Fluxes in Multicomponent Systems

ChEn 6603

Taylor & Krishna §1.1-1.2

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Outline

- Reference velocities
- Types of fluxes (total, convective, diffusive)
  - Total fluxes
  - Diffusive Fluxes
- Example
- Conversion between diffusive fluxes

T&K Table 1.2

Reference Velocities

Denote the velocity of component i as $\mathbf{u}_i$.

What assumptions have we made here?

"Molar-Averaged" velocity $$\mathbf{u} = \sum_{i=1}^{n} x_i \mathbf{u}_i$$ x_i is the mole fraction of component i.

"Mass-Averaged" velocity $$\mathbf{v} = \sum_{i=1}^{n} \omega_i \mathbf{u}_i$$ ω_i is the mass fraction of component i.

"Volume-Averaged" velocity $$\mathbf{u}^V = \sum_{i=1}^{n} \phi_i \mathbf{u}_i$$

$\phi_i \equiv c_i \bar{V}_i$ is the volume fraction of component i.

$c_i = x_i c = \rho_i / M_i$ - molar concentration of i.

$\bar{V}_i$ - partial molar volume of component i (EOS).

Arbitrary reference velocity $$\mathbf{u}^a = \sum_{i=1}^{n} a_i \mathbf{u}_i \qquad \sum_{i=1}^{n} a_i = 1$$ a_i is an arbitrary weighting factor.

Why $\sum a_i = 1$?

How do we define a_i such that $\mathbf{u}^a = \mathbf{u}_j$?

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Types of Fluxes

- Total Flux
  - Amount of a quantity passing through a unit surface area per unit time.
- Convective Flux:
  - Amount of a quantity passing through a unit surface area per unit time that is carried by some reference velocity.
- Diffusive Flux:
  - Amount of a quantity passing through a unit surface area per unit time due to diffusion.
  - The difference between the Total Flux and the Convective Flux.
  - Cannot be defined independently of the total & convective fluxes!

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Total Fluxes

Total Fluxes may be written in terms of a component's *velocity* and *specific density*

Mass Flux of component i:

$$\begin{aligned}\mathbf{n}_i &\equiv \omega_i \rho \mathbf{u}_i \\ &= \rho_i \mathbf{u}_i\end{aligned}$$

ρ - mixture mass density

Total Mass Flux:

$$\begin{aligned}\mathbf{n} &\equiv \sum_{i=1}^{n} \mathbf{n}_i \\ &= \sum_{i=1}^{n} \rho_i \mathbf{u}_i, \\ &= \rho \mathbf{v}\end{aligned}$$

Molar Flux of component i:

$$\begin{aligned}\mathbf{N}_i &\equiv x_i c \mathbf{u}_i \\ &= c_i \mathbf{u}_i\end{aligned}$$

Total Molar Flux:

$$\begin{aligned}\mathbf{N}_t &= \sum_{i=1}^{n} \mathbf{N}_i \\ &= \sum_{i=1}^{n} c_i \mathbf{u}_i \\ &= c\mathbf{u}\end{aligned}$$

Note: there is a typo in T&K eq. (1.2.5)

Diffusive Fluxes

Concepts:

- The *total* flux is partitioned into a *convective* and *diffusive* flux.
- The *convective flux* is defined in terms of an *average velocity*.
- The *diffusive flux* is defined as the difference between the *total* and *convective* fluxes. It is only defined once we have chosen a convective flux!

Mass diffusive flux of component i relative to a mass-averaged velocity.

Total mass flux of component i

Convective flux of component i due to a mass-averaged velocity

$$
\begin{aligned}
\mathbf{j}_i &= \mathbf{n}_i - \rho_i \mathbf{v} \\
&= \rho_i (\mathbf{u}_i - \mathbf{v}) \\
&= \mathbf{n}_i - \omega_i \mathbf{n}_t
\end{aligned}
$$

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Diffusive Fluxes

Diffusion fluxes are defined as motion relative to some *reference velocity.*

(*Diffusion flux*) = (*Total Flux*) - (*convective flux*)

Diffusion Flux	Total Flux	Convective Flux	Comments
$\mathbf{j}_i$	$\mathbf{n}_i$	$\rho_i \mathbf{v}$	Mass diffusive flux relative to a mass-averaged velocity
$\mathbf{j}_i^u$	$\mathbf{n}_i$	$\rho_i \mathbf{u}$	Mass diffusive flux relative to a molar-averaged velocity
$\mathbf{J}_i$	$\mathbf{N}_i$	$c_i \mathbf{u}$	Molar diffusive flux relative to a molar-averaged velocity
$\mathbf{J}_i^v$	$\mathbf{N}_i$	$c_i \mathbf{v}$	Molar diffusive flux relative to a mass-averaged velocity

$$\begin{aligned} \mathbf{j}_i &= \mathbf{n}_i - \rho_i \mathbf{v} \\ &= \rho_i (\mathbf{u}_i - \mathbf{v}) \\ &= \mathbf{n}_i - \omega_i \mathbf{n}_t \end{aligned}$$

$$\begin{aligned} \mathbf{J}_i &= \mathbf{N}_i - c_i \mathbf{u} \\ &= c_i (\mathbf{u}_i - \mathbf{u}) \\ &= \mathbf{N}_i - x_i \mathbf{N}_t \end{aligned}$$

Linear Dependence of Diffusive Fluxes

- Appropriately weighted diffusive fluxes sum to zero. Why?
- Total fluxes are all independent.
- Convective fluxes are not all independent.

For mass diffusive flux relative to mass-averaged velocity: $\sum_{i=1}^{n} \mathbf{j}_i = 0$

From the previous slide: $\mathbf{j}_i = \rho_i \left(\mathbf{u}_i - \mathbf{v} \right)$

$$\begin{aligned} \sum_{i=1}^{n} \mathbf{j}_i &= \sum_{i=1}^{n} (\rho_i \mathbf{u}_i - \rho_i \mathbf{v}) \\ &= \rho \sum_{i=1}^{n} (\omega_i \mathbf{u}_i - \omega_i \mathbf{v}), \\ &= -\rho \mathbf{v} + \rho \sum \omega_i \mathbf{u}_i \\ &= -\rho \mathbf{v} + \rho \mathbf{v}, \\ &= 0. \end{aligned}$$

Note: typo in table 1.3 (missing v superscript) $\sum_{i=1}^{n} \frac{\omega_i}{x_i} \mathbf{J}_i^v = 0$

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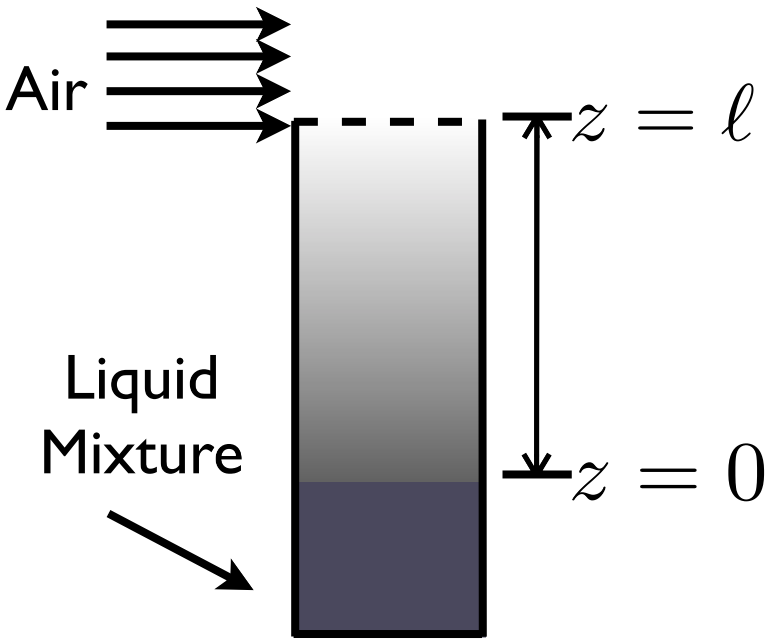
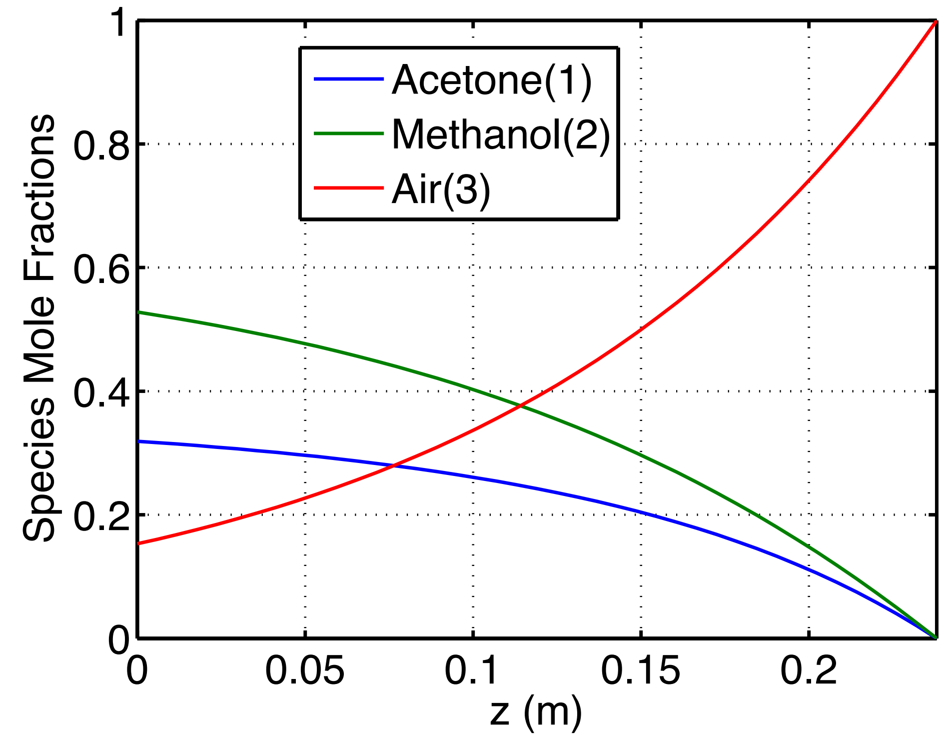
Example - Stefan Tube



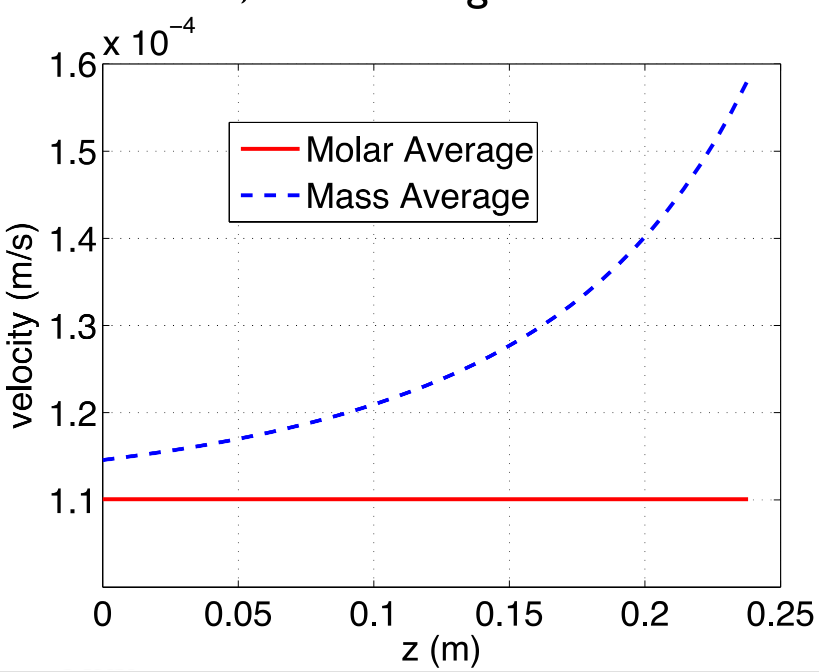
At steady state (1D),

$$\begin{aligned} \mathbf{n}_i &= \alpha_i \\ \mathbf{N}_i &= \beta_i \end{aligned}$$

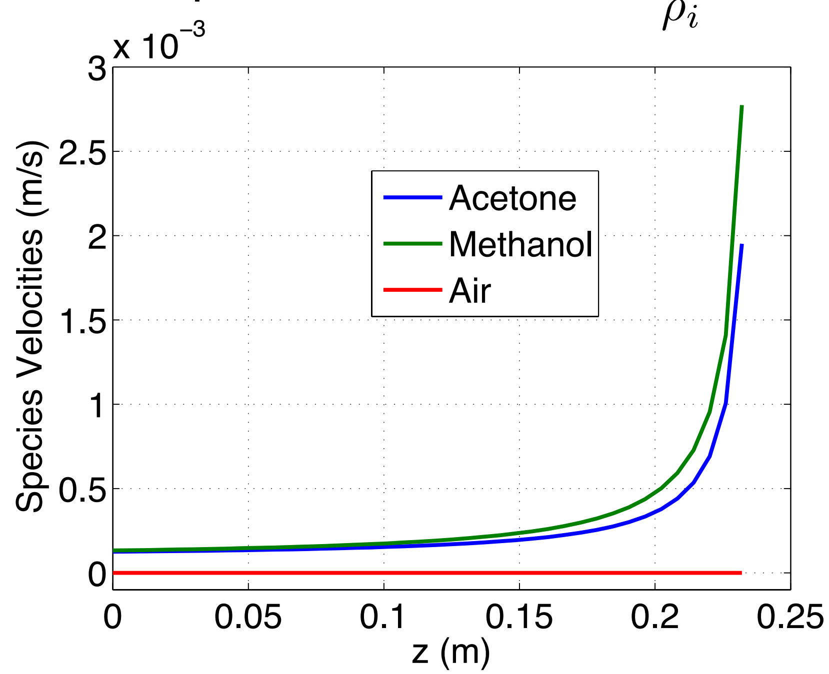
We will show this later...



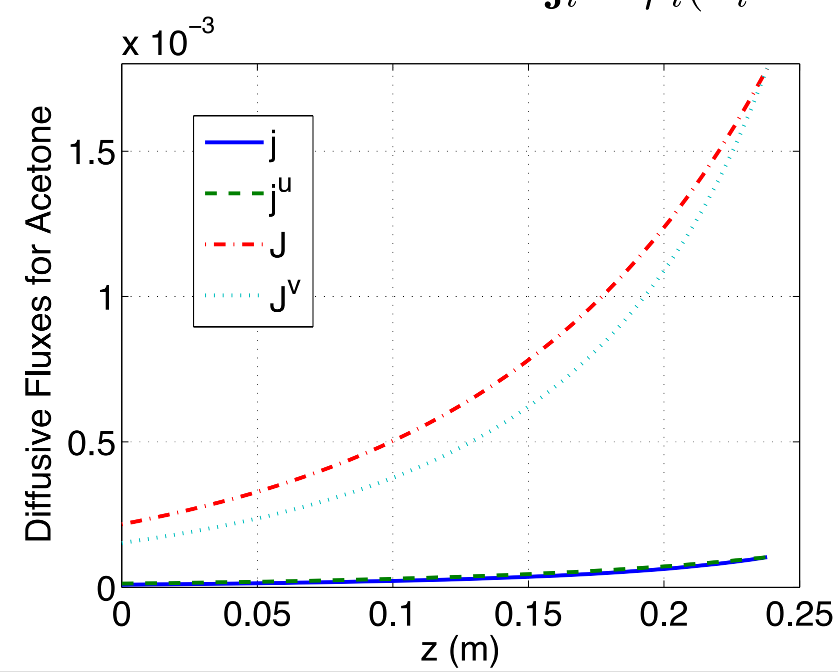
Molar, mass averaged velocities



Species velocities $\mathbf{u}_i = \dfrac{\mathbf{n}_i}{\rho_i}$



Acetone diffusive fluxes $\mathbf{j}_i = \rho_i(\mathbf{u}_i - \mathbf{v})$



Conversion Between Fluxes

We can convert between various diffusive fluxes via linear transformations.

Conversion between mass diffusive fluxes relative to mass and molar reference velocities.

$$
\begin{aligned}
(\mathbf{j}^u) &= [B^{uo}](\mathbf{j}) \\
(\mathbf{j}) &= [B^{ou}](\mathbf{j}^u)
\end{aligned}
$$

To form $[B^{uo}]^{-1}$ this must be an n-1 dimensional system of equations! (why?)

Derivation of $[B^{ou}]$...

$$\mathbf{j}_i^u = \rho_i(\mathbf{u}_i - \mathbf{u})$$

$$
\begin{aligned}
\sum_{i=1}^{n} \mathbf{j}_i^u &= \sum_{i=1}^{n} \rho_i \mathbf{u}_i - \sum_{i=1}^{n} \rho_i \mathbf{u}, \\
&= \rho \mathbf{v} - \rho \mathbf{u}, \\
\frac{1}{\rho} \sum_{i=1}^{n} \mathbf{j}_i^u &= \mathbf{v} - \mathbf{u}.
\end{aligned}
$$

$$\mathbf{j}_i = \rho_i(\mathbf{u}_i - \mathbf{v})$$

Let's try to get a $\mathbf{j}_i^u$ on the RHS ⇒ add & subtract $\rho_i\mathbf{u}$.

$$
\begin{aligned}
\mathbf{j}_i &= \rho_i(\mathbf{u}_i - \mathbf{v}), \\
&= \underbrace{\rho_i(\mathbf{u}_i - \mathbf{u})}_{\mathbf{j}_i^u} + \rho_i(\mathbf{u} - \mathbf{v})
\end{aligned}
$$

$$\mathbf{j}_i = \mathbf{j}_i^u - \omega_i \sum_{j=1}^{n} \mathbf{j}_j^u$$

This is an n-dimensional set of equations. If we derive $[B^{ou}]$ from this, it will not be full-rank.

Derivation of $[B^{ou}]$ (cont'd)

$$\mathbf{j}_i = \mathbf{j}_i^u - \omega_i \sum_{j=1}^{n} \mathbf{j}_j^u$$

separate out $\mathbf{j}_n^u$

$$\mathbf{j}_i = \mathbf{j}_i^u - \omega_i \left[\mathbf{j}_n^u + \sum_{j=1}^{n-1} \mathbf{j}_j^u \right]$$

$$\sum_{i=1}^{n} \frac{x_i}{\omega_i} \mathbf{j}_i^u = 0 \quad \Rightarrow \quad \mathbf{j}_n^u = -\frac{\omega_n}{x_n} \sum_{i=1}^{n-1} \frac{x_i}{\omega_i} \mathbf{j}_i^u$$

eliminate $\mathbf{j}_n^u$

Eliminate $\mathbf{j}_n^u$ from the above equation...

$$\begin{aligned} \mathbf{j}_i &= \mathbf{j}_i^u - \omega_i \sum_{j=1}^{n-1} \left[-\frac{\omega_n}{x_n} \frac{x_j}{\omega_j} \mathbf{j}_j^u + \mathbf{j}_j^u \right], \\ &= \sum_{j=1}^{n-1} \left[\delta_{ij} - \omega_i \left(1 - \frac{\omega_n}{x_n} \frac{x_j}{\omega_j} \right) \right] \mathbf{j}_j^u \end{aligned}$$

gather terms on $\mathbf{j}_n^u$

we have n-1 of these equations (i=1...n-1)

$$(\mathbf{j}) = [B^{ou}](\mathbf{j}^u)$$

$$B_{ij}^{ou} = \delta_{ij} - \omega_i \left(1 - \frac{\omega_n}{x_n} \frac{x_j}{\omega_j} \right)$$

The inverse $[B^{uo}]=[B^{ou}]^{-1}$ can be obtained from equations A.3.21-A.3.23 in T&K (note the typo in A.3.22).

$$\begin{aligned} [B]^{-1} &= [A]^{-1} - \tfrac{1}{\alpha} [A]^{-1} (u) (v)^{\mathsf{T}} [A]^{-1}, \\ \alpha &= 1 + (v)^{\mathsf{T}} [A]^{-1} (u) \end{aligned}$$

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