Ch E 345 - Chemical Reactor Analysis 1
Seminar #8

March 24, 2017

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1. A batch reactor is used to produce ethanoic acid by the hydrolysis of methyl acetate. The reaction is:

$$CH_3COOCH_3 + H_2O \rightarrow CH_3CO_2H + CH_3OH$$

The reaction is pseudo-first order overall because of the excess of water:

$$-r_{CH_3COOCH_3} = k\left[CH_3COOCH_3\right]$$

At 25°C the apparent rate constant has a value $k = 3.51\times10^{-3}\ \text{min}^{-1}$, and at 35°C $k = 8.84\times10^{-3}\ \text{min}^{-1}$. The heat of formation data, $\Delta H^o_{f,298}$, are given below. Assume that the heat of reaction does not change with temperature.

methanol	-238.7 kJ/mol		ethanoic acid	-484.4 kJ/mol
water	-286.0 kJ/mol		methyl acetate	-447.8 kJ/mol

The reactor volume is 1000 litres. At time zero the reactor is filled with reactants at 25°C. A heating coil is then activated, with heat transfer fluid at 100°C. The heat transfer area is 1.5 m^2 and the overall heat transfer coefficient is 1000 W/(m^2K). Calculate the time required to achieve 95 % conversion of the methyl acetate and the temperature in the reactor at that time.

Assume that the density is a constant 1000 kg/m^3.

The initial concentration of methyl acetate is 5 mol/L.

Assume that the specific heat of the mixture is a constant equal to 4180 J/kg•K.

2. Consider an adiabatic constant pressure batch reactor in which a second order gas phase reaction occurs:

$$A + B \rightarrow C \qquad (-r_A) = k\, C_A\, C_B$$

The rate constant is independent of temperature and equals $0.01\ m^3/mol \cdot s$. The initial reactor temperature is 450 K and the pressure is 100 kPa. The initial volume of the reactor is 1.0 m^3. The reactor initially contains 30% by volume A, 30% B and 40% inerts. The heat capacity of the mixture is a constant $C_V = 1000\ J/kg\ K$. The average molecular mass of the initial material is 30 g/mol. The internal energy change on reaction is a constant $\Delta U_R = -60\ kJ/mol$. Calculate

a) The time required to reach 80% conversion.

b) The reactor volume at 80% conversion.

c) The reactor temperature at 80% conversion.

Solution to problem 1

The reaction is:

$$CH_3COOCH_3 + H_2O \rightarrow CH_3CO_2H + CH_3OH$$

$$A + B \rightarrow C + D$$

The reaction is pseudo-first order overall because of the excess of water:

$$-r_{CH_3COOCH_3} = k\left[CH_3COOCH_3\right]$$

The problem concerns a first order reaction in a batch reactor. The first step is to determine the rate constant as a function of temperature. The Arrhenius equation gives:

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{-E}{R_g}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Substitute the numbers to get:

$$\ln\left(\frac{3.51\times10^{-3}}{8.84\times10^{-3}}\right) = \frac{-E}{8.314}\left(\frac{1}{298} - \frac{1}{308}\right)$$

Solving gives $E = 70,554\frac{\text{J}}{\text{mol}}$ and $A_0 = 7.954\times10^{9}\ \text{min}^{-1}$. Next we determine the enthalpy change of reaction. The enthalpy of reaction equals the enthalpy of formation of the products minus the reactants:

$$\Delta H_R^0 = (-484.4) + (-238.7) - (-286) - (-447.8) = 10.7\frac{\text{kJ}}{\text{mol}} \equiv 10700\frac{\text{J}}{\text{mol}}$$

The reaction is endothermic. The mole balance for the reactor, which is constant volume, is:

$$-\frac{1}{V}\frac{d\,N_A}{d\,t} = \left(-r_A\right) \qquad \Rightarrow \qquad \frac{d\,X_A}{d\,t} = k\left(1 - X_A\right)$$

The general energy balance equation can be written as:

$$\frac{dT}{dt} = \frac{q}{\left(\sum_{j=1}^{n} N_j C_{Vj}\right)} - \frac{(-r_A)V\left(\Delta U_{R,A}\right)}{\left(\sum_{j=1}^{n} N_j C_{Vj}\right)}$$

The heat transfer occurs with a heating coil containing a fluid at a constant temperature. Also, we assume that the total heat capacity of the mixture is constant and also that the enthalpy of reaction is constant. Because the reaction mixture is a liquid, we can use the enthalpy change of reaction rather than the internal energy, and the constant pressure heat capacity. Making these substitutions gives.

$$\frac{dT}{dt} = \frac{U\,A\left(T_\infty - T\right)}{m_t\,\overline{C}_P} - \frac{\left(\Delta H_{R,\mathrm{A}}\right)k\,C_{\mathrm{A0}}\left(1 - X_\mathrm{A}\right)V}{m_t\,\overline{C}_P}$$

The mass of the tank is the product of the volume and density. The volume is 1 m^3, so the mass is 1000 kg. Substitute the numbers into the mole and energy balance equations:

$$\frac{d\,X_\mathrm{A}}{d\,t} = 7.954\times10^{9}\exp\left(\frac{-70,554}{8.314T}\right)\left(1 - X_\mathrm{A}\right) = 7.954\times10^{9}\exp\left(\frac{-8486.2}{T}\right)\left(1 - X_\mathrm{A}\right)$$

$$\frac{dT}{dt} = \frac{(1000)1.5\left(373.15 - T\right)}{(1000)(4180)} - \frac{\left(10700\right)7.954\times10^{9}\exp\left(\frac{-8486.2}{T}\right)\left(5\times10^{-3}\right)\left(1 - X_\mathrm{A}\right)1}{(1000)(4180)}$$

Simplify the equations:

$$\frac{d\,X_\mathrm{A}}{d\,t} = 7.954\times10^{9}\exp\left(\frac{-8486.2}{T}\right)\left(1 - X_\mathrm{A}\right)$$

$$\frac{dT}{dt} = 4.306\times10^{-4}\left(373.15 - T\right) - \left(1.02\times10^{5}\right)\exp\left(\frac{-8486.2}{T}\right)\left(1 - X_\mathrm{A}\right)$$

The initial conversion is zero and the initial temperature is 298.15 K. Solve the equations using POLYMATH. The required fractional conversion of methyl acetate 0.95. This level of conversion occurs at 440.045 s and the corresponding temperature is 311 K.

Solution to problem 2

The mole balance equation is:

$$-\frac{1}{V}\frac{dN_A}{dt} = k\left(\frac{N_A}{V}\right)^2$$

In terms of fractional conversion:

$$\frac{dX}{dt} = \frac{k N_{A0}}{V}(1-X)^2$$

The reactor volume depends on the temperature and the number of moles present. The stoichiometric table can be written:

	initial	**final**
A	N_{A0}	$N_{A0}(1-X)$
B	N_{A0}	$N_{A0}(1-X)$
C	0	$N_{A0}X$
inert	$\frac{4}{3}N_{A0}$	$\frac{4}{3}N_{A0}$
total	$\frac{10}{3}N_{A0}$	$\frac{10}{3}N_{A0} - N_{A0}X$

The reactor volume is obtained using the ideal gas law:

$$V = V_0\frac{N_T}{N_{T0}}\frac{T}{T_0} = V_0\left(\frac{\frac{10}{3}N_{A0} - N_{A0}X}{\frac{10}{3}N_{A0}}\right)\frac{T}{T_0}V = \frac{V_0}{T_0}T(1-0.3X)$$

Substitute the volume into the mole balance equation:

$$\frac{dX}{dt} = \frac{T_0\ k\ N_{A0}}{V_0\ T(1-0.3X)}(1-X)^2$$

The initial number of moles is given by:

$$N_{A0} = 0.3\left(\frac{PV_0}{R_g T_0}\right)_0 = \frac{(0.3)(100,000)(1)}{(8.314)(450)} = 8.01\ \text{mol}$$

Substitute the numbers into the mole balance equation:

$$\frac{dX}{dt} = \frac{36.05\left(1-X\right)^2}{T\left(1-0.3X\right)}$$

The energy balance for the adiabatic reactor is:

$$\frac{dT}{dt} = \frac{(-r_A)V\left(\Delta H_{R,A}\right)}{m_t \bar{C}_P}$$

The constant pressure heat capacity can be evaluated from the constant volume value given by using the ideal gas assumption:

$$\bar{C}_P = \bar{C}_V + R_g M = 1000\,\frac{\text{J}}{\text{kg•K}} + 8.314\frac{\text{J}}{\text{mol•K}} \times \frac{1}{0.03}\frac{\text{mol}}{\text{kg}} = 1277.13$$

The enthalpy of reaction is related to the internal change of reaction:

$$\left(\Delta H_{R,A}\right) = \left(\Delta U_{R,A}\right) + \Delta N R_g T = (-60000 - 8.314T)$$

Substitute the volume into the energy balance, and the rate etc:

$$\frac{dT}{dt} = -\frac{k\left(N_{A0}\right)^2\left(1-X\right)^2\left(\Delta H_{R,A}\right)}{V m_t \bar{C}_P} = -\frac{T_0 k\left(N_{A0}\right)^2\left(1-X\right)^2\left(\Delta H_{R,A}\right)}{V_0 T\left(1-0.3X\right) m_t \bar{C}_P}$$

The total mass in the system is:

$$m_t = \frac{PV M_m}{R_g T} = \frac{(100,000)(1)\left(30\times10^{-3}\right)}{(8.314)(450)} = 0.801\text{ kg}$$

Substitute the numbers into the energy balance:

$$\frac{dT}{dt} = -\frac{0.282\left(1-X\right)^2\left(-60000 - 8.314T\right)}{T\left(1-0.3X\right)}$$

Solve the mole and energy balance simultaneously. When the conversion is 80%, the time is 68.2 seconds and the temperature is 860 K. Substitute into the equation for the volume and calculate the volume is 1.45 m^3.