Steady-State Nonisothermal Reactors

Lecture 5

General algorithm of Chemical Reaction Engineering

- 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

- Mole balance
- Rate laws
- Stoichiometry
- Energy balance

- Combine and Solve

Why we need energy balance?

Let's consider an exothermic reaction in a flow reactor: $A \rightarrow B$

1. Mole balance: $$\frac{dX}{dV} = -\frac{r_A}{F_{A0}}$$

2. Rate law: $$-r_A = kC_A$$

$$k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

3. Stoichiometry: $$C_A = C_{A0}(1 - X)$$

4. Combining: $$\frac{dX}{dV} = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]\frac{1 - X}{v_0}$$

- Now we need to provide relationship between X and T to solve the equation – the **Energy Balance**:

Lecture plan:

- Develop general energy balance equation
- Derive energy balance equation for adiabatic operation
- Derive energy balance for operation with thermal exchange
  - constant temperature
  - co-current flow of heat transfer fluid
  - counter-current flow of heat transfer fluid

The Energy balance

- According to the 1st Law of Thermodynamics, for closed system

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

- For an open system we need to take into account mass and energy flow through the system...

The mass and energy balance

- For an open system:

Flow In

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

Generation rate

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

$$\sum_i \int r_i dV$$

Flow Out

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

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

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

$$\dot{W} = -\sum_{i=1} F_i P V_{mi} \Big|_{in} + \sum_{i=1} F_i P V_{mi} \Big|_{out} + \dot{W}_s$$

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

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

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

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: $E_i \cong U_i$
- now we insert this into energy equation and re-group

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

- now we need to find how to deal with enthalpies…

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

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

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

- The energy balance

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

Heat of the reaction at temperature T $\Delta H_{Rx}=\frac{d}{a}H_D+\frac{c}{a}H_C-\frac{b}{a}H_B-H_A$

The Enthalpies

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

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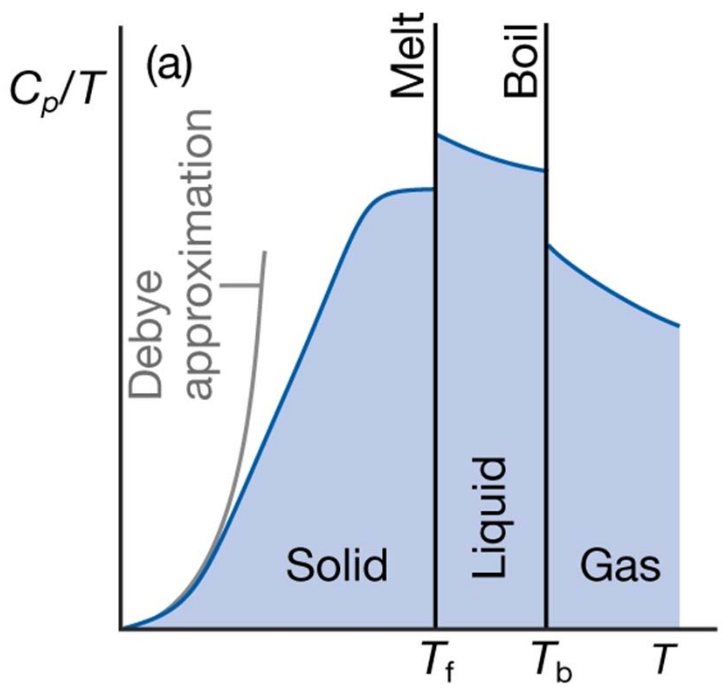
$$H(T) = H(T_{ref}) + \int_0^{T_f} C_p(s)dT + \Delta_{fus}H +$$

$$+\int_{T_f}^{T_b} C_p(l)dT + \Delta_{vap}H + \int_{T_b}^{T} C_p(g)dT$$



The Enthalpies

- 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

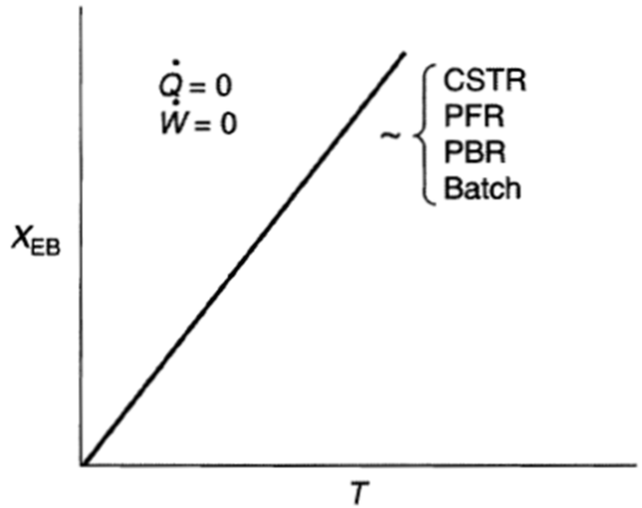
$$\Delta H_{Rx}(T) = \Delta H_{Rx}^{\theta}(T_R) + \Delta C_P(T - T_R)$$

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

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

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

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



- 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 $C_A = C_{A0}\left(1 - X\right)\dfrac{T}{T_0}; C_B = C_{B0}X\dfrac{T}{T_0}$
- Energy balance

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

- when pure A enters and ΔC_P=0.

Example 8-3: Butane isomerization

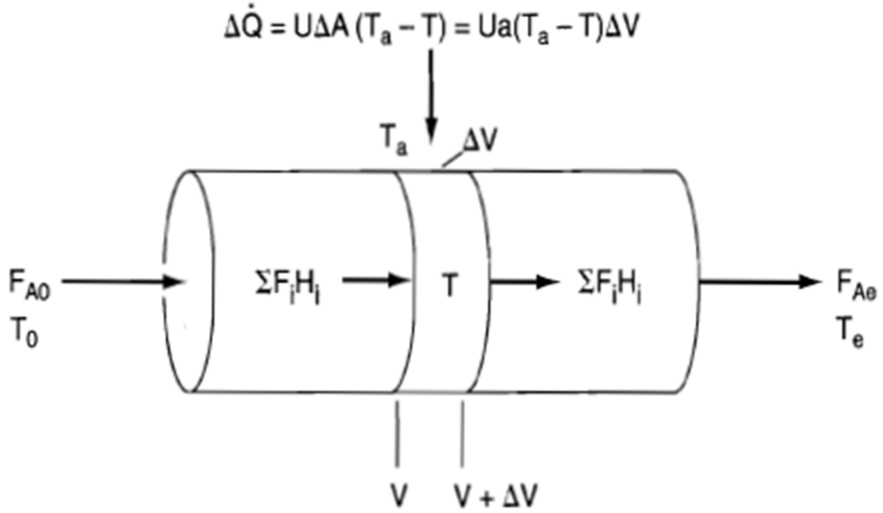
- Reaction carried out adiabatically in the liquid phase using trace amounts of liquid catalyst.
  - reaction rate 31.1h^{-1} at 360K
  - feed enters at 330K
  - $\Delta H^0_{Rx} = -6900 J/mol$; Activ.energy $E = 65.7 kJ/mol$

    $K_C = 3.03 \, at \, 60^0 C$; $C_{A0} = 9.3 kmol/m^3$

    $C_{Pi-b} = C_{Pn-b} = 141 kJ/molK$; $C_{Pi-p} = 161 kJ/molK$
  - Calculate the PFR and CSTR volumes required for 163 kmol/h production at 70% conversion of a mixture 90 mol% n-butane and 10% inert

Steady state tubular reactor with heat exchange

- If the heat is added or removed through the walls



- Energy balance

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

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

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

Steady state tubular reactor with heat exchange

- Combining and taking the limit:

$$Ua\left(T_a - T\right) + \frac{d\sum_{i=1} F_i \cdot H_i}{dV} = 0$$

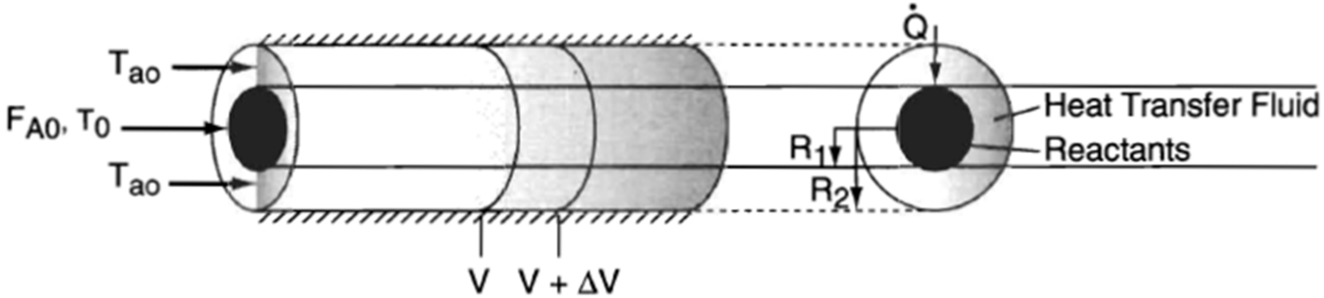
$$Ua\left(T_a - T\right) + \sum_{i=1} \frac{dF_i}{dV} \cdot H_i + \sum_{i=1} C_{Pi} \frac{dT}{dV} \cdot F_i = 0$$

- From mole balance: $\frac{dF_i}{dV} = r_i = -v_i r_A$

$$\frac{dT}{dV} = \frac{r_A \Delta H_{Rx} - Ua\left(T_a - T\right)}{\sum_{i=1} C_{Pi} \cdot F_i}$$

Balance on the coolant heat transfer

- Co-current flow

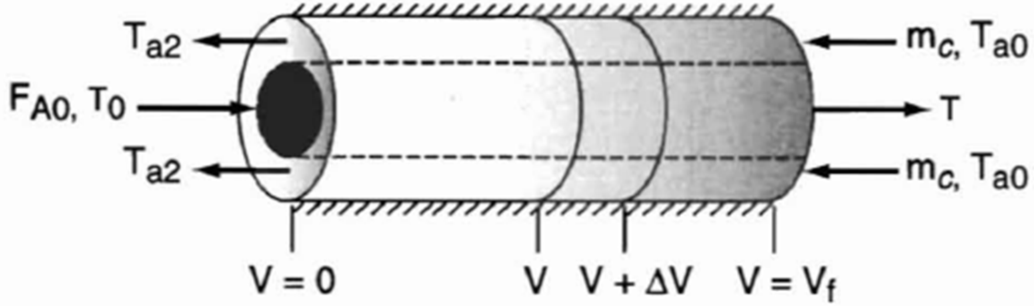


$$\dot{m}_c H_c\big|_V - \dot{m}_c H_c\big|_{V+\Delta V} + Ua\Delta V\left(T - T_a\right) = 0$$

$$\dot{m}_c \frac{dH_c}{dV} + Ua\left(T - T_a\right) = 0$$

$$\frac{dT_a}{dV} = \frac{Ua\left(T - T_a\right)}{\dot{m}_c C_{Pc}}$$

- Counter current flow



$$\frac{dT_a}{dV} = \frac{Ua\left(T_a - T\right)}{\dot{m}_c C_{Pc}}$$

Problems (for the class)

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