Problem 4.
Consider the reaction between o-nitrochlorobenzene (ONCB) and ammonia, to produce nitroaniline (NA). The reaction is \( \text{ONCB} + 2\text{NH}_3 \rightarrow \text{NA} + \text{NH}_4\text{Cl} \) or \( \text{A} + 2\text{B} \rightarrow \text{C} + \text{D} \). This is conducted along with water (inert), in a batch reactor. The reactor has cooling coils. The normal operation is as follows:

1. The reactor is charged with 3.17 kmol ONCB, 43 kmol of NH\(_3\) and 103.6 kmol of water.
2. From 0 to 45 mins the reaction is carried out at 175 °C. The cooling coil has water circulating in it and the flow rate is adjusted so that the reaction bath is at a temperature of 175 °C. The maximum temperature of the coolant is 25 °C and \( UA = 35.85 \text{ kcal/min/°C} \).
3. From 45 to 55 mins, it is either operated isothermally at the same temperature or operated adiabatically.
   a. When we say it is operated adiabatically, it just means that we cut off the coolant supply. When operated adiabatically the temperature will increase a bit and the reaction will be quicker.
4. From 55 min to next 23 h it is operated with cooling on. The temperature at the beginning of this stage may be higher than 175 °C, but with maximum cooling, it will be brought in to control.

A. Plot the temperature as a function of time.

B. If the reactor is charged with 9.044 kmol of ONCB, 33 kmol of NH\(_3\) and 103 kmol of water, and the coolant is not cut off, determine the temperature profile.

C. With the coolant cut off for 10 minutes, determine the profile.

Additional data:

\[ -r_A = kC_A C_B \]  with \( k = 0.00017 \frac{m^3}{\text{kmol} \times \text{min}} \) at 188 °C , \( E = 11273 \text{ cal/mol} \)

Density data is not given, but we are told that normally the reactant volume will be 3.26 \( m^3 \) and with 9.044 kmol ONCB batch, it is 5.119 \( m^3 \).

\( \Delta H = -5.9 \times 10^5 \text{ kcal/kmol} \), and is roughly independent of temperature.

\( C_{p-A} = 40 \text{ cal/mol/K} \), \( C_{p-B} = 8.38 \text{ cal/mol/K} \), \( C_{p-w} = 18 \text{ cal/mol/K} \).

The normal operating pressure is 34 atm but if it exceeds 47 atm, a safety valve will open. Water from the reacting bath will evaporate and cool the bath. If the safety valve doesn’t function, the pressure can build up further.

Solution:

First, the rate constant is to be written as \( k = 37.5984 \times e^{-\frac{5673.4}{T}} \text{ m}^3/\text{kmol/min} \)
A. For normal operation, \( C_{A0} = 3.17/3.26 = 0.9724 \text{ kmol/m}^3 \). \( C_{B0} = 13.19 \text{ kmol/m}^3 \).

Rate constant at the operating temperature = \( 1.1895 \times 10^{-4} \text{ m}^3/\text{kmol min} \).

Mass balance: \( \frac{dN_A}{dt} = r_A V \), Energy balance: \((-r_A)V(-\Delta H) = \sum_i (N_i C_{p,i}) \frac{dT}{dt} + UA(T - T_c) \)

For this case, \( N_{A0} \frac{dx}{dt} = Vk C_A C_B = Vk C_{A0} (1 - x) (C_{B0} - 2C_{A0}x) \)

\[
\frac{dx}{dt} = k (1 - x) C_{A0} \left( \frac{C_{B0}}{C_{A0}} - 2x \right)
\]

For normal operation, \( C_{A0} = 3.17/3.26 = 0.9724 \text{ kmol/m}^3 \). \( C_{B0} = 13.19 \text{ kmol/m}^3 \).

\[
\frac{C_{B0}}{C_{A0}} = \frac{N_{B0}}{N_{A0}} = \frac{43}{3.17} = 13.565
\]

\[
\frac{dx}{dt} = k (1 - x) C_{A0} \left( \frac{C_{B0}}{C_{A0}} - 2x \right) = k C_{A0} (1 - x) (\Theta - 2x)
\]

\[
\frac{dx}{(1 - x)(13.565 - 2x)} = 1.1566 \times 10^{-4} dt
\]

\[
\left( \frac{1}{(1 - x)(13.565 - 2x)} \right) dx = \frac{1}{11.565} \left( \frac{2}{13.565 - 2x} - \frac{1}{13.565 - 2x} \right) dx = 1.1566 \times 10^{-4} dt
\]

\[
\frac{1}{11.565} \left( -\ln(1 - x) + \ln(13.565 - 2x) - \ln(13.565) \right) = 1.1566 \times 10^{-4} t
\]

Without using the numbers, we can show that \( t = \frac{1}{k C_{A0}} \left( \frac{1}{\Theta - 2} \right) \ln \left( \frac{\Theta - 2x}{\Theta (1 - x)} \right) \)

\[
\frac{1}{11.565} \ln \left( \frac{13.565 - 2x}{13.565 (1 - x)} \right) = 1.1566 \times 10^{-4} t
\]

\[
\frac{1}{11.565} \ln \left( \frac{13.565 - 2x}{13.565 (1 - x)} \right) = 1.1566 \times 10^{-4} t
\]

\[
\ln \left( \frac{13.565 - 2x}{13.565 (1 - x)} \right) = 1.33761 \times 10^{-3} t
\]
At 45 mins, \( \ln \left( \frac{13.565 - 2x}{13.565 (1 - x)} \right) = 1.33761 \times 10^{-3} \times 45 = 0.0602 \)

\[
\frac{13.565 - 2x}{13.565 (1 - x)} = 1.062
\]

\[
(13.565 - 2x) = 14.4067 - 14.4067x
\]

Conversion = 0.0678, i.e. about 7%

Heat generation rate = \( (-r_A) V (-\Delta H) \). Since the operation is isothermal, the rate constant \( k \) will be a constant for this phase. The reaction rate will be a maximum at the very beginning since the concentration of A and B are the highest at that time. Then,

Maximum rate of heat generation rate =

\[
= (-r_A) \bigg|_{t=0} V (-\Delta H)
\]

\[
= kC_{A0}C_{B0}V (-\Delta H)
\]

\[
= 1.1895 \times 10^{-4} \times 0.9724 \times 13.19 \times 3.26 \times 5.9 \times 10^5
\]

\[
= 2934 \text{ kcal/min}
\]

Maximum possible heat removal rate

\[
UA(T - T_c) = 35.85 \times (175 - 25) = 5378 \text{ kcal/min}
\]

Therefore, with feedback control, it is easy to maintain the temperature of the bath.

In the second phase, the operation is adiabatic.

\( C_{A0} = 0.90643 \text{ kmol/m}^3 \), \( C_{B0} = 12.1275 \text{ kmol/m}^3 \).

The equations to be solved are

\[
\frac{dx}{dt} = k(1-x)C_{A0}\left( \frac{C_{B0}}{C_{A0}} - 2x \right)
\]

\[
k = 37.5984 \times e^{-\frac{5673.4}{T}}
\]

\[
(-r_A)V(-\Delta H) = \sum_i (N_iC_{p-i}) \frac{dT}{dt} + UA(T - T_c)
\]

i.e.

\[
\frac{dx}{dt} = k(1-x)C_{A0}\left( \frac{C_{B0}}{C_{A0}} - 2x \right) \quad \text{and} \quad \frac{dT}{dt} = \frac{(-r_A)V(-\Delta H) - UA(T - T_c)}{\sum_i (N_iC_{p-i})}
\]
Performing the integration numerically, we get the conversion to be 0.085 and the temperature to be 188.7 °C.
Max rate is 0.0020 kmol/min. Max heat generated at this stage is 3861 kcal/min which is less than Max heat removal capacity (5869 kcal/min)

If full supply of coolant is used in the third stage, then numerical integration shows that the bath will cool down, as shown below.

Thus, with feedback loop it is easy to operate at 188.7 C for the rest of the time. Such operation for 23 h gives 94.5% conversion, as shown below. Had they operated isothermally in the second and third stage, the final conversion would have been 87.2%
B. New values of inputs, but second stage is operated without cutting the coolant supply.

Initial concentration is 1.7668 and 6.4466 kmol/m$^3$ for A and B respectively.

Max heat removal is the same, viz. 5378 kcal/min, Max heat generated is 4091 kcal/min. So the first stage is fine.

Ratio of $C_{B0}/C_{A0} = 3.6488$

At the end of the first stage, conversion is 0.033608 and the concentration of A and B are 1.7074 and 6.3278 kmol/m$^3$ respectively.

Running the second stage isothermally, we find max heat generation rate at the end is 3836 kcal/min, well below the max heat removal capacity (5378 kcal/min). The conversion is 0.0407.

The third stage, run isothermally gives the following, about 59% conversion after 23 hours.

C.

Initial concentration is 1.7668 and 6.4466 kmol/m$^3$ for A and B respectively.

Max rate is 0.0014
Max heat removal is the same, viz. 5378 kcal/min, Max heat generated is 4091 kcal/min. So the first stage is fine.
Ratio of $C_{B0}/C_{A0} = 3.6488$

At the end of the first stage, conversion is 0.033608 and the concentration of A and B are 1.7074 and 6.3278 kmol/m$^3$ respectively.

At the end of second stage, conversion is 0.043 and temperature is 195 °C.

K is 0.0002044 m3/kmol/min. Max rate is 0.0022 kmol/min

Max heat generated at this stage is 6570 kcal/min, which is more than the max possible heat removal rate (6095 kcal/min)

Third stage: Operated with maximum coolant supply gives the following.

The temperature increase is less than 0.5 °C/min in the beginning, so it is difficult to notice the problem at that stage!

Summary:

1. For ‘regular’ input, cutting off the coolant for 10 mins (45 to 55 min) is not a problem.
2. For the larger input, isothermal operation is not a problem.
3. Larger input and cutting off coolant is problematic.