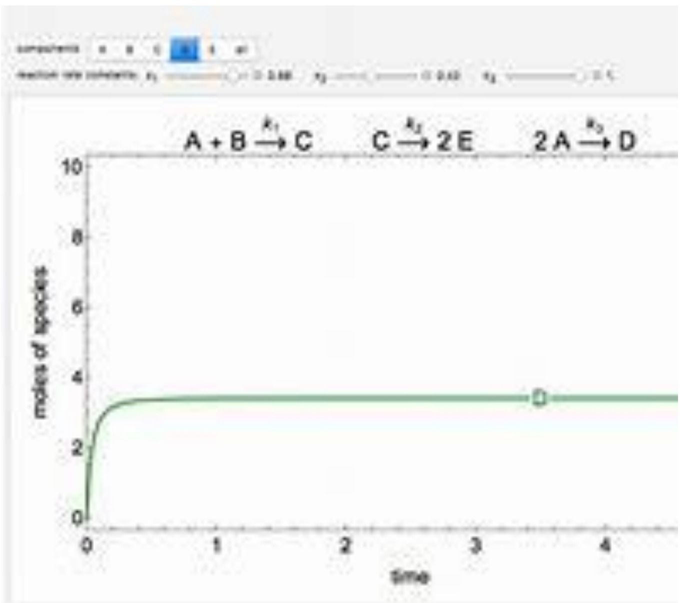
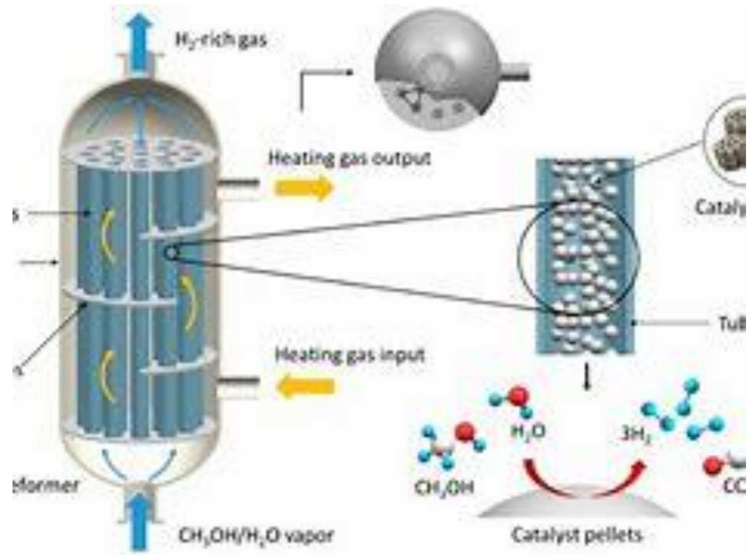
Reactor Design II





Week 4

Multiple Reactions and Semibatch Reactor

Saba A. Gheni, Ph.D.

Chemical Engineering Department

ghenis@tu.edu.iq

Introduction

- Chemical Reaction Engineering (CRE) involves the study of reaction rates, mechanisms, and reactor design.

- This lecture focuses on the role of semibatch reactors in maximizing selectivity and optimizing reaction conditions.

Topics to be Addressed

- - Fundamentals of Semibatch Reactors
- - Mole Balances and Stoichiometry
- - Rate Laws and Reversible Reactions
- - Numerical Analysis using Polymath
- - Practical Examples and Case Studies

Objectives

- By the end of this lecture, students will be able to:

- - Understand the operational principles of semibatch reactors.
- - Apply mole balances, rate laws, and stoichiometry to reactor design.
- - Analyze reversible reactions in semibatch reactors.
- - Utilize numerical methods for reactor analysis.

Introduction

- Semibatch reactors are highly effective for controlling reaction dynamics, especially in liquid-phase reactions where selectivity is crucial.
- This session explores theoretical foundations, practical applications, and numerical approaches using Polymath for analysis.

Selectivity in Multiple Reactions

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

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

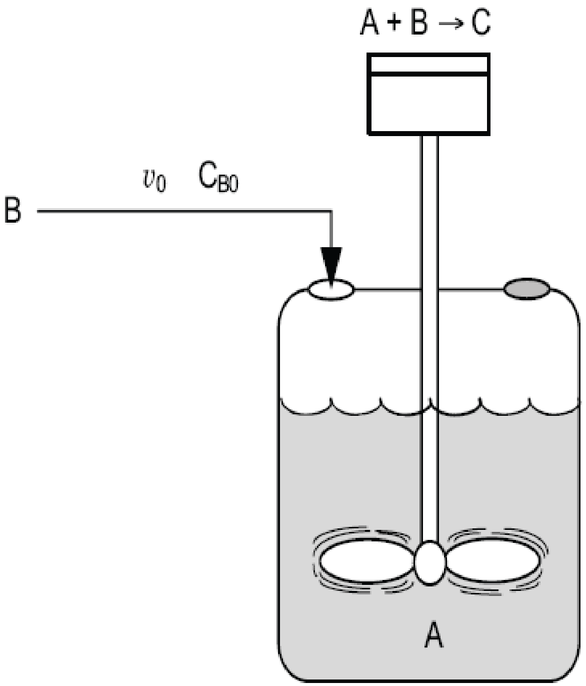
	Selectivity	Yield
Instantaneous	$S_{D/U} = r_D / r_U$	$Y_D = r_D / -r_A$
Overall	$\hat{S}_{D/U} = F_D / F_U$	$\hat{Y}_D = F_D / (F_{A0} - F_A)$

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

Keep C_A high and C_B low.

Semibatch Reactors

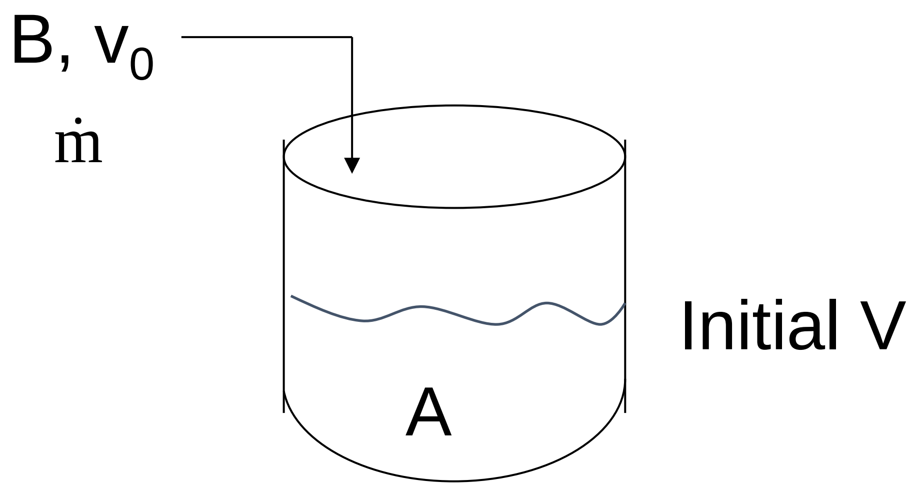
- Semibatch reactors can be very effective in maximizing selectivity in liquid phase reactions.
- The reactant that starts in the reactor is always the limiting rea



Semibatch Reactors

<u>Semibatch reactors</u>

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



Liquid level and volume increase

Semibatch Reactors

1) Mass Balance:

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

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

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

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

$$t = 0 \quad V = V_0 \qquad V = V_0 + \upsilon_0 t$$

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

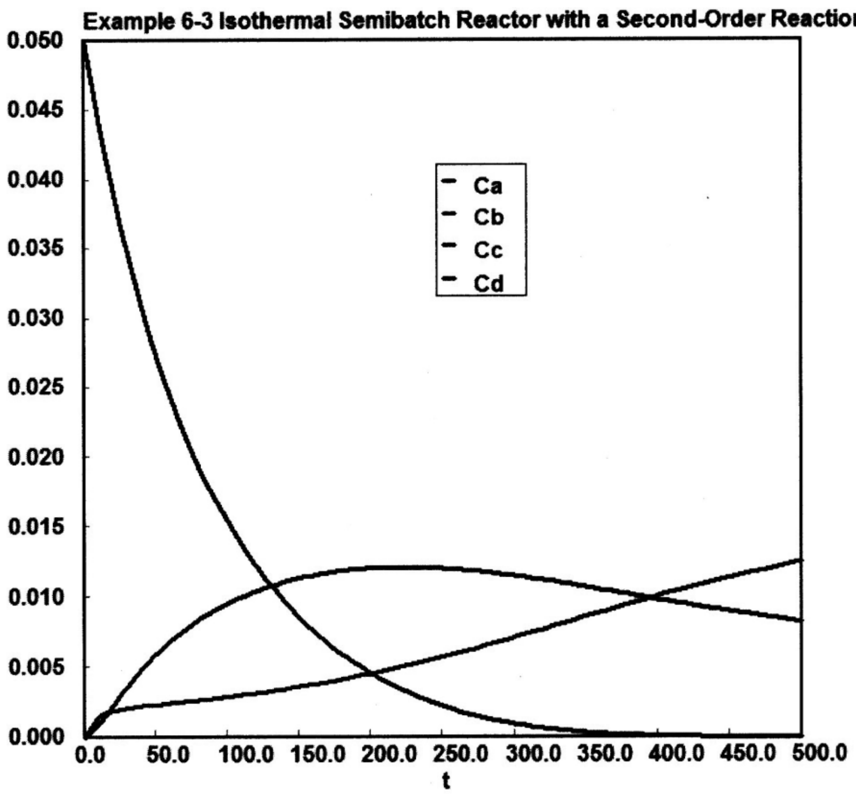
6 ra = -k*Ca*Cb

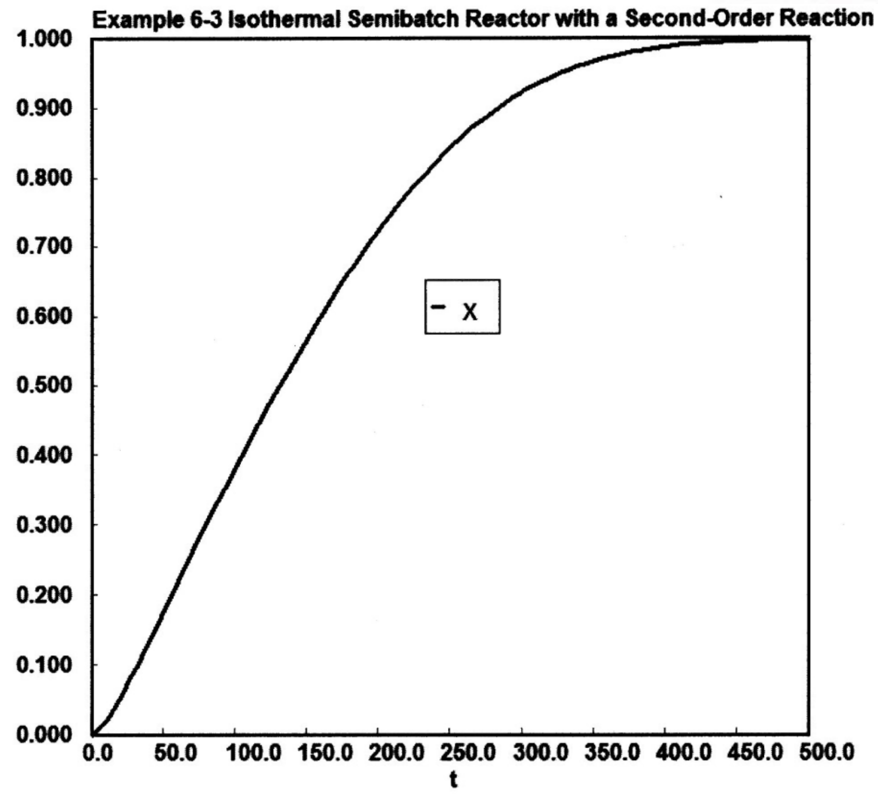
7 Cao = 0.05

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:

$$A + B \rightleftarrows C + D$$

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

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

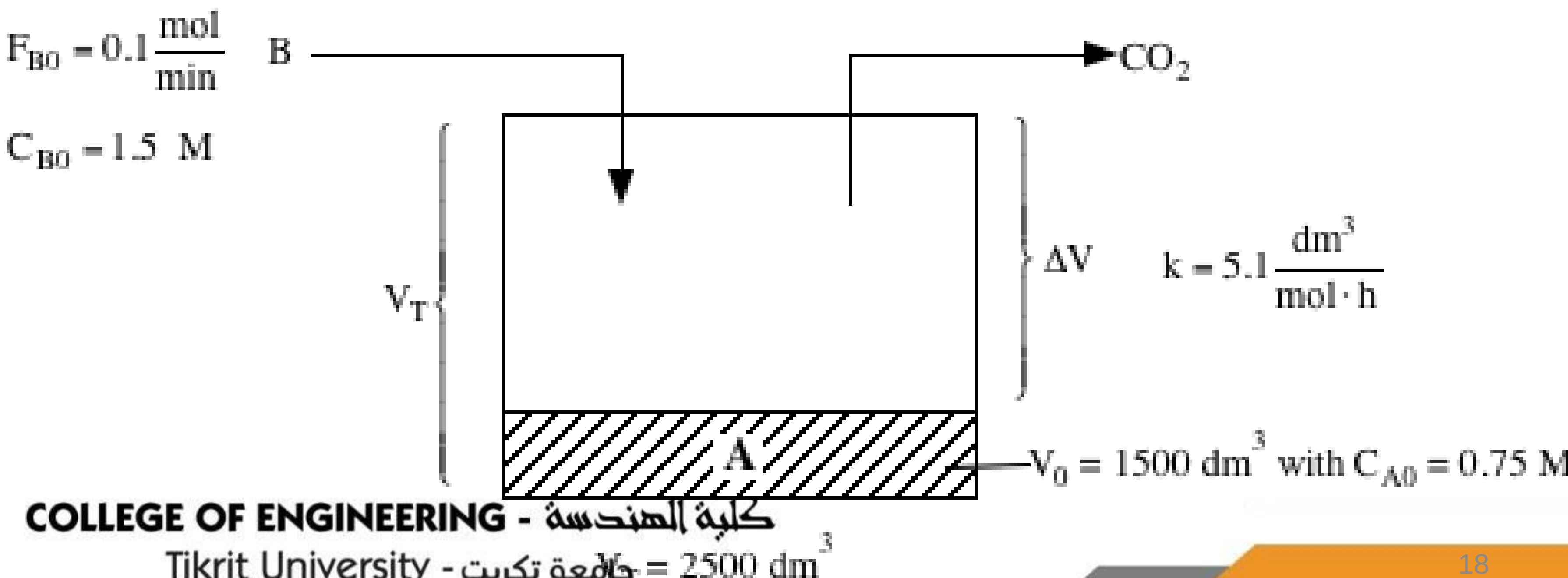
X_e changes with time.

Example 1:Semibatch Reactors

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

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

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



طريقك إلى النجاح
YOUR WAY TO SUCCESS

Semibatch Reactors in terms of Moles

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

Mole Balances

$$A \qquad (1) \quad \frac{dN_a}{dt} = r_A V$$

$$B \qquad (2) \quad \frac{dN_b}{dt} = F_{B0} + r_B V$$

$$C \qquad (3) \quad \frac{dN_c}{dt} = r_C V$$

$$D \qquad (4) \quad N_D = N_C$$

$$CO_2 \qquad 0 = -F_{CO_2} + r_{CO_2} V$$

$$(5) \quad F_{CO_2} = r_{CO_2} V$$

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

Stoichiometry

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

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

$$(8)\quad MW = 44$$

$$(9)\quad RHO = 1000$$

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

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

Rate Laws

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

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

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

Rest of the Polymath Statements
Similar to Concentration Program

Semibatch: Moles, N_a, N_b, etc.

POLYMATH Report
Ordinary Differential Equations

Calculated values of DEQ variables

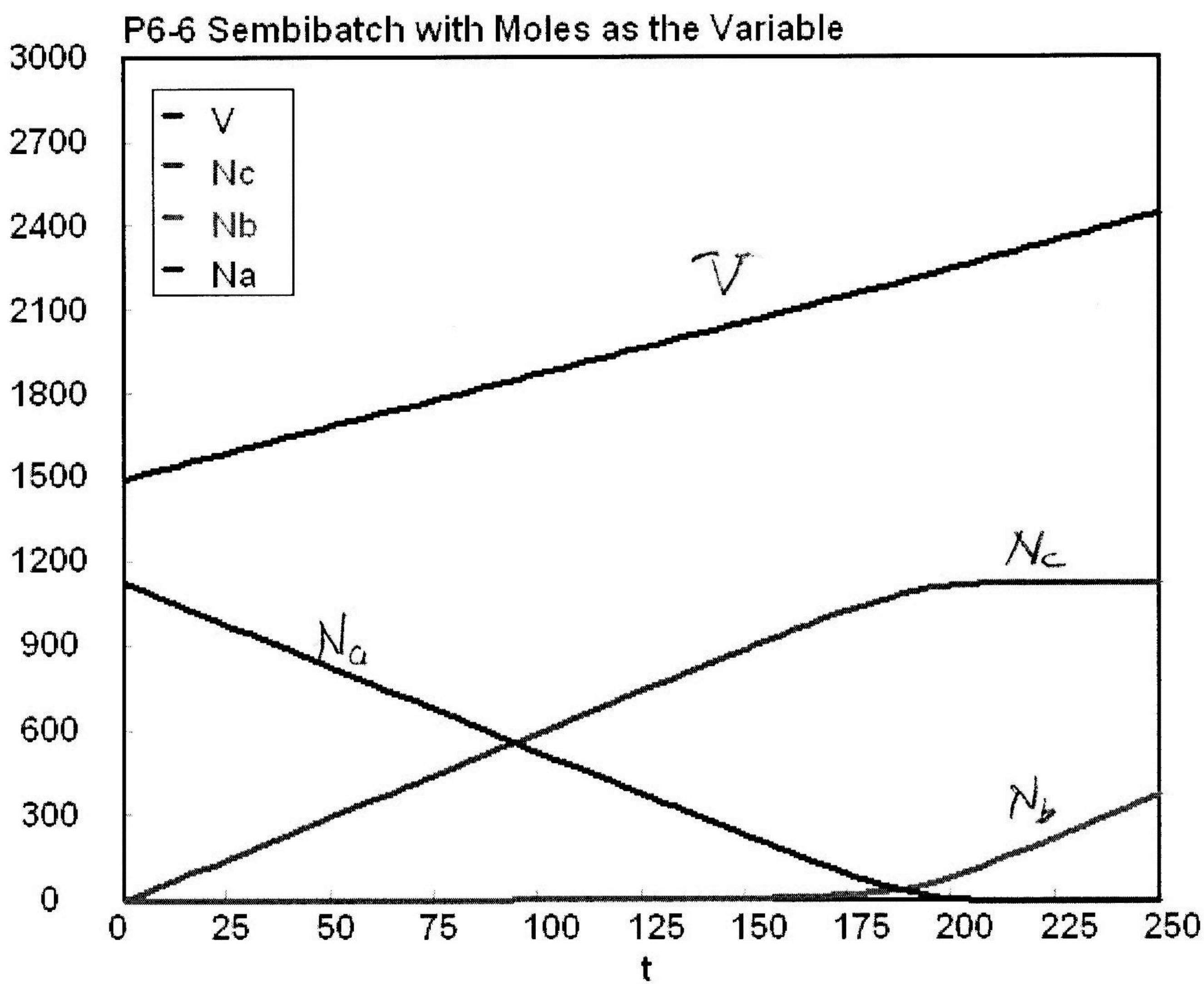
	Variable	Initial value	Minimal value	Maximal value	Final value
1	Ca	0.75	8.845E-14	0.75	8.845E-14
2	Cao	0.75	0.75	0.75	0.75
3	Cb	0	0	0.15303	0.15303
4	Cbo	1.5	1.5	1.5	1.5
5	Cc	0	0	0.4967829	0.45909
6	Cd	0	0	0.4967829	0.45909
7	Fbo	6.	6.	6.	6.
8	FCO2	0	0	5.987114	1.692E-10
9	k	5.1	5.1	5.1	5.1
10	MWCO2	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.

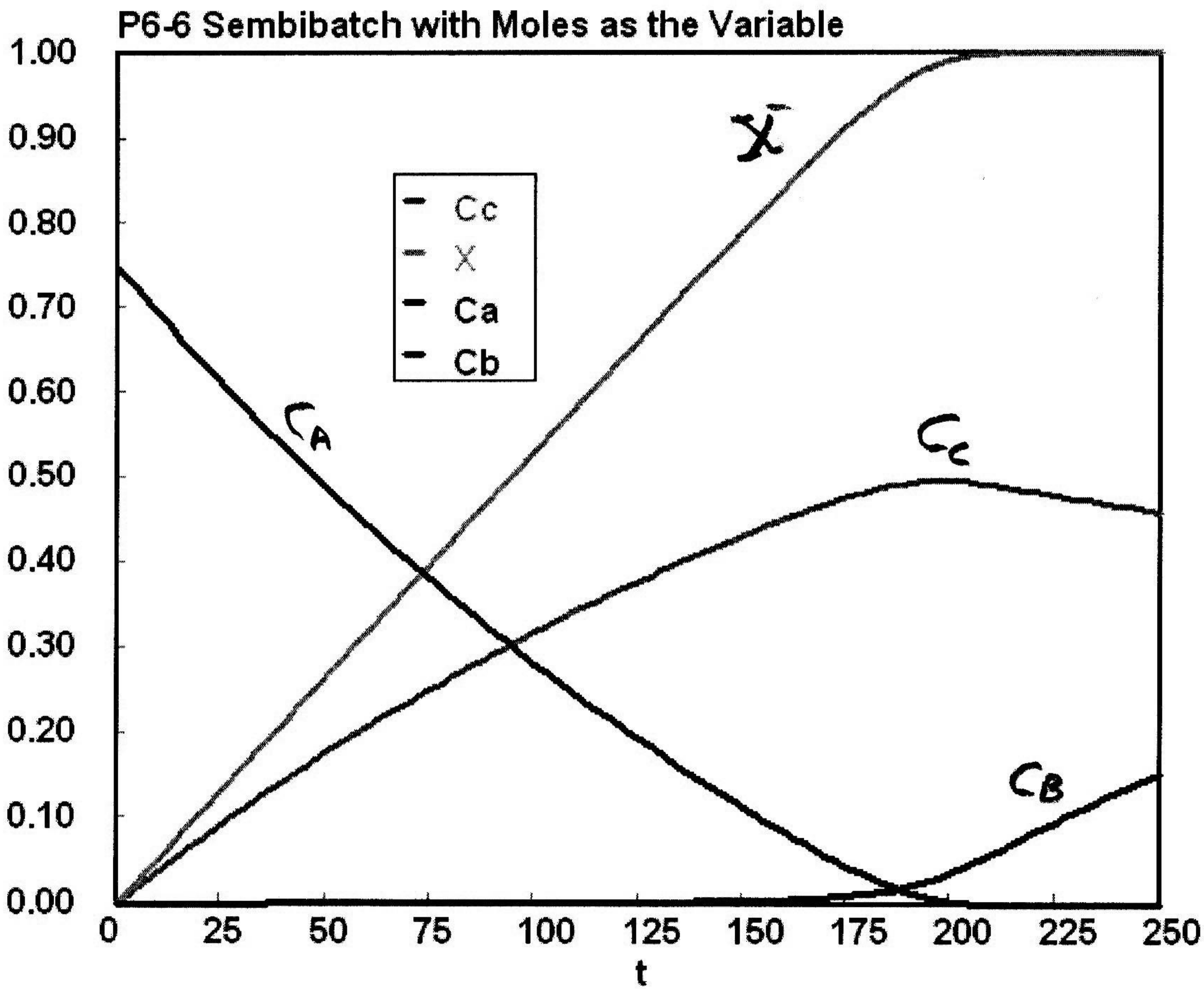
Differential equations

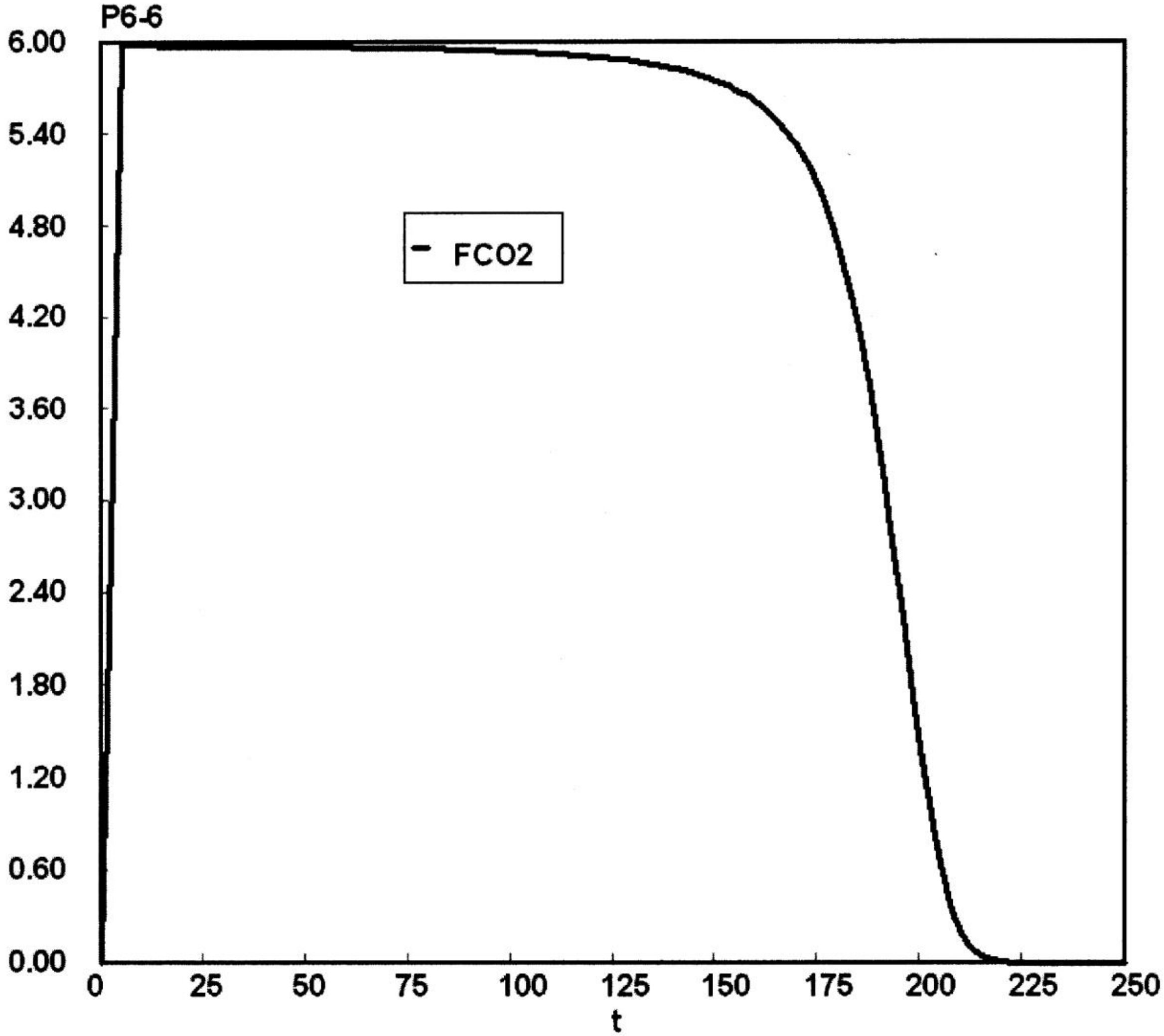
1 d(V)/d(t) = vo-vCO2
2 d(Nc)/d(t) = -ra*V
3 d(Nb)/d(t) = Fbo+ra*V
4 d(Na)/d(t) = ra*V

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

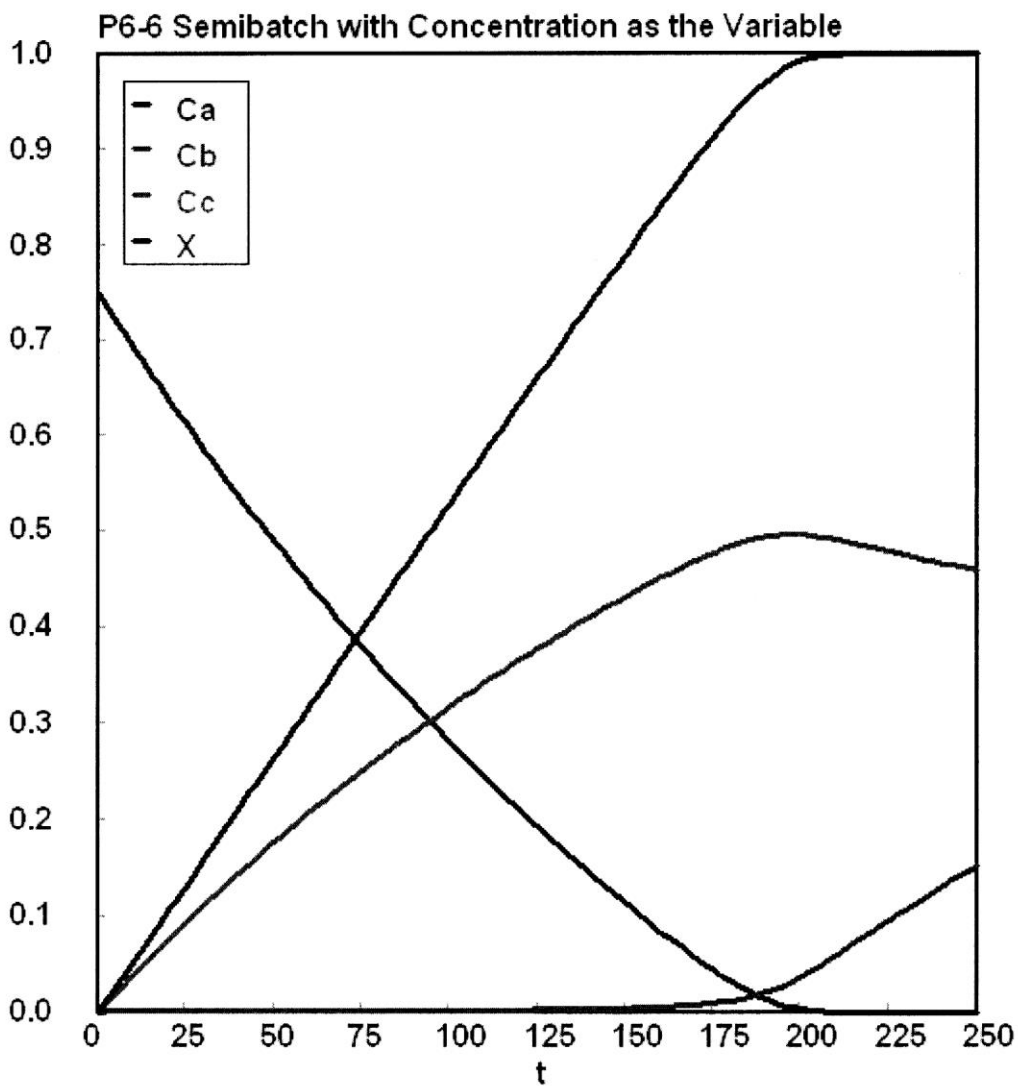
	Variable	Initial value	Minimal value	Maximal value	Final value
1	Ca	0.75	8.846E-14	0.75	8.846E-14
2	Cao	0.75	0.75	0.75	0.75
3	Cb	0	0	0.15303	0.15303
4	Cbo	1.5	1.5	1.5	1.5
5	Cc	0	0	0.496826	0.45909
6	CC	0	0	0.496827	0.45909
7	Cd	0	0	0.496827	0.45909
8	Fbo	6.	6.	6.	6.
9	FCO2	0	0	5.987132	1.692E-10
10	k	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.

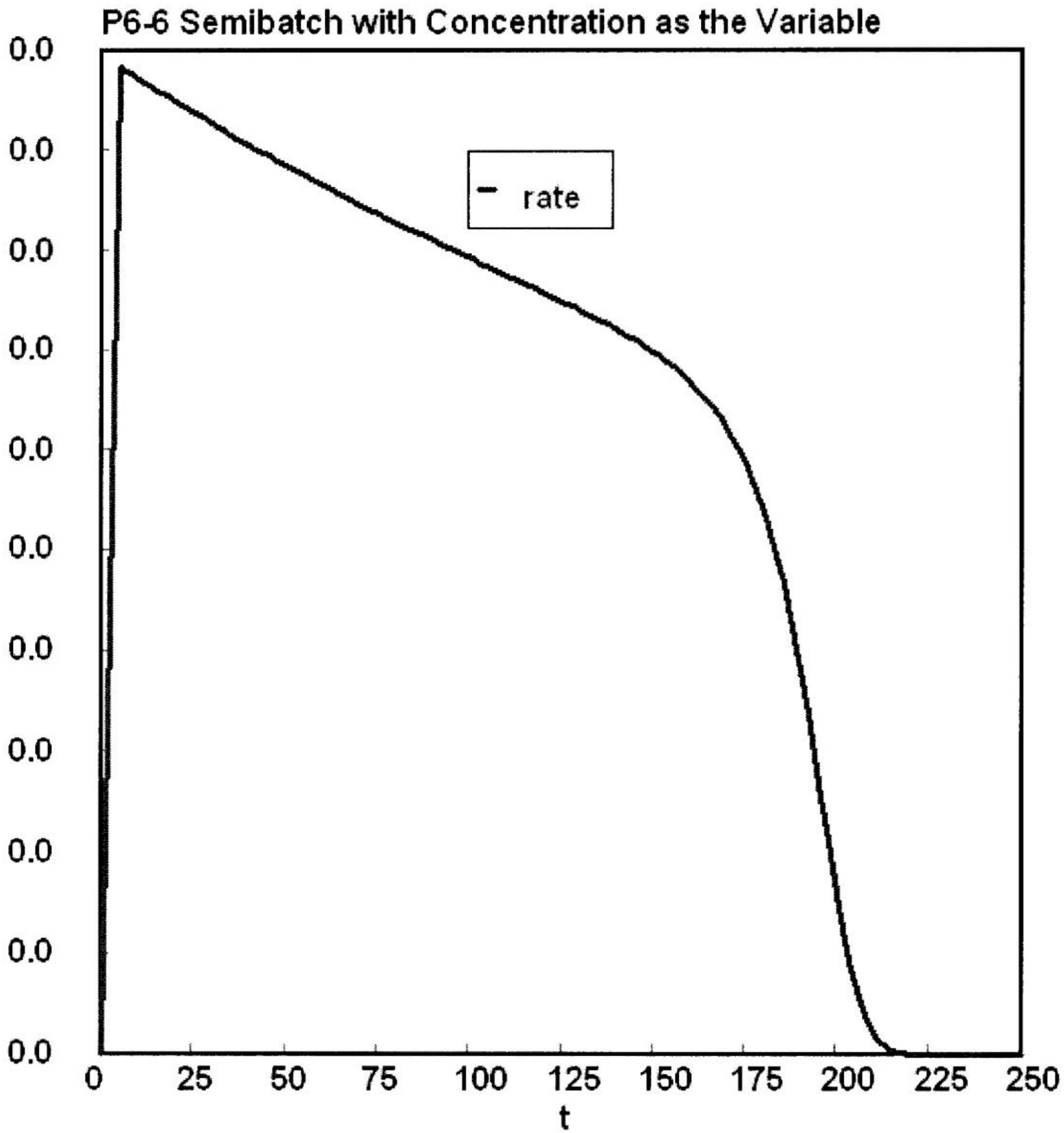
Differential equations

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

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

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

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	

Are you ready?

Summary

- In this lecture, we discussed:
- - The unique features and applications of semibatch reactors.
- - How to maximize selectivity in multiple reactions.
- - Key concepts: mole balances, rate laws, and stoichiometry.
- - Numerical approaches for analyzing semibatch reactor performance.
- Semibatch reactors are versatile tools in chemical engineering, enabling precise control over reaction dynamics for optimized outcomes.