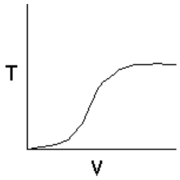
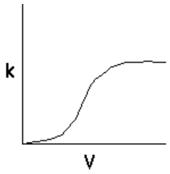
Ch 8: Steady – State Non-isothermal Reactor Design

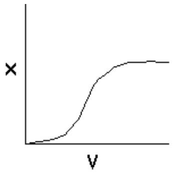
Energy Balances, Rationale and Overview

Calculate the volume necessary to achieve a conversion, X, in a PFR for a first-order, exothermic reaction carried out adiabatically.

For an adiabatic, exothermic reaction the temperature profile might look something like this:







The combined mole balance, rate law, and stoichiometry yield:

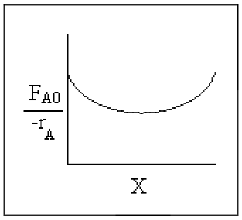
$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \qquad r_A = -k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] C_A$$

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

To solve this equation we need to relate **X** and **T**. We will use the **Energy Balance** to relate X and T. For example, for an adiabatic reaction, $A \rightarrow B$, the energy balance can be written in the form

$$T = T_0 + \frac{(-\Delta Hrx)X}{Cp_A}$$

set X, then calculate T, -V_A, and $\frac{F_{A0}}{-r_A}$, increment X, then plot $\frac{F_{A0}}{-r_A}$ vs. X



1. Adiabatic (Q = 0); CSTR, PFR, Batch and PBR:

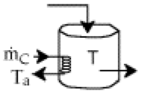
$$\dot{W}_s = \Delta\hat{C}_P = 0$$

$$\boxed{X_{EB} = \frac{\sum\theta_i\hat{C}_{P_i}(T-T_0)}{-\Delta H_{Rx}}}$$

$$X = \frac{\tilde{C}_{P_A}(T-T_0)}{-\Delta H_{Rx}}$$

$$\boxed{T = T_0 + \frac{(-\Delta H_{Rx})X}{\sum\theta_i C_{P_i}}}$$

2. CSTR with heat exchanger, UA(Ta-T) and large coolant flow rate.



$$\boxed{X_{EB} = \frac{\left(\frac{UA}{F_{A0}}(T-T_a)\right)+\sum\theta_i\tilde{C}_{P_i}(T-T_0)}{-\Delta H_{Rx}}}$$

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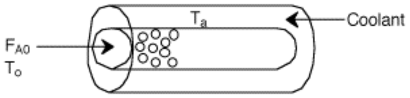
3 . PFR/PBR with heat exchange



3A. In terms of conversion, X

$$\boxed{\frac{dT}{dW} = \frac{\frac{Ua}{\rho_B}(T_a-T)+r'_A\Delta H_{Rx}(T)}{F_{A0}\left(\sum\theta_i\tilde{C}_{P_i}+\Delta C_P X\right)}}$$

3B. In terms of molar flow rates, F_i

$$\boxed{\frac{dT}{dW} = \frac{\frac{Ua}{\rho_B}(T_a-T)+r'_A\Delta H_{Rx_{ij}}(T)}{\sum F_i C_{P_i}}}$$

4. <u>For Multiple Reactions</u>

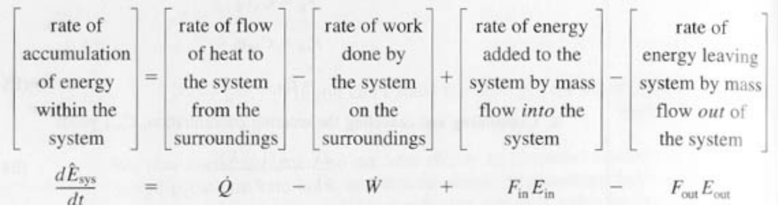
$$\boxed{\frac{dT}{dV} = \frac{\frac{Ua}{\rho_B}(T_a - T) + \Sigma r_{ij}\Delta H_{Rx_{ij}}}{\Sigma F_i C_{P_i}}}$$

5. <u>Coolant Balance</u>

$$\boxed{\frac{dT_A}{dV} = \frac{Ua(T - T_a)}{\dot{m}_c Cp_c}}$$

These are eq'ns we will use to solve rxn engineering problems with heat changes.

3. Energy Balance



$$\begin{bmatrix}\text{rate of}\\ \text{accumulation}\\ \text{of energy}\\ \text{within the}\\ \text{system}\end{bmatrix} = \begin{bmatrix}\text{rate of flow}\\ \text{of heat to}\\ \text{the system}\\ \text{from the}\\ \text{surroundings}\end{bmatrix} - \begin{bmatrix}\text{rate of work}\\ \text{done by}\\ \text{the system}\\ \text{on the}\\ \text{surroundings}\end{bmatrix} + \begin{bmatrix}\text{rate of energy}\\ \text{added to the}\\ \text{system by mass}\\ \text{flow } \textit{into} \text{ the}\\ \text{system}\end{bmatrix} - \begin{bmatrix}\text{rate of}\\ \text{energy leaving}\\ \text{system by mass}\\ \text{flow } \textit{out} \text{ of}\\ \text{the system}\end{bmatrix}$$

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

Typical units for each term are J/s; i.e. Watts

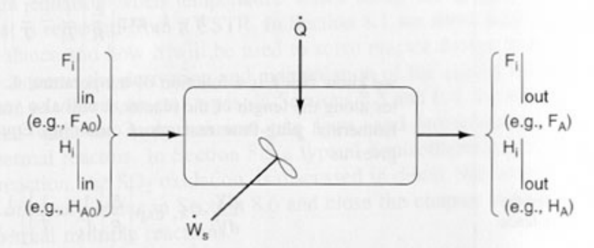


Figure 8-1 Energy balance on an open system: schematic.

Energy Balance

1st Law of Thermodynamics:

dE = dQ – dW (for a closed system)

Energy of the system

Heat flow to the system

Work done by the system on the surroundings

$$\frac{dE}{dt} = \dot{Q} - \dot{W} + \underbrace{F_{in} E_{in}}_{\text{rate of energy added to the system by mass flow}} - F_{out}\ E_{out} \qquad \{\text{for an open system}\}$$

Evaluation of the Work Term:

$$\dot{W} = \underset{\downarrow}{W_f} + \underset{\downarrow}{W_s}$$

flow shaft

$$= -\sum_{i=1}^{n} F_i \cdot P \cdot \tilde{V}_i \Big|_{in} + \sum_{i=1}^{n} F_i \cdot P \cdot \tilde{V}_i \Big|_{out} + W_s$$

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

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

$$\dot{Q} - \dot{W}_s + \sum F_{i0} E_{i0}\Big|_{IN} - \sum F_i E_i \Big|_{OUT} = \frac{dE_{system}}{dt} \qquad \textbf{(1)}$$

1. Replace E_i by $E_i = H_i - PV_i$
2. Express H_i in terms of enthalpies of formation and heat capacities
3. Express F_i in terms of either conversion or rates of reaction
4. Define ΔH_{RX}
5. Define ΔC_P
6. Manipulate so that the overall energy balance is either in terms of the Equations above 1.A, 1.B, 2, 3A, 3B, or 4 depending on the application

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Step 1:

Substitute

$$E_i = U_i\ , \qquad \dot{W} = \dot{W}_s + \sum F_{i0} P_{i0} \tilde{V}_{i0} - \sum F_i P_i \tilde{V}_i \quad \text{and} \quad H_i = U_i + P_i \tilde{V}_i$$

into equation (1) to obtain the General Energy Balance Equation.

General Energy Balance:

$$\boxed{\dot{Q} - \dot{W}_s + \sum F_{i0} H_{i0} - \sum F_i H_i = \frac{dE_{system}}{dt}}$$

For steady state operation:

$$\boxed{\dot{Q} - \dot{W}_s + \sum F_{i0} H_{i0} - \sum F_i H_i = 0}$$

We need to put the above equation into a form that we can easily use to relate X and T in order to size reactors. To achieve this goal, we write the molar flow rates in terms of conversion and the enthalpies as a function of temperature. We now will "dissect" both Fi and Hi.

Flow Rates, Fi

For the generalized reaction:

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

$$F_A = F_{A0}(1-X), \;\; F_B = F_{A0}\left(\Theta_B - \frac{b}{a}X\right) \qquad (2)$$

In general,

$$F_i = F_{A0}\,(\Theta_i + \nu_i\,X) \qquad \text{where} \;\; \Theta_i = \frac{F_{i0}}{F_{A0}} \qquad (3)$$

$$\nu_A = -1 \;\; \nu_B = -\frac{b}{a} \qquad \nu_C = \frac{c}{a} \qquad \nu_D = \frac{d}{a}$$

Then

$$\sum_{i=1}^{n} H_{i0}\cdot F_{i0} - \sum_{i=1}^{n} H_i \cdot F_i = F_{A0}\left[(H_{A0} - H_A) + (H_{B0} - H_B)\,\Theta_B\right] + \ldots\ldots\ldots\ldots$$

$$= F_{A0}\sum_{i=1}^{n}\left[(H_{i0} - H_i)\,\Theta_i\right] - \sum_{i=1}^{n}\left[\underbrace{(\nu_i \cdot H_i)}_{\Delta H_{RX}} F_{A0}\cdot X\right] \qquad (4)$$

$$\Delta H_{RX} = \frac{d}{a}H_D + \frac{c}{a}H_C - \frac{b}{a}H_B - H_A \qquad (5)$$

$$\sum F_{i0}\,H_{i0} - \sum F_i\,H_i = F_{A0}\sum \Theta_i\,(H_{i0} - H_i) - \Delta H_{RX}(T)\,F_{A0}\,X \qquad (6)$$

$$\text{for st - st}\left\{\frac{dE}{dt} = 0\right\}; \text{ combining (1) and (6):}$$

$$\dot{Q} - \dot{W} + F_{A0}\sum_{i=1}^{n}\Theta_i\,(H_{i0} - H_i) - \Delta H_{RX}(T)\,F_{A0}\,X = 0 \qquad (7)$$

If a phase change takes place, it will be included in ΔH_{RX}.

Assuming no phase change:

$$H_i = H_i^{o}(T_R) + \Delta H_{Qi} \qquad (8)$$

Enthalpy of formation at T_R (ref. temp.)

Change in enthalpy when T is changed from T_R to T.

If there is a phase change:

$$H_i = H_i^{o}(T_R) + \int_{T_R}^{T_M} C_{ps,i} \cdot dT + \Delta H_{mi}(T_m) + \int_{T_R}^{T} C_{pl,i}\, dT \qquad (9)$$

$$\Delta H_{Qi} = \int_{T_1}^{T_2} C_{pi} \cdot dT \quad \text{(if no phase change)} \qquad (10)$$

$$H_i = H_i^{o}(T_R) + \int_{T_R}^{T} C_{pi} \cdot dT \qquad (11)$$

$$C_p = \alpha_i + \beta_i \cdot T + \gamma_i \cdot T^2$$

$$H_i - H_{i0} = \int_{T_{i0}}^{T} C_{pi} \cdot dT = C_{pi} \cdot [T - T_{i0}] \qquad (12)$$

Substitute into (7) :

$$\boxed{\dot{Q} - \dot{W} + F_{A0} \sum_{i=1}^{n} \Theta_i \cdot C_{pi} \cdot [T - T_{i0}] - \Delta H_{RX}(T)\, F_{A0}\, X = 0} \qquad (13)$$

Combine eq'n (11) & (5)

$$\boxed{\Delta H_{RX} = \Delta H_{RX}^{o} + \Delta C_p\, (T - T_R)} \qquad (14)$$

where

$$\Delta H_{RX}^{o} = \frac{d}{a} H_D^{o}(T_R) + \frac{c}{a} H_C^{o}(T_R) - \frac{b}{a} H_B^{o}(T_R) - H_A^{o}(T_R) \qquad (15)$$

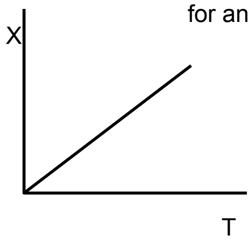
$$\Delta C_p = \frac{d}{a} C_{pD} + \frac{c}{a} C_{pC} - \frac{b}{a} C_{pB} - C_{pA} \qquad (16)$$

Combine (13) and (14)

$$\dot{Q} - \dot{W} + F_{A0}\sum_{i=1}^{n}\Theta_i \cdot C_{pi} \cdot [T - T_{i0}] - \left[\Delta H_{RX}{}^{o} + \Delta C_p\,(T - T_R)\right]\cdot F_{A0}\,X = 0 \qquad (17)$$

Adiabatic Operation:

$$\left.\begin{matrix}\dot{W}_s = 0\\ \dot{Q} = 0\end{matrix}\right\} \qquad X = \frac{\sum \Theta_i\,C_{pi}\,(T - T_{io})}{-\left[\Delta H_{RX}{}^{o} + \Delta C_p\,(T - T_R)\right]}$$



for an exothermic, adiabatic rxn

for an exo. rxn why does X increase?

This is from E balance, not mole balance.

$$\left|\Delta H_{RX}{}^{o}\right| > \left|\Delta C_p\,(T - T_R)\right|$$

so X vs T is linear!!!

Adiabatic Tubular Reactor

Rearrange (18):

$$T = \frac{X\cdot\left[-H_{RX}{}^{o}\right] + \sum \Theta_i \cdot C_{pi}\,T_o + X\cdot\Delta C_p\cdot T_R}{\sum \Theta_i \cdot C_{pi} + X\cdot\Delta C_p} \qquad (19)$$

Combine with differential mole balance:

$$F_{A0}\,\frac{dX}{dV} = -r_A\,(X, T) \qquad (20)$$

To obtain T, X and conc'n profiles along the reactor!

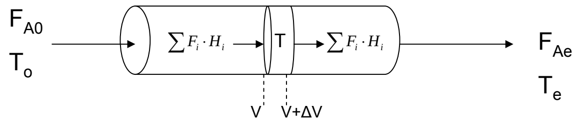
Use (19) to construct a table of T vs X.

Obtain k(T) as a function of X → $-r_A$ as a function of X.

Look at Table 8-2A.

Steady – State Tubular Reactor with Heat Exchange:

$$\Delta\dot{Q} = U \cdot \Delta A\,(Ta - T) = Ua \cdot (Ta - T) \cdot \Delta V \qquad \text{assume } \dot{W}s = 0$$



$$\Delta\dot{Q} + \sum F_i \cdot H_i\big|_V - \sum F_i \cdot H_i\big|_{V+\Delta V} = 0 \qquad (1)$$

The heat flow to the reactor $\Delta\dot{Q}$

Overall heat transfer coefficient (U)

Heat exchange area (ΔA)

Difference between ambient temperature (Ta) and reactor temperature (T)

$$\Delta\dot{Q} = U \cdot \Delta A\,(Ta - T) = Ua \cdot \Delta V \cdot (Ta - T) \qquad (2)$$

$\frac{A}{V} = \frac{4}{D}$ → Diameter of reactor

If ΔV → 0

$$Ua\,(Ta - T) = \frac{d \sum (F_i \cdot H_i)}{dV} \qquad (3)$$

$$\text{mole balance}: \frac{dF_i}{dV} = r_i = \nu_i\,(-r_A) \qquad (4)$$

diff. Eq'n (3)

$$Ua\,(Ta - T) = \frac{\sum dF_i}{dV} \cdot H_i - \sum F_i \frac{dH_i}{dV} \qquad (5)$$

$$H_i = C_{pi} \cdot dT$$

$$\frac{dH_i}{dV} = C_{pi} \cdot \frac{dT}{dV} \qquad (6)$$

Combine (5) & (4) & (6)

$$Ua\,(Ta - T) = \underbrace{\sum \nu_i \cdot H_i}_{\Delta H_{RX}} \cdot (-r_A) - \sum F_i \cdot C_{pi} \frac{dT}{dV} \qquad (7)$$

→ Rearrange:

$$\frac{dT}{dV} = \frac{\overbrace{r_A \cdot \Delta H_{RX}}^{\text{Heat generated}} - \overbrace{Ua\,(T - Ta)}^{\text{Heat removed}}}{\sum F_i \cdot C_{pi}} \qquad (8)$$

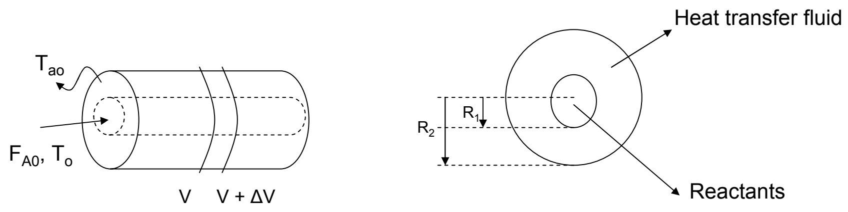
$$F_i = F_{A0} \cdot (\Theta + \nu_i\ X)$$

Substitute into (8) $$\frac{dT}{dV} = \frac{Ua\,(Ta - T) + r_A \cdot \Delta H_{RX}}{F_{A0} \cdot \left(\sum \Theta_i + \nu_i\ X + \Delta C_p \cdot X\right)} \qquad \{\text{for a PFR}\}$$

for a PBR {dW = ρ_b dV} $$\frac{dT}{dW} = \frac{\frac{Ua}{\rho_b} \cdot (Ta - T) + (r_A') \cdot \Delta H_{RX}}{\sum F_i \cdot C_{pi}}$$

These eq'ns will be coupled with mole balance eq'ns $$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

Balance on the Coolant Heat Transfer Fluid:



The fluid will keep the rxn temperature constant for endo/exo – thermic rxns

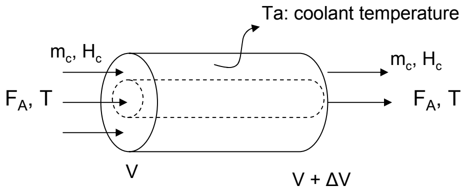
You might have

A. Co – current Flow

B. Counter – current Flow

A. Co – Current Flow

The Energy Balance



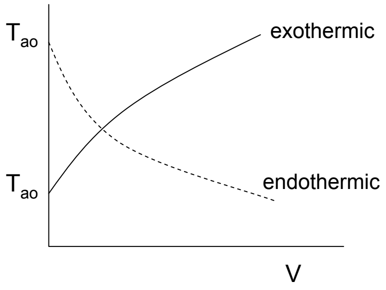
$$\dot{E}_{in}\Big|_{V} - \dot{E}_{out}\Big|_{V+\Delta V} + \dot{Q}_{conduction} = 0$$

$$\dot{m}_c\, H_c\Big|_{V} - \dot{m}_c\, H_c\Big|_{V+\Delta V} + Ua\,(T - Ta)\,\Delta V = 0$$

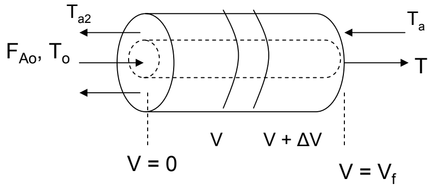
Divide by ΔV and take limit as ΔV → 0

$$\dot{m}_c \cdot \frac{dH_c}{dV} + Ua\,(T - Ta) = 0$$

$$\frac{dH_c}{dV} = C_p \frac{dT_a}{dV} \qquad \Rightarrow \frac{dT_a}{dV} = \frac{Ua\,(T - Ta)}{\dot{m}_c \cdot C_p}$$



B. Counter – Current Flow



$$\frac{dT_a}{dV} = \frac{Ua\,(Ta - T)}{\dot{m}_c \cdot C_{pc}}$$

At the entrance X = 0; V = 0; $T_a = T_{a2}$

At the exit V = V_f; $T_a = T_{ao}$

The sol’n to the counter-current flow problem to find {T X} is a trial & error procedure.

Assume a coolant temp at the entrance (T_{a2})

Solve ODEs to calculate X, T and Ta as a function of V:

Find $T_a(V = V_o)$

If $\left|T_a(V = V_o) - T_{a2}\right| < \varepsilon \rightarrow T_a(V = V_o) = T_{a2}$

Else assume another T_{a2}

Equilibrium Conversion

As T ↗ X ↗ {For endothermic rxns}

As T ↗ X ↘ {For exothermic rxns}

Exothermic Rxns:

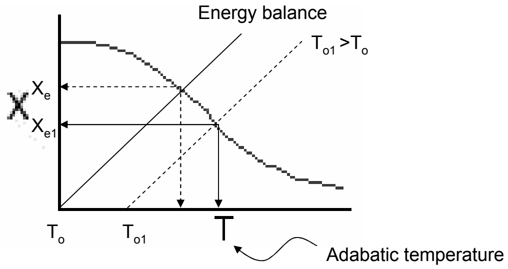
$$\mathrm{Xe} = \frac{\mathrm{Kc}}{1+\mathrm{Kc}} \quad \{\text{1st order rxn}\}$$

From Le Chaltlier's Law

(Kc ↘ as T ↗ if ΔH<0) exothermic

$$K_c = \frac{K_p}{(RT)^{\gamma}}$$

To find the max X in an exothermic rxn carried adiabatically:

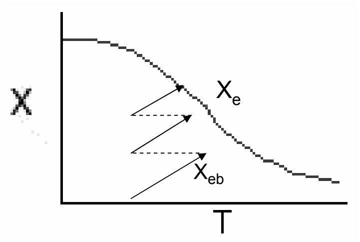


$$X_e = \frac{\sum \Theta_i \cdot C_{pi} \cdot (T - T_o)}{-\Delta H_{RXN}(T)}$$

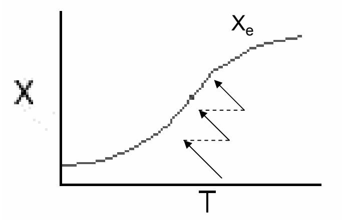
$$\left\{\begin{array}{l}\text{if } T_o \text{ is changed to } T_{o1} \\ \text{as } T \nearrow \; X_e \searrow\end{array}\right\}$$

$$\left\{\begin{array}{l}\dfrac{d\ln K_p}{dT} = \dfrac{\Delta H_{RXN}(T)}{R \cdot T^2} = \dfrac{\Delta H^o{}_{RXN}(T_R) + \Delta \tilde{C}_p (T - T_R)}{R \cdot T^2} \\ \text{if } \Delta \tilde{C}_p = 0 \\ K_p(T_2) = K_p(T_1)\exp\left\{\dfrac{\Delta H^o{}_{RXN}(T_R)}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)\right\}\end{array}\right\}$$

To increase the conversion in an exothermic rxn, use multiple reactors with interstate cooling:



For Endothermic Rxn (you need heating)



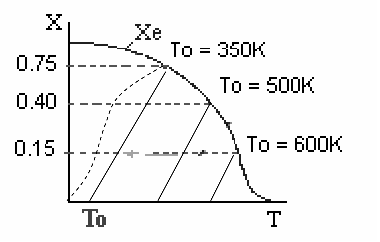
Optimum Feed Temperature

Adiabatic Reactor of fixed size

Reversible & Exothermic Rxn

$$T = T_o - \frac{\Delta H_{rx}}{C_{pA}} \cdot X$$

if $\Delta H_{rx} < 0$ as X ↗ ; T ↗



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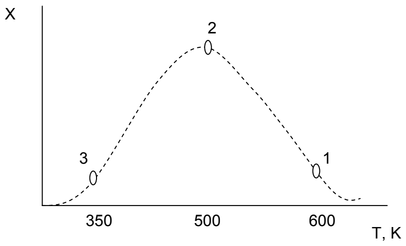


As T ↗ Xe ↗ but the $(-r_A)$ decreases!

(so the conversion is achieved at the end of the reactor)

So there must be an optimum temperature to achieve max X.

Curve A: Rxn rate slow, rxn dictated by rate of rxn and reactor volume

As T ↗ , r ↗ , X ↗

Curve B: Rxn rate very rapid. Virtual equilibrium reached in X dictated by equilibrium conversion

Adiabatic Rxn Algorithm

Suppose $A \Leftrightarrow 2B$

1. Choose X

Calculate T $T = T_0 - \frac{\Delta H_{RX} X}{\sum \theta_i C_{pi}}$

Calculate k $k = Ae^{-E/RT}$

Calculate T/T$_o$

Calculate C$_A$ $C_A = \frac{C_{A0}(1-X)}{1+\varepsilon X}\left(\frac{T}{T_0}\right)$

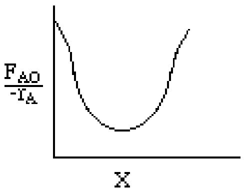
Calculate C$_B$ $C_B = \frac{C_{A0}X}{1+\varepsilon X}\left(\frac{T}{T_0}\right)$

Calculate K$_C$ $K_C = K_{C1}\exp\left[\frac{\Delta H_{RX}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$

Calculate -r$_A$ $-r_A = k\left(C_A - \frac{C_B^2}{K_C}\right)$

2. Increment X and then repeat calculations.

3. When finished, plot $\frac{F_{A0}}{-r_A}$ vs. X or use some numerical technique to find V.



Levenspiel Plot for an exothermic, adiabatic reaction.

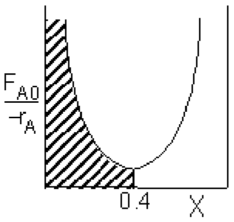
Consider:

CSTR: $V_1 = \left(\frac{F_{Ao}}{-r_{A1}}\right)X_1$ $\qquad$ $V_2 = \left(\frac{F_{Ao}}{-r_{A2}}\right)(X_2 - X_1)$

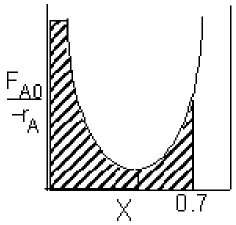
PFR: $V_1 = \int_0^{X_1}\left(\frac{F_{Ao}}{-r_A}\right)dX$ $\qquad$ $V_2 = \int_{X_1}^{X_2}\left(\frac{F_{Ao}}{-r_A}\right)dX$

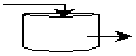
PFR Shaded area is the volume.

For an exit conversion of 40%

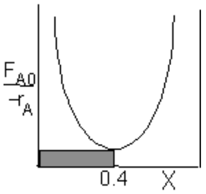


For an exit conversion of 70%

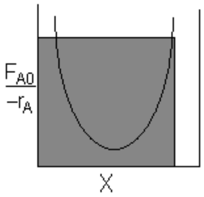


CSTR  Shaded area is the reactor volume.

For an exit conversion of 40%

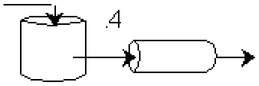


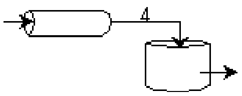
For an exit conversion of 70%



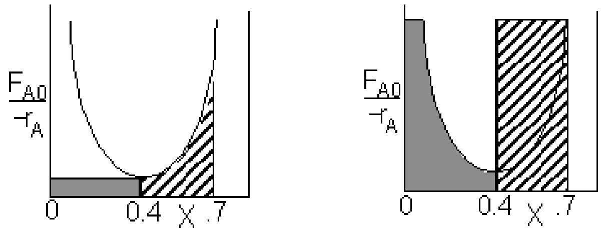
We see for 40% conversion very little volume is required.

CSTR+PFR



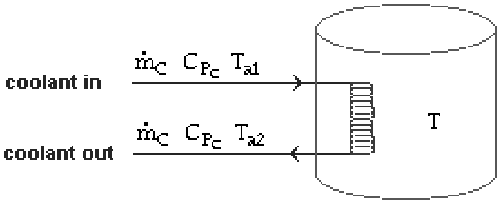


For an intermediate conversion of 40% and exit conversion of 70%



Looks like the best arrangement is a CSTR with a 40% conversion followed by a PFR up to 70% conversion.

Evaluating the Heat Exchanger Term



Energy transferred between the reactor and the coolant:

$$\dot{Q} = \dot{m}_C C_{Pc} \left(T_{a1} - T_{a2}\right)$$

Assuming the temperature inside the CSTR, T, is spatially uniform:

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

At high coolant flow rates the exponential term will be small, so we can expand the exponential term as a Taylor Series, where the terms of second order or greater are neglected, then:

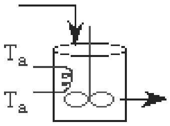
$$\dot{Q} = UA\left(T_{a1} - T\right)$$

Since the coolant flow rate is high, $T_{a1} \cong T_{a2} \cong T_a$:

$$\boxed{\dot{Q} = UA\left(T_a - T\right)}$$

Multiple Steady States (MSS)

$$\dot{Q} - \dot{W}_S - F_{A0}\,\Sigma\,\Theta_i \tilde{C}_{Pi}\left(T - T_0\right) + \left(r_A V\right)\left(\Delta H_R(T)\right) = \Sigma N_i C_{Pi}\frac{dT}{dt}$$



$\dot{W}_S \cong 0$

$$\left[X\left(-\Delta H_R(T)\right)\right] - \left[C_{P0}(1+\kappa)\left(T - T_C\right)\right] = \left(\frac{\Sigma N_i C_{Pi}}{F_{A0}}\right)\frac{dT}{dt}$$

$$G(T) \quad - \quad R(T) = \left(\frac{\Sigma N_i C_{Pi}}{F_{A0}}\right)\frac{dT}{dt}$$

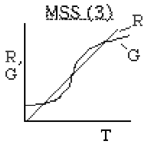
where

$$\boxed{G(T) = \left(\frac{-r_A V}{F_{A0}}\right)\left(-\Delta H_R(T)\right) = X\left(-\Delta H_R(T)\right)}$$

Heat generated term

$$\boxed{R(T) = C_{P0}\left(1+\kappa\right)\left(T - T_C\right)}$$

Heat removed term

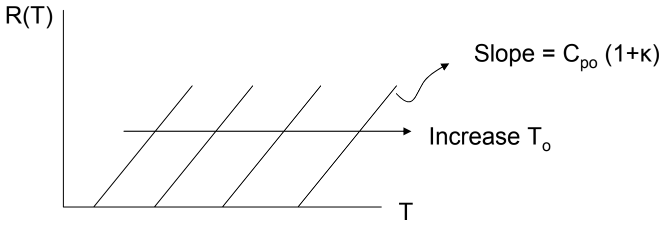


R > G: Temp. will decrease

R < G: Temp. will increase

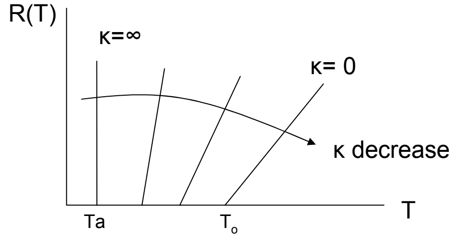
R(T):

Varying Entering Temperature



Vary non-adiabatic parameter κ:

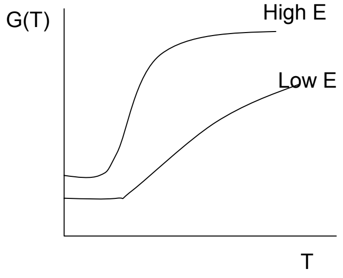
if you increase F_{A0} (molar flow rate) or decrease heat – exch area then κ will decrease

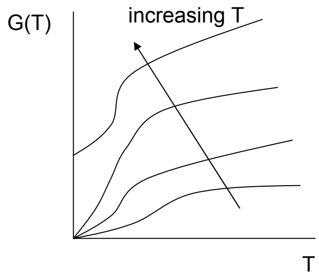


$$\left\{ \kappa = \frac{\mathrm{Ua}}{\mathrm{F_{A0}\ C_{p0}}} \right\}$$

$$\mathrm{T_c} = \frac{\mathrm{T_0} + \kappa \cdot \mathrm{T_a}}{1 + \kappa}$$

G(T)





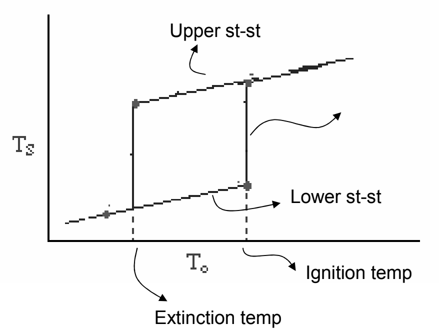
For a first order rxn:

$$X = \frac{\tau \cdot k}{1 + \tau \cdot k}$$

Ignition – Extinction Curve:

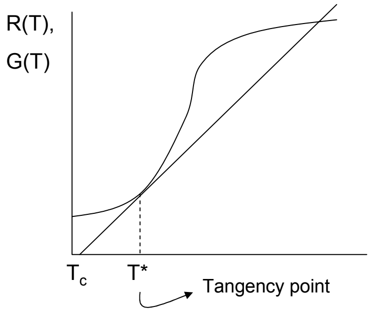
The point of intersection of G(T) and R(T) give $T_{st\text{-}st}$.

By plotting $T_{st\text{-}st}$ vs T_o, we obtain ignition – extinction curve.



As T_o ↗ $T_{st\text{-}st}$ ↘

Runaway Rxns in a CSTR:



$$T_c = \frac{T_0 + \kappa \cdot T_a}{1 + \kappa}$$

$$\Delta T_{rc} = T^* - T_c = \frac{R \cdot T^{*2}}{E}$$

Reactor T

if this diff. is exceeded, transition to the upper st – st will occur.

At this high temp, it is undesirable or even dangerous.

PFR

$$\frac{dT}{dV} = \frac{Ua\,(T_a - T) + (-r_A)(-\Delta H_{Rxn}(T))}{\sum_{i=1}^{m} F_i\, C_{pi}} \qquad \text{(for a single rxn)}$$

When q multiple rxns occur with m species:

$$\frac{dT}{dV} = \frac{Ua\,(T_a - T) + \sum_{i=1}^{q} (-r_{ij})\left[-\Delta H_{Rxn,ij}(T)\right]}{\sum_{j=1}^{m} F_j\, C_{pj}} \qquad \begin{array}{l} i: \text{rxn} \\ j: \text{species} \end{array}$$

Ex: Rxn 1:

$$A \xrightarrow{k_1} B$$

$$B \xrightarrow{k_2} C$$

$$\frac{dT}{dV} = \frac{Ua\,(T_a - T) + (-r_{1A})\left[-\Delta H_{Rxn,1A}(T)\right] + (-r_{2B})\left[-\Delta H_{Rxn,2B}(T)\right]}{F_A\, C_{pA} + F_B\, C_{pB} + F_C\, C_{pC}}$$

CSTR

$$\dot{Q} - \dot{W}_s + F_{A0} \sum_{i=1}^{n} \Theta_i \cdot C_{pi} \cdot [T - T_0] - \left[\Delta H_{RXN}(T)\right] \cdot \left[r_A V\right] = 0 \quad \text{(for a single rxn)}$$

When q multiple rxns take place

$$\dot{Q} - \cancelto{0}{\dot{W}_s} + F_{A0} \sum_{i=1}^{n} \Theta_i \cdot C_{pi} \cdot [T - T_0] - V \cdot \sum_{i=1}^{q} r_{ij} \Delta H_{RXN,ij}(T) = 0$$

$$UA(T_a - T) + F_{A0} \sum_{i=1}^{n} \Theta_i \cdot C_{pi} \cdot [T - T_0] - V \cdot \sum_{i=1}^{q} r_{ij} \Delta H_{RXN,ij}(T) = 0$$

CHAPTER 9

Nonisothermal Reactors

9.1 | The Nature of the Problem

In Chapter 3, the isothermal material balances for various ideal reactors were derived (see Table 3.5.1 for a summary). Although isothermal conditions are most useful for the measurement of kinetic data, real reactor operation is normally nonisothermal. Within the limits of heat exchange, the reactor can operate isothermally (maximum heat exchange) or adiabatically (no heat exchange); recall the limits of reactor behavior given in Table 3.1.1. Between these bounds of heat transfer lies the most common form of reactor operation—the nonisothermal regime (some extent of heat exchange). The three types of reactor operations yield different temperature profiles within the reactor and are illustrated in Figure 9.1.1 for an exothermic reaction.

If a reactor is operated at nonisothermal or adiabatic conditions then the material balance equation must be written with the temperature, T, as a variable. For example with the PFR, the material balance becomes:

$$\frac{dF_i}{dV_R} = \upsilon_i \mathrm{r}(F_i, T) \tag{9.1.1}$$

Since the reaction rate expression now contains the independent variable T, the material balance cannot be solved alone. The solution of the material balance equation is only possible by the simultaneous solution of the energy balance. Thus, for nonisothermal reactor descriptions, an energy balance must accompany the material balance.

9.2 | Energy Balances

Consider a generalized flow reactor as illustrated in Figure 9.2.1. Applying the first law of thermodynamics to the reactor shown in Figure 9.2.1, the following is obtained:

$$\begin{aligned} Q - (\overline{W}_s + P_{\text{out}} V_{\text{out}} - P_{\text{in}} V_{\text{in}}) = {} & \overline{U}_{\text{out}} + \overline{m}_{\text{out}}\left(\overline{z}_{\text{out}} (g/g_c) + \tfrac{1}{2} u_{\text{out}}^2/g_c\right) \\ & - \overline{U}_{\text{in}} - \overline{m}_{\text{in}}\left(\overline{z}_{\text{in}} (g/g_c) + \tfrac{1}{2} u_{\text{in}}^2/g_c\right) \end{aligned} \tag{9.2.1}$$

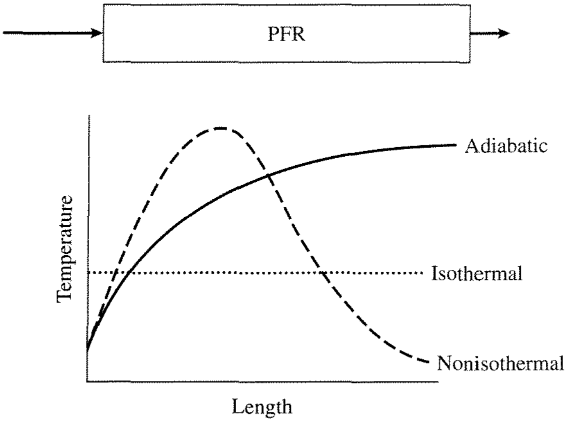


Figure 9.1.1 |
Temperature profiles in a PFR accomplishing an exothermic reaction.

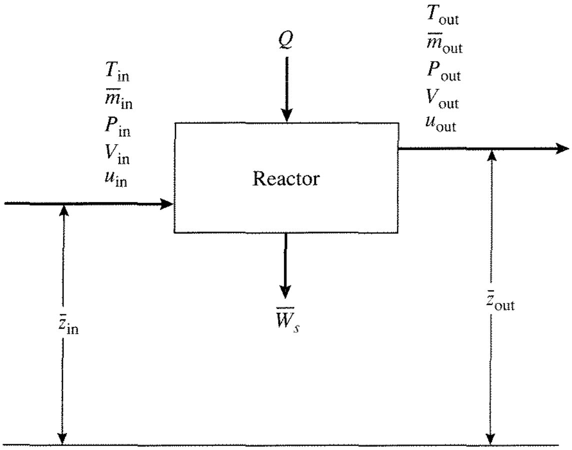


Figure 9.2.1 |
Schematic of flow reactor and energy terms.

where $\overline{W}_s$ is "shaft work," that is, pump or turbine work, $\overline{U}_i$ is the internal energy of stream i, $\overline{m}_i$ is the mass of stream i, P_i is the pressure of stream i, V_i is the volume of mass i, u_i is the velocity of stream i, $\overline{z}_i$ is the height of stream i above a datum plane, and g_c is the gravitational constant, for i denoting either the outlet or inlet stream. For most normal circumstances:

$$\overline{W}_s = 0 \tag{9.2.2}$$

and

$$\overline{m}_{\text{out}}\left(\bar{z}_{\text{out}}(g/g_c) + \tfrac{1}{2}u_{\text{out}}^2/g_c\right) \cong \overline{m}_{\text{in}}\left(\bar{z}_{\text{in}}(g/g_c) + \tfrac{1}{2}u_{\text{in}}^2/g_c\right)$$

Using these assumptions to simplify Equation (9.2.1) yields:

$$Q = (\overline{U}_{\text{out}} + P_{\text{out}}V_{\text{out}}) - (\overline{U}_{\text{in}} + P_{\text{in}}V_{\text{in}}) \tag{9.2.3}$$

Recall that the enthalpy, H, is:

$$H = \overline{U} + PV \tag{9.2.4}$$

Thus, Equation (9.2.3) can be written as:

$$Q = H_{\text{out}} - H_{\text{in}} \tag{9.2.5}$$

However, since it is more typical to deal with rates of energy transfer, $\dot{Q}$, rather than energy, Q, when dealing with reactors, Equation (9.2.5) can be differentiated with respect to time to give:

$$\dot{Q} = h_{\text{out}}\dot{m}_{\text{out}} - h_{\text{in}}\dot{m}_{\text{in}} \tag{9.2.6}$$

where $\dot{Q}$ is the rate of heat transfer, h_i is the enthalpy per unit mass of stream i, and $\dot{m}$ is the mass flow rate of stream i. Generalizing Equation (9.2.6) to multi-input, multi-output reactors yields a generalized energy balance subject to the assumptions stated above:

$$\dot{Q} = \sum_{\substack{\text{outlet}\\\text{streams}}} h_{\text{out}}\dot{m}_{\text{out}} - \sum_{\substack{\text{inlet}\\\text{streams}}} h_{\text{in}}\dot{m}_{\text{in}} \qquad \left(\begin{array}{c}\text{conservation}\\\text{of energy}\end{array}\right) \tag{9.2.7}$$

$$0 = \sum_{\substack{\text{outlet}\\\text{streams}}} \dot{m}_{\text{out}} - \sum_{\substack{\text{inlet}\\\text{streams}}} \dot{m}_{\text{in}} \qquad \left(\begin{array}{c}\text{conservation}\\\text{of mass}\end{array}\right) \tag{9.2.8}$$

Note that the enthalpy includes sensible heat and heat of reaction effects as will be illustrated below.

For a closed reactor (e.g., a batch reactor), the potential and kinetic energy terms in Equation (9.2.1) are not relevant. Additionally, $\overline{W}_s \cong 0$ for most cases (including the work input from the stirring impellers). Since most reactions carried out in closed reactors involve condensed phases, $\Delta(PV)$ is small relative to $\Delta\overline{U}$, and for this case is:

$$Q = \Delta\overline{U} = \overline{U}_{\text{products}} - \overline{U}_{\text{reactants}} \tag{9.2.9}$$

or from Equations (9.2.9) and (9.2.4):

$$Q = \Delta H, PV = \text{constant} \qquad \text{(conservation of energy)} \tag{9.2.10}$$

9.3 | Nonisothermal Batch Reactor

Consider the batch reactor schematically illustrated in Figure 9.3.1. Typically, reactants are charged into the reactor from point (I), the temperature of the reactor

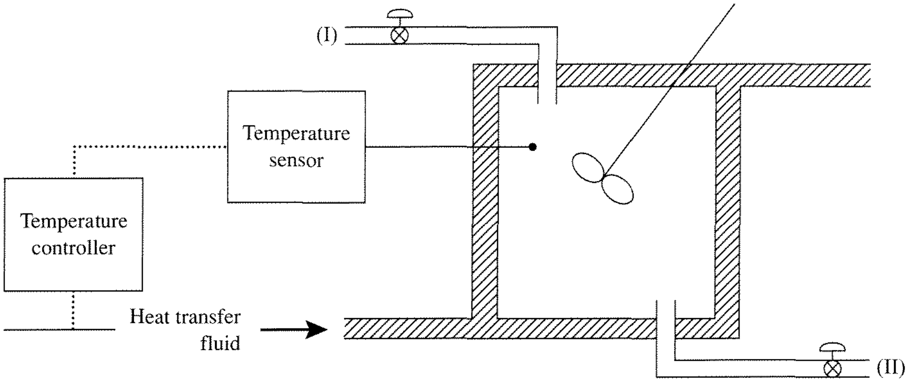


Figure 9.3.1 |
Schematic of a batch reactor.

is increased by elevating the temperature in the heat transfer fluid, a temperature maximum is reached, the reactor is then cooled by decreasing the temperature of the heat transfer fluid and products discharged via point (II).

To describe this process, material and energy balances are required. Recall that the mass balance on a batch reactor can be written as [refer to Equation (3.2.1)]:

$$\frac{1}{V}\frac{dn_i}{dt} = v_i \mathrm{r}(n_i, T) \tag{9.3.1}$$

If in the rare case that the reactor is accomplishing a constant pressure gas-phase reaction at nonisothermal conditions:

$$V = V_0(1 + \varepsilon_i f_i)\left(\frac{T}{T^0}\right) \tag{9.3.2}$$

To solve the mass balance, it must be accompanied by the simultaneous solution of the energy balance (i.e., the solution of Equation (9.2.9)). To do this, Equation (9.2.9) can be written in more convenient forms. Consider that the enthalpy contains both sensible heat and heat of reaction effects. That is to say that Equation (9.2.10) can be written as:

heat exchange = (change in sensible heat effects)
+ (the energy consumed or released
by reaction) (9.3.3)

or

$$Q = \int_{T_{\text{initial}}, \Phi_{\text{initial}}}^{T_{\text{final}}, \Phi_{\text{final}}} \left(\overline{MS}\langle \overline{C}_p \rangle dT + \Delta H_r d\Phi\right) \tag{9.3.4}$$

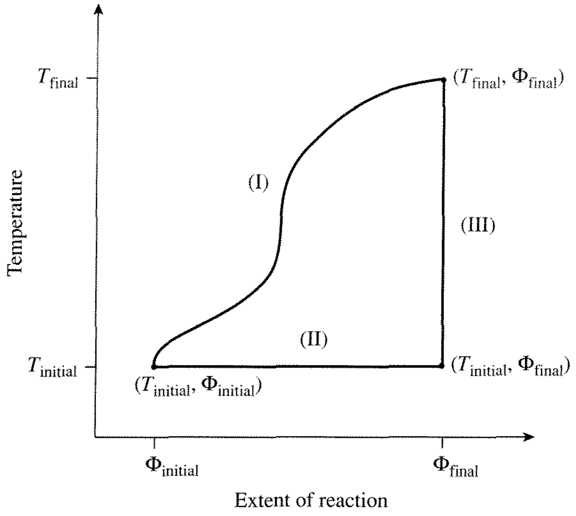


Figure 9.3.2 |
Enthalpy pathways.

where Φ is the extent of reaction (see Chapter 1), ΔH_r is the heat of reaction, $\overline{MS}$ is the total mass of the system, and $\langle \overline{C}_p \rangle$ is an average heat capacity per unit mass for the system. Since enthalpy is a state variable, the solution of the integral in Equation (9.3.4) is path independent. Referring to Figure 9.3.2, a simple way to analyze the integral [pathway (I)] is to allow the reaction to proceed isothermally [pathway (II)] and then evaluate the sensible heat changes using the product composition [pathway (III)]. That is,

$$Q = \Delta H_r|_{T_{\text{initial}}}(\Phi_{\text{final}} - \Phi_{\text{initial}}) + \int_{T_{\text{initial}}}^{T_{\text{final}}} \overline{MS}_{\text{final}} \langle C_{p_{\text{final}}} \rangle dT \tag{9.3.5}$$

where a positive value for the heat of reaction denotes an endothermic reaction. Since the reaction-rate expressions normally employ moles of species in their evaluation:

$$\int_{T_{\text{initial}}}^{T_{\text{final}}} \overline{MS}_{\text{final}} \langle \overline{C}_{p_{\text{final}}} \rangle dT = \int_{T_{\text{initial}}}^{T_{\text{final}}} \sum_i (n_i C_{p_i}) dT \tag{9.3.6}$$

where n_i is the moles of species i, and C_{p_i} is the molar heat capacity of species i. Note also that the heat exchange is the integral over time of the heat transfer rate, that is,

$$Q = \int \dot{Q} dt = \int U A_H (T^* - T) dt \tag{9.3.7}$$

where U is an overall heat transfer coefficient, A_H is the heat transfer area, and T^* is the reference temperature. Combining Equations (9.3.7), (9.3.6), and (9.3.5) and recalling the definition of the extent of reaction in terms of the fractional conversion [Equation (1.2.10)] gives:

$$\int_0^t UA_H(T^* - T)d\bar{t} = \frac{-\Delta H_r|_{T^0}}{v_\ell} n_\ell^0 f_\ell + \sum_i \left(n_i \int_{T_{\text{initial}}}^{T_{\text{final}}} C_{p_i} dT \right) \tag{9.3.8}$$

or in differential form:

$$UA_H(T^* - T) = \frac{-\Delta H_r|_{T^0}}{v_\ell} n_\ell^0 \frac{df_\ell}{dt} + \sum_i (n_i C_{p_i}) \frac{dT}{dt} \tag{9.3.9}$$

Notice that [see Equations (1.2.10) and (1.3.2)]:

$$\frac{n_\ell^0}{-v_\ell} \frac{df_\ell}{dt} = \frac{d\Phi}{dt} = \mathrm{r}V \tag{9.3.10}$$

Using Equation (9.3.10) in Equation (9.3.9) yields:

$$UA_H(T^* - T) = \Delta H_r|_{T^0} \mathrm{r}V + \sum_i (n_i C_{p_i}) \frac{dT}{dt} \tag{9.3.11}$$

Equations (9.3.11), (9.3.9), and (9.3.8) each define the energy balance for a batch reactor.

EXAMPLE 9.3.1

Show that the general energy balance, Equation (9.3.9), can simplify to an appropriate form for either adiabatic or isothermal reactor operation.

■ Answer

For adiabatic operation there is no heat transfer to the surroundings (i.e., $U = 0$). For this case, Equation (9.3.9) can be written as:

$$0 = \frac{-\Delta H_r|_{T^0}}{v_\ell} n_\ell^0 \frac{df_\ell}{dt} + \sum_i (n_i C_{p_i}) \frac{dT}{dt}$$

or when integrated as:

$$T = T^0 + \frac{\Delta H_r|_{T^0} n_\ell^0 f_\ell}{v_\ell \sum_i (n_i C_{p_i})} \tag{9.3.12}$$

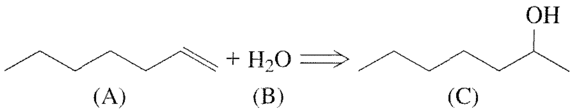
If the reactor is operated at isothermal conditions, then no sensible heat effects occur and Equation (9.3.9) becomes:

$$UA_H(T^* - T^0) = \frac{-\Delta H_r|_{T^0}}{v_\ell} n_\ell^0 \frac{df_\ell}{dt} \tag{9.3.13}$$

The description of the nonisothermal batch reactor then involves Equation (9.3.1) and either Equation (9.3.9) or (9.3.11) for nonisothermal operation or Equation (9.3.12) for adiabatic operation. Notice that for adiabatic conditions, Equation (9.3.12) provides a relationship between T and f_ℓ. Insertion of Equation (9.3.12) into Equation (9.3.1) allows for direct solution of the mass balance.

EXAMPLE 9.3.2

The hydration of 1-hexene to 2-hexanol is accomplished in an adiabatic batch reactor:



The reactor is charged with 1000 kg of a 10 wt. % H_2SO_4 solution and 200 kg of 1-hexene at 300 K. Assuming that the heat capacities for the reactants and products do not vary with temperature, the heat of reaction does not vary with temperature, and the presence of H_2SO_4 is ignored in the calculation of the heat capacity, determine the time required to achieve 50 percent conversion and the reactor temperature at that point.

Data:

	C_p (cal/(mol-K))	ΔH_f^0 (kcal/mol)
1-hexene	43.8	−10.0
H_2O	16.8	−68.0
2-hexanol	54.0	−82.0

reaction rate constant: $k = 10^4 \exp[-10^4/(R_g T)]$ (s^{-1})

■ Answer

The material balance on the batch reactor is:

$$\frac{dC_A}{dt} = -kC_A$$

or

$$\frac{df_A}{dt} = k(1 - f_A)$$

since the reaction is first-order (units on k and large excess of water; 1-hexene is the limiting reagent). The energy balance is:

$$T = T^0 + \frac{\Delta H_r|_{T^0} n_\ell^0 f_\ell}{\upsilon_\ell \sum_i (n_i C_{p_i})}$$

where $\upsilon_\ell = -1$. In order to calculate the heat of reaction, the standard heats of formation can be used as follows:

$$\Delta H_r^0 = -82 + 68 + 10 = -4 \text{ kcal/mol}$$

Thus, the energy balance equation can be written:

$$T = T^0 + \frac{(4000)\, n_A^0 f_A}{n_A^0 (1 - f_A) C_{p_A} + n_A^0 (\overline{M} - f_A) C_{p_B} + n_A^0 f_A C_{p_C}}$$

where

$$\overline{M} = n_B^0 / n_A^0$$

The values of n_A^0 and n_B^0 are:

$$n_A^0 = (2 \times 10^5\,\text{g})(1\,\text{mol}/84\,\text{g}) = 2381\,\text{mol}$$
$$n_B^0 = (9 \times 10^5\,\text{g})(1\,\text{mol}/18\,\text{g}) = 50000\,\text{mol}$$

so that:

$$n_B^0 / n_A^0 = 21$$

By placing the values for n_A^0, $\overline{M}$, T^0, and the C_p into the energy balance, the result is:

$$T = 300 + \frac{4000\, f_A}{421.8 - 7.8\, f_A}$$

The material balance equation is then solved with $k(T)$ being first converted to $k(f_A)$ by substitution of the energy balance for T:

$$k = 10^4 \exp\left[\frac{-10^4}{R_g\left(300 + \dfrac{4000\, f_A}{421.8 - 7.8\, f_A}\right)}\right]$$

The material balance equation must be solved numerically to give $t = 1111$ s or 18.52 min. The reactor temperature at this point is obtained directly from the energy balance with $f_A = 0.5$ to give $T = 304.8$ K.

EXAMPLE 9.3.3

Consider accomplishing the reaction $A + B \Rightarrow C$ in a nonisothermal batch reactor. The reaction occurs in the liquid phase. Find the time necessary to reach 80 percent conversion if the coolant supply is sufficient to maintain the reactor wall at 300 K.

Data:

$C_A^0 = 0.5$ mol/L $\qquad \Delta H_r = -15$ kJ/mol

$C_B^0 = 0.6$ mol/L $\qquad UA_H = 50$ J/(s-K)

$C_{p_A} = C_{p_B} = 65$ J/(mol-K) $\qquad C_{p_C} = 150$ J/(mol-K)

$n_A^0 = 100$ mol

$$k = 5 \times 10^{-3} \exp\left[\frac{20000\ \text{J/mol}}{R_g}\left(\frac{1}{300} - \frac{1}{T}\right)\right] \text{(L/mol/s)}$$

■ Answer

The material balance for the batch reactor is:

$$\frac{df_A}{dt} = kC_A^0(1 - f_A)(1.2 - f_A)$$

The energy balance can be written as:

$$UA_H(T^* - T) = \Delta H_r n_A^0 \frac{df_A}{dt} + [n_A^0(1 - f_A)C_{p_A} + n_A^0(1.2 - f_A)C_{p_B} + n_A^0 f_A C_{p_C}]\frac{dT}{dt}$$

The material and energy balance equations must be solved simultaneously. A convenient form for solution by numerical techniques is:

$$\frac{df_A}{dt} = g(T, f_A) = k(T)C_A^0(1 - f_A)(1.2 - f_A)$$

$$\frac{dT}{dt} = \frac{UA_H(300 - T) - \Delta H_r n_A^0 g(T, f_A)}{n_A^0(1 - f_A)C_{p_A} + n_A^0(1.2 - f_A)C_{p_B} + n_A^0 f_A C_{p_C}}$$

with $f_A = 0$ and $T = 300$ K at $t = 0$. The results are shown in Figure 9.3.3. From the data given in Figure 9.3.3, it takes 462 s to reach a fractional conversion of 0.8. Additionally, the final temperature is 332 K. Notice that the final temperature is not the maximum temperature achieved during the reaction, in contrast to adiabatic operation.

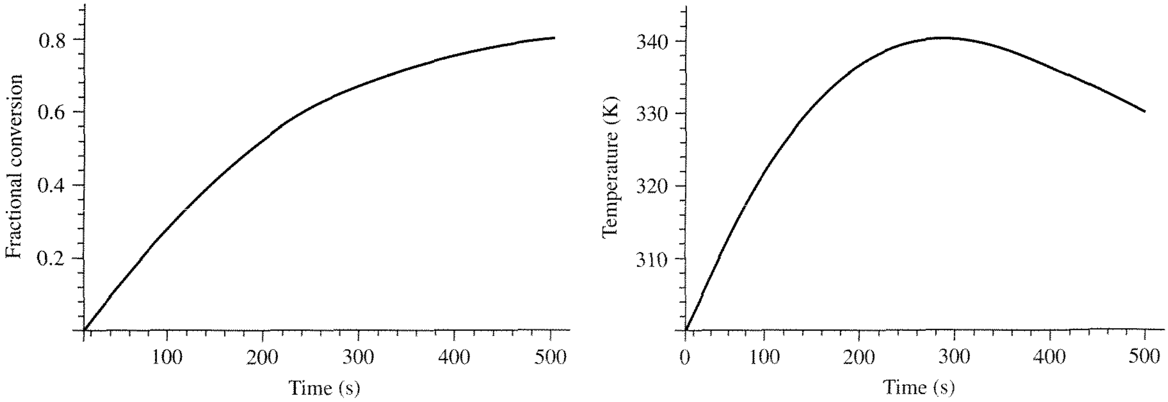


Figure 9.3.3 | Fractional conversion and temperature profiles for the reactor described in Example 9.3.3.

VIGNETTE 9.3.1

M. Kladko [*CHEMTECH*, **1** (1971) 141] presented an interesting case study of performing a liquid-phase, exothermic isomerization reaction. In a 50 gal steam-heated reactor, the reaction of $A \rightarrow B$ was adequately conducted with a 1:1 ratio of A to solvent. However, when scaling-up to a 750 gal glass-lined reactor with a reactant-to-solvent ratio of 2:1, the batch exothermed violently and the reaction ran out of control. The batch erupted through a safety valve and vented. Thus, the effects of the ratio of heat transfer area to reactor volume are nicely demonstrated in this case study. For small vessels the ratio of heat transfer area to reaction volume is higher than for larger vessels and thus the exothermic heat of reaction more efficiently removed.

The analysis of this problem led to the solution illustrated below. A reactor was constructed as a semibatch reactor (solvent initially charged into the reactor and reactant fed over time) and a heating and cooling cycle employed (see Figure 9.3.4). The reactor was operated and the results are shown in Figures 9.3.5–9.3.7.

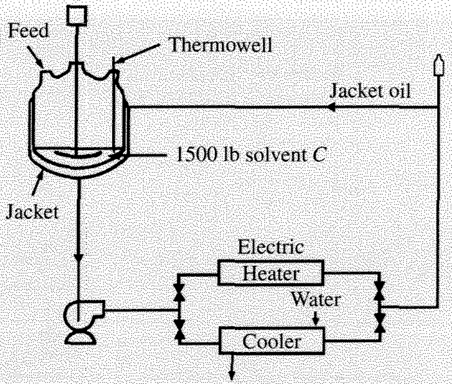


Figure 9.3.4 | Plant installation for "semibatch" isomerization showing heating/cooling circuits. [Adapted from "The Case of a Real Engineering Design Problem" by M. Kladko, *CHEMTECH* (now *Chemical Innovation*), **1** (1971) 141, with permission of the author and the American Chemical Society, copyright 1971.]

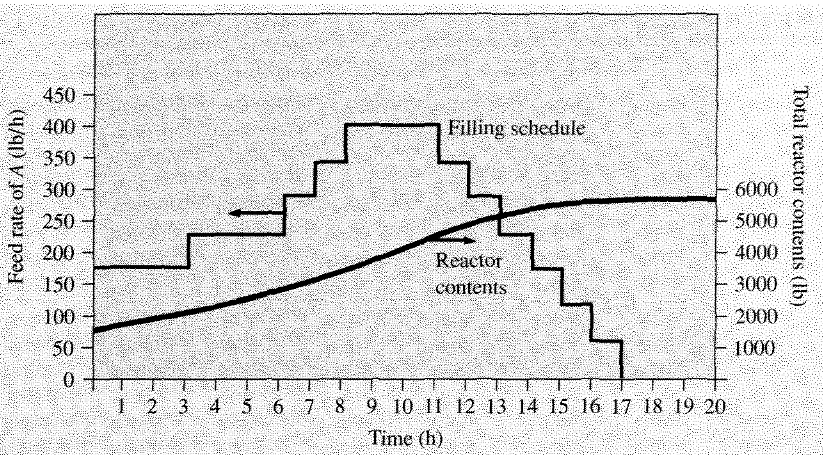


Figure 9.3.5 | Reactor filling schedule and total contents versus time for "semibatch" operation. [Adapted from "The Case of a Real Engineering Design Problem" by M. Kladko, *CHEMTECH* (now *Chemical Innovation*), **1** (1971) 141, with permission of the author and the American Chemical Society, copyright 1971.]

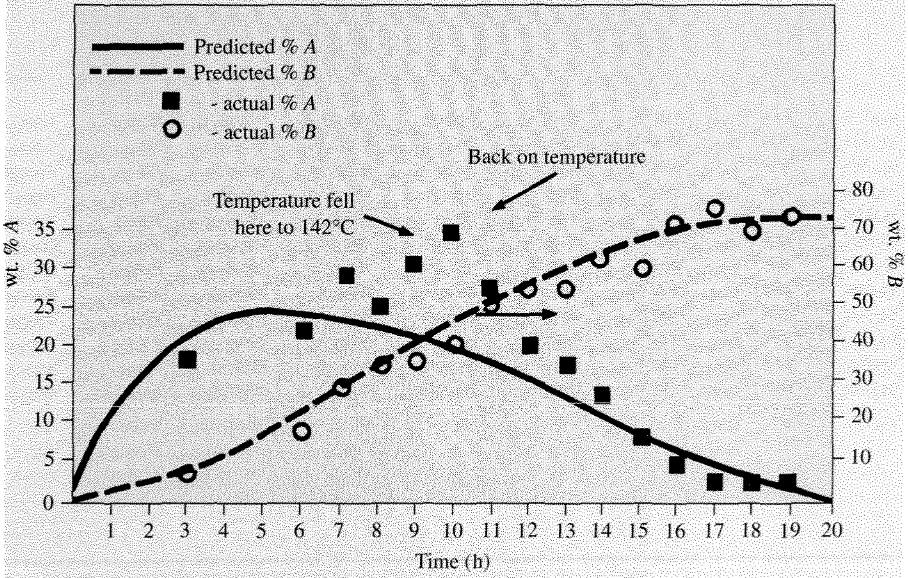


Figure 9.3.6 | Predicted and actual percent *A* and *B* versus time. [Adapted from "The Case of a Real Engineering Design Problem" by M. Kladko, *CHEMTECH* (now *Chemical Innovation*), **1** (1971) 141, with permission of the author and the American Chemical Society, copyright 1971.]

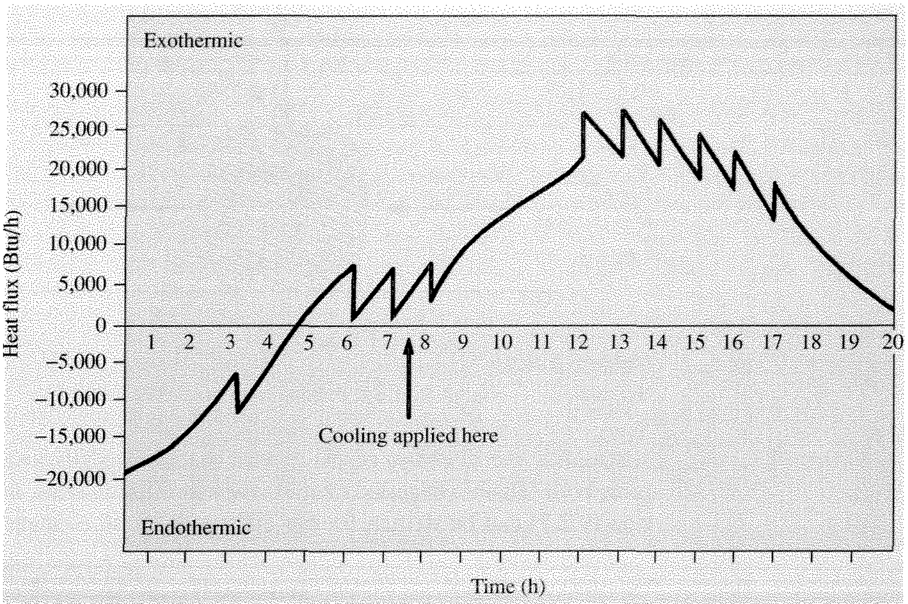


Figure 9.3.7 | Heat flux versus time. [Adapted from "The Case of a Real Engineering Design Problem" by M. Kladko, *CHEMTECH* (now *Chemical Innovation*), **1** (1971) 141, with permission of the author and the American Chemical Society, copyright 1971.]

9.4 | Nonisothermal Plug Flow Reactor

Consider a PFR operating at nonisothermal conditions (refer to Figure 9.4.1). To describe the reactor performance, the material balance, Equation (9.1.1), must be solved simultaneously with the energy balance, Equation (9.2.7). Assuming that the PFR is a tubular reactor of constant cross-sectional area and that T and C_i do not vary over the radial direction of the tube, the heat transfer rate $\dot{Q}$ can be written for a differential section of reactor volume as (see Figure 9.4.1):

$$d\dot{Q} = U(T^* - T)dA_H = U(T^* - T)\frac{4}{d_t}dV_R \qquad (9.4.1)$$

since

$$dA_H = \pi d_t dz \quad \text{(differential area for heat transfer)}$$

and

$$dV_R = \frac{\pi d_t^2}{4}dz \quad \text{(differential reactor volume)}$$

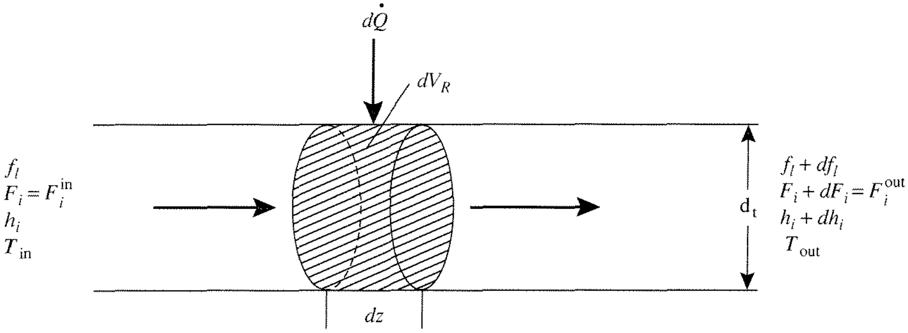


Figure 9.4.1 |
Schematic of differential fluid volume in a nonisothermal PFR.

where d_t is the diameter of the tubular reactor. Recall again that the enthalpy contains both sensible heat and heat of reaction effects. Thus, the energy balance Equation (9.2.7) can be written for the differential fluid element of the PFR as:

$$d\dot{Q} = \sum_i \left(F_i^{\text{out}} \int_{T^0}^{T_{\text{out}}} C_{p_i} dT \right) - \sum_i \left(F_i^{\text{in}} \int_{T^0}^{T_{\text{in}}} C_{p_i} dT \right) - \frac{\Delta H_r|_{T^0}}{v_\ell} F_\ell^0 df_\ell \quad (9.4.2)$$

where the heat of reaction is evaluated at a reference temperature T^0 and C_{p_i} is the molar heat capacity of species i. Normally, T^0 is taken as the reactor entrance temperature.

EXAMPLE 9.4.1

Show that the general energy balance, Equation (9.4.2), can simplify to an appropriate form for either adiabatic or isothermal reactor operation.

■ Answer

For adiabatic operation $d\dot{Q} = 0$. Thus, Equation (9.4.2) simplifies to:

$$\sum_i \left(F_i^{\text{out}} \int_{T^0}^{T_{\text{out}}} C_{p_i} dT \right) - \sum_i \left(F_i^{\text{in}} \int_{T^0}^{T_{\text{in}}} C_{p_i} dT \right) = \frac{\Delta H_r|_{T^0}}{v_\ell} F_\ell^0 df_\ell \quad (9.4.3)$$

If T^0 is the temperature at the reactor entrance and the conversion is zero at this point, then Equation (9.4.3) can be written for any point in the PFR as:

$$\sum_i F_i \int_{T^0}^{T} C_{p_i} dT = \frac{\Delta H_r|_{T^0}}{v_\ell} F_\ell^0 f_\ell \quad (9.4.4)$$

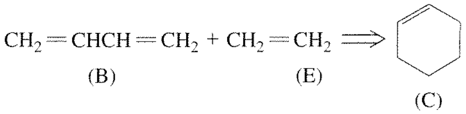
Equation (9.4.4) relates the conversion to the temperature for an adiabatic PFR. If the reactor is operated isothermally, then:

$$d\dot{Q} = -\frac{\Delta H_r|_{T^0}}{v_\ell} F_\ell^0 df_\ell \quad (9.4.5)$$

EXAMPLE 9.4.2

(From C. G. Hill, *An Introduction to Chemical Engineering Kinetics and Reactor Design*, Wiley, 1977, pp. 362–364.)

Butadiene and ethylene can be reacted together to form cyclohexene as follows:



If equimolar butadiene and ethylene at 450°C and 1 atm are fed to a PFR operating adiabatically, what is the space time necessary to reach a fractional conversion of 0.10?

Data:

$k = 10^{7.5} \exp[-27{,}500/(R_g T)]$ L/mol/s
$\Delta H_r = -30000$ cal/mol
$C_{p_B} = 36.8$ cal/mol/K
$C_{p_E} = 20.2$ cal/mol/K
$C_{p_C} = 59.5$ cal/mol/K

■ Answer

Assume that each C_{p_i} is not a strong function of temperature over the temperature range obtained within the PFR (i.e., each is not a function of T). The material and energy balance equations are:

$$\frac{dF_B}{dV_R} = -kC_B^2 = -k(C_B^0)^2\left[\frac{1 - f_B}{1 + \varepsilon_B f_B}\right]^2\left(\frac{T^0}{T}\right)^2$$

and

$$\sum_i F_i \int_{T^0}^{T} C_{p_i}\, dT = \frac{\Delta H_r|_{T^0}}{v_B} F_B^0 f_B$$

Since $F_B = F_B^0(1 - f_B) = C_B \text{v}$:

$$\frac{dF_B}{dV_R} = -F_B^0 \frac{df_B}{dV_R} = -\frac{F_B^0}{\text{v}_0}\frac{df_B}{d(V_R/\text{v}_0)} = -C_B^0 \frac{df_B}{d\tau}$$

Thus, the material balance can be written as:

$$\frac{df_B}{d\tau} = kC_B^0\left[\frac{1 - f_B}{1 - 0.5\, f_B}\right]^2\left(\frac{T^0}{T}\right)^2$$

since $\varepsilon_B = 0.5\left[\frac{1-2}{|-1|}\right] = -0.5$. Now for the energy balance,

$$\sum_i F_i \int_{T^0}^{T} C_{p_i}\, dT = \sum_i F_i C_{p_i} \int_{T^0}^{T} dT \quad \text{since } C_{p_i} \neq C_{p_i}(T)$$

Thus,

$$\sum_i F_i C_{p_i} \int_{T^0}^{T} dT = F_B^0(1-f_B)(36.8)(T-T^0) + F_B^0(1-f_B)(20.2)(T-T^0) + F_B^0 f_B(59.5)(T-T^0)$$

or

$$\sum_i F_i C_{p_i} \int_{T^0}^{T} dT = (57 + 2.5 f_B) F_B^0 (T - T^0)$$

The energy balance then becomes:

$$(57 + 2.5 f_B) F_B^0 (T - T^0) = \frac{(-30{,}000)}{(-1)} F_B^0 f_B$$

or

$$T = 723 + \frac{(30{,}000) f_B}{57 + 2.5 f_B}$$

The solution of the material balance equation:

$$\tau = \int_0^{0.10} \frac{df_B}{kC_B^0 \left[\dfrac{1 - f_B}{1 - 0.5 f_B}\right]^2 \left(\dfrac{723}{T}\right)^2}$$

with T from the energy balance gives a value of $\tau = 47.1$ s. Additionally, the exit temperature is 775 K.

VIGNETTE 9.4.1

Over the first year of a child's life in the United States, the child receives vaccines for immunization against hepatitis B, diphtheria, tetanus, pertussis (whooping cough), haemophilus influenzae, polio, measles, mumps, rubella, and chicken pox. Numerous vaccines are based on viruses in some form. The growth of viral-based vaccines typically occurs in bioreactors that are just tanks. However, when the aqueous medium that is used to grow the viral products is to be expelled, it must be "decontaminated." To do so, the fluid is mixed with H_2O_2 and flows through a tubular reactor. The H_2O_2 is used to kill any living material in the tubular reactor. Thus, τ must be fixed to a sufficiently long time to assure complete death of all living matter prior to exiting the reactor. The temperature of this reactor must be maintained below a critical value so that the hydrogen peroxide does not decompose to form dioxygen. Thus, the material balance for the reactor must be solved simultaneously with the energy balance as illustrated in Section 9.4 to properly define the correct τ for complete decontamination.

The energy balance for the PFR can also be written as follows by combining Equations (9.4.1) and (9.4.2):

$$U(T^* - T)\frac{4}{d_t}\,dV_R = \sum_i F_i C_{p_i}\,dT - \frac{\Delta H_r|_{T^0}}{v_\ell} F_\ell^0\,df_\ell \tag{9.4.6}$$

or

$$U(T^* - T)\frac{4}{d_t} = \sum_i F_i C_{p_i}\frac{dT}{dV_R} - \frac{\Delta H_r|_{T^0}}{v_\ell} F_\ell^0 \frac{df_\ell}{dV_R} \tag{9.4.7}$$

Using the fact that:

$$F_\ell^0 \frac{df_\ell}{dV_R} = (-v_\ell)\mathrm{r}$$

Equation (9.4.7) can be written as:

$$\sum_i F_i C_{p_i}\frac{dT}{dV_R} = (-\Delta H_r|_{T^0})\mathrm{r} - U(T - T^*)\frac{4}{d_t} \tag{9.4.8}$$

Thus, the material and energy balances for the PFR can be written as ($F_\ell = C_\ell \mathrm{v} = C_\ell \pi d_t^2 u/4$; $dV_R = \pi d_t^2\,dz/4$):

$$\left.\begin{aligned} -u\frac{dC_\ell}{dz} &= (-v_\ell)\mathrm{r} \\ u\rho\bar{C}_p\frac{dT}{dz} &= (-\Delta H_r|_{T^0})\mathrm{r} - \frac{4U}{d_t}(T - T^*) \end{aligned}\right\} \tag{9.4.9}$$

with $C_\ell = C_\ell^0$ and $T = T^0$ at $z = 0$, where u is the superficial linear velocity, ρ is the average density of the fluid, and $\bar{C}_p$ is the average heat capacity per unit mass. Equation (9.4.9) is only applicable when the density of the fluid is not changing in the reactor and when $\bar{C}_p$ is not a function of temperature, since the following relationship is used to obtain Equation (9.4.9):

$$\sum F_i C_{p_i} = \mathrm{v}\rho\bar{C}_p \tag{9.4.10}$$

EXAMPLE 9.4.3

A PFR of dimensions $L = 2$ m and $d_t = 0.2$ m is accomplishing a homogeneous reaction. The inlet concentration of the limiting reactant is $C_\ell^0 = 0.3$ kmol/m^3 and the inlet temperature is 700 K. Other data are: $-\Delta H_r|_{T^0} = 10^4$ kJ/kmol, $\bar{C}_p = 1$ kJ/(kg-K), $E = 100$ kJ/mol, $\rho = 1.2$ kg/m^3, $u = 3$ m/s, and $\bar{A} = 5$ s^{-1}. Calculate the dimensionless concentration ($y = C_\ell/C_\ell^0$) and temperature ($\theta = T/T^0$) profiles for adiabatic ($U = 0$) and nonisothermal ($U = 70$ J/(m^2-s-K)) operations. (Example adapted from J. Villadsen and M. L. Michelsen, *Solution of Differential Equation Models by Polynomial Approximation*, Prentice-Hall, Englewood Cliffs, 1978, p. 59.)

■ Answer

From the units on $\bar{A}$, it is clear that the reaction rate is first order. Using Equation (9.4.9) with a first-order reaction rate expression gives:

$$-u\frac{dC_\ell}{dz} = \bar{A}\exp[-E/(R_gT)]C_\ell$$

$$u\rho\bar{C}_p\frac{dT}{dz} = (-\Delta H_r)\bar{A}\exp[-E/(R_gT)]C_\ell - \frac{4U}{d_t}(T - T^0)$$

Let $x = z/L$, $y = C_\ell/C_\ell^0$ and $\bar{\theta} = T/T^0$. Using these dimensionless variables in the material and energy balance relationships yields:

$$\frac{dy}{dx} = -(\bar{D}a)y\exp\left[\gamma\left(1 - \frac{1}{\bar{\theta}}\right)\right]$$

$$\frac{d\bar{\theta}}{dx} = \beta_T(\bar{D}a)y\exp\left[\gamma\left(1 - \frac{1}{\bar{\theta}}\right)\right] - H_w(\bar{\theta} - 1)$$

with $y = 1$ at $x = 0$ and where:

$$\bar{D}a = \frac{L\bar{k}}{u}, \quad \bar{k} = \bar{A}\exp[-E/(R_gT^0)]$$

$$\beta_T = \frac{C_\ell^0(-\Delta H_r)}{\rho\tau T^0}$$

$$\gamma = \frac{E}{R_gT^0}$$

$$H_w = \frac{4U}{d_t}\left(\frac{L}{\rho\bar{C}_pu}\right)$$

Notice that all the groupings $\bar{D}a$, β_T, γ, and H_w are dimensionless. For adiabatic operation, $H_w = 0$. For this case, the mass balance equation can be multiplied by β_T and added to the energy balance to give:

$$\frac{d}{dx}(\bar{\theta} + \beta_T y) = 0$$

Integration of this equation with $y = \bar{\theta} = 1$ at $x = 0$ leads to:

$$\bar{\theta} = 1 + \beta_T(1 - y) \tag{9.4.11}$$

Equation (9.4.11) is the adiabatic relationship between temperature and conversion in dimensionless form. The mass balance can then be written as:

$$\frac{dy}{dx} = -(\bar{D}a)y\exp\left[\frac{\gamma\beta_T(1 - y)}{1 + \beta_T(1 - y)}\right]$$

with

$$y = 1 \text{ at } x = 0$$

The solution of this differential equation is straightforward and is shown in Figure 9.4.2. For the nonisothermal case, the material and energy balances must be solved simultaneously by

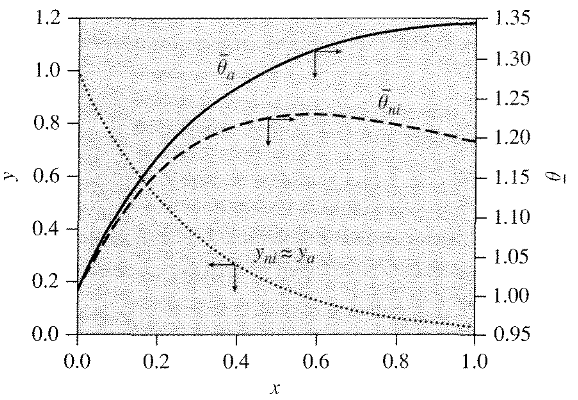


Figure 9.4.2 | Dimensionless concentration and temperature profiles for adiabatic and nonisothermal operation. y_a and $\bar{\theta}_a$ are for adiabatic conditions while y_{ni} and $\bar{\theta}_{ni}$ are for nonisothermal operation.

numerical methods. The nonisothermal results are plotted also in Figure 9.4.2. Notice that there is a maximum in the value of $\bar{\theta}_{ni}$ that occurs at $x = 0.57$ and gives $T = 860$ K. The maximum in the temperature profile from nonisothermal operation is normally denoted as the *hot spot* in the reactor.

9.5 | Temperature Effects in a CSTR

Although the assumption of perfect mixing in the CSTR implies that the reactor contents will be at uniform temperature (and thus the exit stream will be at this temperature), the reactor inlet may not be at the same temperature as the reactor. If this is the case and/or it is necessary to determine the heat transferred to or from the reactor, then an energy balance is required.

The energy balance for a CSTR can be derived from Equation (9.2.7) by again carrying out the reaction isothermally at the inlet temperature and then evaluating sensible heat effects at reactor outlet conditions, that is,

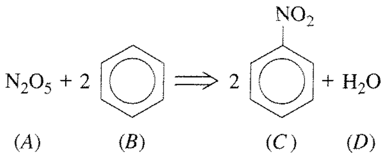
$$\dot{Q} = \frac{F_\ell^0 (\Delta H_r|_{T^0})(f_\ell^f - f_\ell^0)}{(-v_\ell)} + \sum\left(F_i^f \int_{T^0}^{T^f} C_{p_i} dT\right) \tag{9.5.1}$$

where the superscript f denotes the final or outlet conditions. For adiabatic operation, $\dot{Q} = 0$.

EXAMPLE 9.5.1

The nitration of aromatic compounds is a highly exothermic reaction that generally uses catalysts that tend to be corrosive (e.g., HNO_3/H_2SO_4). A less corrosive reaction employs N_2O_5

as the nitrating agent as illustrated below:



If this reaction is conducted in an adiabatic CSTR, what is the reactor volume and space time necessary to achieve 35 percent conversion of N_2O_5? The reaction rate is first order in A and second order in B.

Data:

$\Delta H_r = -370.1$ kJ/mol
$C_{p_A} = 84.5$ J/(mol-K)
$C_{p_B} = 137$ J/(mol-K)
$C_{p_C} = 170$ J/(mol-K)
$C_{p_D} = 75$ J/(mol-K)

$T^0 = 303$ K
$F_A^0 = 10$ mol/min
$F_B^0 = 30$ mol/min
$\text{v} = 1000$ L/min
$C_A^0 = 0.01$ mol/L

$$k = 0.090 \exp\left[\frac{(40 \text{ kJ/mol})}{R_g}\left(\frac{1}{303} - \frac{1}{T}\right)\right] \qquad (\text{L/mol})^2 (\text{min})^{-1}$$

■ Answer

The reaction occurs in the liquid-phase and the concentrations are dilute so that mole change with reaction does not change the overall density of the reacting fluid. Thus,

$$C_A = C_A^0(1 - f_A), \qquad F_A = F_A^0(1 - f_A)$$
$$C_B = C_A^0(3 - 2f_A), \qquad F_B = F_A^0(3 - 2f_A)$$
$$F_C = 2F_A^0 f_A, \qquad F_D = F_A^0 f_A$$

The material balance on the CSTR can be written as:

$$V = \frac{F_A^0 f_A}{k(C_A^0)^3(1 - f_A)(3 - 2f_A)^2}$$

The energy balance for the adiabatic CSTR is:

$$0 = \Delta H_r F_A^0 f_A + F_A^0(1 - f_A)C_{p_A}(T - T^0) + F_A^0(3 - 2f_A)C_{p_B}(T - T^0) + 2F_A^0 f_A C_{p_C}(T - T^0) + F_A^0 f_A C_{p_D}(T - T^0)$$

For $f_A = 0.35$, the energy balance yields $T = 554$ K. At 554 K, the value of the rate constant is $k = 119.8$ $\text{L}^2/(\text{mol}^2\text{-min})$. Using this value of k in the material balance gives $V = 8{,}500$ L and thus $\tau = 8.5$ min.

EXAMPLE 9.5.2

Consider the aromatic nitration reaction illustrated in Example 9.5.1. Calculate the reactor volume required to reach 35 percent conversion if the reactor is now cooled.

Data:

$$
\begin{aligned}
UA_H &= 9000\ \text{J/(min-K)}\\
T_C^0 &= 323\ \text{K (and is constant)}\\
\text{v} &= 100\ \text{L/min}\\
C_A^0 &= 0.10\ \text{mol/L}
\end{aligned}
$$

All other data are from Example 9.5.1.

■ Answer

The material balance equation remains the same as in Example 9.5.1. The energy balance is now:

$$
\begin{aligned}
UA_H(T_C^0 - T) = \Delta H_r F_A^0 f_A + F_A^0(1 - f_A)C_{p_A}(T - T^0) + F_A^0(3 - 2f_A)C_{p_B}(T - T^0)\\
+ 2F_A^0 f_A C_{p_C}(T - T^0) + F_A^0 f_A C_{p_D}(T - T^0)
\end{aligned}
$$

when $f_A = 0.35$, the energy balance yields $T = 407$ K. At 407 K, the reaction rate constant is $k = 5.20\ \text{L}^2/(\text{mol}^2\text{-min})$. Using this value of k and $C_A^0 = 0.10$ mol/L in the material balance equation gives $V = 196$ L.

9.6 | Stability and Sensitivity of Reactors Accomplishing Exothermic Reactions

Consider the CSTR illustrated in Figure 9.6.1. The reactor is accomplishing an exothermic reaction and therefore must transfer heat to a cooling fluid in order to remain at temperature T. Assume that the heat transfer is sufficiently high to maintain the reactor wall temperature at T_c. Therefore,

$$
\dot{Q} = \underbrace{UA_H(T - T_c)}_{\text{heat removed from reactor}} = \underbrace{\text{v}_c C_{p_c}(T_c - T_c^0)}_{\text{sensible heat change of coolant}} \tag{9.6.1}
$$

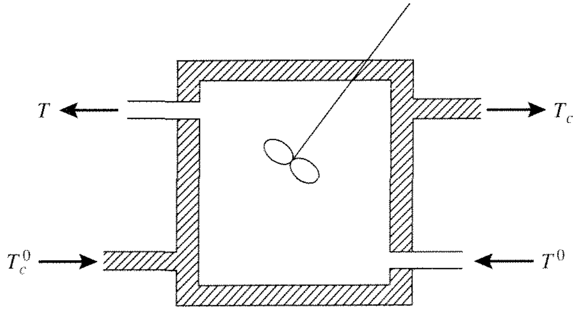


Figure 9.6.1 |
Schematic illustration of a CSTR that is maintained at temperature T by transferring heat to a coolant fluid ($T_c > T_c^0$).

where v_c is the volumetric flow rate of the coolant and C_{p_c} is the heat capacity of the coolant and is not a function of temperature. Solving for T_c and then substituting the expression back into the heat transfer equation yields:

$$\dot{Q} = \frac{UA_H \mathrm{v}_c C_{p_c}}{UA_H + \mathrm{v}_c C_{p_c}}(T - T_c^0) = \lambda_\lambda (T - T_c^0) \tag{9.6.2}$$

The energy balance on the CSTR can be written as [from Equation (9.5.1) with a first-order reaction rate expression]:

$$\dot{Q} = \frac{\Delta H_r|_{T^0} F_\ell^0 (f_\ell - f_\ell^0)}{(-\upsilon_\ell)} + \sum\left(F_i \int_{T^0}^{T} C_{p_i} dT\right)$$

or since:

$$-\upsilon_\ell \mathrm{r} V = F_\ell^0 (f_\ell - f_\ell^0) \qquad \text{(material balance)}$$

as:

$$\dot{Q} = (\Delta H_r|_{T^0}) k C_\ell V + \mathrm{v}^p \rho C_p (T - T^0) \qquad \text{(first-order reaction rate)} \tag{9.6.3}$$

where v^p is the volumetric flow rate of the product stream and ρ and C_p are the average density and heat capacity of the outlet stream. Rearranging Equation (9.6.3) and substituting Equation (9.6.2) for $\dot{Q}$ gives (note that $\dot{Q}$ is heat removed):

$$\frac{\lambda_\lambda}{\mathrm{v}^p \rho C_p}(T_c^0 - T) = \frac{k C_\ell \tau (\Delta H_r|_{T^0})}{\rho C_p} + (T - T^0) \tag{9.6.4}$$

Let:

$$\alpha\alpha_1 = \frac{\lambda_\lambda}{\mathrm{v}^p \rho C_p}$$

$$\alpha\alpha_2 = \frac{-k\tau(\Delta H_r|_{T^0})}{\rho C_p}$$

so that Equation (9.6.4) can be written as:

$$(1 + \alpha\alpha_1)T - (T^0 + \alpha\alpha_1 T_c^0) = \alpha\alpha_2 C_\ell \tag{9.6.5}$$

Since:

$$C_\ell = C_\ell^0/(1 + k\tau)$$

from the solution of the material balance equation, Equation (9.6.5) can be formulated as:

$$(1 + \alpha\alpha_1)T - (T^0 + \alpha\alpha_1 T_c^0) = \frac{\alpha\alpha_2 C_\ell^0}{1 + k\tau} \tag{9.6.6}$$

$$Q_r \text{ (heat removed)} = Q_g \text{ (heat generated)}$$

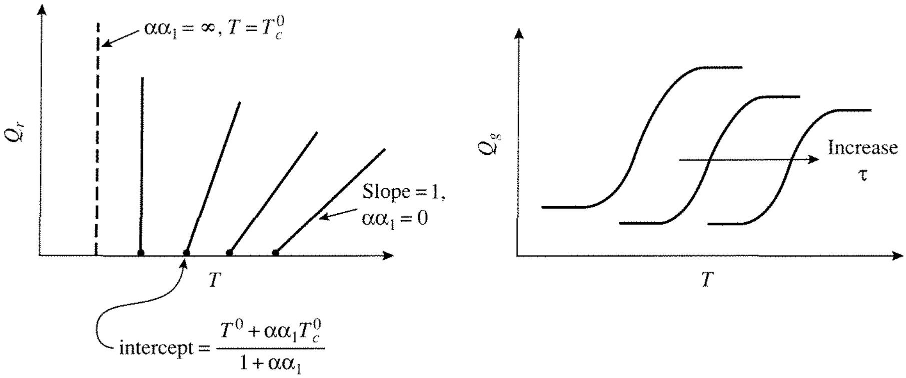


Figure 9.6.2 |
Schematic illustration of Q_r and Q_g as functions of T.

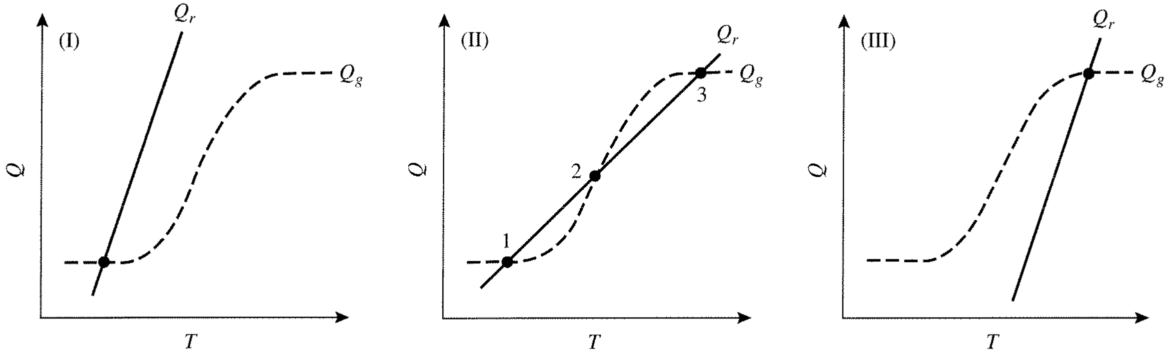


Figure 9.6.3 |
Steady-state solutions to Equation (9.6.3).

If Q_r and Q_g are plotted versus the reaction temperature, T, the results are illustrated in Figure 9.6.2. A solution of Equation (9.6.6) occurs when Q_r equals Q_g, and this can happen as shown in Figure 9.6.3. Notice that for cases (I) and (III) a single solution exists. However, for case (II) three steady-states are possible. An important question of concern with case (II) is whether all three steady-states are stable. This is easy to rationalize as follows. At steady-state 1, if T is increased then $Q_r > Q_g$ so the reactor will return to point 1. Additionally, if T is decreased, $Q_g > Q_r$ so the reactor will also return to point 1 in this case. Thus, steady-state 1 is stable since small perturbations from this position cause the reactor to return to the steady-state. Likewise steady-state 3 is a stable steady-state. However, for steady-state 2, if T is increased, $Q_g > Q_r$ and the reactor will move to position 3. If T is decreased below that of point 2, $Q_r > Q_g$ and the reactor will move to point 1. Therefore, steady-state 2 is unstable. It is important to determine the stability of reactor operation since perturbations from steady-state always occur in a real system. Finally, what determines whether the reactor achieves steady-state 1 or 3 is the start-up of the reactor.

EXAMPLE 9.6.1

Calculate the steady-states for the following reactor configuration. Is there an unstable steady-state?

Data:
$A + B \Rightarrow 2C$ in the liquid phase, $V = 1$ L, $k = 33 \times 10^9 \exp[-20{,}000/(R_g T)]$ L/(mol · min), $-\Delta H_r = 20$ kcal/mol, $C_A^0 = 20$ mol/L, $C_B^0 = 3$ mol/L, v = 100 cm^3/min, $T^0 = 17$°C, $T_c^0 = 87$°C, $\rho C_p = 650$ cal/(L · °C), $U = 0.1$ cal/(cm^2 · min · K), and $A_H = 250$ cm^2.

■ Answer

The reaction rate expression is:

$$(-v_B)\mathrm{r} = kC_A C_B = k(C_B^0)^2 (1 - f_B)(\overline{M} - f_B),\ \overline{M} = C_A^0/C_B^0$$

giving the following material balance:

$$0 = C_B^0 f_B - \tau k (C_B^0)^2 (1 - f_B)(\overline{M} - f_B)$$

Therefore,

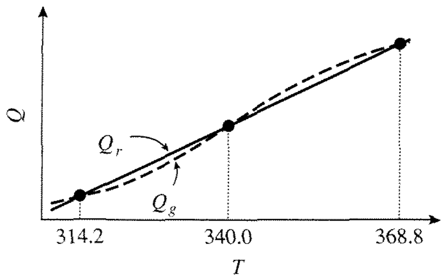
$$Q_r = (1 + \alpha\alpha_1) T - (T^0 + \alpha\alpha_1 T_c^0)$$

$$Q_g = \frac{-k(C_B^0)^2 \tau (\Delta H_r)(1 - f_B)(\overline{M} - f_B)}{\rho C_p}$$

First, solve the material balance equation for f_B (gives two values for f_B—one will have physical meaning) at a particular T and next calculate Q_r and Q_g. A sampling of results is provided below (assume $\mathrm{v}_c C_{p_c} \gg UA_H$ for the calculation of Q_r):

T (K)	f_B	Q_r	Q_g
310	0.049	0.77	4.55
320	0.124	14.62	11.45
330	0.264	28.46	24.40
340	0.461	42.31	42.50
350	0.658	56.20	60.77
360	0.807	70.00	74.78
370	0.898	83.80	82.85

If these data are plotted, they yield:



Thus, there are three steady-states and they are:

Steady-state	T (K)	T (°C)	f_B
1	314.2	41.2	0.079
2	340.0	67.0	0.460
3	368.8	95.8	0.888

Steady-state 2 is unstable. Notice the vast differences in f_B for the three steady-states. Thus, it is clear that attempts by a naïve designer to operate at steady-state 2 would not succeed since the reactor would not settle into this steady-state at all.

In addition to knowing the existence of multiple steady-states and that some may be unstable, it is important to assess how stable the reactor operation is to variations in the processing parameters (i.e., the sensitivity). In the above example for the CSTR, it is expected that the stable steady-states have low sensitivity to variations in the processing parameters, while clearly the unstable steady-state would not.

To provide an example of how the sensitivity may be elucidated, consider a tubular reactor accomplishing an exothermic reaction and operating at nonisothermal conditions. As described in Example 9.4.3, hot spots in the reactor temperature pro-

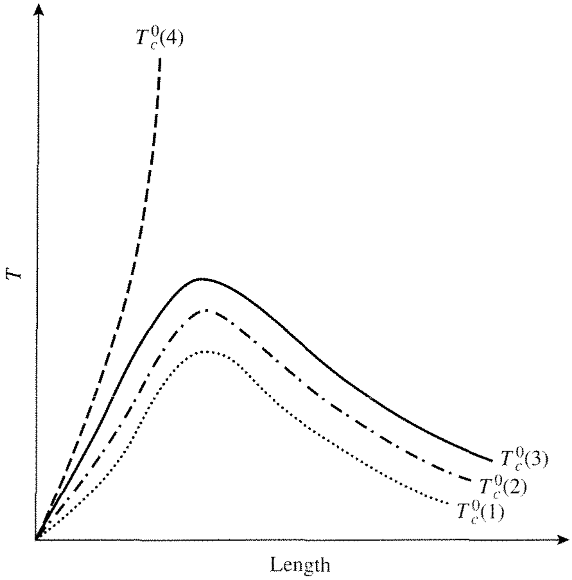


Figure 9.6.4 |
Temperature profiles in a tubular reactor operating nonisothermally and conducting an exothermic reaction. T_c^0 is the temperature of the coolant fluid.

file can occur for this situation. Figure 9.6.4 illustrates what a typical reactor temperature profile would look like. Consider what could happen as the temperature of the coolant fluid, T_c^0, increases. As T_c^0 becomes warmer $T_c^0(i+1) > T_c^0(1)$, $i = 1$, 2, 3, then less heat is removed from the reactor and the temperature at the reactor hot spot increases in value. Eventually, heat is generated at a sufficiently high rate that it cannot be removed [illustrated for $T_c^0(4)$] such that the hot spot temperature exceeds some physical limit (e.g., phase change of fluid, explosions or fire, the catalyst melts, etc.) and this condition is called *runaway*. Thus, reactor operation close to a runaway point would not be prudent, and determining the sensitivity towards the tendency of runaway a critical factor in the reactor analysis. Several criteria have been developed to assess the sensitivity of reactors; each involves the use of critical assumptions [see, for example, G. F. Froment and K. B. Bischoff, *Chemical Reaction Analysis and Design,* Wiley, New York, 1977, Chapter 1]. Here, an example of how reactor stability can be assessed is illustrated and was provided by J. B. Cropley.

EXAMPLE 9.6.2

A tubular reactor packed with a heterogeneous catalyst is accomplishing an oxidation reaction of an alcohol to an aldehyde. The reactions are:

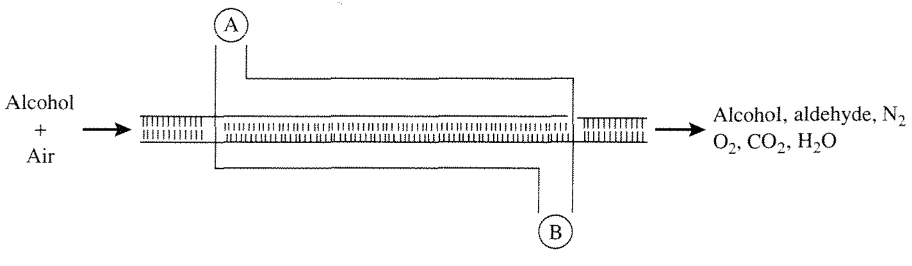
$$\text{alcohol} + \text{air} \Rightarrow \text{aldehyde} + \text{air} \Rightarrow CO_2 + H_2O$$

In this series reaction pathway, the desired species is the aldehyde. Since both reactions are exothermic (second reaction is highly exothermic), the reactor is operated nonisothermally. The reactor is a shell-and-tube heat exchanger consisting of 2500 tubes of 1 inch diameter. Should the heat exchanger be operated in a cocurrent or countercurrent fashion in order to provide a greater stabilization against thermal runaway?

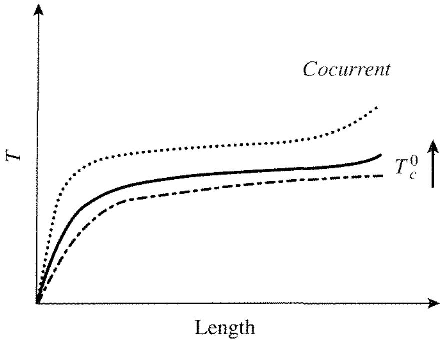
■ Answer

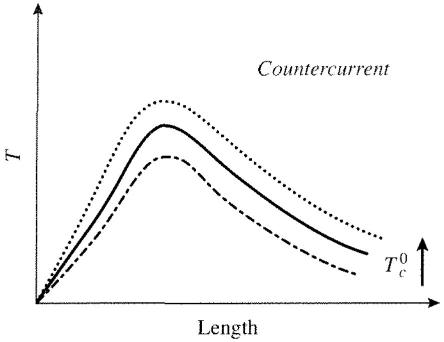
Since this example comes from the simulation of a real reactor, the amount of data necessary to completely describe it is very high. Thus, only the trends observed will be illustrated in order to conserve the length of presentation.

Schematically, the reactor can be viewed as:

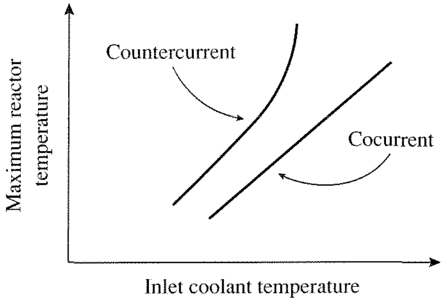


The cooling fluid is fed at point A or at point B for cocurrent and countercurrent operation, respectively. Next, the reactor temperature profiles from the two modes of operation are illustrated. The three profiles in each graph are for different coolant feed temperatures, T_c^0. Notice that a hot spot occurs with countercurrent operation. In order to access the sensitivity,





Cropely suggests plotting the maximum temperature in the reactor as a function of the inlet coolant temperature. The results look like:



The slope of the line would be an indication of the reactor stability to variations in the inlet coolant temperature. Clearly, cocurrent operation provides better sensitivity and this conclusion is a general one. The reason for this is that by operating in a cocurrent manner the greatest ability to remove heat [largest ΔT ($T_{\text{reactor}} - T_{\text{coolant}}$)] can occur in the region of highest heat generation within the reactor.

Exercises for Chapter 9

1. Calculate the final temperature and time required to reach 50 percent conversion in the batch reactor described in Example 9.3.2 if the heat of reaction is now −40 kcal/mol. Do you think that this time is achievable in a large reactor system?
2. Find the final temperature and time required to reach 90 percent conversion in the reactor system of Exercise 1.

3. Plot the fractional conversion and temperature as a function of time for the batch reactor system described in Example 9.3.3 if the reactor is now adiabatic ($U = 0$). Compare your results to those for the nonisothermal situation given in Figure 9.3.3. How much energy is removed from the reactor when it is operated nonisothermally?
4. Consider what happens in the batch reactor given in Example 9.3.3 if the wall temperature does not remain constant. For comparison to the constant wall temperature, calculate the fractional conversion and reactor temperature as a function of time when:

$$T^* = 300 + 0.1t$$

where t is in seconds.
5. Calculate the exit temperature and τ for the PFR described in Example 9.4.2 when mole change with reaction is ignored (i.e., $\varepsilon_B = 0$). How much error is introduced by making this change?
6. Calculate the exit temperature and τ for the PFR described in Example 9.4.2 when the temperature effects on the concentration are ignored. Is this a reasonable simplification or not?
7. An adiabatic PFR can be described by the following set of equations:

$$\frac{dy}{dx} = -4y \exp\left[18\left(1 - \frac{1}{\bar{\theta}}\right)\right]$$

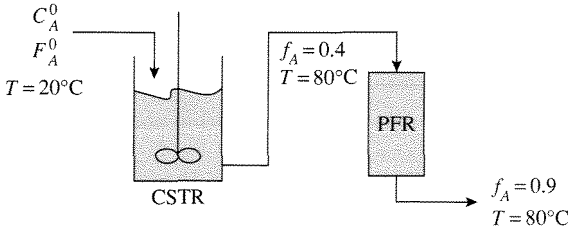
$$\frac{d\bar{\theta}}{dx} = 0.2y \exp\left[18\left(1 - \frac{1}{\bar{\theta}}\right)\right]$$

$$y = \bar{\theta} = 1 \text{ at } x = 0$$

Solve these equations and plot y and $\bar{\theta}$ as a function of x for 0 (entrance) $\leq x \leq 1$ (exit). What happens if the heat of reaction is doubled?
8. Ascertain whether the following exothermic reaction:

$$A + A \underset{k_2}{\overset{k_1}{\rightleftarrows}} P + P \qquad k_1 = 30 \text{ L mol}^{-1}\text{ min}^{-1},\ k_2 = 0.1 \text{ L mol}^{-1}\text{ min}^{-1}$$

(k_1 and k_2 at 80°C) could be carried out in the reactor shown below:



Calculate the volume and heat removed from the CSTR and the PFR. Do the magnitudes of the heat being removed appear feasible? Why or why not?

Data:

$$C_{p_A} = 45 \text{ cal mol}^{-1}\text{ K}^{-1}$$
$$C_{p_P} = 40 \text{ cal mol}^{-1}\text{ K}^{-1}$$
$$-\Delta H_r = 10{,}000 \text{ cal mol}^{-1}$$
$$C_A^0 = 1.5 \text{ mol L}^{-1}$$
$$F_A^0 = 100 \text{ mol min}^{-1}$$

9. The ester of an organic base is hydrolyzed in a CSTR. The rate of this irreversible reaction is first-order in each reactant. The liquid volume in the vessel is 6500 L. A jacket with coolant at 18°C maintains the reactant mixture at 30°C. Additional data:

Ester feed stream—1 M, 30°C, 20 L/s
Base feed stream—4 M, 30°C, 10 L/s
Rate constant = $10^{14}\exp(-11{,}000/T)$ $\text{M}^{-1}\text{s}^{-1}$, T in K
$\Delta H_r = -45$ kcal/mol ester

The average heat capacity is approximately constant at 1.0 kcal L^{-1} $°\text{C}^{-1}$.

(a) What is the conversion of ester in the reactor?

(b) Calculate the rate at which energy must be removed to the jacket to maintain 30°C in the reactor. If the heat transfer coefficient is 15 kcal $\text{s}^{-1}\text{m}^{-2}\text{ K}^{-1}$, what is the necessary heat transfer area?

(c) If the coolant supply fails, what would be the maximum temperature the reactor could reach?

10. A reaction is carried out in an adiabatic CSTR with a volume of 10,000 L. The feed solution with reactant A, at a concentration of 5 M, is supplied at 10 L s^{-1}. The reaction is first-order with rate constant:

$$k = 10^{13}\exp(-12500/T)\ \text{s}^{-1}, \text{ where } T \text{ is in K}$$

The density is 1000 kg m^{-3} and $C_p = 1.0$ kcal $\text{kg}^{-1}\text{K}^{-1}$. The heat of reaction is $\Delta H_r = -70$ kJ mol^{-1}.

(a) Calculate the reactor temperature and exit concentration for feed temperatures of 280, 300, and 320 K.

(b) To maintain the reactor temperature below 373 K, a well-mixed cooling jacket at 290 K is used. Show that it is possible to get 90 percent conversion in this reactor with a feed temperature of 320 K. Do you anticipate any start-up problems?

11. The reversible, first-order reaction shown below takes place in a CSTR.

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

The following data are known:

$$k_1 = 10^3 \exp(-2500/T)\ \mathrm{s}^{-1},\ T \text{ in K}$$
$$\Delta H_r = -10\ \mathrm{kcal\ mol}^{-1}$$
$$K = 8 \text{ at } 300\ \mathrm{K}$$
$$C_p = 1\ \mathrm{kcal\ kg}^{-1}\mathrm{K}^{-1}$$
$$\rho = 1\ \mathrm{kg\ L}^{-1}$$

(a) For a reactor space time of 10 min, what is the conversion for a 300 K operating temperature? What is the conversion at 500 K? (Remember: the equilibrium constant depends on temperature.)

(b) If the feed temperature is 330 K and the feed concentration is 5 M, what is the necessary heat-removal rate per liter of reactor volume to maintain a 300 K operating temperature?

STEADY-STATE NONISOTHERMAL REACTOR DESIGN
(5)

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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***

NONISOTHERMAL REACTOR: RATIONALE

EXAMPLE No. 0

- **LET US CALCULATE THE VOLUME OF A PLUG FLOW REACTOR NECESSARY TO ACHIEVE 70% CONVERSION. THE CHEMICAL REACTION IS EXOTHERMIC 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:** $v = v_0; F_A = C_A v_0; F_{A0} = C_{A0} v_0; C_A = C_{A0}(1-X)$

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

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

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

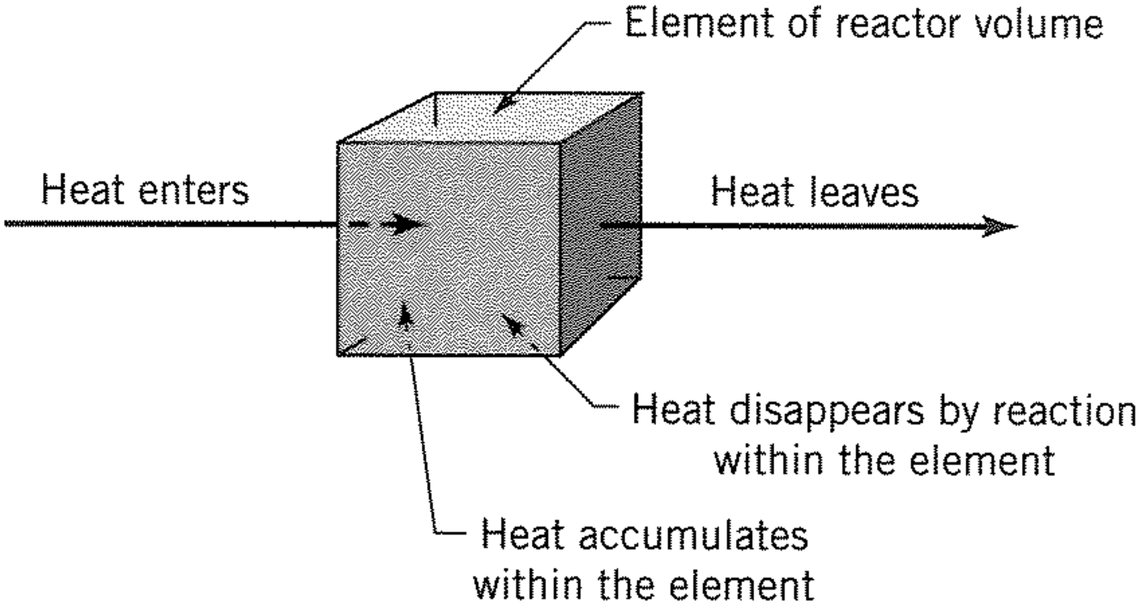


Figure 4.3 Energy balance for an element of volume of the reactor.

THERMAL ENERGY CONSERVATION: BASIC EQUATION

RATE OF ACCUMULATION OF INTERNAL ENERGY WITHIN SYSTEM (WATTS)

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)

$$\frac{dE_{sys}}{dt} = \sum_{i=1}^{n} F_{i0} H_{i0} - \sum_{i=1}^{n} F_i H_i + \dot{Q} - \dot{W}_S \qquad \mathbf{(5.1)}$$

RATE OF FLOW OF HEAT TO THE SYSTEM FROM 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:**

IN $\longrightarrow \sum H_{i0}F_{i0} = H_{A0}F_{A0} + H_{B0}F_{B0} + H_{C0}F_{C0} + H_{D0}F_{D0} + H_{I0}F_{I0}$

OUT $\longrightarrow \sum H_{i}F_{i} = H_{A}F_{A} + H_{B}F_{B} + H_{C}F_{C} + H_{D}F_{D} + H_{I}F_{I}$

SUBSTITUTING

$$F_A = F_{A0}(1-X); \quad F_B = F_{A0}(\theta_B - \frac{b}{a}X);$$

NOTE: $\theta_i = \frac{F_{i0}}{F_{A0}}$

$$F_C = F_{A0}(\theta_C + \frac{c}{a}X); \quad F_D = F_{A0}(\theta_D + \frac{d}{a}X); \quad F_I = F_{A0}\theta_I;$$

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

$$\sum_{i=1}^{n} F_{i0}H_{i0} - \sum_{i=1}^{n} F_i H_i = F_{A0}\begin{bmatrix} (H_{A0}-H_A)+(H_{B0}-H_B)\theta_B + \\ (H_{C0}-H_C)\theta_C + (H_{D0}-H_D)\theta_D + \\ (H_{I0}-H_I)\theta_I \end{bmatrix}$$

$$-\left[\frac{d}{a}H_D + \frac{c}{a}H_C - \frac{b}{a}H_B - H_A\right]F_{A0}X$$

$$= F_{A0}\sum_{i=1}^{n}\theta_i (H_{i0}-H_i) - \Delta H_{Rx}(T)F_{A0}X \qquad \textbf{(5.2)}$$

$\Delta H_{Rx}(T):$ **HEAT OF REACTION AT TEMPERATURE *T (Joules per mole of A reacted);* THE ENTHALPIES H_A, H_B,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,

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

$$\Rightarrow \qquad H_i - H_{i0} = \int_{T_{i0}}^{T} C_{pi}\,dT \qquad \textbf{(5.3)}$$

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 ΔC_p :**

$$\Delta H_{Rx}(T) = \Delta H^0_{Rx}(T_R) + \int_{T_R}^{T} \Delta C_p dT \qquad \textbf{(5.4)}$$

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**

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

(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**

$$H_i - H_{i0} = \int_{T_{i0}}^{T} C_{pi}\,dT = \overline{C_{pi}}(T - T_{i0}) \qquad \textbf{(5.3)'}$$

AND EQUATION (5.4) BECOMES

$$\Delta H_{Rx}(T) = \Delta H^0_{Rx}(T_R) + \overline{\Delta C_p}(T - T_R) \qquad \textbf{(5.4)'}$$

WHERE

$$\overline{C_{pi}} = \frac{\int_{T_{i0}}^{T} C_{pi}\,dT}{T - T_{i0}} \qquad \textbf{AND} \qquad \overline{\Delta C_p} = \frac{\int_{T_R}^{T} \Delta C_p\,dT}{T - T_R}$$

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**

$$\dot{Q} - \dot{W}_S - F_{A0}\sum_{i=1}^{n}\theta_i\overline{C_{pi}}(T - T_{i0}) - F_{A0}X\left[\Delta H^{0}_{Rx}(T_R) + \overline{\Delta C_p}(T - T_R)\right] = 0 \qquad \textbf{(5.6)}$$

ENERGY BALANCE IN TERMS OF MEAN OR CONSTANT HEAT CAPACITIES

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

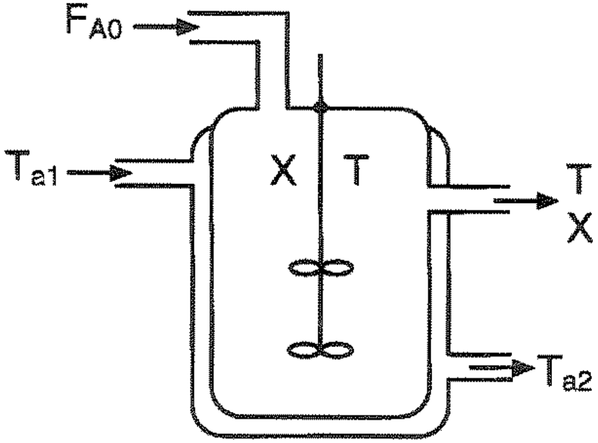
EXAMPLE No.1:
HEAT OF REACTION

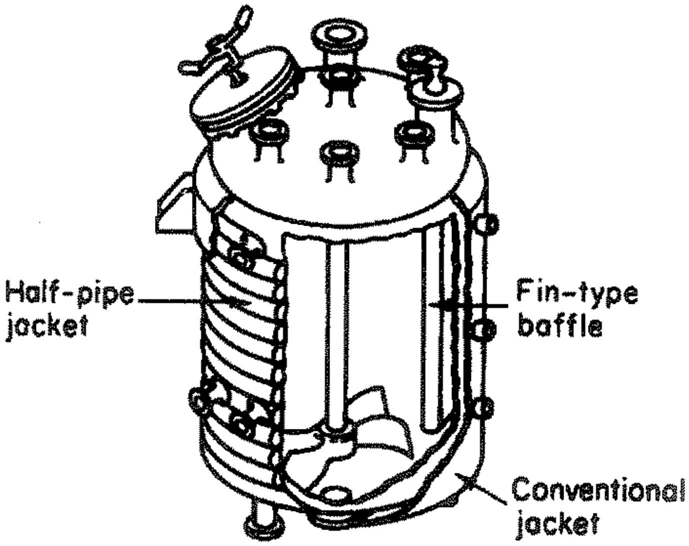
- **THE HEAT OF REACTION IS THE ENERGY CHANGE OF THE REACTION OVERALL. IT IS THE DIFFERENCE BETWEEN THE ENTHALPY OF THE PRODUCTS AND THE ENTHALPY OF THE REACTANTS.**
- **CALCULATE THE HEAT OF REACTION FOR THE SYNTHESIS OF AMMONIA FROM HYDROGEN AND NITROGEN AT 150^{0}C IN kcal/mole AND IN kJoule/mole OF HYDROGEN REACTED.**

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

- **THE HEATS OF FORMATION OF ALL THE ELEMENTS ARE ZERO AT 25 ^{0}C. THE HEATS OF FORMATION OF COMPOUNDS AT 25 ^{0}C ARE TABULATED.**
- **1 cal = 4.184 Joule**

THERMAL ENERGY CONSERVATION: HEAT ADDED TO A CSTR





RATE OF HEAT TRANSFER (WATTS)

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

T:REACTION TEMPERATURE (K)

U:OVERALL HEAT TRANSFER COEFFICIENT (W/m^{2}K)

A:HEAT-EXCHANGE AREA (m^2)

T_a=T_{a1}=T_{a2}:INLET TEMPERATURE OF HIGH FLOW RATE COOLANT (K)

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:**

PFR $\longrightarrow$

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

a*: HEAT- EXCHANGE AREA PER UNIT VOLUME OF PFR = *4/D* FOR TUBULAR PFR OF DIAMETER *D

PBR $\longrightarrow$

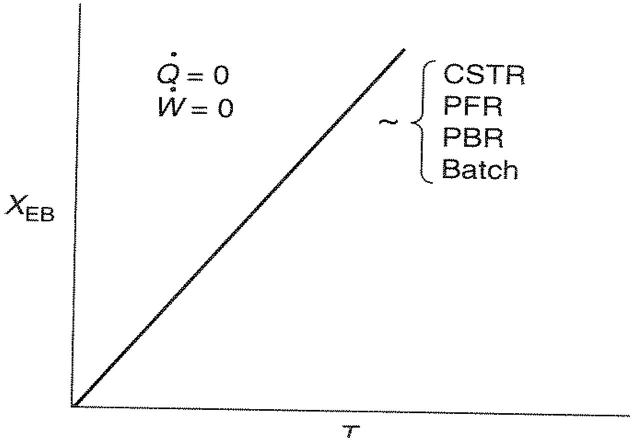
$$\frac{d\dot{Q}}{dW} = \frac{Ua}{\rho_b}(T_a - T)$$

BULK DENSITY OF CATALYST (g/cm^3 of reactor bed)

THERMAL ENERGY CONSERVATION: NONISOTHERMAL CONTINUOUS-FLOW REACTORS

- **CONSIDER A SYSTEM AT STEADY-STATE, NO SHAFT WORK $\dot{W}_S = 0$, ADIABATIC OPERATION $\dot{Q} = 0$. IN MANY INSTANCES, $\Delta H^0_{Rx}(T_R) >> \overline{\Delta C_p}(T - T_R)$ 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:**

$$X = \frac{\sum_{i=1}^{n} \theta_i \overline{C_{pi}}(T - T_{i0})}{-\Delta H^0_{Rx}(T_R)}$$



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* REALTIONSHIP IS PROVIDED BY THE ENERGY BALANCE EQUATION

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

TABLE 8-1. CSTR ALGORITHM

The first-order irreversible liquid-phase reaction

$$A \longrightarrow B$$

is carried out adiabatically.

1. **CSTR design equation:**

$$V = \frac{F_{A0}X}{-r_A} \tag{T8-1.1}$$

2. **Rate law:** $-r_A = kC_A$ (T8-1.2)

with $k = Ae^{-E/RT}$ (T8-1.3)

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

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

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_{A0}, and F_{i0} are specified and the reactor volume, V, must be determined. The procedure is:

5A. Solve for the temperature, T, for pure A entering, and $\tilde{C}_{p_A} = \tilde{C}_{p_B} (\Delta\hat{C}_p = 0)$. For the adiabatic case, solve Equation (8-52) for T:

$$T = T_0 + \frac{X(-\Delta H^\circ_{Rx})}{\tilde{C}_{p_A}} \tag{T8-1.5}$$

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

$$T = \frac{F_{A0}X(-\Delta H^\circ_{Rx}) + F_{A0}\tilde{C}_{p_A}T_0 + UAT_a}{F_{A0}\tilde{C}_{p_A} + UA} \tag{T8-1.6}$$

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_{A0}, V, and F_{i0} 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.**

$$X_{EB} = \frac{\tilde{C}_{p_A}(T - T_0)}{-[\Delta H^\circ_{Rx}(T_R)]} \tag{T8-1.7}$$

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

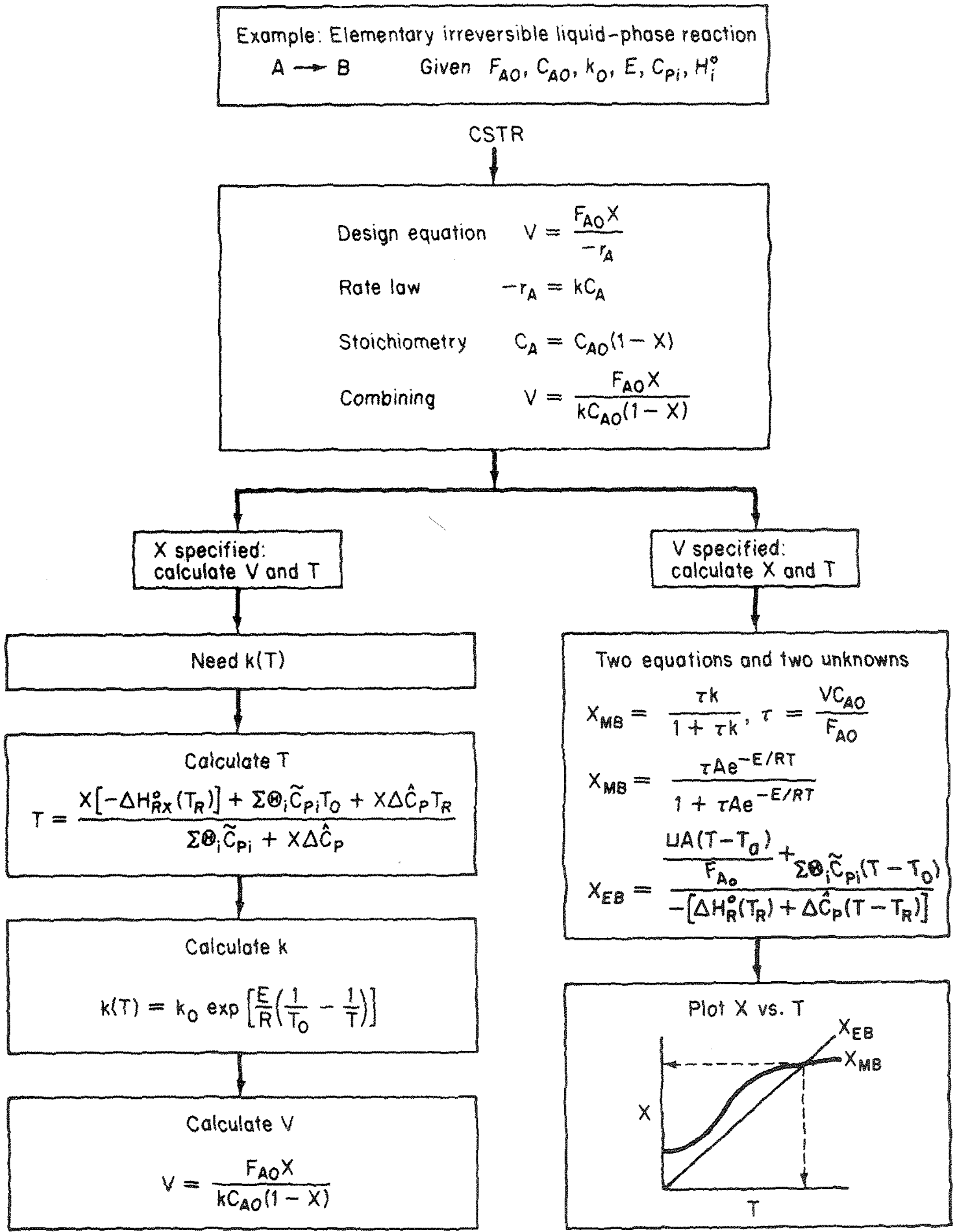
$$X_{EB} = \frac{UA(T-T_a)/F_{A0} + \tilde{C}_{p_A}(T-T_0)}{-\Delta H^\circ_{Rx}} \tag{T8-1.8}$$

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

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

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].

Algorithm



EXAMPLE No.2:
DESIGN OF A CSTR

- **PROPYLENE GLYCOL IS PRODUCED BY THE HYDROLYSIS OF PROPYLENE OXIDE:**

$$(CH_2)(CH)O(CH_3) + H_2O \xrightarrow{CATALYST} (CH_2)OH(CH)OH(CH_3)$$

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

- **(2) 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 ^{0}C PRIOR TO MIXING, BUT THERE IS AN IMMEDIATE 9.4 ^{0}C TEMPERATURE RISE UPON MIXING OF THE TWOO FEED STREAMS CAUSED BY THE HEAT OF MIXING. THE ENTERING TEMPERATURE OF ALL FEED STREAMS IS TAKEN TO BE 24 ^{0}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**

$$A = 16.96 \cdot 10^{12}\, h^{-1}; E = 75311 kJ/kmole; R = 8.3144 J/moleK;$$

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 34^0C AT 1 atm). WITH THE MIXTURE YOU ARE USING, YOU FEEL THAT YOU CANNOT EXCEED AN OPERATING TEMPERATURE OF 52^0C, 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 m^2 WITH THE COOLING WATER FLOW RATE SUFFICIENTLY LARGE THAT A CONSTANT TEMPERATURE OF 29.5 ^{0}C CAN BE MAINTAINED. THE OVERALL HEAT-TRANSFER COEFFICIENT IS** $U = 568 W/m^2 K$ **. WILL THE REACTOR SATISFY THE CONSTRAINT OF 52^0C MAXIMUM TEMPERATURE IF THE COOLING COIL IS USED?**

EXAMPLE No.2: EFFECT OF COOLING COIL

- **NLES Solution**

Variable	Value	f(x)	Ini Guess
X	0,3326428	2,874E-10	0
T	311,68313	-8,842E-09	0
A	2,084E+12		
B	2,392E-13		

$$X = 33\%;$$

$$T = 312K$$

- **NLES Report (safenewt)**

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

- Explicit equations as entered by the user
- [1] A = 2084E09
- [2] B = exp(-9058/T)

THERMAL ENERGY CONSERVATION: APPLICATION TO ADIABATIC TUBULAR REACTORS

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

$$-\sum_{i=1}^{n} \theta_i \overline{C_{pi}} (T - T_{i0}) = X \left[\Delta H_{Rx}^{0}(T_R) + \overline{\Delta C_p}(T - T_R) \right]$$

- **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:** $A \underset{k_2}{\overset{k_1}{\Leftrightarrow}} B$
- **RATE EQUATION FOR *A*:** $-r_A = -\dfrac{dC_A}{dt} = k_1 C_A - k_2 C_B$
- **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

$$\mathrm{A} \rightleftarrows \mathrm{B}$$

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

Mole balance:

$$\frac{dX}{dV} = \frac{-r_{\mathrm{A}}}{F_{\mathrm{A}0}} \tag{T8-2.1}$$

Rate law:

$$-r_{\mathrm{A}} = k\left(C_{\mathrm{A}} - \frac{C_{\mathrm{B}}}{K_{\mathrm{C}}}\right) \tag{T8-2.2}$$

with

$$k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] \tag{T8-2.3}$$

$$K_C = K(T_2) \exp\left[\frac{\Delta H^\circ_{\mathrm{Rx}}}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)\right] \tag{T8-2.4}$$

Stoichiometry: Gas, $\varepsilon = 0$, $P = P_0$

$$C_{\mathrm{A}} = C_{\mathrm{A}0}(1-X)\,\frac{T_0}{T} \tag{T8-2.5}$$

$$C_{\mathrm{B}} = C_{\mathrm{A}0}X\,\frac{T_0}{T} \tag{T8-2.6}$$

Combine:

$$-r_{\mathrm{A}} = kC_{\mathrm{A}0}\left[(1-X) - \frac{X}{K_C}\right]\frac{T_0}{T} \tag{T8-2.7}$$

Energy balance:

To relate temperature and conversion we apply the energy balance to an adiabatic PFR. If all species enter at the same temperature, $T_{i0} = T_0$. Solving Equation (8-50) to obtain the function of conversion yields

$$T = \frac{X[-\Delta H^\circ_{\mathrm{Rx}}(T_R)] + \sum \Theta_i \tilde{C}_{pi} T_0 + X\,\Delta\hat{C}_p T_R}{\sum \Theta_i \tilde{C}_{pi} + X\,\Delta\hat{C}_p} \tag{T8-2.8}$$

If pure A enters and $\Delta\hat{C}_p = 0$, then

$$T = T_0 + \frac{X[-\Delta H^\circ_{\mathrm{Rx}}(T_R)]}{\tilde{C}_{p_{\mathrm{A}}}} \tag{T8-2.9}$$

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,

$$V = F_{\mathrm{A}0}\int_0^{X_3} \frac{dX}{-r_{\mathrm{A}}} = F_{\mathrm{A}0}\int_0^{X_3}\left(\frac{1}{-r_{\mathrm{A}}}\right)dX \tag{T8-2.10}$$

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 $-r_{\mathrm{A}}$ using Equation (T8-2.7).
7. Calculate $(1/-r_{\mathrm{A}})$.
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. $(1/-r_{\mathrm{A}})$.
10. Use numerical integration formulas, for example,

$$V = F_{\mathrm{A}0}\int_0^{X_3}\left(\frac{1}{-r_{\mathrm{A}}}\right)dX = \frac{3}{8}h\left[\frac{1}{-r_{\mathrm{A}}(x=0)} + \frac{3}{-r_{\mathrm{A}}(X_1)} + \frac{3}{-r_{\mathrm{A}}(X_2)} + \frac{1}{-r_{\mathrm{A}}(X_3)}\right] \tag{T8-2.11}$$

with

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

B. Ordinary Differential Equation (ODE) Solver

1. $$\frac{dX}{dV} = \frac{kC_{\mathrm{A}0}}{F_{\mathrm{A}0}}\left[(1-X) - \frac{X}{K_C}\right]\frac{T_0}{T} \tag{T8-2.12}$$
2. $$k = k_1(T_1)\exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] \tag{T8-2.13}$$
3. $$K_C = K_{C2}(T_2)\exp\left[\frac{\Delta H_{\mathrm{Rx}}}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)\right] \tag{T8-2.14}$$
4. $$T = T_0 + \frac{X[-\Delta H_{\mathrm{Rx}}(T_R)]}{\tilde{C}_{p_{\mathrm{A}}}} \tag{T8-2.15}$$
5. Enter parameter values k_1, E, R, K_{C2}, $\Delta H_{\mathrm{Rx}}(T_R)$, $\tilde{C}_{p_{\mathrm{A}}}$, $C_{\mathrm{A}0}$, T_0, T_1, T_2.
6. Enter in intial values $X = 0$, $V = 0$ and final values $X = X_{\mathrm{f}}$ and $V = V_{\mathrm{f}}$.

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 UNDE 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:** $C_{P(n-B)} = C_{P(i-B)} = 141 J/moleK$
- **i-PENTANE:** $C_{P(i-P)} = 161 J/moleK; E = 65.7 kJ/mole;$

$$K_c = 3.03\_at\_60^0 C; C_{A0} = 9.3 kmole/m^3$$

EXAMPLE No.3: DESIGN OF A PFR

POLYMATH PROGRAM

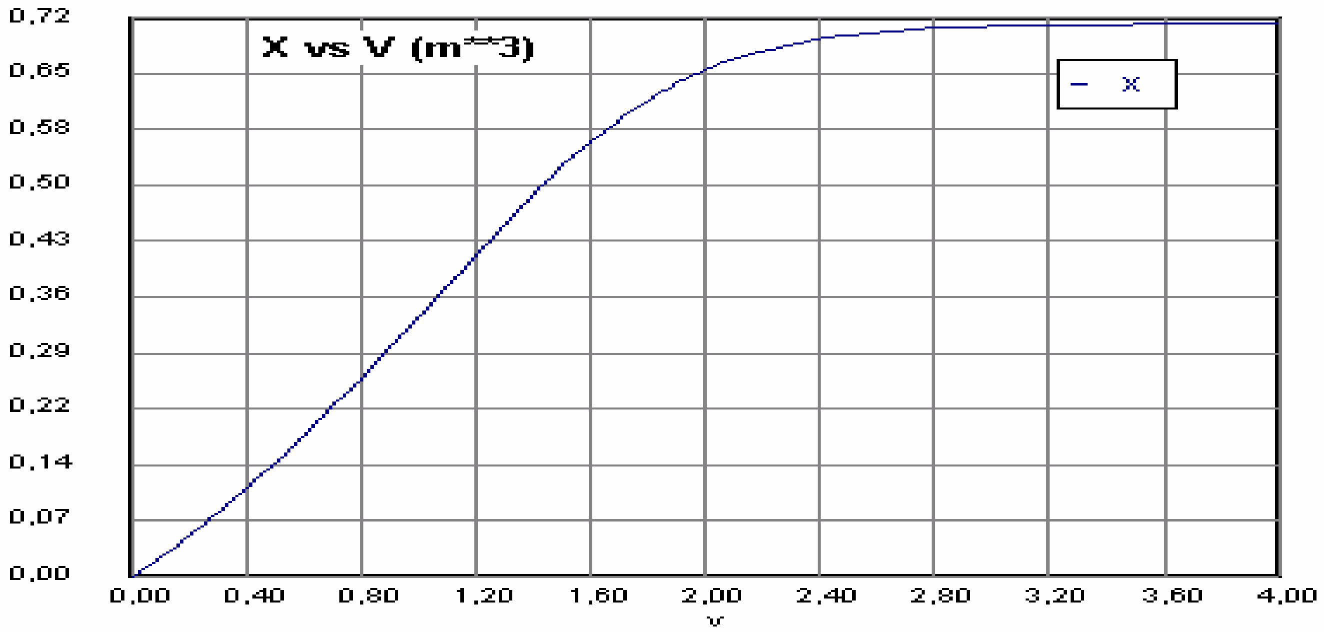
- **ODE Report (RKF45)**

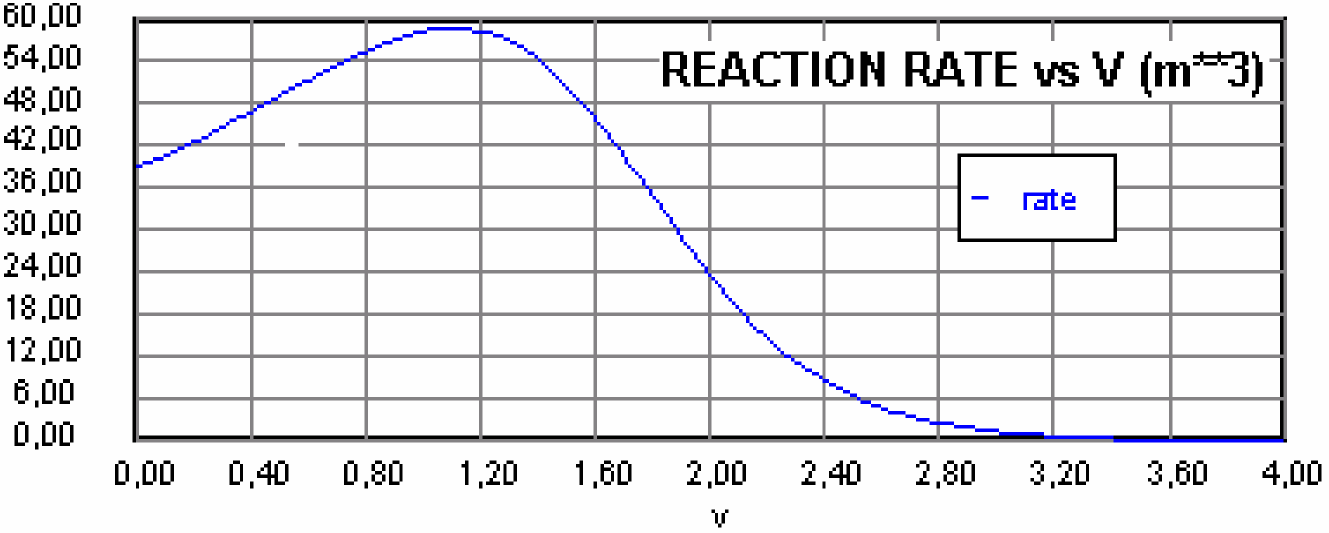
- Differential equations as entered by the user
- [1] d(X)/d(v) = -ra/Fa0

- 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

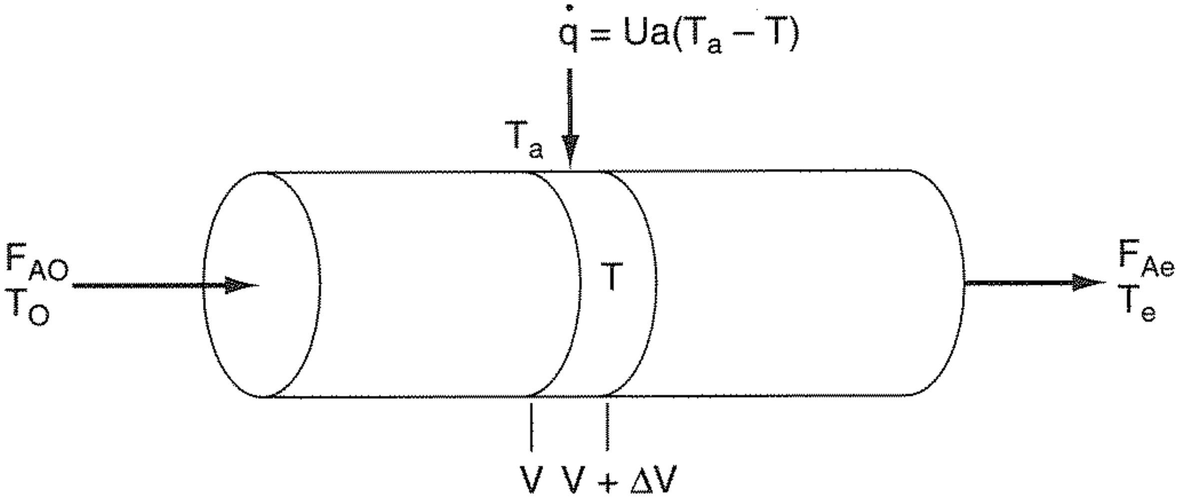
- Independent variable
- variable name : v
- initial value : 0
- final value : 4

EXAMPLE No.3: DESIGN OF A PFR





THERMAL ENERGY CONSERVATION: APPLICATION TO TUBULAR REACTORS WITH HEAT EXCHANGE



$$\dot{Q} - F_{A0}\int_{T_0}^{T}\sum_{i=1}^{n}\theta_i C_{pi}\,dT - F_{A0}X\left[\Delta H_{Rx}^{0}(T_R) + \int_{T_R}^{T}\Delta C_p\,dT\right] = 0$$

THERMAL ENERGY CONSERVATION: APPLICATION TO TUBULAR REACTORS WITH HEAT EXCHANGE

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

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

- **THE MOLE BALANCE IS**

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

2 EQUATIONS FOR 2 UNKNOWNS: X AND T

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:** $CH_3COCH_3 \rightarrow CH_2CO + CH_4$

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

  $$A \rightarrow B + C$$

  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.**

HEATS OF FORMATION AT 298 K

$$H^0_{Rx}(T_R)_A = -216.67 kJ/mole;$$

$$H^0_{Rx}(T_R)_B = -61.09 kJ/mole;$$

$$H^0_{Rx}(T_R)_C = -74.81 kJ/mole;$$

TEMPERATURE-DEPENDENT HEAT CAPACITIES

$$C_{PA} = 26.63 + 0.183T - 45.86 \cdot 10^{-6} T^2 (J/moleK);$$

$$C_{PB} = 20.04 + 0.0945T - 30.95 \cdot 10^{-6} T^2 (J/moleK);$$

$$C_{PA} = 13.39 + 0.077T - 18.71 \cdot 10^{-6} T^2 (J/moleK);$$

EXAMPLE No.4: ADIABATIC CASE

- **ODE Report (RKF45)**

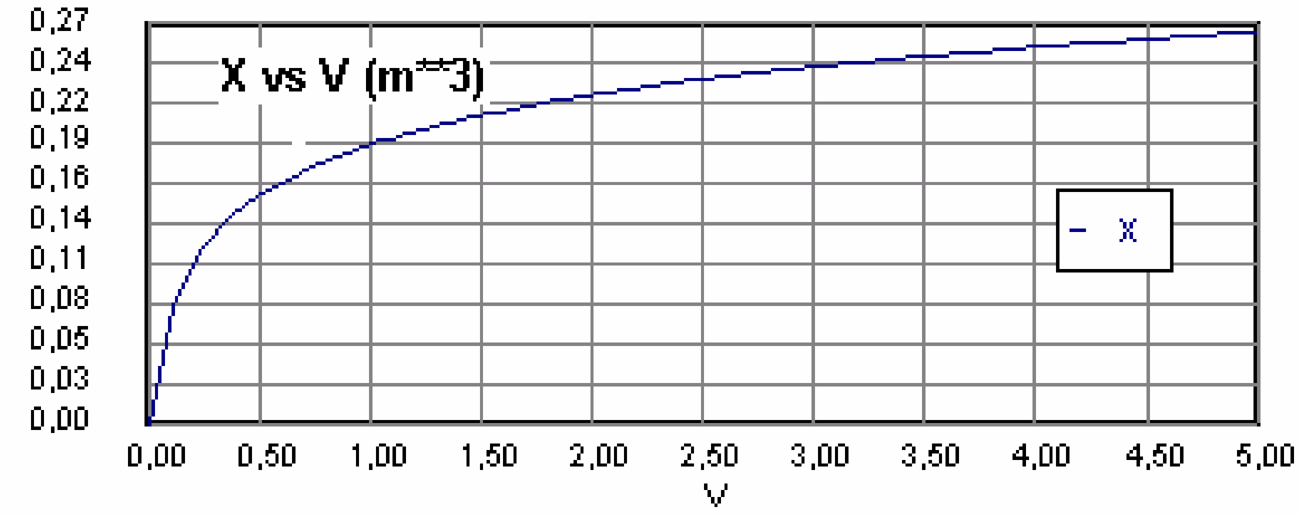
  Differential equations as entered by the user
- [1] d(X)/d(V) = -ra/Fao
- [2] d(T)/d(V) = -ra*(-deltaH)/(Fao*Cpa+X*delCp)

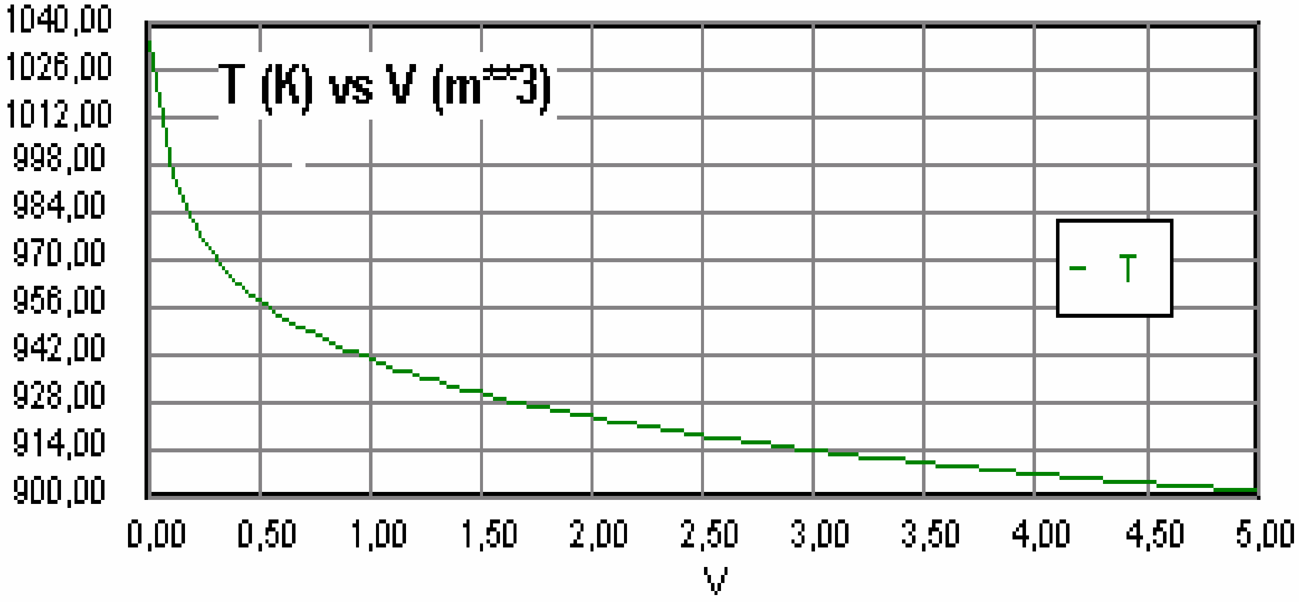
POLYMATH PROGRAM

- 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 = -k*Cao*(1-X)/(1+X)*To/T

- Independent variable
- variable name : V
- initial value : 0
- final value : 5

EXAMPLE No.4: ADIABATIC CASE





EXAMPLE No.4: CONCLUSION FOR ADIABATIC CASE

- **FOR THE ADIABATIC CASE, THE REACTION DIES OUT AFTER 2.5 m^3, 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 N_2 WHICH COULD SUPPLY THE SENSIBLE HEAT FOR THIS ENDOTHERMIC 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)**

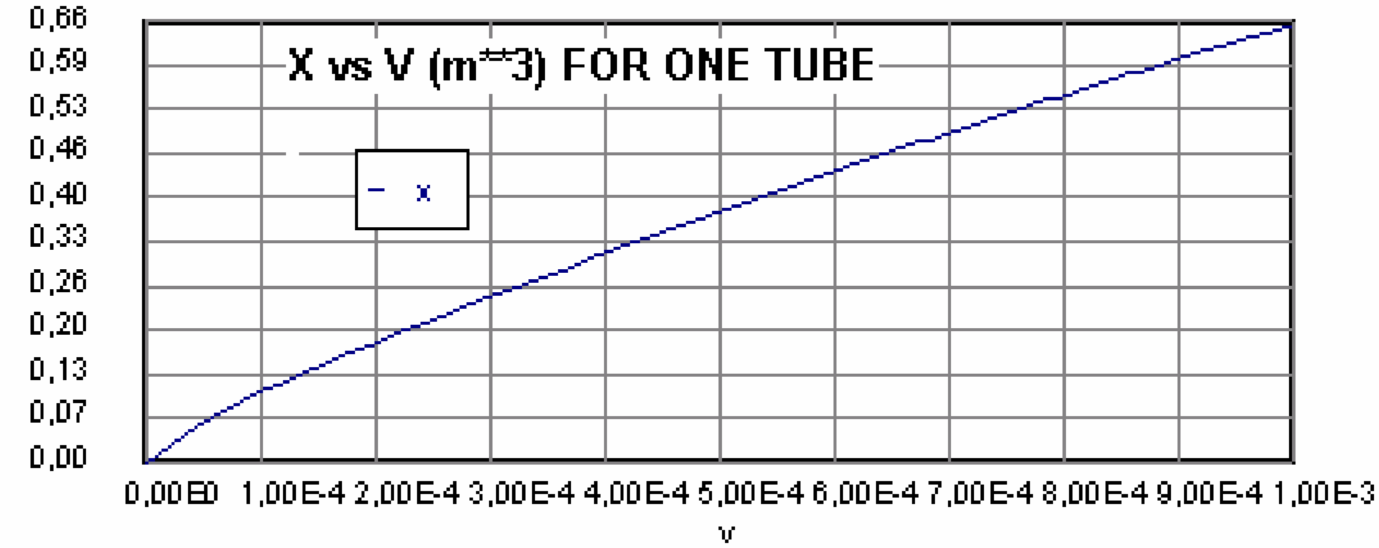
  Differential equations as entered by the user
- `[1]` d(x)/d(v) = -ra/fa0
- `[2]` d(t)/d(v) = (ua*(ta-t)+ra*dh)/(fa0*(cpa+x*dcp))

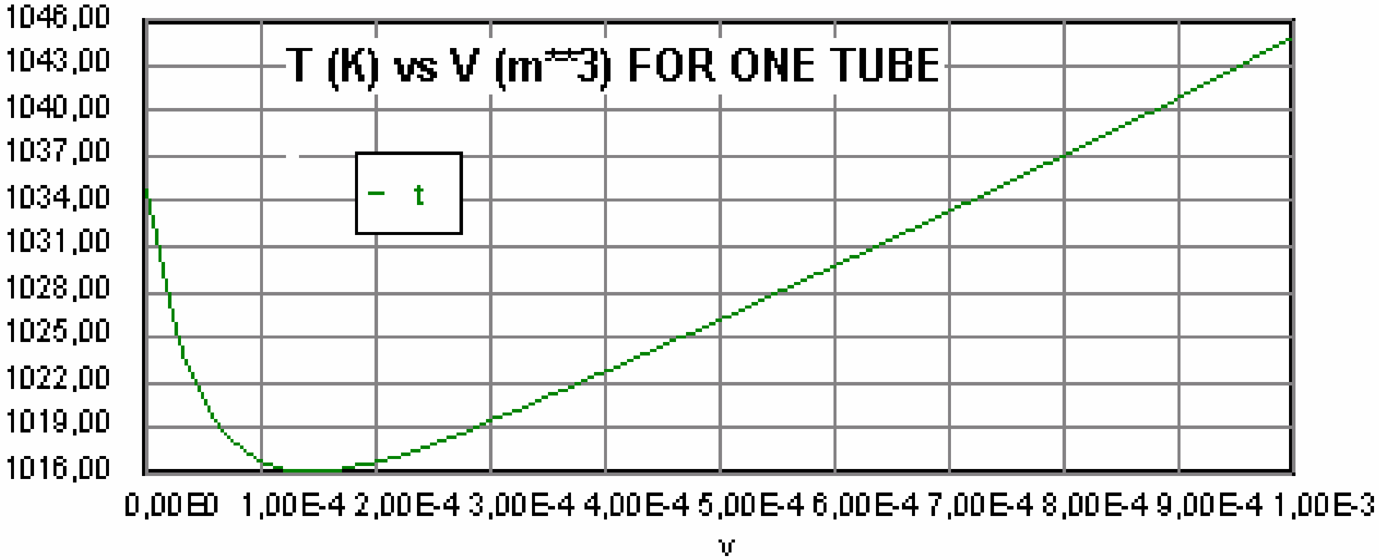
POLYMATH PROGRAM

- 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*t
- `[5]` dcp = 68e-01-115e-04*t-381e-08*t*t
- `[6]` ca0 = 188e-01
- `[7]` t0 = 1035
- `[8]` term = -127e-08*(t^3-298^3)
- `[9]` dh = 80770+68e-01*(t-298)-575e-05*(t^2-298^2)+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

EXAMPLE No.4: HEAT EXCHANGER CASE





EXAMPLE No.4:
CONCLUSION FOR HEAT EXCHANGER CASE

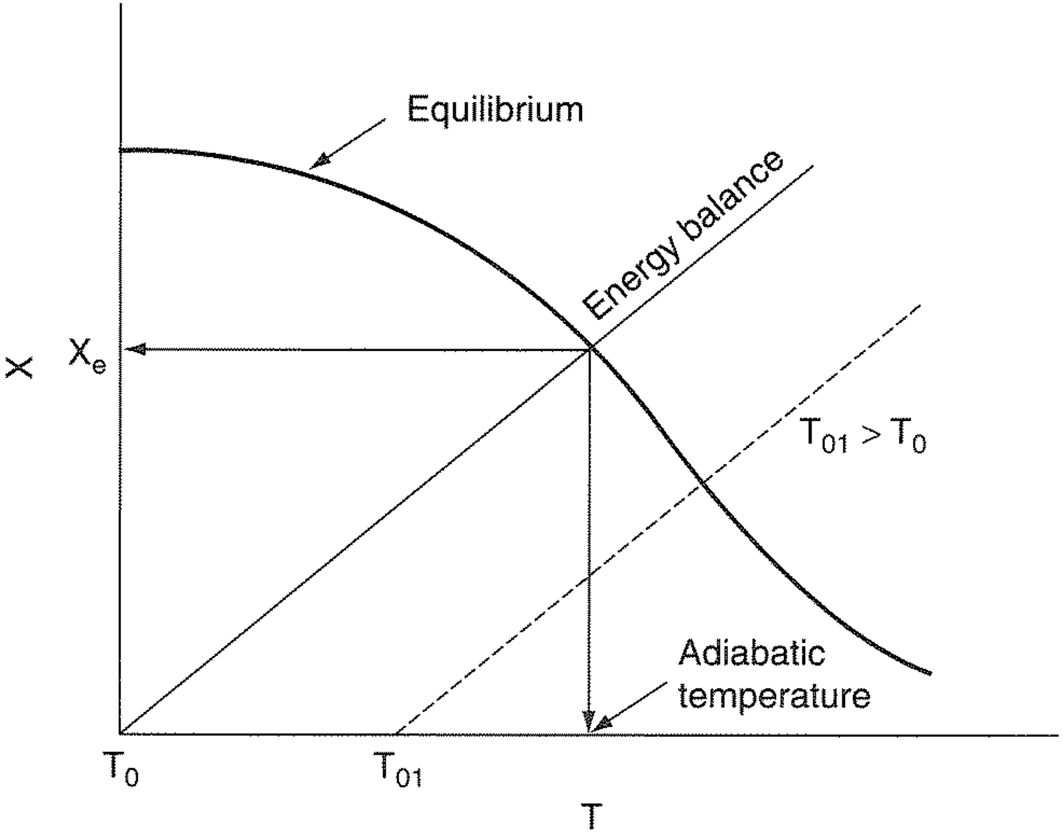
- **THE REACTOR TEMPERATURE GOES THROUGH A MINIMUM ALONG THE LENGTH OF THE REACTOR. AT THE FRONT OF THE REACTOR, THE REACTION TAKES PLACE VERY RAPIDLY, DRAWING ENERGY FROM THE SENSIBLE HEAT OF THE GAS CAUSING THE GAS TEMPERATURE TO DROP BECAUSE THE HEAT EXCHANGER CANNOT SUPPLY ENERGY AT THE EQUAL OR GREATER RATE. THIS DROP IN TEMPERATURE, COUPLED WITH THE CONSUMPTION OF REACTANTS, SLOWS THE REACTION RATE AS WE MOVE DOWN THE REACTOR. BECAUSE OF THIS SLOWER REACTION RATE, THE HEAT EXCHANGER SUPPLIES ENERGY AT A RATE GREATER THAN THE REACTION DRAWS ENERGY FROM THE GASES AND, AS A RESULT, THE TEMPERATURE INCREASES.**

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 TEMPERATUTE 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:**

$$H_A^0(298K) = -40000cal/mole; H_B^0(298K) = -60000cal/mole;$$

$$C_{PA} = 50cal/moleK; C_{PB} = 50cal/moleK; K_e = 10^5\_at\_298K;$$

- **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 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 $20 dm^3/s$ 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:

$\alpha = 0.019 / kg\_cat.$ for particle diameter D_1

$\alpha = 0.0075 / kg\_cat.$ for particle diameter D_2

a) Plot the temperature T, conversion X and pressure $y = P/P_0$ along the length of the reactor that is as a function of the catalyst mass w.
b) Vary the parameters α and P_0 to learn the ranges of values in which they dramatically affect conversion.

Additional information:

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

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

$k = 0.133 \cdot \exp\left[\frac{E}{R}\left(\frac{1}{450} - \frac{1}{T}\right)\right] \frac{dm^3}{kg \cdot cat \cdot s}$ with $E = 31.4 kJ/mol; R = 8.314 J/mol \cdot K$

Example No.6: Plug flow reactor

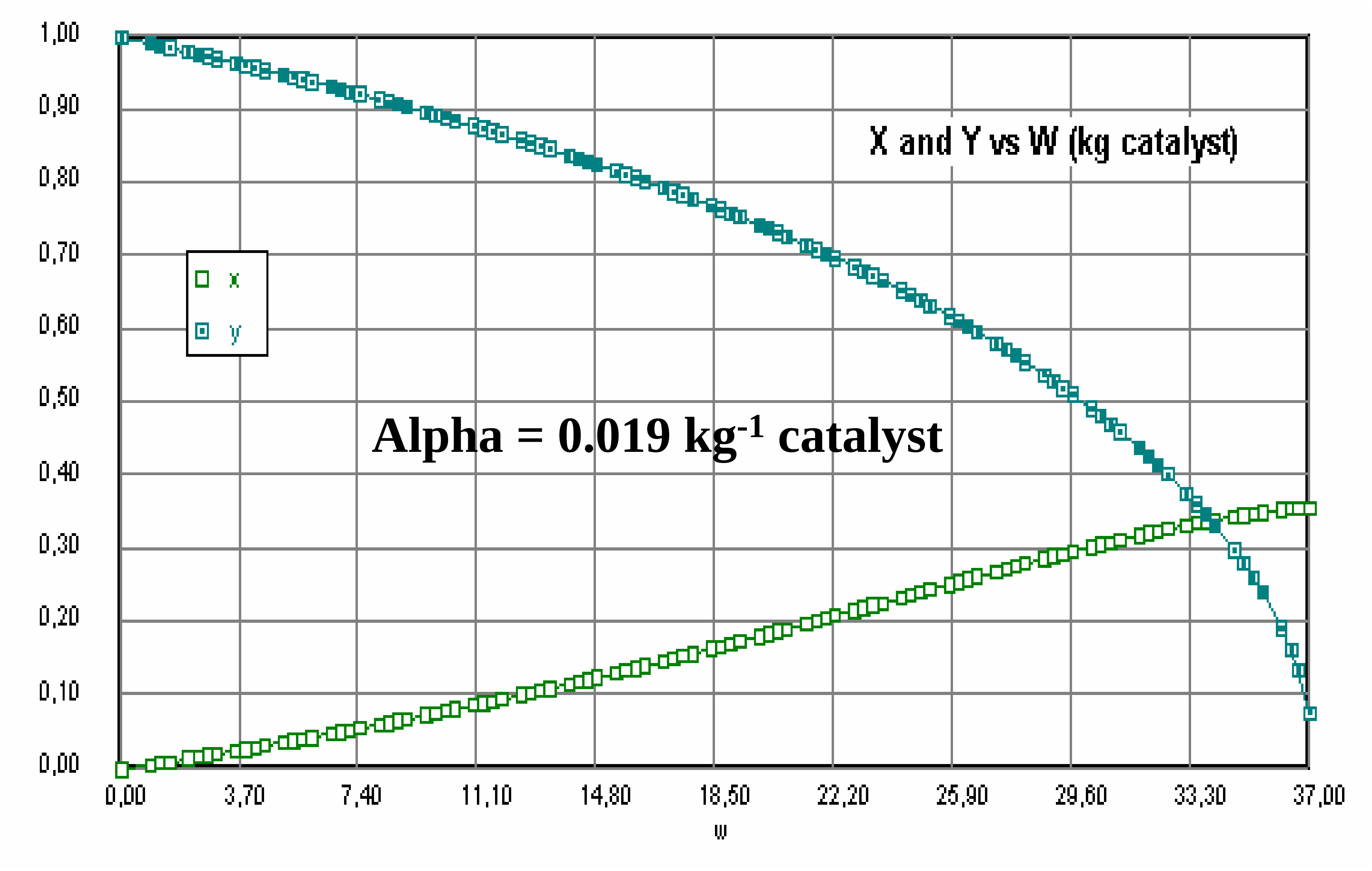
- **ODE Report (RKF45)**

- Differential equations as entered by the user
- [1] d(t)/d(w) = ra*dhr/(fao*cpa)
- [2] d(x)/d(w) = -ra/fao
- [3] d(y)/d(w) = -(1+x)*(t/450)*alpha/(2*y)

- Explicit equations as entered by the user
- [1] fao = 542E-02
- [2] dhr = -20000
- [3] cpa = 40
- [4] alpha = 19E-03
- [5] k = 133E-03*exp(37766E-01*(1/450-1/t))
- [6] cao = 271E-03
- [7] ca = cao*(1-x)*(450/t)/(1+x)*y
- [8] ra = -k*ca
- [9] rate = -ra

- 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