

Kinetics and Reactor Design HW12

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Assigned: April 25, 2023

Due: May 8, 2023

1 Problem Statement

1.1 P13-2_B (a,b)

P13-2_B The following is an excerpt from *The Morning News*, Wilmington, Delaware (August 3, 1977): “Investigators sift through the debris from blast in quest for the cause [that destroyed the new nitrous oxide plant]. A company spokesman said it appears more likely that the [fatal] blast was caused by another gas—ammonium nitrate—used to produce nitrous oxide.” An 83% (wt) ammonium nitrate and 17% water solution is fed at 200°F to the CSTR operated at a temperature of about 510°F. Molten ammonium nitrate decomposes directly to produce gaseous nitrous oxide and steam. It is believed that pressure fluctuations were observed in the system and, as a result, the molten ammonium nitrate feed to the reactor may have been shut off approximately 4 min prior to the explosion.

(a) Can you explain the cause of the blast?

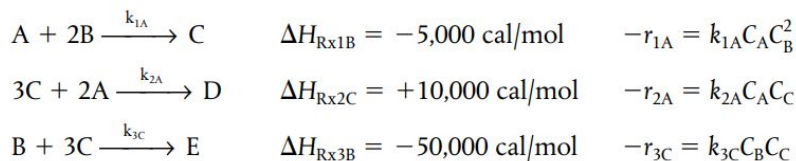
(b) If the feed rate to the reactor just before shutoff was 310 lb_m of solution per hour, what was the exact temperature in the reactor just prior to shutdown? Use the data to calculate the exact time it took for the reactor to explode after the feed was shut off to the reactor.



Figure 1

1.2 P13-9_B(a-f)

P13-9_B The following reactions are taking place in a 2000-dm³ liquid-phase batch reactor under a pressure of 400 psig



The initial temperature is 450 K and the initial concentrations of A, B, and C are 1.0, 0.5, and 0.2 mol/dm³, respectively. The coolant flow rate was at its maximum value so that $T_{a1} = T_{a2} = T_a = 400 \text{ K}$, so that the product, the exchange area, and the overall heat transfer coefficient, UA , is $UA = 100 \text{ cal/s} \cdot \text{K}$.

- (a) If $Q_r > Q_g$ at time $t = 0$, and there is no failure of the heat exchange system, is there any possibility that the reactor will run away? Explain.
- (b) What is Q_r at $t = 0$?
- (c) What is Q_g at $t = 0$?
- (d) What is the initial rate of increase in temperature, (i.e., dT/dt) at $t = 0$?

$$\frac{dT}{dt} = \underline{\hspace{2cm}}$$

- (e) Suppose that the ambient temperature T_a is lowered from 400 K to 350 K; what is the initial rate of reactor temperature change?

$$\frac{dT}{dt} = \underline{\hspace{2cm}}$$

Plot the temperatures and all the concentrations as a function of time up to $t = 1000 \text{ s}$.

- (f) A suggestion was made to add 50 moles of inerts at a temperature of 450 K. Will the addition of the inerts make runaway more likely or less likely? How? Show quantitatively.

Additional information:

As a first approximation, assume all heats of reaction are constant (i.e., $\Delta C_{p_{ij}} \cong 0$). Specific reaction rates at 450 K are

$$\begin{array}{lll} k_{1A} = 1 \times 10^{-3} (\text{dm}^3/\text{mol})^2/\text{s} & C_{p_A} = 10 \text{ cal/mol/K} & C_{p_D} = 80 \text{ cal/mol/K} \\ k_{2A} = \frac{1}{3} \times 10^{-3} (\text{dm}^3/\text{mol})^2/\text{s} & C_{p_B} = 10 \text{ cal/mol/K} & C_{p_E} = 50 \text{ cal/mol/K} \\ k_{3C} = 0.6 \times 10^{-3} (\text{dm}^3/\text{mol})^2/\text{s} & C_{p_C} = 50 \text{ cal/mol/K} & \end{array}$$

Figure 2

2 Problem Solution

2.1 P13-2_B (a,b)

a) Adiabatic reactor

$$(-\Delta H_R)(r_A V) = N_A C_{P_A} \frac{dT}{dt} \quad (1)$$

$$\frac{dT}{dt} = \frac{\Delta H_{Rxn}}{C_{P_A}} k(T) \quad (2)$$

$$C_{P_A} = 0.38 Btu/lb_m \quad (3)$$

$$\Delta H_{Rxn}^\circ = -336 Btu/lb_m \text{ at } 500F \quad (4)$$

$$T_0 = 510^\circ F = 980^\circ R \quad (5)$$

$$k \text{ at } 510F = 0.307 [=] h^{-1} \quad (6)$$

$$k \text{ at } 560F = 2.912 [=] h^{-1} \quad (7)$$

$$k(T) = \frac{k \text{ at } 510F}{60} \times \left(\frac{E}{R} \left(\frac{1}{970} - \frac{1}{T} \right) \right) \quad (8)$$

$$\frac{E}{R} = \ln \frac{k_2}{k_1} \left(\frac{T_1 T_2}{T_2 - T_1} \right) = 44518^\circ R \quad (9)$$

$$k(T) = \frac{0.307}{60} \times \left(44518^\circ R \left(\frac{1}{970} - \frac{1}{T} \right) \right) \quad (10)$$

$$\frac{dT}{dt} = \frac{Q_g - Q_r}{N_A C_{P_A}} \quad (11)$$

$$Q_r = 0[C_{P_A}(T - 660) + \Theta_W(1134 + C_{P_W}(T - 960))] \quad (12)$$

$$Q_g = (\Delta H_R)(r_A V) \quad (13)$$

$$\frac{dT}{dt} = \frac{(\Delta H_R)(r_A V)}{\Sigma N_i C_{P_i}} \quad (14)$$

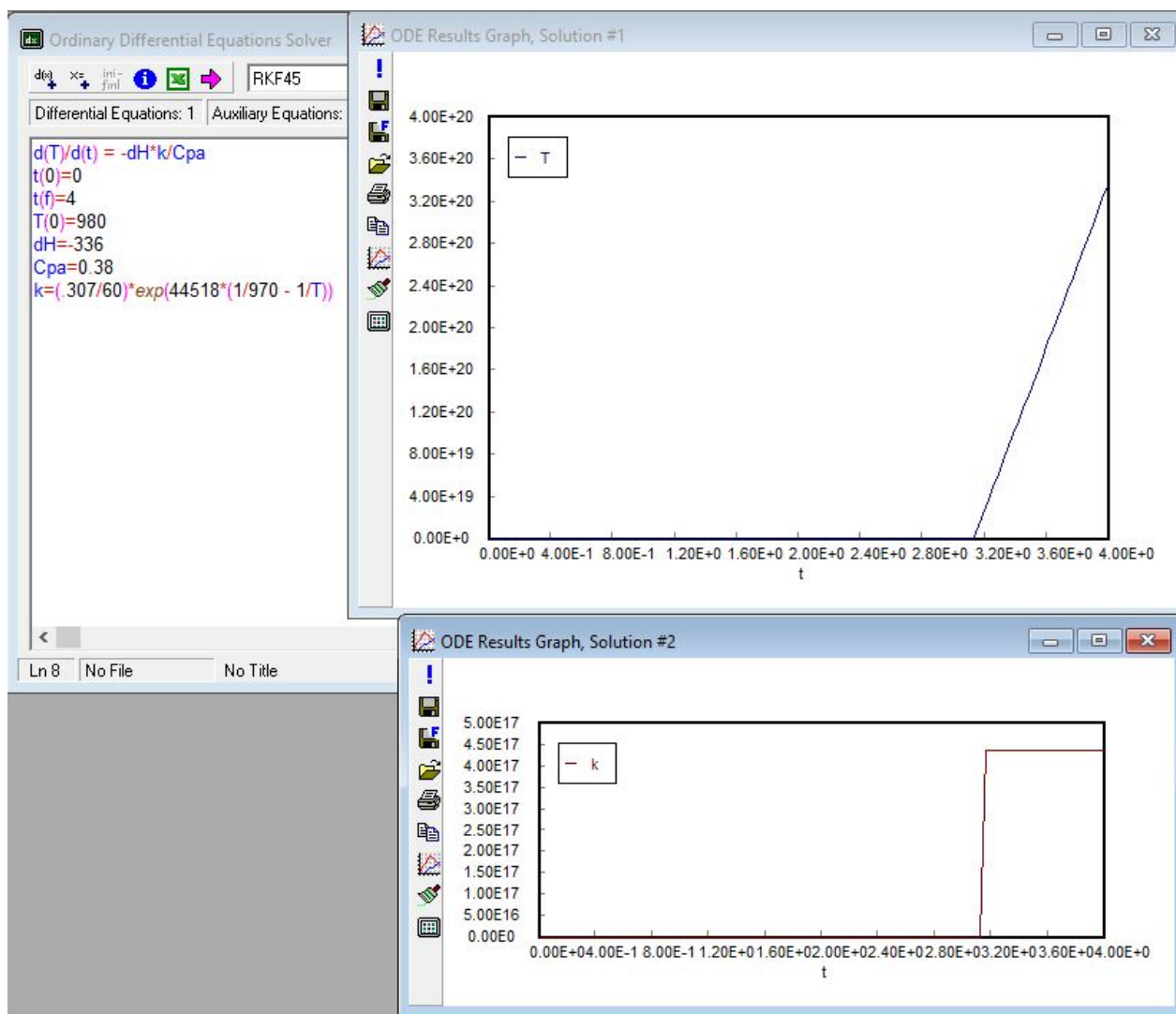


Figure 3: Temperature and k graph as a function of time (in minutes)

As shown by the figure, the temperature rose exponentially (as did the reaction rate) at around the 3 minute mark. The explosion happened because the elevated temperature of the CSTR caused a runaway reaction.

b) Using the data (from the graph) the exponential increase started at $t = 3.15$ minutes. Modeling the same reaction for $T_0 = 100^\circ\text{F}$ yields a constant temperature of 100°F over 4 minutes. For $T_0 = 500^\circ\text{F}$, the temperature increases, but there is no spike within the 4 minutes, so no explosion. I would control the startup and shutdown of such a reaction by carefully monitoring the temperature of the reactor as well as modeling out the kinetics of the reaction to ensure that a runaway reaction can't occur. If the flow rate was increased, Q_g would have decreased and Q_r would return as a non-zero value. This would have significantly decreased change of temperature with time and might have avoided the disaster. If the feed was colder, then Q_r would have been larger and further minimized chances of runaway

reaction.

2.2 P13-9_B(a-f)

a) There is a possibility that the reaction will run away. Producing more C from reaction 1 will result in an increase in the reaction rate of reaction 3. Reaction 3 is highly exothermic, therefore there is a risk of a runaway reaction.

b)

$$Q_r|_{t=0} = UA(T_0 - T_a) = (100)(450 - 400) = 5000 \text{ cal/s} \quad (15)$$

c)

$$Q_g|_{t=0} = r_{1B0}V\Delta H_{Rx1B} + r_{2C0}V\Delta H_{Rx2C} + r_{3B0}V\Delta H_{Rx3B} \quad (16)$$

$$r_{1B0} = 2r_{1A0} = -2k_{1A}C_{A0}C_{B0}^2 = -.0005 \frac{\text{mol}}{\text{s} \times \text{dm}^3} \quad (17)$$

$$r_{2C0} = 1.5r_{2A0} = -1.5k_{2A}C_{A0}C_{C0} = -.0001 \frac{\text{mol}}{\text{s} \times \text{dm}^3} \quad (18)$$

$$r_{3B0} = \frac{1}{3}r_{3C0} = -\frac{1}{3}k_{3C}C_{B0}C_{C0} = -.00002 \frac{\text{mol}}{\text{s} \times \text{dm}^3} \quad (19)$$

$$V = 2000 \text{ dm}^3 \quad (20)$$

$$Q_g|_{t=0} = 5000 \text{ cal/s} \quad (21)$$

d)

$$\frac{dT}{dt}|_{t=0} = \frac{Q_g - Q_r}{N_{A0}C_{PA} + N_{B0}C_{PB} + N_{C0}C_{PC}} = 0 \quad (22)$$

e)

$$Q_r|_{t=0}(T_a = 350K) = UA(T_0 - T_a) = 10000 \text{ cal/s} \quad (23)$$

$$\frac{dT}{dt}|_{t=0} = \frac{Q_g - Q_r}{N_{A0}C_{PA} + N_{B0}C_{PB} + N_{C0}C_{PC}} = \frac{-5000}{2000[(1)(10) + (0.5)(10) + (0.2)(5)]} = -0.1 \text{ K/s} \quad (24)$$

f) Adding 50 moles of inerts at 450K will make runaways less likely. This is due to the denominator of the term in parts d and e now having an additional inert term. The inerts will have some value N_I and C_{PI} , which will increase the denominator. This would result in any temperature changes (in any direction) being slowed down. Effectively, the inert acts as an insulator and prevents fast temperature fluctuations.