CHEMICAL REACTION ENGINEERING (SKF3223)

Chapter 7: Steady-state Non Isothermal Reactors

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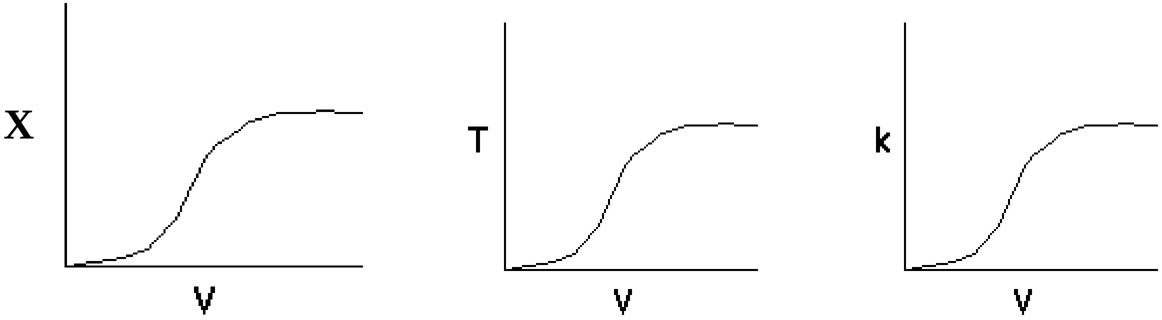
Heat effects in chemical reactors

- Most reactions are not carried out isothermally
- Temperature varies along PFR or heat is removed from CSTR

RECALL!! **Mole balance (design equation):**

PFR: $\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$ CSTR: $V = \frac{F_{A0}X}{-r_A}$ BATCH: $\frac{dX}{dt} = \frac{-r_A V}{N_{A0}}$

Exothermic reaction carried out adiabatically



ALGORITHM – eg: PFR

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

2 Rate Law: $$r_A=kC_A$$

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

3 Stoichiometry (liquid phase): $$v=v_0 \qquad F_A=C_Av_0 \qquad F_{A0}=C_{A0}v_0$$

$$C_A=C_{A0}(1-X)$$

4 Combine: $$\frac{dX}{dV}=k_1\exp\left[\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T}\right)\right]\frac{1-X}{\upsilon_0}$$

$$\frac{dX}{dV} = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]\frac{1-X}{\upsilon_0}$$

How we find the solution???

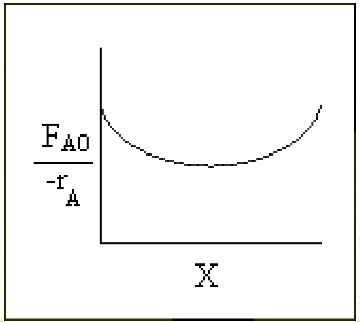
- ❑ We need to relate the conversion (X) to temperature (T) to solve the equation.
- ❑ This is accomplished by energy balance

5 Energy balance: $T = T_0 + \frac{-\Delta H_{Rx}}{C_{PA}} X$

- ➢ We can now form a table like we did in Chapter 2.

Choose X $\longrightarrow$ T $\longrightarrow$ k $\longrightarrow$ K_C $\longrightarrow$ $-r_A$ $\longrightarrow$ $(F_{A0}/-r_A)$

increment X and repeat



THE ENERGY BALANCE

- ☐ Application of 1st Law of Thermodynamic
  - CLOSED system:

$$d\hat{E} = \delta Q - \delta W$$

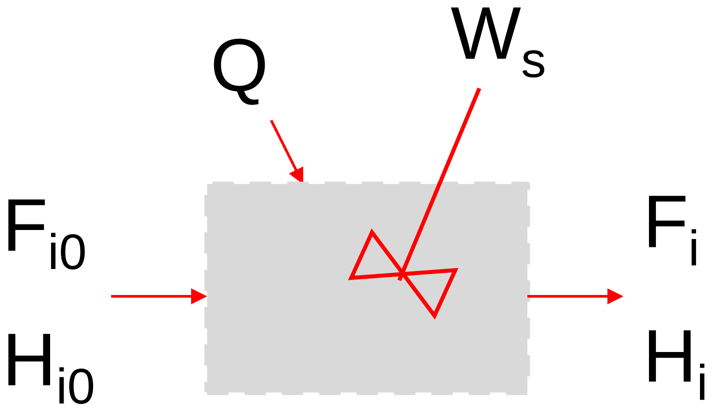
where E = energy of the system, Q = heat flow to the system, and W = work done by the system

  - OPEN system: Continuous-flow reactors

Energy balance on an open system

$$\begin{bmatrix}\text{rate of}\\ \text{accumulation}\\ \text{of energy}\\ \text{in system}\end{bmatrix} = \begin{bmatrix}\text{rate of}\\ \text{flow heat}\\ \text{to the}\\ \text{system}\end{bmatrix} - \begin{bmatrix}\text{rate of}\\ \text{work done}\\ \text{by the}\\ \text{system}\end{bmatrix} + \begin{bmatrix}\text{rate of energy}\\ \text{to the system}\\ \text{by inflow}\\ \text{mass}\end{bmatrix} - \begin{bmatrix}\text{rate of energy}\\ \text{leaving system}\\ \text{by outflow}\\ \text{mass}\end{bmatrix}$$

$$\frac{d\hat{E}}{dt} = \dot{Q} - \dot{W} + F_{in}E_{in} - F_{out}E_{out}$$



Unit: J/s

Work term, W

$$\dot{W} = \overbrace{-\sum_{i=1}^{n} F_i P \upsilon_i \Big|_{in} + \sum_{i=1}^{n} F_i P \upsilon_i \Big|_{out}}^{\text{Flow work: mass into and out of the system}} + \overset{\substack{\text{Shaft work: stirrer (CSTR) or turbine (PFR)} \\ \downarrow}}{\dot{W}_s}$$

$$\Downarrow$$

$$\frac{d\hat{E}_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^{n} \left(E_i + P\upsilon_i\right) F_i \Big|_{in} - \sum_{i=1}^{n} \left(E_i + P\upsilon_i\right) F_i \Big|_{out}$$

$$F_i P v_i = \frac{mol}{s} \frac{Newton}{m^2} \frac{m^3}{mol} = \frac{Newton.m}{s} = Joule/s$$

$$1Pa = 1Newton/m^2 = 1kg.m/s^2/m^2 \qquad v_i = m^3/mol$$

NONISOTHERMAL REACTOR

$$\frac{d\hat{E}_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^{n}(E_i + P\upsilon_i)F_i\Big|_{in} - \sum_{i=1}^{n}(E_i + P\upsilon_i)F_i\Big|_{out}$$

often negligible

Ei, Energy: $E_i = U_i + \cancel{\frac{u_i^2}{2}} + \cancel{gz_i} + \cancel{other}$ $\qquad E_i = U_i$

Hi, Enthalpy (J/mol) or (Btu/Ibmol) or (cal/mol):

$$H_i = U_i + P\upsilon_i$$

$$F_i H_i = F_i (U_i + P\upsilon_i)$$

$$\frac{d\hat{E}_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^{n} F_i H_i\Big|_{in} - \sum_{i=1}^{n} F_i H_i\Big|_{out}$$

Energy Balance: **Non Steady state**

$$\frac{d\hat{E}_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^{n} H_{io}F_{io} - \sum_{i=1}^{n} H_iF_i$$

Energy Balance: **Steady state**

$$\dot{Q} - \dot{W}_S + \sum_{i=1}^{n} F_{i0}H_{i0} - \sum_{i=1}^{n} F_iH_i = 0$$

STEADY STATE ENERGY BALANCE

$$\dot{Q} - \dot{W}_S + \sum_{i=1}^{n} F_{i0} H_{i0} - \sum_{i=1}^{n} F_i H_i = 0$$

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

Inlet & Outlet:

$$In = \Sigma H_{i0} F_{i0} = H_{A0} F_{A0} + H_{B0} F_{B0} + H_{C0} F_{C0} + H_{D0} F_{D0} + H_{I0} F_{I0}$$

$$Out = \Sigma H_i F_i = H_A F_A + H_B F_B + H_C F_C + H_D F_D + H_I F_I$$

Molar flow rate in terms of conversion:

$$F_i = F_{A0}(\Phi_i + v_i X)$$

$$F_A = F_{A0}(1 - X)$$

$$F_B = F_{A0}(\Phi_B - \frac{b}{a} X)$$

$$F_C = F_{A0}(\Phi_C + \frac{c}{a} X)$$

$$F_D = F_{A0}(\Phi_D + \frac{d}{a} X)$$

$$F_I = \Phi_I F_{A0}$$

Inlet - Outlet:

$$\Sigma H_{i0}F_{i0} - \Sigma H_i F_i = F_{A0}(H_{A0} - H_A) + (H_{B0} - H_B)\Phi_B$$
$$+ (H_{C0} - H_C)\Phi_C + (H_{D0} - H_D)\Phi_D + (H_{I0} - H_I)\Phi_I$$
$$-\left(\frac{d}{a}H_D + \frac{c}{a}H_C - \frac{b}{a}H_B - H_A\right)F_{A0}X$$

Heat of reaction at temp. T:

$$\Delta H_{Rx}(T) = \left(\frac{d}{a}H_D(T) + \frac{c}{a}H_C(T) - \frac{b}{a}H_B(T) - H_A(T)\right)$$

Combine:

$$\Sigma H_{i0}F_{i0} - \Sigma H_i F_i = F_{A0}\Sigma\Phi_i(H_{i0} - H_i) - \Delta H_{Rx}(T)F_{A0}X$$

$$\boxed{\dot{Q} - \dot{W}_S + F_{A0}\Sigma\Phi_i(H_{i0} - H_i) - \Delta H_{Rx}(T)F_{A0}X = 0}$$

ENTHALPIES, H

H_i is usually express in terms of heat capacity, C_p

$$H_i = \overbrace{H_i^o(T_R)}^{\text{Can be found from handbook}} + \int_{T_R}^{T} C_{pi}\,dT$$

T reference, 25°C

$$C_{Pi} = J/mol.K = Btu/Ibmol.^{\circ}R = cal/mol.K$$

Inlet & Outlet:

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

$$= \int_{T_{i0}}^{T} C_{pi}\,dT = C_{pi}[T - T_{i0}]$$

Therefore:

$$\boxed{\dot{Q}-\dot{W}_S - F_{A0}\Sigma\Phi_i C_{P_i}[T-T_{i0}] - \Delta H_{Rx}(T)F_{A0}X = 0}$$

Enthalpy of each species:

$$\Delta H_{RX}(T) = \overbrace{\left[\frac{d}{a}H_D^\circ(T_R)+\frac{c}{a}H_C^\circ(T_R)-\frac{b}{a}H_B^\circ(T_R)-H_A^\circ(T_R)\right]}^{\Delta H_{Rx}^\circ(T_R)}$$

$$+\underbrace{\left[\frac{d}{a}C_{P_D}+\frac{c}{a}C_{P_C}-\frac{b}{a}C_{P_B}-C_{P_A}\right]}_{\Delta C_P}(T-T_R)$$

Simplified:

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

ADIABATIC OPERATION

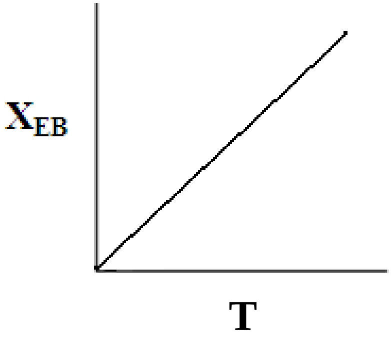
- Reactions in industry are frequently carried out adiabatically with heating and cooling provided either upstream or downstream.
- No heat is gained or lost by the system

$$\dot{Q} = 0,\ \dot{W}_S = 0:$$

$$\boxed{X = \frac{\sum \Phi_i C_{P_i}(T - T_{i0})}{-[\Delta H^\circ_{Rx}(T_R) + \Delta C_P(T - T_R)]}}$$

$$\boxed{\frac{dT}{dV} = \frac{(-r_A)(-[\Delta H^\circ_{Rx}(T_R) + \Delta C_P(T - T_R)])}{F_{A0}(\underbrace{\sum \Phi_i C_{P_i}}_{\text{Feed}} + X\Delta C_P)}}$$

- Relationship between X and T for adiabatic exothermic reactions:
- X_{EB} = conversion from the energy balance



- ➢ CSTR
- ➢ PFR
- ➢ PBR
- ➢ Batch

- Energy balance for adiabatic operation of PFR:

$$\boxed{T = \frac{X[-\Delta H_{Rx}^{\circ}(T_R)] + \Sigma\Phi_i C_{P_i} T_0 + X\Delta C_P T_R}{\Sigma\Phi_i C_{P_i} + X\Delta C_P}}$$

- If pure A enters and $\Delta C_P = 0$, then:

$$\boxed{T = T_0 + \frac{X[-\Delta H_{Rx}^{\circ}(T_R)]}{C_{P_A}}}$$

ALGORITHM- Adiabatic PFR (reversible GAS phase), no Pressure drop

$$\boxed{A \leftrightarrow B}$$

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

Integrating: $V = \displaystyle\int_0^{X_3} \frac{F_{A0}}{-r_A} dX$

2 Rate Law:

$$-r_A = k\left(C_A - \frac{C_B}{K_C} \right)$$

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

$$K_C = K_{C2}(T_2)\exp\left[\frac{\Delta H^\circ_{Rx}}{R}\left(\frac{1}{T_2} - \frac{1}{T} \right) \right]$$

3 Stoichiometry (gas phase):

$$\varepsilon = 0, \quad P = P_0$$

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

$$C_B = C_{A0} X$$

4 Combine:

$$-r_A = kC_{A0}\left((1 - X) - \frac{X}{K_C} \right)\frac{T_0}{T}$$

$$V = \int_0^{X_3} \frac{F_{A0}}{kC_{A0}\left((1 - X) - \frac{X}{K_C} \right)} dX$$

5 Energy Balance, Q=0, W=0, Pure A, ΔC_P=0:

$$T = T_0 + \frac{X[-\Delta H^\circ_{Rx}(T_R)]}{C_{P_A}}$$

6 SOLVE:

i Set X = 0

ii Calculate T using: $T = T_0 + \dfrac{X[-\Delta H^{\circ}_{Rx}(T_R)]}{C_{P_A}}$

iii Calculate k using: $k = k_1(T_1)\exp\left[\dfrac{E}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T}\right)\right]$

iv Calculate K_C using: $K_C = K_{C2}(T_2)\exp\left[\dfrac{\Delta H^{\circ}_{Rx}}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T}\right)\right]$

v Calculate T_0/T (gas phase)

vi Calculate $-r_A$ using: $-r_A = kC_{A0}\left((1-X) - \dfrac{X}{K_C}\right)\dfrac{T_0}{T}$

vii Calculate $F_{A0}/-r_A$

viii If X is less than the X3 specified, increment X () and go to Step 2

ix Prepare table of X vs ($F_{A0}/-r_A$)

x Use numerical integration formulas (**Simpson's rule**) or graphical method (Levenspiel plot)

ALGORITHM- **Adiabatic CSTR (LIQUID phase)**

$$\boxed{A \leftrightarrow B}$$

1 Mole balance: $V = \dfrac{F_{A0}X}{-r_A}$

2 Rate Law:

$$-r_A = k\left(C_A - \frac{C_B}{K_C}\right)$$

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

$$K_C = K_{C2}(T_2)\exp\left[\frac{\Delta H^\circ_{Rx}}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)\right]$$

3 Stoichiometry (liquid phase):

$$v = v_0$$

$$C_A = C_{A0}(1 - X)$$

$$C_B = C_{A0}X$$

4 Combine:

$$-r_A = kC_{A0}\left[1 - \left(1 + \frac{1}{K_C}\right)X\right]$$

$$V = \frac{F_{A0}X}{kC_{A0}\left[1 - \left(1 + \frac{1}{K_C}\right)X\right]}$$

5 Energy Balance, Q=0, W=0, Pure A, ΔC_P=0:

$$T = T_0 + \frac{X[-\Delta H^\circ_{Rx}(T_R)]}{C_{P_A}}$$

6 SOLVE : Table 8-4 (pg. 526)

C1 Given X
Find T and V

Solution:
Calc T → cal k → calc K_C → calc $-r_A$ → calc V

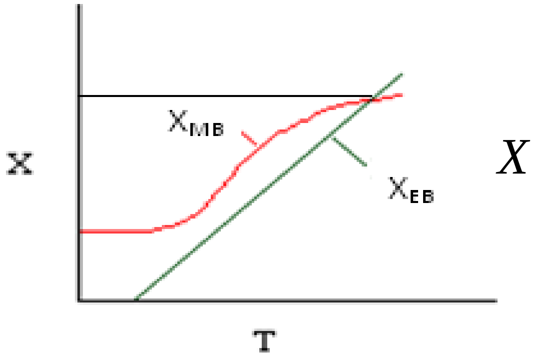
C2 Given T
Find X and V

Solution:
Calc k → cal K_C → calc X → calc $-r_A$ → calc V

C3 Given V
Find X at T

Solution:
Plot X_{EB} vs. T and X_{MB} vs. T on the same graph

$$X_{MB} = drive\ from\ step$$
$$4\ combine$$



$$X_{EB} = \frac{\Sigma\Theta_i C_{P_i}(T - T_0)}{-\Delta H_{Rx}(T)}$$

5 Energy Balance, **Pure A**,
Q=0, W=0, $\Delta C_P=0$:

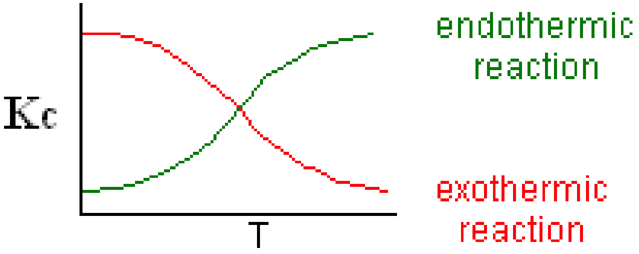
$$T = T_0 + \frac{X[-\Delta H^\circ_{Rx}(T_R)]}{C_{P_A}}$$

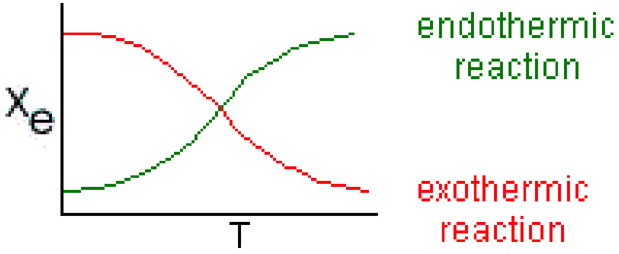
5 Energy Balance, **More than 1 reactant including inert**,
Q=0, W=0, $\Delta C_P=0$:

$$T = T_0 + \frac{X[-\Delta H^\circ_{Rx}(T_R)]}{\Sigma\Theta_i C_{Pi}}$$

<u>Exothermic</u> ΔH is negative

<u>Endothermic</u> ΔH is positive





ALGORITHM- **for HEAT EFFECTS-PFR/PBR/CSTR**

$$A \leftrightarrow B$$

① Mole balance:

X as the reaction variable	F as the reaction variable
$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$ $\quad V = \frac{F_{A0}X}{-r_A}$	$\frac{dF_A}{dV} = r_A$ $\quad V = \frac{F_{A0} - F_A}{-r_A}$

② Rate Law:

$$-r_A = k\left(C_A - \frac{C_B}{K_C}\right) \qquad k = k_1(T_1)\exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] \qquad K_C = K_{C2}(T_2)\exp\left[\frac{\Delta H^\circ_{Rx}}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)\right]$$

③ Stoichiometry, no ΔP:

Gas phase	Liquid phase
$C_A = C_{A0}\frac{(1-X)}{(1+\varepsilon X)}\frac{T_0}{T}$ $\quad C_B = C_{A0}\frac{(\Phi_B - X)}{(1+\varepsilon X)}\frac{T_0}{T}$	$C_A = C_{A0}(1-X)$ $\quad C_B = C_{A0}(\Phi_B + X)$
$C_A = C_{T0}\frac{F_A}{F_T}\frac{T_0}{T}$ $\quad C_B = C_{T0}\frac{F_B}{F_T}\frac{T_0}{T}$	$C_A = \frac{F_A}{v_0}$ $\quad C_B = \frac{F_B}{v_0}$

④ Combine

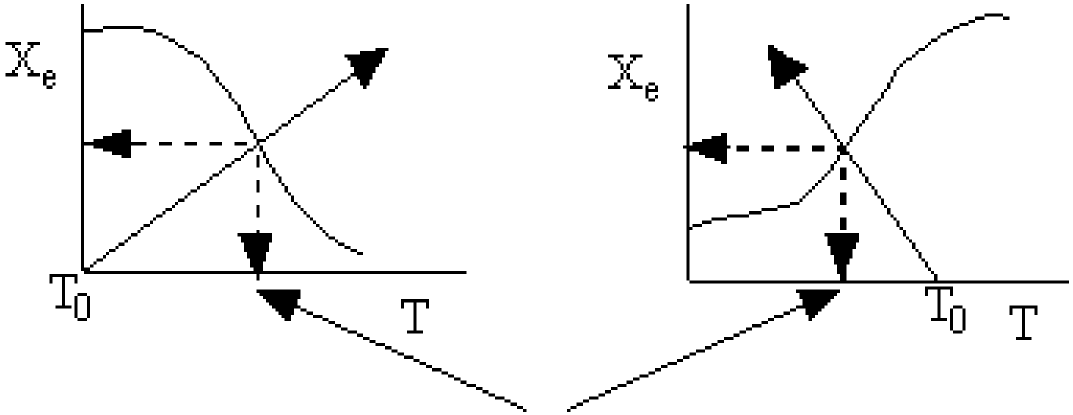
⑤ Energy Balances:

Refer TABLE 8-1
(pg. 476-478)

REVERSIBLE REACTION

- Determination of the maximum conversion, X_{EB}

Exothermic Endothermic

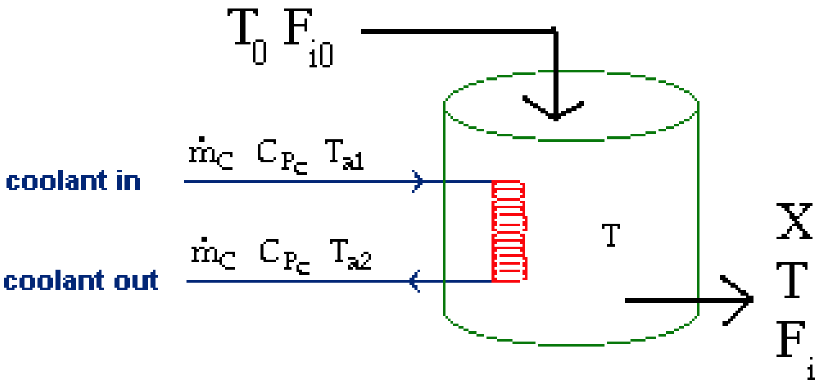


Adiabatic temperature

1st Order : $$X_e = \frac{K_C}{1+K_C}$$

$$X_{EB} = \frac{\Sigma\Theta_i C_{P_i}(T-T_0)}{-\Delta H_{Rx}(T)}$$

Evaluating the Heat Exchanger Term



Heat transfer to a CSTR: $\dot{Q} = \dot{m}_c C_{P_c} \{(T_{a1} - T)[1 - \exp(\frac{-UA}{\dot{m}_c C_{P_c}})]\}$

Since the coolant flow rate is high, T_a is constant: $\dot{Q} = UA(T_a - T)$

$$X = \frac{\frac{UA}{F_{A0}}(T - T_a) + \Sigma\Theta_i C_{P_i}(T - T_0)}{[-\Delta H^\circ_{Rx}(T_R)]}$$

Multiple Reactions with Heat Effects

PFR:

$$\frac{dT}{dV}=\frac{Ua(T_a-T)+\Sigma(-r_{ij})[-\Delta H_{Rxij}(T)]}{\Sigma F_j C_{P_j}}$$

i = Reaction number
j = Species

CSTR:

$$UA(T_a-T)-F_{A0}\,\Sigma\Theta_i C_{P_i}(T-T_0)+V\,\Sigma r_{ij}\,\Delta H_{Rxij}(T)=0$$

REFERENCES

Main Reference:

1. Fogler,H.S., "*Elements of Chemical Reaction Engineering*", 4th Edition,Prentice Hall, New Jersey, 2006.

Other References:

1. Davis, M.E and Davis, R.J, *"Fundamentals of Chemical Reaction Engineering",* Mc-Graw-Hill, New York, 2003
2. Schmidt, L.D, "*The Engineering of Chemical Reactions"*, Oxford, New York, 1998
3. Levenspiel,O., "*Chemical Reaction Engineering*", 3rd Edition, Wiley,New York, 1998
4. Smith,J., "*Chemical Engineering Kinetics*", 3rd Edition, McGraw-Hill, New York, 1981