Ch E 345 - Chemical Reactor Analysis I
Seminar #7

March 17, 2017

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1. A first order endothermic reaction, $A \rightarrow B$, is carried out in a constant volume batch reactor. The enthalpy of reaction is 50,000 J/mol. The first order rate constant is given by:

$$k = 0.20 \exp\left(\frac{-10,000}{R_g T}\right) \quad \text{min}^{-1}$$

The reactor volume is 1 m^3 and contains 1000 kg of mixture. There are initially 10,000 mol of reactant A in the reactor. The reactor is heated to 400°C, during which time 10% of the initial A reacts. Once the temperature reaches 400°C, the reactor operates adiabatically. The heat capacity of the reaction mixture is a constant 2000 J/kgK.

a) After the heating stops, how much time is required to achieve a final conversion of 70% of the A originally present before the heating started?
b) What is the final temperature in the reactor?

2. Consider a constant volume batch reactor in which a liquid phase reaction occurs. The reaction is a catalytic reaction (solid catalyst is used), and is represented by the following overall reaction, with second order kinetics:

$$A + B \rightarrow C + D \qquad (-r_A) = k\, C_A\, C_B \quad \frac{\text{mol of A}}{\text{s} \cdot \text{kgcat}}$$

The kgcat term means kg of catalyst and concentrations are in mol/m^3. The reaction rate constant is:

$$k = 1 \times 10^{-5} \exp\left(\frac{-2500}{T}\right) \quad \frac{\text{m}^6}{\text{mol} \cdot \text{s} \cdot \text{kgcat}}$$

One cubic metre (1000 kg) of a fluid solution containing 2000 mol of A and 2000 mol of B are placed in the reactor. At time zero, 10 kg of catalyst is added to the reactor and the reaction starts.

(a) If the reactor is operated isothermally at a temperature of 100°C, calculate how much time is required to reach 80% conversion.
(b) If the reactor is operated adiabatically, and the initial temperature of the mixture is 27°C, calculate the temperature of the reaction mixture when the conversion is 80%.

$$\Delta H_{R,A} = -50,000 \ \frac{\text{J}}{\text{mol}}, \quad \text{Heat capacity of fluid} = 4000 \ \frac{\text{J}}{\text{kg} \cdot \text{K}}$$

$$\text{Heat capacity of catalyst} = 10,000 \ \frac{\text{J}}{\text{kg} \cdot \text{K}}$$

Solutions - Seminar #7

Problem 1:

The reaction is carried out in a constant volume batch reactor. The reactor is heated to an initial operating temperature and then operated adiabatically.

$$\mathrm{A} \rightarrow \mathrm{B} \qquad \left(\text{-}r_{\mathrm{A}}\right) = kC_{\mathrm{A}}$$

The solution requires the simultaneous solution of the mole and energy balance equations. The mole balance is:

$$-\frac{1}{V}\frac{dN_{\mathrm{A}}}{dt} = \left(-r_{\mathrm{A}}\right) = k\mathrm{C}_{\mathrm{A}} = k\frac{N_{\mathrm{A}}}{V}$$

The volume cancels. Writing in terms of the fractional conversion gives:

$$\frac{dX_{\mathrm{A}}}{dt} = k\left(1 - X_{\mathrm{A}}\right)$$

The energy balance equation can be written as:

$$\frac{dT}{dt} = \frac{\left(-\Delta U_{R,\mathrm{A}}\right)\left(-r_{\mathrm{A}}\right)V}{\sum N_i C_{Vi}}$$

The heat capacity of the reaction mixture is given as a constant based on the reactant mass. Mass is conserved. Furthermore, $\Delta V_R = \Delta H_R$ because moles are conserved on reaction. The energy balance can thus be written:

$$\frac{dT}{dt} = \frac{\left(-\Delta U_{R,\mathrm{A}}\right)\left(-r_{\mathrm{A}}\right)V}{m_t \bar{C}_V}$$

To eliminate one of the differential equations, substitute the mole balance into the energy balance:

$$\frac{dT}{dt} = -\frac{\left(-\Delta U_{R,\mathrm{A}}\right)}{m_t \bar{C}_V}\frac{dN_{\mathrm{A}}}{dt} = \frac{\left(-\Delta U_{R,\mathrm{A}}\right)}{m_t \bar{C}_V} N_{\mathrm{A0}}\frac{dX_{\mathrm{A}}}{dt}$$

Eliminate the t variable and integrate:

$$T = T_0 + \frac{\left(-\Delta U_{R,\mathrm{A}}\right)}{m_t \bar{C}_V} N_{\mathrm{A0}}\left(X_{\mathrm{A}} - X_{\mathrm{A0}}\right)$$

At time $t = 0$, the conversion is 0.1. Substitute the expression for T into the mole balance:

$$\frac{dX_A}{dt} = 20\exp\left(-\frac{10,000}{8.314} \bullet \frac{1}{T_0 + \left(\frac{-\Delta U_{R,A}}{m_t \bar{C}_V}\right) N_{A0}\left(X_A - X_{A0}\right)}\right)\left(1 - X_A\right)$$

Substitute the numbers:

$$\frac{dX_A}{dt} = 20\ \exp\left(\frac{-1202.79}{673 + \left(\frac{-50,000}{1000 \times 2000}\right) 10,000\left(X_A - 0.1\right)}\right)\left(1 - X_A\right)$$

$$\frac{dX_A}{dt} = 20\ \exp\left(\frac{-1202.79}{673 - 250\left(X_A - 0.1\right)}\right)\left(1 - X_A\right)$$

Solve the equation numerically to find t when $X_A = 0.7$. The solution is $t = 43.9$ min.

Solution to problem 2

The reaction and the rate expression are given by:

$$\text{A + B} \rightarrow \text{C + D} \qquad \left(-r_{\text{A}}\right) = kC_{\text{A}}C_{\text{B}}$$

The reaction is catalytic and the rate has units of $\dfrac{\text{mol}}{\text{s}\cdot\text{kgcat}}$. The concentration has units of $\dfrac{\text{mol}}{\text{m}^3}$.

The rate constant is equal to $k = 1\times10^{-5}\exp\left(-\dfrac{2500}{T}\right)$ with units of $k \equiv \dfrac{m^6}{\text{mol}\cdot\text{s}\cdot\text{kgcat}}$. The reactor is constant volume batch reactor. The mole balance is: $\left(\text{note that } C_{\text{A}} = C_{\text{B}}\right)$

$$-\frac{1}{W}\frac{dN_A}{dt} = kC_{\text{A}}C_{\text{B}} = kC_{\text{A}}^2 = k\left(\frac{N_{\text{A}}}{V}\right)^2$$

Written in terms of fractional conversion:

$$\frac{1}{W}\frac{dX_{\text{A}}}{dt} = k\frac{N_{\text{A0}}}{V^2}\left(1-X_{\text{A}}\right)^2$$

Part (a):

The reactor is isothermal at $T = 100°\text{C}$ where $k = 1.23\times10^{-8}$. The mole balance is:

$$\frac{dX_{\text{A}}}{\left(1-X_{\text{A}}\right)^2} = \frac{kN_{\text{A0}}W}{V^2}dt = \frac{(10)(2000)\left(1.23\times10^{-8}\right)}{1^2}dt$$

Integrate:

$$\left.\frac{1}{1-X_{\text{A}}}\right|_0^{0.8} = 2.46\times10^{-4}t = 4$$

$$t = 16260 \text{ s} \quad \text{or} \quad t = 4.52 \text{ h}$$

Part (b):

The reactor is adiabatic, therefore we need the adiabatic reaction line, which is obtained from the energy balance. For a catalytic reactor, the energy balance is:

$$\sum F_i C_{Pi} \frac{dT}{dt} + (\Delta H_R)(-r_A)W = 0$$

Both the fluid and catalyst must be considered in the energy balance. The ΔH_R and C_P are taken as constant. The energy balance including fluid and catalyst is:

$$\left(m_f C_{P_f} + m_c C_{P_C}\right)\frac{dT}{dt} - \Delta H_R \frac{dN_A}{dt} = 0$$

The dt term cancels and the following result is obtained:

$$\left(m_f C_{P_f} + m_c C_{P_c}\right) dT + \Delta H_R N_{A0}\, dX_A = 0$$

The equation is integrated and the numerical values substituted for a conversion of 0.8:

$$\left[(1000)(4000) + (10)(10{,}000)\right]\left(T_f - 27\right) = (50{,}000)(2000)(0.8)$$

Solve for the final temperature:

$$T_f = 46.51°\text{C}$$