CEN 786, Spring 2020
Project 3 (Credit where due, all problems taken from Scott Fogler's Textbook. I modified some slightly to reinforce concepts from class.)
Due: Friday 3/13/2020

1. Consider the hydration of propylene oxide (A) using water (B) to produce propylene glycol (C).

$$A + B \rightarrow C$$

   The reaction may be considered irreversible. Further, under the conditions here, water is in considerable excess so the reaction is pseudo first order in propylene oxide.

$$r = k \cdot C_A$$

   You carry out the reaction in a 500 gallon CSTR that is equipped with a heat exchanger. Initially, the tank is filled with water at a concentration of 3.45 lb-mol ft^{-3} at a temperature of 75°F. The feed stream consists of propylene oxide (80 lb-mol h^{-1}), water (1000 lb-mol h^{-1}), and methanol (100 lb-mol h^{-1}); the combined feed stream enters the reactor at a temperature of 75°F. The cooling water enters the heat exchanger at 60∘F, and you may assume that the cooling water flowrate is sufficiently high to keep the cooling water temperature constant.

   You additionally have the following data available:

$$\Delta H_{rxn} = -36,000 \text{ BTU lb-mol}^{-1} \text{ at T} = 536.73°R$$
$$C_{PA} = 35 \text{ BTU lb-mol}^{-1} °R^{-1}$$
$$C_{PB} = 18 \text{ BTU lb-mol}^{-1} °R^{-1}$$
$$C_{PC} = 46 \text{ BTU lb-mol}^{-1} °R^{-1}$$
$$C_{PM} = 19.5 \text{ BTU lb-mol}^{-1} °R^{-1}$$
$$V_A = 1.083 \text{ ft}^3 \text{ mol}^{-1}$$
$$V_B = 0.290 \text{ ft}^3 \text{ mol}^{-1}$$
$$V_M = 0.649 \text{ ft}^3 \text{ mol}^{-1}$$
$$UA = 16,000 \text{ BTU h}^{-1} °R^{-1}$$

   The rate constant for this reaction can be computed in units of h^{-1} using the following equation:

$$k = 16.96 \times 10^{12} \; exp\left(\frac{-32,400}{RT}\right)$$

   (a) How many steady states are possible in this system?

(b) Compare rates of heat generation and heat removal as a function of Temperature to characterize the stability of each steady state.

(c) Create a Taylor series expansion about the steady state solution in order to linearize the (transient) material and energy balances that describe this system. Find the eigenvalues associated with each steady state solution and determine whether perturbations in temperature and/or concentration at each steady state will a) grow with time, b) decay with time (asympotic stability), and/or show oscillatory behavior

(d) For the case where the reactor is initially filled with water and held at a temperature of 75°F, simulate the reactor startup period to determine 1) how long it takes for the reactor to reach steady state and 2) the fractional conversion of A and reactor Temperature at steady state.

(e) Simulate the case where the reactor is allowed to reach steady state and operate at steady state for 10 hours. At that time, the heat transfer coefficient is reduced in half due to a problem in the cooling line. This persists for 30 minutes, and then the original working capacity is restored. What happens in this case?

2. For this problem, we will simulate an industrial explosion that occurred as a result of a runaway reaction.

A batch reactor at the Monsanto plant in Sauget, Illinois exploded on August 8 (I don't know the year). The reactor was convert o-nitrochlorobenzene (A) and ammonia (B) into used to produce nitroanilane (C). The reaction additionally produces ammonium chloride (D) as a side product. Here, we use the usual shorthand:

$$A + 2B \rightarrow C + D$$
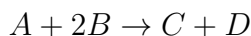
The reaction is first order in both A and B. It is typically carried out isothermally at 175°C and 500 psi. The ambient temperature of the cooling water in the heat exchanger is typically 25°C. For usual operation, the reactor was charged with 3.17 kmol of A, 103.6 kmol of water (solvent) and 43 kmol of NH_3, which typically utilized about 1/3 of the total volume of the batch reactor (3.26 m^3). It was well-known that the heat exchanger used to cool this reactor was faulty. It would fail from time to time resulting in a total loss of coolant flow (i.e., UA = 0) to the reactor; however, plant operators were typically able to bring the heat exchanger back on line with about 10 minutes. This was a common occurrence, and there had never previously been ill effects. Knowing that this reaction is exothermic and had the potential to run away, the reactor was outfitted with a rupture disk that was designed to break at 700psi (which corresponds to a reactor temperature of 265°C considering the vapor pressure of the mixture). In the event of rupture, the reactor contents would evaporate and discharge through the rupture disk, cooling the reactor and preventing further runaway. The real danger is that if the temperature in the reactor ever exceeds 300°C, a secondary decomposition occurs that is extremely exothermic and generates a lot of gas-phase decomposition products (and hence creates a huge spike in reactor pressure). The reactor will explode if the temperature hits 300°C

As the story goes, (From Fogler), someone in management noticed that the reactor was running well below full capacity (i.e., only a third of its volume was utilized). It was suggested to fill the reactor more completely to maximize productivity and profit; accordingly, the reactor on the date in question was instead charged with 9.044 kmol of A, 33.0 kmol of NH3, and 103.7 kmol of water. This increased the liquid volume to 5.119 m^3.

You also have the following information:

$$\Delta H_{rxn} = -5.9 \times 10^5 \text{ kcal kmol}^{-1}$$
$$C_{PA} = 40 \text{ cal mol}^{-1} \text{ K}^{-1}$$
$$C_{PB} = 8.38 \text{ cal mol}^{-1} \text{ K}^{-1}$$
$$C_{PW} = 18 \text{ cal mol}^{-1} \text{ K}^{-1}$$
$$UA = 35.85 \text{ kcal min}^{-1} \text{ K}^{-1} \text{ at max capacity}$$
$$k0 = 0.00017 \text{ m}^3 \text{ kmol}^{-1} \text{ min}^{-1}$$
$$T0 = 461 \text{ K}$$
$$E_A = 11,273 \text{ cal mol}^{-1}$$

Note, even though it is not strictly true, you may assume that ΔCp is zero for this system. It may be helpful to write your material an energy balances as functions of fractional conversion of A instead of concentrations.

On the day of the incident, the reaction was initiated at 9:55PM. Startup proceeded normally, and isothermal operation was maintained at 175°C for 45 minutes. At that time, the heat exchanger failed, and the reactor operation became adiabatic for 10 minutes. As usual, operations personnel responded quickly and restored the cooling flow to its maximum capacity, restoring cooling to the unit; however, the runaway had initiated, and the cooling capacity could not keep pace with heat generation. The final problem is that the rupture disk, which was supposed to break at 265°C, failed.

(a) Starting at a time of 0 (or 9:55PM), prepare a temperature vs. time plot for this scenario.

(b) How long did it take for the reactor to explode?