CHE 318 L10

Jan-26 2026

Recap unsteady state M.T

$$[In] - [Out] + [Gen] = [Acc]$$

① $[In] - [out] \Rightarrow -\frac{\partial N_A}{\partial z}$ (1D)

$-\nabla \cdot \vec{N}_A$ (Any coordinate)

② [Gen] term: typically chemical reaction

Form Gen = r_A = concentration · k

Unit? matching Acc [mol]/[m^3]/[s]

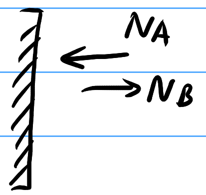
k lumped term ⇒ unit 1/[s]

But many different forms!

E.g. Surface reaction

$$r_A = k \cdot (\overset{\text{surface conc}}{C_{As}} - \underset{\text{bulk conc}}{C_A})$$

B.C for reaction



$$xA \rightarrow yB + w\underset{\text{solid}}{D}$$

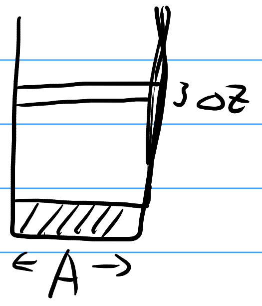
$$\frac{N_A}{x} = -\frac{N_B}{y}$$

$$\underset{A}{CH_4(g)} \longrightarrow \underset{\text{coke}}{C(s)} + \underset{B}{4H(g)}$$ (assumption, not real reaction)

$N_A = r_A$

$N_B = -4 r_A$ $\Rightarrow \frac{N_A}{1} = -\frac{N_B}{4}$

Solving U.S.S for stagnant B



Governing Eq (M.B)

$$\frac{\partial C_A}{\partial t} = - \frac{\partial N_A}{\partial z}$$

$$N_A = - C_T D_{AB} \frac{\partial x_A}{\partial z} + x_A (N_A + N_B)$$

Cannot directly say $N_B = 0$!

Constraints between N_A & N_B

$$\frac{\partial C_T}{\partial t} = - \frac{\partial N_T}{\partial z} = - \frac{\partial N_A}{\partial z} - \frac{\partial N_B}{\partial z} = 0$$

$$\frac{\partial N_A}{\partial z} = - \frac{\partial N_B}{\partial z}$$ N_T is constant

B.C.s

$x_A(z=0,t) = x_{A0}$ $x_A(L,t) = 0$

$N_B(z=0,t) = 0$ $\longrightarrow$ $N_A(0,t) = - \frac{C_T D_{AB}}{1-x_{A0}} \frac{\partial x_A}{\partial z}\Big|_{z=0}$

z=0

No flux BC

$$\frac{\partial C_A}{\partial t} = C_T \frac{\partial x_A}{\partial t} = - \frac{\partial \left(- C_T D_{AB} \frac{\partial x_A}{\partial z}\right)}{\partial z} - \frac{\partial [x_A \cdot (N_A + N_B)]}{\partial z}$$

2 parts

$$= -C_T D_{AB} \frac{\partial^2 x_A}{\partial z^2} - \frac{\partial x_A}{\partial z} \cdot (N_A + N_B)$$

$$\cancel{- x_A \frac{\partial (N_A + N_B)}{\partial z}}$$

What is $N_T = N_A + N_B$?

$$N_T(z \neq 0, t) = N_T(z=0,t) = N_A(0,t) + \cancel{N_B(0,t)}$$

$$= - \frac{C_T D_{AB}}{1-x_{A0}} \frac{\partial x_A}{\partial z}\Big|_{z=0}$$

Not a constant over t !

Final expression for Govern. Equ.

$$\frac{\partial x_A}{\partial t} = + D_{AB}\frac{\partial^2 x_A}{\partial z^2} + \left[\frac{D_{AB}}{1-x_{A0}} \underbrace{\left.\frac{\partial x_A}{\partial z}\right|_{z=0}}_{\text{inital gradient !}}\right]\frac{\partial x_A}{\partial z}$$

And initial conditions

$x_A(z\neq 0, 0) = 0$ Analytical solution exhists

See Bird Transport phenomena 20.1

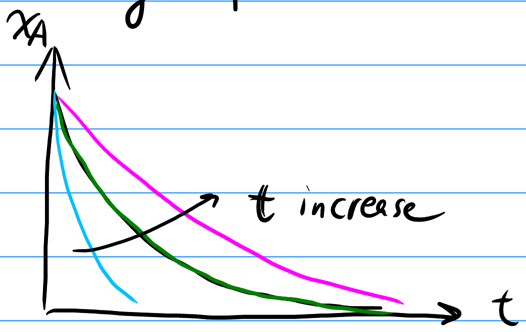
Solution

$$X = \frac{x_A(z)}{x_{A0}} = \frac{1 - \mathrm{erf}\left(\frac{z}{\sqrt{4D_{AB}t}} - \varphi\right)}{1 + \mathrm{erf}(\varphi)}$$

φ is a constant that satisfies

$$x_{A0} = \left[1 + \left[\sqrt{\pi}\,(1+\mathrm{erf}\varphi)\,\varphi \exp\varphi^2\right]^{-1}\right]^{-1}$$

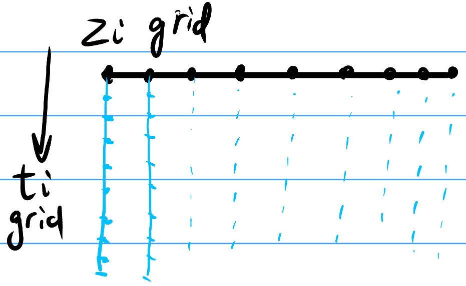
We usualy refer to a table for x_{A0} ..... φ solution



$$\varphi = v_z^{*}\sqrt{t/D_{AB}}$$
$$= \frac{N_{A0}}{c_T}\sqrt{t/D_{AB}}$$

Detailed solution byond 318 but useful in other courses

Numerical solution scheme



$$\frac{\partial x_A}{\partial t} \Rightarrow x(z_i, t+\Delta t) = x(z_i, t) + \Delta x$$

$\Delta x \Leftarrow \Big\{$

$\frac{\partial^2 x_A}{\partial z^2} \xrightarrow{F.D.}$  $= \frac{x_{i+1} - 2x_i + x_{i-1}}{\Delta z^2}$

$\frac{\partial x_A}{\partial z} \xrightarrow{F.D.}$  $= \frac{x_{i+1} - x_{i-1}}{2\Delta z}$

At each time step

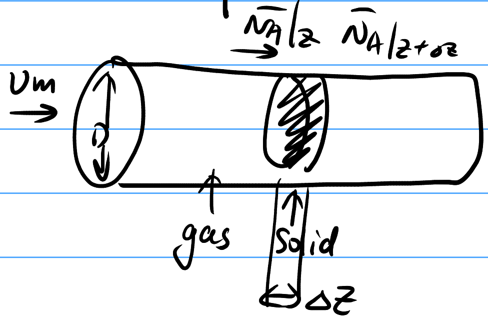
① Calculate
- F.D $\frac{\partial^2 x_A}{\partial z^2}$
- F.D $\frac{\partial x_A}{\partial z}$
- F.D $\frac{\partial x_A}{\partial z}\Big|_{z=0}$

② Calculate Δx

③ Add $x_{i+1} = x_i + \Delta x$ for each gridpoint

increase t

Example 2 Reaction through catalyst wall



Reaction & M.T.

In the catalyst region Rate of reaction

$r = k(C_{As} - C_A)$

$$\text{In} - \text{Out} + \boxed{\text{Gen}}^{\neq 0} = \text{Acc}$$

cross-sectional area of tube ⇐

$$\boxed{\frac{\pi D^2}{4}}\left(N_A|_z - N_A|_{z+\Delta z}\right) + \pi D\cdot\Delta z\cdot k(C_{As} - C_A)$$

$$= \frac{\pi D^2}{4}\cdot\frac{\partial C_A}{\partial t}$$

Surface reaction rate

$= (\text{Area\_surf})\cdot k(C_{As} - C_A)$

$= (\pi\cdot D\cdot\Delta z)\cdot[k(C_{As} - C_A)]$

$$\hookrightarrow \quad -\frac{\partial N_A}{\partial z} + \left(\frac{4k}{D}\right)(C_{As} - C_A) = \frac{\partial C_A}{\partial t}$$

Use flux eq with υ_m (easier!)

$$N_A = -D_{AB}\frac{\partial C_A}{\partial z} + C_A\cdot \upsilon_m$$

Constant υ_m case

$$\frac{\partial N_A}{\partial z} = -D_{AB}\frac{\partial^2 C_A}{\partial z^2} + \frac{\partial C_A}{\partial z}\upsilon_m$$

$$\Downarrow$$

$$\frac{\partial C_A}{\partial t} = -\left(-D_{AB}\frac{\partial^2 C_A}{\partial z^2} + \frac{\partial C_A}{\partial z}\upsilon_m\right) + \frac{4k}{D}(C_{As} - C_A)$$

1) Need initial & BC
2) Numerical integration