Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.
Multiple Reactions with Heat Effects
Multiple Reactions with Heat Effects

**PFR/PBR:**

\[
\frac{dT}{dV} = \frac{Ua(T_a - T) + \sum_{i=1}^{n} (-r_{ij})(\Delta H_{Rxij})}{\sum_{j=1}^{m} F_j C_{pj}}
\]

**CSTR:**

\[
UA(T_a - T) - F_{A0} \sum_{j=1}^{m} C_{pi} \theta_i (T - T_0) \sum_{i=1}^{q} (r_{ij})H_{Rxij}(T) = 0
\]

These equations are coupled with the mole balances and rate law equations.
Multiple Reactions with Heat Effects

Multiple Reactions

Make sure each rate of reaction and rate law are in respect to the same species (example, A); Subscripts must agree

\[
\frac{dT}{dV} = \frac{Q_g - Q_r}{\sum F_i C_{pi}} \\
Q_g = \sum r_{ij} \Delta H_{Rxij} = r_{1A} \Delta H_{Rx1A} + r_{2A} \Delta H_{Rx2A}
\]
Multiple Reactions with Heat Effects

Multiple Reactions

1) Mole Balances:— every species (no conversion!)

2) Rate Laws:
   – relative rates
   – net rates

3) Stoichiometry:

\[ C_A = C_{T0} \frac{F_A}{F_T} p \frac{T_0}{T} \]

\[ \frac{dp}{dW} = -\alpha \frac{F_T}{2 p} \frac{T}{F_{T0} T_0} \]
Multiple Reactions with Heat Effects

Multiple Reactions

4) Heat Effects:

\[
\frac{dT}{dV} = \frac{Q_g - Q_r}{\sum F_i C_{pi}}
\]

\( Q_g \) = heat produced

\( Q_r \) = heat removed

\( Q_g = \sum r_{ij} \Delta H_{Rij} \) \hspace{1cm} (must have matching i, j)

\( Q_r = Ua(T - T_a) \)
Multiple Reactions with Heat Effects

4) Heat Effects:

\[ \frac{dT}{dV} = \frac{Q_g - Q_r}{\sum F_i C_{pi}} \]

\[ Q_g = r_{1A} \Delta H_{R1A} + r_{2A} \Delta H_{R2A} \]

\[ Q_r = Ua(T - T_a) \]

\[ \sum F_i C_{pi} = F_A C_{PA} + F_B C_{PB} + F_C C_{PC} + F_D C_{PD} \]

\[ \frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_i C_{Pcool}} \]

5) Parameters

\[ E_1, E_2, F_{A0}, Ua, \ldots \text{etc} \]
4) Heat Effects:

\[
\frac{dT}{dV} = \frac{Q_g - Q_r}{\sum F_i C_{pi}} \quad (23)
\]

\[
\Delta H_{Rx1A} = -12kJ \ (\text{mole of A reacted in reaction 1})
\]

\[
\Delta H_{Rx2B} = +8kJ \ (\text{mole of B reacted in reaction 2})
\]

\[
Q_g = r_{1A} \Delta H_{Rx1A} + r_{2B} \Delta H_{Rx2B}
\]

Use relative rates of reaction to get \( r_{2B} \) in terms of the rate law that is given for reaction 2, e.g.,

\[
(2) \quad 3 \text{A} + 2\text{B} \rightarrow 2\text{D}
\]

\[
-r_{2A} = k_{2A} C_A^3 C_B^2 \quad \text{then} \quad r_{2B} = \frac{2}{3} r_{2A}
\]
The complex gas phase reactions

(1) \[ A + 2B \rightarrow C \quad -r_{1A} = k_{1A}C_AC_B^2 \quad \Delta H_{RX1B} = -15,000 \text{ cal/mol B} \]

(2) \[ A + C \rightarrow 2D \quad -r_{2C} = k_{2C}C_AC_C \quad \Delta H_{RX2A} = -10,000 \text{ cal/mol A} \]

take place in a 10 dm$^3$ PFR with a heat exchanger. Plot the temperature, concentrations, molar flow rates down the length of the reactor for the following operations. E.g., Note any maximums or minimums on your plot along with how they change for the different types of operations.

(a) Adiabatic operation
(b) Heat exchange with constant $T_a$
(c) Co current heat exchange
(d) Counter current heat exchange
(e) For parts (c) and (d), plot $Q_r$ and $Q_g$ down the length of the reactor. What do you observe?

*Additional Information*

\[
\begin{align*}
C_{P_A} &= 10 \text{ cal/mol/K} & C_{P_C} &= 30 \text{ cal/mol/K} \\
C_{P_B} &= 10 \text{ cal/mol/K} & C_{P_D} &= 20 \text{ cal/mol/K} \\
k_{1A} &= 40 \left( \text{dm}^3/\text{mol} \right)^2/\text{s/K} \text{ at } 300K \text{ and } E_1 = 8,000 \text{ cal/mol} \\
k_{2C} &= 2 \left( \text{dm}^3/\text{mol} \right)^2/\text{s/K} \text{ at } 300K \text{ and } E_2 = 12,000 \text{ cal/mol} \\
C_{T_0} &= 0.2 \text{ mol/dm}^3 & C_{P_{\text{cool}}} &= 1 \text{cal/g/K} & m_{\text{cool}} &= 20 \text{g/s} \\
U_a &= 80 \text{ cal/dm}^3/\text{s/K} & T_{ao} &= 325K & T_0 &= 300K \\
F_{A0} &= 5 \text{ mol/s} & F_{B0} &= 10 \text{ mol/s} & F_{C0} &= 0 & F_{D0} &= 0
\end{align*}
\]
# Ordinary Differential Equations

## Calculated values of DEQ variables

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<th>Variable</th>
<th>Initial value</th>
<th>Final value</th>
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## Differential equations

1. \( \frac{d(Fa)}{d(V)} = ra \)
2. \( \frac{d(Fb)}{d(V)} = rb \)
3. \( \frac{d(Fc)}{d(V)} = rc \)
4. \( \frac{d(Fd)}{d(V)} = rd \)
5. \( \frac{d(T)}{d(V)} = \frac{(Qg-qr)*sumFiCpi}{Ua*(T-Ta)/m/Cpco} \)
6. \( \frac{d(Ta)}{d(V)} = Ua*(T-Ta)/m/Cpco \)

## Explicit equations

1. \( E2 = 12000 \)
2. \( y = 1 \)
3. \( R = 1.987 \)
4. \( Ft = Fa+Fb+Fc+Fd \)
5. \( To = 300 \)
6. \( k2c = 2*exp((E2/R)*(1/300-1/T)) \)
7. \( E1 = 8000 \)
8. \( Cto = 0.2 \)
9. \( Ca = Cto*(Fb/Ft)*(To/T)y \)
10. \( Cc = Cto*(Fc/Ft)*(To/T)y \)
11. \( r2c = -k2c*Cao*Cc \)
12. \( Cpco = 10 \)
13. \( m = 50 \)
14. \( Cb = Cto*(Fb/Ft)*(To/T)y \)
15. \( k1a = 40*exp((E1/R)*(1/300-1/T)) \)
16. \( rla = -k1a*Cao*Cb^2 \)
17. \( r1b = 2*r1a \)
18. \( rb = r1b \)
19. \( r2a = r2c \)
20. \( DH1b = -15000 \)
21. \( DH2a = -10000 \)
22. \( rlc = r1a \)
23. \( Ta55 = 325 \)
24. \( Cpd = 20 \)
25. \( Cpc = 10 \)
26. \( Cpb = 10 \)
27. \( Cpa = 30 \)
28. \( sumFiCpi = Cpa*Fa+Cpb+Fb+Cpc+Fc+Cpd*Fd \)
29. \( rc = r1c+r2c \)
30. \( Ua = 80 \)
31. \( r2d = -2*r2c \)
32. \( ra = r1a+r2a \)
33. \( rd = r2d \)
34. \( Qg = r1b*DH1b+r2a*DH2a \)
35. \( Qr = Ua*(T-Ta) \)
Lecture 18 Multiple Reactions with Heat Exchange Constant Ta

- T
- $T_a$

- $F_a$
- $F_b$
- $F_c$
- $F_d$

Lecture 18 Multiple Reactions with Heat Exchange Constant Ta

- $Q_g$
- $Q_r$

Lecture 18 Multiple Reactions with Heat Exchange Constant Ta
Multiple Reactions with **Heat Effects**

Multiple Reactions

4) Heat Effects:

\[
\frac{dT}{dV} = (-r_A)(-\Delta H_{Rx}) - \frac{Ua(T - T_a)}{\sum F_i C_{Pi}}
\]

\[
\frac{dT}{dV} = \frac{Q_g - Q_r}{\sum F_i C_{Pi}}
\]

*\(Q_g\) = heat produced

*\(Q_r\) = heat removed

\[
Q_g = \sum r_{ij} \Delta H_{Rij}
\]

(must have matching i, j)
Multiple Reactions with Heat Effects in a PFR and CSTR

Examples:

(1) $A + 2B \rightarrow C$

$-r_{1A} = k_{1A} C_A C_B^2$

and

$\Delta H_{R1A} = -20,000 \text{ cal/mol A}$

(2) $2A + 3C \rightarrow D$

$-r_{2C} = k_{2C} C_A^2 C_C^3$

and

$\Delta H_{R2A} = 10,000 \text{ cal/mol A}$
Example A: Liquid Phase CSTR

(1) \[ A + 2B \rightarrow C \quad -r_{1A} = k_{1A} C_A C_B^2 \]

NOTE: The specific reaction rate \( k_{1A} \) is defined with respect to species A.

(2) \[ 3C + 2A \rightarrow D \quad -r_{2C} = k_{2C} C_C^3 C_A^2 \]

NOTE: The specific reaction rate \( k_{2C} \) is defined with respect to species C.
Example A: Liquid Phase CSTR

The complex liquid phase reactions take place in a 2,500 dm$^3$ CSTR. The feed is equal molar in A and B with $F_{A0} = 200$ mol/min, the volumetric flow rate is 100 dm$^3$/min and the reaction volume is 50 dm$^3$.

Find the concentrations of A, B, C and D existing in the reactor along with the existing selectivity.

Plot $F_A$, $F_B$, $F_C$, $F_D$ and $S_{C/D}$ as a function of V
Example A: Liquid Phase CSTR

Solution

Liquid Phase CSTR

1) Mole Balances:

(1) \[ f(C_A) = \nu_0 C_{A0} - \nu_0 C_A + r_A V \]

(2) \[ f(C_B) = \nu_0 C_{B0} - \nu_0 C_B + r_B V \]

(3) \[ f(C_C) = -\nu_0 C_C + r_C V \]

(4) \[ f(C_D) = -\nu_0 C_D + r_D V \]

2) Net Rates:

(5) \[ r_A = r_{1A} + r_{2A} \]
3) Stoichiometry:

\[
(16) \quad C_A = \frac{F_A}{\nu_0} \\
(17) \quad C_B = \frac{F_B}{\nu_0} \\
(18) \quad C_C = \frac{F_C}{\nu_0} \\
(19) \quad C_D = \frac{F_D}{\nu_0}
\]

4) Parameters:

\[
(20) \quad \nu_0 = 100 \text{ dm}^3/\text{min} \\
(21) \quad k_{1A} = 10 \left(\text{dm}^3/\text{mol}\right)^2/\text{min} \\
(22) \quad k_{2C} = 15 \left(\text{dm}^3/\text{mol}\right)^4/\text{min}
\]
Example B: Liquid Phase PFR

Takes place in a PFR. The feed is equal molar in A and B and F\textsubscript{A0} = 200 mol/min and the volumetric flow rate is 100 dm\textsuperscript{3}/min. The reaction volume is 50 dm\textsuperscript{3} and the rate constants are:

\[ k_{1A} = 10 \left( \text{dm}^3/\text{mol} \right)^2 / \text{min} \]
\[ k_{2C} = 15 \left( \text{dm}^3/\text{mol} \right)^4 / \text{min} \]

Rate laws are the same as Example A.

Plot F\textsubscript{A}, F\textsubscript{B}, F\textsubscript{C}, F\textsubscript{D} and S\textsubscript{C/D} as a function of V.
Example B: Liquid Phase PFR

1) Mole Balances:

\[
\begin{align*}
(1) & \quad \frac{dF_A}{dV} = r_A \\
(2) & \quad \frac{dF_B}{dV} = r_B \\
(3) & \quad \frac{dF_C}{dV} = r_C \\
(4) & \quad \frac{dF_D}{dV} = r_D
\end{align*}
\]

\(F_{A0} = 200 \text{ mol/min}\)

\(F_{B0} = 200 \text{ mol/min}\)

\(V_F = 50 \text{ dm}^3\)
Example B: Liquid Phase PFR

2) Net Rates:

(5) \[ r_A = r_{1A} + r_{2A} \]

(6) \[ r_B = r_{1B} \]

(7) \[ r_C = r_{1C} + r_{2C} \]

(8) \[ r_D = r_{2D} \]

2) Rate Laws:

(9) \[ r_{1A} = -k_{1A} C_A C_B^2 \]

(10) \[ r_{2C} = -k_{2C} C_A^2 C_C^3 \]
Example B: **Liquid Phase PFR**

2) **Relative Rates:**

\[
\frac{r_{1A}}{-1} = \frac{r_{1B}}{-2} = \frac{r_{1C}}{1} \quad \text{Reaction 1}
\]

(11) \( r_{1B} = 2r_{1A} \)

(12) \( r_{1C} = -r_{1A} \) \quad \text{Reaction 2}

\[
\frac{r_{2A}}{-2} = \frac{r_{2C}}{-3} = \frac{r_{2D}}{1}
\]

(13) \( r_{2A} = \frac{2}{3} r_{2C} \)

(14) \( r_{2D} = -\frac{1}{3} r_{2C} \)
Example B: Liquid Phase PFR

2) Rate Laws:

\[ r_{1A} = -k_{1A} C AC_B^2 \] (5) \[ k_{1A} = k_{1A1} \exp\left[(E_1/R)(1/T_1 - 1/T)\right] \] (6)

\[ r_{2C} = -k_{2C} C_A^2 C_C^3 \] (7) \[ k_{2C} = k_{2C2} \exp\left[(E_2/R)(1/T_2 - 1/T)\right] \] (8)

\[ r_A = r_{1A} + r_{2B} \] (9) \[ r_B = r_{1B} \] (10)

\[ r_C = r_{1C} + r_{2C} \] (11) \[ r_D = r_{2D} \] (12)

\[ r_{1C} = -r_{1A} \] (13) \[ r_{1B} = 2r_{1A} \] (13)

\[ r_{2A} = 2/3r_{2C} \] (15) \[ r_{2D} = -1/3r_{2C} \] (16)
Example B: Liquid Phase PFR

3) Stoichiometry:

\[ C_A = C_{T0} \frac{F_A}{F_T} p \frac{T_0}{T} \]  \hspace{1cm} (17) \hspace{1cm} \[ C_B = C_{T0} \frac{F_B}{F_T} p \frac{T_0}{T} \]  \hspace{1cm} (18)

\[ C_C = C_{T0} \frac{F_C}{F_T} p \frac{T_0}{T} \]  \hspace{1cm} (19) \hspace{1cm} \[ C_D = C_{T0} \frac{F_D}{F_T} p \frac{T_0}{T} \]  \hspace{1cm} (20)

\[ F_T = F_A + F_B + F_C + F_D \]  \hspace{1cm} (21) \hspace{1cm} \[ \frac{dp}{dV} = -\alpha \rho \frac{F_T}{2p} \frac{T}{F_{T0}} \frac{T}{T_0} \]  \hspace{1cm} (22)
Multiple Reactions with Heat Effects

4) Heat Effects:

\[ \frac{dT}{dV} = \frac{Q_g - Q_r}{\sum F_i C_{pi}} \]  \hspace{.5cm} (23)
\[ \frac{dT_a}{dV} = \frac{U a (T - T_a)}{\dot{m}_i C_{pcool}} \]  \hspace{.5cm} (26)  \hspace{.5cm} Co-Current

\[ Q_g = r_{1A} \Delta H_{R1A} + r_{2A} \Delta H_{R2A} \]  \hspace{.5cm} (24)
\[ Q_r = U a (T - T_a) \]  \hspace{.5cm} (25)

\[ \sum C_P = F_A C_{PA} + F_B C_{PB} + F_C C_{PC} + F_D C_{PD} \]  \hspace{.5cm} (27)

Parameters:

\[ E_1, \ E_2, \ F_{A0}, \ldots \]
Selectivity

If one were to write $S_{C/D}=F_C/F_D$ in the Polymath program, Polymath would not execute because at $V=0$, $F_C=0$ resulting in an undefined volume (infinity) at $V=0$. To get around this problem we start the calculation $10^{-4}$ dm$^3$ from the reactor entrance where $F_D$ will not be zero and use the following IF statement.

(15) \[ S_{C/D} = \begin{cases} \frac{F_C}{F_D} & \text{if } (V > 0.001) \\ 0 & \text{else} \end{cases} \]
Selectivity

3) Stoichiometry:

\[ C_A = \frac{F_A}{\nu_0} \quad (16) \]
\[ C_B = \frac{F_B}{\nu_0} \quad (17) \]
\[ C_C = \frac{F_C}{\nu_0} \quad (18) \]
\[ C_D = \frac{F_D}{\nu_0} \quad (19) \]

Parameters:

\[ \nu_0 = 100 \text{ dm}^3/\text{min} \quad (20) \]
\[ k_{1A} = 10 \left( \text{dm}^3/\text{mol} \right)^2/\text{min} \quad (21) \]
\[ k_{2C} = 15 \left( \text{dm}^3/\text{mol} \right)^4/\text{min} \quad (22) \]
End of Web Lecture 23
Class Lecture 18