STEADY-STATE NONISOTHERMAL REACTOR DESIGN
(5)

Marcel Lacroix
Université de Sherbrooke
STEADY-STATE NONISOTHERMAL REACTOR DESIGN: OBJECTIVE

• WE NOW EXAMINE THE EFFECTS OF HEAT IN CHEMICAL REACTORS.
• THE BASIC DESIGN EQUATIONS, RATE LAWS AND STOICHIOMETRIC RELATIONSHIPS DERIVED AND USED FOR ISOTHERMAL REACTORS ARE STILL VALID FOR NONISOTHERMAL REACTORS.
• THE MAJOR DIFFERENCE IN NONISOTHERMAL REACTORS IS THAT THE TEMPERATURE VARIES ALONG THE LENGTH OF THE PFR OR HEAT IS TRANSFERRED TO OR FROM THE CSTR
EXAMPLE No. 0

- LET US CALCULATE THE VOLUME OF A PLUG FLOW REACTOR NECESSARY TO ACHIEVE 70% CONVERSION. THE CHEMICAL REACTION IS EXOTHERMNIC AND THE REACTOR IS OPERATED ADIABATICALLY. AS A RESULT, THE TEMPERATURE WILL INCREASE WITH CONVERSION DOWN THE LENGTH OF THE REACTOR.
NONISOTHERMAL REACTOR: RATIONALE

1. DESIGN EQUATION: \[ \frac{dX}{dV} = \frac{-r_A}{F_{A0}} \]

2. RATE LAW: \[ -r_A = kC_A \]

3. STOICHIOMETRY: \[ \nu = \nu_0 ; F_A = C_A \nu_0 ; F_{A0} = C_{A0} \nu_0 ; C_A = C_{A0} (1 - X) \]

4. COMBINING: \[ \frac{dX}{dV} = \frac{k(1 - X)}{\nu_0} \quad \text{WITH} \quad k = k_1 \exp \left[ \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) \right] \]

\[ \Rightarrow \quad \frac{dX}{dV} = k_1 \exp \left[ \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) \right] \frac{1 - X}{\nu_0} \]

WE NEED ANOTHER RELATIONSHIP RELATING \( X \) TO \( T \) OR \( T \) AND \( V \) TO SOLVE THIS EQUATION. THE ENERGY BALANCE WILL PROVIDE US WITH THIS RELATIONSHIP.
THERMAL ENERGY CONSERVATION

ACCUMULATION = INLET – OUTLET + GENERATION

Figure 4.3 Energy balance for an element of volume of the reactor.
THERMAL ENERGY CONSERVATION: BASIC EQUATION

RATE OF ACCUMULATION OF INTERNAL ENERGY WITHIN SYSTEM (WATTS)

\[
\frac{dE_{sys}}{dt} = \sum_{i=1}^{n} F_i H_i^{0} - \sum_{i=1}^{n} F_i H_i + \dot{Q} - \dot{W}_S
\]  

(5.1)

- RATE OF ENERGY CARRIED IN AND OUT OF THE SYSTEM BY THE MOLES OF EACH SPECIES (\(F_i\): molar flow rate, moles of i per second; \(H_i\): enthalpy, Joules per mole)
- RATE OF ENERGY CARRIED IN AND OUT OF THE SYSTEM BY THE MOLES OF EACH SPECIES (\(F_i\): molar flow rate, moles of i per second; \(H_i\): enthalpy, Joules per mole)
- RATE OF FLOW OF HEAT TO THE SYSTEM FROM SURROUNDINGS (WATTS)
- RATE OF FLOW OF HEAT TO THE SYSTEM FROM SURROUNDINGS (WATTS)
- RATE OF SHAFT WORK DONE BY THE SYSTEM ON SURROUNDINGS (WATTS)
- RATE OF SHAFT WORK DONE BY THE SYSTEM ON SURROUNDINGS (WATTS)
THERMAL ENERGY CONSERVATION: DISSECTING MOLAR FLOW RATES TO OBTAIN HEAT OF REACTION

• GENERALIZED EQUATION, \[ A + \frac{b}{a} B \rightarrow \frac{c}{a} C + \frac{d}{a} D \]

• THE INLET AND OUTLET TERMS BECOME:

\[
\text{IN} \rightarrow \sum H_{i_0} F_{i_0} = H_{A_0} F_{A_0} + H_{B_0} F_{B_0} + H_{C_0} F_{C_0} + H_{D_0} F_{D_0} + H_{I_0} F_{I_0}
\]

\[
\text{OUT} \rightarrow \sum H_{i} F_{i} = H_{A} F_{A} + H_{B} F_{B} + H_{C} F_{C} + H_{D} F_{D} + H_{I} F_{I}
\]

SUBSTITUTING

\[
F_{A} = F_{A_0} (1 - X); \quad F_{B} = F_{A_0} (\theta_{B} - \frac{b}{a} X); \quad \text{NOTE: } \theta_{i} = \frac{F_{i_0}}{F_{A_0}}
\]

\[
F_{C} = F_{A_0} (\theta_{C} + \frac{c}{a} X); \quad F_{D} = F_{A_0} (\theta_{D} + \frac{d}{a} X); \quad F_{I} = F_{A_0} \theta_{I};
\]

M. Lacroix

Nonisothermal Reactor Design
THERMAL ENERGY CONSERVATION: DISSECTING MOLAR FLOW RATES TO OBTAIN HEAT OF REACTION

\[
\sum_{i=1}^{n} F_{i0} H_{i0} - \sum_{i=1}^{n} F_{i} H_{i} = F_{A0} \left[ (H_{A0} - H_{A}) + (H_{B0} - H_{B})\theta_{B} + (H_{C0} - H_{C})\theta_{C} + (H_{D0} - H_{D})\theta_{D} + (H_{I0} - H_{I})\theta_{I} 
\right.
\]

\[
\left. - \left[ \frac{d}{a} H_{D} + \frac{c}{a} H_{C} - \frac{b}{a} H_{B} - H_{A} \right] F_{A0} X \right]
\]

\[
= F_{A0} \sum_{i=1}^{n} \theta_{i} (H_{i0} - H_{i}) - \Delta H_{Rx}(T) F_{A0} X \quad (5.2)
\]

\[\Delta H_{Rx}(T): \text{HEAT OF REACTION AT TEMPERATURE } T \text{ (Joules per mole of A reacted);} \text{ THE ENTHALPIES } H_{A}, H_{B}, \text{etc. ARE EVALUATED AT THE TEMPERATURE AT THE OUTLET OF THE SYSTEM } T.\]
THERMAL ENERGY CONSERVATION: DISSECTING THE ENTHALPIES

• FOR A SINGLE-PHASE CHEMICAL REACTION, THE ENTHALPY OF SPECIES $i$ AT TEMPERATURE $T$ IS RELATED TO THE ENTHALPY OF FORMATION AT THE REFERENCE TEMPERATURE $T_R$ BY

$$H_i = H_i^0(T_R) + \int_{T_R}^{T} C_{pi} dT$$

THEREFORE,

$$H_i - H_{i0} = \left[ H_i^0(T_R) + \int_{T_R}^{T} C_{pi} dT \right] - \left[ H_i^0(T_R) + \int_{T_R}^{T_{i0}} C_{pi} dT \right]$$

$$\Rightarrow H_i - H_{i0} = \int_{T_{i0}}^{T} C_{pi} dT \quad (5.3)$$
THERMAL ENERGY CONSERVATION: DISSECTING THE ENTHALPIES

• THE HEAT OF REACTION AT ANY TEMPERATURE $T$ IS ALSO EXPRESSED IN TERMS OF THE HEAT OF REACTION AT A REFERENCE TEMPERATURE (298K) AND AN INTEGRAL INVOLVING $\Delta C_p$:

$$\Delta H_{Rx}(T) = \Delta H_{Rx}^0 (T_R) + \int_{T_R}^{T} \Delta C_p dT$$  \hspace{1cm} (5.4)

WHERE

$$\Delta C_p = \frac{d}{a} C_{pD} + \frac{c}{a} C_{pC} - \frac{b}{a} C_{pB} - C_{pA}$$
THERMAL ENERGY CONSERVATION: FINAL FORM OF THE ENERGY BALANCE EQUATION

• SUBSTITUTING (5.3) AND (5.4) IN (5.2) AND REPLACING (5.2) IN (5.1), THE STEADY-STATE ENERGY BALANCE EQUATION BECOMES

\[
\dot{Q} - \dot{W}_S - F_{A0} \int_{T_{i0}}^{T} \sum_{i=1}^{n} \theta_i c_{pi} dT - F_{A0} \alpha X \left[ \Delta H_{Rx}^0 (T_R) + \int_{T_R}^{T} \Delta C_p dT \right] = 0
\]

(5.5)

ENERGY BALANCE IN TERMS OF TEMPERATURE DEPENDENT HEAT CAPACITIES

WHEN THE REACTANTS ENTER THE SYSTEM AT THE SAME TEMPERATURE, \( T_{i0} = T_0 \)
THERMAL ENERGY CONSERVATION: DISSECTING THE ENTHALPIES

• FOR CONSTANT OR MEAN HEAT CAPACITIES, EQUATION (5.3) BECOMES

\[ H_i - H_{i0} = \int_{T_{i0}}^{T} C_{pi} \, dT = \overline{C}_{pi} (T - T_{i0}) \quad (5.3)' \]

AND EQUATION (5.4) BECOMES

\[ \Delta H_{Rx} (T) = \Delta H^0_{Rx} (T_R) + \overline{\Delta C}_{p} (T - T_R) \quad (5.4)' \]

WHERE

\[ \overline{C}_{pi} = \frac{\int_{T_{i0}}^{T} C_{pi} \, dT}{T - T_{i0}} \quad \text{AND} \quad \overline{\Delta C}_{p} = \frac{\int_{T_R}^{T} \Delta C_{p} \, dT}{T - T_R} \]
THERMAL ENERGY CONSERVATION:
FINAL FORM OF THE ENERGY BALANCE EQUATION
FOR CONSTANT OR MEAN HEAT CAPACITIES

• SUBSTITUTING (5.3)' AND (5.4)' IN (5.2) AND
REPLACING (5.2) IN (5.1), THE STEADY-STATE
ENERGY BALANCE EQUATION BECOMES

\[
\dot{Q} - \dot{W}_S - F_{A0} \sum_{i=1}^{n} \theta_i \bar{C}_{pi} (T - T_{i0}) - F_{A0} X \left[ \Delta H^0_{Rx} (T_R) + \bar{C}_p (T - T_R) \right] = 0
\]

(5.6)

ENERGY BALANCE IN TERMS OF
MEAN OR CONSTANT HEAT
CAPACITIES

WHEN THE REACTANTS ENTER
THE SYSTEM AT THE SAME
TEMPERATURE, T_{i0} = T_0

M. Lacroix
Nonisothermal Reactor Design 13
EXAMPLE No.1:
HEAT OF REACTION


• CALCULATE THE HEAT OF REACTION FOR THE SYNTHESIS OF AMMONIA FROM HYDROGEN AND NITROGEN AT 1500°C IN kcal/mole AND IN kJoule/mole OF HYDROGEN REACTED.

\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]

• THE HEATS OF FORMATION OF ALL THE ELEMENTS ARE ZERO AT 25 °C. THE HEATS OF FORMATION OF COMPOUNDS AT 25 °C ARE TABULATED.

• 1 cal = 4.184 Joule
THERMAL ENERGY CONSERVATION:
HEAT ADDED TO A CSTR

\[ \dot{Q} = UA(T_a - T) \]

- \( \dot{Q} \): Rate of heat transfer (Watts)
- \( U \): Overall heat transfer coefficient (W/m²K)
- \( A \): Heat-exchange area (m²)
- \( T_a \): Reaction temperature (K)
- \( T \): Temperature (K)

**Example:**

- \( F_{A0} \)
- \( T_{a1} \)
- \( T_{a2} \)

**Diagram:**
- CSTR with inlet and outlet streams.
- Heat exchanger with multiple components.

**Equation:**

\[ \dot{Q} = UA(T_a - T) \]

- \( T_a = T_{a1} = T_{a2} \): Inlet temperature of high flow rate coolant (K)

**Diagram notes:**
- Half-pipe jacket
- Fin-type baffle
- Conventional jacket

M. Lacroix

Nonisothermal Reactor Design
THERMAL ENERGY CONSERVATION: HEAT ADDED TO A PFR AND TO A PBR

- WHEN THE HEAT FLOW VARIES ALONG THE LENGTH OF THE REACTOR, THE HEAT FLUX EQUATION MUST BE INTEGRATED ALONG THE LENGTH OF THE REACTOR TO OBTAIN THE TOTAL HEAT ADDED TO THE REACTOR:

\[
\frac{d\dot{Q}}{dV} = Ua(T_a - T)
\]

- PFR: VOLUME HEAT EXCHANGE PER UNIT VOLUME OF PFR

\[
\frac{d\dot{Q}}{dW} = \frac{Ua}{\rho_b} (T_a - T)
\]

- PBR: HEAT EXCHANGE TO BULK DENSITY OF CATALYST IN Reactor Bed

\( a: \) HEAT-EXCHANGE AREA PER UNIT VOLUME OF PFR

\( = \frac{4}{D} \) FOR TUBULAR PFR OF DIAMETER \( D \)
THERMAL ENERGY CONSERVATION:
NONISOTHERMAL CONTINUOUS-FLOW REACTORS

- CONSIDER A SYSTEM AT STEADY-STATE, NO SHAFT WORK \( \hat{W}_s = 0 \), ADIABATIC OPERATION \( \hat{Q} = 0 \). IN MANY Instances, \( \Delta H^0_{Rx, R} (T_R) \gg \Delta C_p (T - T_R) \) AND THE ENERGY BALANCE EQUATION (5.6) GIVES US THE EXPLICIT RELATIONSHIP BETWEEN \( X \) AND \( T \) NEEDED TO BE USED IN CONJUNCTION WITH THE MOLE BALANCE TO SOLVE THE TYPE OF PROBLEMS DISCUSSED EARLIER:

\[
X = \sum_{i=1}^{n} \theta_i \overline{C}_{pi} (T - T_{i0}) - \Delta H^0_{Rx} (T_R)
\]
THERMAL ENERGY CONSERVATION:
APPLICATION TO CSTRs

• ALTHOUGH THE CSTR IS WELL MIXED AND THE TEMPERATURE IS UNIFORM THROUGHOUT THE VESSEL, IT DOES NOT IMPLY THAT THE REACTION IS CARRIED OUT ISOTHERMALLY.

• THE DESIGN EQUATION FOR THE CSTR (MOLE BALANCE) IS

\[ V = \frac{F_{A0} X}{-r_A} \]

AND THE X VERSUS T REALTIONSHP IS PROVIDED BY THE ENERGY BALANCE EQUATION

\[ \frac{\dot{Q} - \dot{W}_S}{F_{A0}} - \sum_{i=1}^{n} \theta_i \bar{C}_{pi} (T - T_{i0}) = X \left[ \Delta H_{Rx}^0 (T_R) + \bar{\Delta C}_p (T - T_R) \right] \]
The first-order irreversible liquid-phase reaction

\[ A \rightarrow B \]

is carried out adiabatically.

1. **CSTR design equation:**

   \[ V = \frac{F_{Ao}X}{-r_A} \tag{T8-1.1} \]

2. **Rate law:**

   \[-r_A = kC_A \tag{T8-1.2} \]

   with

   \[ k = Ae^{-E/RT} \tag{T8-1.3} \]

3. **Stoichiometry (liquid-phase, \( v = v_0 \)):**

   \[ C_A = C_{Ao}(1 - X) \]

4. **Combining yields**

   \[ V = \frac{v_0}{Ae^{-E/RT}} \left( \frac{X}{1 - X} \right) \tag{T8-1.4} \]

**Case A.** The variables \( X, v_0, C_{Ao}, \) and \( F_{Ao} \) are specified and the reactor volume, \( V \), must be determined. The procedure is:

5A. Solve for the temperature, \( T \), for pure \( A \) entering, and \( \tilde{C}_{R_A} = \tilde{C}_{R_B}(\Delta \tilde{C}_P = 0) \).

   For the adiabatic case, solve Equation (8-52) for \( T \):

   \[ T = T_0 + \frac{X(-\Delta H_{R_A})}{\tilde{C}_{R_A}} \tag{T8-1.5} \]

   For the nonadiabatic case with \( Q = UA(T_0 - T) \), solve Equation (8-51) for \( T \):

   \[ T = \frac{F_{Ao}X(-\Delta H_{R_A}) + F_{Ao}\tilde{C}_{R_A}T_0 + UAT_0}{F_{Ao}\tilde{C}_{R_A} + UA} \tag{T8-1.6} \]

6A. Calculate \( k \) from the Arrhenius equation.

7A. Calculate the reactor volume, \( V \), from Equation (T8-1.4).

**Case B.** The variables \( v_0, C_{Ao}, V, \) and \( F_{Ao} \) are specified and the exit temperature, \( T \), and conversion, \( X \), are unknown quantities. The procedure is:

5B. Solve the energy balance (adiabatic) for \( X \) as a function of \( T \).

   \[ X_{EB} = \frac{\tilde{C}_{R_A}(T - T_0)}{\Delta H_{R_A}(T_0)} \tag{T8-1.7} \]

   For the nonadiabatic with \( Q = UA(T_0 - T) \) case, solve Equation (8-51) for \( X_{EB} \):

   \[ X_{EB} = \frac{UA(T - T_0)/F_{Ao} + \tilde{C}_{R_A}(T - T_0)}{-\Delta H_{R_A}} \tag{T8-1.8} \]

6B. Solve Equation (T8-1.4) for \( X \) as a function of \( T \).

   \[ X_{MB} = \frac{\tau Ae^{-E/RT}}{1 + \tau Ae^{-E/RT}} \text{ where } \tau = V/v_0 \tag{T8-1.9} \]

7B. Find the values of \( X \) and \( T \) that satisfy both the energy balance [Equation (T8-1.7)] and the mole balance [Equation (T8-1.9)]. This result can be achieved either numerically or graphically [plotting \( X \) vs. \( T \) using Equations (T8-1.7) and (T8-1.9) on the same graph].

### Example: Elementary irreversible liquid-phase reaction

\[ A \rightarrow B \; \text{Given } F_{Ao}, C_{Ao}, k_A, E, C_P, H_P \]

**CSTR**

- **Design equation**
  \[ V = \frac{F_{Ao}X}{-r_A} \]

- **Rate law**
  \[-r_A = kC_A \]

- **Stoichiometry**
  \[ C_A = C_{Ao}(1 - X) \]

- **Combining**
  \[ V = \frac{F_{Ao}X}{kC_{Ao}(1 - X)} \]

**Algorithm**

1. **X specified:** Calculate \( V \) and \( T \)
2. **V specified:** Calculate \( X \) and \( T \)

   - Two equations and two unknowns
   - Equations:
     - \[ X_{MB} = \frac{\tau k}{1 + \tau k} \]
     - \[ V = \frac{V C_{Ao}}{F_{Ao}} \]
     - \[ X_{MB} = \frac{\tau A e^{-E/RT}}{1 + \tau A e^{-E/RT}} \]
     - \[ X_{EB} = \frac{U A(T - T_0)}{\Delta H_{R_A}(T_0) + \Delta \tilde{C}_P(T - T_0)} \]

3. Plot \( X \) vs. \( T \)
EXAMPLE No.2:
DESIGN OF A CSTR

• PROPYLENE GLYCOL IS PRODUCED BY THE HYDROLYSIS OF PROPYLENE OXIDE:

\[(CH_2)(CH)O(CH_3) + H_2O \xrightarrow{\text{CATALYST}} (CH_2)OH(CH)OH(CH_3)\]

THE REACTION TAKES PLACE AT ROOM TEMPERATURE WHEN CATALYSED WITH SULFURIC ACID. YOU ARE IN CHARGE OF AN ADIABATIC CSTR PRODUCING PROPYLENE GLYCOL BY THIS METHOD. UNFORTunately, THE REACTOR IS BEGINNING TO LEAK AND YOU MUST REPLACE IT (SULFURIC ACID IS CORROSIVE AND MILD STEEL IS A POOR MATERIAL FOR CONSTRUCTION). THERE IS A NICE OVERFLOW CSTR OF 1136-LITER CAPACITY STANDING IDLE. IT IS GLASS-LINED AND YOU WOULD LIKE TO USE IT. YOU ARE FEEDING 1136 kg/h (19.6 kmole/h) OF PROPYLENE OXIDE (P.O.) TO THE REACTOR. THE FEED STREAM CONSISTS OF (1) AN EQUIVOLUMETRIC MIXTURE OF P.O. (1320 l/h) AND METHANOL (1320 l/h).
EXAMPLE No.2: DESIGN OF A CSTR

- WATER CONTAINING 0.1% OF SULFURIC ACID. THE VOLUMETRIC FLOW RATE OF WATER IS 6600 l/h. THE CORRESPONDING MOLAR FEED RATES OF METHANOL AND WATER ARE 32.66 kmole/h AND 365 kmole/h, RESPECTIVELY. THE TEMPERATURE OF BOTH FEED STREAMS IS 14.5 °C PRIOR TO MIXING, BUT THERE IS AN IMMEDIATE 9.4 °C TEMPERATURE RISE UPON MIXING OF THE TWO FEED STREAMS CAUSED BY THE HEAT OF MIXING. THE ENTERING TEMPERATURE OF ALL FEED STREAMS IS TAKEN TO BE 24 °C. FOR THE OPERATING CONDITIONS, IT WAS FOUND THAT THE REACTION IS FIRST-ORDER IN PROPYLENE OXIDE CONCENTRATION AND APPARENT ZERO-ORDER IN EXCESS WATER WITH THE SPECIFIC REACTION RATE \( k = A \exp(-E / RT) \) WHERE

\[
A = 16.96 \cdot 10^{12} \, h^{-1}; \quad E = 75311 kJ / kmole; \quad R = 8.3144 J / moleK;
\]
EXAMPLE No.2: DESIGN OF A CSTR

• THERE IS AN IMPORTANT CONSTRAINT ON YOUR OPERATION. PROPYLENE OXIDE IS A RATHER LOW-BOILING SUBSTANCE (BOILING POINT OF 34°C AT 1 atm). WITH THE MIXTURE YOU ARE USING, YOU FEEL THAT YOU CANNOT EXCEED AN OPERATING TEMPERATURE OF 52°C, OR YOU WILL LOSE TOO MUCH OXIDE BY VAPORIZATION THROUGH THE VENT SYSTEM. CAN YOU USE THE IDLE CSTR AS A REPLACEMENT FOR THE LEAKING ONE IF IT WILL BE OPERATED ADIABATICALLY? IF SO, WHAT WILL BE THE CONVERSION OF OXIDE TO GLYCOL?

• NEXT EXAMINE THE EFFECT OF USING A COOLING COIL OF SURFACE 3.716 m² WITH THE COOLING WATER FLOW RATE SUFFICIENTLY LARGE THAT A CONSTANT TEMPERATURE OF 29.5°C CAN BE MAINTAINED. THE OVERALL HEAT-TRANSFER COEFFICIENT IS \( U = 568 \, W / m^2 K \). WILL THE REACTOR SATISFY THE CONSTRAINT OF 52°C MAXIMUM TEMPERATURE IF THE COOLING COIL IS USED?
EXAMPLE No.2: EFFECT OF COOLING COIL

- **NLES Solution**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>f(x)</th>
<th>Ini Guess</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>0.3326428</td>
<td>2.874E-10</td>
<td>0</td>
</tr>
<tr>
<td>T</td>
<td>311.68313</td>
<td>-8.842E-09</td>
<td>0</td>
</tr>
<tr>
<td>A</td>
<td>2.084E+12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2.392E-13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ X = 33\%; \]
\[ T = 312K \]

- **NLES Report (safenewt)**

  - **Nonlinear equations as entered by the user**
  - \[ f(X) = X-(16867e-01*(T-297)+3877e-01*(T-3025E-01))/(84608+293E-01*(T-293)) = 0 \]
  - \[ f(T) = X-A*B/(1+A*B) = 0 \]

  - **Explicit equations as entered by the user**
  - \[ A = 2084E09 \]
  - \[ B = \exp(-9058/T) \]
THERMAL ENERGY CONSERVATION:
APPLICATION TO ADIABATIC TUBULAR REACTORS

• ENERGY BALANCE WITH $\dot{Q} = 0$ AND $\dot{W}_S = 0$:

$$- \sum_{i=1}^{n} \theta_i C_{pi} (T - T_{i0}) = X \left[ \Delta H_{Rx0} (T_R) + \Delta C_p (T - T_R) \right]$$

• MOLE BALANCE:

$$F_{A0} \frac{dX}{dV} = -r_A (X, T)$$

• SOLUTION OF THESE EQUATIONS YIELDS THE TEMPERATURE, CONVERSION AND CONCENTRATION PROFILES ALONG THE LENGTH OF THE REACTOR.
NOTE ON FIRST-ORDER REVERSIBLE REACTIONS

• BASIC REACTION: \( A \rightleftharpoons B \)

• RATE EQUATION FOR \( A \): \(- r_A = -\frac{dC_A}{dt} = k_1 C_A - k_2 C_B\)

• STOICHIOMETRY: \( C_A = C_{A0} (1 - X_A) \); \( C_B = C_{A0} (\theta_B + X_A) \)
  WITH \( \theta_B = C_{B0} / C_{A0} \)

• AT EQUILIBRIUM,

  RATE OF DISAPPEARANCE OF \( A \)= RATE OF FORMATION OF \( B \)

  \[
  \frac{dC_A}{dt} = 0 \Rightarrow k_1 C_A = k_2 C_B \Rightarrow K_C = \frac{k_1}{k_2} = \frac{C_B}{C_A} = \frac{(\theta_B + X_A)}{(1 - X_A)}
  \]
The elementary reversible gas-phase reaction

$$A \xrightarrow{\text{r}} B$$

is carried out in a PFR in which pressure drop is neglected and pure A enters the reactor.

**Mole balance:**

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$  \hspace{1cm} (T8-2.1)

**Rate law:**

$$-r_A = k \left( \frac{C_A}{K_C} - \frac{C_B}{K_C} \right)$$  \hspace{1cm} (T8-2.2)

with

$$k = k_i \exp \left[ \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) \right]$$  \hspace{1cm} (T8-2.3)

$$K_C = K(T_2) \exp \left[ \frac{\Delta H_{R2}^o}{R} \left( \frac{1}{T_2} - \frac{1}{T} \right) \right]$$  \hspace{1cm} (T8-2.4)

**Stoichiometry:**

Gas, \( e = 0 \), \( P = P_0 \)

$$C_A = C_{A0}(1 - X) \frac{T_0}{T}$$  \hspace{1cm} (T8-2.5)

$$C_B = C_{A0}X \frac{T_0}{T}$$  \hspace{1cm} (T8-2.6)

**Combine:**

$$-r_A = kC_{A0}(1 - X) - \frac{X}{K_C} \frac{T_0}{T}$$  \hspace{1cm} (T8-2.7)

**Energy balance:**

To relate temperature and conversion we apply the energy balance to an adiabatic PFR. If all species enter at the same temperature, \( T_{in} = T_0 \).

Solving Equation (8-50) to obtain the function of conversion yields

$$T = \frac{X(-\Delta H_{R2}^o(T_R)) + \sum \Theta_i \tilde{C}_{pi} T_0 + X \Delta \tilde{C}_p T_R}{\sum \Theta_i \tilde{C}_{pi} + X \Delta \tilde{C}_p}$$  \hspace{1cm} (T8-2.8)

If pure A enters and \( \Delta \tilde{C}_p = 0 \), then

$$T = T_0 + \frac{X(-\Delta H_{R2}^o(T_R))}{\tilde{C}_{pa}}$$  \hspace{1cm} (T8-2.9)

Equations (T8-2.1) through (T8-2.9) can easily be solved using either Simpson’s rule or an ODE solver.

---

**A. Numerical Technique**

Integrating the PFR mole balance,

$$V = F_{A0} \int_0^{r_3} \frac{dX}{-r_A} = F_{A0} \int_0^{r_3} \left( \frac{1}{-r_A} \right) dX$$  \hspace{1cm} (T8-2.10)

1. Set \( X = 0 \).
2. Calculate \( T \) using Equation (T8-2.9).
3. Calculate \( k \) using Equation (T8-2.3).
4. Calculate \( K_C \) using Equation (T8-2.4).
5. Calculate \( T_0/T \) (gas phase).
6. Calculate \(-r_A \) using Equation (T8-2.7).
7. Calculate \((1/r_A) \).
8. If \( X \) is less than the \( X_3 \) specified, increment \( X \) (i.e., \( X_{i+1} = X_i + \Delta X \)) and go to step 2.
9. Prepare table of \( X \) vs. \((1/r_A) \).
10. Use numerical integration formulas, for example,

$$V = F_{A0} \int_0^{r_3} \left( \frac{1}{-r_A} \right) dX = \frac{3}{8} \left[ \frac{1}{-r_A(X = 0)} + \frac{3}{-r_A(X_1)} + \frac{3}{-r_A(X_2)} + \frac{1}{-r_A(X_3)} \right]$$  \hspace{1cm} (T8-2.11)

with

$$h = \frac{X_3}{3}$$

**B. Ordinary Differential Equation (ODE) Solver**

1. \( \frac{dX}{dV} = \frac{kC_{A0}}{F_{A0}} \left( 1 - X \right) - \frac{X}{K_C} \frac{T_0}{T} \) \hspace{1cm} (T8-2.12)
2. \( k = k_i(T_i) \exp \left[ \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) \right] \)  \hspace{1cm} (T8-2.13)
3. \( K_C = K_{C2}(T_2) \exp \left[ \frac{\Delta H_{R2}^o}{R} \left( \frac{1}{T_2} - \frac{1}{T} \right) \right] \)  \hspace{1cm} (T8-2.14)
4. \( T = T_0 + \frac{X(-\Delta H_{R2}^o(T_R))}{\tilde{C}_{pa}} \)  \hspace{1cm} (T8-2.15)
5. Enter parameter values \( k_i, E, R, K_{C2}, \Delta H_{R2}^o(T_R), \tilde{C}_{pa}, C_{A0}, T_0, T_1, T_2 \).
6. Enter inital values \( X = 0, V = 0 \) and final values \( X = X_f \) and \( V = V_f \).
EXAMPLE No.3: DESIGN OF A PFR

• NORMAL BUTANE, $C_4H_{10}$ IS TO BE ISOMERIZED TO ISOBUTANE IN A PLUG FLOW REACTOR. ISOBUTANE IS A VALUABLE PRODUCT THAT IS USED IN THE MANUFACTURE OF GASOLINE ADDITIVES. FOR EXAMPLE, ISOBUTANE CAN BE FURTHER REACTED TO FORM ISOOCTANE. THE REACTION IS TO BE CARRIED OUT ADIABATICALLY IN THE LIQUID PHASE UNDER HIGH PRESSURE USING ESSENTIALLY TRACE AMOUNTS OF A LIQUID CATALYST WHICH GIVES A SPECIFIC REACTION RATE OF 31.1 h$^{-1}$ AT 360 K. CALCULATE THE PFR VOLUME NECESSARY TO PROCESS 163 mole/h OF A MIXTURE 90 mole% n-BUTANE AND 10 mole% i-PENTANE, WHICH IS CONSIDERED AN INERT. THE FEED ENTERS AT 330 K. THE REACTION IS $n-C_4H_{10} \leftrightarrow i-C_4H_{10}$

• BUTANE: $C_{P(n-B)} = C_{P(i-B)} = 141J/moleK$

• i-PENTANE:

$$C_{P(i-P)} = 161J/moleK; E = 65.7kJ/mole;$$

$$K_c = 3.03 \text{ at } 60^0C; C_{A0} = 9.3kmole/m^3$$
EXAMPLE No.3: DESIGN OF A PFR

- **ODE Report (RKF45)**

- Differential equations as entered by the user
  - [1] \( \frac{d(X)}{d(v)} = -\frac{ra}{Fa0} \)

- Explicit equations as entered by the user
  - [1] \( Ca0 = 93e-01 \)
  - [2] \( Fa0 = 9e-01*163 \)
  - [3] \( T = 330+433e-01*X \)
  - [4] \( Kc = 303e-02*exp(-8303e-01*((T-333)/(T*333))) \)
  - [5] \( k = 311e-01*exp(7906*(T-360)/(T*360)) \)
  - [6] \( Xe = Kc/(1+Kc) \)
  - [7] \( ra = -k*Ca0*(1-(1+1/Kc)*X) \)
  - [8] \( rate = -ra \)

- Independent variable
  - variable name: \( v \)
  - initial value: 0
  - final value: 4

POLYMATH PROGRAM
EXAMPLE No.3: DESIGN OF A PFR

![Graph of X vs V (m^3)](image)

![Graph of REACTION RATE vs V (m^4)](image)
THERMAL ENERGY CONSERVATION: APPLICATION TO TUBULAR REACTORS WITH HEAT EXCHANGE

\[ \dot{Q} = F_{A0} \left[ \sum_{i=1}^{n} \theta_i C_{pi} \frac{dT}{dT} \right] - F_{A0} X \left[ \Delta H_{Rx}^0 (T_R) + \int_{T_R}^{T} \Delta C_p dT \right] = 0 \]
THERMAL ENERGY CONSERVATION: APPLICATION TO TUBULAR REACTORS WITH HEAT EXCHANGE

- DIFFERENTIATING WITH RESPECT TO THE VOLUME, RECALLING \(- r_A = F_{A0} \frac{dX}{dV}\) AND \(d Q/ dV = Ua(T_a - T)\), THE ENERGY BALANCE YIELDS:

\[
\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)(-\Delta H_{Rx}(T))}{F_{A0} \left( \sum_{i=1}^{n} \theta_i C_{pi} + X\Delta C_p \right)} = g(X, T)
\]

- THE MOLE BALANCE IS

\[
\frac{dX}{dV} = -\frac{r_A}{F_{A0}} = f(X, T)
\]

M. Lacroix  Nonisothermal Reactor Design 31
EXAMPLE No.4: DESIGN OF A TUBULAR REACTOR

• ONE OF THE KEY STEPS IN THE DESIGN OF AN ACETIC ANHYDRIDE MANUFACTURING FACILITY IS THE VAPOR-PHASE CRACKING OF ACETONE TO KETENE AND METHANE:  
\[ \text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_2\text{CO} + \text{CH}_4 \]

\( (acetone) \rightarrow (ketene) + (methane) \)

\[ A \rightarrow B + C \]

THE REACTION IS FIRST-ORDER WITH RESPECT TO ACETONE AND THE SPECIFIC REACTION RATE CAN BE EXPRESSED BY \( \ln(k) = 34.34 - 34222 / T \) WHERE \( k \) IS IN RECIPROCAL SECONDS AND \( T \) IS IN KELVIN. IN THIS DESIGN, IT IS DESIRED TO FEED 8000 kg OF ACETONE PER HOUR TO A TUBULAR REACTOR. THE REACTOR CONSISTS OF A BANK OF 1000 TUBES (O.D. = 26.6 mm). WE WILL CONSIDER TWO CASES:

(1) THE REACTOR IS OPERATED ADIABATICALLY;
EXAMPLE No.4: DESIGN OF A TUBULAR REACTOR

(2) THE REACTOR IS SURROUNDED BY A HEAT EXCHANGER WHERE THE HEAT-TRANSFER COEFFICIENT IS $U = 110 W/m^2 K$ AND THE AMBIANT TEMPERATURE IS 1150 K.

- THE INLET TEMPERATURE AND PRESSURE ARE THE SAME FOR BOTH CASES AT 1035 K AND 162 kPa, RESPECTIVELY.

\[ H^0_{Rx}(T_R)_A = -216.67 \text{kJ/mole}; \]
\[ H^0_{Rx}(T_R)_B = -61.09 \text{kJ/mole}; \]
\[ H^0_{Rx}(T_R)_C = -74.81 \text{kJ/mole}; \]

HEATS OF FORMATION AT 298 K

\[ C_{PA} = 26.63 + 0.183T - 45.86 \cdot 10^{-6} T^2 \text{ (J/moleK)}; \]
\[ C_{PB} = 20.04 + 0.0945T - 30.95 \cdot 10^{-6} T^2 \text{ (J/moleK)}; \]
\[ C_{PA} = 13.39 + 0.077T - 18.71 \cdot 10^{-6} T^2 \text{ (J/moleK)}; \]

TEMPERATURE-DEPENDENT HEAT CAPACITIES
EXAMPLE No.4: ADIABATIC CASE

- **ODE Report (RKF45)**
  Differential equations as entered by the user
  - [1] \[ \frac{d(X)}{d(V)} = -\frac{ra}{Fao} \]
  - [2] \[ \frac{d(T)}{d(V)} = -\frac{ra*(-deltaH)}{(Fao*Cpa+X*delCp)} \]

- **Explicit equations as entered by the user**
  - [1] \[ Fao = 383e-01 \]
  - [2] \[ Cpa = 2663e-02+183e-03*T-4586e-02*10^(-6)*T^2 \]
  - [3] \[ delCp = 68e-01-115e-01*10^(-3)*T-381e-02*10^(-6)*T^2 \]
  - [4] \[ k = 82e-01*10^{14}*\exp(-34222/T) \]
  - [5] \[ Cao = 188e-01 \]
  - [6] \[ To = 1035 \]
  - [7] \[ Tr = 298 \]
  - [8] \[ deltaH = 80770+68e-01*(T-Tr)-575e-02*10^(-3)*(T^2-Tr^2)-127e-02*10^(-6)*(T^3-Tr^3) \]
  - [9] \[ ra = -\frac{k*Cao*(1-X)}{(1+X)*To/T} \]

- **Independent variable**
  - variable name : V
  - initial value : 0
  - final value : 5
EXAMPLE No.4: ADIABATIC CASE

Graph 1: $X$ vs $V$ (m$^3$)

Graph 2: $T$ (K) vs $V$ (m$^3$)
EXAMPLE No.4: CONCLUSION FOR ADIABATIC CASE

• FOR THE ADIABATIC CASE, THE REACTION DIES OUT AFTER 2.5 m³, OWING TO THE LARGE DROP IN TEMPERATURE, AND VERY LITTLE CONVERSION IS ACHIEVED BEYOND THIS POINT.

• ONE WAY TO INCREASE THE CONVERSION WOULD BE TO ADD A DILUENT SUCH AS N₂ WHICH COULD SUPPLY THE SENSIBLE HEAT FOR THIS ENDOOTHERMIC REACTION. HOWEVER, IF TOO MUCH DILUENT IS ADDED, THE CONCENTRATION AND RATE WILL BE QUITE LOW. ON THE OTHER HAND, IF TOO LITTLE DILUENT IS ADDED, THE TEMPERATURE WILL DROP AND EXTINGUISH THE REACTION.
EXAMPLE No.4: HEAT EXCHANGER CASE

- **ODE Report (RKF45)**
  - Differential equations as entered by the user
    - [1] \( \frac{dx}{dv} = -\frac{ra}{fa0} \)
    - [2] \( \frac{dt}{dv} = \frac{ua*(ta-t)+ra*dh}{fa0*(cpa+x*dcp)} \)

- **Explicit equations as entered by the user**
  - [1] \( fa0 = 376e-04 \)
  - [2] \( ua = 16500 \)
  - [3] \( ta = 1150 \)
  - [4] \( cpa = 266e-01+183e-03*t-459e-07*t^2 \)
  - [5] \( dcp = 68e-01-115e-04*t-381e-08*t^2 \)
  - [6] \( ca0 = 188e-01 \)
  - [7] \( t0 = 1035 \)
  - [8] \( \text{term} = -127e-08*(t^3-298^3) \)
  - [9] \( dh = 80770+68e-01*(t-298)-575e-05*(t^2-298^2)+\text{term} \)
  - [10] \( ra = -ca0*358e-02*\exp(34222*(1/t0-1/t))*(1-x)*(t0/t)/(1+x) \)

- **Independent variable**
  - **variable name**: v
  - **initial value**: 0
  - **final value**: 0,001

**POLYMATH PROGRAM**

37
EXAMPLE No.4: HEAT EXCHANGER CASE

**X vs V (m³) FOR ONE TUBE**

- **x**

**T (K) vs V (m³) FOR ONE TUBE**

- **t**
EXAMPLE No.4:
CONCLUSION FOR HEAT EXCHANGER CASE

EQUILIBRIUM CONVERSION

\[ A \Leftrightarrow B \]

• THE HIGHEST CONVERSION THAT CAN BE ACHIEVED IN REVERSIBLE REACTIONS IS THE EQUILIBRIUM CONVERSION.

• FOR ENDOThERMIC REACTIONS, THE EQUILIBRIUM CONVERSION INCREASES WITH INCREASING TEMPERATURE UP TO A MAXIMUM OF 1.

• FOR EXOTHERMIC REACTIONS, THE EQUILIBRIUM CONVERSION DECREASES WITH INCREASING TEMPERATURE.
EQUILIBRIUM CONVERSION: EXOTHERMIC REACTIONS

To determine the maximum conversion that can be achieved in an exothermic reaction carried out adiabatically, we find the intersection of the equilibrium conversion as a function of temperature with temperature-conversion relationships from the energy balance.
EXAMPLE No.5: ADIABATIC EQUILIBRIUM TEMPERATURE

• FOR THE ELEMENTARY SOLID-CATALYSED LIQUID-PHASE REACTION $A \Leftrightarrow B$, DETERMINE THE ADIABATIC EQUILIBRIUM TEMPERATURE AND CONVERSION WHEN PURE $A$ IS FED TO THE REACTOR AT A TEMPERATURE OF 300 K.

• ADDITIONAL INFORMATION:

\[ H_A^0(298K) = -40000 \text{cal/mole}; H_B^0(298K) = -60000 \text{cal/mole}; \]
\[ C_{PA} = 50 \text{cal/moleK}; C_{PB} = 50 \text{cal/moleK}; K_e = 10^5 \text{ at 298K}; \]

• WHAT CONVERSION COULD BE ACHIEVED IF TWO INTERSTAGE COOLERS HAVING THE CAPACITY TO COOL THE EXIT STREAM AT 350 K WERE EMPLOYED? ALSO, DETERMINE THE HEAT DUTY OF EACH EXCHANGER FOR A MOLAR FEED RATE OF $A$ OF 40 moles/s. ASSUME THAT 95% OF EQUILIBRIUM CONVERSION IS ACHIEVED IN EACH REACTOR. THE FEED TEMPERATURE TO THE FIRST REACTOR IS 300 K.
Example No.6:
Non isothermal Plug Flow Flow Reactor
The elementary irreversible gas-phase reaction $A \rightarrow B + C$ is carried out adiabatically in a PFR packed with a catalyst. Pure A enters the reactor at a volumetric flow rate of $20\text{dm}^3/s$ at a pressure of 10 atm and a temperature of 450K.

The pressure drop in the reactor is given by $\frac{dP}{dW} = -\frac{\alpha}{2} \left( \frac{T}{T_0} \right) \frac{P}{(P/P_0)} (1 + \varepsilon X)$. The reactor can be packed with one of two particle sizes:

$\alpha = 0.019/\text{kg}\_\text{cat}$. for particle diameter $D_1$

$\alpha = 0.0075/\text{kg}\_\text{cat}$. for particle diameter $D_2$

a) Plot the temperature $T$, conversion $X$ and pressure $\gamma = P/P_0$ along the length of the reactor that is as a function of the catalyst mass $w$.

b) Vary the parameters $\alpha$ and $P_0$ to learn the ranges of values in which they dramatically affect conversion.

Additional information:

$C_{PA} = 40J/mol\cdot K$; $C_{PB} = 25J/mol\cdot K$; $C_{PC} = 15J/mol\cdot K$

$H_A^0 = -70kJ/mol$; $H_B^0 = -50kJ/mol$; $H_C^0 = -40kJ/mol$. All heats of formation are referenced to 273 K.

$k = 0.133 \cdot \exp \left[ \frac{E}{R \left( \frac{1}{450} - \frac{1}{T} \right)} \right] \frac{dm^3}{kg\cdot\text{cat}\cdot s}$ with $E = 31.4kJ/mol; R = 8.314J/mol\cdot K$
Example No.6: Plug flow reactor

- **ODE Report (RKF45)**

- Differential equations as entered by the user
  - [1] \( \frac{d(t)}{d(w)} = \frac{r_a*d_{hr}}{f_{ao}*c_{pa}} \)
  - [2] \( \frac{d(x)}{d(w)} = -\frac{r_a}{f_{ao}} \)
  - [3] \( \frac{d(y)}{d(w)} = -(1+x)\frac{t}{450}\alpha/(2*y) \)

- Explicit equations as entered by the user
  - [1] \( f_{ao} = 542E-02 \)
  - [2] \( d_{hr} = -20000 \)
  - [3] \( c_{pa} = 40 \)
  - [4] \( \alpha = 19E-03 \)
  - [5] \( k = 133E-03*\exp(37766E-01*(1/450-1/t)) \)
  - [6] \( c_{ao} = 271E-03 \)
  - [7] \( c_a = c_{ao}(1-x)(450/t)/(1+x)y \)
  - [8] \( r_a = -k*c_a \)
  - [9] \( \text{rate} = -r_a \)

- Independent variable
  - variable name: \( w \)
  - initial value: 0
  - final value: 37
Example No.6: Plug flow reactor

Alpha = 0.019 kg\(^{-1}\) catalyst
Example No.6: Plug flow reactor

\[ \text{Alpha} = 0.0075 \text{ kg}^{-1} \text{ catalyst} \]