CHE 318 Lecture 11

Unsteady State Mass Transfer

Dr. Tian Tian

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Recap

- Step-by-step solution to U.S.S. evaporation through stagnant air
- Mass balance & flux analysis for catalyst on wall system

Learning Outcomes

After today's lecture, you will be able to:

- **Derive** mass balance and flux with reaction terms
- **Identify** B.C. and I.C. for reaction-related problems
- **Apply** simplifications for U.S.S. problems with generation terms

U.S.S Example 2: Transport Through A Reactive Wall

Question: A gas mixture of CO_2 (A) in argon (B) is flown through a cylindrical pipe of diameter D and length L with constant velocity v_m. The pipe is covered with a porous material to absorb CO_2. The porous material is coated uniformed on the inner wall of the pipe. While A is flowing through the pipe, it is being absorbed by a first-order reaction

$$r_A = k(c_{A,s} - c_A)$$

Where $c_{A,s}$ is the surface concentration on the absorbing material and c_A is the conentration of A in the gas mixture. We assume the concentration $c_A(z)$ in the gas phase is uniform in the radial direction. The total pressure p_T and temperature T are both kept constant.

Can you estimate the concentration of CO_2 at the end of the pipe?

Step 1: Mass Balance

Consider a differential gas-phase control volume of thickness Δz that intersects the catalytic wall.

$$\text{In} - \text{Out} + \text{Generation} = \text{Accumulation} \tag{1}$$

$$\tag{2}$$

$$\frac{\pi D^2}{4}\left(N_A\big|_z - N_A\big|_{z+\Delta z}\right) + \pi D\,\Delta z\,k\,(c_{A,s} - c_A) = \frac{\pi D^2}{4}\,\frac{\partial C_A}{\partial t} \tag{3}$$

$$-\frac{\partial N_A}{\partial z} + \frac{4k}{D}\,(c_{A,s} - c_A) = \frac{\partial c_A}{\partial t} \tag{4}$$

Step 2: Coupling With Flux Equation

Use the convection–diffusion flux (constant v_m):

$$N_A = -\,D_{AB}\,\frac{\partial c_A}{\partial z} + c_A\,v_m \tag{5}$$

When v_m is constant, differentiate over N_A becomes:

$$\frac{\partial N_A}{\partial z} = -\,D_{AB}\,\frac{\partial^2 c_A}{\partial z^2} + v_m\,\frac{\partial c_A}{\partial z} \qquad (v_m = \text{const}) \tag{6}$$

Step 3: General Equation for M.T + Surface Reaction

$$\frac{\partial c_A}{\partial t} = -\left(-\,D_{AB}\,\frac{\partial^2 c_A}{\partial z^2} + v_m\,\frac{\partial c_A}{\partial z}\right) + \frac{4k'}{D}\,(c_{A,s} - c_A) \tag{7}$$

$$= D_{AB}\,\frac{\partial^2 c_A}{\partial z^2} - v_m\,\frac{\partial c_A}{\partial z} + \frac{4k}{D}\,(c_{A,s} - c_A) \tag{8}$$

Need:

- initial condition $c_A(z, 0)$
- boundary conditions at $z = 0$ and $z = L$

Solve:

- analytical (special cases)
- numerical integration (finite difference)

Simplifications for Solving U.S.S. Problems

We can make some assumptions that do not have significant impact on the results:

- **Assumption 1**: convection $\gg$ diffusion
  - We can write $D_{AB}\frac{\partial^2 c_A}{\partial z^2} \approx 0$
  - Only need v_m to solve the U.S.S. problem
  - Typically tolerable error in industrial pipes
- **Asumption 2**: system close to steady state
  - U.S.S –> S.S.? Just let $\partial c_A/\partial t = 0$
  - Can compare with other S.S. solutions!

Solutions to Simplified U.S.S. Governing Equations

After removing the $\partial c_A/\partial t$ and $D_{AB}\frac{\partial^2 c_A}{\partial z^2}$ terms, we have

$$\frac{4k}{D}\left(c_{A,s} - c_A\right) = v_m \frac{dc_A}{dz} \tag{9}$$

$$\int_0^z \frac{4k}{Dv_m} dz = \int_{c_{Ai}}^{c_A} \frac{dc_A}{c_{A,s} - c_A} \tag{10}$$

$$\frac{4k}{Dv_m} z = -\ln\left(\frac{c_{A,s} - c_A(z)}{c_{A,s} - c_{A0}}\right) \tag{11}$$

We get $c_A(z)$ profile, where $c_{A0} = c_A(z = 0)$

$$c_A(z) = c_{A,s} - \left(c_{A,s} - c_{A0}\right) \exp\left(-\frac{4k}{Dv_m} z\right) \tag{12}$$

Interpretation of $c_A(z)$ Profile

For this problem, because the surface reaction occurs, we no longer have a linear c_A profile. It decays with a length scale of $Dv_m/4k$.

- At the exit of the pipe, concentration of $c_A(L)$ is no less than $c_{A,s}$!
- Decay length $L_d \approx \frac{Dv_m}{4k}$
- Faster flushing incomplete absorption
- Is N_A constant inside the tube?

- What is the unit of k in this case?

We will investigate these questions in the second half of the course!

Case 3: Catalytic Conversion of D → E (1D, Steady State)

Question: A binary gas mixture containing species D and E occupies a stagnant gas film of thickness L in the z-direction. At $z = 0$, the gas is in contact with a solid catalyst surface that **instantaneously** and **completely** converts D to E. At $z = L$, the gas composition is maintained at known values. Assumpt constant T and total pressure p_T and 100% conversion rate. The reaction between D and E follows:

$$m\text{D} \rightarrow n\text{E}$$

Develop the governing differential equation for N_D and c_D the molar flux of species D in the gas phase at steady state.

Step 1: Mass Balance

At anywhere outside the boundary, we have:

$$[\text{In}] - [\text{Out}] + [\text{Gen}] = [\text{Acc}] \tag{13}$$

$$-\frac{\partial N_D}{\partial z} + 0 = \frac{\partial c_D}{\partial t} \tag{14}$$

- Catalyst at the bottom of the reactor $\quad[\text{Gen}] = 0$
- How do we get the boundary condition?

Step 2: Flux Equation

The reaction at the bottom catalyst is very fast, we can use the "general case" flux equation

$$N_D = -D_{DE}\frac{\partial c_D}{\partial z} + \frac{c_D}{c_T}(N_D + N_E) \tag{15}$$

- How do we get relation between N_D and N_E?
- What are the boundary conditions?

Diffusion-Controlled Reaction: Explanations

In this system we have two conditions **instantaneous** and **complete** reaction. They have distinct meanings

- **Instantaneous**: the reaction rate at the boundary does not depend on the actual concentration, but rather what ever molar flux is at that interface (**diffusion-controlled**)
  - Often we will have $c_{D,z=0} = 0$ (all D at interface consumed instantly)
- **Complete**: the conversion between D and E occur 100%, meaning the fluxes of D and E follow **stoichiometry**
  - Stoichiometry: $mD \to nE$
  - Flux continuity $N_D/m + N_E/n = 0$

Step 3: Conditions And Solutions

We have in general $N_D/m = -N_E/n$

$$-\frac{\partial}{\partial z}\left[-D_{DE}\frac{\partial c_D}{\partial z} + \frac{c_D}{c_T}(N_D + N_E)\right] = \frac{\partial c_D}{\partial t} \tag{16}$$

$$-\frac{\partial}{\partial z}\left[-D_{DE}\frac{\partial c_D}{\partial z} + \frac{c_D}{c_T}N_D(1 - \frac{n}{m})\right] = \frac{\partial c_D}{\partial t} \tag{17}$$

At steady state, we have

`N_D = \left[-\frac{D_{DE}}{1 - \frac{c_D}{c_T} (1 - \frac{n}{m})}\right]{d c_D}{dz}`

The steady state solution can be easily integrated

Catalyst In Wall: Simulation Demo

A slighted adapted demo from lecture 3 (x_A profile). Can we modify the molar flux by interface reaction stoichiometry?

Conclusion of Unsteady State Mass Transport

We will cover until **this point** in the mid-term exam!

To solve unsteady and steady state problem, use the following steps:

1. Draw scheme and list physical quantities / conditions
2. Write mass balance equation
3. Is it steady-state or unsteady-state?
4. If unsteady state, write flux equation in differential form
5. If steady state, use one of the solution examples
6. Do integration / calculation

Summary

- Writing mass balance equation for unsteady state problems
- Apply conditions for reaction
- Apply conditions for fluxes

Summary

- Unsteady state mass transfer governing equation
- Step-by-step solution to diffusion through stagnant B
- Diffusion and reaction system setup