Chemical Reaction Engineering

Steady-State Non-isothermal Reactor Design

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Introduction

➢ For the non-isothermal liquid phase reaction to take place in plug flow reactor

$$A \longrightarrow B \qquad -r_A = kC_A$$

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \qquad k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

$$v = v_0 \qquad F_A = C_A v_0 \qquad F_{A0} = C_{A0} v_0 \qquad C_A = C_{A0}(1 - X)$$

$$\Rightarrow \quad -r_A = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] C_{A0}(1 - X)$$

$$\Rightarrow \quad \frac{dX}{dV} = \frac{k(1 - X)}{v_0}$$

Introduction

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

➢ To find a relation between X and T, then Energy balance is required

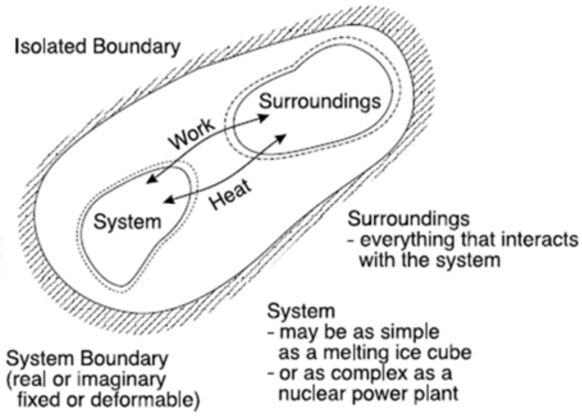
$$T = T_0 + \frac{-\Delta H_{Rx}}{C_{P_A}} X$$

the temperature-conversion relationship if the reaction is adiabatic.

First Law of Thermodynamics: Closed System

For a *closed system*, the energy balance is

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



$d\hat{E}$ the change in total energy of the system,

δQ, the heat flow **to** the system,

δW, the work done **by** the system **on** the surroundings,

The δ's signify that δQ and δW are not exact differentials of a state function.

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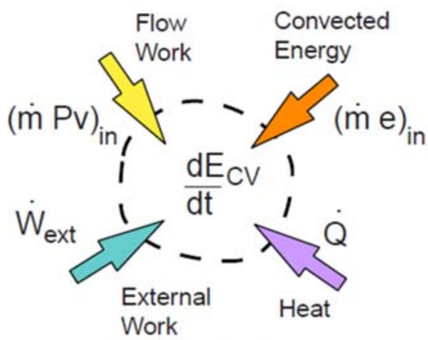
First Law of Thermodynamics: Open System

The continuous-flow reactors are *open systems*



[Rate of accumulation of energy *within* the system] = [Rate of flow of heat *to* the system *from* the surroundings] − [Rate of work *done* by the system *on* the surroundings] + [Rate of energy added to the system by mass flow *into* the system] − [Rate of energy leaving system by mass flow *out* of the system]

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

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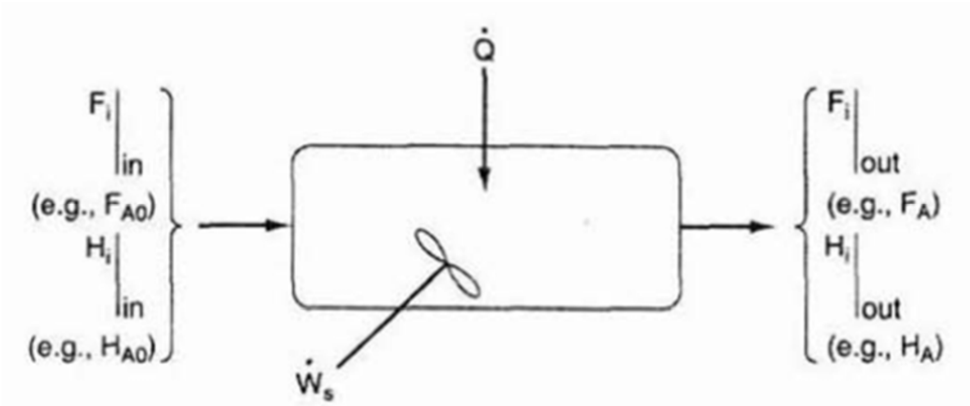
First Law of Thermodynamics: Open System



assume the contents of the system volume are well mixed.

- The unsteady-state energy balance for an open well-mixed system

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

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First Law of Thermodynamics: Open System

$$\dot{W} = \overbrace{-\sum_{i=1}^{n} F_i P \tilde{V}_i \Big|_{in} + \sum_{i=1}^{n} F_i P \tilde{V}_i \Big|_{out}}^{\text{[Rate of flow work]}} + \dot{W}_s$$

where P is the pressure (Pa) [1 Pa = 1 Newton/m^2 = 1 kg • m/s^2/m^2] and $\tilde{V}_i$ is the specific molar volume of species i (m^3/mol of i).

- Flow work is work that is necessary to get the mass into and our of the system which is

$$F_i \cdot P \cdot \tilde{V}_i$$

where F_i is in mol/s, P is Pa (1 Pa = 1 Newton/m^2), and $\tilde{V}_i$ is m^3/mol.

$$F_i \cdot P \cdot \tilde{V}_i \; [=] \; \frac{\text{mol}}{\text{s}} \cdot \frac{\text{Newton}}{\text{m}^2} \cdot \frac{\text{m}^3}{\text{mol}} = (\text{Newton} \cdot \text{m}) \cdot \frac{1}{\text{s}} = \text{Joules/s} = \text{Watts}$$

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First Law of Thermodynamics: Open System

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

$$E_i = U_i + \frac{u_i^2}{2} + gz_i + \text{other}$$

In almost all chemical reactor situations, the kinetic, potential, and "other" energy terms are negligible in comparison with the enthalpy, heat transfer, and work terms,

$$E_i = U_i$$

- Define the enthalpy as

$$H_i = U_i + P\tilde{V}_i$$

$$(H_i) = \frac{\text{J}}{\text{mol } i} \text{ or } \frac{\text{Btu}}{\text{lb mol } i} \text{ or } \frac{\text{cal}}{\text{mol } i}$$

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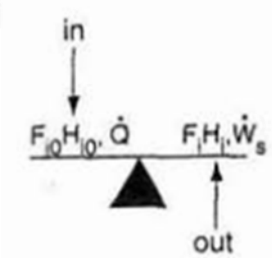
First Law of Thermodynamics: Open System

$$F_i H_i = F_i(U_i + P\tilde{V}_i)$$

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

- Or

$$\dot{Q} - \dot{W}_s + \sum_{i=1}^{n} F_{i0} H_{i0} - \sum_{i=1}^{n} F_i H_i = \frac{d\hat{E}_{sys}}{dt}$$



at steady state.

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

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Heat of Reaction

➤ For the reaction

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

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

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

the molar flow rate of species i $\quad F_i = F_{A0}(\Theta_i + \nu_i X)$

for Reaction $A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D$

$$F_A = F_{A0}(1 - X) \qquad F_C = F_{A0}\left(\Theta_C + \frac{c}{a}X\right) \qquad F_I = \Theta_I F_{A0}$$

$$F_B = F_{A0}\left(\Theta_B - \frac{b}{a}X\right) \qquad F_D = F_{A0}\left(\Theta_D + \frac{d}{a}X\right) \qquad \Theta_i = \frac{F_{i0}}{F_{A0}}$$

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Heat of Reaction

$$\sum_{i=1}^{n} H_{i0}F_{i0} - \sum_{i=1}^{n} F_i H_i = F_{A0}[(H_{A0} - H_A) + (H_{B0} - H_B)\Theta_B + (H_{C0} - H_C)\Theta_C + (H_{D0} - H_D)\Theta_D + (H_{I0} - H_I)\Theta_I] - \underbrace{\left(\frac{d}{a}H_D + \frac{c}{a}H_C - \frac{b}{a}H_B - H_A\right)}_{\Delta H_{Rx}} F_{A0}X$$

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

Heat of reaction

➡ $$\sum_{i=1}^{n} F_{i0}H_{i0} - \sum_{i=1}^{n} F_i H_i = F_{A0}\sum_{i=1}^{n} \Theta_i (H_{i0} - H_i) - \Delta H_{Rx}(T) F_{A0}X$$

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

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Dissecting the Enthalpies

The molal enthalpy of species i at a particular temperature and pressure, H_i,

$$H_i = H_i^\circ(T_R) + \Delta H_{Qi}$$

$H_i^\circ(T_R)$ enthalpy of formation of species i at some reference temperature T_R

ΔH_{Qi}, the change in enthalpy, that results when the temperature is raised from the reference temperature, T_R, to some temperature T

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

$$\Rightarrow \quad H_i = H_i^\circ(T_R) + \int_{T_R}^{T} C_{P_i}\, dT$$

And $\quad C_{P_i} = \alpha_i + \beta_i T + \gamma_i T^2$

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Dissecting the Enthalpies

if the enthalpy of formation is given at a reference temperature where the species is a solid, then the enthalpy, $H(T)$, of a gas at temperature T is

$$\begin{bmatrix}\text{Enthalpy of}\\ \text{species}\\ i \text{ in the gas}\\ \text{at } T\end{bmatrix} = \begin{bmatrix}\text{Enthalpy of}\\ \text{formation}\\ \text{of species}\\ i \text{ in the solid}\\ \text{phase}\\ \text{at } T_R\end{bmatrix} + \begin{bmatrix}\Delta H_Q \text{ in heating}\\ \text{solid from}\\ T_R \text{ to } T_m\end{bmatrix} + \begin{bmatrix}\text{Heat of}\\ \text{melting}\\ \text{at } T_m\end{bmatrix}$$

$$+ \begin{bmatrix}\Delta H_Q \text{ in heating}\\ \text{liquid from}\\ T_m \text{ to } T_b\end{bmatrix} + \begin{bmatrix}\text{Heat of}\\ \text{vaporation}\\ \text{at } T_b\end{bmatrix} + \begin{bmatrix}\Delta H_Q \text{ in heating}\\ \text{gas from}\\ T_b \text{ to } T\end{bmatrix}$$

$$H_i(T) = H_i^\circ(T_R) + \int_{T_R}^{T_m} C_{Ps_i} dT + \Delta H_{mi}(T_m) + \int_{T_m}^{T_b} C_{Pg_i} dT + \Delta H_{vi}(T_b) + \int_{T_b}^{T} C_{Pg_i} dT$$

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Dissecting the Enthalpies

the change in enthalpy ($H_i - H_{i0}$) when the reacting fluid is heated without phase change from its entrance temperature, T_{i0}, to a temperature T,

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

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

Substituting for H_i and H_{i0}

$$\dot{Q} - \dot{W}_s - F_{A0} \sum_{i=1}^{n} \Theta_i \int_{T_{i0}}^{T} C_{P_i}\, dT - \Delta H_{Rx}(T) F_{A0} X = 0$$

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Dissecting the Enthalpies

Relating $\Delta H_{Rx}(T)$, $\Delta H^\circ_{Rx}(T_R)$, and ΔC_p

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

where the enthalpy of each species is

$$H_i = H_i^\circ(T_R) + \int_{T_R}^{T} C_{P_i}\, dT$$

$$\Delta H_{Rx}(T) = \left[\frac{d}{a} H_D^\circ(T_R) + \frac{c}{a} H_C^\circ(T_R) - \frac{b}{a} H_B^\circ(T_R) - H_A^\circ(T_R)\right] + \int_{T_R}^{T} \left[\frac{d}{a} C_{p_D} + \frac{c}{a} C_{p_C} - \frac{b}{a} C_{p_B} - C_{p_A}\right] dT$$

$$\Delta H^\circ_{Rx}(T_R) = \frac{d}{a} H_D^\circ(T_R) + \frac{c}{a} H_C^\circ(T_R) - \frac{b}{a} H_B^\circ(T_R) - H_A^\circ(T_R)$$

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Dissecting the Enthalpies

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

$$\Delta H_{Rx}(T) = \Delta H^\circ_{Rx}(T_R) + \int_{T_R}^{T} \Delta C_p \, dT$$

Mean Heat Capacities

$$\Delta H_{Rx}(T) = \Delta H^\circ_{Rx}(T_R) + \Delta \hat{C}_p (T - T_R)$$

Where $$\Delta \hat{C}_p = \frac{\int_{T_R}^{T} \Delta C_p \, dT}{T - T_R}$$

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Dissecting the Enthalpies

Also $$\sum \Theta_i \int_{T_{i0}}^{T} C_{pi} \, dT = \sum \Theta_i \tilde{C}_{pi}(T - T_{i0})$$

$\tilde{C}_{pi}$ is the mean heat capacity of species i between T_{i0} and T:

$$\tilde{C}_{pi} = \frac{\int_{T_{i0}}^{T} C_{pi} \, dT}{T - T_{i0}}$$

$$\dot{Q} - \dot{W}_s - F_{A0} \sum \Theta_i \tilde{C}_{pi}(T - T_{i0}) - F_{A0} X [\Delta H^\circ_{Rx}(T_R) + \Delta \hat{C}_p (T - T_R)] = 0$$

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Dissecting the Enthalpies

Variable Heat Capacities

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

$$\Delta H_{Rx}(T) = \Delta H^\circ_{Rx}(T_R) + \int_{T_R}^{T} (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2)\, dT$$

$$\Delta H_{Rx}(T) = \Delta H^\circ_{Rx}(T_R) + \Delta\alpha(T - T_R) + \frac{\Delta\beta}{2}(T^2 - T_R^2) + \frac{\Delta\gamma}{3}(T^3 - T_R^3)$$

where

$$\Delta\alpha = \frac{d}{a}\alpha_D + \frac{c}{a}\alpha_C - \frac{b}{a}\alpha_B - \alpha_A$$

$$\Delta\beta = \frac{d}{a}\beta_D + \frac{c}{a}\beta_C - \frac{b}{a}\beta_B - \beta_A$$

$$\Delta\gamma = \frac{d}{a}\gamma_D + \frac{c}{a}\gamma_C - \frac{b}{a}\gamma_B - \gamma_A$$

Dissecting the Enthalpies

$$\sum_{i=1}^{n} \Theta_i \int_{T_0}^{T} C_{pi}\, dT = \int_{T_0}^{T} (\Sigma\, \alpha_i\Theta_i + \Sigma\, \beta_i\Theta_i T + \Sigma\, \gamma_i\Theta_i T^2)\, dT$$

$$= \Sigma\, \alpha_i\Theta_i(T - T_0) + \frac{\Sigma\, \beta_i\Theta_i}{2}(T^2 - T_0^2) + \frac{\Sigma\, \gamma_i\Theta_i}{3}(T^3 - T_0^3)$$

$$\dot{Q} - \dot{W}_s - F_{A0}\left[\alpha_i\Theta_i(T - T_0) + \frac{\Sigma\, \beta_i\Theta}{2}(T^2 - T_0^2) + \frac{\Sigma\, \gamma_i\Theta_i}{3}(T3 - T_0^3)\right]$$

$$- F_{A0}X\left[\Delta H^\circ_{Rx}(T_R) + \Delta\alpha(T - T_R) + \frac{\Delta\beta}{2}(T^2 - T_R^2) + \frac{\Delta\gamma}{3}(T^3 - T_R^3)\right] = 0$$

Dissecting the Enthalpies

For the case of constant heat capacities,

$$H_i = H_i^\circ(T_R) + \int_{T_R}^{T} C_{P_i}\, dT = H_i^\circ(T_R) + C_{P_i}(T - T_R)$$

$$\Delta H_{\mathrm{Rx}}(T) = \left[\frac{d}{a}H_{\mathrm{D}}^\circ(T_R) + \frac{c}{a}H_{\mathrm{C}}^\circ(T_R) - \frac{b}{a}H_{\mathrm{B}}^\circ(T_R) - H_{\mathrm{A}}^\circ(T_R)\right] + \left[\frac{d}{a}C_{P_{\mathrm{D}}} + \frac{c}{a}C_{P_{\mathrm{C}}} - \frac{b}{a}C_{P_{\mathrm{B}}} - C_{P_{\mathrm{A}}}\right](T - T_R)$$

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

The steady-state energy balance is

$$\dot{Q} - \dot{W}_s - F_{A0}\sum_{i=1}^{n}\Theta_i C_{P_i}(T - T_{i0}) - [\Delta H_{\mathrm{Rx}}^\circ(T_R) + \Delta C_P(T - T_R)]F_{A0}X = 0$$

Dissecting the Enthalpies

In most systems, the work term, $\dot{W}_s$, can be neglected

$$\dot{Q} - F_{A0}\Sigma\Theta_i C_{P_i}(T - T_{i0}) - [\Delta H_{Rx}^\circ(T_R) + \Delta C_P(T - T_R)]F_{A0}X = 0$$

Example

Calculate the heat of reaction for the synthesis of ammonia from hydrogen nitrogen at 150°C in kcal/mol of N_2 reacted *and also* in kJ/mol of H_2 reacted.

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

$$\Delta H^\circ_{Rx}(T_R) = 2H^\circ_{NH_3}(T_R) - 3H^\circ_{H_2}(T_R) - H^\circ_{N_2}(T_R)$$

The heats of formation of the elements (H_2, N_2) are zero at 25°C.

$$\Delta H^\circ_{Rx}(T_R) = 2H^\circ_{NH_3}(T_R) - 3(0) - 0 = 2H^\circ_{NH_3} = 2(-11{,}020)\ \frac{\text{cal}}{\text{mol N}_2}$$

$$= -22{,}040 \text{ cal/mol N}_2 \text{ reacted}$$

or

$$\Delta H^\circ_{Rx}(298\text{ K}) = -22.04 \text{ kcal/mol N}_2 \text{ reacted}$$

$$= -92.22 \text{ kJ/mol N}_2 \text{ reacted}$$

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Example Cont.

$C_{P_{H_2}} = 6.992$ cal/mol $H_2 \cdot K$ $\quad$ $C_{P_{N_2}} = 6.984$ cal/mol $N_2 \cdot K$ $\quad$ $C_{P_{NH_3}} = 8.92$ cal/mol $NH_3 \cdot K$

$$\Delta C_P = 2C_{P_{NH_3}} - 3C_{P_{H_2}} - C_{P_{N_2}} = 2(8.92) - 3(6.992) - 6.984$$

$$= -10.12 \text{ cal/mol N}_2 \text{ reacted} \cdot \text{K}$$

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

$$\Delta H_{Rx}(423\text{ K}) = -22{,}040 + (-10.12)(423 - 298)$$

$$= -23{,}310 \text{ cal/mol N}_2 = -23.31 \text{ kcal/mol N}_2$$

The heat of reaction based on the moles of H_2 reacted is

$$\Delta H_{Rx}(423\text{ K}) = \frac{1\text{ mol N}_2}{3\text{ mol H}_2}\left(-97.53\ \frac{\text{kJ}}{\text{mol N}_2}\right) = -32.51\ \frac{\text{kJ}}{\text{mol H}_2} \text{ at } 423\text{ K}$$

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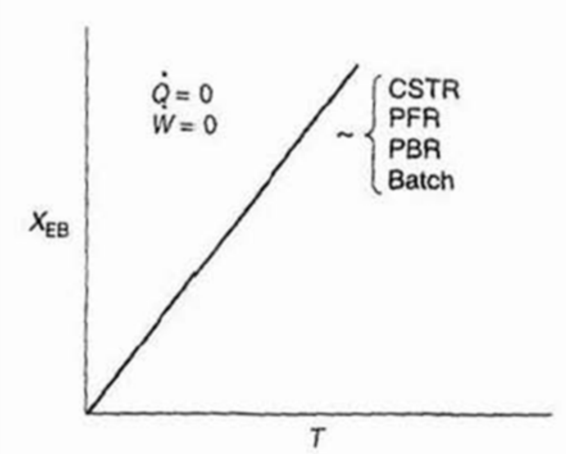
Adiabatic Operation

$$\dot{Q} - F_{A0}\Sigma\Theta_i C_{P_i}(T - T_{i0}) - [\Delta H^{\circ}_{Rx}(T_R) + \Delta C_P(T - T_R)]F_{A0}X = 0$$

$$\dot{Q} = 0$$

$$X = \frac{\Sigma\,\Theta_i C_{P_i}(T - T_{i0})}{-[\Delta H^{\circ}_{Rx}(T_R) + \Delta C_P(T - T_R)]}$$



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Adiabatic Operation

Adiabatic Tubular Reactor

rearrange

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

This equation will be coupled with the differential mole balance

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

to obtain the temperature, conversion, and concentration profiles along the length of the reactor.

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Example

Normal butane, C_4H_{10}, is to be isomerized to isobutane in a plug-flow reactor.

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 and CSTR volumes necessary to process 100,000 gal/day (163 kmol/h) at 70% conversion of a mixture 90 mol % *n*-butane and 10 mol % *i*-pentane, which is considered an inert. The feed enters at 330 K.

Additional information:

$\Delta H_{Rx} = -6900$ J/mol · butane, Activation energy = 65.7 kJ/mol

$K_C = 3.03$ at 60°C, $C_{A0} = 9.3$ kmol/dm³ = 9.3 kmol/m³

Butane

$C_{P_{n\text{-}B}} = 141$ J/mol · K

$C_{P_{i\text{-}B}} = 141$ J/mol · K = 141 kJ/kmol · K

i-Pentane

$C_{P_{i\text{-}P}} = 161$ J/mol · K

Example Cont.

Example Cont.

Example Cont.

Tubular Reactor with Heat Exchange

carry out an energy balance on the volume ΔV with $\dot{W}_s = 0$.

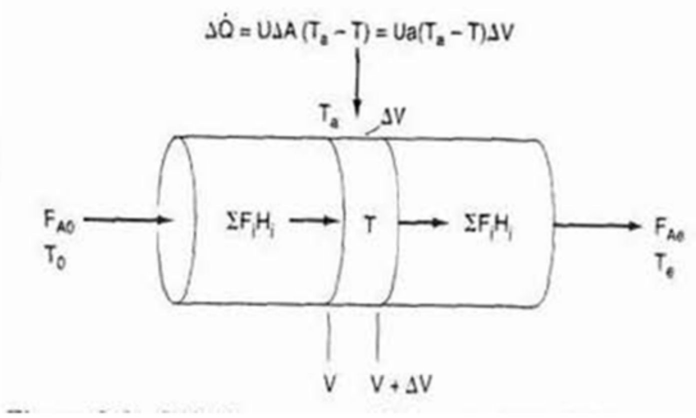
$$\Delta \dot{Q} + \Sigma F_i H_i|_V - \Sigma F_i H_i|_{V+\Delta V} = 0$$

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

where a is the heat exchange area per unit volume of reactor.

$$a = \frac{A}{V} = \frac{\pi D L}{\frac{\pi D^2 L}{4}} = \frac{4}{D}$$

where D is the reactor diameter.



Tubular Reactor with Heat Exchange

as $\Delta V \rightarrow 0$,

$$Ua(T_a - T) - \frac{d\Sigma(F_i H_i)}{dV} = 0$$

Expanding

$$Ua(T_a - T) - \Sigma \frac{dF_i}{dV} H_i - \Sigma F_i \frac{dH_i}{dV} = 0$$

From a mole balance on species i,

$$\frac{dF_i}{dV} = r_i = \nu_i(-r_A)$$

Differentiating the enthalpy Equation

$$\frac{dH_i}{dV} = C_{P_i} \frac{dT}{dV}$$

Tubular Reactor with Heat Exchange

$$Ua(T_a - T) - \underbrace{\Sigma \nu_i H_i}_{\Delta H_{Rx}}(-r_A) - \Sigma F_i C_{P_i} \frac{dT}{dV} = 0$$

Rearranging,

$$\frac{dT}{dV} = \frac{\overbrace{r_A \Delta H_{Rx}}^{\text{Heat "Generated"}} - \overbrace{Ua(T - T_a)}^{\text{Heat Removed}}}{\Sigma F_i C_{P_i}}$$

in terms of conversion $F_i = F_{A0}(\Theta_i + \nu_i X)$

$$\Rightarrow \quad \frac{dT}{dV} = \frac{Ua(T_a - T) + (r_A)(\Delta H_{Rx})}{F_{A0}(\Sigma \Theta_i C_{P_i} + \Delta C_P X)}$$

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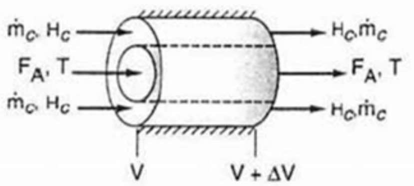
Tubular Reactor with Heat Exchange

For a packed-bed reactor $dW = \rho_b \, dV$ where ρ_b is the bulk density,

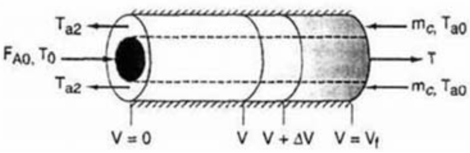
$$\frac{dT}{dW} = \frac{\frac{Ua}{\rho_b}(T_a - T) + (r_A')(\Delta H_{Rx})}{\Sigma F_i C_{P_i}}$$

If the coolant temperature varies down the reactor

the variation of coolant temperature T_a down the length of reactor is



$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_c C_P}$$ Co-Current Flow



$$\frac{dT_a}{dV} = \frac{Ua(T_a - T)}{\dot{m}_c C_{P_c}}$$ Counter Current Flow

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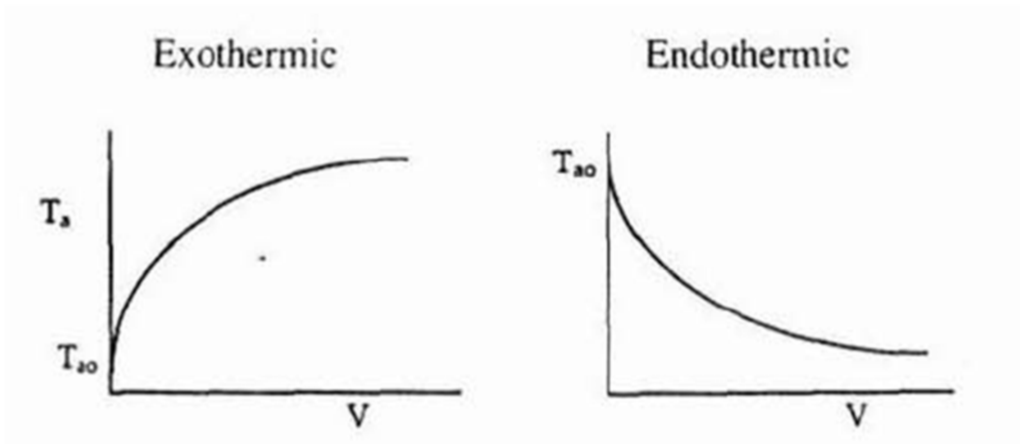
Tubular Reactor with Heat Exchange



Heat Transfer Fluid Temperature Profiles

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Equilibrium Conversion

➢ For the reversible liquid phase exothermic reaction

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

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

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

At equilibrium $\quad -r_A \equiv 0$

$$\Rightarrow \quad X_e = \frac{K_C}{1+K_C}$$

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Equilibrium Conversion

X_e can be calculated directly using Figure 8-4(a).

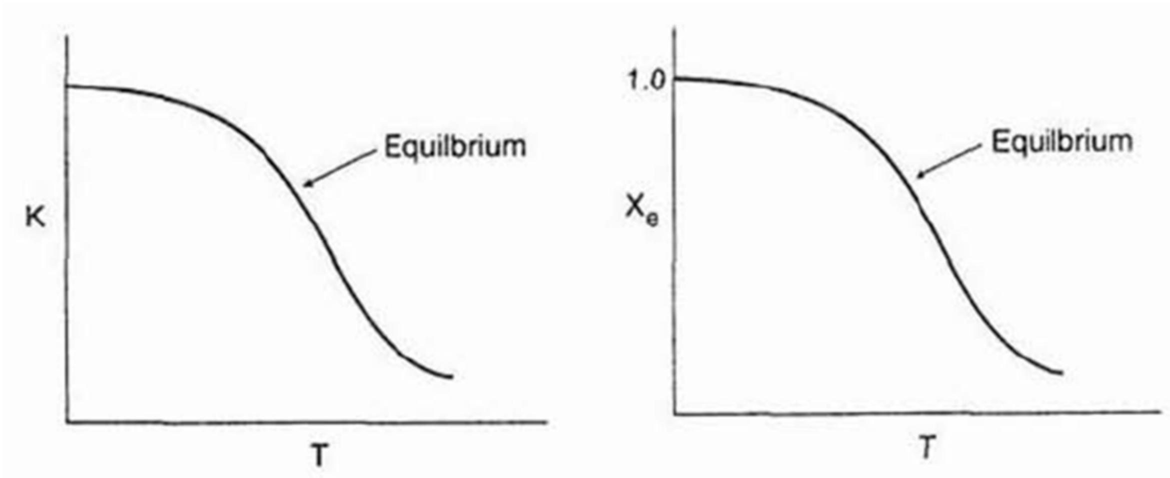


Figure 8-4 Variation of equilibrium constant and conversion with temperature for an exothermic reaction.

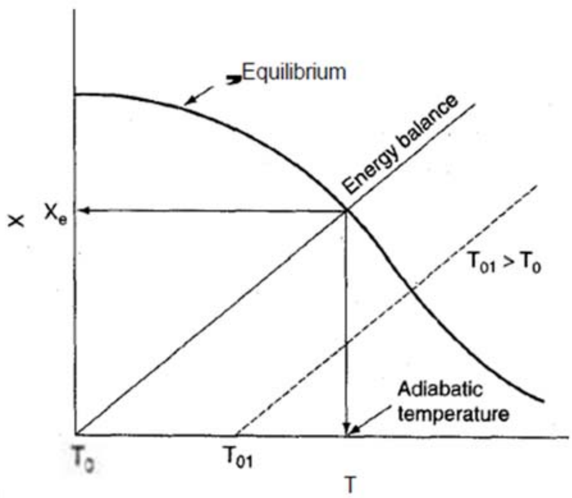
Equilibrium Conversion

- 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

$$X_{EB} = \frac{\sum \Theta_i \tilde{C}_{pi}(T - T_0)}{-\Delta H_{Rx}(T)}$$

If the entering temperature is increased from T_0 to T_{01},

The energy balance line will be shifted to the right **and** will be parallel to the original line, as shown by the dashed line



Example

For the elementary solid-catayzed liquid-phase reaction

$$A \rightleftarrows B$$

make a plot of equilibrium conversion as a function of temperature. Determine the adiabatic equilibrium temperature and conversion when pure A is fed to the reactor at a temperature of 300 K.

Additional information:

$$H_A^\circ(298\ K) = -40{,}000\ cal/mol \qquad H_B^\circ(298\ K) = -60{,}000\ cal/mol$$

$$C_{P_A} = 50\ cal/mol \cdot K \qquad C_{P_B} = 50\ cal/mol \cdot K$$

$$K_e = 100{,}000 \text{ at } 298\ K$$

Example Cont.

Example Cont.

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Example Cont.

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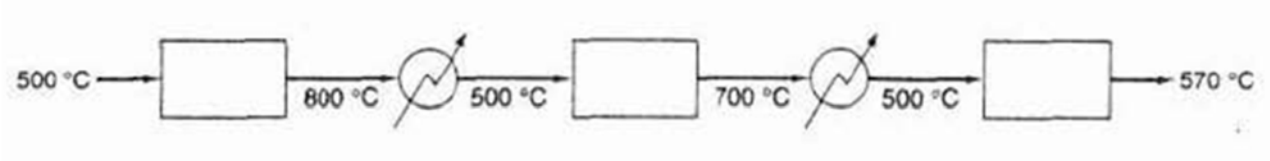
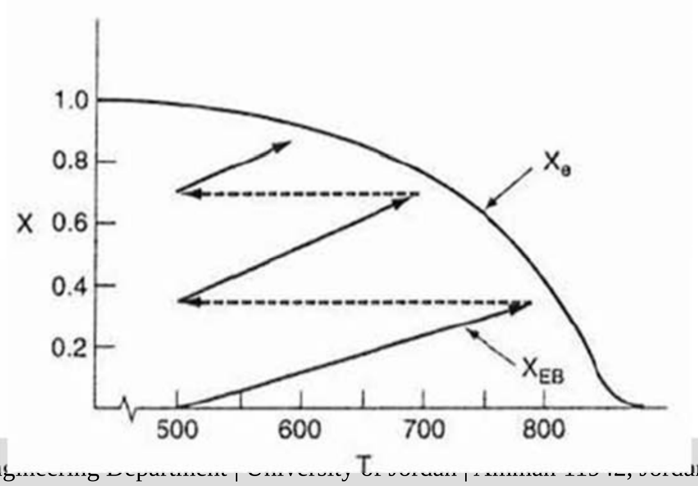
Equilibrium Conversion

Reactor Staging with Interstate Cooling of Heating

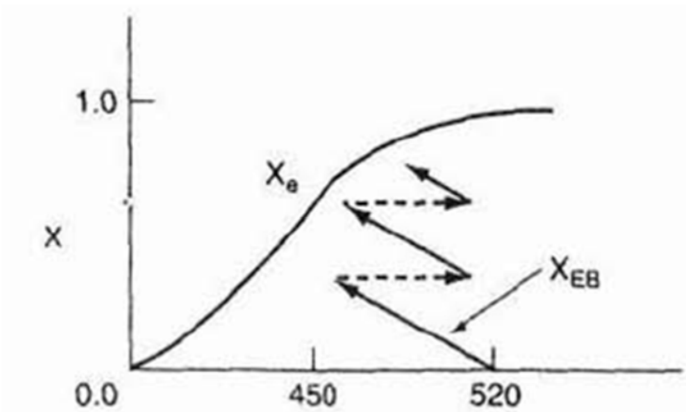
➢ Higher conversions can be achieved for adiabatic operations by connecting reactors in series with interstage cooling





Equilibrium Conversion

Endothermic Reactions.



Interstage heating

Temperature–conversion trajectory for interstage heating of an endothermic reaction

Example

What conversion could be achieved in Example 8-6 if two interstage coolers that had the capacity to cool the exit stream to 350 K were available? Also determine the heat duty of each exchanger for a molar feed rate of A of 40 mol/s. Assume that 95% of equilibrium conversion is achieved in each reactor. The feed temperature to the first reactor is 300 K.

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Example Cont.

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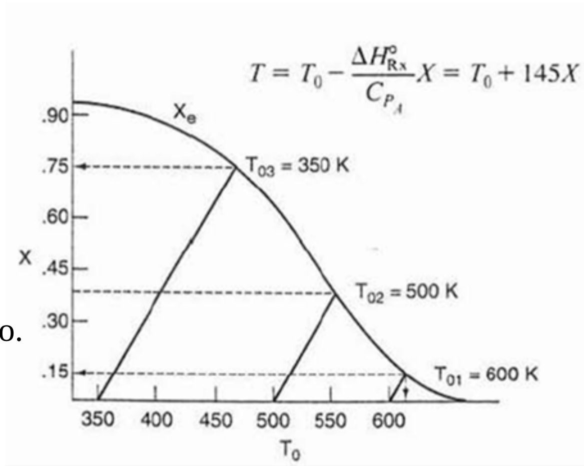
Example Cont.

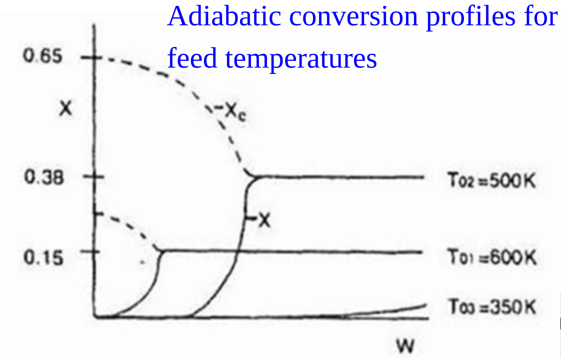
Equilibrium Conversion

Optimum Feed Temperature

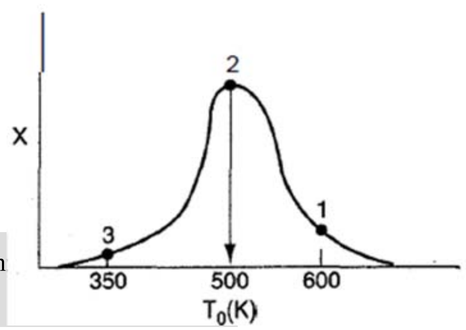
- The reaction is reversible and exothermic.
- At one temperature extreme, using a very high feed temperature, the specific reaction rate will be large and the reaction will proceed rapidly,
- But the equilibrium conversion will be close to zero.
- Consequently, very little product will be formed



Adiabatic conversion profiles for different feed temperatures



Finding the optimum Feed temperature



CSTR with Heat Effects

$$\dot{Q} - \dot{W}_s - F_{A0}\sum_{i=1}^{n}\int_{T_{i0}}^{T}\Theta_i C_{pi}\,dT - \left[\Delta H^\circ_{Rx}(T_R) + \int_{T_R}^{T}\Delta C_p\,dT\right]F_{A0}X = 0$$

OR for the case of *constant or mean heat capacities*

$$\dot{Q} - \dot{W}_s - F_{A0}\Sigma\Theta_i C_{P_i}(T - T_{i0}) - [\Delta H^\circ_{Rx}(T_R) + \Delta C_P(T - T_R)]F_{A0}X = 0$$

Where For CSTR $(F_{A0}X = -r_A V)$

➡ the steady-state balance

$$\dot{Q} - \dot{W}_s - F_{A0}\Sigma\Theta_i C_{P_i}(T - T_{i0}) + (r_A V)(\Delta H_{Rx}) = 0$$

$\dot{W}_s = 0$, $Q = 0$,

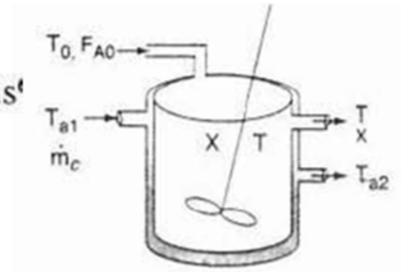
$$X = \frac{\sum \Theta_i \tilde{C}_{pi}(T - T_{io})}{-[\Delta H^\circ_{Rx}(T_R) + \Delta\hat{C}_p(T - T_R)]}$$

CSTR with Heat Effects

The $\dot{Q}$ Term in the CSTR

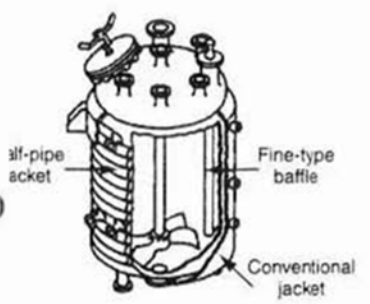
The rate of heat transfer *from* the exchanger *to* the reactor is

$$\dot{Q} = \frac{UA(T_{a1} - T_{a2})}{\ln[(T - T_{a1})/(T - T_{a2})]}$$



assume a quasi-steady state for the coolant flow (i.e., $dT_a/dt = 0$).

$$\begin{bmatrix}\text{Rate of}\\ \text{energy}\\ \textit{in}\\ \text{by flow}\end{bmatrix} - \begin{bmatrix}\text{Rate of}\\ \text{energy}\\ \textit{out}\\ \text{by flow}\end{bmatrix} - \begin{bmatrix}\text{Rate of}\\ \text{heat transfer}\\ \textit{from}\text{ exchanger}\\ \textit{to}\text{ reactor}\end{bmatrix} = 0$$



$$\dot{m}_c C_{P_c}(T_{a1} - T_R) - \dot{m}_c C_{P_c}(T_{a2} - T_R) - \frac{UA(T_{a1} - T_{a2})}{\ln(T - T_{a1})/(T - T_{a2})} = 0$$

where C_{P_C} is the heat capacity of the coolant fluid

CSTR with Heat Effects

$$\dot{Q} = \dot{m}_c C_{p_c}(T_{a1} - T_{a2}) = \frac{UA(T_{a1} - T_{a2})}{\ln(T - T_{a1})/(T - T_{a2})}$$

Solving for the exit temperature of the coolant fluid

$$T_{a2} = T - (T - T_{a1}) \exp\left(\frac{-UA}{\dot{m}_c C_{p_c}}\right)$$

But $\dot{Q} = \dot{m}_c C_{p_c}(T_{a1} - T_{a2})$

Substituting for T_{a2}

$$\dot{Q} = \dot{m}_c C_{p_c}\left\{(T_{a1} - T)\left[1 - \exp\left(\frac{-UA}{\dot{m}_c C_{p_c}}\right)\right]\right\}$$

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CSTR with Heat Effects

For large values of the coolant flow rate, the exponent will be small
expanded in a Taylor series ($e^{-x} = 1 - x + \cdots$)

$$\dot{Q} = \dot{m}_c C_{p_c}(T_{a1} - T)\left[1 - \left(1 - \frac{UA}{\dot{m}_c C_{p_c}}\right)\right]$$

Then $\dot{Q} = UA(T_a - T)$ where $T_{a1} \cong T_{a2} = T_a$.

$$\dot{Q} - \dot{W}_s - F_{A0}\Sigma\Theta_i C_{P_i}(T - T_{i0}) + (r_A V)(\Delta H_{Rx}) = 0$$

$\dot{W}_s = 0$, neglecting ΔC_P,

$$\frac{UA}{F_{A0}}(T_a - T) - \Sigma\Theta_i C_{p_i}(T - T_0) - \Delta H^\circ_{Rx} X = 0$$

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CSTR with Heat Effects

Solving for X

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

Rearranging

$$T = \frac{UAT_a + \sum F_{i0} C_{pi} T_0 + (-\Delta H_{Rx})(-r_A V)}{UA + \sum F_{i0} C_{pi}}$$

But $V = \frac{F_{A0} X}{-r_A(X,T)}$ by letting $\Sigma\Theta_i C_{P_i} = C_{P_0}$

$$C_{P_0}\left(\frac{UA}{F_{A0}C_{P_0}}\right)T_a + C_{P_0}T_0 - C_{P_0}\left(\frac{UA}{F_{A0}C_{P_0}} + 1\right)T - \Delta H^\circ_{Rx}X = 0$$

Let $\kappa = \frac{UA}{F_{A0}C_{P_0}}$ and $T_c = \frac{\kappa T_a + T_0}{1 + \kappa}$ Then $-X\Delta H^\circ_{Rx} = C_{P_0}(1 + \kappa)(T - T_c)$

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CSTR with Heat Effects

$$X = \frac{C_{P_0}(1 + \kappa)(T - T_c)}{-\Delta H^\circ_{Rx}}$$

$$T = T_c + \frac{(-\Delta H^\circ_{Rx})(X)}{C_{P_0}(1 + \kappa)}$$

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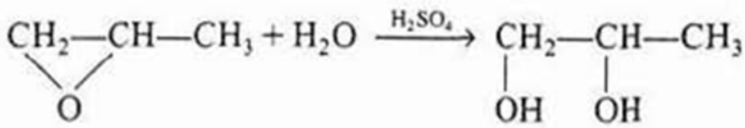
Example

Propylene glycol is produced by the hydrolysis of propylene oxide:



You are feeding 2500 lb/h (43.04 lb mol/h) of propylene oxide (P.O.) to the reactor. The feed stream consists of (1) an equivolumetric mixture of propylene oxide (46.62 ft^3/h) and methanol (46.62 ft^3/h), and (2) water containing 0.1 wt % H_2SO_4. The volumetric flow rate of water is 233.1 ft^3/h, which is 2.5 times the methanol–P.O. flow rate. The corresponding molar feed rates of methanol and water are 71.87 and 802.8 lb mol/h, respectively. The water–propylene oxide–methanol mixture undergoes a slight decrease in volume upon mixing

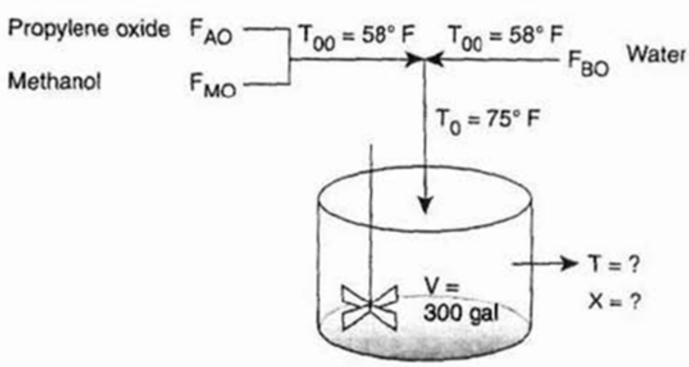
(approximately 3%), but you neglect this decrease in your calculations. The temperature of both feed streams is 58°F prior to mixing, but there is an immediate 17°F temperature rise upon mixing of the two feed streams caused by the heat of mixing. The entering temperature of all feed streams is thus taken to be 75°F (Figure E8-8.1).

Example Cont.

$k = Ae^{-E/RT} = 16.96 \times 10^{12}(e^{-32{,}400/RT})\ h^{-1}$ The units of E are Btu/lb mol.

not exceed an operating temperature of 125°F, 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?



Example Cont.

Example Cont.

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Example Cont.

Example

A cooling coil has been located in equipment storage for use in the hydration of propylene oxide discussed in Example 8-8. The cooling coil has 40 ft^2 of cooling surface and the cooling water flow rate inside the coil is sufficiently large that a constant coolant temperature of 85°F can be maintained. A typical overall heat-transfer coefficient for such a coil is 100 $Btu/h \cdot ft^2 \cdot °F$. Will the reactor satisfy the previous constraint of 125°F maximum temperature if the cooling coil is used?

Example Cont.

Example Cont.

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