“Unsteady” Mass-Transfer Models

ChEn 6603
Outline

- Context for the discussion
- Solution for transient binary diffusion with constant $c_t, N_t$.
- Solution for multicomponent diffusion with $c_t, N_t$.
- Film theory revisited (surface renewal models)
- Transient diffusion in droplets, bubbles
Film theory - so far we assumed steady state, no reaction in bulk (only potentially at interface)

- Mass Transfer Coefficients used to simplify problem - don’t fully resolve diffusive fluxes.
- Bootstrap problem solved (via definition of $[\beta]$) to obtain total species fluxes.

Unsteady cases?

- What if we want to know the transient concentration profiles?
- What if we want to consider the effects of transient (perhaps turbulent) mixing near the interface?

Here we consider **unsteady** film-theory approaches...

Hung Le and Parviz Moin.
http://www.stanford.edu/group/ctr/gallery/003_2.html
Solution Options

\[ \frac{\partial c_i}{\partial t} = -\nabla \cdot N_i + r_i \]

Describes evolution of \( c_i \) at all points in space/time, but requires \( N_i \), which may involve solution of the momentum equations...

Solve the problem numerically

- Allows us to incorporate “full” description of the physics
  - may be quite complex (particularly if we must solve for a non-trivial velocity profile...)
- Could also simplify portions (constant \([D], c_t\), etc.)
- Can solve this for a variety of BCs, ICs

Make enough assumptions/simplifications to solve this analytically

- Different BC/IC may require different form for analytic solution
- We already did this for effective binary and linearized theory for a few simple problems (2-bulb problem, Loschmidt tube)
  - T&K chapters 5 & 6.
- Here we show a few more techniques, based on unsteady film theory
  - Don’t resolve mass transfer completely - get a coarser description of the diffusive fluxes...

\[
(J) = c_t[k^*](\Delta x) \\
(N) = [\beta](J)
\]

Approximation for diffusive flux (total flux).
Binary Formulation (1/2)

\[
\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i + r_i
\]

What are the assumptions?

\[
c_t \frac{\partial x_i}{\partial t} = -\nabla \cdot N_i
\]

What happened here?

\[
c_t \frac{\partial x_i}{\partial t} + N_t \cdot \nabla x_i = -\nabla \cdot J_i
\]

One-dimensional...

\[
c_t \frac{\partial x_i}{\partial t} + N_t \frac{\partial x_i}{\partial z} = -\frac{\partial}{\partial z} J_i
\]

Problem statement: semi-infinite diffusion

BCs & ICs

\[
\begin{align*}
z \geq 0, \quad t = 0, & \quad x_i = x_{i\infty}. \quad \text{(Initial condition)} \\
z = 0, \quad t > 0, & \quad x_i = x_{i0}. \quad \text{(Boundary condition)} \\
z \rightarrow \infty, \quad t > 0, & \quad x_i = x_{i\infty}. \quad \text{(Boundary condition)}
\end{align*}
\]

valid for “short” contact times (more later)
Observation: since \( x \) is dimensionless, \( z, t, D \) must appear in a dimensionless combination in the solution.

\[ \zeta = \frac{z}{\sqrt{4t}} \]

chosen for convenience, \( \zeta^2/D \) is dimensionless

\[ \frac{\partial}{\partial t} = \frac{d}{dz} \frac{\partial}{\partial t} = -\frac{1}{2} \frac{\zeta}{t} \frac{d}{d\zeta} \]

\[ \frac{\partial}{\partial z} = \frac{d}{dz} \frac{\partial}{\partial z} = \frac{\zeta}{z} \frac{d}{dz} \]

\[ \frac{\partial^2}{\partial z^2} = \frac{d^2}{dz^2} \left( \frac{\partial}{\partial z} \right)^2 = \frac{\zeta^2}{z^2} \frac{d}{d\zeta} \]

Solve using order reduction

\[ D \frac{d^2 x}{d\zeta^2} + 2(\zeta - \phi) \frac{dx}{d\zeta} = 0 \]

\[ \phi \equiv \frac{N_t}{c_t} \sqrt{t} \]

\[ x_1 = x_{1,0} \quad \zeta = 0 \]

\[ x_1 = x_{1,\infty} \quad \zeta = \infty \]
Binary Formulation (3/3)

\[
\frac{x_1 - x_{1,0}}{x_{1,\infty} - x_{1,0}} = \frac{1 - \text{erf} \left( \frac{\zeta - \phi}{\sqrt{D}} \right)}{1 + \text{erf} \left( \frac{\phi}{\sqrt{D}} \right)}
\]

Calculate \( J_1 \) at \( z=0 \),

\[
J_{1,0} = c_t \sqrt{\frac{D}{\pi t}} \frac{\exp \left( \frac{-\phi^2}{D} \right)}{1 + \text{erf} \left( \frac{\phi}{\sqrt{D}} \right)} (x_{1,0} - x_{1,\infty})
\]

Mass Transfer Coefficients (binary system):

Low-flux limit (as \( N_t \to 0 \))

\[
J_{1,0} = c_t \sqrt{\frac{D}{\pi t}} (x_{1,0} - x_{1,\infty})
\]

\[
k = \sqrt{\frac{D}{\pi t}}
\]

\[
\Xi = \frac{\exp \left( \frac{-\phi^2}{D} \right)}{1 + \text{erf} \left( \frac{\phi}{\sqrt{D}} \right)}
\]

\[
J_{1,0} = c_t k \Xi (x_{1,0} - x_{1,\infty}) = c_t k^\bullet (x_{1,0} - x_{1,\infty})
\]

\[
N_{1,0} = c_t \beta_0 k^\bullet (x_{1,0} - x_{1,\infty})
\]
Multicomponent System

\[ \frac{\partial (x)}{\partial t} + \frac{N_t}{c_t} \frac{\partial (x)}{\partial z} = [D] \frac{\partial^2 (x)}{\partial z^2} \]
\[ \zeta = \frac{z}{\sqrt{4t}} \quad \phi \equiv \frac{N_t}{c_t} \sqrt{t} \]

This has the analytic solution (see T&K 9.3.1-9.3.2):

\[ (x - x_\infty) = \left[ [I] - \text{erf} \left( (\zeta - \phi) [D]^{-\frac{1}{2}} \right) \right] \left[ [I] + \text{erf} \left( \phi [D]^{-\frac{1}{2}} \right) \right]^{-1} (x_0 - x_\infty) \]

\[ J_0 = \frac{c_t}{\sqrt{\pi t}} [D]^{\frac{1}{2}} \exp \left( \phi [D]^{-\frac{1}{2}} \right) \left[ [I] + \text{erf}[\phi [D]^{-\frac{1}{2}}] \right]^{-1} (x_0 - x_\infty) \]

Low-flux limit (as \( N_t \to 0 \))

\[ J_0 = \frac{c_t}{\sqrt{\pi t}} [D]^{\frac{1}{2}} (x_0 - x_\infty) \]

\[ [k] = (\pi t)^{-\frac{1}{2}} [D]^{\frac{1}{2}} \quad [\Xi] = \exp \left( \phi [D]^{-\frac{1}{2}} \right) \left[ [I] + \text{erf}[\phi [D]^{-\frac{1}{2}}] \right]^{-1} \]

\[ (J_0) = c_t [k][\Xi](x_0 - x_\infty) = c_t [k^\bullet](x_0 - x_\infty) \]
\[ (N_0) = c_t [\beta_0][k^\bullet](x_0 - x_\infty) \]

Possible approaches:

- Solve the transient problem (be aware of the "short" time assumption)
- Use this information to formulate other steady-state models (e.g. turbulent mixing from bulk to surface)
Surface Renewal Models

\[
(J_0) = c_t[k][\Xi](x_0 - x_\infty) = c_t[k^\bullet](x_0 - x_\infty)
\]

\[
(N_0) = c_t[\beta_0][k^\bullet](x_0 - x_\infty)
\]

\[
[k] = (\pi t)^{-\frac{1}{2}} [D]^{\frac{1}{2}}
\]

(J), (N) are functions of time since [k] is a function of time.

Idea: develop a model for \( k \) that approximates the effects of transients near the surface.

Concept:
“Fresh” fluid from bulk is transported to the interface, where diffusion occurs for some time, \( t \). Then this is transported back to the bulk and replaced by more “fresh” fluid.

Initial & Boundary conditions:
- \( z = 0, \quad x_i = x_{i0} \quad t > 0 \)
- \( z \geq 0, \quad x_i = x_{i\infty} \quad t = 0 \)
- \( z \to \infty, \quad x_i = x_{i\infty} \quad t > 0 \)

Assumes that the “bulk” is unaffected by mass transfer (“short” contact times)

Age distribution function, \( \psi(t) \), determines how long a fluid parcel is at the interface. (will affect expression for \([k]\))
Surface-Renewal Models

Age distribution function, \( \psi(t) \), determines how long a fluid parcel is at the interface. (will affect expression for \([k]\))

\[
k_{ij}(t) = \sqrt{\frac{D_{ij}}{\pi t}} \quad k_{ij} = \int_0^\infty k_{ij}(t)\psi(t)dt
\]

Attempts to model a statistically stationary process (fast mixing, no saturation to bulk) by a steady state \([k]\).

Higbie model (1935)

Assumes that all fluid parcels stay at the interface for a fixed amount of time, \(t_e\).

\[
\psi(t) = \begin{cases} 
\frac{1}{t_e} & t \leq t_e \\
0 & t > t_e 
\end{cases} \quad \rightarrow \quad [k] = \frac{2}{\sqrt{\pi t_e}}[D]^{1/2}
\]

Note typo in T&K 9.3.33 (\(t\) vs. \(t_e\))

Danckwerts model (1951)

Fluid parcels have a greater chance of being replaced the longer they are at the interface.

\[
\psi(t) = s \exp(-st) \quad \rightarrow \quad [k] = \sqrt{s}[D]^{1/2}
\]

\(s\) - rate of surface renewal (1/sec) (fraction of surface area replaced by fresh fluid in unit time)
For “small” Fo (Fo\ll 1), we are safe to use surface renewal concepts. What happens at “large” Fo (Fo \to 1)?

\[ \Delta x_i = x_{iI} - \langle x_i \rangle \quad \langle x_i \rangle \text{ - “mixing cup” average} \]
Fractional Approach to EQ

\[
\begin{align*}
(J_0) &= c_t[k][\Xi](x_0 - x) = c_t[k^\bullet](x_0 - x) & x_\infty \text{ is changing!} \\
(N_0) &= c_t[\beta_0][k^\bullet](x_0 - x) \\
\end{align*}
\]

(this solution is not valid)

\[
F \equiv \frac{(x_{10} - \langle x \rangle)}{(x_{10} - x_I)} \quad \text{Binary}
\]

\[
(x_0 - \langle x \rangle) = [F](x_0 - x_I) \quad \text{Multicomponent}
\]

\[x_0 - \text{initial/boundary composition (t=0)}\]

\[x_I - \text{interface composition (constant in time)}\]

\[\langle x \rangle - \text{average composition (changing in time), use in place of } x_\infty.\]

For a spherical droplet/particle:

\[
[F] = \left[ [I] - \frac{6}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} \exp \left[ -m^2 \pi^2 F_{oref} [D'] \right] \right]
\]

\[
[D'] = \frac{1}{D_{ref}} [D] \quad F_{oref} \equiv D_{ref} \frac{t}{r_0^2}
\]

\[\text{note: } \frac{6}{\pi^2} \sum_{m=1}^{\infty} m^{-2} = 1\]

\[
\text{Sh} \equiv [k] \cdot 2r_0[D]^{-1} \quad \text{Sherwood number related to } \partial F / \partial F_{oref}
\]

\[
[\text{Sh}] = \frac{2}{3} \pi^2 \left[ \sum_{m=1}^{\infty} \exp \left[ -m^2 \pi^2 F_{oref} [D'] \right] \right] \left[ \sum_{m=1}^{\infty} \frac{1}{m^2} \exp \left[ -m^2 \pi^2 F_{oref} [D'] \right] \right]^{-1}
\]

\[
\text{remember that these are matrix functions!}
\]

\[\text{Limiting cases:}\]

\[
F_{oref} \to \infty \quad \Rightarrow \quad \text{Sh} = \frac{2}{3} \pi^2 [I] \quad \Rightarrow \quad [k] = \frac{\pi^2}{3r_0} [D]
\]

See fig. 9.7 (L'Hopital's rule)

\[
F_{oref} \ll 1 \quad \Rightarrow \quad [k] = \frac{2}{\sqrt{\pi t}} [D]^{1/2}
\]