FACULTÉ DES SCIENCES ET TECHNIQUES DE SETTAT

DEPARTMENT OF CHEMISTRY AND ENVIRONMENT

Expression of Flux Density in the Case of Absorption with First-Order Chemical Reaction

Anas TASSAOUI

October 13, 2024

Introduction

In various chemical engineering processes, understanding the concentration profile of a reacting species within a medium is crucial. This document provides a detailed step-by-step solution to the steady-state diffusion-reaction problem of a species A undergoing a first-order reaction within a one-dimensional liquid film of thickness δ.

Governing Equation

The starting point is Fick's second law of diffusion with a reaction term. For steady-state conditions (i.e., $\partial C_A/\partial t = 0$), the equation simplifies to:

$$D_A \frac{d^2 C_A}{dx^2} - r_A = 0 \tag{1}$$

where:

- D_A is the diffusion coefficient of species A (units: $\mathrm{m^2/s}$),
- C_A is the concentration of species A as a function of position x (units: $\mathrm{mol/m^3}$),
- r_A is the rate of consumption (or generation) of species A due to reaction (units: $\mathrm{mol/(m^3 \cdot s)}$).

Reaction Rate

We are considering a first-order reaction, meaning the rate of reaction is directly proportional to the concentration of species A:

$$r_A = k_1 C_A \tag{2}$$

where:

- k_1 is the first-order reaction rate constant (units: $\mathrm{s^{-1}}$).

Boundary Conditions

The system is defined within a liquid film of thickness δ, and the concentration of species A is specified at both boundaries:

$$\text{At } x = 0: \qquad C_A = C_A^i \tag{3}$$
$$\text{At } x = \delta: \qquad C_A = C_A^L \tag{4}$$

Here:

- C_A^i is the concentration of species A at the beginning of the liquid film ($x = 0$),
- C_A^L is the concentration of species A at the end of the liquid film ($x = \delta$).

Derivation of the Differential Equation

Substituting the reaction rate expression (Equation (2)) into the governing equation (Equation (1)), we obtain:

$$D_A \frac{d^2 C_A}{dx^2} - k_1 C_A = 0 \tag{5}$$

Dividing both sides by D_A to simplify:

$$\frac{d^2 C_A}{dx^2} - \frac{k_1}{D_A} C_A = 0 \tag{6}$$

Characteristic Equation

This is a linear, homogeneous, second-order ordinary differential equation with constant coefficients. To solve it, we consider the characteristic equation associated with it.

Let $C_A = e^{mx}$, where m is a constant to be determined. Substituting into Equation (6):

$$\begin{aligned}
\frac{d^2}{dx^2} e^{mx} - \frac{k_1}{D_A} e^{mx} &= 0 \\
m^2 e^{mx} - \frac{k_1}{D_A} e^{mx} &= 0 \\
\left(m^2 - \frac{k_1}{D_A} \right) e^{mx} &= 0
\end{aligned} \tag{7}$$

Since $e^{mx} \neq 0$, the characteristic equation is:

$$m^2 - \frac{k_1}{D_A} = 0 \tag{8}$$

Solving for m, we get:

$$m = \pm\sqrt{\frac{k_1}{D_A}} = \pm\beta \tag{9}$$

where we define:

$$\beta = \sqrt{\frac{k_1}{D_A}} \tag{10}$$

General Solution

The general solution to the differential equation is a linear combination of the exponential solutions:

$$C_A(x) = Ae^{\beta x} + Be^{-\beta x} \tag{11}$$

Alternatively, we can express this solution using hyperbolic functions for convenience:

$$C_A(x) = C_1 \sinh(\beta x) + C_2 \cosh(\beta x) \tag{12}$$

Recall that:

$$\sinh(\beta x) = \frac{e^{\beta x} - e^{-\beta x}}{2} \tag{13}$$

$$\cosh(\beta x) = \frac{e^{\beta x} + e^{-\beta x}}{2} \tag{14}$$

Using hyperbolic functions often simplifies the algebra when applying boundary conditions.

Applying Boundary Conditions

We will now determine the constants C_1 and C_2 using the boundary conditions.

At $x = 0$

Applying the first boundary condition (Equation (3)):

$$\begin{aligned} C_A(0) &= C_1 \sinh(0) + C_2 \cosh(0) \\ C_A^i &= C_1 \times 0 + C_2 \times 1 \\ \Rightarrow C_2 &= C_A^i \end{aligned} \tag{15}$$

At $x = \delta$

Applying the second boundary condition (Equation (4)):

$$\begin{aligned} C_A(\delta) &= C_1 \sinh(\beta\delta) + C_2 \cosh(\beta\delta) \\ C_A^L &= C_1 \sinh(\beta\delta) + C_A^i \cosh(\beta\delta) \end{aligned} \tag{16}$$

Solving for C_1:

$$C_1 = \frac{C_A^L - C_A^i \cosh(\beta\delta)}{\sinh(\beta\delta)} \tag{17}$$

Final Expression for $C_A(x)$

Substituting C_1 and C_2 back into the general solution (Equation (12)):

$$C_A(x) = \left(\frac{C_A^L - C_A^i \cosh(\beta\delta)}{\sinh(\beta\delta)}\right) \sinh(\beta x) + C_A^i \cosh(\beta x) \tag{18}$$

To simplify this expression, we can combine terms using the identity for $\sinh(\beta(\delta - x))$.

Hyperbolic Identity

The following identity is useful for simplification:

$$\sinh(\beta(\delta - x)) = \sinh(\beta\delta)\cosh(\beta x) - \cosh(\beta\delta)\sinh(\beta x) \tag{19}$$

Simplifying the Expression

Multiplying numerator and denominator by $\sinh(\beta\delta)$ to have a common denominator:

$$C_A(x) = \frac{[C_A^L - C_A^i \cosh(\beta\delta)]\sinh(\beta x) + C_A^i \sinh(\beta\delta)\cosh(\beta x)}{\sinh(\beta\delta)} \tag{20}$$

Using the hyperbolic identity (Equation (19)) to combine terms:

$$\begin{aligned} C_A(x) &= \frac{C_A^L \sinh(\beta x) + C_A^i \left[\sinh(\beta\delta)\cosh(\beta x) - \cosh(\beta\delta)\sinh(\beta x)\right]}{\sinh(\beta\delta)} \\ &= \frac{C_A^L \sinh(\beta x) + C_A^i \sinh(\beta(\delta - x))}{\sinh(\beta\delta)} \end{aligned} \tag{21}$$

Final Solution

The concentration profile of species A as a function of position x within the liquid film is given by:

$$C_A(x) = \frac{C_A^i \sinh\big(\beta(\delta - x)\big) + C_A^L \sinh\big(\beta x\big)}{\sinh\big(\beta\delta\big)} \tag{22}$$

This expression allows us to calculate the concentration of species A at any position x within the film, taking into account both diffusion and the first-order reaction.

Verification of Boundary Conditions

To ensure the correctness of our solution, we verify that it satisfies the given boundary conditions.

At $x = 0$

Substituting $x = 0$ into Equation (22):

$$\begin{aligned} C_A(0) &= \frac{C_A^i \sinh(\beta\delta) + C_A^L \sinh(0)}{\sinh(\beta\delta)} \\ &= \frac{C_A^i \sinh(\beta\delta) + 0}{\sinh(\beta\delta)} \\ &= C_A^i \end{aligned} \tag{23}$$

At $x = \delta$

Substituting $x = \delta$ into Equation (22):

$$
\begin{aligned}
C_A(\delta) &= \frac{C_A^i \sinh(\beta(\delta - \delta)) + C_A^L \sinh(\beta\delta)}{\sinh(\beta\delta)} \\
&= \frac{C_A^i \sinh(0) + C_A^L \sinh(\beta\delta)}{\sinh(\beta\delta)} \\
&= C_A^L
\end{aligned} \tag{24}
$$

Thus, the solution satisfies both boundary conditions.

Physical Interpretation

The concentration profile described by Equation (22) reflects the balance between diffusion and reaction within the film. The hyperbolic sine functions account for the exponential decay (or growth) of concentration due to the reaction, modulated by the position within the film.

The parameter β is a measure of the relative rates of reaction and diffusion:

$$\beta = \sqrt{\frac{k_1}{D_A}} \tag{25}$$

- A larger β indicates a faster reaction rate relative to diffusion, leading to a steeper concentration gradient.
- A smaller β suggests that diffusion dominates over the reaction, resulting in a more uniform concentration profile.

Limiting Cases

No Reaction ($k_1 = 0$)

When there is no reaction, $k_1 = 0$, so $\beta = 0$. The hyperbolic sine functions reduce to linear functions:

$$
\begin{aligned}
&\sinh(\beta x) \approx \beta x \quad \text{(for small } \beta x\text{)} \\
&\sinh(\beta\delta) \approx \beta\delta
\end{aligned} \tag{26}
$$

Substituting into Equation (22):

$$C_A(x) = \frac{C_A^i(\beta(\delta - x)) + C_A^L(\beta x)}{\beta\delta}$$
$$= C_A^i\left(1 - \frac{x}{\delta}\right) + C_A^L\left(\frac{x}{\delta}\right) \tag{27}$$

This is the linear concentration profile expected for steady-state diffusion without reaction.

Reaction-Dominated Regime ($k_1 \gg D_A$)

When the reaction rate is much greater than the diffusion rate, $\beta\delta \gg 1$. The hyperbolic sine functions can be approximated using exponential functions:

$$\sinh(\beta x) \approx \frac{1}{2}e^{\beta x} \tag{28}$$
$$\sinh(\beta\delta) \approx \frac{1}{2}e^{\beta\delta} \tag{29}$$

Substituting into Equation (22):

$$C_A(x) \approx \frac{C_A^i e^{\beta(\delta - x)} + C_A^L e^{\beta x}}{e^{\beta\delta}}$$
$$= C_A^i e^{-\beta x} + C_A^L e^{-\beta(\delta - x)} \tag{30}$$

If C_A^L is negligible compared to C_A^i, the concentration decays exponentially from the initial value.

Calculation of Flux at the Interface

To determine the flux of species A at the interface ($x = 0$) of the liquid film, we use Fick's first law of diffusion:

$$J_A = -D_A \frac{dC_A}{dx} \tag{31}$$

We need to compute the derivative of the concentration profile $C_A(x)$ with respect to x, and then evaluate it at $x = 0$.

Differentiating the Concentration Profile

Recall that the concentration profile is given by:

$$C_A(x) = \frac{C_A^i \sinh\left(\beta(\delta - x)\right) + C_A^L \sinh\left(\beta x\right)}{\sinh\left(\beta\delta\right)} \tag{32}$$

Differentiating $C_A(x)$ with respect to x:

$$\frac{dC_A}{dx} = \frac{1}{\sinh\left(\beta\delta\right)}\left[-C_A^i \beta \cosh\left(\beta(\delta - x)\right) + C_A^L \beta \cosh\left(\beta x\right)\right] \tag{33}$$

$$= \frac{\beta}{\sinh\left(\beta\delta\right)}\left[-C_A^i \cosh\left(\beta(\delta - x)\right) + C_A^L \cosh\left(\beta x\right)\right] \tag{34}$$

Flux at the Interface ($x = 0$)

Evaluating the derivative at $x = 0$:

$$\left.\frac{dC_A}{dx}\right|_{x=0} = \frac{\beta}{\sinh\left(\beta\delta\right)}\left[-C_A^i \cosh\left(\beta\delta\right) + C_A^L \cosh(0)\right] \tag{35}$$

$$= \frac{\beta}{\sinh\left(\beta\delta\right)}\left[-C_A^i \cosh\left(\beta\delta\right) + C_A^L \times 1\right] \tag{36}$$

Substituting back into Fick's first law (Equation (31)):

$$J_A = -D_A \left.\frac{dC_A}{dx}\right|_{x=0} \tag{37}$$

$$= -D_A \left(\frac{\beta}{\sinh\left(\beta\delta\right)}\left[-C_A^i \cosh\left(\beta\delta\right) + C_A^L\right]\right) \tag{38}$$

$$= D_A \frac{\beta}{\sinh\left(\beta\delta\right)}\left[C_A^i \cosh\left(\beta\delta\right) - C_A^L\right] \tag{39}$$

Final Expression for the Flux

Thus, the flux of species A at the interface ($x = 0$) is given by:

$$J_A = D_A \beta \frac{C_A^i \cosh\left(\beta\delta\right) - C_A^L}{\sinh\left(\beta\delta\right)} \tag{40}$$

References

1. Bird, R. B., Stewart, W. E., Lightfoot, E. N. (2007). *Transport Phenomena* (2nd ed.). John Wiley Sons.

2. Cussler, E. L. (2009). *Diffusion: Mass Transfer in Fluid Systems* (3rd ed.). Cambridge University Press.