

Module 4: Multicomponent Transport

Lecture 33: Multi-component Mixtures

Multi-component equations in terms of fluxes

a) Continuity for each chemical species

$$\frac{D\rho_i}{Dt} = -\rho_i(\nabla \cdot \underline{v}) - (\nabla \cdot \underline{j}_i) + r_i \quad (3.7.1)$$

$i = 1, 2, \dots, n$

$\text{g/cm}^3\text{-s}$

mass flux relative to mass – average velocity \underline{v}

Summing over i one obtains:

Conservation of Total Mass

$$\frac{\partial \rho}{\partial t} + (\nabla \cdot \rho \underline{v}) = 0 \quad (3.7.2)$$

b) Equation of Motion

$$\rho \frac{D\underline{v}}{Dt} = -\nabla(\underline{\tau} + p\underline{\delta}) + \sum_{i=1}^n \rho_i \underline{g}_i \quad (3.7.3)$$

$\underline{\pi}$

body force per unit mass

c) Equation of energy

$$\rho \frac{D}{Dt} \left(\hat{U} + \frac{1}{2} U^2 \right) = -(\nabla \cdot \underline{q}) - \nabla \cdot [\underline{\pi} \cdot \underline{v}] + \sum_{i=1}^n \underline{n}_i \cdot \underline{g}_i \quad (3.7.4)$$

Multicomponent energy
flux relative to \underline{v}
 Mass Average Velocity
 mass flux

For a complete description of a system, one needs:

- a) A thermal equation of state $p = p(\rho, T, X_i)$
- b) A caloric equation of state $\hat{U} = \hat{U}(\rho, T, X_i)$
- c) Information on reaction kinetics (r_i term in 3.7.1)
- d) Explicit expressions for the fluxes ($\underline{j}_i, \underline{q}, \underline{\pi}$) in terms of the gradients and transport coefficients.

Equations (3.7.1), (3.7.3) and (3.7.4) can also be written in terms of fluxes, defined with respect to a coordinate system fixed in space, i.e.,

$$\begin{aligned} \underline{n}_i &= \rho w_i \underline{v} + \underline{j}_i & i = 1, 2, \dots, n \\ \underline{\phi} &= \rho \underline{v} \underline{v} + \underline{\pi} \\ \underline{e} &= \rho \left(\hat{U} + \frac{1}{2} \rho v^2 \right) \underline{v} + \underline{q} + [\underline{\pi} \cdot \underline{v}] \end{aligned} \quad (3.7.5)$$

Then, we get the Equations of

$$\text{Continuity: } \frac{\partial \rho_i}{\partial t} = -(\nabla \cdot \underline{n}_i) + r_i \quad (3.7.6)$$

$$\text{Motion: } \frac{\partial(\rho \underline{v})}{\partial t} = -[\nabla \cdot \underline{\phi}] + \sum_{i=1}^n \rho_i \cdot \underline{g}_i \quad (3.7.7)$$

$$\text{Energy: } \frac{\partial}{\partial t} \rho \left\{ \hat{U} + \frac{1}{2} \rho v^2 \right\} = -[\nabla \cdot \underline{e}] + \sum_{i=1}^n n_i \cdot \underline{g}_i \quad (3.7.8)$$

Note: There is no need to add a term describing thermal energy release by homogeneous chemical reactions. This is included implicitly in \hat{U} in equations (3.7.4) and (3.7.8).

Multi-component Fluxes

Driving forces Fluxes	Velocity gradients	Temperature gradient	Concentration gradient Pressure gradient External force differences
Momentum (second order tensor)	Newton's law (μ, k)		
Energy (vector)		Fourier's law [k]	Dufour Effect [D_A^T]
Mass (vector)		Soret effect [D_A^T]	Fick's law [D_{AB}]

According to the thermodynamics of irreversible processes, there will be a contribution to each flux due to each driving force in the system. This coupling can occur only between flux – force pairs that are tensors of equal order or which differ in order by two.

Therefore,

a) The momentum flux depends only on the velocity gradients. For Newtonian fluids,

$$\underline{\underline{\tau}} = -\mu \left(\nabla \underline{v} + (\nabla \underline{v})^T \right) + \left(\frac{2}{3} \mu - k \right) (\nabla \cdot \underline{v}) \underline{\underline{\sigma}} \quad (3.7.9)$$

Dyadic
Transpose
Viscosity
Bulk Viscosity (\approx zero)
of $(\nabla \underline{v})$

b) The energy flux depends on the temperature gradient (Conduction), the interdiffusion of the various species present, and the Dufour or diffusion – thermo effect. Thus,

$$\underline{q} = \underline{q}^{(c)} + \underline{q}^{(d)} + \underline{q}^{(x)} \quad \text{or}$$

$$\underline{q} = -k \nabla T + \sum_{i=1}^n \bar{H}_i \underline{j}_i + \underline{q}^{(x)} \quad (3.7.10)$$

Partial molal enthalpy quite complex for multi-component systems .

Usually negligible

Note: Equation (3.7.10) neglects radiant energy flux and j_i in this equation is the mass flux of the i-th species defined w.r.t. the mass average velocity.

c) Mass flux depends on three “mechanical driving forces” that tend to produce movement of a species relative to the mean fluid motion (i.e., (i) concentration

gradient, (ii) pressure gradient, and (iii) external force acting unequally on the various species), as well as on (iv) the temperature gradient (thermo – diffusion or Soret Effect)

$$d) \text{ Thus the total flux : } \underline{j}_i = \underline{j}_i^{(x)} + \underline{j}_i^{(p)} + \underline{j}_i^{(s)} + \underline{j}_i^{(T)} \quad (3.7.11)$$

With

(i) Ordinary (Concentration) Diffusion

Partial molal Gibb's free energy

$$\underline{j}_i^{(x)} = \frac{C^2}{\rho RT} \sum_{j=1}^n M_i M_j D_{ij} \left[X_j \sum_{\substack{k=1 \\ k \neq j}}^n \left(\frac{\partial \bar{G}_i}{\partial X_k} \right)_{T, P, X_s, s \neq j, k} \nabla X_k \right] \quad (3.7.12)$$

Multi-component diffusion coefficients

(ii) Pressure diffusion (important in centrifuge separations)

$$\underline{j}_i^{(p)} = \frac{C^2}{\rho RT} \sum_{j=1}^n M_i M_j D_{ij} \left[X_j M_j \left(\frac{\bar{V}_j}{M_j} - \frac{1}{\rho} \right) \nabla p \right] \quad (3.7.13)$$

(iii) Forced diffusion (important in ionic systems; Force = (charge) x (electric field))

$$\underline{j}_i^{(g)} = -\frac{C^2}{\rho RT} \sum_{j=1}^n M_i M_j D_{ij} \left[X_j M_j \left(\underline{g}_j - \sum_{k=1}^n \frac{\rho_k}{\rho} \underline{g}_k \right) \right] \quad (3.7.14)$$

If gravity is the only external force, then $\Rightarrow j_i^{(g)} = 0$

(iv) Thermal diffusion (usually small)

$$\underline{j}_i^{(T)} = -\underset{\uparrow}{D_i^T} \nabla \ln T \quad (3.7.15)$$

Multi-component thermal diffusion coefficients

The above equations can be derived from an “entropy balance” equation.

For $n > 2$ $D_{ij} \neq D_{ji}$, and there are $\frac{n(n-1)}{2}$ independent diffusivities.