Lecture 10

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.

Lecture 10 – Tuesday

- Block 1: **Mole Balances**
- Block 2: **Rate Laws**
- Block 3: **Stoichiometry**
- Block 4: **Combine**

- Definition of Selectivity
- Semibatch Reactors

Selectivity in Multiple Reactions

$$A + B \xrightarrow{k_D} D \qquad r_D = k_D C_A^2 C_B \qquad \text{(Desired)}$$

$$A + B \xrightarrow{k_U} U \qquad r_U = k_U C_A C_B^2 \qquad \text{(Undesired)}$$

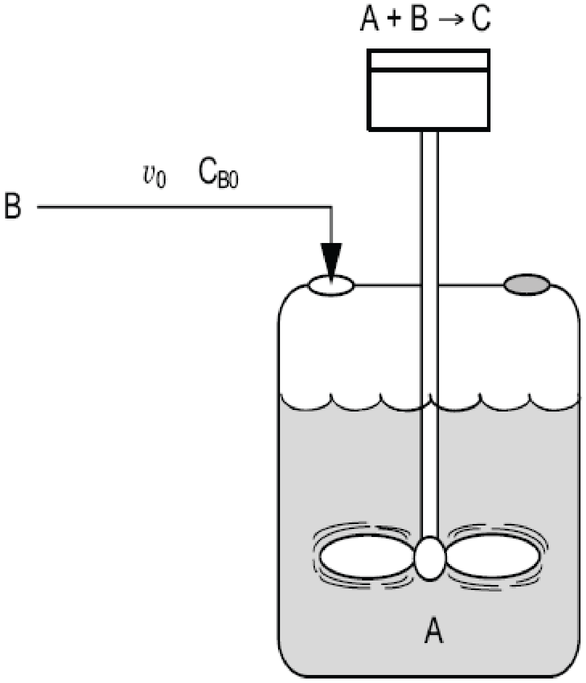
	Selectivity	Yield
Instantaneous	$S_{D/U} = r_D / r_U$	$Y_D = r_D / -r_A$
Overall	$\hat{S}_{D/U} = F_D / F_U$	$\hat{Y}_D = F_D / (F_{A0} - F_A)$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_D C_A^2 C_B}{k_u C_A C_B^2} = \frac{k_D C_A}{k_U C_B}$$

Keep C_A high and C_B low.

Semibatch Reactors

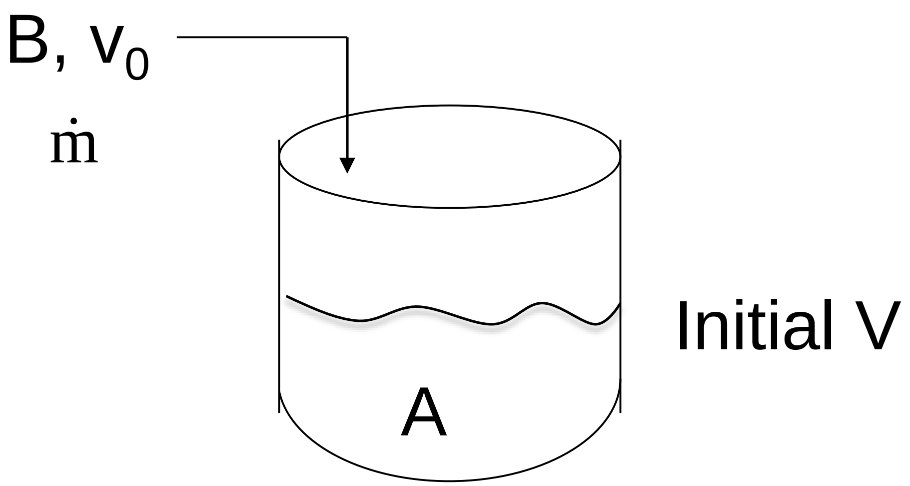
- Semibatch reactors can be very effective in maximizing selectivity in liquid phase reactions.
- The reactant that starts in the reactor is always the limiting reactant.



Semibatch Reactors

Semibatch reactors

$$A + B \rightarrow C + D$$



Liquid level and volume increase

Semibatch Reactors

1) Mass Balance:

$$\frac{dm}{dt} = \dot{m}$$

$$\dot{m} = \upsilon_0 \rho_0 \qquad and \qquad m = V\rho_0$$

$$\frac{dm}{dt} = \rho_0 \frac{dV}{dt} = \rho_0 \upsilon_0$$

$$\frac{dV}{dt} = \upsilon_0$$

$$t = 0 \quad V = V_0$$

$$\boxed{V = V_0 + \upsilon_0 t}$$

Semibatch Reactors

1) Mole Balance on Species A:

[in] – [out] + [gen] = [acc]

$$0 - 0 + r_A V = \frac{dN_A}{dt}$$

$$\frac{dN_A}{dt} = \frac{d[C_A V]}{dt} = V\frac{dC_A}{dt} + C_A\frac{dV}{dt}$$

$$\frac{dV}{dt} = \upsilon_0$$

$$\frac{dC_A}{dt} = r_A - \frac{\upsilon_0 C_A}{V}$$

Semibatch Reactors

1) Mole Balance on Species B:

$$F_{B0} - 0 + r_B V = \frac{dN_B}{dt}$$

$$\frac{dN_B}{dt} = \frac{d[C_B V]}{dt} = V\frac{dC_B}{dt} + C_B\frac{dV}{dt}$$

$$F_{B0} = C_{B0}\upsilon_0 \qquad \frac{dV}{dt} = \upsilon_0$$

$$\frac{dC_B}{dt} = r_B + \frac{(C_{B0} - C_B)\upsilon_0}{V}$$

Semibatch Reactors

1) Mass and Mole Balance Summary

$$(1)\quad \frac{dC_A}{dt} = r_A - \frac{\upsilon_0 C_A}{V}$$

$$(2)\quad \frac{dC_B}{dt} = r_B - \frac{\upsilon_0 (C_{B0} - C_B)}{V}$$

$$(3)\quad \frac{dC_C}{dt} = r_C - \frac{\upsilon_0 C_C}{V}$$

$$(4)\quad \frac{dC_D}{dt} = r_D - \frac{\upsilon_0 C_D}{V}$$

$$(5)\quad V = V_0 + \upsilon_0 t$$

Semibatch Reactors

2) Rate Laws

$$(6) \quad r_A = kC_AC_B$$

3) Stoichiometry

$$\frac{-r_A}{1} = \frac{-r_B}{1} = \frac{r_C}{1} = \frac{r_D}{1}$$

$$(7) \quad r_B = r_A$$

$$(8) \quad r_C = -r_A$$

$$(9) \quad r_D = -r_A$$

$$(10) \quad X = \frac{N_{A0} - N_A}{N_{A0}}$$

$$(11) \quad N_{A0} = C_{A0}V_0$$

$$(12) \quad N_A = C_AV$$

4) Parameters $C_{A0},\ V_0,\ \upsilon_0,\ k,\ C_{B0}$

Semibatch Reactors

POLYMATH Report
Ordinary Differential Equations

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	Ca	0.05	7.731E-06	0.05	7.731E-06
2	Cao	0.05	0.05	0.05	0.05
3	Cb	0	0	0.0125077	0.0125077
4	Cbo	0.025	0.025	0.025	0.025
5	Cc	0	0	0.0121468	0.0083256
6	Cd	0	0	0.0121468	0.0083256
7	k	2.2	2.2	2.2	2.2
8	ra	0	-0.0001644	0	-2.127E-07
9	rate	0	0	0.0001644	2.127E-07
10	t	0	0	500.	500.
11	V	5.	5.	30.	30.
12	vo	0.05	0.05	0.05	0.05
13	Vo	5.	5.	5.	5.
14	X	0	0	0.9990722	0.9990722

Differential equations

1 d(Ca)/d(t) = ra- vo*Ca/V

2 d(Cb)/d(t) = ra+ (Cbo-Cb)*vo/V

3 d(Cc)/d(t) = -ra-vo*Cc/V

4 d(Cd)/d(t) = -ra-vo*Cd/V

Explicit equations

1 vo = 0.05

2 Vo = 5

3 V = Vo+vo*t

4 k = 2.2

5 Cbo = 0.025

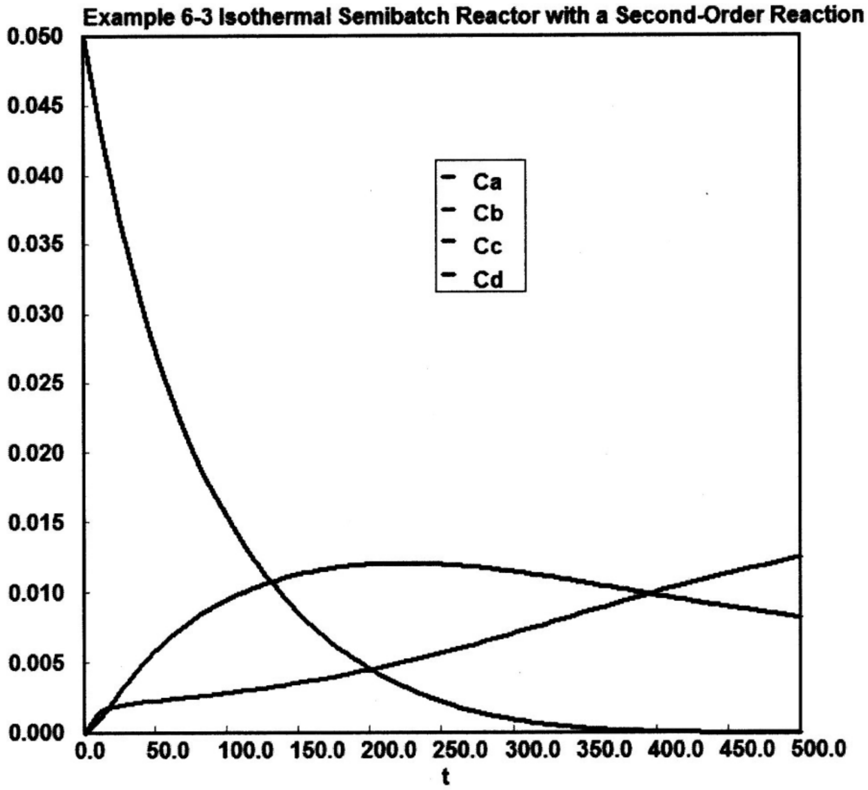
6 ra = -k*Ca*Cb

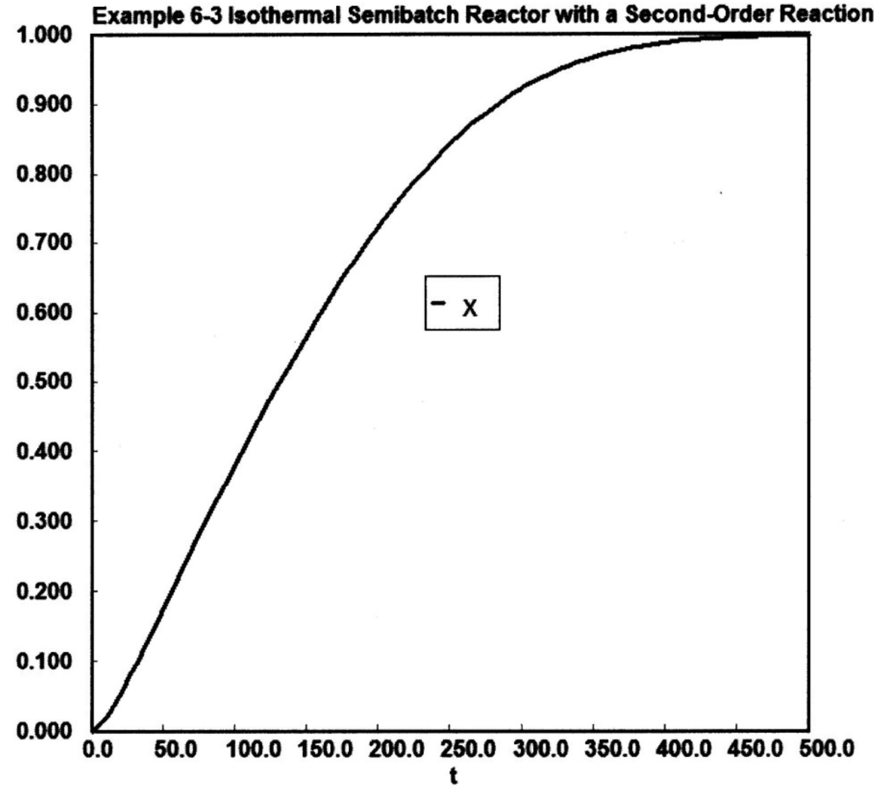
7 Cao = 0.05

8 rate = -ra

9 X = (Cao*Vo-Ca*V)/(Cao*Vo)

Semibatch Reactors





Equilibrium Conversion in Semibatch Reactors with Reversible Reactions

Consider the following reaction:

$$\mathrm{A} + \mathrm{B} \rightleftarrows \mathrm{C} + \mathrm{D}$$

Everything is the same as for the irreversible case, except for the rate law:

$$-r_A = k_A \left[C_A C_B - \frac{C_C C_D}{K_C} \right]$$

Equilibrium Conversion in Semibatch Reactors with Reversible Reactions

Where:

$$C_A = \frac{N_{A0}(1-X)}{V}$$

$$C_B = \frac{(F_{B0}t - N_{A0}X)}{V}$$

$$C_C = C_D = \frac{N_{A0}X}{V}$$

At equilibrium, $-r_A = 0$ then

$$K_C = \frac{C_{Ce}C_{De}}{C_{Ae}C_{Be}} = \frac{N_{Ce}N_{De}}{N_{Ae}N_{Be}} = \frac{N_{A0}X_e^2}{(1-X_e)(F_{B0}t - N_{A0}X_e)}$$

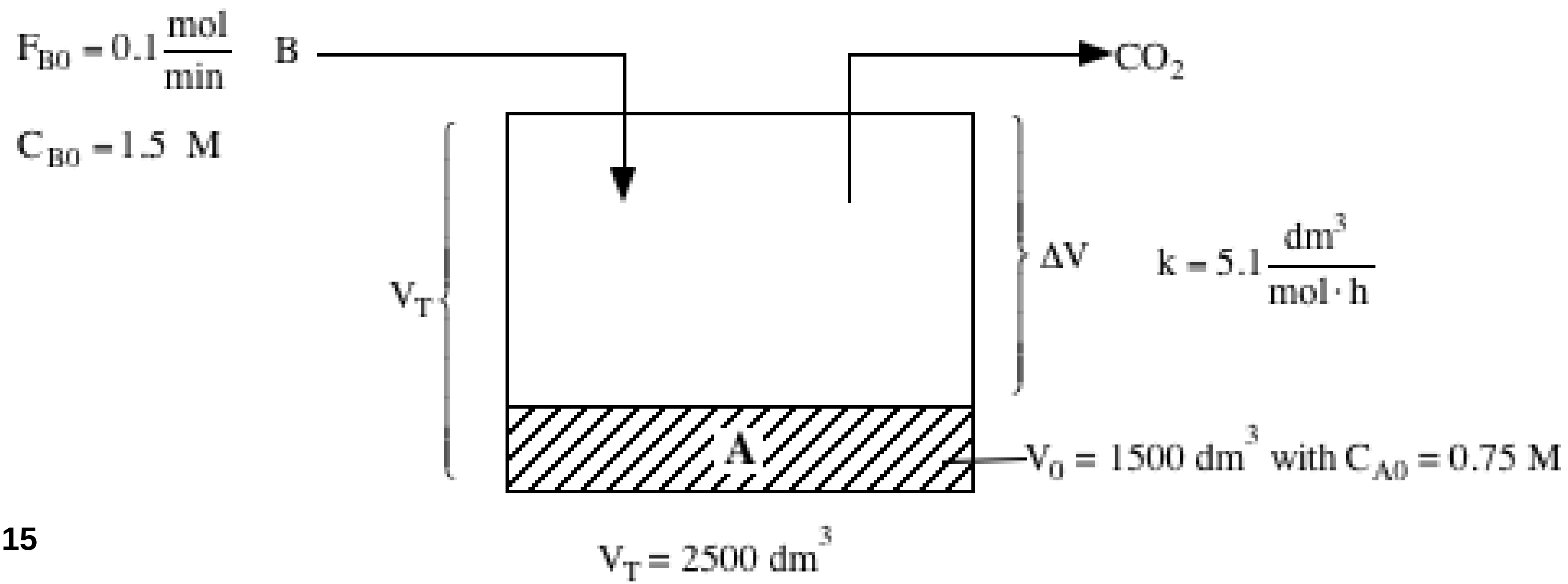
X_e changes with time.

P6-6$_B$ - Semibatch Reactors

Sodium Bicarbonate + Ethylene Chlorohydrin → Ethylene Glycol + NaCl + $CO_2\uparrow$

$$NaCHO_3 + CH_2OHCH_2Cl \rightarrow (CH_2OH)_2 + NaCl + CO_2\uparrow$$

$$A + B \rightarrow C + D + CO_2\uparrow$$



P6-6$_B$ - Semibatch Reactors

Semibatch Reactors in terms of **Moles**

$$A + B \rightarrow C + D + CO_2$$

Mole Balances

A	(1)	$\dfrac{dN_a}{dt} = r_A V$
B	(2)	$\dfrac{dN_b}{dt} = F_{B0} + r_B V$
C	(3)	$\dfrac{dN_c}{dt} = r_C V$
D	(4)	$N_D = N_C$
CO_2		$0 = -F_{CO_2} + r_{CO_2} V$
	(5)	$F_{CO_2} = r_{CO_2} V$

Stoichiometry

$$-r_A = -r_B = r_C = r_D = r_{CO_2}$$

(6) $$\frac{dV}{dt} = \upsilon_0 - \upsilon_{CO_2}$$

(7) $$\upsilon_{CO_2} = \frac{F_{CO_2} MWCO_2}{RHO}$$

(8) $$MW = 44$$

(9) $$RHO = 1000$$

(10) $$C_a = N_A / V$$

(11) $$C_B = N_B / V$$

Rate Laws

(12) $$r_A = -kC_A C_B$$

(13) $$X = \frac{N_{a0} - N_a}{N_{a0}}$$

(14) $$N_{a0} = V_0 C_{a0}$$

Rest of the Polymath Statements Similar to Concentration Program

P6-6 Semibatch: Moles, N_a, N_b, etc.

POLYMATH Report
Ordinary Differential Equations

Calculated values of DEQ variables

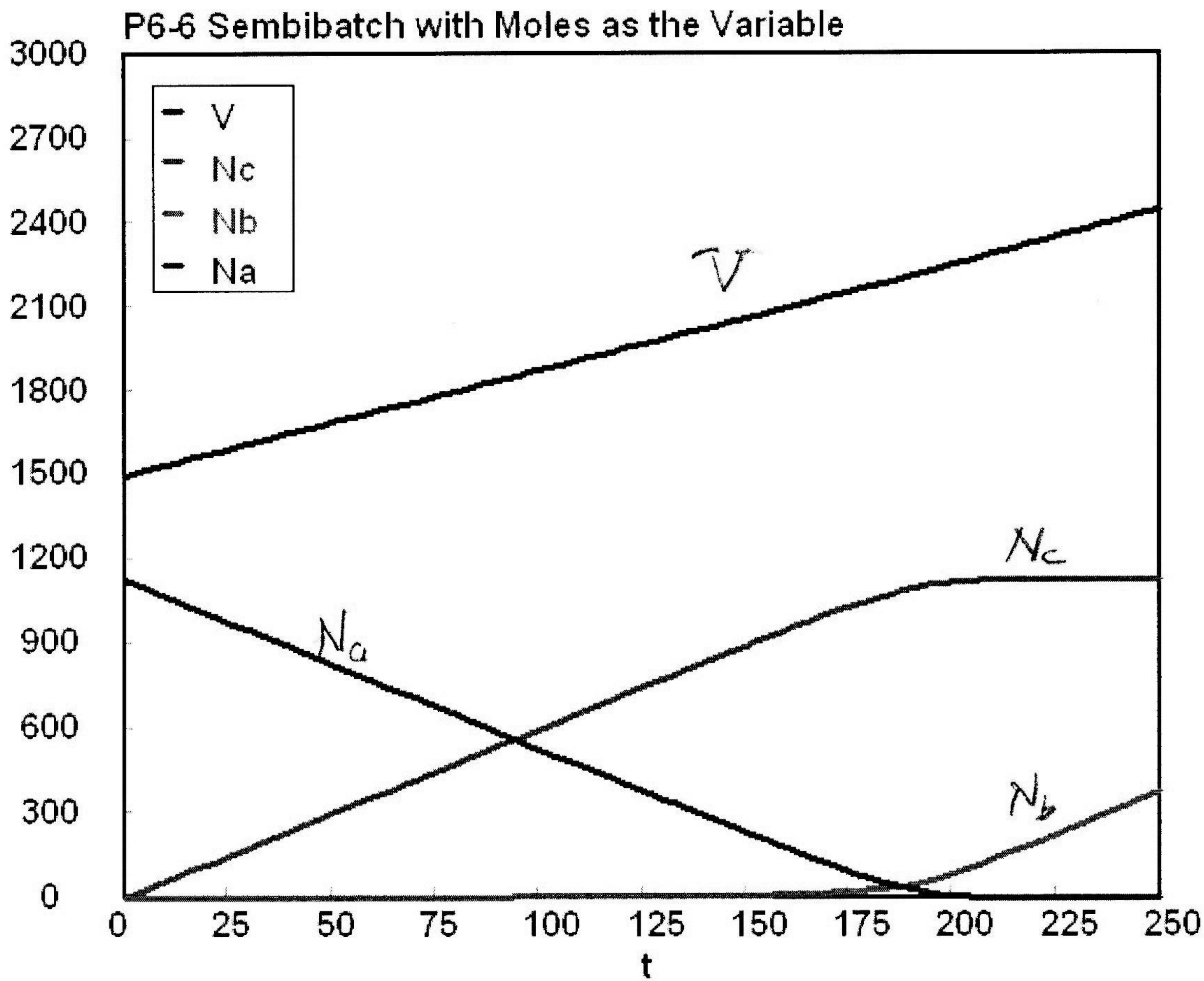
	Variable	Initial value	Minimal value	Maximal value	Final value
1	Ca	0.75	8.845E-14	0.75	8.845E-14
2	Cao	0.75	0.75	0.75	0.75
3	Cb	0	0	0.15303	0.15303
4	Cbo	1.5	1.5	1.5	1.5
5	Cc	0	0	0.4967829	0.45909
6	Cd	0	0	0.4967829	0.45909
7	Fbo	6.	6.	6.	6.
8	FCO2	0	0	5.987114	1.692E-10
9	k	5.1	5.1	5.1	5.1
10	MWCO2	44.	44.	44.	44.
11	Na	1125.	2.167E-10	1125.	2.167E-10
12	Nao	1125.	1125.	1125.	1125.
13	Nb	0	0	375.	375.
14	Nc	0	0	1125.	1125.
15	ra	0	-0.0039389	0	-6.903E-14
16	rho	1000.	1000.	1000.	1000.
17	t	0	0	250.	250.
18	V	1500.	1500.	2450.5	2450.5
19	vCO2	0	0	0.263433	7.443E-12
20	vo	4.	4.	4.	4.
21	X	0	0	1.	1.

Differential equations

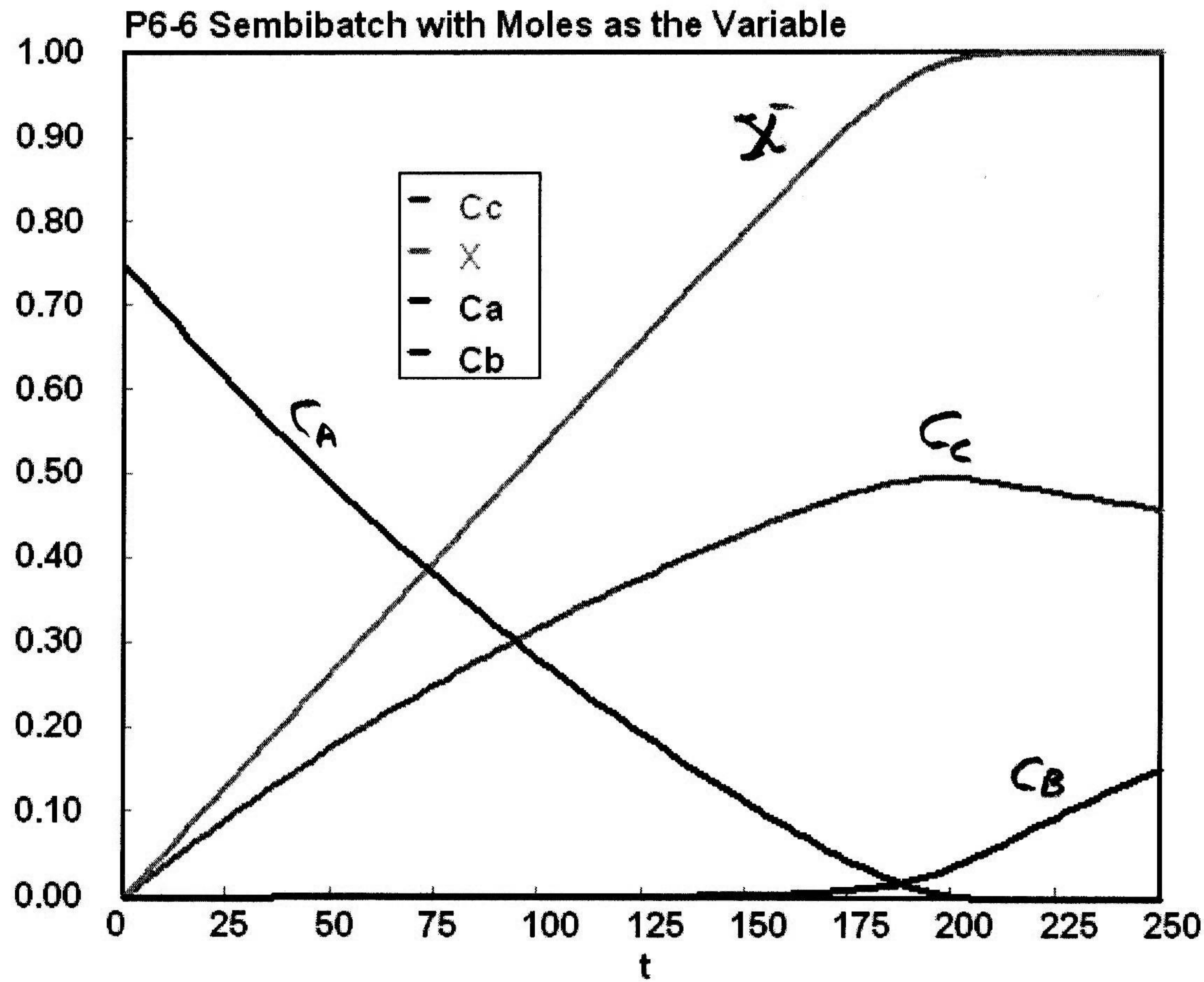
1 d(V)/d(t) = vo-vCO2
2 d(Nc)/d(t) = -ra*V
3 d(Nb)/d(t) = Fbo+ra*V
4 d(Na)/d(t) = ra*V

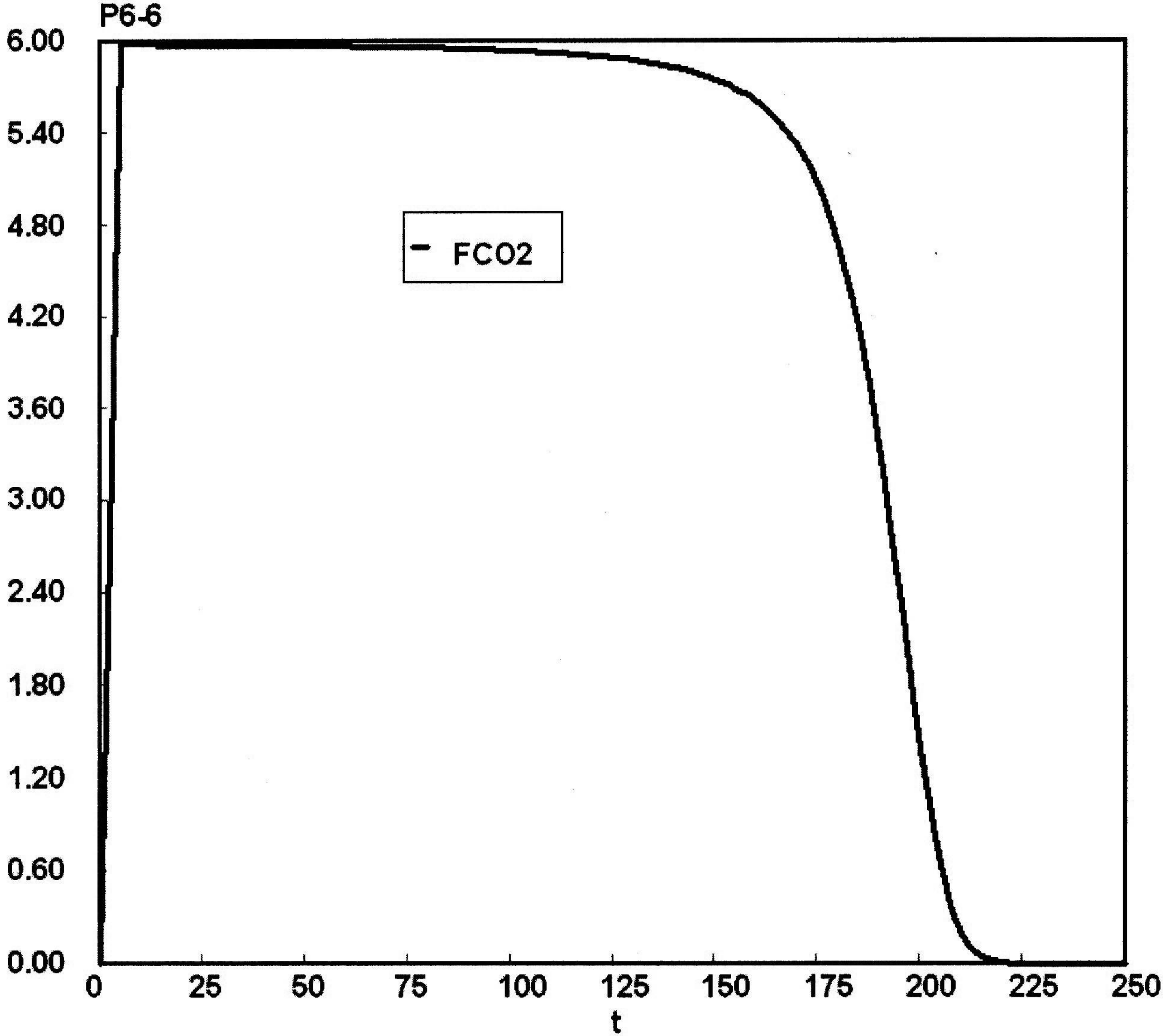
Explicit equations

1 Cbo = 1.5
2 Fbo = 6
3 Cao = 0.75
4 Cc = Nc/V
5 Nao = 1125
6 X = (Nao-Na)/Nao
7 k = 5.1
8 rho = 1000
9 MWCO2 = 44
10 Ca = Na/V
11 Cb = Nb/V
12 ra = -k*Ca*Cb
13 vo = Fbo/Cbo
14 FCO2 = -ra*V
15 vCO2 = FCO2*MWCO2/rho
16 Cd = Cc



P6-6 Sembibatch with Moles as the Variable
3000
2700
2400
2100
1800
1500
1200
900
600
300
0
V
Nc
Nb
Na
0
25
50
75
100
125
150
175
200
225
250
t


P6-6 Sembibatch with Moles as the Variable
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0
25
50
75
100
125
150
175
200
225
250
t
Cc
X
Ca
Cb


P6-6
6.00
5.40
4.80
4.20
3.60
3.00
2.40
1.80
1.20
0.60
0.00
FCO2
0
25
50
75
100
125
150
175
200
225
250
t

P6-6 Semibatch: Concentrations C_A, C_B, C_C

POLYMATH Report
Ordinary Differential Equations

Calculated values of DEQ variables

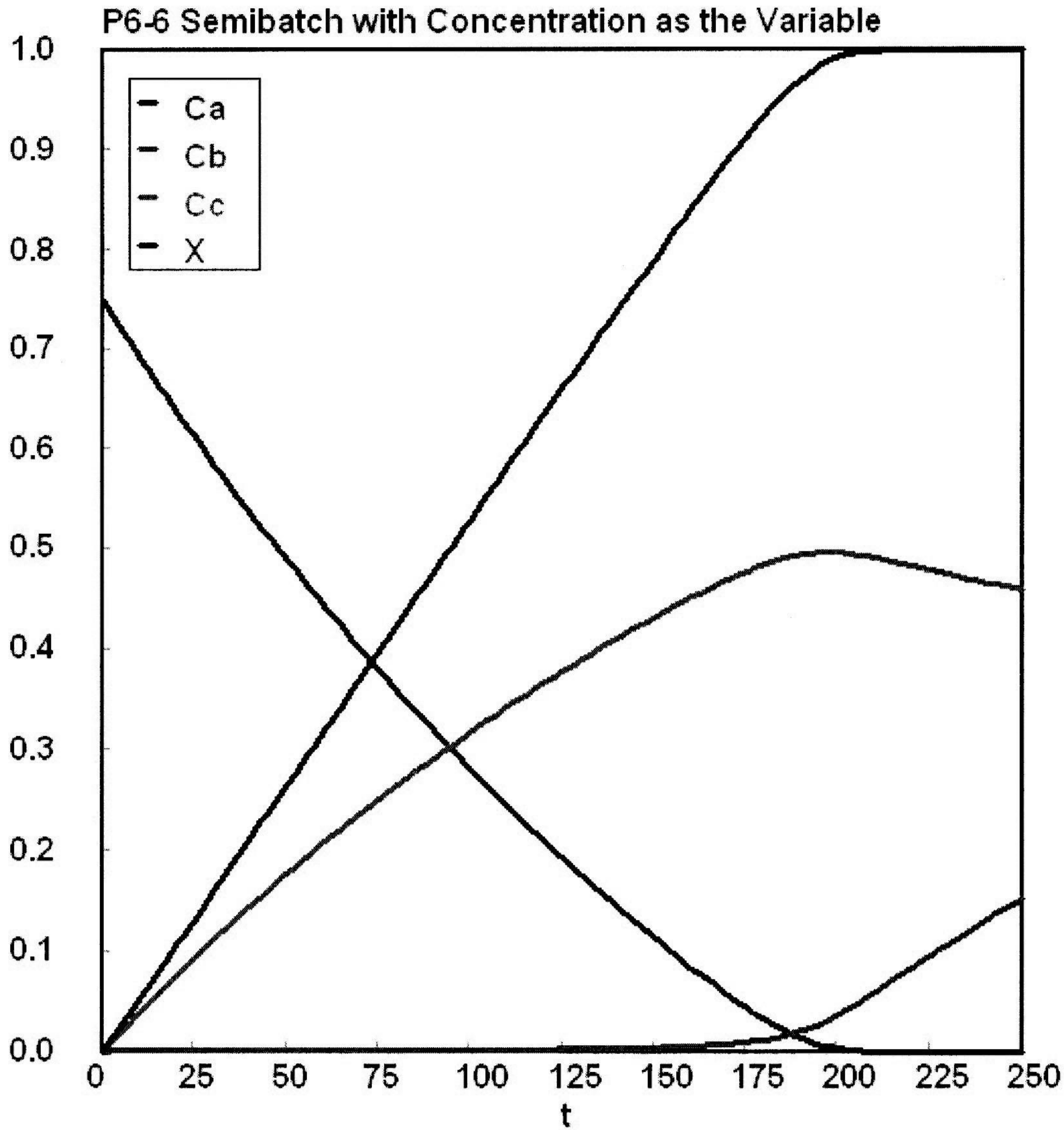
	Variable	Initial value	Minimal value	Maximal value	Final value
1	Ca	0.75	8.846E-14	0.75	8.846E-14
2	Cao	0.75	0.75	0.75	0.75
3	Cb	0	0	0.15303	0.15303
4	Cbo	1.5	1.5	1.5	1.5
5	Cc	0	0	0.496826	0.45909
6	CC	0	0	0.496827	0.45909
7	Cd	0	0	0.496827	0.45909
8	Fbo	6.	6.	6.	6.
9	FCO2	0	0	5.987132	1.692E-10
10	k	5.1	5.1	5.1	5.1
11	MWCO2	44.	44.	44.	44.
12	Na	1125.	2.168E-10	1125.	2.168E-10
13	Nao	1125.	1125.	1125.	1125.
14	NC	0	0	1125.	1125.
15	Nc	0	0	1125.	1125.
16	ra	0	-0.0039413	0	-6.904E-14
17	rate	0	0	0.0039413	6.904E-14
18	rho	1000.	1000.	1000.	1000.
19	t	0	0	250.	250.
20	V	1500.	1500.	2450.5	2450.5
21	vCO2	0	0	0.2634338	7.444E-12
22	vo	4.	4.	4.	4.
23	Vo	1500.	1500.	1500.	1500.
24	X	0	0	1.	1.

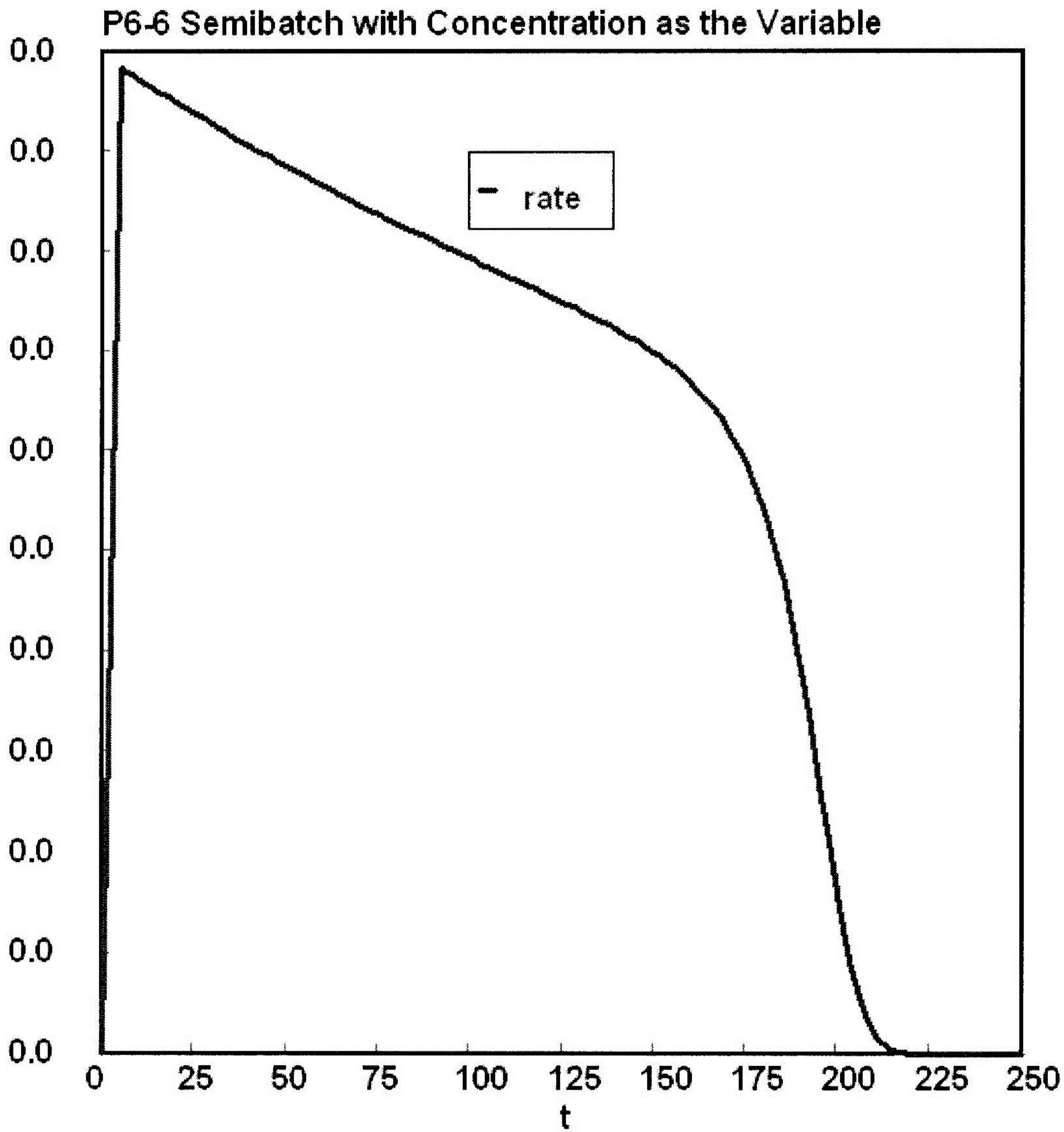
Differential equations

1 d(Ca)/d(t) = ra + ((vo-vCO2) / V) * (- Ca)
2 d(Cb)/d(t) = ra + vo*Cbo/V + ((vo-vCO2) / V) * (-Cb)
3 d(Cc)/d(t) = -ra + ((vo-vCO2) / V) *(-Cc)
4 d(V)/d(t) = vo-vCO2

Explicit equations

1 Cd = Cc
2 Fbo = 6
3 Cao = 0.75
4 Vo = 1500
5 Na = Ca*V
6 k = 5.1
7 ra = -k * Ca * Cb
8 Nao = Cao*Vo
9 rate = -ra
10 rho = 1000
rho=1000g per dm^3
11 MWCO2 = 44
12 FCO2 = - ra*V
13 NC = Nao-Na
14 Cbo = 1.5
15 vo = Fbo / Cbo
16 vCO2 = MWCO2*FCO2/rho
17 CC = NC/V
18 Nc = Cc * V
19 X = 1 - Ca * V / (Cao*Vo)


P6-6 Semibatch with Concentration as the Variable
Ca
Cb
Cc
X
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
25
50
75
100
125
150
175
200
225
250
t



P6-6 Semibatch with Concentration as the Variable
0.0
0.0
0.0
0.0
0.0
0.0
0.0
0.0
0.0
0.0
0.0
rate
0
25
50
75
100
125
150
175
200
225
250
t

Semibatch Reactors

Three Forms of the **Mole Balances** applied to Semibatch Reactors:

1. Molar Basis	$\frac{dN_A}{dt} = r_A V$ $\frac{dN_B}{dt} = F_{B0} + r_B V$	
2. Concentration Basis	$\frac{dC_A}{dt} = r_A - C_A \frac{\upsilon_0}{V}$ $\frac{dC_B}{dt} = r_B + \left(C_{B0} - C_B\right)\frac{\upsilon_0}{V}$	$\frac{dN_A}{dt} = r_A V$ $\frac{dN_B}{dt} = F_{B0} + r_B V$
3. Conversion	$\frac{dX}{dt} = \frac{-r_A V}{N_{A0}}$	

Semibatch Reactors

Consider the following elementary reaction:

$$A+B \rightarrow C+D$$

$$-r_A=kC_AC_B$$

The combined **Mole Balance**, **Rate Law**, and **Stoichiometry** may be written in terms of number of moles, conversion, and/or concentration:

Conversion	Concentration	No. of Moles
$\frac{dX}{dt}=\frac{k(1-X)(N_{Bi}+F_{B0}t-N_{A0}X)}{V_0+\upsilon_0 t}$	$\frac{dC_A}{dt}=r_A-C_A\frac{\upsilon_0}{V}$	$\frac{dN_A}{dt}=r_AV$
	$\frac{dC_B}{dt}=r_A+(C_{B0}-C_B)\frac{\upsilon_0}{V}$	$\frac{dN_B}{dt}=F_{A0}+r_BV$

Polymath Equations

Conversion	Concentration	Moles
d(X)/d(t) = -ra*V/Nao	d(Ca)/d(t) = ra - (Ca*vo)/V	d(Na)/d(t) = ra*V
ra = -k*Ca*Cb	d(Cb)/d(t) = rb + ((Cbo-Cb)*vo)/V	d(Nb)/d(t) = rb*V + Fbo
Ca = Nao*(1 - X)/V	ra = -k*Ca*Cb	ra = -k*Ca*Cb
Cb = (Nbi + Fbo*t - Nao*X)/V	rb = ra	rb = ra
V = Vo + vo*t	V = Vo + vo*t	V = Vo + vo*t
Vo = 100	Vo = 100	Vo = 100
vo = 2	vo = 2	vo = 2
Nao = 100	Fbo = 5	Fbo = 5
Fbo = 5	Nao = 100	Ca = Na/V
Nbi = 0	Cbo = Fbo/vo	Cb = Nb/V
k = 0.1	k = 0.01	k = 0.01
	Na = Ca*V	
	X = (Nao-Na)/Nao	

End of Lecture 10