“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 \([D], c_t, \text{etc.}\))
- 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 (1/3)

\[ \frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i + r_i \]

What are the assumptions?

\[ c_t \frac{\partial x_i}{\partial t} = -\nabla \cdot \mathbf{N}_i \]

What happened here?

\[ c_t \frac{\partial x_i}{\partial t} + \mathbf{N}_t \cdot \nabla x_i = -\nabla \cdot \mathbf{J}_i \]

One-dimensional...

\[ c_t \frac{\partial x_i}{\partial t} + N_t \frac{\partial x_i}{\partial z} = -\frac{\partial}{\partial z} \mathbf{J}_i \]

Problem statement:
semi-infinite diffusion

BCs & ICs

\[ z \geq 0, \quad t = 0, \quad x_i = x_{i\infty}. \quad \text{(Initial condition)} \]
\[ z = 0, \quad t > 0, \quad x_i = x_{i0}. \quad \text{(Boundary condition)} \]
\[ z \to \infty, \quad t > 0, \quad x_i = x_{i\infty}. \quad \text{(Boundary condition)} \]

valid for “short” contact times (more later)
Binary Formulation (2/3)

\[ \frac{\partial x_1}{\partial t} + \frac{N_t}{c_t} \frac{\partial x_1}{\partial z} = D \frac{\partial^2 x_1}{\partial z^2} \]

**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

\[ \frac{\partial}{\partial t} = \frac{d}{d\zeta} \frac{\partial \zeta}{\partial t} = -\frac{1}{2} \frac{\zeta}{t} \frac{d}{d\zeta} \]
\[ \frac{\partial}{\partial z} = \frac{d}{d\zeta} \frac{\partial \zeta}{\partial z} = \frac{\zeta}{z} \frac{d}{d\zeta} \]
\[ \frac{\partial^2}{\partial \zeta^2} = \frac{d^2}{d\zeta^2} \left( \frac{\partial \zeta}{\partial z} \right)^2 = \frac{\zeta^2}{z^2} \frac{d}{d\zeta} \]

\[ c_t \left( \frac{-\zeta}{2t} \right) \frac{dx}{d\zeta} + N_t \left( \frac{\zeta}{z} \right) \frac{dx}{d\zeta} = c_tD_i \frac{\zeta^2}{z^2} \frac{d^2 x}{d\zeta^2} \]
\[ \left( -2\zeta + \frac{N_t z}{c_t} \right) \frac{dx}{d\zeta} = D \frac{d^2 x}{d\zeta^2} \]

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

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

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

Solve using order reduction

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

Note that this is a function of both \( z \) and \( t \).
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 \( z=0 \),

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

What happens to \( J_1 \) as \( z \to \infty \)?

Mass Transfer Coefficients (binary system):

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

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

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

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

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

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

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

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

Low-flux limit (as \(N_t \to 0\)) \(J_0 = \frac{c_t}{\sqrt{\pi t}} [D]^{\frac{1}{2}} (x_0 - x_\infty)\)

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

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

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

Possible approaches:

- Solve the transient problem (beware 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.

How would we handle this problem?

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 \([k]\))

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

Higbie model (1935)

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

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

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)

See T&K §9.1

\[
\kappa_{ij}(t) = \frac{1}{\gamma_{ij} t}
\]

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

For “small” \( F_o \) (\( F_o \ll 1 \)), we are safe to use surface renewal concepts. What happens at “large” \( F_o \) (\( F_o \to 1 \))?

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

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

\( x_\infty \) is changing!

(this solution is not valid)

\[ F \equiv \frac{(x_{10} - \langle x_1 \rangle)}{(x_{10} - x_{1I})} \]
Binary

\[ (x_0 - \langle x \rangle) = [F](x_0 - x_I) \]
Multicomponent

\( x_0 \) - initial/boundary composition (t=0)
\( x_I \) - interface composition (constant in time)
\( \langle x \rangle \) - average composition (changing in time), use in place of \( x_\infty \).

For a spherical droplet/particle:

\[ [F] = \left[ [I] - \frac{6}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} \exp \left[-m^2\pi^2 F_{0\text{ref}} [D']\right] \right] \]

\[ [D'] = \frac{1}{D_{\text{ref}}} [D] \]
\( F_{0\text{ref}} \equiv D_{\text{ref}} \frac{t}{r_0^2} \)

note:
\( \frac{6}{\pi^2} \sum_{m=1}^{\infty} m^{-2} = 1 \)

\[ Sh \equiv [k] \cdot 2r_0[D]^{-1} \]
Sherwood number related to \( \partial F/\partial Fo \).

\[ [Sh] = \frac{2}{3} \pi^2 \left[ \sum_{m=1}^{\infty} \exp \left[-m^2\pi^2 F_{0\text{ref}} [D']\right] \right] \left[ \sum_{m=1}^{\infty} \frac{1}{m^2} \exp \left[-m^2\pi^2 F_{0\text{ref}} [D']\right] \right]^{-1} \]

\[ F_{0\text{ref}} \to \infty \implies Sh = \frac{2}{3} \pi^2 [I] \implies [k] = \frac{\pi^2}{3r_0} [D] \]
See fig. 9.7 (L'Hopital's rule)

Remember that these are matrix functions!

Limiting cases:

\[ F_{0\text{ref}} \ll 1 \implies [k] = \frac{2}{\sqrt{\pi t}} [D]^{1/2} \]