Lecture 9: Conservation of species mass

I. Bulk conservation of species mass

A. Mass vs. molar units

* Today we will talk about the balance equation for species mass in a mixture

* We need to briefly remind ourselves about molar units vs mass units (§1.2, p. 3-5)

(*) Tip: Just look these up. They can be confusing!

	mass units	molar units
species concentration	ρ_i	c_i
total concentration	$\rho = \sum_i \rho_i$	$c = \sum_i c_i$
velocity	$\underline{v} = \sum_i \frac{\rho_i \underline{v}_i}{\rho}$	$\underline{v}^{(M)} = \sum_i \frac{c_i \underline{v}_i}{c}$
flux relative to $\underline{v}$	$\underline{j}_A = -\rho D_{AB} \nabla w_A$	$\underline{J}_A = -\frac{\rho D_{AB}}{M_A} \nabla w_A$
flux relative to $\underline{v}^M$	$\underline{j}_i^{(M)} = -c M_A D_{AB} \nabla x_A$	$\underline{J}_i^{(M)} = -c D_{AB} \nabla x_A$
total flux	$\underline{n}_i$	$\underline{N}_i$
	$= \rho_i \underline{v} + \underline{j}_i$	$= c_i \underline{v} + \underline{J}_i$
	$= \rho_i \underline{v}^M + \underline{j}_i^{(M)}$	$= c_i \underline{v}^M + \underline{J}_i^{(M)}$

* In most chemical diffusion problems, we want molar units, so we can deal with chemical reactions.

  For most fluid flow problems, we want $\underline{v}$ (not $\underline{v}^{(M)}$), because it is conventional (& what we measure/observe easily).

* Recall: $\sum_i j_i = 0$, $\sum J_i^{(M)} = 0$, $\sum_i j_i^{(M)} \neq 0$, $\sum_i J_i \neq 0$

$$x_i = \frac{c_i}{c}, \quad w_i = \frac{\rho_i}{\rho}$$

B. Species Diffusion Equation

* Let's use our general property balance to derive the species diffusion equation.

$$\frac{\partial b}{\partial t} = - \underline{\nabla} \cdot \underline{F} + B_V$$

$b = c_i$ (molar units)

$\underline{F} = \underline{N}_i$ (molar units, total flux)

$B_V = R_{v,i}$ total rate of formation of i per volume by homogeneous chemical reactions

* Plug it all in

$$\boxed{\frac{\partial c_i}{\partial t} = - \underline{\nabla} \cdot N_i + R_{v,i}}$$

↖ Not super practical, we want a PDE for $c_i(\underline{r}, t)$.

* Let's plug some more things in, to see if we can get the equation in terms of C only.

* Assumption 1: Binary mixture

$$\underline{N}_i = \underline{N}_A = c_A \underline{v} + \underline{J}_A$$

$$\underline{J}_A = \frac{\rho D_{AB}}{M_A} \underline{\nabla} w_A$$

$$\frac{\partial c_A}{\partial t} = - \underline{\nabla} \cdot (c_A \underline{v}) - \underline{\nabla} \cdot \left(\frac{\rho D_{AB}}{M_A} \underline{\nabla} w_A \right) + R_{v,A}$$

- Recall: $\rho_A = M_A c_A$, $\omega_A = \rho_A/\rho = \dfrac{M_A c_A}{\rho}$

$$\underline{\nabla}\cdot\left(\frac{\rho D_{AB}}{M_A}\underline{\nabla}\omega_A\right) = \underline{\nabla}\cdot\left(\rho D_{AB}\nabla\left(\frac{\omega_A}{M_A}\right)\right) \quad \leftarrow M_A \text{ const}$$
$$= \underline{\nabla}\cdot\left(\rho D_{AB}\nabla\left(\frac{M_A c_A}{M_A \rho}\right)\right)$$
$$= \underline{\nabla}\cdot\left(\rho D_{AB}\nabla\left(c_A/\rho\right)\right)$$

* Assumption 2: $\rho = \text{const}$ (incompressible)

$$\underline{\nabla}\cdot\left(\rho D_{AB}\nabla\left(c_A/\rho\right)\right) = \underline{\nabla}\cdot\left(D_{AB}\nabla c_A\right)$$

* Assumption 3: $D_{AB} = \text{constant}$

$$\underline{\nabla}\cdot\left(D_{AB}\nabla c_A\right) = D_{AB}\nabla^2 c_A$$

* Put all together:

$$\frac{\partial c_A}{\partial t} + \underbrace{\underline{\nabla}\cdot(c_A\underline{v})} = D_{AB}\nabla^2 c_A + R_{v,A}$$

can simplify: $\underline{\nabla}\cdot(c_A\underline{v}) = c_A \underbrace{\underline{\nabla}\cdot\underline{v}}_{\text{zero (incompressible)}} + \underline{v}\cdot\underline{\nabla}c_A$

$$\boxed{\frac{\partial c_A}{\partial t} + \underline{v}\cdot\underline{\nabla}c_A = D_{AB}\nabla^2 c_A + R_{v,A}}$$

or

$$\boxed{\frac{D c_A}{D t} = D_{AB}\nabla^2 c_A + R_{v,A}}$$

* Comments:
  - Note the 3 assumptions: Binary, incompressible, const D_{AB}.
  - Same equation holds for c_B.

- Similarities to heat equation. Same exact mathematical form! Similar assumptions! Similar meaning of terms!

$$\frac{DT}{Dt} = \alpha \nabla^2 T + \frac{\dot{w}}{\rho \hat{C}_p}$$

C. Multicomponent Diffusion

* Multicomponent diffusion is hard (in general). There are some cases that we can do useful things, though.
* The most common useful multicomponent diffusion case is "pseudo-binary" diffusion.
  - An abundant gas or solvent
  - Two or more dilute components (e.g. solute)
  - Incompressible.

  Example: salt in water

  - pure water: $c = \frac{1000g}{L} \cdot \frac{mol}{18.02g} \simeq 56\,M$.
  - salt is usually mM quantities

* Define dilute solution diffusivity

$$D_i \equiv \lim_{x_i \to 0} D_{is}$$

s ← solvent (abundant species)

D_i ← now a constant

(only binary diffusivity w/ major component is relevant)

* Simplifies species mass balance

$N_i = c_i \underline{v} + \underline{J}_i$, $J_i = D_i \underline{\nabla} c_i$ } follow previous steps

$$\boxed{\frac{Dc_i}{Dt} = D_i \nabla^2 c_i + R_{v,i}}$$

* Some severe limitations! phase separating species, multicomponent gas mixtures, ionic solutions/liquids

II. Mass Transfer at Interfaces

* Just like heat transfer, we will need boundary conditions for our mass diffusion equation.

These are based on the interfacial species mass balance:

$$\left[\left(\underline{f} + b(\underline{v} - \underline{v}_I)\right)_2 - \left(\underline{f} + b(\underline{v} - \underline{v}_I)\right)_1\right] \cdot \underline{n}_I = B_s$$

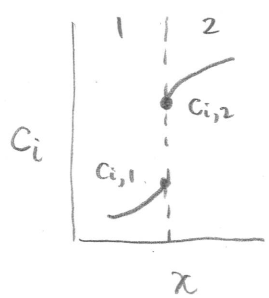
* Let's plug in specific quantities for mass transfer

- let $\underline{v} = 0$, $\underline{v}_I = 0$ (stationary fluid & interface)
- $\underline{f} = \underline{J}_i$ (diffusive flux of i)
- $B_s = R_{s,i}$ total rate per volume of formation of i by heterogeneous chemical reactions

$$\boxed{\underline{J}_{i,2} \cdot \underline{n}_I - \underline{J}_{i,1} \cdot \underline{n}_I = R_{s,i}}$$

* Let's look at some practical cases. Again, note the similarities to heat transfer (and differences).

- Case 1: species equilibrium (Dirichlet)



- very small distances / intimate touching

$$\underline{J}_{i,2} \cdot \underline{n}_I = \underline{J}_{i,1} \cdot \underline{n}_I = 0$$

no flux of species = local equilibrium

- careful! Phase boundaries are governed by chemical potentials!

$$\boxed{\mu_{i,1} = \mu_{i,2}}$$

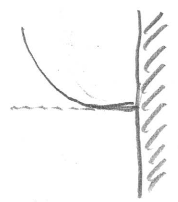
- often, we can make this a bit more simple by using a partition coefficient

$$\boxed{c_{i,1} = K_i \, c_{i,2}}$$

- Can get K_i different ways: VLE, LLE, SLE, (ex. Henry's law), solubility data, etc.

• Case 2: known flux (Neumann)

- a wall or symmetry (no flux)



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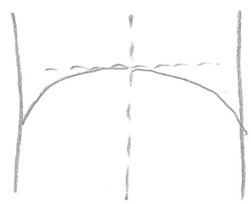
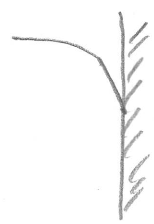


$$\boxed{\underline{J}_i \cdot \underline{n} = 0} \quad \text{or} \quad \boxed{\frac{\partial c_i}{\partial n} = 0}$$

- flux due to reaction at surface (heterogeneous)



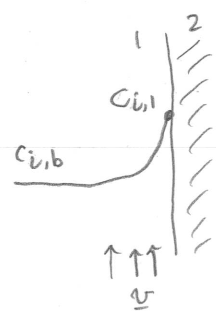
$$\boxed{\underline{J}_i \cdot \underline{n} = R_{s,i}} \quad \text{or} \quad \boxed{\frac{\partial c_i}{\partial n} = -\frac{R_{s,i}}{D_i}}$$

• Case 3: Flux is a function of c_i (Robin)

- convection

$$\boxed{\underline{J}_i \cdot \underline{n} = k_{c,i}(c_{i,1} - c_{i,b})}$$

mass transfer coefficient of i



(dissolving salt)

$$\boxed{\frac{\partial c_i}{\partial n} = -\frac{k_{c,i}}{D_i}(c_{i,1} - c_{i,b})}$$

"definition" of mass transfer coefficient