T&K §5.1.2

Fick's Second Law

CHEN 6603

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Fick's 2nd Law

Assume no reaction

Mass Form

$$\frac{\partial(\rho)}{\partial t} = -\nabla \cdot (\mathbf{n}) = -\nabla \cdot \mathbf{v}(\rho) - \nabla \cdot (\mathbf{j})$$

Assume ρ_t is constant

$$\frac{\partial(\omega)}{\partial t} = -\nabla \cdot \mathbf{v}(\omega) - \frac{1}{\rho_t}\nabla \cdot (\mathbf{j})$$

$$(\mathbf{j}) = -\rho_t[D^o](\nabla\omega)$$

$$\frac{\partial(\omega)}{\partial t} + \nabla \cdot \mathbf{v}(\omega) = \nabla \cdot [D^o](\nabla\omega)$$

Assume $[D^o]$ is constant

$$\boxed{\frac{\partial(\omega)}{\partial t} + \nabla \cdot \mathbf{v}(\omega) = [D^o](\nabla^2\omega)}$$

Fick's Law (simplified)

Molar Form

$$\frac{\partial(c)}{\partial t} = -\nabla \cdot (\mathbf{N}) = -\nabla \cdot \mathbf{u}(c) - \nabla \cdot (\mathbf{J})$$

Assume c_t is constant

$$\frac{\partial(x)}{\partial t} = -\nabla \cdot \mathbf{u}(x) - \frac{1}{c_t}\nabla \cdot (\mathbf{J})$$

$$(\mathbf{J}) = -c_t[D](\nabla x)$$

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

Assume $[D]$ is constant

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

- Does this describe multicomponent effects?
- When is it reasonable to assume that $[D]$ is constant?

Scaling & Fick's Second Law

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

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

$t^* = \dfrac{t}{\tau}$ Dimensionless time

$\mathbf{x}^* = \dfrac{\mathbf{x}}{\ell}$ Dimensionless space

$D^* = D\dfrac{\tau}{\ell^2}$ Dimensionless diffusivity

If D^*=1 then $\tau = \dfrac{\ell^2}{D}$

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

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Diffusion Equations

"Generic" simplified form: $$\frac{\partial \phi}{\partial t} + \nabla \cdot \mathbf{v}\phi = D_\phi \nabla^2 \phi$$

<u>Temperature</u> (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.

For systems with flow

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

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

<u>Velocity</u> (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.

<u>Species</u> (Fick's 2nd Law)

- Constant properties
- Pressure is constant
- Body forces act equally
- No reaction.
- No thermal diffusion (Soret effect)

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

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

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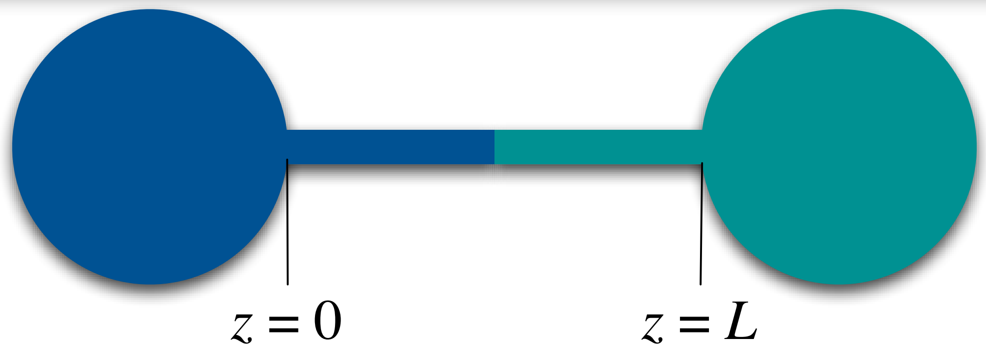
Example: 2 Bulb Problem

(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.



$$\begin{aligned} x_i &= x_{i0} & z &= 0, \\ x_i &= x_{iL} & z &= L, \end{aligned}$$

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

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

At "steady state,"

$$\begin{aligned} [D](\nabla^2 x) &= 0, \\ \frac{\mathrm{d}^2(x)}{\mathrm{d}z^2} &= 0, \\ \frac{\mathrm{d}(x)}{\mathrm{d}z} &= (C_1), \\ (x) &= (C_1)z + (C_2), \end{aligned}$$

Equations are decoupled because diffusive fluxes are constant.

get C_1, C_2 using the BCs,

$$(x) = \frac{(x_L) - (x_0)}{L} z + (x_0)$$

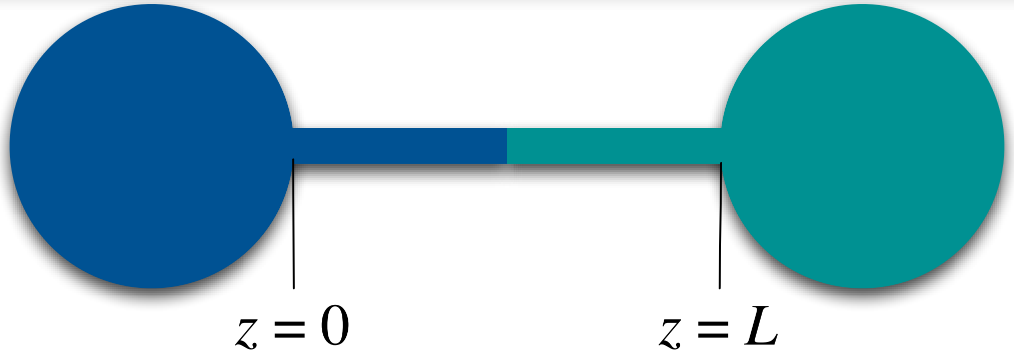
Diffusive fluxes can be calculated using:

$$\begin{aligned} (J) &= -c_t [D] \left(\frac{\partial x}{\partial z} \right), \\ &= -\frac{c_t}{L} [D] (x_L - x_0). \end{aligned}$$

Example - Balance on "Bulbs"

<u>Assume</u>:

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



$$
\begin{aligned}
x_i &= x_{i0} \qquad z = 0, \\
x_i &= x_{iL} \qquad z = L,
\end{aligned}
$$

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

What assumptions have been made?

Mole balance on a bulb:

$$
\begin{aligned}
c_t \frac{\partial x_i}{\partial t} &= -\nabla \cdot \mathbf{N}_i \\
\int_{\mathsf{V}} c_t \frac{\partial x_i}{\partial t} \, \mathrm{dV} &= -\int_{\mathsf{S}} \mathbf{N}_i \cdot \mathbf{a} \, \mathrm{dS} \\
c_t \mathsf{V} \frac{\partial x_i}{\partial t} &= -\mathbf{N}_i A = -\mathbf{J}_i A \qquad (\text{because } \mathbf{u} = 0) \,.
\end{aligned}
$$

?

Need to get $\mathbf{J}_i$...

For the bulb at z=0:

$$
\begin{aligned}
c_t V_0 \frac{\mathrm{d}x_i^0}{\mathrm{d}t} &= -\mathbf{J}_i A \\
V_0 \frac{\mathrm{d}x_i^0}{\mathrm{d}t} &= A \sum_{j=1}^{n-1} D_{ij} \frac{x_j^L - x_j^0}{L} \\
\frac{\mathrm{d}(x^0)}{\mathrm{d}t} &= \frac{A}{LV_0}[D]\left((x^L)-(x^0)\right)
\end{aligned}
$$

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

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

What were the assumptions?

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

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

$$
\begin{aligned}
\frac{\mathrm{d}(x^0)}{\mathrm{d}t} &= \frac{A}{LV_0}\left(1+\frac{V_0}{V_L}\right)[D]\left((x^\infty)-(x^0)\right) \\
&= \beta[D]\left((x^\infty)-(x^0)\right),
\end{aligned}
$$

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

$$
\beta \equiv \frac{A}{LV_0}\left(1+\frac{V_0}{V_L}\right)
$$

Constant for a given geometry.

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Solution Strategy

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

<u>Solution Options</u>:

- 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 $(\mathbf{J})$.

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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: $$\frac{\mathrm{d}^2 T}{\mathrm{d}z^2} = 0,$$

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

Heat flux: $$q = -k\frac{\mathrm{d}T}{\mathrm{d}z} = -\frac{k}{L}(T_L - T_0).$$

$$(x) = \frac{(x_L) - (x_0)}{L} z + (x_0)$$

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

$$\mathrm{Le}_{ij} = \frac{k}{\rho c_p D_{ij}}$$

If we know Le, ρ, k, c_p, we can find D_{ij}. More later.