Fluxes in Multicomponent Systems

ChEn 6603

Taylor & Krishna §1.1-1.2
Outline

Reference velocities

Types of fluxes (total, convective, diffusive)

• Total fluxes
• Diffusive Fluxes

Example

Conversion between diffusive fluxes
Reference Velocities

Denote the velocity of component $i$ as $u_i$. What assumptions have we made here?

“Molar-Averaged” velocity

$$u = \sum_{i=1}^{n} x_i u_i$$

$x_i$ is the mole fraction of component $i$.

“Mass-Averaged” velocity

$$v = \sum_{i=1}^{n} \omega_i u_i$$

$\omega_i$ is the mass fraction of component $i$.

“Volume-Averaged” velocity

$$u^V = \sum_{i=1}^{n} \phi_i u_i$$

$\phi_i \equiv c_i \bar{V}_i$ 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

$$u^a = \sum_{i=1}^{n} a_i u_i$$

$$\sum_{i=1}^{n} a_i = 1$$

$a_i$ is an arbitrary weighting factor.

Why $\sum a_i = 1$?

How do we define $a_i$ such that $u^a = u_j$?
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!
Total Fluxes

Total Fluxes may be written in terms of a component’s velocity and specific density.

Mass Flux of component $i$:

$$n_i = \omega_i \rho u_i$$
$$= \rho_i u_i$$

$\rho$ - mixture mass density

Total Mass Flux:

$$n = \sum_{i=1}^{n} n_i$$
$$= \sum_{i=1}^{n} \rho_i u_i$$
$$= \rho v$$

Molar Flux of component $i$:

$$N_i = x_i c u_i$$
$$= c_i u_i$$

Total Molar Flux:

$$N_i = \sum_{i=1}^{n} N_i$$
$$= \sum_{i=1}^{n} c_i u_i$$
$$= c u$$

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!

\[
\mathbf{j}_i = \mathbf{n}_i - \rho_i \mathbf{v} = \rho_i (\mathbf{u}_i - \mathbf{v}) = \mathbf{n}_i - \omega_i \mathbf{n}_t
\]
Diffusive Fluxes

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

\[(\text{Diffusion flux}) = (\text{Total Flux}) - (\text{convective flux})\]

<table>
<thead>
<tr>
<th>Diffusion Flux</th>
<th>Total Flux</th>
<th>Convective Flux</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(j_i)</td>
<td>(n_i)</td>
<td>(\rho_i \mathbf{v})</td>
<td>Mass diffusive flux relative to a mass-averaged velocity</td>
</tr>
<tr>
<td>(j_i^u)</td>
<td>(n_i)</td>
<td>(\rho_i \mathbf{u})</td>
<td>Mass diffusive flux relative to a molar-averaged velocity</td>
</tr>
<tr>
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</tr>
</tbody>
</table>

\[
\begin{align*}
    j_i &= n_i - \rho_i \mathbf{v} \\
         &= \rho_i (\mathbf{u}_i - \mathbf{v}) \\
         &= n_i - \omega_i n_t \\
    J_i &= N_i - c_i \mathbf{u} \\
         &= c_i (\mathbf{u}_i - \mathbf{u}) \\
         &= N_i - x_i N_t
\end{align*}
\]
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:
\[ \sum_{i=1}^{n} j_i = 0 \]

From the previous slide:
\[ j_i = \rho_i (u_i - v) \]
\[
\sum_{i=1}^{n} j_i = \sum_{i=1}^{n} (\rho_i u_i - \rho_i v) \\
= \rho \sum_{i=1}^{n} (\omega_i u_i - \omega_i v), \\
= -\rho v + \rho \sum_{i=1}^{n} \omega_i u_i \\
= -\rho v + \rho v, \\
= 0.
\]

Note: typo in table 1.3 (missing \( v \) superscript)
\[ \sum_{i=1}^{n} \frac{\omega_i J_{v}^{x_i}}{x_i} = 0 \]
Example - Stefan Tube

At steady state (1D),

\[ n_i = \alpha_i \]
\[ N_i = \beta_i \]

We will show this later...

Molar, mass averaged velocities

Species velocities \[ u_i = \frac{n_i}{\rho_i} \]

Acetone diffusive fluxes \[ j_i = \rho_i(u_i - v) \]
Conversion Between Fluxes

We can convert between various diffusive fluxes via linear transformations.

\begin{align*}
(j^u) &= [B^{uo}](j) & \text{(why?) To form } [B^{uo}]^{-1} \text{ this must be an } n-1 \text{ dimensional system of equations!}
(j) &= [B^{ou}](j^u)
\end{align*}

Derivation of \([B^{ou}]\...\)

\begin{align*}
j_i^u &= \rho_i(u_i - u) \\
\sum_{i=1}^{n} j_i^u &= \sum_{i=1}^{n} \rho_i u_i - \sum_{i=1}^{n} \rho_i u, \\
&= \rho v - \rho u, \\
\frac{1}{\rho} \sum_{i=1}^{n} j_i^u &= v - u.
\end{align*}

\begin{align*}
j_i &= \rho_i(u_i - v), \\
&= \rho_i(u_i - u) + \rho_i(u - v)
\end{align*}

Let’s try to get a \(j_i^u\) on the RHS ⇒ add & subtract \(\rho_i u\).

\begin{align*}
j_i &= j_i^u - \omega_i \sum_{j=1}^{n} j_j^u
\end{align*}

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)

\[
\begin{align*}
\mathbf{j}_i &= \mathbf{j}^u_i - \omega_i \sum_{j=1}^{n} \mathbf{j}^u_j \\
\mathbf{j}_i &= \mathbf{j}^u_i - \omega_i \left[ \mathbf{j}^u_n + \sum_{j=1}^{n-1} \mathbf{j}^u_j \right]
\end{align*}
\]

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

\[
\begin{align*}
\mathbf{j}_i &= \mathbf{j}^u_i - \omega_i \sum_{j=1}^{n-1} \left[ -\frac{\omega_n}{x_n} \frac{x_j}{\omega_j} \mathbf{j}^u_j + \mathbf{j}^u_j \right], \\
&= \sum_{j=1}^{n-1} \left[ \delta_{ij} - \omega_i \left( 1 - \frac{\omega_n}{x_n} \frac{x_j}{\omega_j} \right) \right] \mathbf{j}^u_j \\
&\text{we have } n-1 \text{ of these equations (i=1...n-1)}
\end{align*}
\]

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

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

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).

\[
[B]^{-1} = [A]^{-1} - \frac{1}{\alpha} [A]^{-1} (u) (v)^T [A]^{-1},
\]

\[
\alpha = 1 + (v)^T [A]^{-1} (u)
\]