Lecture 22

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.

Web Lecture 22
Class Lecture 18-Thursday 3/21/2013

Multiple Reactions with Heat Effects

Multiple Reactions with Heat Effects

PFR/PBR:

$$\frac{dT}{dV}=\frac{Ua\left(T_a-T\right)+\sum_{i=1}^{n}\left(-r_{ij}\right)\left(\Delta H_{Rxij}\right)}{\sum_{j=1}^{m}F_jC_{Pj}}$$

CSTR:

$$\mathrm{UA}\left(\mathrm{T_a}-\mathrm{T}\right)-\mathrm{F_{A0}}\sum_{j=1}^{m}\mathrm{C_{Pi}}\theta_i\left(\mathrm{T}-\mathrm{T_0}\right)\sum_{i=1}^{q}\left(\mathrm{r_{ij}}\right)\mathrm{H_{Rxij}}\left(\mathrm{T}\right)=0$$

These equations are coupled with the **mole balances** and **rate law** equations.

Multiple Reactions with Heat Effects

Multiple Reactions

Make sure it is in respect to A; Subscripts must agree

$$\frac{dT}{dV} = \frac{Q_g - Q_r}{\sum F_i C_{Pi}} \qquad Q_g = \sum r_{ij} \Delta H_{Rxij} = r_{1A} \Delta H_{Rx1A} + r_{2A} \Delta H_{Rx2A}$$

Multiple Reactions with Heat Effects

Multiple Reactions

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

2) Rate Laws:

– relative rates

– net rates

3) Stoichiometry:

$$C_A = C_{T0}\frac{F_A}{F_T}y\frac{T_0}{T}$$

$$\frac{dy}{dW} = \frac{-\alpha}{2y}\frac{F_T}{F_{T0}}\frac{T}{T_0}$$

Multiple Reactions with Heat Effects

Multiple Reactions

4) Heat Effects:

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

$$Q_g = \text{heat produced}$$

$$Q_r = \text{heat removed}$$

$$Q_g = \sum r_{ij} \Delta H_{Rxij} \qquad \text{(must have matching i, j)}$$

$$Q_r = Ua(T - T_a)$$

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

$$E_1,\ E_2,\ F_{A0}, Ua, \ldots etc$$

Multiple Reactions with Heat Effects

4) Heat Effects:

$$\frac{dT}{dV} = \frac{Q_g - Q_r}{\sum F_i C_{Pi}} \qquad (23)$$

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

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

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

Use relative rates of reaction

to get r_{2B} in terms of the rate law that is given for reaction 2,

e.g., (2) $3A + 2B \text{-->} 2D$

$$-r_{2A} = k_{2A} C_A^3 C_B \quad \text{then} \quad r_{2B} = \frac{2}{3} r_{2A}$$

The complex gas phase reactions

$$(1) \qquad A + 2B \rightarrow C \qquad -r_{1A} = k_{1A} C_A C_B^2 \qquad \Delta H_{Rx1B} = -15{,}000 \ \text{cal/mol B}$$

$$(2) \qquad A + C \rightarrow 2D \qquad -r_{2C} = k_{2C} C_A C_C \qquad \Delta H_{Rx2A} = -10{,}000 \ \text{cal/mol A}$$

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

$$C_{P_A} = 10 \ \text{cal/mol/K} \qquad C_{P_C} = 30 \ \text{cal/mol/K}$$

$$C_{P_B} = 10 \ \text{cal/mol/K} \qquad C_{P_D} = 20 \ \text{cal/mol/K}$$

$$k_{1A} = 40 \ \left(\text{dm}^3/\text{mol}\right)^2/\text{s}/\text{K} \ \text{at} \ 300\text{K} \ \text{and} \ E_1 = 8{,}000 \ \text{cal/mol}$$

$$k_{2C} = 2 \ \left(\text{dm}^3/\text{mol}\right)^2/\text{s}/\text{K} \ \text{at} \ 300\text{K} \ \text{and} \ E_2 = 12{,}000 \ \text{cal/mol}$$

$$C_{T_0} = 0.2 \ \text{mol/dm}^3 \ , \quad C_{P_{Cool}} = 1 \text{cal/g/K} \ , \quad \dot{m}_{Cool} 20 \text{g/s}$$

$$Ua = 80 \ \text{cal/dm}^3/\text{s}/\text{K} \ , \ T_{ao} = 325\text{K} \ , \ T_0 = 300\text{K}$$

$$F_{A0} = 5 \ \text{mol/s} \ , \ F_{B0} = 10 \ \text{mol/s} \ , \ F_{C0} = 0 \ , \ F_{D0} = 0$$

POLYMATH Report
Ordinary Differential Equations

Calculated values of DEQ variables

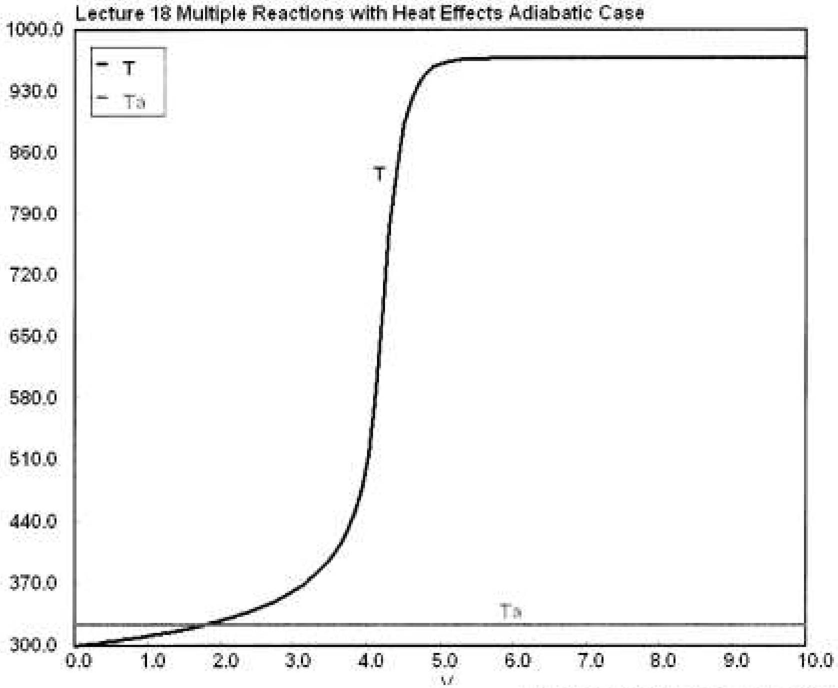
	Variable	Initial value	Final value
1	Ca	0.0666667	2.49E-05
2	Cb	0.1333333	0.0611818
3	Cc	0	0.0012689
4	Cpa	10.	10.
5	Cpb	10.	10.
6	Cpc	30.	30.
7	Cpco	10.	10.
8	Cpd	20.	20.
9	Cto	0.2	0.2
10	DH1b	-1.5E+04	-1.5E+04
11	DH2a	-10000.	-10000.
12	E1	8000.	8000.
13	E2	1.2E+04	1.2E+04
14	Fa	5.	0.0019942
15	Fb	10.	4.900364
16	Fc	0	0.1016299
17	Fd	0	4.896376
18	Ft	15.	9.900364
19	k1a	40.	6734.733
20	k2c	2.	4369.388
21	m	50.	50.
22	Qg	1422.222	20.21055
23	Qr	-2000.	1126.152
24	R	1.987	1.987
25	r1a	-0.0474074	-0.0006277
26	r1b	-0.0948148	-0.0012553
27	r1c	0.0474074	0.0006277
28	r2a	0	-0.000138
29	r2c	0	-0.000138
30	r2d	0	0.0002761
31	ra	-0.0474074	-0.0007657
32	rb	-0.0948148	-0.0012553
33	rc	0.0474074	0.0004896
34	rd	0	0.0002761
35	sumFiCpi	150.	150.
36	T	300.	485.4075
37	Ta	325.	471.3306
38	Ta55	325.	325.
39	To	300.	300.
40	Ua	80.	80.
41	V	0	10.
42	y	1.	1.

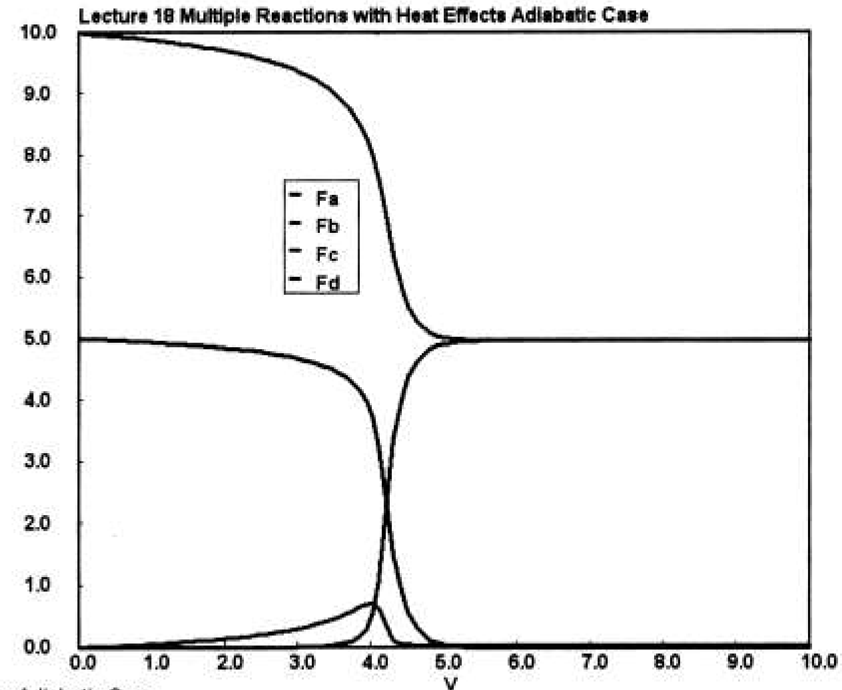
Differential equations

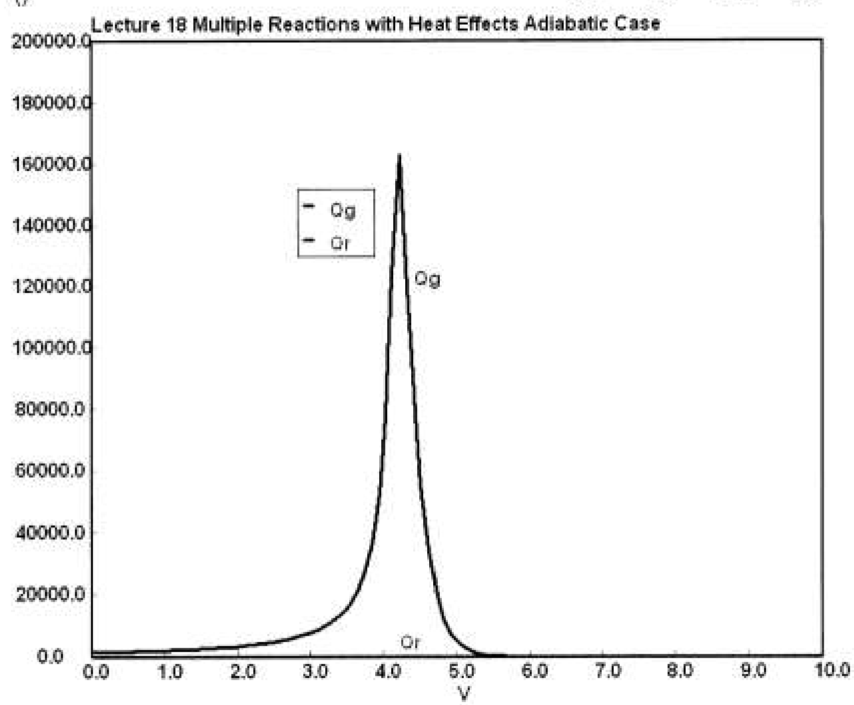
1 d(Fa)/d(V) = ra
2 d(Fb)/d(V) = rb
3 d(Fc)/d(V) = rc
4 d(Fd)/d(V) = rd
5 d(T)/d(V) = (Qg-Qr)/sumFiCpi
6 d(Ta)/d(V) = Ua*(T-Ta)/m/Cpco

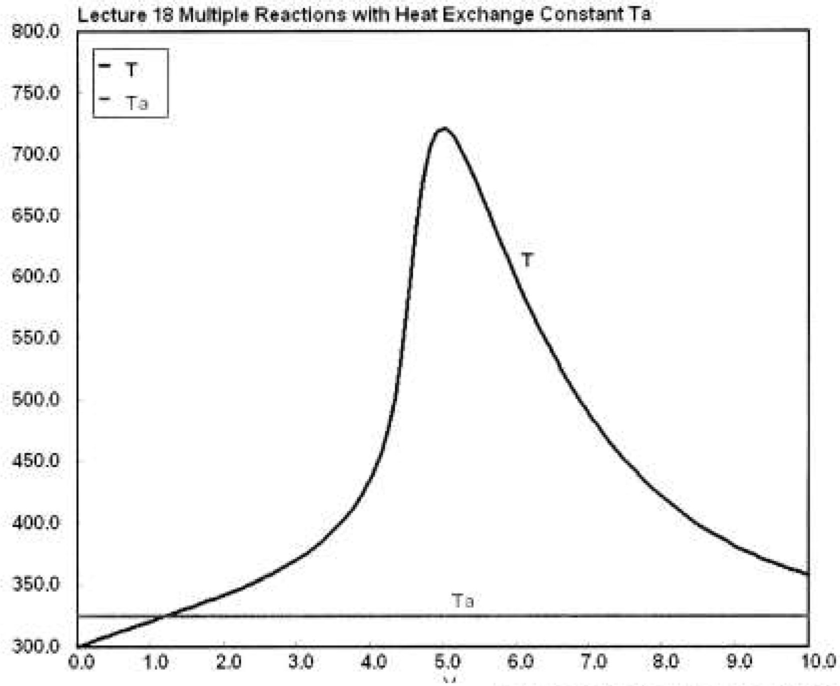
Explicit equations

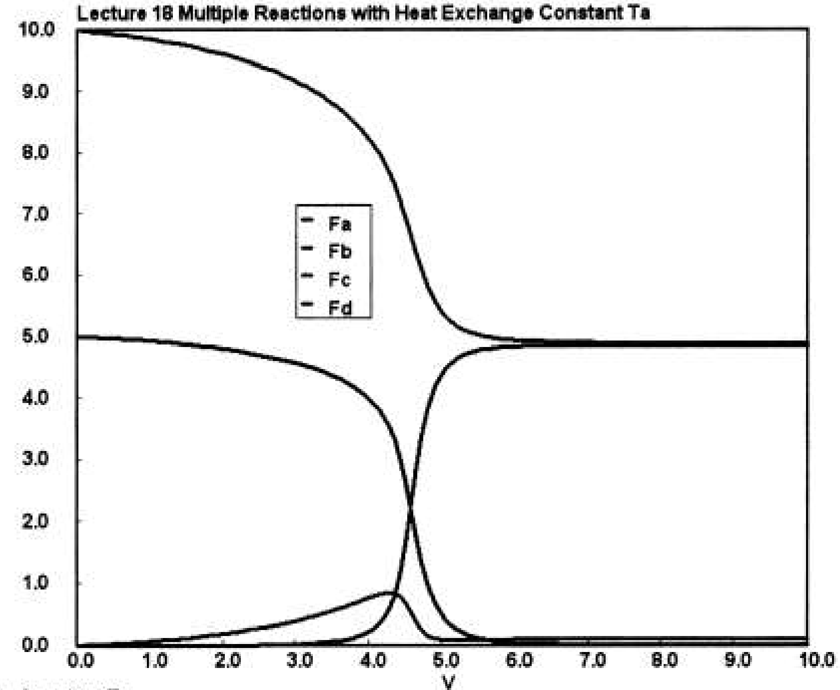
1 E2 = 12000
2 y = 1
3 R = 1.987
4 Ft = Fa+Fb+Fc+Fd
5 To = 300
6 k2c = 2*exp((E2/R)*(1/300-1/T))
7 E1 = 8000
8 Cto = 0.2
9 Ca = Cto*(Fa/Ft)*(To/T)*y
10 Cc = Cto*(Fc/Ft)*(To/T)*y
11 r2c = -k2c*Ca*Cc
12 Cpco = 10
13 m = 50
14 Cb = Cto*(Fb/Ft)*(To/T)*y
15 k1a = 40*exp ((E1/R)*(1/300-1/T))
16 r1a = -k1a*Ca*Cb^2
17 r1b = 2*r1a
18 rb = r1b
19 r2a = r2c
20 DH1b = -15000
21 DH2a = -10000
22 r1c = -r1a
23 Ta55 = 325
24 Cpd = 20
25 Cpa = 10
26 Cpb = 10
27 Cpc = 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)

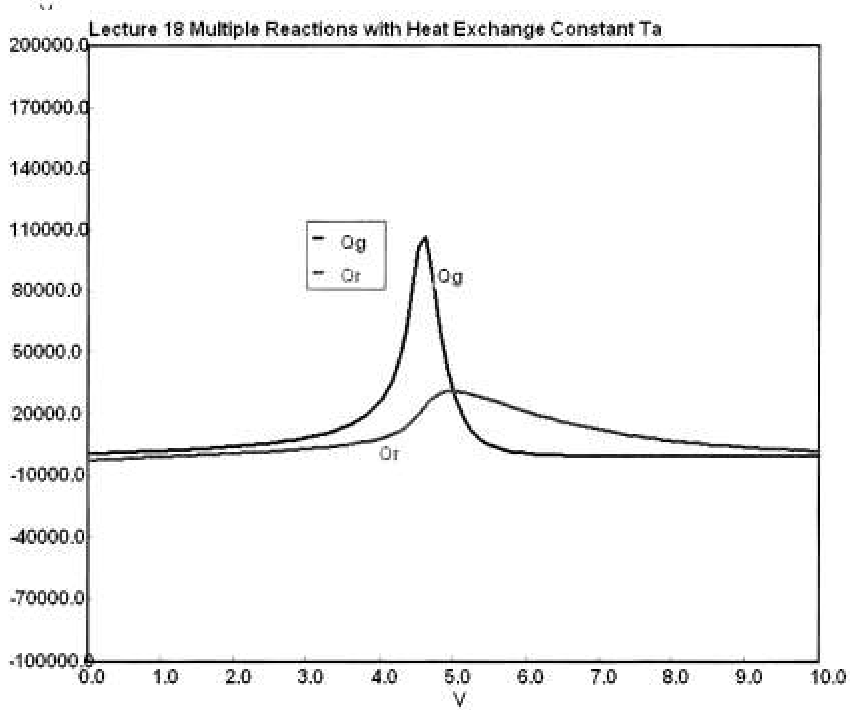

Lecture 18 Multiple Reactions with Heat Effects Adiabatic Case
T
Ta
1000.0
930.0
860.0
790.0
720.0
650.0
580.0
510.0
440.0
370.0
300.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0

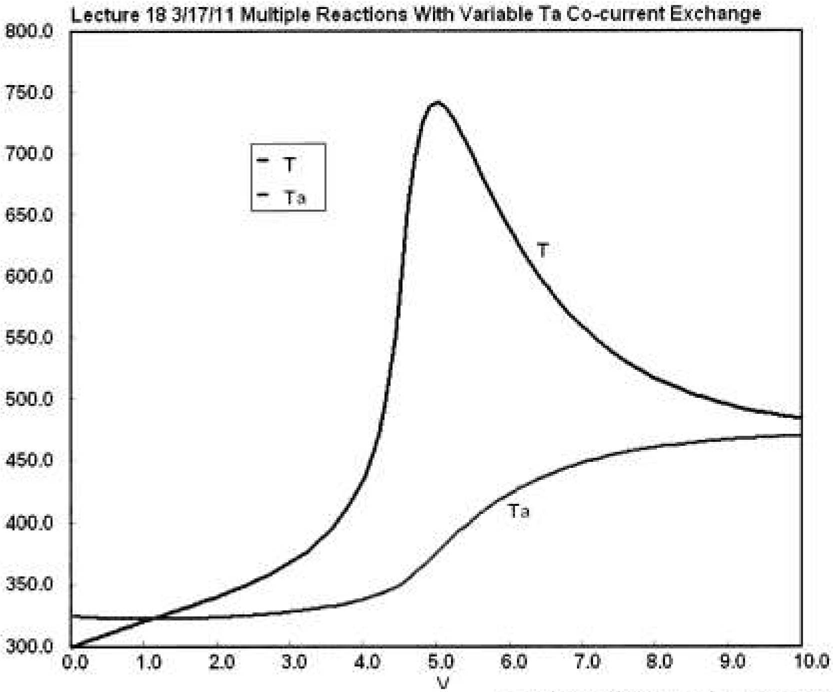

Lecture 18 Multiple Reactions with Heat Effects Adiabatic Case
Fa
Fb
Fc
Fd
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
V

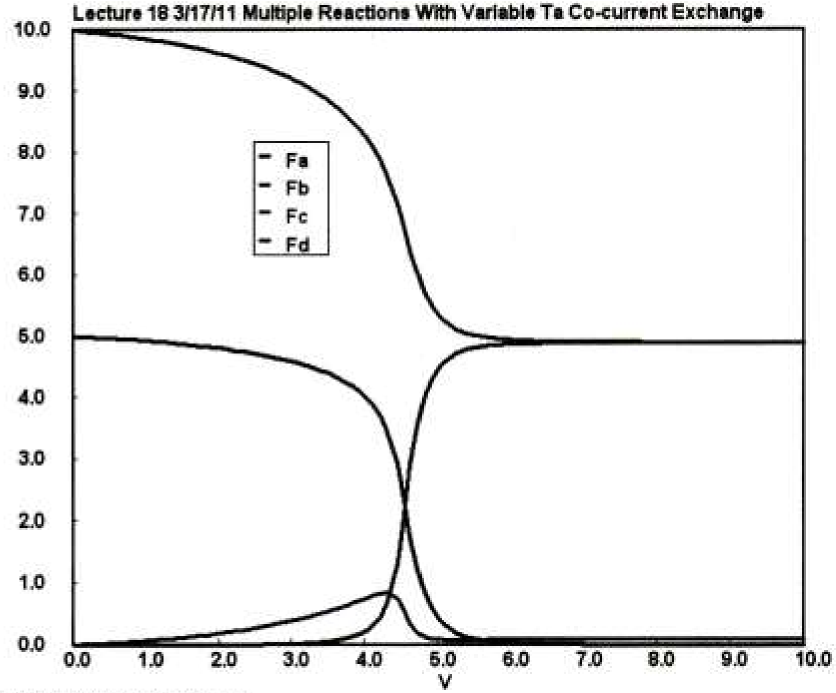

Lecture 18 Multiple Reactions with Heat Effects Adiabatic Case
Qg
Qr
200000.0
180000.0
160000.0
140000.0
120000.0
100000.0
80000.0
60000.0
40000.0
20000.0
0.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
V

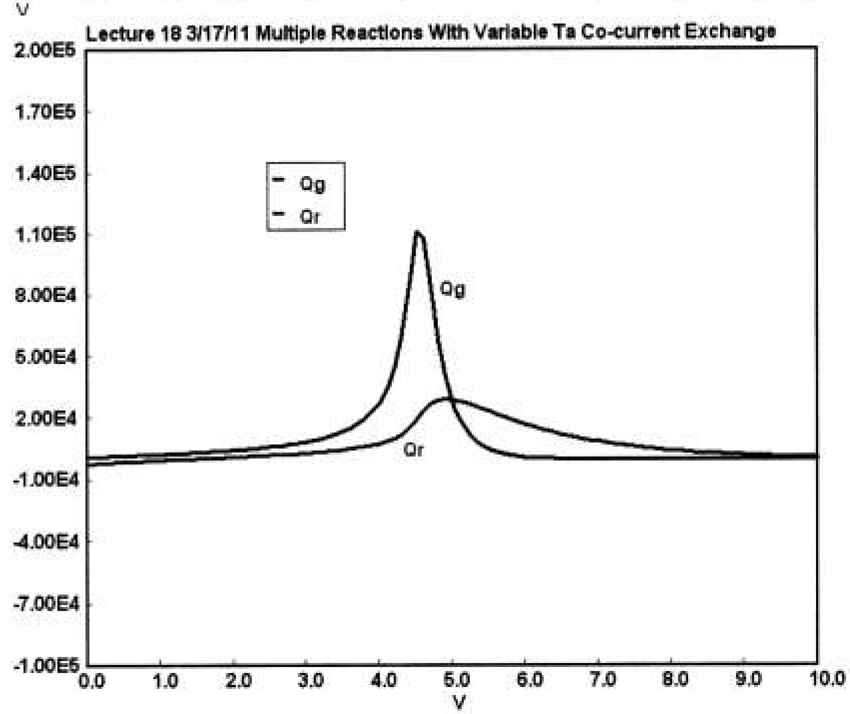

Lecture 18 Multiple Reactions with Heat Exchange Constant Ta
T
Ta
800.0
750.0
700.0
650.0
600.0
550.0
500.0
450.0
400.0
350.0
300.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0


Lecture 18 Multiple Reactions with Heat Exchange Constant Ta
Fa
Fb
Fc
Fd
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
V


Lecture 18 Multiple Reactions with Heat Exchange Constant Ta
Qg
Qr
200000.0
170000.0
140000.0
110000.0
80000.0
50000.0
20000.0
-10000.0
-40000.0
-70000.0
-100000.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
V


Lecture 18 3/17/11 Multiple Reactions With Variable Ta Co-current Exchange
800.0
750.0
700.0
650.0
600.0
550.0
500.0
450.0
400.0
350.0
300.0
0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0
V
T
Ta


Lecture 18 3/17/11 Multiple Reactions With Variable Ta Co-current Exchange
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0
V
Fa
Fb
Fc
Fd


Lecture 18 3/17/11 Multiple Reactions With Variable Ta Co-current Exchange
2.00E5
1.70E5
1.40E5
1.10E5
8.00E4
5.00E4
2.00E4
-1.00E4
-4.00E4
-7.00E4
-1.00E5
0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0
V
Qg
Qr

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:

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

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

and

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

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

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

and

$$\Delta H_{R2A} = 10{,}000\,\mathrm{cal/mol\ A}$$

Example A: Liquid Phase CSTR

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

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

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

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 reation 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) $$f(C_A) = \upsilon_0 C_{A0} - \upsilon_0 C_A + r_A V$$

(2) $$f(C_B) = \upsilon_0 C_{B0} - \upsilon_0 C_B + r_B V$$

(3) $$f(C_C) = -\upsilon_0 C_C + r_C V$$

(4) $$f(C_D) = -\upsilon_0 C_D + r_D V$$

2) Net Rates:

(5) $$r_A = r_{1A} + r_{2A}$$

Example A: Liquid Phase CSTR

3) Stoichiometry:

(16) $$C_A = F_A / \upsilon_0$$

(17) $$C_B = F_B / \upsilon_0$$

(18) $$C_C = F_C / \upsilon_0$$

(19) $$C_D = F_D / \upsilon_0$$

4) Parameters:

(20) $$\upsilon_0 = 100\ dm^3 / min$$

(21) $$k_{1A} = 10 \left(dm^3 / mol\right)^2 / min$$

(22) $$k_{2C} = 15 \left(dm^3 / mol\right)^4 / min$$

Example B: Liquid Phase PFR

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

$$k_{1A} = 10\left(dm^3/mol\right)^2/\min$$

$$k_{2C} = 15\left(dm^3/mol\right)^4/\min$$

Rate laws are the same as Example A.

Plot F_A, F_B, F_C, F_D and $S_{C/D}$ as a function of V.

Example B: Liquid Phase PFR

1) Mole Balances:

(1) $$\frac{dF_A}{dV} = r_A \qquad (F_{A0} = 200 \ \text{mol/min})$$

(2) $$\frac{dF_B}{dV} = r_B \qquad (F_{B0} = 200 \ \text{mol/min})$$

(3) $$\frac{dF_C}{dV} = r_C \qquad V_F = 50 \ \text{dm}^3$$

(4) $$\frac{dF_D}{dV} = r_D$$

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:

$$\frac{r_{1A}}{-1} = \frac{r_{1B}}{-2} = \frac{r_{1C}}{1}$$ Reaction 1

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

(12) $$r_{1C} = -r_{1A}$$ Reaction 2

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

(13) $$r_{2A} = 2/3\, r_{2C}$$

(14) $$r_{2D} = -1/3\, r_{2C}$$

Example B: Liquid Phase PFR

2) Rate Laws:

$$r_{1A} = -k_{1A} C_A C_B^2 \quad (5) \qquad k_{1A} = k_{1A1} \exp\left[\left(E_1/R\right)\left(1/T_1 - 1/T\right)\right] (6)$$

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

$$r_A = r_{1A} + r_{2B} \quad (9) \qquad r_B = r_{1B} \ (10)$$

$$r_C = r_{1C} + r_{2C} \quad (11) \qquad r_D = r_{2D} \ (12)$$

$$r_{1C} = -r_{1A} \quad (13) \qquad r_{1B} = 2r_{1A} \ (13)$$

$$r_{2A} = 2/3 r_{2C} \quad (15) \qquad r_{2D} = -1/3 r_{2C} \ (16)$$

Example B: Liquid Phase PFR

3) Stoichiometry:

$$C_A = C_{T0}\frac{F_A}{F_T}y\frac{T_0}{T} \quad (17) \qquad C_B = C_{T0}\frac{F_B}{F_T}y\frac{T_0}{T} \quad (18)$$

$$C_C = C_{T0}\frac{F_C}{F_T}y\frac{T_0}{T} \quad (19) \qquad C_D = C_{T0}\frac{F_D}{F_T}y\frac{T_0}{T} \quad (20)$$

$$F_T = F_A + F_B + F_C + F_D \quad (21) \qquad \frac{dy}{dV} = \frac{-\alpha\rho}{2y}\frac{F_T}{F_{T0}}\frac{T}{T_0} \quad (22)$$

Multiple Reactions with Heat Effects

4) Heat Effects:

$$\frac{dT}{dV} = \frac{Q_g - Q_r}{\sum F_i C_{Pi}} \qquad (23)$$

$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_i C_{Pcool}} \qquad (26)$$

$$Q_g = r_{1A} \Delta H_{R1A} + r_{2A} \Delta H_{R2A} \qquad (24)$$

$$Q_r = Ua(T - T_a) \qquad (25)$$

$$\sum C_P = F_A C_{PA} + F_B C_{PB} + F_C C_{PC} + F_D C_{PD} \qquad (27)$$

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.

$$\tilde{S}_{C/D} = if\ \ (V > 0.001)\ \ then\ \left(\frac{F_C}{F_D}\right)\ else\ \ (0) \tag{15}$$

Selectivity

3) Stoichiometry:

(16) $$C_A = F_A / \upsilon_0$$

(17) $$C_B = F_B / \upsilon_0$$

(18) $$C_C = F_C / \upsilon_0$$

(19) $$C_D = F_D / \upsilon_0$$

Parameters:

(20) $$\upsilon_0 = 100\ \mathrm{dm^3/min}$$

(21) $$k_{1A} = 10\left(\mathrm{dm^3/mol}\right)^2/\mathrm{min}$$

(22) $$k_{2C} = 15\left(\mathrm{dm^3/mol}\right)^4/\mathrm{min}$$

End of Web Lecture 22
Class Lecture 18