

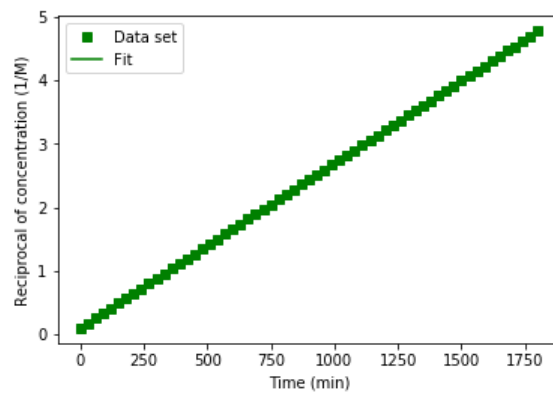
CHBE 355 Kinetics and Reactor Design - Final Examination (Worked Solutions)

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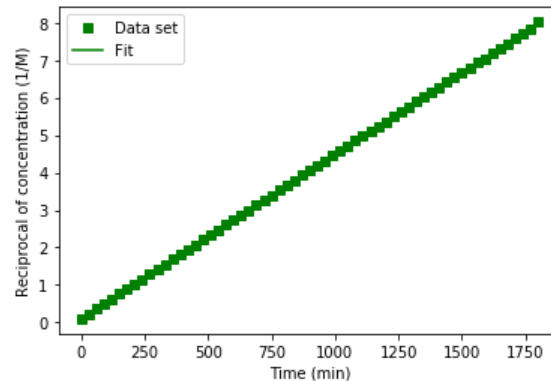
1 Determining order of reaction and parameters to Arrhenius Equation

Since we are given 2 sets of experimental data at varying temperatures, we can find the temperature dependant reaction rate constant for both experiments along with the order of reaction to then determine the pre-exponential factor A and activation energy E_A . From the statistical analysis such as linear and non-linear regression, it is concluded that:



The coefficient of determination for the fit for the dataset is 0.9999940936683402
The model for the dataset $1/C = 0.10135397375444688 + [0.00259469] * \text{time}$

Figure 1: Reciprocal of concentration vs time graph for experiment 1 ($T = 50$)



The coefficient of determination for the fit for the dataset is 0.9999822252064176
The model for the dataset $1/C = 0.10733849751221491 + [0.00437959] * \text{time}$

Figure 2: Reciprocal of concentration vs time graph for experiment 1 ($T = 60$)

Given that the reaction rate constant can be expressed as:

$$k = Ae^{-E_A/RT}$$

And we have 2 solutions. We can assume A and E_A are constant within the temperature range for this experiment and PBR:

$$\begin{aligned}\frac{k_1}{k_2} &= e^{\frac{-E_A}{RT_1} - \frac{-E_A}{RT_2}} \\ &= \exp\left(\frac{-E_A \times RT_2 + E_A \times RT_1}{R^2 T_1 T_2}\right) \\ \ln \frac{k_1}{k_2} &= \left(\frac{-E_A \times RT_2 + E_A \times RT_1}{R^2 T_1 T_2}\right) \\ E_A &= \frac{R^2 T_1 T_2 \ln \frac{k_1}{k_2}}{RT_1 - RT_2} \\ &= \frac{8.3145^2 \times 323 \times 333 \times \ln \frac{0.00259469}{0.00437959}}{8.3145 \times 323 - 8.3145 \times 333} \\ &= 46815.50118 \text{ Jmol}^{-1} \text{ K}^{-1} \\ A &= \frac{0.00259469}{\exp\left(\frac{46815.50118}{8.3145 \times 323}\right)} \\ &= 96554.6349 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}\end{aligned}$$

Therefore, at $T = 150^\circ \text{C} = 423 \text{K}$:

$$\begin{aligned}k_{ov} &= 96554.6349 e^{\frac{-46815.50118}{8.3145 \times 423}} \\ &= 0.1598991487\end{aligned}$$

2 Analysis of Catalyst and Determination of Effectiveness Factors

2.1 Shell Balance

At steady state:

$$\begin{aligned}\frac{dC_A}{dt} &= \text{Flux}_{in} - \text{Flux}_{out} - (-r_{LH}) \\ &= W_A|_r 2\pi r h - W_A|_{r+\Delta r} 2\pi(r + \Delta r)h - k_{LH} a C_A^2 \Delta V\end{aligned}$$

Determining differential volume unit:

$$\begin{aligned}\Delta V &= \pi h((r + \Delta r)^2 - r^2) \\ &= \pi h(r^2 + 2\pi r \Delta r + \Delta r^2 - r^2) \\ &= 2\pi r \Delta r h\end{aligned}$$

Divide the shell balance above by the differential volume unit:

$$\begin{aligned}0 &= \frac{W_A|_r 2\pi r h - W_A|_{r+\Delta r} 2\pi(r + \Delta r)h}{2\pi r \Delta r h} - k_{ov} C_A^2 \\ 0 &= \frac{1}{r} \left(\frac{W_A|_r 2r - W_A|_{r+\Delta r} (r + \Delta r)}{\Delta r} \right) - k_{ov} C_A^2 \\ 0 &= \frac{-1}{r} \frac{d}{dr} (W_A|_r r) - k_{ov} C_A^2\end{aligned}$$

Using Fick's law, assuming only diffusion:

$$\begin{aligned} W_A|_r &= J_A|_r + x_A W \\ &= -D_{eff} \frac{dC_A}{dr} \end{aligned}$$

Substituting back into shell balance:

$$\begin{aligned} 0 &= \frac{-1}{r} \frac{d}{dr} \left(-r D_{eff} \frac{dC_A}{dr} \right) - k_{ov} C_A^2 \\ 0 &= \frac{D_{eff}}{r} \frac{d}{dr} \left(r \frac{dC_A}{dr} \right) - k_{ov} C_A^2 \\ \frac{k_{ov}}{D_{eff}} C_A^2 &= \frac{1}{r} \left(r \frac{d^2 C_A}{dr^2} + \frac{dC_A}{dr} \right) \\ &= \frac{d^2 C_A}{dr^2} + \frac{1}{r} \frac{dC_A}{dr} \end{aligned}$$

Therefore final flux mass transfer ODE:

$$\begin{aligned} \frac{d^2 C_A}{dr^2} + \frac{1}{r} \frac{dC_A}{dr} &= \frac{k_{ov}}{D_{eff}} C_A^2 \\ &= \frac{k_{ov} R^2 C_{A,surf}}{D_{eff}} \times \frac{C_A^2}{R^2 C_{A,surf}} \end{aligned}$$

The dimensionless Thiele Modulus is:

$$\Phi^2 = \frac{k_{ov} R^2 C_{A,surf}}{D_{eff}}$$

Finally, the simplified ODE is:

$$\frac{d^2 C_A}{dr^2} + \frac{1}{r} \frac{dC_A}{dr} = \frac{\Phi^2}{R^2 C_{A,surf}} C_A^2$$

The shooting method can now be employed to solve the ODE for a range of values for $C_{A,surf}$. This will model the concentration inside the catalyst and the range of $C_{A,surf}$ values.

2.2 Internal and Overall Effectiveness Factors

$$\begin{aligned} \eta &= \frac{\left| -D_{eff} \frac{dC_A}{dr} \right|_{r=R} 2\pi R h}{k_{ov} C_{A,surf}^2 \pi R^2 h} \\ &= \frac{2D_{eff} \frac{dC_A}{dr} \Big|_{r=R}}{k_{ov} C_{A,surf}^2 R} \\ \Omega &= \frac{k_{conv} \eta}{k_{conv} + \eta k_{conv} (1 - \phi_{cat})} \end{aligned}$$

Where $k_{conv} = \frac{D_A}{\delta}$: Equating the rate of transport through the boundary layer and the true rate of reaction inside the catalyst we get:

$$\begin{aligned} k_{conv} (C_{A,bulk} - C_{A,surf}) 2\pi R h &= \eta k_{ov} C_{A,surf}^2 \pi R^2 (1 - \phi_{cat}) \\ k_{conv} (C_{A,bulk} - C_{A,surf}) 2\pi R h &= \frac{2D_{eff} \frac{dC_A}{dr} \Big|_{r=R}}{k_{ov} C_{A,surf}^2 R} k_{ov} C_{A,surf}^2 \pi R^2 (1 - \phi_{cat}) \\ k_{conv} (C_{A,bulk} - C_{A,surf}) &= D_{eff} \frac{dC_A}{dr} \Big|_{r=R} (1 - \phi_{cat}) \\ C_{A,surf} &= \frac{k_{conv} C_{A,bulk} + D_{eff} \frac{dC_A}{dr} \Big|_{r=R} (1 - \phi_{cat})}{k_{conv}} \end{aligned}$$

$\left. \frac{dC_A}{dr} \right|_{r=R}$ can be found via the shooting method performed on the second order ODE describing the mass transfer of species A inside the catalyst. By doing so, a corrected value of the surface concentration can be obtained. It follows that the internal effectiveness and overall effectiveness can also be calculated. $C_{A,bulk}$ can also be described as the concentration of species A in the PBR.

A quadratic can also be formed to relate $C_{A,surf}$ to $C_{A,bulk}$.

$$\begin{aligned} k_{conv}(C_{A,bulk} - C_{A,surf})2\pi Rh &= \eta k_{ov} C_{A,surf}^2 \pi R^2 (1 - \phi_{cat}) \\ k_{conv}(C_{A,bulk} - C_{A,surf}) &= \eta k_{ov} C_{A,surf}^2 \frac{R}{2} (1 - \phi_{cat}) \end{aligned}$$

Where the above equation can be written as a polynomial of order 2 with respect to $C_{A,surf}$.

$$C_{A,surf} = \frac{-k_{conv} \pm \sqrt{k_{conv}^2 + 2R\eta(1 - \phi_{cat})k_{conv}k_{ov}C_{A,bulk}}}{\eta k_{ov}(1 - \eta_{cat}R)}$$

Because η depends on $C_{A,surf}$, and $C_{A,surf}$ depends on both $C_{A,bulk}$ and η , and hence Ω , there is a circular loop of calculations. What is recommended is to solve this problem for a range of $C_{A,surf}$ values.

3 PBR Analysis

3.1 Rate Law Derivation

After calculating the overall effectiveness factor Ω , a mathematical relationship can be drawn to calculate $-r_A$ for the PBR analysis.

$$\begin{aligned} -r_A &= -r_{ov} \\ &= \Omega k_{ov} C_{A,bulk} \end{aligned}$$

Where $C_{A,bulk}$ is the variable used to represent the concentration of species A in the reactor. Now the parameters of the system of ODEs will be derived to describe the behaviour of conversion X_A , dimensionless pressure y , temperature T and coolant temperature T_c .

$$\begin{aligned} \Delta &= b - a = 1 \\ \mathcal{E} &= \frac{\Delta}{a} y_{A_o} = 0.1 \\ F_A &= F_{A_o}(1 - X_A) \\ C_A &= \frac{F_{A_o}(1 - X_A)}{v_o \left(\frac{P_o}{P} \right) \left(\frac{T}{T_o} \right) \left(\frac{z}{z_o} \right) (1 + \mathcal{E}X_A)} \end{aligned}$$

Assuming ideal gas behaviour, and assuming $y = \frac{P}{P_o}$,

$$C_A = \frac{C_{A_o}(1 - X_A)yT_o}{T(1 + \mathcal{E}X_A)}$$

3.2 Pressure Drop

Ergun Equation:

$$\begin{aligned} \frac{dP}{dz} &= \frac{-1.75G^2}{\rho_o D_p g_c} \left(\frac{1 - \phi_b}{\phi_b^3} \right) \left(\frac{v}{v_o} \right) \\ &= \frac{-1.75G^2}{\rho_o D_p g_c} \left(\frac{1 - \phi_b}{\phi_b^3} \right) \left(\frac{P_o}{P} \right) \left(\frac{F}{F_o} \right) \left(\frac{T}{T_o} \right) \\ \frac{dz}{dW} &= \frac{1}{\rho_{cat}(1 - \rho_b)A_c} \\ \frac{dP}{dW} &= \frac{-\alpha}{2} \left(\frac{P_o}{P} \right) \left(\frac{T}{T_o} \right) (1 + \mathcal{E}X_A) \end{aligned}$$

Let $y = \frac{P}{P_o}$:

$$\frac{dy}{dW} = \frac{-\alpha}{2} \left(\frac{1}{y} \right) \left(\frac{T}{T_o} \right) (1 + \mathcal{E}X_A)$$

3.3 Energy Balance

$$0 = \dot{Q} - \cancel{\dot{W}_S} - F_{A_o} \sum \theta_i \int_{T_o}^T C p_i dT - F_{A_o} X_A \left[\Delta H_{rxn}^o + \int_{T_{ref}}^T \Delta C p_{rxn} dT \right]$$

Heat generation term:

$$\begin{aligned} 0 &= UA(T - T_c) + \sum F_i H_i|_V - \sum F_i H_i|_{V+\Delta V} \\ \frac{d}{dV} \left(\sum F_i H_i \right) &= U\alpha(T - T_c) \\ \sum \left(H_i \frac{dF_i}{dV} + F_i C p_i \frac{dT}{dV} \right) &= U\alpha(T - T_c) \\ \sum H_i \frac{dF_i}{dV} &= (-r_A) \Delta H_{rxn} \\ \sum F_i C p_i \frac{dT}{dV} &= F_{A_o} \frac{dT}{dV} \left(\sum \theta_i C p_i + X_A \Delta C p_{rxn} \right) \end{aligned}$$

Substituting the last two terms into the general mole balance we get:

$$\begin{aligned} (-r_A) \Delta H_{rxn} + F_{A_o} \frac{dT}{dV} \left(\sum \theta_i C p_i + X_A \Delta C p_{rxn} \right) &= -U\alpha(T - T_c) \\ \frac{dT}{dV} &= \frac{-U\alpha(T - T_c) - (-r_A) \Delta H_{rxn}}{F_{A_o} \left(\sum \theta_i C p_i + X_A \Delta C p_{rxn} \right)} \end{aligned}$$

Assuming heat capacities are independent of temperature we get:

$$\frac{dT}{dV} = \frac{-U\alpha(T - T_c) - (-r_A) H_{rxn}^o + \Delta C p_{rxn} (T - T_{ref})}{F_{A_o} \left(\sum \theta_i C p_i + X_A \Delta C p_{rxn} \right)}$$

For co-current flow:

$$\begin{aligned} \dot{m}_c H_c|_V - \dot{m}_c H_c|_{V+\Delta V} + UA(T - T_c) &= 0 \\ \frac{\dot{m}_c H_c|_V - \dot{m}_c H_c|_{V+\Delta V}}{\Delta V} &= -U\alpha(T - T_c) \\ -\dot{m}_c \frac{dH_c}{dV} &= -U\alpha(T - T_c) \\ \dot{m}_c C p_{cool} \frac{dT_c}{dV} U\alpha(T - T_c) & \\ \frac{dT_c}{dV} &= \frac{U\alpha(T - T_c)}{\dot{m}_c C p_{cool}} \end{aligned}$$

Since some of the variables in the ODEs above are in the form:

$$\frac{d\gamma}{dV}$$

The derivative must be with respect to the weight of the catalyst bed. The chain rule can be used to convert the associated ODEs to the correct independent variable by using density. We are given 2g of catalyst is fitted into a 1L reactor during the experimental phase. The density is then calculated to be: $\rho_B = 2 \text{ kg m}^{-3}$. We now have:

$$\begin{aligned} V &= \frac{1}{\rho_B} W \\ \frac{dV}{dW} &= \frac{1}{\rho_B} \end{aligned}$$

Therefore, our system of equations are:

$$\begin{aligned}
k_{ov} &= A e^{\frac{-E_A}{RT}} \\
C_{A,surf} &= \frac{k_{conv} C_{A,bulk} + D_{eff} \frac{dC_A}{dr} \Big|_{r=R} (1 - \phi_{cat})}{k_{conv}} \\
\eta &= \frac{2 D_{eff} \frac{dC_A}{dr} \Big|_{r=R}}{k_{ov} C_{A,surf} R} \\
\Omega &= \frac{k_{conv} \eta}{k_{conv} + \eta k_{conv} (1 - \phi_{cat})} \\
-r_A &= \Omega k_{ov} C_A^2 \\
\frac{dX_A}{dW} &= \frac{1}{\rho_B} \frac{-r_A}{F_{A_o}} \\
\frac{dy}{dW} &= \frac{-\alpha}{2} \left(\frac{1}{y} \right) \left(\frac{T}{T_o} \right) (1 + \mathcal{E} X_A) \\
\frac{dT}{dW} &= \frac{1}{\rho_B} \frac{U \alpha (T - T_c) - (-r_A) [\Delta^o H_{rxn} + \Delta C p_{rxn} (T - T_{ref})]}{F_{A_o} [\sum \theta_i C p_i + X_A \Delta C p_{rxn}]} \\
\frac{dT_c}{dW} &= \frac{1}{\rho_B} \frac{U \alpha (T - T_c)}{\dot{m}_c C p_{cool}}
\end{aligned}$$