 0$; and at $z = \xi$, $p = p_\xi$. To determine $p_\xi$, Newton's second law of motion is written for the piston:

$$\frac{d}{dt}(Mv) = -Mg - p_a A + p_\xi A$$

where $v$ = $\frac{d\xi}{dt}$ (at z = $\xi$) and at $t = 0, \xi = \xi_0$. Hence,

$$M\frac{d}{dt}\left[\frac{d\xi}{dt}\right] = -Mg - p_a A + p_\xi A$$

or,

$$p_\xi = \frac{1}{A}\left\{M\frac{d}{dt}\left[\frac{d\xi}{dt}\right] + M\,g\right\} + p_a \qquad \text{(E41N)}$$

Example 2 Consider a solid sphere of radius *a*, and temperature $T_0$ situated in an infinite volume of gas. The gas consists of two components, *A* and *B*, which can undergo a reversible transformation: $A \Leftrightarrow B$. The kinetics of the reaction are described by $R_B''' = k_A''' C_A - k_B''' C_B$, where $k_A'''$ and $k_B'''$ are functions of temperature only.

Defining the constant $K$ = $k_A''' / k_B'''$ and $K$ = $f(T)$ yields $R_B''' = \frac{k_A'''}{K}\left[(1+K)X_A - 1\right]C$, where $C$ = total mass concentration and $X_A$ = mole fraction of *A*.

Far from sphere the gas temperature is $T_\infty$ and the mole fraction of *A* is $X_{A\infty}$. Analyze the situation under the following assumptions: steady state, the gas phase is ideal, the values of $c_p$, $k$ and $\mu$ are the same for *A* and *B*, there is no natural convection and only concentration diffusion is important.

(a) Give the differential equation and boundary conditions describing the steady state velocity, composition, etc.
(b) Show that the velocity is zero.
(c) Does the presence of the homogeneous reaction change the heat flux from the sphere from the value it would be if there were no homogeneous reaction?

Solution

Based on the above-mentioned problem statement and assumptions the governing conservation equations (for the gas phase) can be written as:

Overall continuity: $$\frac{1}{r^2}\frac{\partial}{\partial r}\left(\rho r^2 v_r\right)=0 \tag{E42A}$$

"B" balance: $$0=D_{AB}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_B}{\partial r}\right)\right]+\frac{k_A'''}{K}\left[(1+K)x_A-1\right]C$$

or,

$$0=D_{AB}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial x_B}{\partial r}\right)\right]+\frac{k_A'''}{k}\left[(1+k)x_A-1\right] \tag{E42B}$$

Momentum: $$0=-\frac{\partial p}{\partial r}-\rho g_r \tag{E42C}$$

Energy: $$\begin{aligned}0=\alpha&\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right)\right]-\\ &\frac{1}{\rho c_p}\left\{\overline{H}_A\left[k_B'''(1+K)x_B-1\right]+\overline{H}_B\left[k_A'''(1+K)x_A-1\right]\right\}C\end{aligned} \tag{E42D}$$

Subject to the following boundary conditions: at $r\to\infty$, $T=T_\infty$, $p=p_\infty$, $x_B\to x_{B\infty}$ (or equals to $1-x_{A\infty}$). In addition, the following interface boundary conditions (at $r$ = $a$) are used:

Species (component "B") balance:

$$\left\|n_B-\rho_B v_s\right\|=r_B''' \tag{E42E}$$

or, since at $r$ = $a$, $r_B'''=0$,

$$n_B-\rho_B v_s=n_B'-\rho_B' v_s \tag{E42F}$$

Finally, $\vec{n}_B=\vec{j}_B=0$.[5] A similar information can also be derived using the molar fluxes:

$$\left\|x_B\rho\left(v_r-v_s\right)+J_{rB}\right\|=R_B''' \tag{E42G}$$

or,

$$x_B\rho\left(v_r-v_s\right)+J_{rB}-x_B'\rho'\left(v_r'-v_s\right)+J_{rB}'=R_B''' \tag{E42H}$$

Finally, $\vec{J}_B=0$.[6]

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[5] Why does the convective part of this mass flux equal to zero?

[6] The reason for the absence of the convective part here is the same as for the mass flux term.

Jump energy balance:

$$\left\| \sum \dot{m}\bar{h}_i + q_n \right\| = r_B''' \tag{E42I}$$

but at $r = a$, $r_B''' = 0$ then:

$$\left\| \sum \dot{m}\bar{h}_i + q_n \right\| = 0$$

and since at $r = a$, $\dot{m} = 0$ [7]:

$$\left\| q_n \right\| = 0$$

or,

$$k\frac{\partial T'}{\partial r} = k'\frac{\partial T'}{\partial r} \tag{E42J}$$

Finally, from the thermodynamic equilibrium, at $r = a$, $T = T' = T_0$.

### 4.3 Free Convection due to Concentration Gradient

Similar to that discussed in Chapter 2 free convective currents can be developed when concentration gradient is presented in the system. In that case,

$$\rho = f(T, p, \omega) \tag{4.3A}$$

Using Taylor's series expansion,

$$\rho = \rho_R + \left(\frac{\partial \rho}{\partial T}\right)_{\rho,\omega}(T - T_R) + \left(\frac{\partial \rho}{\partial p}\right)_{T,\omega}(p - p_R) + \left(\frac{\partial \rho}{\partial \omega}\right)_{T,p}(\omega - \omega_R) \tag{4.3B}$$

and since $\beta_T = -\frac{1}{\rho_R}\left(\frac{\partial \rho}{\partial T}\right)\rho,\omega$ and $\beta_\omega = \frac{1}{\rho_R}\left(\frac{\partial \rho}{\partial \omega}\right)_{T,p}$, where $\beta_\omega$ is the quantity defined analogously to $\beta$ (so-called concentration expansion coefficient) and is normally neglected.[8]

$$\rho = \rho_R\left[1 - \beta_T(T - T_R) + \beta_\omega(\omega - \omega_R)\right] \tag{4.3C}$$

Thus, our momentum equation becomes (taking $\rho = \rho_R$):

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[7] The information is derived from the overall (jump) mass balance at the interface.

[8] This quantity is symbolized $\zeta$ in Bird et al. (1960, p. 563).

$$\rho \frac{D\vec{v}}{Dt} = -\nabla P - \rho\beta_T (T - T_R)\vec{G} + \rho\beta_\omega (\omega - \omega_R)\vec{G} + \mu\nabla \cdot \underline{\dot{\gamma}} \tag{4.3D}$$

where $P = p + \rho \vec{G}$

In dimensionless form,

$$\frac{D\vec{v}^{\,*}}{Dt^*} = -\nabla^* P^* - \left(\frac{\beta_T \Delta TGL}{U^2}\right)\vec{G}^{\,*}\ T^* + \left(\frac{\beta_\omega \Delta\omega GL}{U^2}\right)\vec{G}^{\,*}\ \omega^* + \left(\frac{\mu}{\rho UL}\right)\nabla^* \cdot \underline{\dot{\gamma}}^{\,*} \tag{4.3E}$$

where the terms in the first, second and third brackets on the right-hand side of the equation are heat-transfer Grashof number $Gr_T$, mass-transfer Grashof number $Gr_\omega$, and the reciprocal of the Reynolds number, respectively.

## References

1. Bird, R.B., Stewart, W.E., Lightfoot, E.N., 1960, **Transport Phenomena**, Wiley, New York.
2. Bird, R.B., Stewart, W.E., Lightfoot, E.N., 2002, **Transport Phenomena**, **2nd Edition**, Wiley, New York.

## Problems

1. In the food processing industry, many products are separated from their original natural structure by a process called leaching. Examples of this process are the production of soluble instant coffee, where ground roasted coffee is leached with fresh water, as well as the leaching of oils from various seeds using organic solvents. In studying the rate of leaching of a substance *A* from solid particles by a solvent *B*, it is postulated that the rate-controlling step is the diffusion of *A* from the particle surface through a stagnant liquid film of thickness $\delta$ out into the main stream (see Figure P4.1). The molar solubility of *A* in *B* is $c_{A0}$, and the concentration of *A* in the main stream is $c_{A\delta}$.

   (a) Write a differential equation for $c_A$ as a function of *z*. Assume that $D_{AB}$ is constant and that *A* is only slightly soluble in *B*. Neglect the curvature of the particle.
   (b) Show that, in the absence of chemical reaction in the liquid phase, the concentration profile is linear.
   (c) Show that the rate of leaching is given by $N_{Az} = D_{AB}(c_{A0} - c_{A\delta})/\delta$.

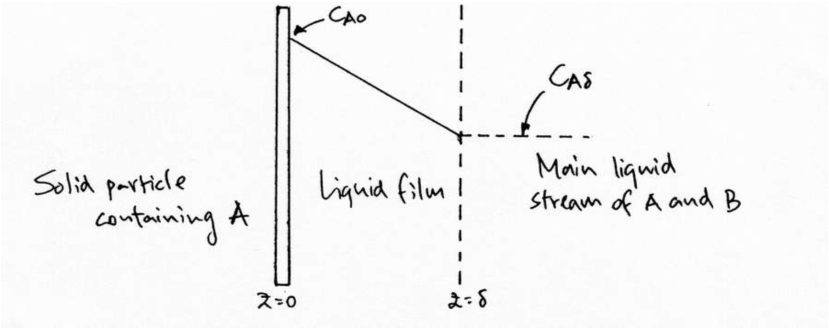

**Figure P4.1. Leaching of A by diffusion into a stagnant liquid film of B**

2. A layer of pure carbon deposited on a solid surface burns with oxygen according to the following reaction:

$$2C(s) + O_2 \rightarrow 2CO(g)$$

The reaction occurs only at the gas/solid interface. The carbon is consumed and the thickness of the layer $\delta$ decreases (see Figure P4.2).

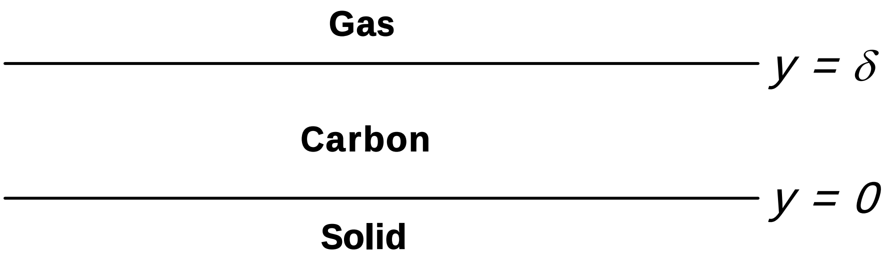

**Figure P4.2. Carbon deposition layer of Problem 2**

In the gas phase at $y = \delta$, denote the molar fluxes (with respect to fixed coordinates) of oxygen and carbon monoxide as $N_{O_2}$ and $N_{CO}$ and the molar concentrations of the respective components as $c_{O_2}$ and $c_{CO}$. Derive the equation relating the molar fluxes, concentrations and the velocity of the interface of the reaction is instantaneous.

3. A droplet of water, initially having a radius $a_0$ and a temperature $T_0$, is suspended in air, which is initially at a temperature $T_\infty$. At time $t = 0$ the droplet is exposed to the air. Assume the following:

- The pressure in the gas phase at the surface of the droplet is one atmospheric.
- Far from the droplet the gas is motionless.
- Constant properties (no natural convection); no dissipation.
- Radial flow only
- Air is insoluble in the droplet

- The diffusion flux is $\vec{j} = -\rho D \nabla w$ (i.e., neglect thermal and pressure diffusions)
- The simplified jump (interface) balances apply.

(a) Set up the equations governing this situation.
(b) Give the required initial and boundary conditions to solve the set of equations proposed in (a).

4. The process of chemical vapor deposition (CVD) is used to grow thin solid films on solid substrates. The film is deposited from the gas phase by reaction at the surface. An example of this process is the growth of solid silicon (Si) from the decomposition of silane ($SiH_4$) gas according to the following reaction:

$$SiH_4(g) \rightarrow Si(s) + 2H_2(g)$$

where gaseous hydrogen is produced.

A silicon film is grown on a motionless substrate exposed to a two-dimensional stagnation flow. At $z = L$ the gas consists of a mixture of $SiH_4$ at low concentration (say, mass fraction equals to $\omega_L$) in hydrogen. Also at this point the flow is directed toward the surface with a uniform velocity $V$. The substrate is assumed to be infinite in extent and the film thickness is assumed to be uniform so that the velocity, temperature and composition fields are two-dimensional. The substrate is at a uniform temperature $T_0$ and the gas at $z = L$ is at a temperature $T_L$ and a pressure $P_L$. The situation is sketched in Figure P4.4.

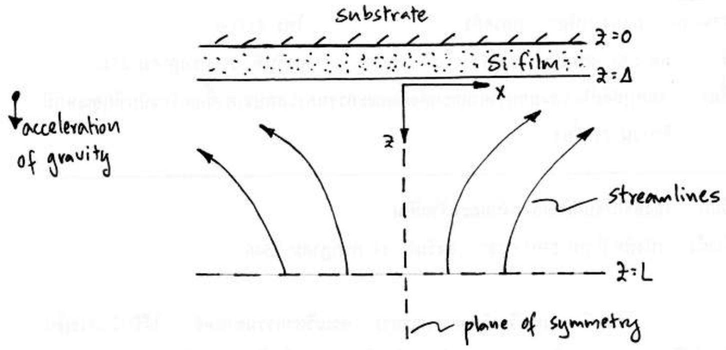

**Figure P4.4. Chemical vapor deposition of solid silicon on a solid substrate**

The proposed reaction occurs only on the surface of the film, or, initially, on the surface of the substrate. It can also be assumed that silicon is non-volatile and the energy dissipation, thermal diffusion[9] and pressure diffusion may be neglected. In addition, it can be assumed that the gases form an ideal solution and follow the ideal gas law.

Assume that the fluid properties are constant and that the rate of the above reaction may be written as:

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[9] This assumption is indeed not realistic but is made here only for the sake of simplicity.

$$R'''_{Si} = Kc_{SiH_4}$$

where $R'''_{Si}$ is the rate of deposition of Si per unit area, $c_{SiH_4}$ is the molar concentration of $SiH_4$ in the gas phase at $y = \Delta$, and $K$ is the reaction rate constant, which is a strong function of temperature.

(a) Give the differential equations governing the flow, thermal and concentration fields in the solid and gas phases.
(b) Give the boundary conditions needed for a complete mathematical specification of the process.

5. A droplet of substance *A* is suspended in a stream of gas *B*. The droplet radius is $r_1$. It is also postulated that there is a spherical stagnant gas film of radius $r_2$ around the droplet. The concentration of *A* in the gas phase is $x_{A1}$ at $r = r_1$ and $x_{A2}$ at $r = r_2$.

(a) Show that, for steady state diffusion, $r^2N_{Ar}$, where $N_{Ar}$ is the molar flux of *A* in the radial direction, is a constant and set this constant equal to $r_1^2 N_{Ar1}$, the value at the droplet interface.
(b) Show that the result in (a) lead to the following equation for $x_A$ (mole fraction of *A*):

$$r_1^2 N_{Ar1} = -\frac{cD_{AB}}{1-x_A} r^2 \frac{dx_A}{dr}$$

6. Consider a spherical cell (organism) of radius $r_o$ within which respiration occurs at a uniform volumetric rate of $r'''_A = -k_0$; in other words, oxygen (species A) consumption is governed by a zero-order, homogeneous chemical reaction within the cell.

(a) If a molar concentration of $C_A(r_o) = C_{A,o}$ is maintained at the surface of the cell, obtain an expression for the steady radial distribution of oxygen, $C_A(r)$, within the cell by writing an appropriate differential equation and solving it subject to the suitable boundary conditions. A radial symmetry can be assumed at the center of the cell.
(b) Obtain an expression for the rate of oxygen consumption (in mole/s) within the cell, i.e., the rate at which oxygen must be transferred to the cell through its surface. Fick's first law of diffusion can be used to obtain the required expression.

7. Consider a system where a gas is confined between two large parallel plates as shown in Figure P4.7. The gas is initially binary, i.e., some species *A* that is diluted in species *B*; the initial concentration of *A* is $C_{A0}$. The planar surfaces at $y = \pm B$ are coated with a catalyst that promotes a first-order heterogeneous reaction:

$$A \rightarrow P \qquad \text{(P41A)}$$

with a rate:

$$R_A = kC_A \qquad \text{(P41B)}$$

where $R_A$ represents the rate of the surface reaction and *P* is any arbitrary component in the system. At the time $t > 0$ the catalytic reaction is switched on and *A* disappears through this heterogeneous reaction. Note that there is no accumulation of any species on the catalytic surfaces.

(a) Write the differential equation (species balance equation) that can be solved (but do not attempt to solve the equation!) for the transient distributions of *A* in the gas phase.
(b) Give the initial and boundary conditions necessary to completely solve the above equation.

Hint: A symmetry can be assumed along the centerline ($y = 0$) of the system.

**Figure P4.7. A schematic diagram of the diffusion with surface reaction**

8. Consider a situation involving a gaseous mixture of *A* and *B* for which *A* is chemically consumed at the catalytic surface (see Figure P4.8).

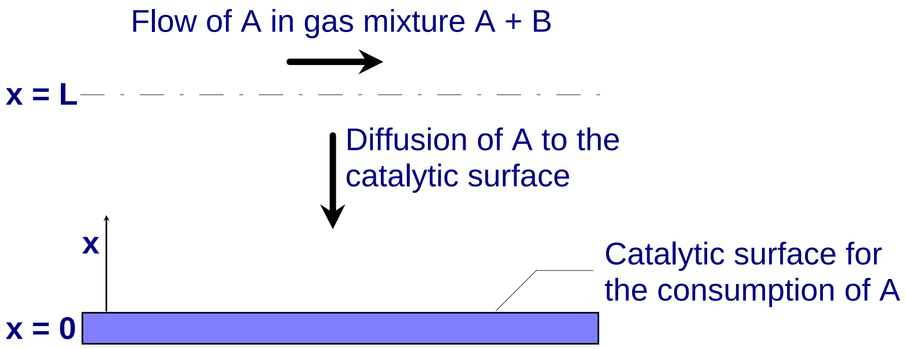

**Figure P4.8. A schematic sketch of the catalytic surface**

The reaction is known to be first order and its rate per unit area of the surface may be expressed as $r_A''' = -k_1 C_A$ where $k_1$ is the reaction rate constant and $C_A$ is the local molar concentration of *A*. Although bulk motion influences the transfer of *A* through the system, it is reasonable to assume, as a first estimate, that the effect of bulk motion is negligible. It is also assumed that *A* arrives the surface as a result of one-dimensional diffusion through a thin stagnant film of thickness *L* within which there is no reaction. At steady state the molar concentration of *A* at $x = L$ is fixed at $C_{A,L}$, which corresponds to the condition in the mainstream of the mixture. Write the differential equation, along with appropriate boundary conditions, and show that the variation of $C_A$ with distance $x$, $C_A(x)$, is given by $\dfrac{C_A(x)}{C_{A,L}} = \dfrac{(D_{AB} + xk_1)}{(D_{AB} + Lk_1)}$.

9. A simple scheme for desalination involves maintaining a thin film of salt water on the lower surface of two infinite parallel plates that are separated by a distance $L$ as shown in Figure P4.9. A low-speed incompressible, fully developed, laminar flow of constant property air is applied between the plates. Evaporation occurs from the liquid film on the lower surface, which is maintained at a temperature $T_0$, while condensation occurs at the upper surface, which is maintained at $T_L$. The corresponding molar concentrations of water vapor at the lower and upper surfaces are $C_{A,0}$ and $C_{A,L}$, respectively.

   (a) Write the differential equations, along with appropriate boundary conditions, which enable one to obtain a steady state expression for the distribution of the water vapor molar concentration in the air.
   (b) Write an additional boundary condition at the lower interface to obtain a steady state expression for the rate at which heat must be supplied to this surface to maintain its temperature at $T_0$.

   Hint: Recall the definition of fully developed flow when simplifying the governing conservation equations. The use of infinite plates also implies that the temperature and species concentration may be assumed to be independent of $x$ and $z$.

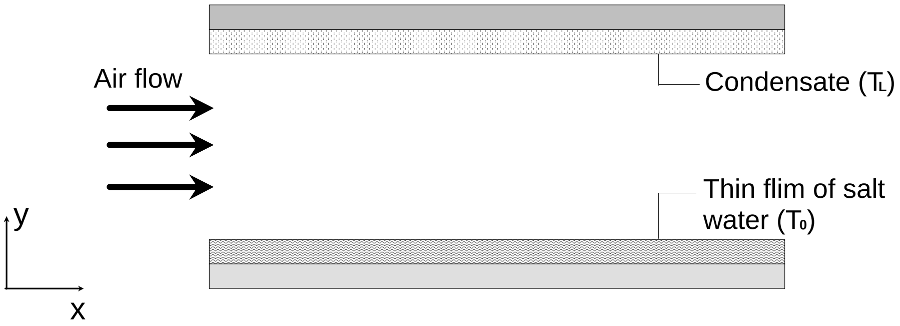

**Figure P4.9. A schematic sketch of a simple desalination process**