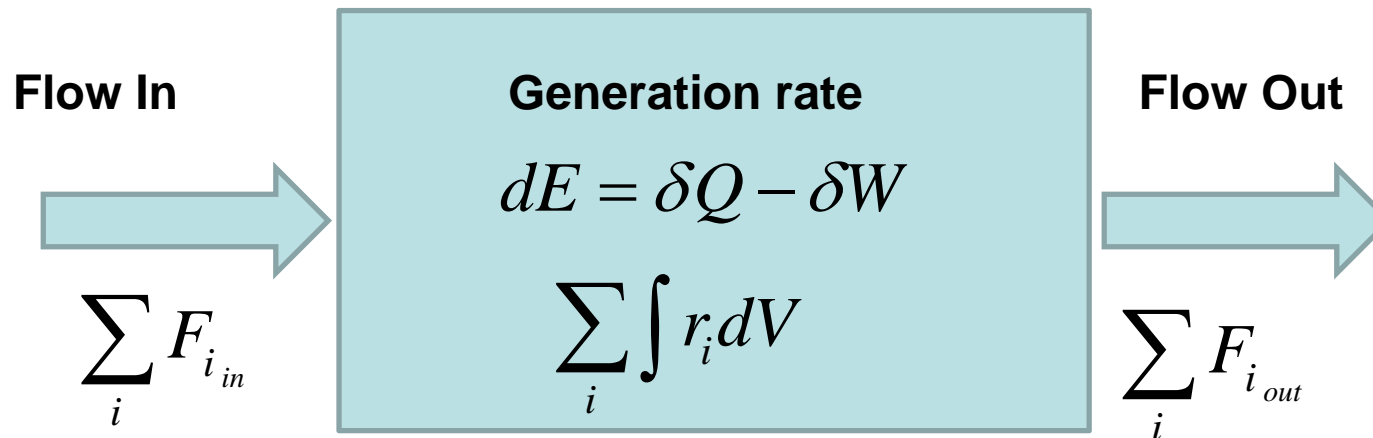# Steady-State Nonisothermal Reactors

Lecture 10

The mass and energy balance

- Most of the reactions are not carried out isothermally.
- Heat generation/ or adsorption can contribute to the temperature of the reaction mixture and e.g. affect the reaction rate

Flow In

Generation rate

$$dE = \delta Q - \delta W$$

$$\sum_i \int r_i dV$$

Flow Out

$$\sum_i F_{i_{in}}$$

$$\sum_i F_{i_{out}}$$

$$\frac{dE_{sys}}{dt} = \dot{Q} - \dot{W} + F_{in} \cdot E_{in} - F_{out} \cdot E_{out}$$

The Energy Balance

$$\frac{dE_{sys}}{dt} = \dot{Q} - \dot{W} + F_{in} \cdot E_{in} - F_{out} \cdot E_{out}$$

- The **work term W** can be separated into **flow work** (work necessary to get the mass in and out of the system) and **shaft work** (stirrer, turbine etc.)

molar volume

$$\dot{W} = -\sum_{i=1} F_i PV_{mi} \bigg|_{in} + \sum_{i=1} F_i PV_{mi} \bigg|_{out} + W_s$$

- now we insert this into energy equation and re-group

$$E_i = U_i + u_i^2/2 + gz_i + other$$

$$\frac{dE_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1} F_i \cdot \left(E_i + PV_{mi} \right) \bigg|_{in} - \sum_{i=1} F_i \cdot \left(E_i + PV_{mi} \right) \bigg|_{out}$$
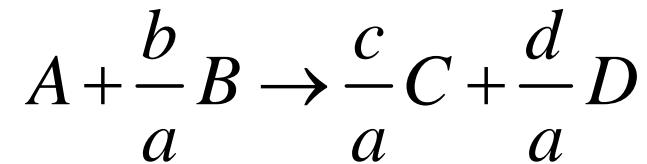
The Energy Balance

$$\frac{dE_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1} F_i \cdot \left(E_i + PV_{mi} \right)\Big|_{in} - \sum_{i=1} F_i \cdot \left(E_i + PV_{mi} \right)\Big|_{out}$$

- neglecting potential and kinetic energy: $E_i \cong U_i$

$$\frac{dE_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1} F_i \cdot H_i\Big|_{in} - \sum_{i=1} F_i \cdot H_i\Big|_{out}$$

- now we insert this into energy equation and re-group

Steady-State operation: the energy balance and Conversion

$$A + \frac{b}{a} B \rightarrow \frac{c}{a} C + \frac{d}{a} D$$

- Flow In: $F_{A0}, F_{B0}, F_{C0}, F_{D0},$

- Flow Out

$$F_A = F_{A0}(1 - X); \ F_B = F_{A0}\left(\Theta_B - \frac{b}{a}X\right);$$

$$F_C = F_{A0}\left(\Theta_C + \frac{c}{a}X\right); \ F_D = F_{A0}\left(\Theta_D + \frac{d}{a}X\right);$$

- The energy balance

$$\dot{Q} - \dot{W}_s + F_{A0}\sum_{i=1}\Theta_i \cdot (H_{i0} - H_i) - \Delta H_{Rx}(T)F_{A0}X = 0$$

$$\Delta H_{Rx} = \frac{d}{a}H_D + \frac{c}{a}H_C - \frac{b}{a}H_B - H_A$$

The Enthalpies

- The enthalpy at a given temperature will equal to the enthalpy of formation + eventual the enthalpy of eventual phase transformation + enthalpy of heating

- If no phase transformation occurs in the reactor

$$\Delta H_{Qi} = \int_{T_1}^{T_2} C_{Pi} dT$$

- Heat capacity dependence on the temperature is usually expressed

$$C_{Pi} = \alpha_i + \beta_i T + \gamma_i T^2$$

- In the most of cases we can assume heat capacity constant

$$\dot{Q} - \dot{W}_s + F_{A0} \sum_{i=1} \Theta_i \cdot C_{Pi} \left(T - T_{i0} \right) - \Delta H_{Rx}(T) F_{A0} X = 0$$

The Enthalpies

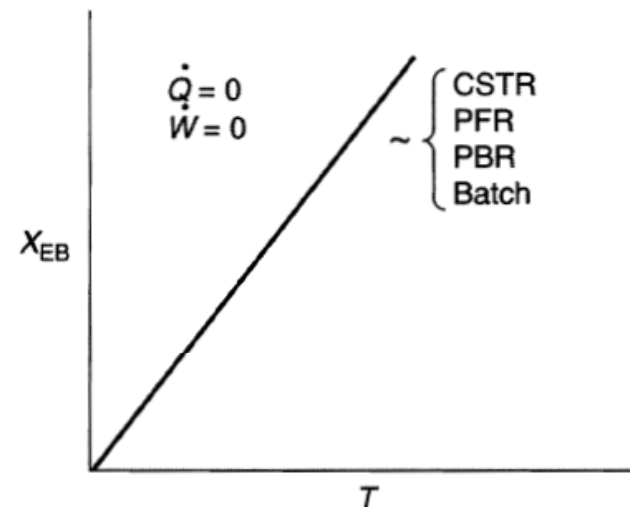$$\Delta H_{Rx}(T) = \Delta H_{Rx}^{\theta}(T_R) + \Delta C_P(T - T_R)$$

- where $\qquad \Delta C_P = \dfrac{d}{a}C_{P_D} + \dfrac{d}{a}C_{P_C} - \dfrac{b}{a}C_{P_B} - C_{PA}$

- in most systems the shaft work can be neglected.
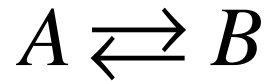- for an **adiabatic** system we can derive an explicit equation:

$$F_{A0}\sum_{i=1}\Theta_i \cdot C_{Pi}(T - T_{i0}) - \left[\Delta H_{Rx}^{\theta}(T) + \Delta C_P(T - T_R)\right]F_{A0}X = 0$$

$$X = \frac{\sum\limits_{i=1}\Theta_i \cdot C_{Pi}(T - T_{i0})}{-\left[\Delta H_{Rx}^{\theta}(T) + \Delta C_P(T - T_R)\right]}$$

- Now it can be solved together with the mole balance equation

Solving for adiabatic tubular reactor

$$A \rightleftarrows B$$

- Mole balance $\dfrac{dX}{dV} = \dfrac{-r_A}{F_{A0}}$

- Rate law $-r_A = k\left(C_A - \dfrac{C_B}{K_C}\right); \; k = k_1(T_1)\exp\left[\dfrac{E}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T}\right)\right]$

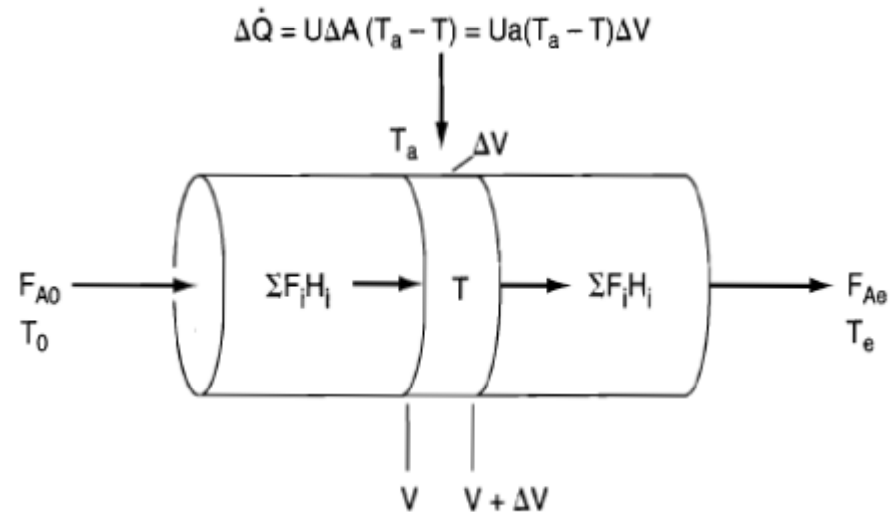- Stoichiometry $C_A = C_{A0}(1 - X)\dfrac{T}{T_0}; C_B = C_{B0}X\dfrac{T}{T_0}$

- Energy balance

$$T = \frac{X\left[-\Delta H_{Rx}^{\theta}(T_R)\right] + \sum\limits_{i=1}\Theta_i C_{Pi}T_0 + X\Delta C_P T_R}{\sum\limits_{i=1}\Theta_i \cdot C_{Pi} + X\Delta C_P} \approx T_0 + \frac{X\left[-\Delta H_{Rx}^{\theta}(T_R)\right]}{C_{PA}}$$

- when pure A enters and $\Delta C_P = 0$.

Steady state tubular reactor with heat exchange
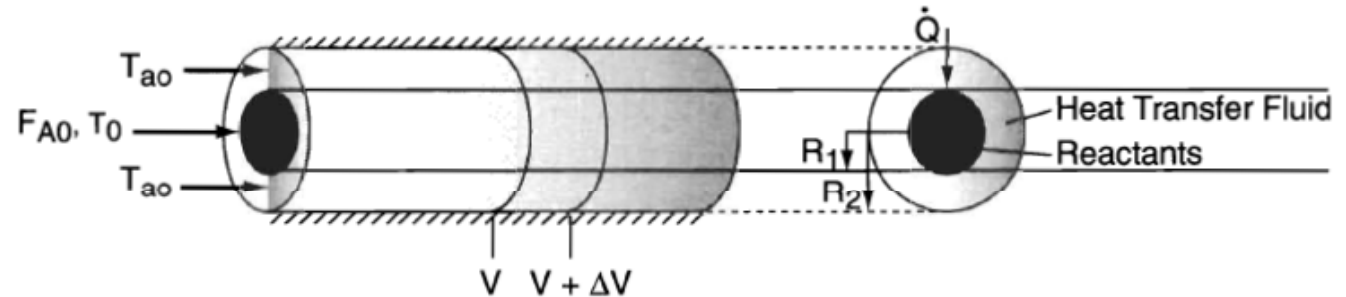
- If the heat is added or removed through the walls

$$\Delta \dot{Q} = U\Delta A (T_a - T) = Ua(T_a - T)\Delta V$$

- Energy balance

$$\Delta \dot{Q} + \sum_{i=1}^{} F_i \cdot H_i \bigg|_V - \sum_{i=1}^{} F_i \cdot H_i \bigg|_{V+\Delta V} = 0$$

$$\Delta \dot{Q} = U \Delta A \left(T_a - T \right) = Ua\Delta V \left(T_a - T \right)$$

$$a = \frac{A}{V} = \frac{4}{D}$$

Balance on the coolant heat transfer

- Co-current flow

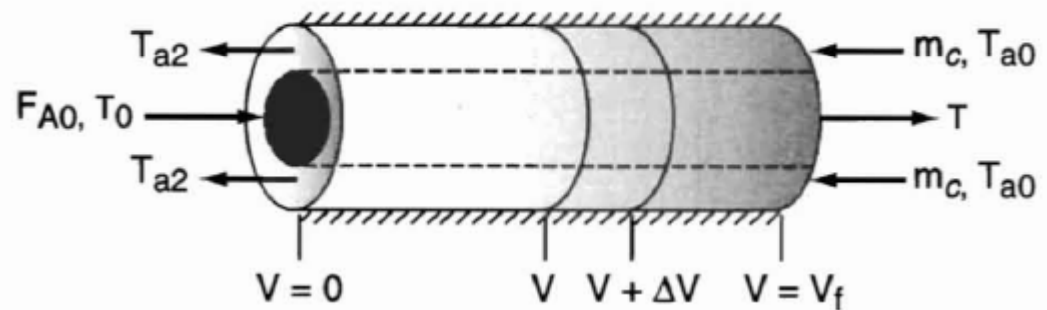$$\dot{m}_c H_c \big|_V - \dot{m}_c H_c \big|_{V+\Delta V} + U a \Delta V (T - T_a) = 0$$

$$\dot{m}_c \frac{dH_c}{dV} + U a (T - T_a) = 0$$

$$\frac{dT_a}{dV} = \frac{U a (T - T_a)}{\dot{m}_c C_{Pc}}$$

- Counter current flow

$$\frac{dT_a}{dV} = \frac{U a (T_a - T)}{\dot{m}_c C_{Pc}}$$

Problems (for the class)

- P8.7: (a)-(d)

Problems (for the class)

- Derive the Briggs-Haldane equation

- **P7-25** (http://www.engin.umich.edu/~cre/07chap/frames.htm). Methanol has been ingested, and after pumping the stomach methanol has an initial concentration of C_{Mi} = 0.25 g/dm^3 in the body:

  1. First prove the equations on the left hand side.

  2. How many grams of ethanol are necessary to retard the formation of formaldehyde so that it will not reach the level to cause blindness if the ethanol is to be injected immediately?

  3. What feed rate of ethanol should be used to prevent formaldehyde from reaching a concentration of 0.16 g/dm^3?

$$r_{p1} = \frac{V_{max1}(C_E)}{C_E + K_{M1}\left(1 + \frac{C_M}{K_{M2}}\right)}$$

$$r_{p2} = \frac{V_{Max2}(C_M)}{C_M + K_{M2}\left(1 + \frac{C_E}{K_{M1}}\right)}$$

$$\frac{dC_{p2}}{dt} = r_{p2} - k_7 C_{p2}$$

- Use the following values for V_{max1} and K_{M1} for ethanol neglecting the reverse reaction of acetaldehyde to ethanol. As a first approximation, use the same values for methanol. Next, vary V_{max2} the initial methanol concentration (0.1 g/dm^3 < C_M < 2 g/dm^3), (0.1 V_{max1} < V_{max2} < 2V_{max1}), k_7, and the intravenous injection rate, r_{IV}.

- There are 10 mg of methanol per 12 ounce can of diet pop. How many cans and how fast must you need to drink then to cause blindness. Just estimate, no need to modify and run the Polymath program.

- K_{M1} (ethanol) = 1.53 mg/dm^3; K_{M2} (methanol) = 1.07 mg/dm^3; V_{max1} (ethanol) = 3.1 mg/(dm^3 • min); V_{max2} (methanol) 2.16 mg/(dm^3 • min)

Problem (at home)

- P7-9:

(*Postacidification in yogurt*) Yogurt is produced by adding two strains of bacteria (*Lactobacillus bulgaricus* and *Streptococcus thermophilus*) to pasteurized milk. At temperatures of 110°F, the bacteria grow and produce lactic acid. The acid contributes flavor and causes the proteins to coagulate, giving the characteristic properties of yogurt. When sufficient acid has been produced (about 0.90%), the yogurt is cooled and stored until eaten by consumers. A lactic acid level of 1.10% is the limit of acceptability. One limit on the shelf life of yogurt is "postacidification," or continued production of acid by the yogurt cultures during storage. The table that follows shows acid production (% lactic acid) in yogurt versus time at four different temperatures.

Time (days)	35°F	40°F	45°F	50°F
1	1.02	1.02	1.02	1.02
14	1.03	1.05	1.14	1.19
28	1.05	1.06	1.15	1.24
35	1.09	1.10	1.22	1.26
42	1.09	1.12	1.22	1.31
49	1.10	1.12	1.22	1.32
56	1.09	1.13	1.24	1.32
63	1.10	1.14	1.25	1.32
70	1.10	1.16	1.26	1.34

Acid production by yogurt cultures is a complex biochemical process. For the purpose of this problem, assume that acid production follows first-order kinetics with respect to the consumption of lactose in the yogurt to produce lactic acid. At the start of acid production the lactose concentration is about 1.5%, the bacteria concentration is 10^{11} cells/dm^3, and the acid concentration at which all metabolic activity ceases is 1.4% lactic acid.

(a) Determine the activation energy for the reaction.

(b) How long would it take to reach 1.10% acid at 38°F?

(c) If you left yogurt out at room temperature, 77°F, how long would it take to reach 1.10% lactic acid?

(d) Assuming that the lactic acid is produced in the stationary state, do the data fit any of the modules developed in this chapter?