Fick’s Second Law

CHEN 6603
Fick’s 2nd Law

**Mass Form**
\[
\frac{\partial (\rho)}{\partial t} = -\nabla \cdot (n) = -\nabla \cdot v(\rho) - \nabla \cdot (j)
\]

**Molar Form**
\[
\frac{\partial (c)}{\partial t} = -\nabla \cdot (N) = -\nabla \cdot u(c) - \nabla \cdot (J)
\]

**Assume \( \rho_t \) is constant**
\[
\frac{\partial (\omega)}{\partial t} = -\nabla \cdot v(\omega) - \frac{1}{\rho_t} \nabla \cdot (j)
\]

\[
(j) = -\rho_t [D^o] (\nabla \omega)
\]

**Fick’s Law (simplified)**
\[
\frac{\partial (\omega)}{\partial t} + \nabla \cdot v(\omega) = \nabla \cdot [D^o](\nabla \omega)
\]

**Assume \([D^o]\) is constant**
\[
\frac{\partial (\omega)}{\partial t} + \nabla \cdot v(\omega) = [D^o](\nabla^2 \omega)
\]

**Assume \( c_t \) is constant**
\[
\frac{\partial (x)}{\partial t} = -\nabla \cdot u(x) - \frac{1}{c_t} \nabla \cdot (J)
\]

\[
(J) = -c_t [D](\nabla x)
\]

\[
\frac{\partial (x)}{\partial t} + \nabla \cdot u(x) = \nabla \cdot [D](\nabla x)
\]

**Assume \([D]\) is constant**
\[
\frac{\partial (x)}{\partial t} + \nabla \cdot u(x) = [D](\nabla^2 x)
\]

- Does this describe multicomponent effects?
- When is it reasonable to assume that \([D]\) is constant?
Scaling & Fick’s Second Law

\[
\frac{\partial (x)}{\partial t} + \nabla \cdot u(x) = [D](\nabla^2 x)
\]

Non-dimensionalization: we have length scale, time scale, and \( D \).

\[
t^* = \frac{t}{\tau}
\]

Dimensionless time

\[
x^* = \frac{x}{\ell}
\]

Dimensionless space

\[
D^* = D \frac{\tau}{\ell^2}
\]

Dimensionless diffusivity

- Given \( D \), we can estimate how long it will require for a species to diffuse distance \( \ell \).
- Given \( D \), we can estimate how far the diffusion boundary layer will reach in time \( \tau \).
- If we measure the time that it takes to detect a species that diffuses some distance \( \ell \) through a pure fluid, we can estimate the binary diffusion coefficient for that species in that fluid at the given temperature and pressure.
Diffusion Equations

“Generic” simplified form: \[
\frac{\partial \phi}{\partial t} + \nabla \cdot \mathbf{v} \phi = D_\phi \nabla^2 \phi
\]

**Temperature** (Fourier’s Law of Conduction)
- constant properties
- No heat released by chemical reactions
- low Mach numbers (negligible viscous heating)
- No species diffusion
- Pressure is steady.

\[
\frac{\partial T}{\partial t} + \nabla \cdot \mathbf{v} T = \frac{k}{\rho c_p} \nabla^2 T
\]

\[
\frac{\partial T}{\partial t} = \frac{k}{\rho c_p} \nabla^2 T
\]

**Velocity** (Newton’s Law of Viscosity)
- constant properties
- pressure & density are constant
- no body forces

\[
\frac{\partial \mathbf{v}}{\partial t} + \nabla \cdot (\mathbf{v} \mathbf{v}) = \frac{\mu}{\rho} \nabla^2 \mathbf{v}
\]

Note: the form without the convective term is meaningless in the case of momentum.

**Species** (Fick’s 2\textsuperscript{nd} Law)
- Constant properties
- Pressure is constant
- Body forces act equally
- No reaction.
- No thermal diffusion (Soret effect)

\[
\frac{\partial (x)}{\partial t} + \nabla \cdot \mathbf{u}(x) = [D](\nabla^2 x)
\]

\[
\frac{\partial (x)}{\partial t} = [D](\nabla^2 x)
\]
Example: 2 Bulb Problem
(Equimolar Counterdiffusion)

Assume:
• $T, p$ are constant
• No reaction
• 1-D domain $z=[0,L]
• Compositions are constant at
domain boundaries $z=0$, $z=L$.
• Ideal gas behavior.

\[ x_i = x_{i0} \quad z = 0, \]
\[ x_i = x_{iL} \quad z = L, \]

Molar reference frame is most convenient,
because $u_z=$constant for an ideal gas mixture
in 1D. (we can also deduce that $u_z=0$)

At “steady state,”

\[ \frac{\partial c_t}{\partial t} = -\nabla \cdot c_t \mathbf{u} + \sum_{i=1}^{n} \frac{s_i}{M_i} \]
\[ c_t = \bar{V}^{-1} = \frac{P}{RT} \]

Equations are decoupled
because diffusive fluxes
are constant.

Diffusive fluxes can
be calculated using:
\[ (J) = -c_t [D] \left( \frac{\partial x}{\partial z} \right), \]
\[ = -\frac{c_t}{L} [D](x_L - x_0). \]

Get $C_1, C_2$ using the BCs,

\[ (x) = \frac{(x_L) - (x_0)}{L} z + (x_0) \]
Example - Balance on “Bulbs”

Assume:
• $T, p$ are constant
• No reaction
• 1-D domain $z = [0, L]$
• Each bulb is well-mixed (no spatial gradients)
• Ideal gas behavior

• @ $t=0$, each bulb has a known composition.
• @ $t=\infty$, we can determine the composition (equilibrium).
• Can we determine the composition in each bulb as a function of time?

Mole balance on a bulb:

\[
\int_V c_t \frac{\partial x_i}{\partial t} \, dV = - \int_S \mathbf{N}_i \cdot \mathbf{a} \, dS
\]

What assumptions have been made?

Need to get $J_i$...
For the bulb at $z=0$:

$$\begin{align*}
    c_t V_0 \frac{dx_0^i}{dt} &= -J_i A \\
    V_0 \frac{dx_0^i}{dt} &= A \sum_{j=1}^{n-1} D_{ij} \frac{x_j^L - x_j^0}{L} \\
    \frac{d(x_0^0)}{dt} &= \frac{A}{L V_0} [D] ((x^L) - (x^0))
\end{align*}$$

Use equilibrium balance to eliminate $(x^L)$: (assume tube has “negligible” volume)

$$\begin{align*}
    V_0 x_0^i + V_L x_i^L &= (V_0 + V_L) x_i^\infty, \\
    x_i^L &= x_i^\infty (1 + V_0/V_L) - x_i^0 V_0/V_L
\end{align*}$$

Recall from our previous discussion (Fick’s second law):

$$\begin{align*}
    (x) &= \frac{(x^L) - (x^0)}{L} z + (x^0) \\
    (J) &= -\frac{c_t}{L} [D](x^L - x^0).
\end{align*}$$

What were the assumptions?

Use equilibrium balance to eliminate $(x^L)$: (assume tube has “negligible” volume)

$$\begin{align*}
    \frac{d(x_0^0)}{dt} &= \frac{A}{L V_0} \left(1 + \frac{V_0}{V_L}\right) [D] ((x^\infty) - (x^0)) \\
    &= \beta [D] ((x^\infty) - (x^0)), \\
    \beta &\equiv \frac{A}{L V_0} \left(1 + \frac{V_0}{V_L}\right)
\end{align*}$$

Must solve this (coupled) system of ODEs for the change in the composition in bulb 0 in time.

Constant for a given geometry.
Solution Strategy

\[
\frac{d(x^0)}{dt} = \beta[D] \left( (x^\infty) - (x^0) \right)
\]

**Solution Options:**

- Solve this as a system of coupled ODEs.
- Make some assumptions to decouple the system.
- **Note:** we have already made some assumptions to get the ODEs and the expression for \((J)\).
Heat Transfer Analogy

From before:
\[
\frac{\partial T}{\partial t} + \nabla \cdot \mathbf{v} T = \frac{k}{\rho c_p} \nabla^2 T,
\]

Steady state, \( \mathbf{v} = 0 \):
\[
\frac{d^2 T}{dz^2} = 0,
\]

Temperature solution:
\[
T = \frac{T_L - T_0}{L} z + T_0,
\]

Heat flux:
\[
q = -k \frac{dT}{dz} = -\frac{k}{L} (T_L - T_0).
\]

\[
(x) = \frac{(x_L) - (x_0)}{L} z + (x_0)
\]
\[
(J) = -\frac{c_t}{L} [D](x_L - x_0)
\]

Le\(_{ij}\) = \(\frac{k}{\rho c_p D_{ij}}\)

If we know Le, \(\rho\), \(k\), \(c_p\), we can find \(D_{ij}\). More later.