CD-ROM INCLUDED

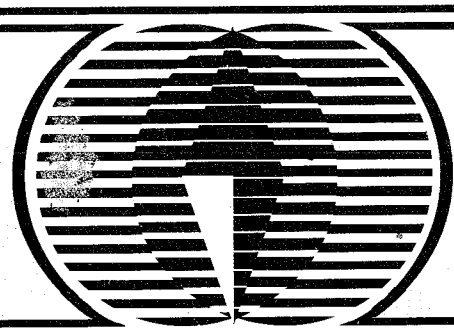
Brian Vicente / Max Nori / H. Scott Fogler

Solutions Manual for

Elements of Chemical Reaction Engineering

Fourth Edition

Prentice Hall International Series in the Physical and Chemical Engineering Sciences



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UNIVERSITY OF MICHIGAN
INTERACTIVE COMPUTER MODULES FOR CHEMICAL ENGINEERING
CHEMICAL REACTION ENGINEERING MODULES

H. Scott Fogler, Project Director

M. Nihat Gürmen, Project Manager (2002-2004)
Susan Montgomery, Project Manager (1991-1993)

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INTERPRETATION OF PERFORMANCE NUMBERS

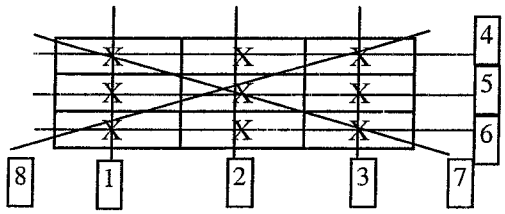
Students should record their Performance Number for each program, along with the name of the program, and turn it in to the instructor. The Performance Number for each program is decoded as described in the following pages.

The official site for the distribution of the modules is
http://www.engin.umich.edu/~cre/icm

Please report problems to icm.support@umich.edu.

ICMs with Windows® interface

Module	Format	Interpretation	Example
KINETIC CHALLENGE I			
	CzBzzAzz	Score = 1.5 * AB.C z = random numbers Note: 75% constitutes mastery.	Perf. No. = 75241692 Score = 1.5*(62.7) = 94 %
KINETIC CHALLENGE II			
	CzBzzAzz	Score = 2.0 * AB.C z = random numbers Note: 75% constitutes mastery.	Perf. No. = 03776467 Score = 2.0*(47.0) = 94 %
MURDER MYSTERY			
	zzAzz	A even: Killer and victim correctly identified A odd: Killer and victim not identified z = random numbers Note: An even number for the middle digit constitutes mastery.	Perf. No. = 50732 Score: No credit
TIC TAC TOE			
	zDzCzBzA	Score = 4.0 * AB.C z = random numbers Configurations	Perf. No. = 77803581 Score = 4*(15.0) = 60 configuration 7 completed



Note: Student receives 20 points for every square answered correctly.
A score of 60 is needed for mastery of this module.

GREAT RACE			
	zzzCzABz	Score = 6.0 * AB.C z = random numbers	Perf. No. = 77738078 Score = 6*(07.3) = 44

Note: A score of 40 is needed for mastery of this module.

ECOLOGY

AzBCzaaD **z = random numbers**
a = random characters

A gives info on r^2 value of the student's linearized plot
A=Y if r^2 >= 0.9
A=A if 0.9 > r^2 >= 0.8
A=X if 0.8 > r^2 >= 0.7
A=F if 0.7 > r^2
A=Q if Wetland Analysis/Simulator portion has not been completed

B gives info on alpha
B=1 to 4 => student's alpha < (simulator's alpha ± 0.5)
B=5 to 9 => student's alpha > (simulator's alpha ± 0.5)
B=X if Wetland Analysis/Simulator portion has not been completed

C indicates number of data points deactivated during analysis
C=number of deactivated data points if at least 1 point has been deactivated
C=a randomly generated letter from A to Y if 0 points deactivated
C=Z if Wetland Analysis/Simulator portion has not been completed

D gives info on solution method used by student
D=1 if polynomial regression was used
D=2 if differential formulas were used
D=3 if graphical differentiation was used
D=4 to 9 if Wetland Analysis/Simulator portion has not been completed

Perf No. = A7213DF2
1) A => 0.9 > r^2 >= 0.8
2) 2 => student's alpha < (simulator's alpha ± 0.5)
3) 1 => one data point was deactivated
4) 2 => differential formulas were used

STAGING

zCBzAFzED **z = random numbers** Perf. No. = 2125482913

Final conversion = 2*AB.C conversion = 2*42.1 = 84.2
Final flow rate = 2*DE.F flow rate = 2*31.2 = 62.4

Please make a pass/fail criterion based on these values.

ICMs with Dos® interface

Module	Format	Interpretation	Example
HETCAT			
	zzABzCD	A=2,3,5,7: interaction done B=2,3,5,7: intro done C=2,3,5,7: review done D denotes how much they did in the interaction: D<2 Not done 2 < D:5 4 Dependences 4 < D:5 6 Parameter values 6<D Mechanism z = random numbers	Perf. No. = 8027435 A: Worked on interaction B: Looked at intro C: Looked at review D: found parameter values, didn't find mechanism
	Note: Performance number given only if student goes through the interaction portion of the module		
HEATFX1			
	zzAzz	A even: score > 85 % z = random numbers	Perf. No. = 53607 Score > 85 %
	Note: Student told they have achieved mastery if their score is greater than 85%		
HEATFX2			
	zzzAzz	A even: completed interaction z = random numbers	Perf. No. = 407582 Interaction not completed
	Note: Performance number given only if student goes through the interaction portion of the module.		

Solutions for Chapter 1 – Mole Balances

Synopsis

General: The goal of these problems are to reinforce the definitions and provide an understanding of the mole balances of the different types of reactors. It lays the foundation for step 1 of the algorithm in Chapter 4.

P1-1. This problem helps the student understand the course goals and objectives.

P1-2. Part (d) gives hints on how to solve problems when they get stuck. Encourages students to get in the habit of writing down what they learned from each chapter. It also gives tips on problem solving.

P1-3. Helps the student understand critical thinking and creative thinking, which are two major goals of the course.

P1-4. Requires the student to at least look at the wide and wonderful resources available on the CD-ROM and the Web.

P1-5. The ICMs have been found to be a great motivation for this material.

P1-6. Uses Example 1-1 to calculate a CSTR volume. It is straight forward and gives the student an idea of things to come in terms of sizing reactors in chapter 4. An alternative to **P1-15**.

P1-7. Straight forward modification of Example 1-1.

P1-8. Helps the student review and member assumption for each design equation.

P1-9 and **P1-10**. The results of these problems will appear in later chapters. Straight forward application of chapter 1 principles.

P1-11. Straight forward modification of the mole balance. Assigned for those who emphasize bioreaction problems.

P1-12. Can be assigned to just be read and not necessarily to be worked. It will give students a flavor of the top selling chemicals and top chemical companies.

P1-13. Will be useful when the table is completed and the students can refer back to it in later chapters. Answers to this problem can be found on Professor Susan Montgomery's equipment module on the CD-ROM. See **P1-17**.

P1-14. Many students like this straight forward problem because they see how CRE principles can be applied to an everyday example. It is often assigned as an in-class problem where parts **(a)** through **(f)** are printed out from the web. Part **(g)** is usually omitted.

P1-15. Shows a bit of things to come in terms of reactor sizing. Can be rotated from year to year with **P1-6**.

P1-16. Open-ended problem.

P1-17. I **always** assign this problem so that the students will learn how to use POLYMATH/MaLab before needing it for chemical reaction engineering problems.

P1-18. Parts **(a)** and **(b)** are open-ended problem.

P1-19 and **P1-20.** Help develop critical thinking and analysis.

CDP1-A Similar to problems 3, 4, 11, and 12.

CDP1-B Points out difference in rate per unit liquid volume and rate per reactor volume.

Summary

	Assigned	Alternates	Difficulty	Time (min)
● P1-1	AA		SF	60
P1-2	I		SF	30
● P1-3	O		SF	30
P1-4	O		SF	30
P1-5	AA		SF	30
P1-6	AA	1-15	SF	15
P1-7	I		SF	15
● P1-8	S		SF	15
P1-9	S		SF	15
P1-10	S		SF	15
P1-11	O		FSF	15

	P1-12	I	– Read Only	SF	30
	P1-13	I		SF	1
	P1-14	O		FSF	30
	P1-15	O		SF	60
	P1-16	S		SF	15
●	P1-17	AA		SF	60
	P1-18	S		SF	30
	P1-19	O		--	30
	P1-20	O		FSF	15
	CDP1-A	AA		FSF	30
	CDP1-B	I		FSF	30

Assigned

● = Always assigned, AA = Always assign one from the group of alternates,
O = Often, I = Infrequently, S = Seldom, G = Graduate level

Alternates

In problems that have a dot in conjunction with AA means that one of the problem, either the problem with a dot or any one of the alternates are always assigned.

Time

Approximate time in minutes it would take a B/B^+ student to solve the problem.

Difficulty

SF = Straight forward reinforcement of principles (plug and chug)
FSF = Fairly straight forward (requires some manipulation of equations or an intermediate calculation).
IC = Intermediate calculation required
M = More difficult
OE = Some parts open-ended.

---

*Note the letter problems are found on the CD-ROM. For example A ≡ CDP1-A.

Summary Table Ch-1

Review of Definitions and Assumptions	1,5,6,7,8,9
Introduction to the CD-ROM	1,2,3,4

Make a calculation	6
Open-ended	8,16

P1-1 Individualized solution.

P1-2 Individualized solution.

P1-3 Individualized solution.

P1-4 Individualized solution.

P1-5 Solution is in the decoding algorithm given with the modules.

P1-6

The general equation for a CSTR is:

$$V = \frac{F_{A0} - F_A}{-r_A}$$

Here r_A is the rate of a first order reaction given by:

$$r_A = -kC_A$$

Given : $C_A = 0.1C_{A0}$, $k = 0.23\ min^{-1}$, $v_0 = 10dm^3\ min^{-1}$, $F_A = 5.0$ mol/hr
And we know that $F_A = C_A v_0$ and $F_{A0} = C_{A0} v_0$
$\Rightarrow C_{A0} = F_{A0}/ v_0 = 0.5\ mol/dm^3$
Substituting in the above equation we get:

$$V = \frac{C_{A0}v_0 - C_A v_0}{kC_A} = \frac{(0.5mol/dm^3)(10dm^3/\min) - 0.1(0.5mol/dm^3)(10dm^3/\min)}{(0.23\min^{-1})(0.1(0.5mol/dm^3))}$$

V = 391.3 dm^3

P1-7

$$t = \int_{N_{A0}}^{N_A} \frac{1}{-k \cdot N_A}\, dN_A$$

$$k = 0.23\min^{-1}$$

From mole balance: $$\frac{dN_A}{dt} = r_A \cdot V$$

Rate law: $-r_A = k \cdot C_A$

$$-r_A = k \cdot \frac{N_A}{V}$$

Combine:

$$\frac{dN_A}{dt} = -k \cdot N_A$$

$$\tau = 0 \int_0^t 1 \, dt = -\left(\frac{1}{k}\right) \cdot \int_{N_{A0}}^{N_A} \frac{1}{N_A} dN_A$$

at $\tau = 0$, $N_{AO} = 100$ mol and $\tau = \tau$, $N_A = (0.01)N_{AO}$

$$\rightarrow t = \frac{1}{k} \ln\left(\frac{N_{A0}}{N_A}\right)$$

$$= \frac{1}{0.23} \ln(100) \quad \text{min} \qquad t = 20 \text{ min}$$

P1-8

a) The assumptions made in deriving the design equation of a batch reactor are:
- Closed system: no streams carrying mass enter or leave the system.
- Well mixed, no spatial variation in system properties
- Constant Volume or constant pressure.

b) The assumptions made in deriving the design equation of CSTR, are:
- Steady state.
- No spatial variation in concentration, temperature, or reaction rate throughout the vessel.

c) The assumptions made in deriving the design equation of PFR are:
- Steady state.
- No radial variation in properties of the system.

d) The assumptions made in deriving the design equation of PBR are:
- Steady state.
- No radial variation in properties of the system.

e) For a reaction,
A→ B
$-r_A$ is the number of moles of A reacting (disappearing) per unit time per unit volume [=] moles/ (dm^3.s).

$-r_A'$ is the rate of disappearance of species A per unit mass (or area) of catalyst [=] moles/ (time. mass of catalyst).
r_A' is the rate of formation (generation) of species A per unit mass (or area) of catalyst [=] moles/ (time. mass catalyst).
$-r_A$ is an ***intensive*** property, that is, it is a function of concentration, temperature, pressure, and the type of catalyst (if any), and is defined at any ***point*** (location) within the system. It is independent of amount. On the other hand, an extensive property is obtained by summing up the properties of individual subsystems within the ***total*** system; in this sense, $-r_A$ is independent of the 'extent' of the system.

P 1-9

Rate of homogenous reaction r_A is defined as the mole of A formed per unit volume of the reactor per second. It is an Intensive property and the concentration, temperature and hence the rate varies with spatial coordinates.

r_A' on the other hand is defined as g mol of A reacted per gm. of the catalyst per second. Here mass of catalyst is the basis as this is what is important in catalyst reactions and not the reactor volume.

Applying general mole balance we get:

$$\frac{dN_j}{dt} = F_{j0} - F_j + \int r_j dV$$

No accumulation and no spatial variation implies

$$0 = F_{j0} - F_j + \int r_j dV$$

Also $r_j = \rho_b r_j'$ and $W = V\rho_b$ where ρ_b is the bulk density of the bed.

$$\Rightarrow \quad 0 = (F_{j0} - F_j) + \int r_j'(\rho_b dV)$$

Hence the above equation becomes

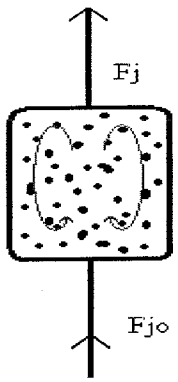
$$W = \frac{F_{j0} - F_j}{-r_j'}$$

We can also just apply the general mole balance as

$$\frac{dN_j}{dt} = (F_{j0} - F_j) + \int r_j'(dW)$$

Assuming no accumulation and no spatial variation in rate, we get the same form as above:

$$W = \frac{F_{j0} - F_j}{-r_j'}$$



P1-10

Mole balance on species j is:

$$F_{j0} - F_j + \int_0^V r_j dV = \frac{dN_j}{dt}$$

Let M_j = molecular wt. of species j

Then $F_{j0}M_j = w_{j0}$ = mass flow rate of j into reactor:

$N_j M_j = m_j$ = mass of species j in the reactor

Multiplying the mole balance on species j by M_j

$$F_{j0}M_j - F_j M_j + M_j \int_0^V r_j dV = M_j \frac{dN_j}{dt}$$

Now M_j is constant:

$$F_{j0}M_j - F_j M_j + \int_0^V M_j r_j dV = \frac{d(M_j N_j)}{dt} = \frac{d(m_j)}{dt}$$

$$w_{j0} - w_j + \int_0^V M_j r_j dV = \frac{dm_j}{dt}$$

P1-11

Applying mole balance to Penicillin: Penicillin is produced in the cells stationary state (See Chapter 7), so there is no cell growth and the nutrients are used in making product.

Let's do part c first.

[In flowrate (moles/time)] $_{penicillin}$ + [generation rate (moles/time)]$_{penicillin}$ – [Out flowrate (moles/time)] $_{penicillin}$ = [rate of accumulation (moles/time)]$_{penicillin}$

$$F_{p,in} + G_p - F_{p,out} = \frac{dNp}{dt}$$

$F_{p,in} = 0$ .....(because no penicillin inflow)

$$G_p = \int_V r_p.dV$$

Therefore,

$$\int_V r_p.dV - F_{p,out} = \frac{dNp}{dt}$$

Assuming steady state for the rate of production of penicillin in the cells stationary state,

$$\frac{dNp}{dt} = 0$$

And no variations

$$\boxed{V = \frac{F_{p,in} - F_{p,out}}{-r_p}}$$

Or,

$$\boxed{V = \frac{F_{p,out}}{r_p}}$$

Similarly, for Corn Steep Liquor with $F_C = 0$

$$\boxed{V = \frac{F_{C0} - F_C}{-r_C} = \frac{F_{C0}}{-r_C}}$$

Assume RNA concentration does not change in the stationary state and no RNA is generated or destroyed.

P1-12 (a)

Ranking of 10 most produced chemicals in 1995 and 2002 are listed in table below:

Rank 2002	Rank 1995	**Chemical**
1	1	**H_2SO_4**
2	2	**N_2**
3	4	**C_2H_4**
4	3	**O_2**
5	9	**C_3H_6**
6	-	**H_2**

7	6	**NH_3**
8	10	**Cl_2**
9	-	**P_2O_5**
10	-	**$C_2H_2Cl_2$**

➔ Chemicals like H_2 , P_2O_5 , $C_2H_2Cl_2$ has come in top 10 chemicals and C_3H_6 has jumped to rank 5 now then rank 9 in 1995 .

P1-12 (b)

Ranking of top 10 chemical companies in sales in year 2003 and 2002:

2003	2002	Company	Chemical Sales ($ million 2003)
1	1	Dow Chemical	32632
2	2	DuPont	30249
3	3	ExxonMobil	20190
4	4	General Electric	8371
5	8	Chevron Phillips	7018
6	5	Huntsman Corp.	6990
7	6	PPG Industries	6606
8	7	Equistar Chemicals	6545
9	11	Air Products	6029
10	9	Eastman Chemicals	5800

source: Chemical and Engineering News may 17,2004

➔ We have Chevron Phillips which jumped to 5 rank in 2003 from 8th rank in 2002 and Air Products coming to 9th rank in 2003 from 11th in 2003.

➔Chemical sales of each company has increased compared to year 2002 from 9%(Eastman Chemical) to28.2%(Chevron Phillips) but Huntsman Corp. has a decrease by 2.9%.

P1-12 (c)

Sulfuric acid is prime importance in manufacturing. It is used in some phase of the manufacture of nearly all industrial products .It is used in production of every other strong acid. Because of its large number of uses, it's the most produced chemical. Sulfuric acid uses are:

➔It is consumed in production of fertilizers such as ammonium sulphate $(NH_4)_2SO_4$ and superphosphate $(Ca(H_2PO_4)_2)$, which is formed when rock phosphate is treated with sulfuric acid.

➔Used as dehydrating agent.

➔Used in manufacturing of explosives, dyestuffs, other acids, parchment paper, glue , purification of petroleum and picking of metals.

➔Used to remove oxides from iron and steel before galvanizing or electroplating.

➔Used in non-ferrous metallurgy, in production of rayon and film.

➔as laboratory reagent and etchant and in storage batteries.

➔It is also general purpose food additive.

P1-12 (d) Annual Production rate of ethylene for year 2002 is $\underline{5.21 \times 10^{10}\ lb/year}$

Annual Production rate of benzene for year 2002 is $\underline{1.58 \times 10^{10}\ lb/year}$

Annual Production rate of ethylene oxide for year 2002 is 7.6×10^9 lb/year

P1-12 (e) Because the basic raw material 'coal and petroleum' for organic chemicals is very limited and their production is not increasing as production of raw material for inorganic chemicals.

P1-13

Type	Characteristics	Phases	Usage	Advantage	Disadvantage
Batch	All the reactants fed into the reactor. During reaction nothing is added or removed. Easy heating or cooling.	1. Liquid phase 2. Gas phase 3. Liquid Solid	1. Small scale pdn. 2. Used for lab experimentation. 3. Pharmaceuticals 4. Fermentation	1. High Conversion per unit volume. 2. Flexibility of using for multiple reactions. 3. Easy to clean	1. High Operating cost. 2. Variable product quality.
CSTR	Continuous flow of reactants and products. Uniform composition throughout.	1. Liquid phase 2. Gas – liquid 3. Solid - liquid	1. Used when agitation required. 2. Series Configuration possible for different configuration streams	1. Continuous Operation. 2.Good Temperature Control 3. Two phase reactions possible. 4.Good Control 5. Simplicity of construction. 6. Low operating cost 7. Easy to clean	1. Lowest conversion per unit volume. 2. By passing possible with poor agitation. 3 High power Input reqd.
PFR	One long reactor or number of CSTR's in series. No radial variations. Conc. changes along the length.	1. Primarily gas Phase	1. Large Scale pdn. 2. Fast reactions 3. Homogenous reactions 4. Heterogeneous reactions 5. Continuous pdn.	1. High conversion per unit volume 2. Easy to maintain (No moving parts) 3. low operating cost 4. continuous operation	1. Undesired thermal gradient. 2. Poor temperature control 3. Shutdown and cleaning expensive.
PBR	Tubular reactor that is packed with solid catalyst particles.	1. Gas Phase (Solid Catalyst) 2.Gas – solid reactions.	1. Used primarily in the heterogeneous gas phase reaction with solid catalyst e.g Fischer tropsch synthesis.	1. High conversion per unit mass of catalyst 2. low operating cost 3. Continuous operation	1. Undesired thermal gradient. 2. Poor temperature control 3. Channeling 4. Cleaning expensive.

P1-14

Given

$A = 2*10^{10}\ ft^2$ $\quad T_{STP} = 491.69R$ $\quad H = 2000\ ft$

$V = 4*10^{13}\ ft^3$ $\quad T = 534.7\ ^\circ R$ $\quad P_O = 1atm$

$R = 0.7302 \frac{atm\ ft^3}{lbmol\ R}$ $\quad y_A = 0.02$ $\quad C_S = 2.04*10^{-10} \frac{lbmol}{ft^3}$

$C = 4*10^5$ cars

F_S = CO in Santa Ana wind $\quad F_A$ = CO emission from autos

$v_A = 3000 \frac{ft^3}{hr}$ per car at STP

P1-14 (a)

Total number of lb moles gas in the system:

$$N := \frac{P_0 \cdot V}{R \cdot T}$$

$$N = \frac{1atm \times (4 \times 10^{13}\ ft^3)}{\left(0.73 \frac{atm.ft^3}{lbmol.R}\right) \times 534.69R} = 1.025 \times 10^{11} \text{ lb mol}$$

P1-14 (b)

Molar flowrate of CO into L.A. Basin by cars.

$$F_A = y_A F_I = y_A \cdot \frac{v_A C P_0}{R T_{STP}}$$

$$F_T = \frac{3000\ ft^3}{hr\ car} \times \frac{1 lbmol}{359\ ft^3} \times 400000\ cars$$ (See appendix B)

$F_A = 6.685 \times 10^4$ lb mol/hr

P1-14 (c)

Wind speed through corridor is v = 15mph

W = 20 miles

The volumetric flowrate in the corridor is

v_O = v.W.H = (15x5280)(20x5280)(2000) ft^3/hr

= $1.673 \times 10^{13}\ ft^3/hr$

P1-14 (d)

Molar flowrate of CO into basin from Sant Ana wind

$F_S := v_0 \cdot C_S$

$= 1.673 \times 10^{13}\ ft^3/hr \times 2.04\times10^{-10}\ lbmol/ft^3$

$F_S = 3.412 \times 10^3\ lbmol/hr$

P1-14 (e)

Rate of emission of CO by cars + Rate of CO by Wind - Rate of removal of CO = $\frac{dN_{CO}}{dt}$

$$F_A + F_S - v_o C_{co} = V\frac{dC_{co}}{dt} \qquad (V=\text{constant}, N_{co} = C_{co}V)$$

P1-14 (f)

$t = 0$, $C_{co} = C_{coO}$

$$\int_0^t dt = V\int_{C_{coO}}^{C_{co}} \frac{dC_{co}}{F_A + F_S - v_o C_{co}}$$

$$t = \frac{V}{v_o}\ln\left(\frac{F_A + F_S - v_o C_{coO}}{F_A + F_S - v_o C_{co}}\right)$$

P1-14 (g)

Time for concentration to reach 8 ppm.

$$C_{CO0} = 2.04\times10^{-8}\frac{lbmol}{ft^3},\ C_{CO} = \frac{2.04}{4}\times10^{-8}\frac{lbmol}{ft^3}$$

From (f),

$$t = \frac{V}{v_o}\ln\left(\frac{F_A + F_S - v_O.C_{CO0}}{F_A + F_S - v_O.C_{CO}}\right)$$

$$= \frac{4\,ft^3}{1.673\times10^{13}\frac{ft^3}{hr}}\ln\left(\frac{6.7\times10^4\frac{lbmol}{hr} + 3.4\times10^3\frac{lbmol}{hr} - 1.673\times10^{13}\frac{ft^3}{hr}\times2.04\times10^{-8}\frac{lbmol}{ft^3}}{6.7\times10^4\frac{lbmol}{hr} + 3.4\times10^3\frac{lbmol}{hr} - 1.673\times10^{13}\frac{ft^3}{hr}\times0.51\times10^{-8}\frac{lbmol}{ft^3}}\right)$$

t = 6.92 hr

P1-14 (h)

(1)

t_o	= 0	t_f	= 72 hrs
C_{co}	= 2.00E-10 lbmol/ft^3	a	= 3.50E+04 lbmol/hr
v_o	= 1.67E+12 ft^3 /hr	b	= 3.00E+04 lbmol/hr

F_s = 341.23 lbmol/hr V = 4.0E+13 ft^3

$$a + b\sin\left(\pi\frac{t}{6}\right) + F_s - v_o C_{co} = V\frac{dC_{co}}{dt}$$

Now solving this equation using POLYMATH we get plot between C_{co} vs t

See Polymath program P1-14-h-1.pol.

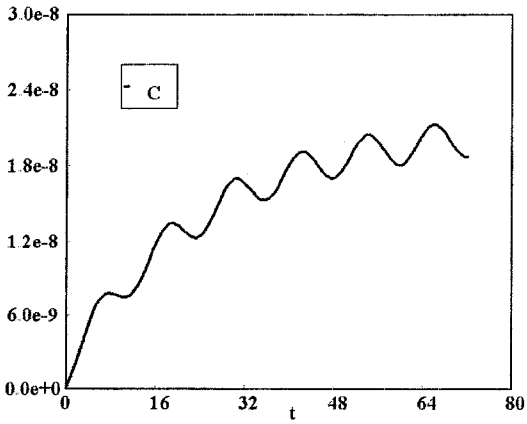
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	72	72
C	2.0E-10	2.0E-10	2.134E-08	1.877E-08
v0	1.67E+12	1.67E+12	1.67E+12	1.67E+12
a	3.5E+04	3.5E+04	3.5E+04	3.5E+04
b	3.0E+04	3.0E+04	3.0E+04	3.0E+04
F	341.23	341.23	341.23	341.23
V	4.0E+13	4.0E+13	4.0E+13	4.0E+13

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(C)/d(t) = (a+b*sin(3.14*t/6)+F-v0*C)/V

Explicit equations as entered by the user
[1] v0 = 1.67*10^12
[2] a = 35000
[3] b = 30000
[4] F = 341.23
[5] V = 4*10^13



(2) t_f = 48 hrs $F_s = 0$ $$a + b\sin\left(\pi\frac{t}{6}\right) - v_o C_{co} = V\frac{dC_{co}}{dt}$$

Now solving this equation using POLYMATH we get plot between C_{co} vs t

See Polymath program P1-14-h-2.pol.

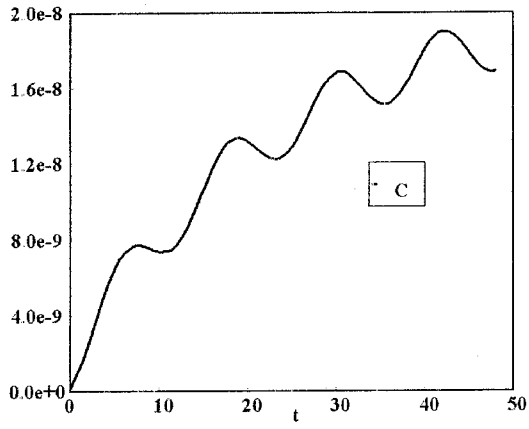
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	48	48
C	2.0E-10	2.0E-10	1.904E-08	1.693E-08
v0	1.67E+12	1.67E+12	1.67E+12	1.67E+12
a	3.5E+04	3.5E+04	3.5E+04	3.5E+04
b	3.0E+04	3.0E+04	3.0E+04	3.0E+04
V	4.0E+13	4.0E+13	4.0E+13	4.0E+13

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(C)/d(t) = (a+b*sin(3.14*t/6)-v0*C)/V

Explicit equations as entered by the user
[1] v0 = 1.67*10^12
[2] a = 35000
[3] b = 30000
[4] V = 4*10^13



(3)

Changing a → Increasing 'a' reduces the amplitude of ripples in graph. It reduces the effect of the sine function by adding to the baseline.

Changing b → The amplitude of ripples is directly proportional to 'b'. As b decreases amplitude decreases and graph becomes smooth.

Changing v_0 → As the value of v_0 is increased the graph changes to a "shifted sin-curve". And as v_0 is decreased graph changes to a smooth increasing curve.

P1-15 (a)

$-r_A = k$ with $k = 0.05$ mol/h dm^3

CSTR: The general equation is

$$V = \frac{F_{A0} - F_A}{-r_A}$$

Here $C_A = 0.01C_{A0}$, $v_0 = 10$ dm^3/min, $F_A = 5.0$ mol/hr
Also we know that $F_A = C_A v_0$ and $F_{A0} = C_{A0} v_0$, $C_{A0} = F_{A0}/ v_0 = 0.5$ mol/dm^3
Substituting the values in the above equation we get,

$$V = \frac{C_{A0}v_0 - C_A v_0}{k} = \frac{(0.5)10 - 0.01(0.5)10}{0.05}$$

→ **V = 99 dm^3**

PFR: The general equation is

$$\frac{dF_A}{dV} = r_A = k \text{ , Now } F_A = C_A v_0 \text{ and } F_{A0} = C_{A0} v_0 \Rightarrow \frac{dC_A v_0}{dV} = -k$$

Integrating the above equation we get

$$\frac{v_0}{k}\int_{C_{A0}}^{C_A} dC_A = \int_0^V dV \Rightarrow V = \frac{v_0}{k}(C_{A0} - C_A)$$

Hence **V = 99 dm^3**
Volume of PFR is same as the volume for a CSTR since the rate is constant and independent of concentration.

P1-15 (b)

- $r_A = kC_A$ with k = 0.0001 s^{-1}

CSTR:
We have already derived that

$$V = \frac{C_{A0}v_0 - C_A v_0}{-r_A} = \frac{v_0 C_{A0}(1-0.01)}{kC_A}$$

k = 0.0001s^{-1} = 0.0001 x 3600 hr^{-1}= 0.36 hr^{-1}

$$\rightarrow V = \frac{(10dm^3/hr)(0.5mol/dm^3)(0.99)}{(0.36hr^{-1})(0.01*0.5mol/dm^3)} \Rightarrow \textbf{V = 2750 dm}^3$$

PFR:
From above we already know that for a PFR

$$\frac{dC_A v_0}{dV} = r_A = kC_A$$

Integrating

$$\frac{v_0}{k}\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = -\int_0^V dV$$

$$\frac{v_0}{k}\ln\frac{C_{A0}}{C_A} = V$$

Again k = 0.0001s^{-1} = 0.0001 x 3600 hr^{-1}= 0.36 hr^{-1}

Substituing the values in above equation we get
V = 127.9 dm^3

P1-15 (c)

- $r_A = kC_A^2$ with k = 3 dm^3/mol.hr

CSTR:

$$V = \frac{C_{A0}v_0 - C_A v_0}{-r_A} = \frac{v_0 C_{A0}(1-0.01)}{kC_A^{\,2}}$$

Substituting all the values we get

$$V = \frac{(10dm^3/hr)(0.5mol/dm^3)(0.99)}{(3dm^3/hr)(0.01*0.5mol/dm^3)^2} \quad \Rightarrow \mathbf{V = 66000\ dm^3}$$

PFR:

$$\frac{dC_A v_0}{dV} = r_A = kC_A^{\,2}$$

Integrating

$$\frac{v_0}{k}\int_{C_{A0}}^{C_A}\frac{dC_A}{C_A^{\,2}} = -\int_0^V dV \quad \Rightarrow \frac{v_0}{k}\left(\frac{1}{C_A} - \frac{1}{C_{A0}}\right) = V$$

$$\Rightarrow V = \frac{10dm^3/hr}{3dm^3/mol.hr}\left(\frac{1}{0.01C_{A0}} - \frac{1}{C_{A0}}\right) = \mathbf{660\ dm^3}$$

P1-15 (d)

$C_A = .001C_{A0}$

$$t = \int_{N_A}^{N_{A0}} \frac{dN}{-r_A V}$$

Constant Volume $V=V_0$

$$t = \int_{C_A}^{C_{A0}} \frac{dC_A}{-r_A}$$

Zero order:

$$t = \frac{1}{k}[C_{A0} - 0.001C_{A0}] = \frac{.999C_{Ao}}{0.05} = 9.99\,h$$

First order:

$$t = \frac{1}{k}\ln\left(\frac{C_{A0}}{C_A}\right) = \frac{1}{0.001}\ln\left(\frac{1}{.001}\right) = 6908\,s$$

Second order:

$$t = \frac{1}{k}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right] = \frac{1}{3}\left[\frac{1}{0.0005} - \frac{1}{0.5}\right] = 666\,h$$

P1-16 Individualized Solution

P1-17 (a)

Initial number of rabbits, x(0) = 500
Initial number of foxes, y(0) = 200
Number of days = 500

$$\frac{dx}{dt} = k_1 x - k_2 xy \quad \text{.....(1)}$$

$$\frac{dy}{dt} = k_3 xy - k_4 y \quad \text{.....(2)}$$

Given,

$k_1 = 0.02 day^{-1}$

$k_2 = 0.00004/(day \times foxes)$

$k_3 = 0.0004/(day \times rabbits)$

$k_4 = 0.04 day^{-1}$

See Polymath program P1-17-a.pol.

POLYMATH Results
Calculated values of the DEQ variables

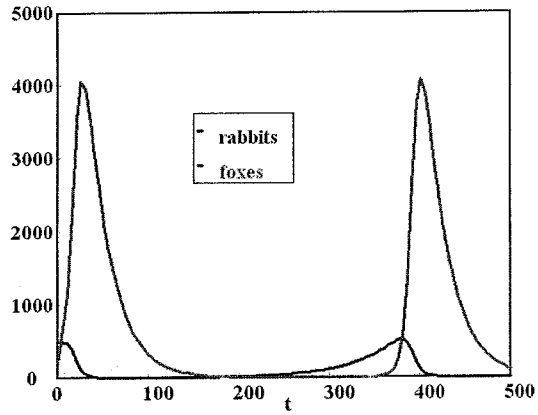
Variable	initial value	minimal value	maximal value	final value
t	0	0	500	500
x	500	2.9626929	519.40024	4.2199691
y	200	1.1285722	4099.517	117.62928
k1	0.02	0.02	0.02	0.02
k2	4.0E-05	4.0E-05	4.0E-05	4.0E-05
k3	4.0E-04	4.0E-04	4.0E-04	4.0E-04
k4	0.04	0.04	0.04	0.04

ODE Report (RKF45)

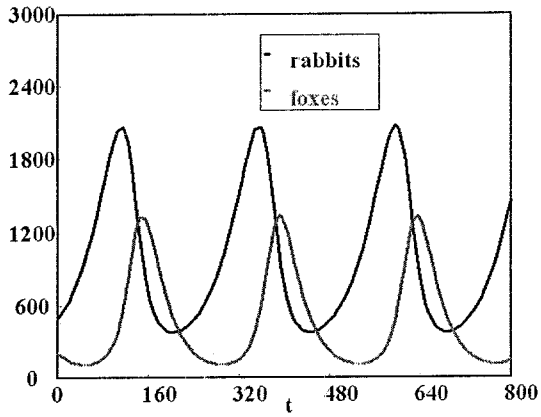
Differential equations as entered by the user
[1] d(x)/d(t) = (k1*x)-(k2*x*y)
[2] d(y)/d(t) = (k3*x*y)-(k4*y)

Explicit equations as entered by the user

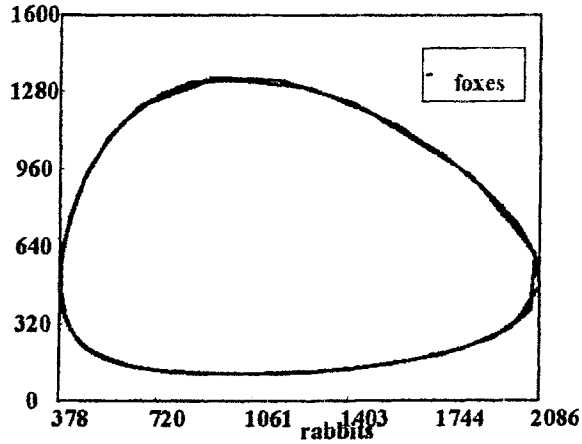
```
[1] k1 = 0.02
[2] k2 = 0.00004
[3] k3 = 0.0004
[4] k4 = 0.04
```



When, $t_{final} = 800$ and $k_3 = 0.00004/(day \times rabbits)$



Plotting rabbits Vs. foxes



P1-17 (b)

POLYMATH Results

See Polymath program P1-17-b.pol.

POLYMATH Results
NLES Solution

Variable	Value	f(x)	Ini Guess
x	2.3850387	2 53E-11	2
y	3.7970279	1.72E-12	2

NLES Report (safenewt)

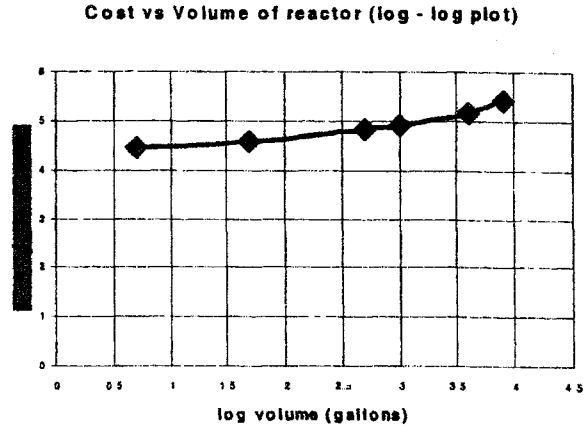
Nonlinear equations
[1] f(x) = x^3*y-4*y^2+3*x-1 = 0
[2] f(y) = 6*y^2-9*x*y-5 = 0

P1-18 (a)

No preheating of the benzene feed will diminish the rate of reaction and thus lesser conversions will be achieved.

P1-18 (b)

An interpolation can be done on the logarithmic scale to find the desired values from the given data.
Now we can interpolate to the get the cost at 6000 gallons and 15000 gallons
Cost of 6000 gal reactor = 1 905 x 10^5 $
Cost of 15000 gal reactor = 5 623 x 10^5 $



P1-18 (c)

We are given C_A is 0.1% of initial concentration
→ $C_A = 0\ 001 C_{A0}$

Also from Example 1.3,

$$V = \frac{v_0}{k}\ln(\frac{C_{A0}}{C_A})$$

Substituting $v_0 = 10$ dm^3/min and
$k = 0.23$ min^{-1} we get

$$V = 300dm^3$$

which is three times the volume of reactor used in Example 1-3.

P1-18 (d) Safety of Plant.

P1-19 Enrico Fermi Problem – no definite solution

P1-20 Enrico Fermi Problem -- no definite solution

P1-21 Individualized solution.

CDP1-A (a)

How many moles of A are in the reactor initially? What is the initial concentration of A?
If we assume ideal gas behavior, then calculating the moles of A initially present in the reactor is quite simple. We insert our variables into the ideal gas equation:

$$n = \frac{PV}{RT} = \frac{(20atm)(200dm^3)}{\left(8.3145\frac{kPa.dm^3}{molK}\right)(500)}\left(\frac{101.33kPa}{1atm}\right) = 97.5moles$$

Knowing the mole fraction of A (y_{Ao}) is 75%, we multiply the total number of moles (N_{To}) by the y_A:

$$molesA = N_{Ao} = 0.75 \times 97.5 = 73.1$$

The initial concentration of A (C_{Ao}) is just the moles of A divided by the volume:

$$C_{Ao} = \frac{moles}{volume} = \frac{N_{Ao}}{V} = \frac{73.1moles}{200dm^3} = 0.37moles/dm^3$$

CDP1-A (b)

Time (t) for a 1st order reaction to consume 99% of A.

$$r_A = \frac{dC_A}{dt}$$

Our first order rate law is: $-r_A = kC_A$

mole balance: $\frac{dC_A}{dt} = -kC_A \Rightarrow -k\int_0^t dt = \int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A}$

$-kt = \ln\left(\frac{C_A}{C_{Ao}}\right)$, knowing C_A=0.01 C_{Ao} and our rate constant (k=0.1 min^{-1}), we can solve for the time of the reaction: $t = -\frac{1}{k}\ln(0.01) = \frac{4.61}{0.1\,min^{-1}} = 46.1\,min$

CDP1-A (c)

Time for 2nd order reaction to consume 80% of A and final pressure (P) at T = 127 C.

rate law: $-r_A = kC_A^2$

mole balance: $\therefore \frac{dC_A}{dt} = -kC_A^2 \Rightarrow -k\int_0^t dt = \int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A^2} \Rightarrow -kt = -\frac{1}{C_A} + \frac{1}{C_{Ao}}$

We can solve for the time in terms of our rate constant (k = 0.7) and our initial concentration (C_{Ao}): $-kt = -\frac{5}{C_{Ao}} + \frac{1}{C_{Ao}}$

$t = \frac{4}{kC_{Ao}} = \frac{4}{(0.7 dm^3/mol\,min)(0.37 mol/dm^3)} = 15.4\,min$. To determine the pressure of the reactor following this reaction, we will again use the ideal gas law. First, we determine the number of moles in the reactor:

$N_T = N_I + N_A + N_B + N_C = 0.25N_{To} + 0.2N_{Ao} + N_B + N_C$

$N_B = N_C = 0.8N_{Ao}$

$N_T = (0.25)N_{To} + (0.2+0.8+0.8)N_{Ao} = 0.25(97.6) + (1.8)(73.2) = 156.1 moles$

$P = \frac{N_T RT}{V} = \frac{(156.1 mole)\left(0.082\frac{dm^3 atm}{molK}\right)(500K)}{200 dm^3} = 32 atm$

CDP1-B

Given: Liquid phase reaction in a foam reactor, A $\rightarrow$ B

Consider a differential element, ΔV of the reactor:

By material balance

$$F_A - (F_A + \Delta F_A) = -r_A(1-e)\Delta V$$

Where, $(1-e)\Delta V$ = fraction of reactor element which is liquid.

or: $$-F_A = -r_A(1-e)\Delta V$$

$$\frac{dF_A}{dV} = r_A(1-e)$$

Must relate $(-r_A)$ to F_A,

where, F_A is the total (gas +liquid) molar flow rate of A.

$-r_A$ =rate of reaction (g mol A per cubic cm. of liquid per sec.); e = volume fraction of gas; F_A = molar flow rate of A (g mol/sec.); V = volume of reactor

Solutions for Chapter 2 - Conversion and Reactor Sizing

Synopsis

General: The overall goal of these problems is to help the student realize that if they have $-r_A=f(X)$ they can "design" or size a large number of reaction systems. It sets the stage for the algorithm developed in Chapter 4.

P2-1. This problem will keep students thinking about writing down what they learned every chapter.

P2-2. This "forces" the students to determine their learning style so they can better use the resources in the text and on the CDROM and the web.

P2-3. ICMs have been found to motivate the students learning.

P2-4. Introduces one of the new concepts of the 4th edition whereby the students "play" with the example problems before going on to other solutions.

P2-5. This is a reasonably challenging problem that reinforces Levenspiels plots.

P2-6. Novel application of Levenspiel plots from an article by Professor Alice Gast at Massachusetts Institute of Technology in CEE.

P2-7. Straight forward problem alternative to problems 8, 9, and 12.

P2-8. To be used in those courses emphasizing bio reaction engineering.

P2-9. The answer gives ridiculously large reactor volume. The point is to encourage the student to question their numerical answers.

P2-10. Helps the students get a feel of real reactor sizes.

P2-11. Great motivating problem. Students remember this problem long after the course is over.

P2-12. Alternative problem to **P2-7** and **P2-9**.

CDP2-A Similar to 2-9

CDP2-B Good problem to get groups started working together (e.g. cooperative learning.

CDP2-C Similar to problems 2-8, 2-9, 2-12.

CDP2-D Similar to problems 2-8, 2-9, 2-12.

Summary

	Assigned	Alternates	Difficulty	Time (min)
P2-1	O			15
● P2-2	A			30
● P2-3	A			30
P2-4	O			75
P2-5	O		M	75
P2-6	S		M	60
● P2-7	AA	8,9,12	FSF	45
P2-8	S		FSF	45
P2-9	AA	7,9,12	SF	45
P2-10	S		SF	15
● P2-11	AA		SF	1
P2-12	AA	7,8,9	SF	60
CDP2-A	O	9,B,C,D	FSF	5
CDP2-B	O	9,B,C,D	FSF	30
CDP2-C	O	9,B,C,D	FSF	30
CDP2-D	O	9,B,C,D	FSF	45

Assigned

● = Always assigned, AA = Always assign one from the group of alternates, O = Often, I = Infrequently, S = Seldom, G = Graduate level

Alternates

In problems that have a dot in conjunction with AA means that one of the problems, either the problem with a dot or any one of the alternates are always assigned.

Time

Approximate time in minutes it would take a B/B^+ student to solve the problem.

Difficulty

SF = Straight forward reinforcement of principles (plug and chug)

FSF = Fairly straight forward (requires some manipulation of equations or an intermediate calculation).
IC = Intermediate calculation required
M = More difficult
OE = Some parts open-ended.

*Note the letter problems are found on the CD-ROM. For example A ≡ CDP1-A.

Summary Table Ch-2

Straight forward	1,2,3,4,10
Fairly straight forward	7,9,12
More difficult	5,6,8
Open-ended	6
Comprehensive	4,5,6,7,8,9,12
Critical thinking	P2-9

P2-1 Individualized solution.

P2-2 Individualized solution.

P2-3 Solution is in the decoding algorithm given with the modules.

P2-4 (a) Example 2-1 through 2-3

If flow rate F_{AO} is cut in half.

$v_1 = v/2$, $F_1 = F_{AO}/2$ and C_{AO} will remain same.

Therefore, volume of CSTR in example 2-3,

$$V_1 = \frac{F_1 X}{-r_A} = \frac{1}{2}\frac{F_{A0} X}{-r_A} = \frac{1}{2}6.4 = 3.2$$

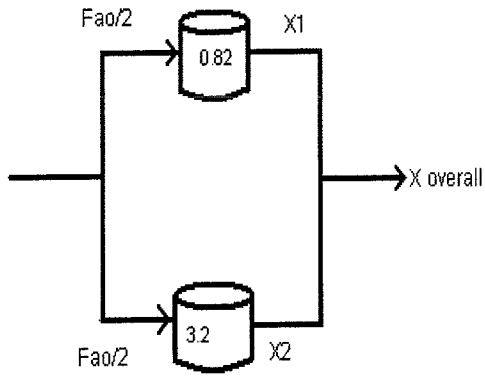
If the flow rate is doubled,

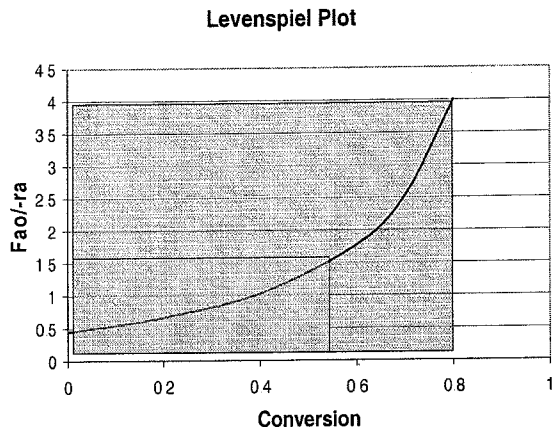
$F_2 = 2F_{AO}$ and C_{AO} will remain same,

Volume of CSTR in example 2-3,

$V_2 = F_2X/-r_A = 12.8\ m^3$

P2-4 (b) Example 2-5





Now, $F_{AO} = 0.4/2 = 0.2$ mol/s,

New Table: Divide each term $\frac{F_{A0}}{-r_A}$ in Table 2-3 by 2.

X	0	0.1	0.2	0.4	0.6	0.7	0.8
$[F_{AO}/-r_A](m^3)$	0.445	0.545	0.665	1.025	1.77	2.53	4

Reactor 1

$V_1 = 0.82 m^3$

$V = (F_{AO}/-r_A)X$

$$0.82 = \left(\frac{F_{A0}}{-r_A}\right)_{X1} (X1)$$

Reactor 2

$V_2 = 3.2\ m^3$

$$3.2 = \left(\frac{F_{A0}}{-r_A}\right)_{X2} (X2)$$

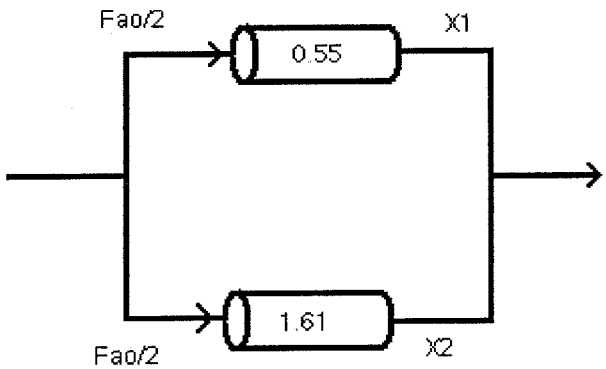
By trial and error we get:

$X_1 = 0.546$ and $X_2 = 0.8$

Overall conversion $X_{0overall} = (1/2)X_1 + (1/2)X_2 = (0.546+0.8)/2 = 0.673$

P2-4 (c) Example 2-6

Now, $F_{AO} = 0.4/2 = 0.2$ mol/s,



$$X_0 = \frac{F_{A01}X_1 + F_{A02}X_2}{F_{A01} + F_{A02}}$$

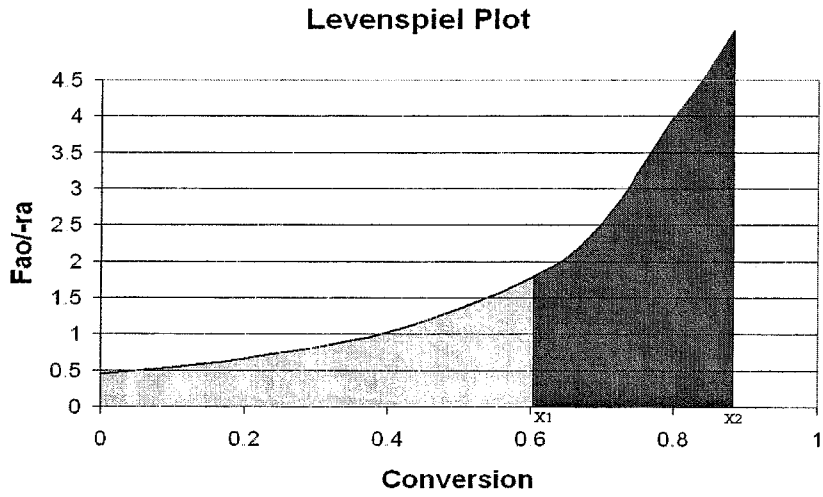
New Table: Divide each term $\frac{F_{A0}}{-r_A}$ in Table 2-3 by 2.

X	0	0.1	0.2	0.4	0.6	0.7	0.8
$[F_{AO}/-r_{Al}(m^3)$	0.445	0.545	0.665	1.025	1.77	2.53	4

$V_1 = 0.551 m^3$ $V_2 = 1.614\ m^3$

$$V_1 = F_{AO}\int_0^X \frac{dX}{-r_A}$$

Plot $F_{A0}/-r_A$ versus conversion. Estimate outlet conversions by computing the integral of the plotted function.



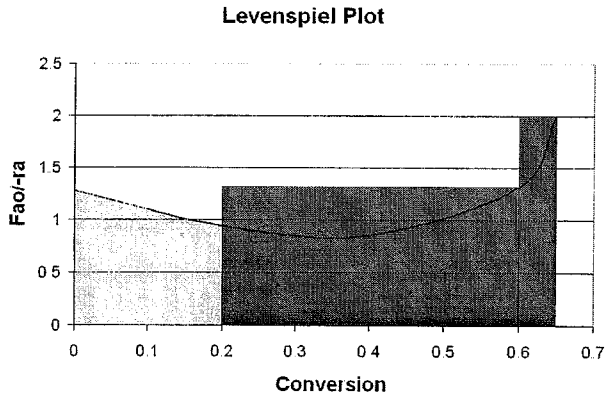
$X_1 = 0.603$ for $V_1 = 0.551 m^3$ $X_2 = 0.89$ for $V_2 = 1.614 m^3$
Overall conversion $X_0 = (1/2)X_1 + (1/2)X_2 = (0.603+0.89)/2 = 0.746$

P2-4 (d) Example 2-7

(1)
For PFR,

$$V_2 = \int_0^{0.2}\left(\frac{F_{AO}}{-r_A}\right)dX$$

$$= 0.222 m^3$$



For first CSTR,

$X_2 = 0.6$, $\frac{F_{AO}}{-rA} = 1.32m^3$, $V_1 = \frac{F_{AO}(X_2 - X_1)}{-rA} = .528m^3$

For second CSTR,

$X_3 = 0.65$, $\frac{F_{AO}}{-rA} = 2.0m^3$, $V_3 = \frac{F_{AO}(X_3 - X_2)}{-rA} = 0.1m^3$

(2)

First CSTR remains unchanged

For PFR:

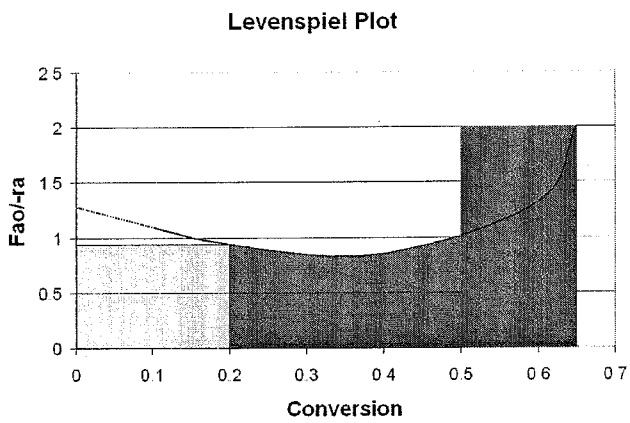
$$V = \int_{0.2}^{0.5} \left(\frac{F_{AO}}{-r_A} \right) dX$$

Using the Levenspiel Plot

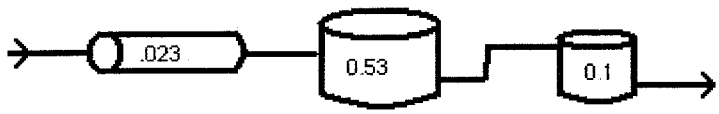
$V_{PFR} = 0.22$

For CSTR,

$$V_{CSTR2} = \frac{F_{AO}(X_3 - X_2)}{-rA} = 0.3m^3$$



(3) The worst arrangement is to put the PFR first, followed by the larger CSTR and finally the smaller CSTR.



Conversion	Original Reactor Volumes	Worst Arrangement
X1 = 0.20	V1 = 0.188 (CSTR)	V1 = 0.23 (PFR)
X2 = 0.60	V2 = 0.38 (PFR)	V2 = 0.53 (CSTR)
X3 = 0.65	V3 = 0.10 (CSTR)	V3 = 0.10 (CSTR)

For PFR,

$X_1 = 0.2$

$$V_1 = \int_{0}^{X_1} \left(\frac{F_{AO}}{-r_A} \right) dX$$

Using trapezoidal rule,

$X_O = 0.1$, $X_1 = 0.1$

$$V_1 = \frac{(X_1 - X_O)}{-rA}\left[f(X_O) + f(X_1)\right]$$

$$= \frac{0.2}{2}[1.28 + 0.98]m^3$$

$$= 0.23m^3$$

For CSTR,

For $X_2 = 0.6$, $\frac{F_{AO}}{-rA} = 1.32m^3$, $V_2 = \frac{F_{AO}}{-r_A}(X_2 - X_1) = 1.32(0.6 - 0.2) = 0.53\ m^3$

For 2nd CSTR,

For $X_3 = 0.65$, $\frac{F_{AO}}{-rA} = 2m^3$, $V_3 = 0.1\ m^3$

P2-4 (e) Example 2-8

$\tau = 5hrs$

$v_0 = 1dm^3/min = 60dm^3/hr$ $C_A = 2.5\ mol/dm^3$ $X = 0.8$

For CSTR, $\tau = \frac{V}{v_0}$

$V = 300dm^3$

(1)

$$-r_A = \frac{C_{A0}X}{\tau} = \frac{2.5 \times 0.8}{5} mol/dm^3 hr$$

$$= 0.4 mol/dm^3 hr$$

(2) $V = 300dm^3$

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

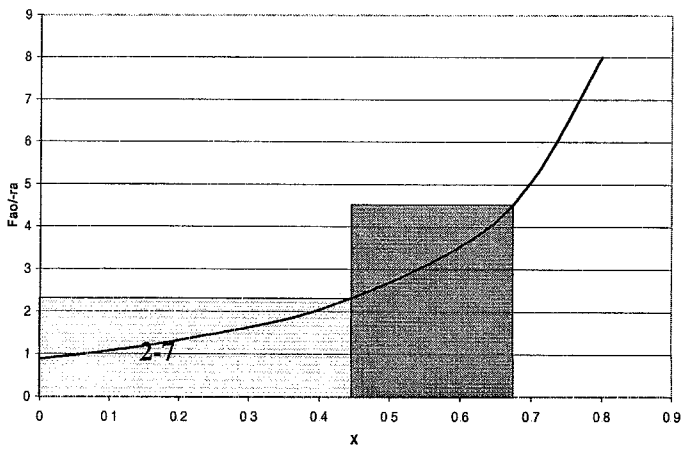
$= 0.5\ mol/dm^3$

P2-5

X	0	0.1	0.2	0.4	0.6	0.7	0.8
$F_{AO}/-r_A\ (m^3)$	0.89	1.08	1.33	2.05	3.54	5.06	8.0

$V = 1.0\ m^3$

Levenspiel plot



P2-5 (a) Two CSTRs in series

For first CSTR,

$V = (F_{Ao}/-r_{AX1})\ X_1$

$\Rightarrow X1 = 0.44$

For second CSTR,

$V = (F_{Ao}/-r_{AX2})\ (X_2 - X_1)$

$\Rightarrow X2 = 0.67$

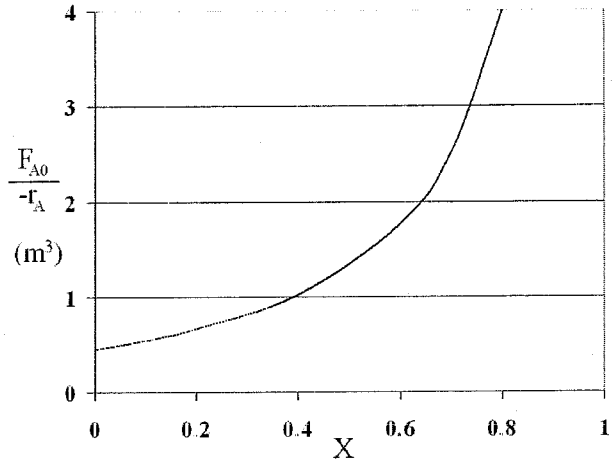
P2-5 (b)

Two PFRs in series

$$V = \int_0^{X_1}\left(\frac{F_{Ao}}{-r_A}\right)dX + \int_{X_1}^{X_2}\left(\frac{F_{Ao}}{-r_A}\right)dX$$

By extrapolating and solving, we get

$X_1 = 0.50$ $X_2 = 0.74$



P2-5 (c)

Two CSTRs in parallel with the feed, F_{AO}, divided equally between two reactors. $F_{ANEW}/-r_{AX1} = 0.5F_{AO}/-r_{AX1}$

$V = (0.5F_{AO}/-r_{AX1})\ X_1$

Solving we get, $X_{out} = 0.60$

P2-5 (d)

Two PFRs in parallel with the feed equally divided between the two reactors.

$F_{ANEW}/-r_{AX1} = 0.5F_{AO}/-r_{AX1}$

By extrapolating and solving as part (b), we get

$X_{out} = 0.74$

P2-5 (e)

A CSTR and a PFR are in parallel with flow equally divided

Since the flow is divided equally between the two reactors, the overall conversion is the average of the CSTR conversion (part C) and the PFR conversion (part D)

$X_o = (0.60 + 0.74) / 2 = 0.67$

P2-5 (f)

A PFR followed by a CSTR,

$X_{PFR} = 0.50$ (using part(b))

$V = (F_{Ao}/-r_{A\text{-}XCSTR})\ (X_{CSTR} - X_{PFR})$

Solving we get, $X_{CSTR} = 0.70$

P2-5 (g)

A CSTR followed by a PFR,

$X_{CSTR} = 0.44$ (using part(a))

$$V = \int_{X_{CSTR}}^{X_{PFR}} \frac{F_{AO}}{-r_A} dX$$

By extrapolating and solving, we get $X_{PFR} = 0.72$

P2-5 (h)

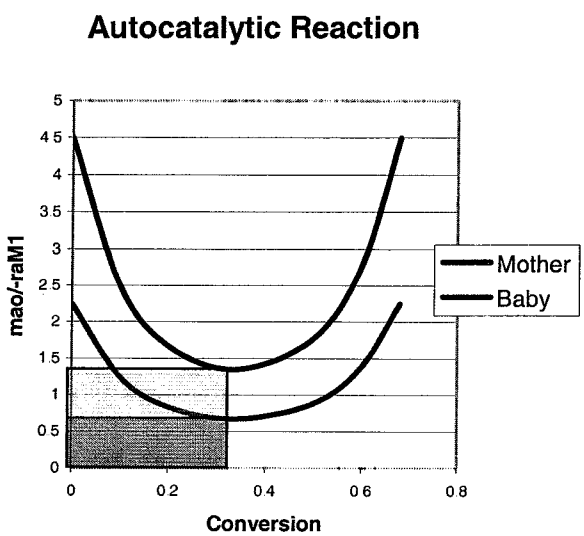
A 1 m^3 PFR followed by two 0.5 m^3 CSTRs,
For PFR,
$X_{PFR} = 0.50$ (using part(b))
$CSTR_1$: $V = (F_{Ao}/-r_{A\text{-}XCSTR})\ (X_{CSTR} - X_{PFR}) = 0.5\ m^3$
$X_{CSTR} = 0.63$
$CSTR_2$: $V = (F_{Ao}/-r_{A\text{-}XCSTR2})\ (X_{CSTR2} - X_{CSTR1}) = 0.5\ m^3$
$X_{CSTR2} = 0.72$

P2-6 (a) Individualized Solution

P2-6 (b)

1) In order to find the age of the baby hippo, we need to know the volume of the stomach.

The metabolic rate, $-r_A$, is the same for mother and baby, so if the baby hippo eats one half of what the mother eats then Fao (baby) = ½ Fao (mother).
The Levenspiel Plot is drawn for the baby hippo below.



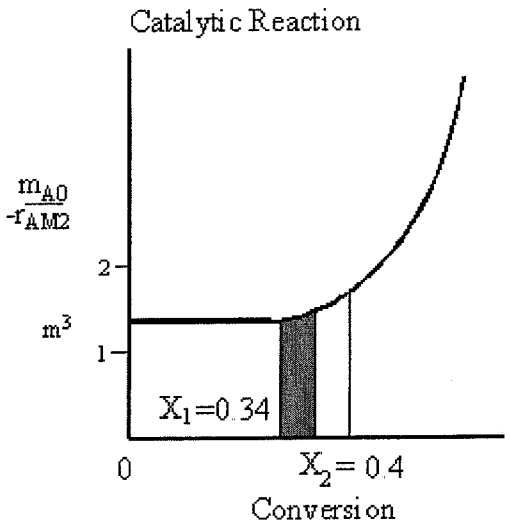
$$V_{baby} = \frac{FaoX}{-r_A} = \frac{1.36}{2} * 0.34 = 0.23m^3$$

Since the volume of the stomach is proportional to the age of the baby hippo, and the volume of the baby's stomach is half of an adult, then the baby hippo is half the age of a full grown hippo.

$$Age = \frac{4.5\ years}{2} = 2.25\ years$$

2) If Vmax and m_{ao} are both one half of the mother's then

$$\frac{m_{Ao}}{-r_{AM2}} = \frac{\left(\frac{1}{2} m_{A0_{mother}}\right)}{-r_{AM2}}$$



and since

$$-r_{AM2} = \frac{v_{\max} C_A}{K_M + C_A} \text{ then}$$

$$-r_{AM2_{baby}} = \frac{\frac{1}{2} v_{\max} C_A}{K_M + C_A} = -\frac{1}{2} r_{AM2_{mother}}$$

$$\left(\frac{m_{Ao}}{-r_{AM2}}\right)_{baby} = \left(\frac{\frac{1}{2} m_{Ao}}{-\frac{1}{2} r_{AM2}}\right)_{mother} = \left(\frac{m_{Ao}}{-r_{AM2}}\right)_{mother}$$

$\frac{m_{Ao}}{-r_{AM2}}$ will be identical for both the baby and mother.

Assuming that like the stomach the intestine volume is proportional to age then the volume of the intestine would be 0.75 m^3 and the final conversion would be 0.40

P2-6 (c)

$V_{stomach} = 0.2\ m^3$

From the web module we see that if a polynomial is fit to the autocatalytic reaction we get:

$$\frac{m_{A0}}{-r_{AM1}} = 127X^4 - 172.36X^3 + 100.18X^2 - 28.354X + 4.499$$

And since $V_{stomach} = \frac{m_{A0}}{-r_{AM1}} X$,

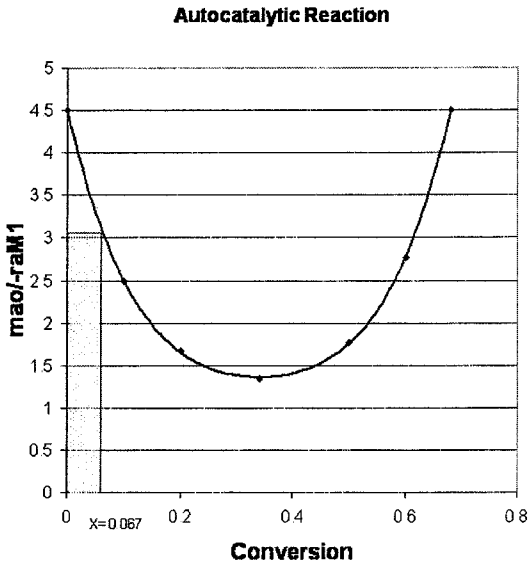
solve $V = 127X^5 - 172.36X^4 + 100.18X^3 - 28.354X^2 + 4.499X = 0.2\ m^3$

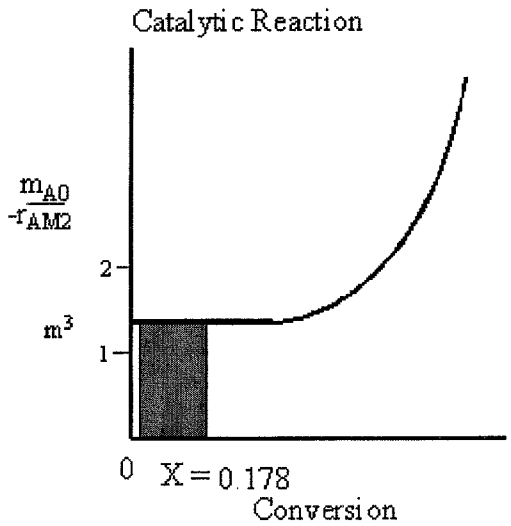
$X_{stomach} = .067$.

For the intestine:

The Levenspiel plot for the intestine is shown below. The outlet conversion is 0.178

Since the hippo needs 30% conversion to survive but only achieves 17.8%, the hippo cannot survive.



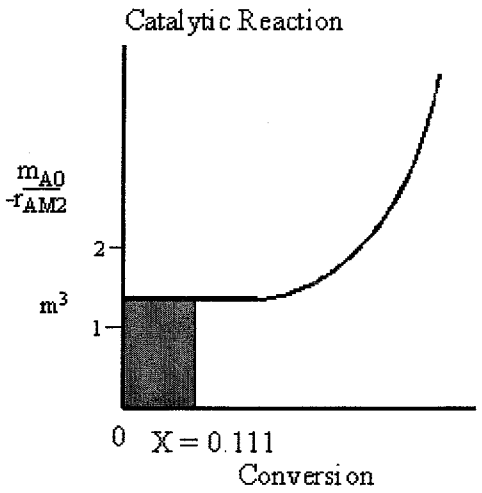


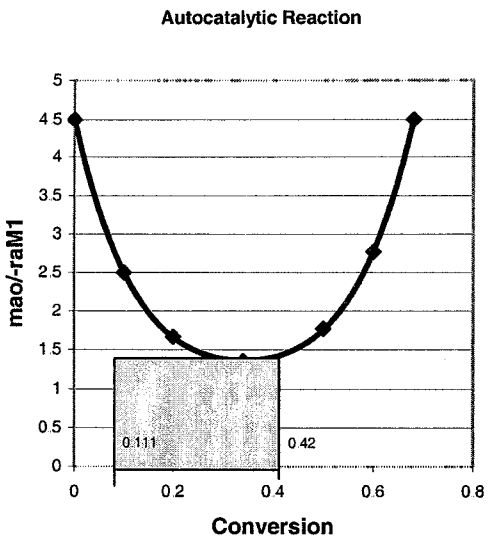
P2-6 (d)

PFR→ CSTR

PFR:

Outlet conversion of PFR = 0.111





CSTR:

We must solve

$V = 0.46 = (X-0.111)(127X^4 - 172.36X^3 + 100.18X^2 - 28.354X + 4.499)$

X=0.42

Since the hippo gets a conversion over 30% it will survive.

P2-7

Exothermic reaction: A → B + C

X	r(mol/dm^3.min)	1/-r(dm^3.min/mol)
0	1	1
0.20	1.67	0.6
0.40	5	0.2
0.45	5	0.2
0.50	5	0.2
0.60	5	0.2
0.80	1.25	0.8
0.90	0.91	1.1

P2-7 (a)

To solve this problem, first plot 1/-rA vs. X from the chart above. Second, use mole balance as given below.

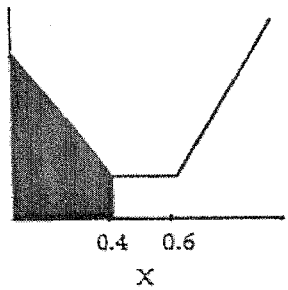
CSTR:

Mole balance: $V_{CSTR} = \frac{F_{A0}X}{-r_A} = \frac{(300mol/\min)(0.4)}{(5mol/dm^3.\min)}$ =>

=>$V_{CSTR} = 24\ dm^3$

PFR:

Mole balance: $V_{PFR} = F_{A0}\int_0^X \frac{dX}{-r_A}$



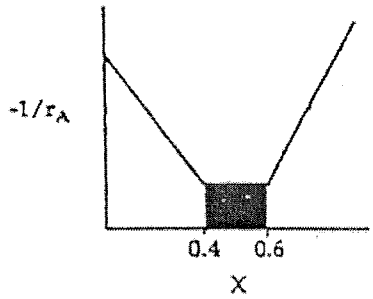
= 300(area under the curve)

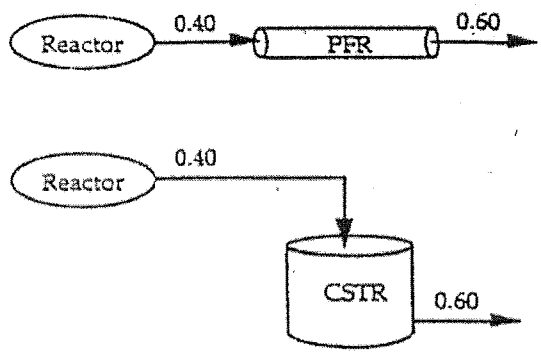
$V_{PFR} = 72\ dm^3$

P2-7 (b)

For a feed stream that enters the reaction with a previous conversion of 0.40 and leaves at any conversion up to 0.60, the volumes of the PFR and CSTR will be identical because of the rate is constant over this conversion range.

$$V_{PFR} = \int_{.4}^{.6} \frac{F_{A0}}{-r_A} dX = \frac{F_{A0}}{-r_A} \int_{.4}^{.6} dX = \frac{F_{A0}}{-r_A} X \Big|_{.4}^{.6}$$





P2-7 (c)

$V_{CSTR} = 105\ dm^3$

Mole balance: $V_{CSTR} = \frac{F_{A0} X}{-r_A}$

$$\frac{X}{-r_A} = \frac{105 dm^3}{300 mol/\min} = 0.35 dm^3 \min/mol$$

Use trial and error to find maximum conversion.

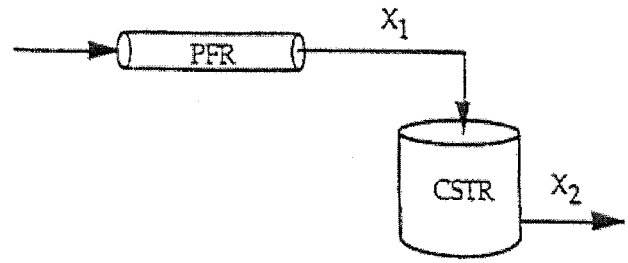
At X = 0.70, 1/-rA = 0.5, and X/-rA = 0.35 dm3.min/mol

Maximum conversion = 0.70

P2-7 (d)

From part (a) we know that $X_1 = 0.40$.

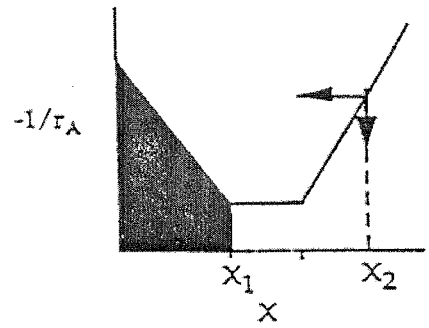
Use trial and error to find X_2.



Mole balance: $V = \dfrac{F_{A0}(X_2 - X_1)}{-r_A\big|_{X_2}}$

Rearranging, we get

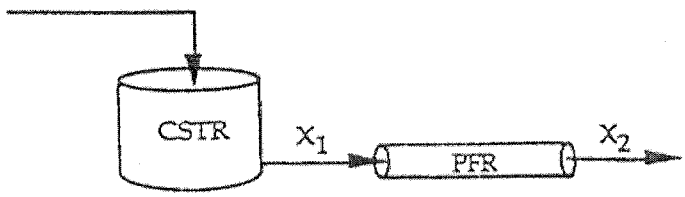
$$\frac{X_2 - 0.40}{-r_A\big|_{X_2}} = \frac{V}{F_{A0}} = 0.008$$



At $X_2 = 0.64$, $\dfrac{X_2 - 0.40}{-r_A\big|_{X_2}} = 0.008$

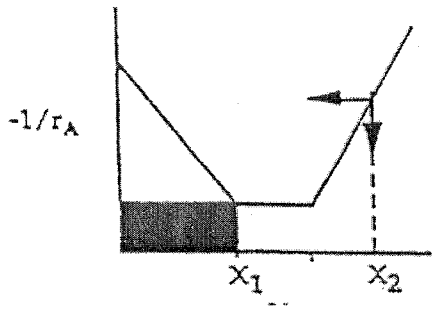
Conversion = 0.64

P2-7 (e)



From part (a), we know that $X_1 = 0.40$. Use trial and error to find X_2.

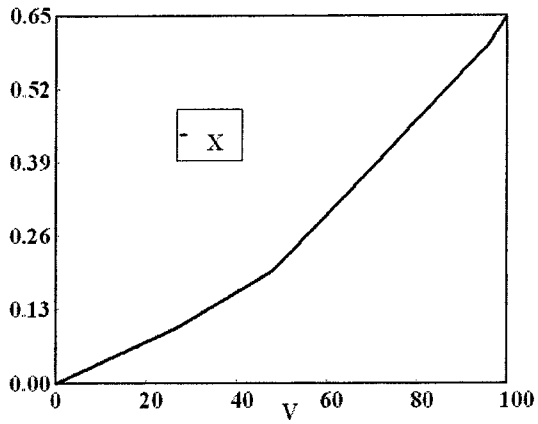
Mole balance: $V_{PFR} = 72 = F_{A0}\int_{0.40}^{X_2} \dfrac{dX}{-r_A} = 300\int_{0.40}^{X_2} \dfrac{dX}{-r_A}$

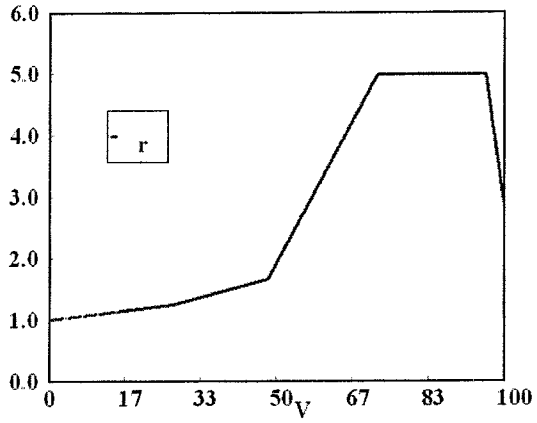


At $X_2 = 0.908$, V = 300 x (area under the curve)
=> V = 300(0.24) = 72dm^3
Conversion = 0.908.

P2-7 (f)

See Polymath program P2-7-f.pol.





P2-8 (a)

$$V = \frac{F_{S0}X}{-r_S}$$

F_{S0} = 1000 g/hr

At a conversion of 40% $\frac{1}{-r_S} = 0.15\frac{dm^3 hr}{g}$

Therefore $V = (0.15)(1000)(0.40) = 60\,dm^3$

P2-8 (b)

At a conversion of 80%, $\frac{1}{-r_S} = 0.8\frac{dm^3 hr}{g}$

F_{S0} = 1000 g/hr

Therefore $V = (0.8)(1000)(0.80) = 640\,dm^3$

P2-8 (c)

$$V_{PFR} = F_{S0}\int_0^X \frac{dX}{-r_S}$$

From the plot of $1/-r_S$ Calculate the area under the curve such that the area is equal to V/F_{S0} = 80 / 1000 = 0.08

X = 12%

For the 80 dm^3 CSTR, $V = 80\,dm^3 = \frac{F_{S0}X}{-r_S}$

$X/-r_s$ = 0.08. From guess and check we get X = 55%

P2-8 (d)

To achieve 80% conversion with a CSTR followed by a CSTR, the optimum arrangement is to have a CSTR with a volume to achieve a conversion of about 45%, or the conversion that corresponds to the minimum value of $1/-r_s$. Next is a PFR with the necessary volume to achieve the 80% conversion following the CSTR. This arrangement has the smallest reactor volume to achieve 80% conversion

For two CSTR's in series, the optimum arrangement would still include a CSTR with the volume to achieve a conversion of about 45%, or the conversion that corresponds to the minimum value of $1/-r_s$, first. A second CSTR with a volume sufficient to reach 80% would follow the first CSTR.

P2-8 (e)

$$-r_s = \frac{kC_S C_C}{K_M + C_S} \text{ and } C_C = 0.1[C_{S0} - C_S] + 0.001$$

$$-r_s = \frac{kC_S\left(0.1[C_{S0} - C_S] + 0.001\right)}{K_M + C_S}$$

$$-\frac{1}{r_s} = \frac{K_M + C_S}{kC_S\left(0.1[C_{S0} - C_S] + 0.001\right)}$$

Let us first consider when C_S is small.

C_{S0} is a constant and if we group together the constants and simplify

$$\text{then } -\frac{1}{r_s} = \frac{K_M + C_S}{k_1 C_S^2 + k_2 Cs}$$

since $C_S < K_M$

$$-\frac{1}{r_s} = \frac{K_M}{k_1 C_S^2 + k_2 Cs}$$ which is consistent with the shape of the graph when X is large (if C_S is small X is large and as C_S grows X decreases).

Now consider when C_S is large (X is small)

As C_S gets larger C_C approaches 0:

$$C_C = 0.1[C_{S0} - C_S] + 0.001 \text{ and } C_S \approx C_{S0}$$

$$\text{If } -r_s = \frac{kC_S C_C}{K_M + C_S} \text{ then } -\frac{1}{r_s} = \frac{K_M + C_S}{kC_S C_C}$$

As C_S grows larger, $C_S >> K_M$

And $-\frac{1}{r_s} = \frac{C_S}{kC_SC_C} = \frac{1}{kC_C}$

And since C_C is becoming very small and approaching 0 at X = 0, $1/-r_s$ should be increasing with C_S (or decreasing X). This is what is observed at small values of X. At intermediate levels of C_S and X, these driving forces are competing and why the curve of $1/-r_S$ has a minimum.

P2-9

Irreversible gas phase reaction

$$2A + B \rightarrow 2C$$

See Polymath program P2-9.pol.

P2-9 (a)

PFR volume necessary to achieve 50% conversion

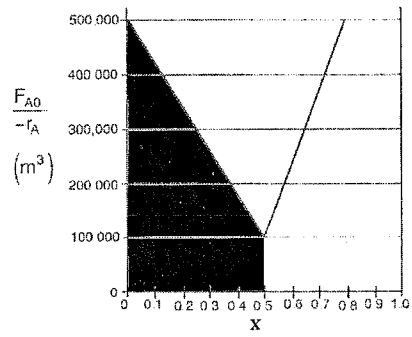
Mole Balance

$$V = F_{A0}\int_{X_1}^{X_2}\frac{dX}{(-r_A)}$$

Volume = Geometric area under the curve of ($F_{A0}/-r_A$) vs X)

$$V = \left(\frac{1}{2}\times 400000\times 0.5\right) + (100000\times 0.5)$$

V = 150000 m^3



P2-9 (b)

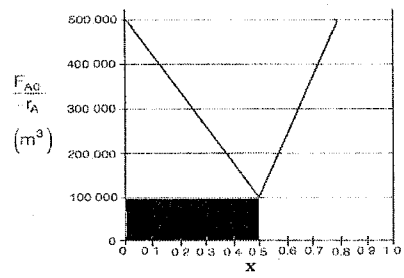
CSTR Volume to achieve 50% conversion

Mole Balance

$$V = \frac{F_{A0}X}{(-r_A)}$$

$$V = 0.5\times 100000$$

V = 50000m^3



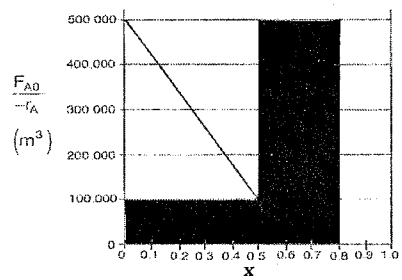
P2-9 (c)

Volume of second CSTR added in series to achieve 80% conversion

$$V_2 = \frac{F_{A0}(X_2 - X_1)}{(-r_A)}$$

$$V_2 = 500000\times(0.8 - 0.5)$$

V_2 = 150000m^3

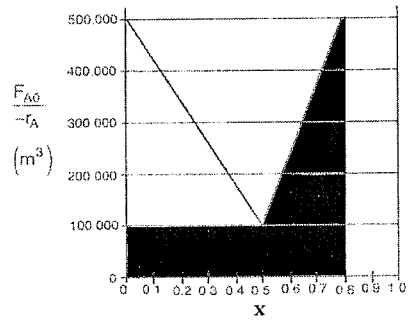


P2-9 (d)

Volume of PFR added in series to first CSTR to achieve 80% conversion

$$V_{PFR} = (\frac{1}{2} \times 400000 \times 0.3) + (100000 \times 0.3)$$

$V_{PFR} = 90000 m^3$



P2-9 (e)

For CSTR,

$V_1 = 60000 m^3$ (CSTR)

Mole Balance

$$V = \frac{F_{A0}X}{(-r_A)}$$

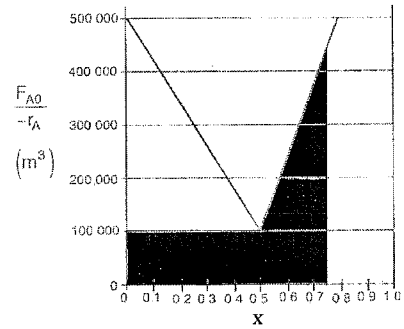
X = 0.515

For PFR,

$V_2 = 60000 m^3$

Mole balance

$$V = F_{A0} \int_{X_1}^{X_2} \frac{dX}{(-r_A)}$$



Eqn. Of 2nd line (sloping upwards)

$$y - 100000 = 1.3 \times 10^6 (x - 0.5)$$

$$60000 = \int_{X_1}^{X_2} (1.3 \times 10^6 (x - 0.51) + 100000) dX$$

=> $X_2 = 0.746$

P2-9 (f)

Real rates would not give that shape. The reactor volumes are absurdly large.

P2-10

Problem 2-10 involves estimating the volume of three reactors from a picture. The door on the side of the building was used as a reference. It was assumed to be 8 ft high.

The following estimates were made:

CSTR

h = 56ft d = 9 ft

$V = \pi r^2 h = \pi(4.5 ft)^2(56 ft) = 3562 ft^3 = 100{,}865 L$

PFR

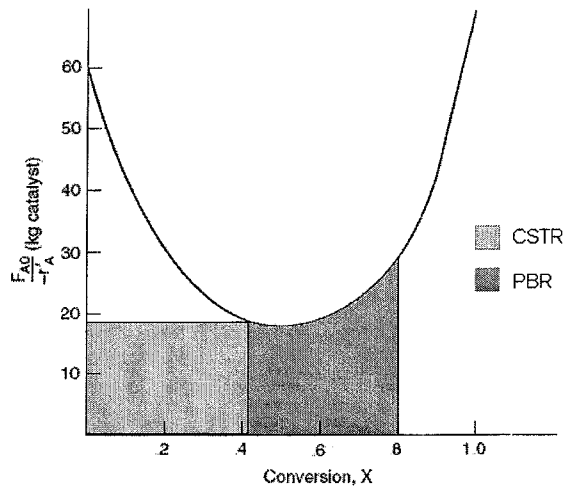
Length of one segment = 23 ft
Length of entire reactor = (23 ft)(12)(11) = 3036 ft
D = 1 ft
$V = \pi r^2 h = \pi(0.5\text{ ft})^2(3036\text{ ft}) = 2384\text{ ft}^3 = 67{,}507\text{ L}$

Answers will vary slightly for each individual.

P2-11 No solution necessary.

P2-12 (a)

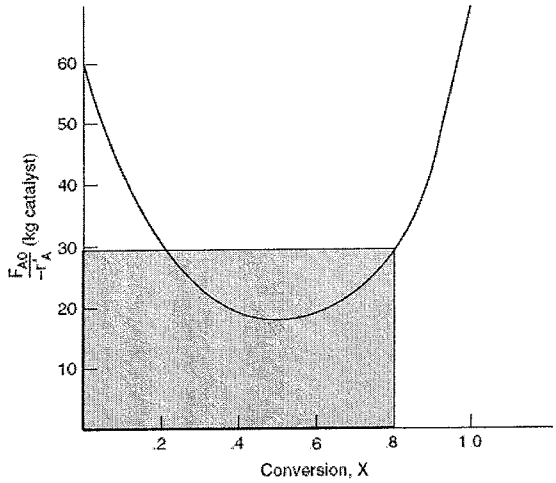
The smallest amount of catalyst necessary to achieve 80 % conversion in a CSTR and PBR connected in series and containing equal amounts of catalyst can be calculated from the figure below.



The lightly shaded area on the left denotes the CSTR while the darker shaded area denotes the PBR. This figure shows that the smallest amount of catalyst is used when the CSTR is upstream of the PBR.
See Polymath program P2-12.pol.

P2-12 (b)

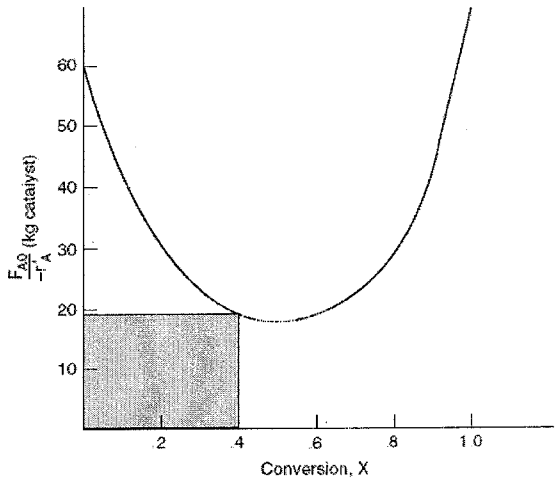
Calculate the necessary amount of catalyst to reach 80 % conversion using a single CSTR by determining the area of the shaded region in the figure below.



The area of the rectangle is approximately 23.2 kg of catalyst.

P2-12 (c)

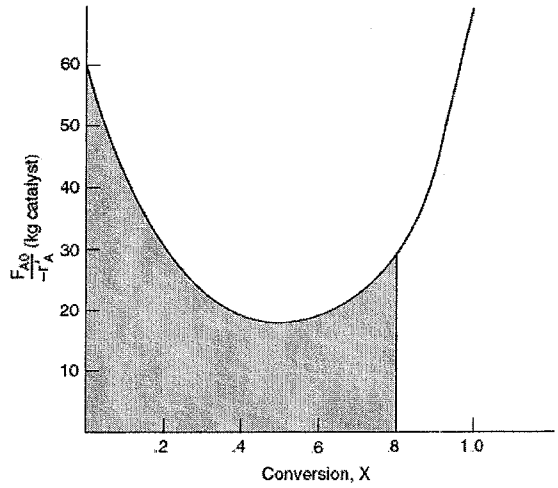
The CSTR catalyst weight necessary to achieve 40 % conversion can be obtained by calculating the area of the shaded rectangle shown in the figure below.



The area of the rectangle is approximately 7.6 kg of catalyst.

P2-12 (d)

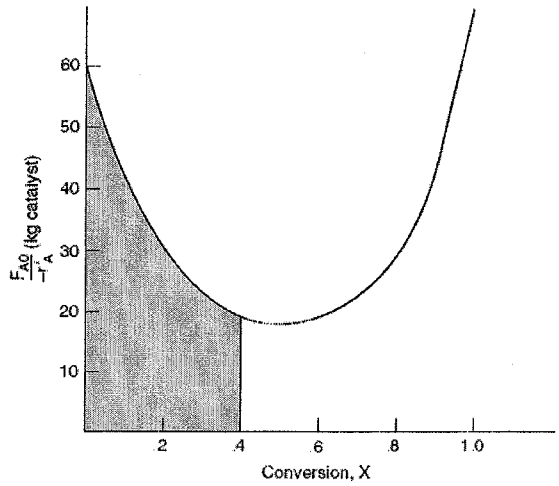
The catalyst weight necessary to achieve 80 % conversion in a PBR is found by calculating the area of the shaded region in the figure below.



The necessary catalyst weight is approximately 22 kg.

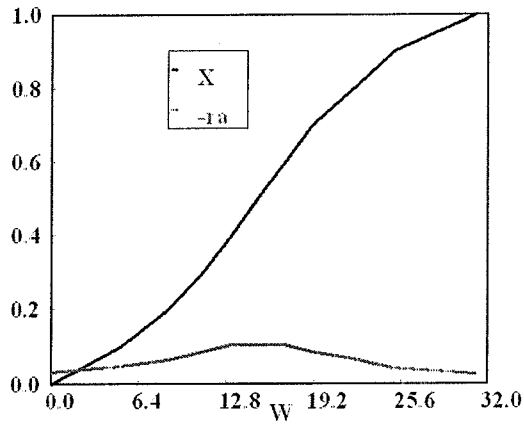
P2-12 (e)

The amount of catalyst necessary to achieve 40 % conversion in a single PBR can be found from calculating the area of the shaded region in the graph below.



The necessary catalyst weight is approximately 13 kg.

P2-12 (f)



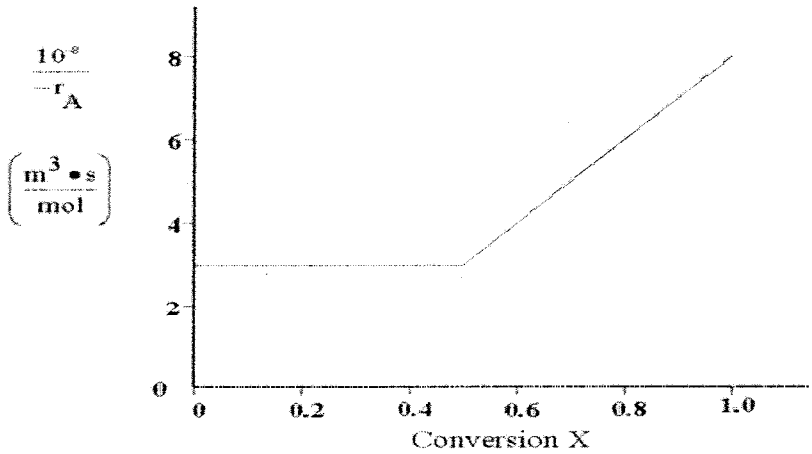
P2-12 (g)

For different ($-r_A$) vs. (X) curves, reactors should be arranged so that the smallest amount of catalyst is needed to give the maximum conversion. One useful heuristic is that for curves with a negative slope, it is generally better to use a CSTR. Similarly, when a curve has a positive slope, it is generally better to use a PBR.

CDP2-A (a)

Over what range of conversions are the plug-flow reactor and CSTR volumes identical?

We first plot the inverse of the reaction rate versus conversion.



Mole balance equations for a CSTR and a PFR:

$$\text{CSTR: } V = \frac{F_{A0}X}{-r_A} \qquad \text{PFR: } V = \int_0^X \frac{dX}{-r_A}$$

Until the conversion (X) reaches 0.5, the reaction rate is independent of conversion and the reactor volumes will be identical.

$$\text{i.e. } V_{PFR} = \int_0^{0.5} \frac{dX}{-r_A} = \frac{F_{A0}}{-r_A}\int_0^{0.5} dX = \frac{F_{A0}X}{-r_A} = V_{CSTR}$$

CDP2-A (b)

What conversion will be achieved in a CSTR that has a volume of 90 L?

For now, we will assume that conversion (X) will be less that 0.5.

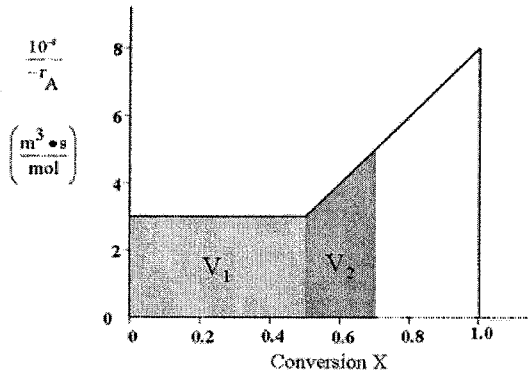
CSTR mole balance:

$$V = \frac{F_{A0}X}{-r_A} = \frac{v_0 C_{A0} X}{-r_A}$$

$$X = \frac{V}{\frac{v_0 C_{A0}}{-r_A}} = \frac{0.09m^3}{5\frac{m^3}{s}\times 200\frac{mol}{m^3}\times 3\times 10^8 \frac{m^3.s}{mol}} = 3\times 10^{-13}$$

CDP2-A (c)

This problem will be divided into two parts, as seen below:



- The PFR volume required in reaching X=0.5 (reaction rate is independent of conversion).

$$V_1 = \frac{F_{A0}X}{-r_A} = \frac{v_0 C_{A0} X}{-r_A} = 1.5\times 10^{11} m^3$$

- The PFR volume required to go from X=0.5 to X=0.7 (reaction rate depends on conversion).

$$V_2 = F_{A0}\int_{0.5}^{0.7}\frac{dX}{-r_A} = v_0 C_{A0} * \left(10^8 \frac{m^3 \bullet s}{mol}\right)\int_{0.5}^{0.7}(10X-2)dX$$

$$-5\frac{m^3}{s} * 200\frac{mol}{m^3} * \left(10^8 \frac{m^3 \bullet s}{mol}\right) * (5X^2 - 2X)\Big|_{0.5}^{0.7}$$

$$= 10^{11} m^3 \left([5(0.7)^2 - 2(0.7)] - [5(0.5)^2 - 2(0.5)]\right)$$

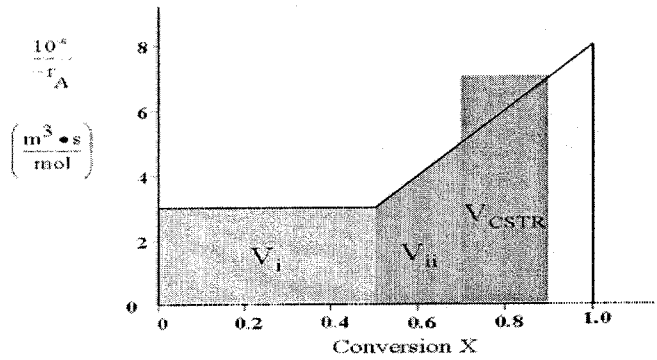
$$= 8 * 10^{10} m^3$$

Finally, we add V_2 to V_1 and get:

$$V_{tot} = V_1 + V_2 = 2.3 \times 10^{11}\ m^3$$

CDP2-A (d)

What CSTR reactor volume is required if effluent from the plug-flow reactor in part (c) is fed to a CSTR to raise the conversion to 90 %



We notice that the new inverse of the reaction rate (1/-rA) is 7*108. We insert this new value into our CSTR mole balance equation:

$$V_{CSTR} = \frac{F_{A0}\Delta X}{-r_A} = \frac{v_0 C_{A0}\Delta X}{-r_A} = 1.4 \times 10^{11} m^3$$

CDP2-A (e)

If the reaction is carried out in a constant-pressure batch reactor in which pure A is fed to the reactor, what length of time is necessary to achieve 40% conversion?

Since there is no flow into or out of the system, mole balance can be written as:

Mole Balance: $r_A V = \frac{dN_A}{dt}$

Stoichiometry: $N_A = N_{A0}(1 - X)$

Combine: $r_A V = N_{A0} \frac{dX}{dt}$

From the stoichiometry of the reaction we know that V = Vo(1+eX) and e is 1. We insert this into our mole balance equation and solve for time (t):

$$-r_A \frac{V_0}{N_{A0}}(1+X) = \frac{dX}{dt}$$

$$\int_0^t dt = C_{A0} \int_0^X \frac{dX}{-r_A(1+X)}$$

After integration, we have:

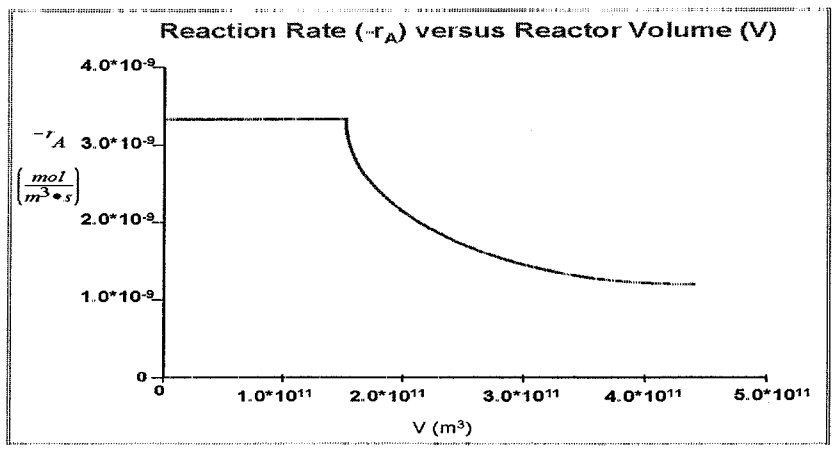
$$t = \frac{1}{-r_A} C_{A0} \ln(1+X)$$

Inserting the values for our variables:
t = 2.02 x 10^{10} s
That is 640 years.

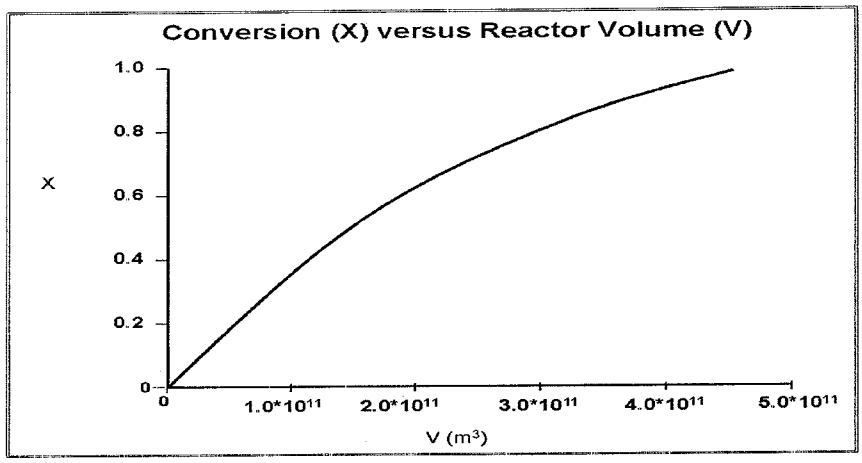
CDP2-A (f)

Plot the rate of reaction and conversion as a function of PFR volume.

The following graph plots the reaction rate ($-r_A$) versus the PFR volume:



Below is a plot of conversion versus the PFR volume. Notice how the relation is linear until the conversion exceeds 50%.



The volume required for 99% conversion exceeds 4*1011 m^3.

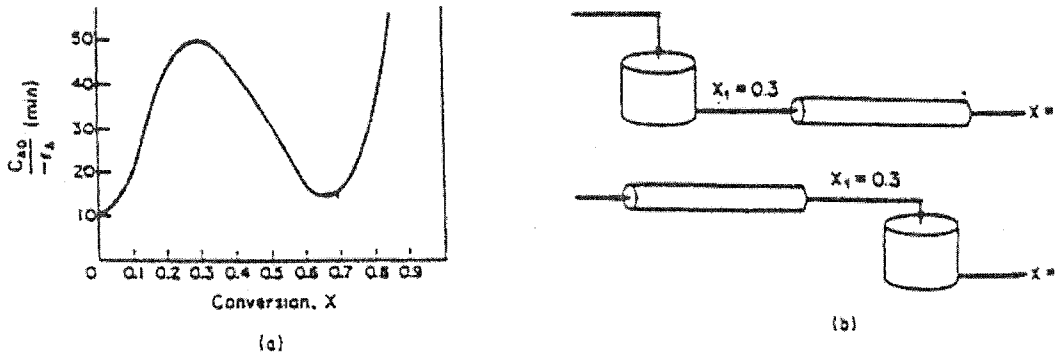
CDP2-A (g)

Critique the answers to this problem.

The rate of reaction for this problem is extremely small, and the flow rate is quite large. To obtain the desired conversion, it would require a reactor of geological proportions (a CSTR or PFR approximately the size of the Los Angeles Basin), or as we saw in the case of the batch reactor, a very long time.

CDP2-B Individualized solution

CDP2-C (a)



For an intermediate conversion of 0.3, Figure below shows that a PFR yields the smallest volume, since for the PFR we use the area under the curve. A minimum volume is also achieved by following the PFR with a CSTR. In this case the area considered would be the rectangle bounded by X =0.3 and X = 0.7 with a height equal to the $C_{A0}/-r_A$ value at X = 0.7, which is less than the area under the curve.

CDP2-C (b)

v_o = 50 l/min

$V = v_o I$, where

I = area considered in part a.

$$I = \int_0^{0.3} \frac{C_{AO}}{-r_A} dX + (0.7-0.3) \left.\frac{C_{AO}}{-r_A}\right|_{X=0.7}$$

$$= (0.3 - 0)(10) + \frac{1}{2}(0.3-0)(50-10) + (0.7-0.3)(15)$$

$$= 15 \text{ min}$$

So $V = v_o I = (50 \text{ l/min})(15 \text{ min}) = 750 \text{ l} = 750 \text{ dm}^3$.

CDP2-C (c)

The smallest area can be achieved by using only one CSTR with this system.

$$I = (0.7-0.0) \left.\frac{C_{AO}}{-r_A}\right|_{X=0.7} = (0.7-0)(15) = 10.5 \text{ min}$$

So $V = v_o I = (50)$ l/min (10.5) min = 525 l

We would further reduce the total volume by using a PFR at first up to the conversion that gives the same $C_{AO}/-r_A$ as X=0.7.

CDP2-C (d)

To obtain equal CSTR and PFR volumes the area under the curve must be equal to the area of the rectangle up to the specified conversion.

By trial and error we see that X=0.45 is a solution. For the CSTR,

$$I = (0.45-0)\left.\frac{C_{AO}}{-r_A}\right|_{X=0.7} = (0.45-0)(37) = 16.65 \text{ min}$$

So $V = v_o I = (50 \text{ l/min})(16.65 \text{ min}) = 832.5 \text{ l}$

For the PFR,

$$I = \int_0^{0.45} \frac{C_{AO}}{-r_A} dX$$

Using Simpson's rule

$$I = \frac{0.05}{3}(10 + 4(15) + 2(20) + 4(35) + 2(43) + 4(48) + 2(50) + 4(48) + 2(43) + 37)$$

$$= \frac{0.05}{3}(10 + 4(15 + 35 + 48 + 48) + 2(20 + 43 + 50 + 43) + 37) = 15.72$$

So $V = v_o I = (50 \text{ l/min})(15.72 \text{ min}) = 786 \text{ l}$ 6% difference, pretty cl

There is also a solution at an X>0.7

Try X = 0.8

For the CSTR

$$I = (0.8-0)(33) = 26.4 \text{ min}$$

For the PFR

$$I = \int_0^{0.8} \frac{C_{AO}}{-r_A} dX$$

$$= \frac{0.1}{3}(10 + 4(20) + 2(43) + 4(50) + 2(43) + 4(32) + 2(17) + 4(15) + 33)$$

$$= \frac{0.1}{3}(10 + 4(20 + 50 + 32 + 15) + 2(43 + 43 + 17) + 33) = 23.9 \text{ min}$$

Try X=0.79

For the CSTR

$$I = (0.79)(30) = 23.7 \text{ min}$$

So $V = v_o I = (50 \text{ l/min})(23.7 \text{ min}) = 1185 \text{ l } (dm^3)$

For the PFR

$$I = 23.9 - \frac{1}{2}(0.8-0.79)(30+33) = 23.9 - 0.315 = 23.58 \text{ min}$$

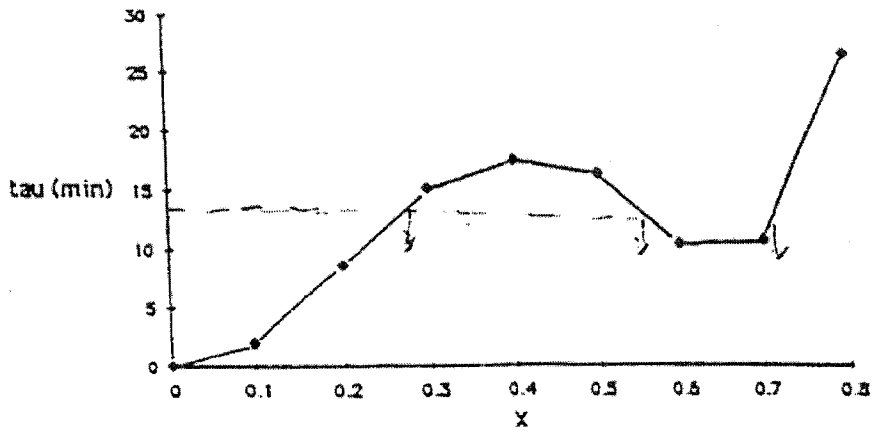
So $V = v_o I = (50 \text{ l/min})(23.58 \text{ min}) = 1179 \text{ l}$

0.5% difference

CDP2-C (e)

$$\tau = \frac{V}{v_o} = \frac{v_o X\left[\frac{C_{Ao}}{(-r_A)_X}\right]}{v_o} = X\frac{C_{Ao}}{(-r_A)_X}$$

X	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
$C_{A0}/-r_A$(min)	10	20	43	50	43	32	17	15	33
τ(min)	0.0	2.0	8.6	15.0	17.2	16.0	10.2	10.5	26.4



For our particular case

$$\tau = \frac{V}{v_o} = \frac{700 \text{ l}}{50 \text{ l/min}} = 14 \text{ min}$$

The graph yields three possible steady states

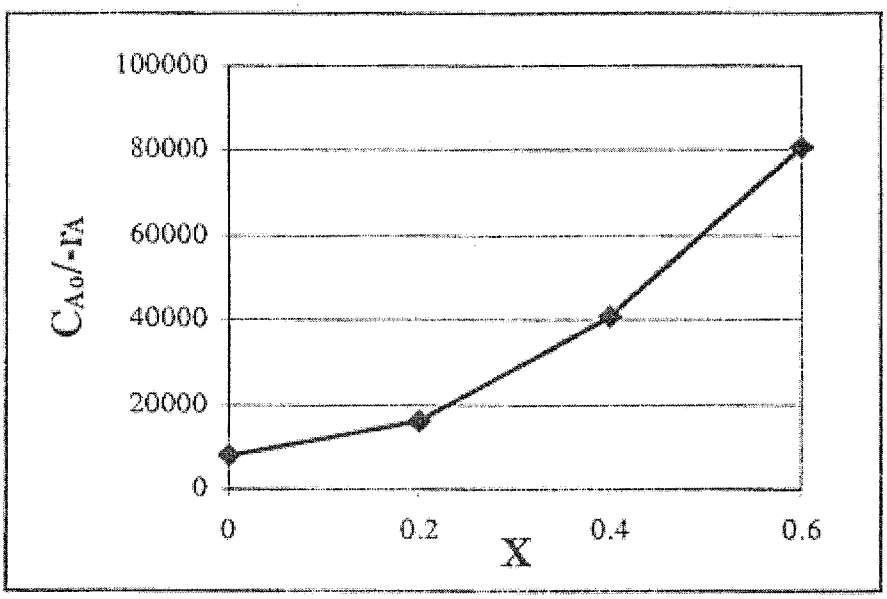
$X_1 = 0.285$, $X_2 = 0.535$, and X_3 0.730.

CDP2-D

Data taken at 1013 kPa (10 atm) and 227°C (500.2 K)

$$y_{Ao} = 0.333 \qquad C_{Ao} = \frac{y_{Ao}P}{RT} = \frac{(0.333)(10)}{(0.082)(500.2)} = 0.08113 \text{ gmol/dm}^3$$

$-r_A$	0.000010	0.000005	0.000002	0.000001
X	0	0.2	0.4	0.6
$C_{Ao}/-r_A$	8112.77	16225.54	40563.84	81127.68



CDP2-D (a)

30% conversion in PFR:

$$\tau_{PFR} = C_{Ao}\int_0^{0.3}\frac{dX}{-r_A} = 4{,}664.84 \text{ s} \quad \Rightarrow \quad V = v_o\tau = (4664.84 \text{ s})\left(\frac{1 \text{ min}}{60 \text{ s}}\right)(2 \text{ m}^3/\text{min}) = 155.5 \text{ m}^3$$

CDP2-D (b)

30 to 50% conversion in CSTR:

$$\tau_{CSTR} = \frac{C_{Ao}(X_2 - X_1)}{-r_{A2}} = 12{,}169.2 \text{ s} \quad \Rightarrow \quad V_{CSTR} = (12{,}169.2 \text{ s})\left(\frac{1 \text{ min}}{60 \text{ s}}\right)(2 \text{ m}^3/\text{min}) = 405.64 \text{ m}^3$$

CDP2-D (c)

Total Volume:

$$V_{Total} = 155.5 + 405.6 = 561.1\ m^3$$

CDP2-D (d)

60% conversion in PFR:

$$\tau_{PFR} = C_{Ao}\int_0^{0.6}\frac{dX}{-r_A} = 20{,}281.9\ s \quad \Rightarrow \quad V_{PFR} = (20{,}281.9\ s)\left(\frac{1\ min}{60\ s}\right)(2\ m^3/min) = 676.06\ m^3$$

80% conversion in PFR:

r_A is not known for X>0.60 – can not do.

CDP2-D (e)

50 % in CSTR:

$$\tau = C_{Ao}\frac{X}{-r_A} = 30{,}422.9\ s$$

$$V = v_o\tau = (30{,}422.9\ s)\left(\frac{1\ min}{60\ s}\right)(2\ m^3/min) = 1014.1\ m^3$$

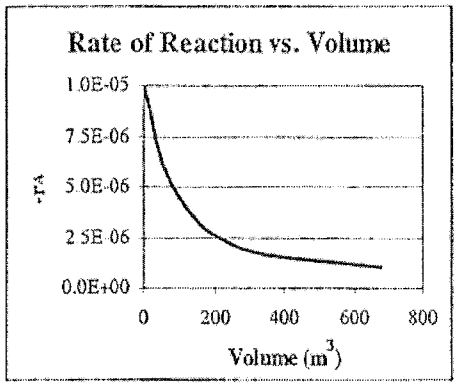
CDP2-D (f)

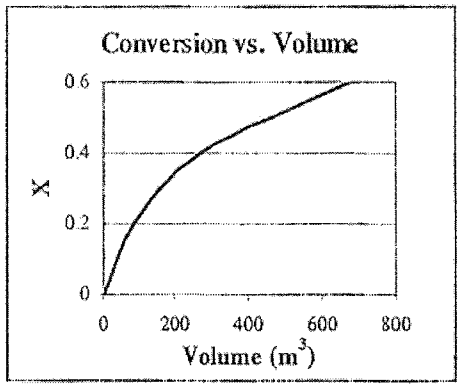
50 to 60% conversion in CSTR:

$$\tau = \frac{C_{Ao}(X_2 - X_1)}{-r_{A2}} = 8112.8$$

$$V = v_o\tau = (8112.8\ s)\left(\frac{1\ min}{60\ s}\right)(2\ m^3/min) = 270.4\ m^3$$

CDP2-D (g)





CDP2-D (h)

Critique
Answers are Valid:

1. Constant Temperature and Pressure
   No heat effects
   No pressure drop
2. Single interpolation to $X_A = 0.15$, 0.30, 0.45, and 0.50 allowable
3. Huge volume (the size of the LA Basin)! Raise T? Raise P?

CDP2-E

For the CSTR:

$$V_1 = \frac{F_{A0}X_1}{-r_A} = F_{A0}(\text{Area})$$

$$\text{Area} = V_1 = 1200\ \text{dm}^3$$

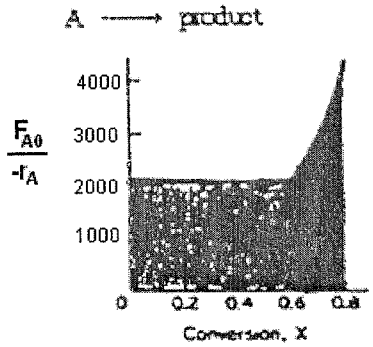
From the graph we can see that $X_1 = 0.60$

For the PFR:

$$V_2 = \frac{F_{A0}(X_2 - X_1)}{-r_A} = F_{A0}(\text{Area under curve})$$

$$\text{Area under curve} = V_2 = 600\ \text{dm}^3$$

From the graph we can see that $X_2 = 0.80$



CDP2-F (a)

Find the conversion for the CSTR and PFR connected in series.

X	$-r_A$	$1/(-r_A)$
0	0.2	5
0.1	0.0167	59.9
0.4	0.00488	204.9
0.7	0.00286	349.65
0.9	0.00204	490.19

400 L CSTR and 100 L PFR Feed is 41% A, 41% B, and 18% I.

$P = 10$ atm $T = 227°C = 500$ K

$$C_{To} = \frac{P}{RT} = \frac{10 \text{ atm}}{(0.082 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(500 \text{ K})} = 0.244 \text{ mol/L}$$

$$C_{Ao} = 0.41 C_{To} = 0.41(0.244 \text{ mol/L}) = 0.1 \text{ mol/L}$$

$$F_{Ao} = \upsilon_o C_{Ao} = 1 \text{ L/s}(0.1 \text{ mol/L}) = 0.1 \text{ mol/s} = 6 \text{ mol/min}$$

There are two possible arrangements of the system:

1. CSTR followed by the PFR
2. PFR followed by the CSTR

Case 1: CSTR → PFR

CSTR: $V_1 = F_{Ao}(\text{Area})$

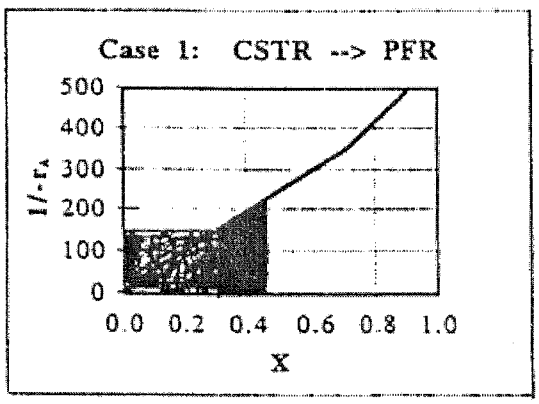
$$\text{Area} = \frac{V_1}{F_{Ao}} = \frac{400}{6} = 66.67$$

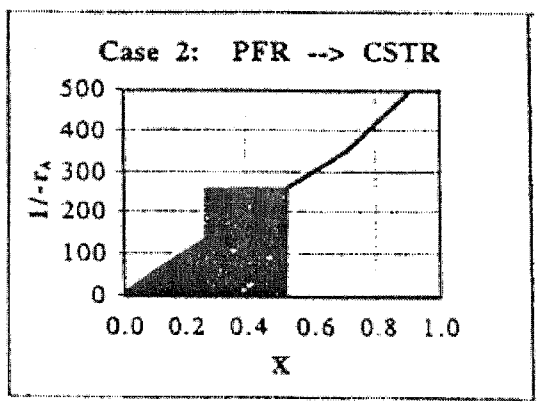
From the graph - $X_1 = 0.36$

PFR: $V_2 = F_{Ao}(\text{Area under curve})$

$$\text{Area under curve} = \frac{V_2}{F_{Ao}} = \frac{100}{6} = 16.667$$

From the graph - $X_2 = 0.445$





Case 2: PFR → CSTR

PFR: Area under curve = 16.67

From the graph - $X_1 = 0.259$

CSTR: Area = 66.67

From the graph - $X_2 = 0.515$

CDP2-F (b)

Two 400 L CSTR's in series.

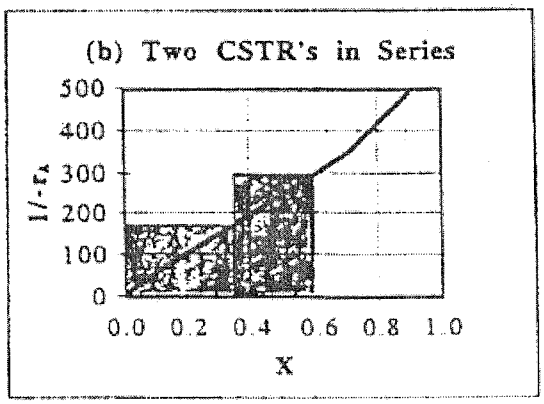
CSTR1: $V = F_{Ao}(\text{Area})$

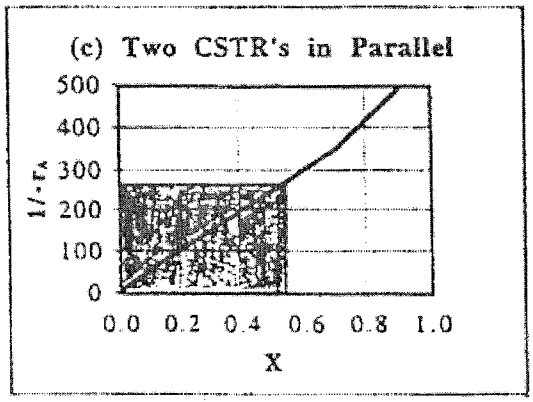
Area = 66.67

From the graph - $X_1 = 0.36$

CSTR2: Area = 66.67

From the graph - $X_2 = 0.595$





CDP2-F (c)

Two 400 L CSTR's in parallel.

To each CSTR goes half of the feed.

$F_{Ao} = 6/2 = 3$ mol/min

$V = F_{Ao}(\text{Area})$

$$\text{Area} = \frac{V}{F_{Ao}} = \frac{400}{3} = 133.3$$

From the graph: $X = 0.52$

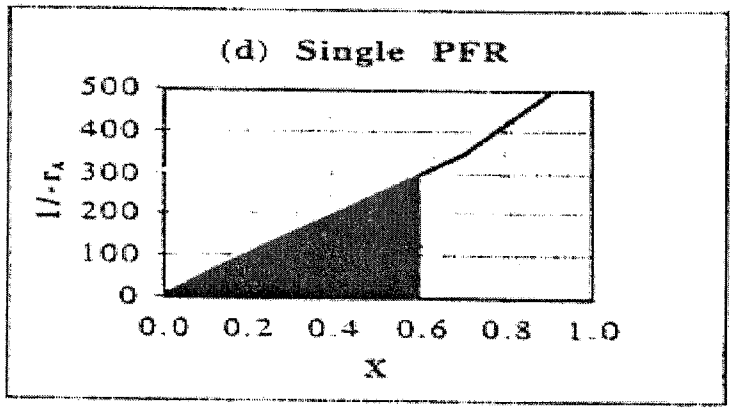
CDP2-F (d)

PFR: $V = F_{Ao}$(Area under curve)

From the graph we can find the area under the curve for a conversion of 0.60:

$$\text{Area} = \frac{(0.60)(300)}{2} = 90$$

$$V = (2 \text{ mol/min})(90) = 180 \text{ L}$$



CDP2-F (e)

Pressure reduced by a factor of 10.

A decrease in pressure would cause a decrease in the overall concentration which would in turn cause a decrease in C_{Ao} and F_{Ao}. By looking at the design equation:

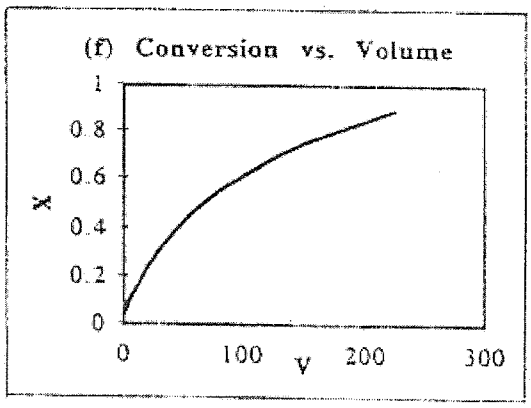
$$V = \frac{F_{Ao}X}{-r_A}$$

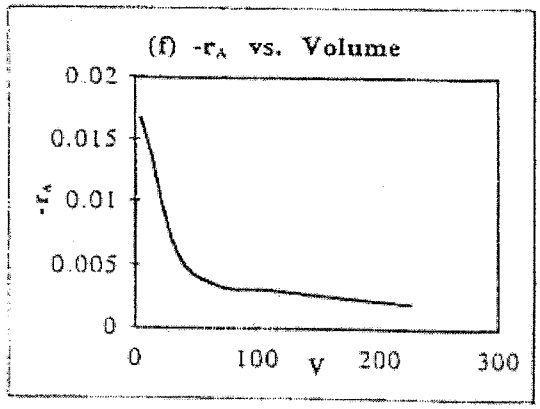
it is apparent that to compensate for the decrease in F_{Ao} there would be and increase in X.

CDP2-F (f)

Use the graph of $1/-r_A$ vs. X to find values for all volumes. (Assume a flow rate of 1 mol/min.) Generate the following table and graphs:

X	$-r_A$	V
0	0.2	0
0.1	0.0167	3.494
0.4	0.00488	42.984
0.7	0.00286	125.878
0.9	0.00204	225.088



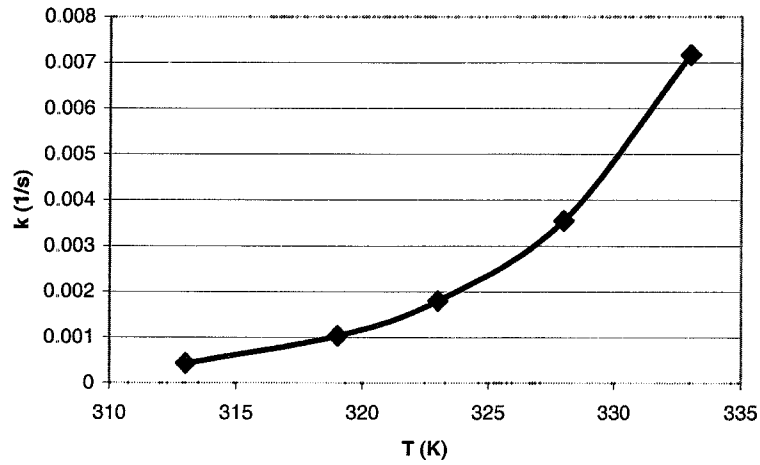


CDP2-F (g) Individualized solution

Solutions for Chapter 3 – Rate Law and Stoichiometry

P3-1 Individualized solution.

P3-2 (a) Example 3-1

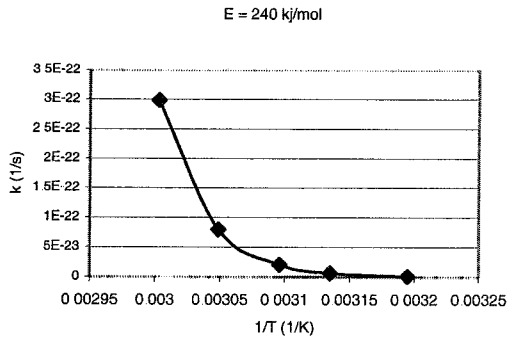


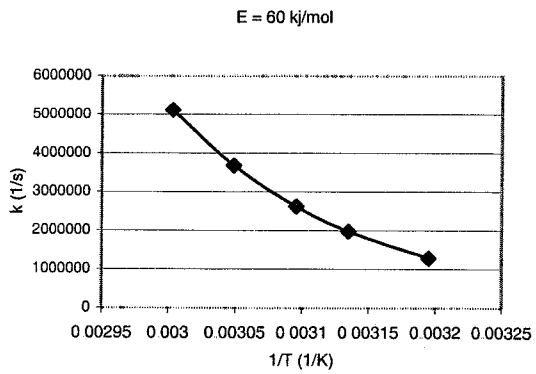
For E = 60kJ/mol

$$k = 1.32\times10^{16}\exp\left(\frac{-60000J}{RT}\right)$$

For E_1 = 240kJ/mol

$$k1 = 1.32\times10^{16}\exp\left(\frac{-240000J}{RT}\right)$$





P3-2 (b) Example 3-2 Yes, water is already considered inert.

P3-2 (c) Example 3-3

The solution to the example at a conversion of 20% would remain unchanged. For 90 % conversions of the caustic soda, the final concentration of glyceryl sterate is 0 instead of a negative concentration. Therefore 90 % of caustic soda is possible.

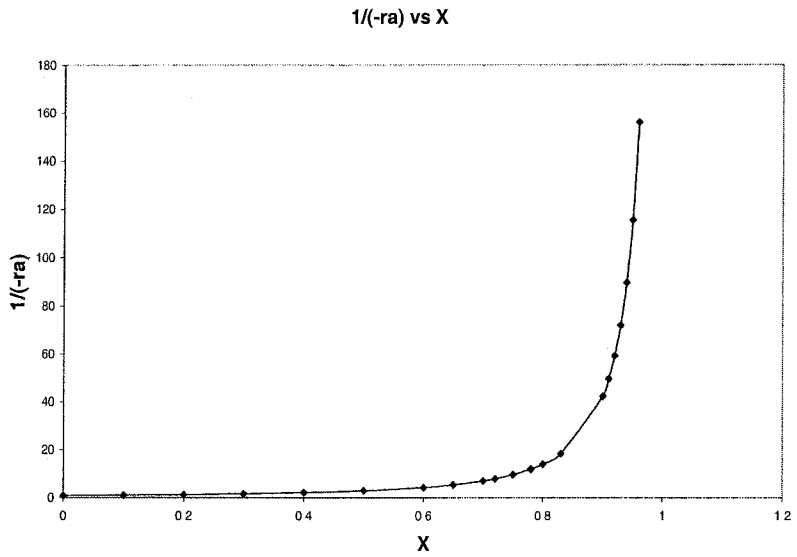
P3-2 (d) Example 3-4 $A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$

So, the minimum value of Θ_B = b/a = $\frac{1/3}{1} = 0.33$

P3-2 (e) Example 3-5

For the concentration of N_2 to be constant, the volume of reactor must be constant. V = V_O.

Plot: $\frac{1}{-r_A} = \frac{0.5(1-0.14X)^2}{(1-X)(0.54-0.5X)}$



The rate of reaction decreases drastically with increase in conversion at higher conversions.

P3-2 (f) Example 3-6

For a given conversion, concentration of B is lower in flow reactor than a constant volume batch reactor. Therefore the reverse reaction decreases.

C_{T0} = constant and inerts are varied.

$N_2O_4 \leftrightarrow 2NO_2$

A $\leftrightarrow$ 2B

Equilibrium rate constant is given by: $K_C = \frac{C_{B,e}^{\ 2}}{C_{A,e}}$

Stoichiometry: $\varepsilon = y_{A0}\delta = y_{A0}(2-1) = y_{A0}$

Constant volume Batch:

$$C_A = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X) \quad \text{and} \quad C_B = \frac{2N_{A0}X}{V_0} = 2C_{A0}X$$

Plug flow reactor:

$$C_A = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} = \frac{C_{A0}(1-X)}{(1+\varepsilon X)} \quad \text{and} \quad C_B = \frac{2F_{A0}X}{v_0(1+\varepsilon X)} = \frac{2C_{A0}X}{(1+\varepsilon X)}$$

$$C_{AO} = \frac{y_{AO}P_O}{RT_O} = y_{AO}(0.07176) mol/dm^3$$

Combining: For constant volume batch:

$$K_C = \frac{C_{B,e}^{\ 2}}{C_{A,e}} = \frac{4C_{Ao}^2X^2}{C_{AO}(1-X)} \qquad \Rightarrow X_e = \sqrt{\frac{K_C(1-X_e)}{4C_{A0}}}$$

For flow reactor:

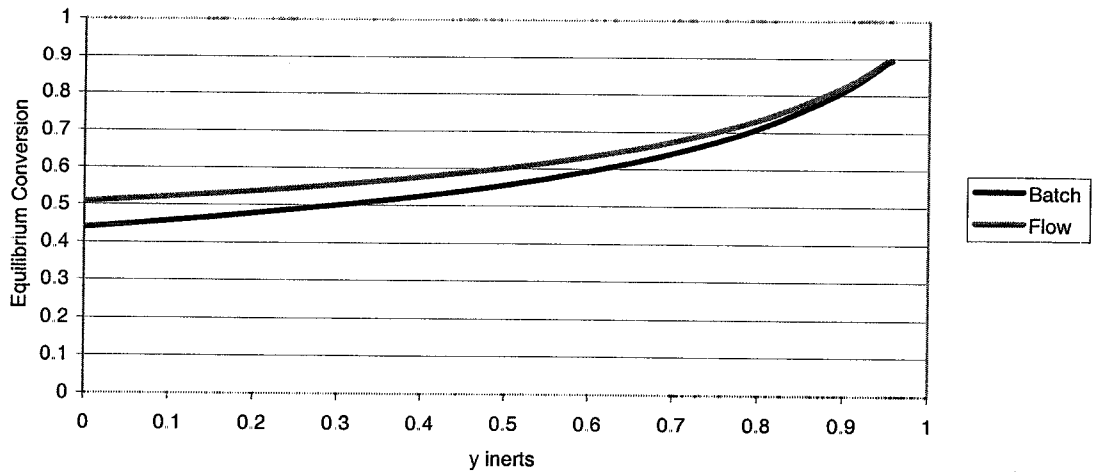
$$K_C = \frac{C_{B,e}^{\ 2}}{C_{A,e}} = \frac{4C_{Ao}^2X^2}{C_{AO}(1-X)(1+\varepsilon X)} \qquad \Rightarrow X_e = \sqrt{\frac{K_C(1-X_e)(1+\varepsilon X_e)}{4C_{A0}}}$$

See Polymath program P3-2-f.pol.

POLYMATH Results
NLES Report (safenewt)

Nonlinear equations
[1] f(Xeb) = Xeb - (kc*(1-Xeb)/(4*Cao))^0.5 = 0
[2] f(Xef) = Xef - (kc*(1-Xef)*(1+eps*Xef)/(4*Cao))^0.5 = 0

Explicit equations
[1] yao = 1
[2] kc = 0.1
[3] Cao = 0.07174*yao
[4] eps = yao



Y_{inert}	Yao	Xeb	Xef
0	1	0.44	0.508
0.1	0.9	0.458	0.5217
0.2	0.8	0.4777	0.537
0.3	0.7	0.5	0.5547
0.4	0.6	0.525	0.576
0.5	0.5	0.556	0.601
0.6	0.4	0.5944	0.633
0.7	0.3	0.6435	0.6743
0.8	0.2	0.71	0.732
0.9	0.1	0.8112	0.8212
0.95	0.05	0.887	0.89
0.956	0.044	0.893	0.896

P3-2 (g) No solution will be given

P3-2 (h)

$$A + \frac{1}{2}B \rightarrow \frac{1}{2}C$$

Rate law: $-r_A = k_A C_A^{\,2} C_B$ and $k_A = 25\frac{1}{s}\left(\frac{dm^3}{mol}\right)^2$

$$\frac{r_A}{-1} = \frac{r_B}{-1/2} = \frac{r_C}{1/2} \qquad \Rightarrow 25C_A^{\,2}C_B = \frac{k_B C_A^{\,2} C_B}{1/2} = \frac{k_C C_A^{\,2} C_B}{-1/2}$$

$$k_C = k_B = 12.5\frac{1}{s}\left(\frac{dm^3}{mol}\right)^2$$

P3-2 (i)

$A + 3B \rightarrow 2C$

Rate law: $-r_A = k_A C_A C_B$ at low temperatures.

At equilibrium,

$$K_C = \frac{C_{C,e}}{C_{A,e}^{\,1/2} C_{B,e}^{\,3/2}} \qquad \Rightarrow C_A^{\,1/2} C_B^{\,3/2} - \frac{C_C}{K_C} = 0$$

At equilibrium, $-r_A = 0$, so we can suggest that $-r_A = k_A\left(C_A^{\,1/2} C_B^{\,1/2} - \frac{C_C}{K_C}\right)$

But at t = 0, $C_C = 0$

So the rate law is not valid at t = 0.

Next guess:

$$K_C^{\,2} = \frac{C_{C,e}^{\,2}}{C_{A,e}C_{B,e}^{\,3}}, \text{ or } \; C_A C_B - \frac{C_C^{\,2}}{K_C^{\,2} C_B^{\,2}} = 0$$

$$\Rightarrow -r_A = k_A\left(C_A C_B - \frac{C_C^{\,2}}{K_C^{\,2} C_B^{\,2}}\right)$$

which satisfies both the initial conditions and equilibrium rate law.

Hence $-r_A = k_A\left(C_A C_B - \frac{C_C^{\,2}}{K_C^{\,2} C_B^{\,2}}\right)$ is the required rate law.

P3-3 Solution is in the decoding algorithm available separately from the author.

P3-4 (a)

Note: This problem can have many solutions as data fitting can be done in many ways.

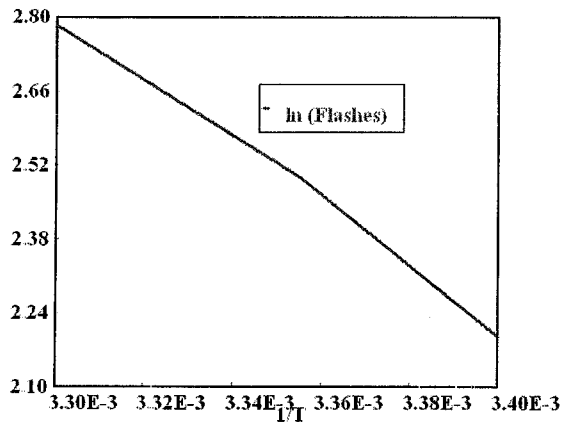
Using Arrhenius Equation

For Fire flies:

T(in K)	1/T	Flashes/ min	ln(flashes/min)
294	0.003401	9	2.197
298	0.003356	12.16	2.498
303	0.003300	16.2	2.785

Plotting ln(flashes/min) vs 1/T,
we get a straight line.

See Polymath program P3-4-fireflies.pol.

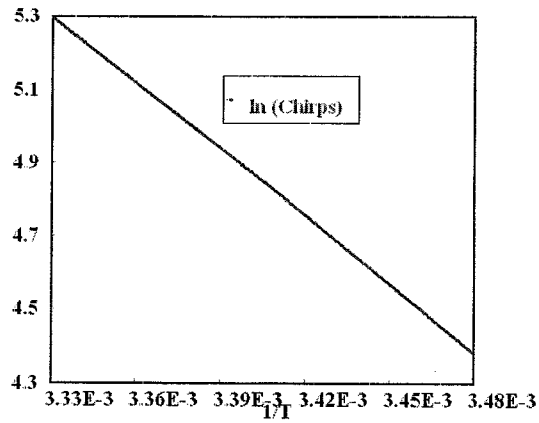


For Crickets:

T(in K)	1/T x10^3	chrips/ min	ln(chirps/ min)
287.2	3.482	80	4.382
293.3	3.409	126	4.836
300	3.333	200	5.298

Plotting ln(chirps/min) Vs 1/T,
we get a straight line.
➔Both, Fireflies and Crickets data
follow the Arrhenius Model.
ln y = A + B/T , and have the same activation energy.

See Polymath program P3-4-crickets.pol.



P3-4 (b)

For Honeybee:

T(in K)	1/T x10^3	V(cm/s)	ln(V)
298	3.356	0.7	-0.357
303	3.300	1.8	0.588
308	3.247	3	1.098

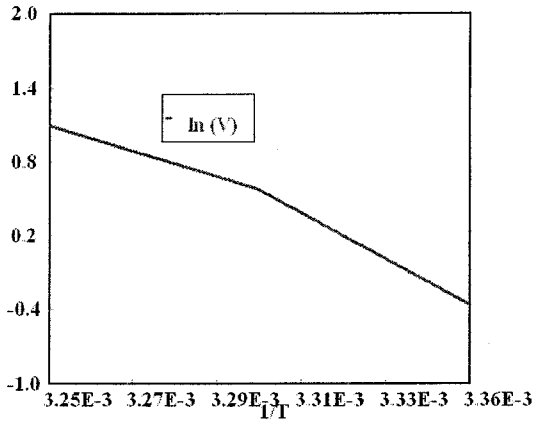
Plotting ln(V) Vs 1/T, almost straight line.

ln(V) = 44.6 – 1.33E4/T

At T = 40°C(313K) V = 6.4cm/s

At T = -5°C(268K) V = 0.005cm/s(But bee would not be alive at this temperature)

See Polymath program P3-4-bees.pol.



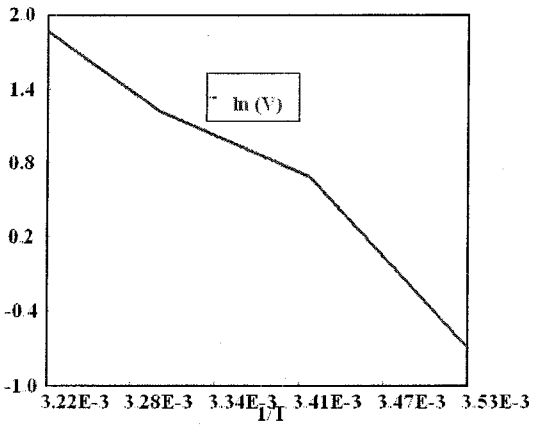
P3-4 (c)

For ants:

T(in K)	1/T x10^3	V(cm/s)	ln(V)
283	3.53	0.5	-0.69
293	3.41	2	0.69
303	3.30	3.4	1.22
311	3.21	6.5	1.87

Plotting ln(V) Vs 1/T, almost straight line.

See Polymath program P3-4-ants.pol.



So activity of bees, ants, crickets and fireflies follow Arrhenius model. So activity increases with an increase in temperature. Activation energies for fireflies and crickets are almost the same.

Insect	Activation Energy
Cricket	52150
Firefly	54800
Ant	95570
Honeybee	141800

P3-4 (d)

There is a limit to temperature for which data for any one of he insect can be extrapolate. Data which would be helpful is the maximum and the minimum temperature that these insects can endure before death. Therefore, even if extrapolation gives us a value that looks reasonable, at certain temperature it could be useless.

P3-5

There are two competing effects that bring about the maximum in the corrosion rate: Temperature and HCN-H_2SO_4 concentration. The corrosion rate increases with increasing temperature and increasing concentration of HCN-H_2SO_4 complex. The temperature increases as we go from top to bottom of the column and consequently the rate of corrosion should increase. However, the HCN concentrations (and the

HCN-H2SO4 complex) decrease as we go from top to bottom of the column. There is virtually no HCN in the bottom of the column. These two opposing factors results in the maximum of the corrosion rate somewhere around the middle of the column.

P3-6 Antidote did not dissolve from glass at low temperatures.

P3-7 (a)

If a reaction rate doubles for an increase in 10°C, at $T = T_1$ let $k = k_1$ and at $T = T_2 = T_1+10$, let $k = k_2 = 2k_1$. Then with $k = Ae^{-E/RT}$ in general, $k_1 = Ae^{-E/RT_1}$ and $k_2 = Ae^{-E/RT_2}$, or

$$\frac{k_2}{k_1} = e^{-\frac{E}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)} \quad \text{or} \quad \frac{E}{R} = -\frac{\ln\left(\frac{k_2}{k_1}\right)}{\left(\frac{1}{T_2}-\frac{1}{T_1}\right)} = -\frac{\ln\left(\frac{k_2}{k_1}\right)}{\frac{(T_1-T_2)}{T_1T_2}}$$

Therefore:

$$E = R\frac{\ln\left(\frac{k_2}{k_1}\right)\left(T_1(T_1+10)\right)}{(T_2-T_1)} = R\frac{(\ln 2)\left(T_1(T_1+10)\right)}{10}$$

$$T_1(T_1+10) = \frac{10E}{R\ln 2}$$

which can be approximated by $T = \frac{10E^{0.5}}{R\ln 2}$

P3-7 (b)

Equation 3-18 is $k = Ae^{-\frac{E}{RT}}$

From the data, at $T_1 = 0°C$, $k_1 = Ae^{-E/RT_1}$, and at $T_2 = 100°C$, $k_2 = Ae^{-E/RT_2}$

Dividing gives $\frac{k_2}{k_1} = e^{-\frac{E}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}$, or

$$E = -\frac{R\ln\left(\frac{k_2}{k_1}\right)}{\left(\frac{1}{T_2}-\frac{1}{T_1}\right)} = -\frac{RT_1T_2}{(T_1-T_2)}\ln\left(\frac{k_2}{k_1}\right)$$

$$E = \frac{\left[1.99\frac{cal}{mol\,K}\right][273\,K][373\,K]}{100\,K}\ln\left(\frac{.050}{.001}\right) = 7960\frac{cal}{mol}$$

$$A = k_1 e^{\frac{E}{RT_1}} = 10^{-3}\,\text{min}^{-1}\exp\left[\frac{7960\frac{cal}{mol}}{\left(1.99\frac{cal}{mol\,K}\right)(273\,K)}\right] = 2100\,\text{min}^{-1}$$

P3-7 (c) Individualized solution

P3-8

When the components inside air bag are ignited, following reactions take place,

$2NaN_3 \rightarrow 2Na + 3N_2$ .....(1)

$10Na + 2KNO_3 \rightarrow K2O + 5Na_2O + N_2$ .....(2)

$K_2O + Na_2O + SiO_2 \rightarrow$ alkaline silicate glass .....(3)

$$5 \times rxn(1) + rxn(2) + rxn(3) = rxn(4)$$

$NaN_3 + 0.2KNO_3 + 0.1SiO_2 \rightarrow 0.4Na_2O + 1.6N_2 +$ complex/10.....(4)

Stoichiometric table:

Species	Symbol	Initial	Change	Final
NaN_3	A	N_A	$-N_AX$	$N_A(1-X)$
KNO_3	B	$N_A\theta_B$	$-0.2X\,N_A$	$N_A(\theta_B - 0.2X)$
SiO_2	C	$N_A\theta_C$	$-0.1XN_A$	$N_A(\theta_C - 0.1X)$
Na_2O	D	0	$0.4XN_A$	$0.4XN_A$
N_2	E	0	$1.6XN_A$	$1.6XN_A$

Given weight of NaN_3 = 150g M_{wt} of NaN_3 = 65

Therefore, no. of moles of NaN_3 = 2.3

1 moles of NaN_3 requires 0.2 mole of KNO_3

=> Moles of B, KNO_3 = 0.2(2.3) = 0.46 moles M_{wt} of KNO_3 = 101.1

Therefore, grams of KNO_3 required = 0.46 x 101.1 = 46.5 g

1 moles of NaN_3 requires 0.1 mole of SiO_2.

Moles of C, SiO_2 = 0.1(2.3) = 0.23 moles M_{wt} of SiO_2 = 60.08

Therefore, grams of SiO2 required = 0.23 x 60.08 = 13.8 g

Following proposals are given to handle all the un-detonated air bags in cars piling up in the junkyards:

- Store cars in cool, dry, ventilated areas.
- Avoid Physical damage of the bag in car.
- It is stable under ordinary conditions of storage. Decomposes explosively upon heating (over 221 °F or 105 °C), shock, concussion, or friction.

- Conditions to avoid: heat, flames, ignition sources and incompatibles.

P3-9 (a)

From the web module we know that $\frac{dX}{dt} = k(1-x)$ and that k is a function of temperature, but not a linear function. Therefore doubling the temperature will not necessarily double the reaction rate, and therefore halve the cooking time.

P3-9 (b)

When you boil the potato in water, the heat transfer coefficient is much larger, but the temperature can only be 100°C.

When you bake the potato, the heat transfer coefficient is smaller, but the temperature can be more than double that of boiling water.

P3-9 (c) No solution will be given

P3-10 (a)

1) $C_2H_6 \rightarrow C_2H_4 + H_2$ Rate law: $-r_A = kC_{C_2H_6}$

2) $C_2H_4 + 1/2O_2 \rightarrow C_2H_4O$ Rate law: $-r_A = kC_{C_2H_4}C_{O_2}^{1/2}$

3) $(CH_3)_3COOC(CH_3)_3 \rightarrow C_2H_6 + 2CH_3COCH_3$

A $\rightarrow$ B + 2C

Rate law: $-r_A = k[C_A - C_B C_C^2/K_C]$

4) $n\text{-}C_4H_{10} \leftrightarrow I\text{-}C_4H_{10}$ Rate law: $-r_A = k[C_{nC_4H_{10}} - C_{iC_4H_{10}}/K_c]$

5) $CH_3COOC_2H_5 + C_4H_9OH \leftrightarrow CH_3COOC_4H_9 + C_2H_5OH$

A + B $\leftrightarrow$ C + D

Rate law: $-r_A = k[C_A C_B - C_C C_D/K_C]$

P3-10 (b)

$2A + B \rightarrow C$

(1) $-r_A = kC_AC_B^2$

(2) $-r_A = kC_B$

(3) $-r_A = k$

(4) $-r_A = kC_AC_B^{-1}$

P3-10 (c)

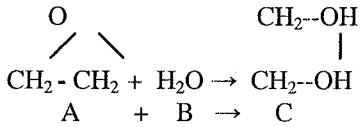
(1) $C_2H_6 \rightarrow C_2H_4 + H_2$ Rate law: $-r_A = kC_{C_2H_6}$

(2) $H_2 + Br_2 \rightarrow 2HBr$ Rate law: $-r_{HBr} = \dfrac{k_1 C_{H_2} C_{Br_2}^{1/2}}{k_2 + \dfrac{C_{HBr}}{C_{Br_2}}}$

(3) $H_2 + I_2 \rightarrow 2HI$ Rate law: $-r_{H_2} = kC_{H_2}C_{I_2}$

P3-11 (a)

Liquid phase reaction,



$CH_2\text{-}CH_2 + H_2O \rightarrow CH_2\text{--}OH\text{--}CH_2\text{--}OH$

A + B → C

C_{AO} = 1 lbmol/ft^3 C_{BO} = 3.47 lbmol/ft^3

Stoichiometric Table:

Species	Symbol	Initial	Change	Remaining
Ethylene oxide	A	C_{AO}=1 lbmol/ft^3	- $C_{AO}X$	$C_A = C_{AO}(1\text{-}X)$ = (1-X) lbmol/ft^3
Water	B	C_{BO}= 3.47 lbmol/ft^3, θ_B=3.47	-$C_{AO}X$	$C_B = C_{AO}(\theta_B - X)$ =(3.47-X) lbmol/ft^3
Glycol	C	0	$C_{AO}X$	$C_C = C_{AO}X$ = X lbmol/ft^3

Rate law: $-r_A = kC_AC_B$

Therefore, $-r_A = k\,C_{AO}^2(1\text{-}X)(\theta_B\text{-}X) = k(1\text{-}X)(3.47\text{-}X)$

At 300K E = 12500 cal/mol, X = 0.9,

$$k = 0.1 dm^3/mol.s = \frac{0.1}{1000} \times 35.315 ft^3/lbmol.s = 0.0035 ft^3/lbmol.s$$

$$\tau_{CSTR} = \frac{C_{AO}X}{-r_A} = \frac{(1)(0.9)}{(0.0035)(1)^2(1-0.9)(3.47-0.9)} = 1000.56\ s^{-1}$$

At 350K,

$k_2 = k\exp((E/R)(1/T\text{-}1/T_2)) = 0.0035\exp((12500/1.987)(1/T\text{-}1/T_2)) = 0.071\ dm^3/mol.s$

Therefore,

$$\tau_{CSTR} = \frac{C_{AO}X}{-r_A} = \frac{(1)(0.9)}{(0.071)(1)^2(1-0.9)(3.47-0.9)} = 49.3 s^{-1}$$

P3-11 (b)

Isothermal, isobaric gas-phase pyrolysis,

$C_2H_6 \rightarrow C_2H_4 + H_2$

A → B + C

Stoichiometric table:

Species	symbol	Entering	Change	Leaving
C_2H_6	A	F_{AO}	-$F_{AO}X$	$F_A = F_{AO}(1\text{-}X)$

C_2H_4	B	0	$+F_{AO}X$	$F_B=F_{AO}X$
H_2	C	0	$+F_{AO}X$	$F_C=F_{AO}X$
		$F_{TO}=F_{AO}$		$F_T=F_{AO}(1+X)$

$\varepsilon = y_{ao}\delta = 1(1+1-1) = 1$

$v = v_o(1+\varepsilon X)$ $\Rightarrow v = v_o(1+X)$

$$C_{AO} = y_{AO}\,C_{TO} = y_{AO}\frac{P}{RT}$$

$$= \frac{(1)(6atm)}{\left(0.082\frac{m^3 atm}{K.kmol}\right)(1100K)} = 0.067 \text{ kmol/m}^3 = 0.067 \text{ mol/dm}^3$$

$$C_A = \frac{F_A}{v} = \frac{F_{AO}(1-X)}{v_O(1+X)} = C_{AO}\frac{(1-X)}{(1+X)} \text{ mol/dm}^3$$

$$C_B = \frac{F_B}{v} = \frac{F_{AO}(X)}{v_O(1+X)} = C_{AO}\frac{X}{(1+X)} \text{ mol/dm}^3$$

$$C_C = \frac{F_C}{v} = \frac{F_{AO}(X)}{v_O(1+X)} = C_{AO}\frac{X}{(1+X)} \text{ mol/dm}^3$$

Rate law:

$$-r_A = kC_A = kC_{AO}\frac{(1-X)}{(1+X)} = 0.067\,k\frac{(1-X)}{(1+X)}$$

If the reaction is carried out in a constant volume batch reactor, $\Rightarrow(\varepsilon = 0)$

$C_A = C_{AO}(1-X)$ mol/dm^3 $C_B = C_{AO}X$ mol/dm^3 $C_C = C_{AO}X$ mol/dm^3

P3-11 (c)

Isothermal, isobaric, catalytic gas phase oxidation,

$$C_2H_4 + \frac{1}{2}O_2 \rightarrow C_2H_4O$$

$$A + \frac{1}{2}B \rightarrow C$$

Stoichiometric table:

Species	Symbol	Entering	Change	Leaving
C_2H_4	A	F_{AO}	$-F_{AO}X$	$F_A=F_{AO}(1-X)$
O_2	B	F_{BO}	$-\theta_B F_{AO}X$	$F_B=F_{AO}(\theta_B-X)$
C_2H_4O	C	0	$+F_{AO}X$	$F_C=F_{AO}X$

$$\theta_B = \frac{F_{BO}}{F_{AO}} = \frac{\frac{1}{2}F_{AO}}{F_{AO}} = \frac{1}{2} \qquad y_{AO} = \frac{F_{AO}}{F_{TO}} = \frac{F_{AO}}{F_{AO}+F_{BO}} = \frac{2}{3}$$

$$\varepsilon = y_{AO}\delta = \frac{2}{3}\left(1--\frac{1}{2}-1\right) = 0.33$$

$$C_{AO} = y_{AO}C_{TO} = y_{AO}\frac{P}{RT} = \frac{2}{3}\frac{(6atm)}{\left(0.082\frac{atm.dm^3}{mol.K}\right)(533K)} = 0.092\frac{mol}{dm^3}$$

$$C_A = \frac{F_A}{v} = \frac{F_{AO}(1-X)}{v_O(1+\varepsilon X)} = \frac{C_{AO}(1-X)}{(1-0.33X)} = \frac{0.092(1-X)}{(1-0.33X)}$$

$$C_B = \frac{F_B}{v} = \frac{F_{AO}\left(\theta_B - \frac{X}{2}\right)}{v_O(1+\varepsilon X)} = \frac{0.046(1-X)}{(1-0.33X)}$$

$$C_C = \frac{F_C}{v} = \frac{F_{AO}X}{v_O(1+\varepsilon X)} = \frac{0.092(X)}{(1-0.33X)}$$

If the reaction follow elementary rate law

Rate law: $-r_A = kC_AC_B^{0.5}$ $\Rightarrow -r_A = k\left\{\frac{0.092(1-X)}{(1-0.33X)}\right\}\left\{\frac{0.046(1-X)}{(1-0.33X)}\right\}^{0.5}$

P3-11 (d)

Isothermal, isobaric, catalytic gas phase reaction in a PBR

$C_6H_6 + 2H_2 \rightarrow C_6H_{10}$

A + 2B → C

Stoichiometric table:

Species	Symbol	Entering	Change	Leaving
Benzene	A	F_{AO}	$-F_{AO}X$	$F_A=F_{AO}(1-X)$
H_2	B	$F_{BO}=2F_{AO}$	$-2F_{AO}X$	$F_B=F_{AO}(\theta_B-2X)$
C_6H_{10}	C	0	$F_{AO}X$	$F_C=F_{AO}X$

$$\theta_B = \frac{F_{BO}}{F_{AO}} = \frac{2F_{AO}}{F_{AO}} = 2$$

$$y_{AO} = \frac{F_{AO}}{F_{TO}} = \frac{F_{AO}}{F_{AO}+F_{BO}} = \frac{1}{3}$$

$$\varepsilon = y_{AO}\delta = \frac{1}{3}(1-2-1) = -\frac{2}{3}$$

$$C_{AO} = C_{TO}y_{AO} = \frac{P}{RT}\left(\frac{1}{3}\right) = \frac{6atm}{\left(0.082\frac{atm.dm^3}{mol.K}\right)(443.2K)}\left(\frac{1}{3}\right) = 0.055mol/dm^3$$

$$C_A = \frac{F_A}{v} = \frac{F_{AO}(1-X)}{v_O(1+\varepsilon X)} = \frac{C_{AO}(1-X)}{\left(1-\frac{2}{3}X\right)} = \frac{0.055(1-X)}{\left(1-\frac{2}{3}X\right)}$$

$$C_B = \frac{F_B}{v} = \frac{F_{AO}(\theta_B - 2X)}{v_O(1+\varepsilon X)} = \frac{0.11(1-X)}{\left(1-\frac{2}{3}X\right)}$$

$$C_C = \frac{F_C}{v} = \frac{F_{AO}X}{v_O(1+\varepsilon X)} = \frac{C_{AO}X}{\left(1-\frac{2}{3}X\right)} = \frac{0.055X}{\left(1-\frac{2}{3}X\right)}$$

If the reaction follow elementary rate law.
Rate law:

$$-r_A' = kC_AC_B^2$$

$$-r_A' = 0.0007k\frac{(1-X)^3}{\left(1-\frac{2}{3}X\right)^3}$$

For a fluidized CSTR:

$$W = \frac{F_{A0}X}{-r_A'}$$

$$W = \frac{F_{A0}X}{0.0007k\frac{(1-X)^3}{\left(1-\frac{2}{3}X\right)^3}}$$

k = 53 $\frac{mol}{kgcat\ \min\ atm^3}$ at 300K

$$k = k_1\exp\left(\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T}\right)\right) = 53\exp\left(\frac{80000}{8.314}\left(\frac{1}{300}-\frac{1}{443}\right)\right) = 1663000\ \frac{mol}{kgcat\ \min\ atm^3}$$

$F_{A0} = C_{A0} * v_0$
$v_0 = 5\ dm^3/min$

$$W = \frac{C_{A0}v_0X}{0.0007k\frac{(1-X)^3}{\left(1-\frac{2}{3}X\right)^3}}$$

at X = 0.8

W = 0.0024 kg of catalyst

P3-12 $C_2H_4 + \frac{1}{2}O_2 \rightarrow C_2H_4O$

$A + \frac{1}{2}B \rightarrow C$

Stoichiometric table for the given problem will be as follows

Assuming gas phase

Species	Symbol	Entering	Change	Leaving
C_2H_4	A	F_{A0}	$-F_{A0}X$	$F_{A0}(1-X)$
O_2	B	$F_{B0} = \Theta_B F_{A0}$	$-1/2\ F_{A0}X$	$F_{A0}(\Theta_B - X/2)$
N_2	I	$F_I = \Theta_I F_{A0}$	-------	$F_{A0}\Theta_I$
C_2H_4O	C	0	$F_{A0}X$	$F_{A0}X$

$$\theta_B = \frac{\frac{1}{2}F_{A0}}{F_{A0}} = \frac{1}{2} \qquad \theta_I = \frac{F_{IO}}{F_{AO}}, F_{IO} = \frac{0.79}{0.21}F_{BO} \qquad \Rightarrow \theta_I = \theta_B \frac{0.79}{0.21} = 1.88$$

$$y_{A0} = \frac{F_{A0}}{F_{T0}} = 0.30, \qquad \varepsilon = y_{A0}\delta = -0.15$$

$$C_{A0} = \frac{y_{A0}P}{RT} = 0.041\frac{mol}{dm^3}$$

$$C_A = \frac{F_{A0}}{v} = C_{A0}\frac{(1-X)}{(1+\varepsilon X)} = \frac{0.041(1-X)}{1-0.15X}$$

$$C_B = \frac{F_B}{v} = C_{A0}\frac{(\frac{1}{2} - \frac{1}{2}X)}{1-0.15X} = \frac{0.020(1-X)}{1-0.15X}$$

$$C_C = \frac{F_C}{v} = \frac{C_{A0}X}{1-0.15X} = \frac{0.041X}{1-0.15X}$$

P3-13 (a)

Let A = ONCB
B = NH_3
C = Nibroanaline
D = Ammonium Chloride

$A + 2B \longrightarrow C + D$

$-r_A = kC_AC_B$

P3-13 (b)

Species	Entering	Change	Leaving
A	F_{A0}	$-F_{A0}X$	$F_{A0}(1-X)$
B	$F_{B0}=\Theta_B F_{A0}$ $=6.6/1.8\ F_{A0}$	$-2\ F_{A0}X$	$F_B=$ $F_{A0}(\Theta_B-2X)$
C	0	$F_{A0}X$	$F_C=F_{A0}X$
D	0	$F_{A0}X$	$F_D=F_{A0}X$

P3-13 (c)

For batch system,

$C_A=N_A/V$ $\qquad -r_A=kN_AN_B/V^2$

P3-13 (d)

$$-r_A=kC_AC_B$$

$$F_A=\frac{N_A}{V}=\frac{N_A}{V_0}=\frac{N_{A0}}{V_0}(1-X)=C_{A0}(1-X),\quad C_A=\frac{F_A}{v}=\frac{F_A}{v_0}=C_{A0}(1-X)$$

$$F_B=\frac{N_B}{V}=\frac{N_B}{V_0}=\frac{N_{A0}}{V_0}(\theta_B-2X)=C_{A0}(\theta_B-2X),\quad C_B=\frac{F_B}{v_0}=C_{A0}(\theta_B-2X)$$

$$-r_A=kC_{A0}^2(1-X)(\theta_B-2X)$$

$$\theta_B=\frac{C_{B0}}{C_{A0}}=\frac{6.6}{1.8}=3.67$$

$$C_{A0}=1.8\frac{kmol}{m^3}$$

$$\boxed{-r_A=k(1.8)^2(1-X)(3.67-2X)}$$

P3-13 (e)

1) At X = 0 and T = 188°C = 461 K

$$-r_{A0}=kC_{A0}^2\theta_B=k_AC_{A0}C_{B0}=0.0017\frac{m^3}{kmol\ \min}\left(1.8\frac{kmol}{m^3}\right)\left(6.6\frac{kmol}{m^3}\right)$$

$$\boxed{-r_{A0}=0.0202\frac{\text{kmol}}{\text{m}^3\ \text{min}}}$$

2) At X = 0 and T = 25C = 298K

$$k = k_O \exp\left(\frac{E}{R}\left(\frac{1}{T_O}+\frac{1}{T}\right)\right)$$

$$k = 0.0017\frac{m^3}{kmol.\min}\exp\left(\frac{11273\frac{cal}{mol}}{1.987\frac{cal}{mol.k}}\left(\frac{1}{461}+\frac{1}{298}\right)\right)$$

$$= 2.12\times10^{-6}\frac{m3}{kmol.\min}$$

$-r_{AO} = kC_{AO}C_{BO} = 2.52 \text{ X } 10^{-5}$ kmol/m^{3}min

3)

$$k = k_0 \exp\left[\frac{E}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)\right]$$

$$k = 0.0017\frac{\text{m}^3}{\text{kmol min}}\exp\left[\frac{11273\frac{cal}{mol}}{1.987\frac{cal}{mol\,K}}\left(\frac{1}{461K}-\frac{1}{561K}\right)\right]$$

$$k = 0.0152\frac{\text{m}^3}{\text{kmol min}}$$

$$-r_{A0} = kC_{A0}C_{B0}$$

$$-r_A = 0.0152\frac{\text{m}^3}{\text{kmol min}}\left(1.8\frac{kmol}{m^3}\right)\left(6.6\frac{kmol}{m^3}\right)$$

$$\boxed{-r_A = 0.1806\frac{\text{kmol}}{\text{m}^3\text{ min}}}$$

P3-13 (f)

$r_A = kC_{AO}^2(1\text{-}X)(\theta_B\text{-}2X)$

At X = 0.90 and T = 188C = 461K

1) at t = 188 C

$$-r_A = \left(0.0017\frac{m^3}{kmol.\min}\right)\left(1.8\frac{kmol}{m^3}\right)^2(1-0.9)(3.67-2(0.9))$$

$$= 0.00103\frac{kmol}{m^3\text{ min}}$$

2)

At X = 0.90 and T = 25C = 298K

$$-r_A = \left(2.12\times10^{-6}\frac{m^3}{kmol.\min}\right)\left(1.8\frac{kmol}{m^3}\right)^2(1-0.9)(3.67-2(0.9))$$

$$=1.28\times10^{-6}\frac{kmol}{m^3\min}$$

3)

At X = 0.90 and T = 288C = 561K

$$-r_A = \left(0.0152\frac{m^3}{kmol.\min}\right)\left(1.8\frac{kmol}{m^3}\right)^2(1-0.9)(3.67-2(0.9))$$

$$=0.00333\frac{kmol}{m^3\min}$$

P3-13 (g)

$v_o = 2m^3/min = 0.002m^3/min$

1)For CSTR at 25C $-r_A = =1.28\times10^{-6}\frac{kmol}{m^3\min}$

$$V=\frac{v_oC_{AO}(1-X)}{-r_{A:X=0.9}}$$

$$=\frac{0.002m^3/\min\times1.8kmol/m^3\times0.1}{1.28\times10^{-6}\frac{kmol}{m^3\min}}=281.25m^3$$

2)At 288C, $-r_A = 0.00333\frac{kmol}{m^3\min}$

$$V=\frac{v_oC_{AO}(1-X)}{-r_{A:X=0.9}}$$

$$V=\frac{0.002m^3/\min\times1.8kmol/m^3\times0.1}{0.00333\frac{kmol}{m^3\min}}=0.108m^3$$

P3-14

$C_6H_{12}O_6 + aO_2 + bNH_3 \rightarrow c(C_{4.4}H_{7.3}N_{0.86}O_{1.2}) + dH_2O + eCO_2$

To calculate the yields of biomass, you must first balance the reaction equation by finding the coefficients a, b, c, d, and e. This can be done with mass balances on each element involved in the reaction. Once all the coefficients are found, you can then calculate the yield coefficients by simply assuming the reaction proceeds to completion and calculating the ending mass of the cells.

P3-14 (a)

Apply mass balance

For C	$6 = 4.4c + e$	For O	$6 + 2a = 1.2c + d + 2e$
For N	$b = 0.86c$	For H	$12 + 3b = 7.3c + 2d$

Also for C, $6(2/3) = 4.4c$ which gives **c = 0.909**

Next we solve for e using the other carbon balance
$6 = 4.4 (0.909) + e$
e = 2

We can solve for b using the nitrogen balance
$b = 0.86c = 0.86* (0.909)$
b = 0.78

Next we use the hydrogen balance to solve for d
$12 + 3b = 7.3c + 2d$
$12 + 3(0.78) = 7.3(0.909) + 2d$
d = 3.85

Finally we solve for a using the oxygen balance
$6 + 2a = 1.2c + d + 2e$
$6 + 2a = 1.2(0.909) + 3.85 + 2(2)$
a = 1.47

P3-14 (b)

Assume 1 mole of glucose (180 g) reacts:

$Y_{c/s}$= mass of cells / mass of glucose = mass of cells / 180 g

mass of cells = c*(molecular weight) = 0.909 mol* (91.34g/mol)

mass of cells = 83.12 g

$Y_{c/s} = 83.12$ g / 180 g
$Y_{c/s}$ = 0.46

$Y_{c/o2}$ = mass of cells / mass of O_2

If we assume 1 mole of glucose reacted, then 1.47 moles of O_2 are needed and 83.12 g of cells are produced.

mass of $O_2 = 1.47$ mol * (32 g/mol)

mass of $O_2 = 47.04$ g

$Y_{c/o2} = 83.12$ g /47.04 g
$Y_{c/o2}$ =1.77

P3-15 (a)

Isothermal gas phase reaction.

$$\frac{1}{2}N_2+\frac{3}{2}H_2 \rightarrow NH_3$$

Making H_2 as the basis of calculation:

$$H_2+\frac{1}{3}N_2 \rightarrow \frac{2}{3}NH_3$$

$$A+\frac{1}{3}B \rightarrow \frac{2}{3}C$$

Stoichiometric table:

Species	Symbol	Initial	change	Leaving
H_2	A	F_{AO}	$-F_{AO}X$	$F_A=F_{AO}(1-X)$
N_2	B	$F_{BO}=\theta_B F_{AO}$	$-F_{AO}X/3$	$F_B=F_{AO}(\theta_B-X/3)$
NH_3	C	0	$+2F_{AO}X/3$	$F_C=(2/3)F_{AO}X$

P3-15 (b)

$$\delta=\left(\frac{2}{3}-\frac{1}{3}-1\right)=-\frac{2}{3}$$

$$\varepsilon=y_{AO}\delta=0.5\times\left(-\frac{2}{3}\right)=-\frac{1}{3}$$

$$C_{AO}=0.5\frac{(16.4atm)}{\left(0.082\frac{atm.dm^3}{mol.K}\right)(500K)}=0.2\ \text{mol/dm}^3$$

$$C_{H_2}=C_A=\frac{C_{AO}(1-X)}{(1+\varepsilon X)}=\frac{0.2(1-X)}{\left(1-\frac{X}{3}\right)}=0.1mol/dm^3$$

$$C_{NH_3}=C_C=\frac{2}{3}\times\frac{C_{AO}(1-X)}{(1+\varepsilon X)}=\frac{2}{3}\times\frac{0.2(X)}{\left(1-\frac{X}{3}\right)}=0.1mol/dm^3$$

P3-15 (c)

$k_{N2} = 40\ dm^3/mol.s$

(1) For Flow system:

$$-r_{N_2} = k_{N_2}\left[C_{N_2}\right]^{1/2}\left[C_{H_2}\right]^{3/2}$$

$$= 40\left(C_{AO}\right)^2\left[\frac{\left(1-\frac{X}{3}\right)}{\left(1-\frac{X}{3}\right)}\right]^{1/2}\left[\frac{(1-X)}{\left(1-\frac{X}{3}\right)}\right]^{3/2}$$

$$-r_{N_2} = 8.3\left[\frac{(1-X)}{\left(1-\frac{X}{3}\right)}\right]^{3/2}$$

(2) For batch system, constant volume.

$$-r_{N_2} = k_{N_2}\left[C_{N_2}\right]^{1/2}\left[C_{H_2}\right]^{3/2}$$

$$= 40\left(C_{AO}\right)^2\left[\left(1-\frac{X}{3}\right)\right]^{1/2}\left[(1-X)\right]^{3/2}$$

$$-r_{N_2} = 1.6\left[1-\frac{X}{3}\right]^{1/2}\left[1-X\right]^{3/2}$$

P3-16 (a)

Liquid phase reaction → assume constant volume

Rate Law (reversible reaction):

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

Stoichiometry:

$$C_A = C_{A0}\left(1-X\right),\ C_B = C_{A0}\left(1-X\right),\ C_C = C_{A0}X$$

To find the equilibrium conversion, set $-r_A = 0$, combine stoichiometry and the rate law, and solve for X_e.

$$C_A C_B K_C = C_C$$

$$C_{A0}^2\left(1-X_e\right)^2 K_C = C_{A0}X_e$$

$$X_e^2 - \left(2+\frac{1}{C_{A0}K_C}\right)X_e + 1 = 0$$

$$X_e = 0.80$$

To find the equilibrium concentrations, substitute the equilibrium conversion into the stiochiometric relations.

$$C_A = C_{A0}(1-X) = 2\frac{mol}{dm^3}(1-0.80) = 0.4\frac{mol}{dm^3}$$

$$C_B = C_{A0}(1-X) = 2\frac{mol}{dm^3}(1-0.80) = 0.4\frac{mol}{dm^3}$$

$$C_A = C_{A0}X = 2\frac{mol}{dm^3} * 0.80 = 1.6\frac{mol}{dm^3}$$

P3-16 (b)

Stoichiometry:

$$\varepsilon = y_{A0}\delta = (1)(3-1) = 2 \text{ and } \theta_C = 0$$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V_0(1+\varepsilon X)} = C_{A0}\frac{(1-X)}{(1+2X)}$$

$$C_C = \frac{N_C}{V} = \frac{3N_{A0}X}{V_0(1+\varepsilon X)} = C_{A0}\frac{3X}{(1+2X)}$$

Combine and solve for X_e.

$$K_C C_{A0}\frac{(1-X_e)}{(1+2X_e)} = \left[C_{A0}\frac{3X_e}{(1+2X_e)}\right]^3$$

$$K_C(1-X_e)(1+2X_e)^2 = 27C_{A0}^2X_e^3$$

$$-\left(4+\frac{27C_{A0}^2}{K_C}\right)X_e^3 + 3X_e + 1 = 0$$

$$X_e = 0.58$$

Equilibrium concentrations:

$$C_{A0} = \frac{P_0}{RT_0} = \frac{10\,atm}{(400\,K)\left(0.082\frac{dm^3\,atm}{mol\,K}\right)} = 0.305\frac{mol}{dm^3}$$

$$C_A = 0.305\frac{(1-0.58)}{(1+2(0.58))} = 0.059\frac{mol}{dm^3}$$

$$C_C = \frac{3(0.58)(0.305)}{(1+2(0.58))} = 0.246\frac{mol}{dm^3}$$

P3-16 (c)

Same reaction, rate law, and initial concentration as part (b) gas phase, batch reaction.

Stoichiometry:

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X)$$

$$C_C = \frac{N_C}{V} = \frac{3N_{A0}X}{V_0} = 3C_{A0}X$$

Combine and solve for X_e

$$K_C C_{A0}(1-X_e) = (3C_{A0}X_e)^3$$

$$X_e = 0.39$$

Equilibrium concentrations

$$C_A = (0.305)(1-0.39) = 0.19\frac{mol}{dm^3}$$

$$C_C = (0.305)(0.39) = 0.36\frac{mol}{dm^3}$$

P3-16 (d)

Gas phase reaction in a constant pressure, batch reactor

Rate law (reversible reaction):

$$-r_A = k\left[C_A - \frac{C_C^3}{K_C}\right]$$

Stoichiometry:

$$\varepsilon = y_{A0}\delta = (1)(3-1) = 2 \text{ and } \theta_C = 0$$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V_0(1+\varepsilon X)} = C_{A0}\frac{(1-X)}{(1+2X)}$$

$$C_C = \frac{N_C}{V} = \frac{3N_{A0}X}{V_0(1+\varepsilon X)} = 3C_{A0}\frac{X}{(1+2X)}$$

Combine and solve for X_e:

$$\frac{K_C C_{A0}(1-X_e)}{1+2X_e} = \left[\frac{3C_{A0}X_e}{1+2X_e}\right]^3$$

$$X_e = 0.58$$

Equilibrium concentrations:

$$C_A = \frac{0.305(1-0.58)}{1+2(0.58)} = 0.059\frac{mol}{dm^3}$$

$$C_C = \frac{3(0.305)(0.58)}{1+2(0.58)} = 0.246\frac{mol}{dm^3}$$

P3-17

Given: Gas phase reaction A + B → 8C in a batch reactor fitted with a piston such that $V = 0.1P_0$

$$k = 1.0\frac{(ft^3)^2}{lb\,mol^2\,\sec}$$

$$-r_A = kC_A^2C_B$$

$N_{A0} = N_{B0}$ at $t = 0$

$V_0 = 0.15\ ft^3$

$T = 140°C = 600°R$ = Constant

P3-17 (a)

$$y_{A0} = \frac{N_{A0}}{N_{A0}+N_{B0}} = 0.5$$

$$\delta = 8-1-1 = 6$$

$$\varepsilon = y_{A0}\delta = 3$$

Now $V = \frac{V_0P_0}{P\left(\frac{T}{T_0}\right)}(1+\varepsilon X)$ and $\frac{T}{T_0}=1$, $P_0 = 10V_0$, and $P = 10V$

Therefore $V = \frac{10V_0^2}{10V}(1+\varepsilon X)$ or $V^2 = V_0^2(1+\varepsilon X)$

$$N_A = N_{A0}[1-X] \qquad N_B = N_{A0}[\theta_B - X] \qquad \theta_B = \frac{N_{B0}}{N_{A0}} = 1$$

$$-r_A = kC_A^2C_B = \frac{kN_A^2N_B}{V^3} = \frac{kN_{A0}^3[1-X]^3}{V_0^3(1+\varepsilon X)^{\frac{3}{2}}} \qquad N_{A0} = \left(\frac{y_{A0}P_0}{RT}\right)V_0$$

Therefore

$$-r_A = k\left(\frac{y_{A0}P_0}{RT}\right)\frac{[1-X]^3}{(1+\varepsilon X)^{\frac{3}{2}}}$$

$$-r_A = 5.03*10^{-9}\frac{[1-X]^3}{(1+3X)^{\frac{3}{2}}}\frac{lb\,mol}{ft^3\,\sec}$$

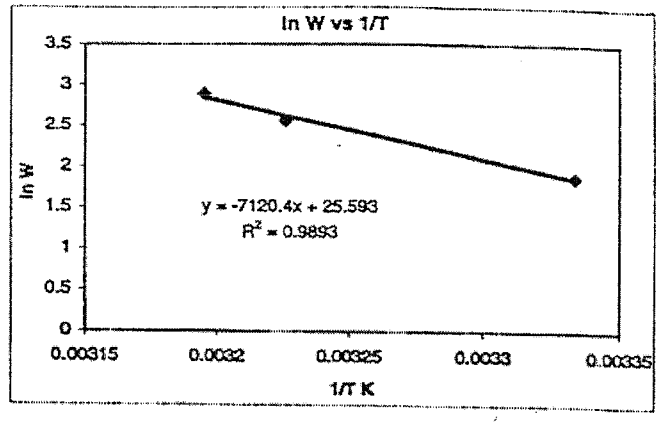
P3-17 (b)

$$V^2 = V_0^2(1+\varepsilon X)$$
$$0.2^2 = 0.15^2(1+\varepsilon X)$$
$$X = 0.259$$
$$-r_A = 8.63*10^{-10}\frac{lb\,mol}{ft^3\,\sec}$$

P3-18 No solution will be given.
P3-19 No solution will be given.
P3-20 No solution will be given.

CDP3-A

W	lnW	T	1/T
6.5	1.871802	300	0.003333
13	2.564949	310	0.003226
18	2.890372	313	0.003195



From the graph:
E = 7120

$$\ln W = -7120.4*\left(\frac{1}{41.5+273}\right)+25.593 = 2.95$$

$$W(41.5°C) = 19.2 cm/s$$

CDP3-B

Polanyi equation: $E = C - \alpha(-\Delta H_R)$
We have to calculate E for the reaction

$CH_3\bullet + RBr \rightarrow CH_3Br + R\bullet$

Given: $\Delta H_R = -6$ kcal/mol
From the given data table, we get

$6.8 = C - \alpha(17.5)$

and $6.0 = C - \alpha(20)$

=> C = 12.4 KJ/mol and $\alpha = 0.32$
Using these values, and $\Delta H_R = -6$ kcal/mol, we get **E = 10.48 KJ/mol**

CDP3-C (a)

A → B

Rate law at low temperature: $-r_A = kC_A$

The rate law t higher temperature must:
1) Satisfy thermodynamics relationships at equilibrium, and
2) Reduce to irreversible rate law when the concentration of one or more of the reaction products is zero.

Also, We know, $$K_C = \frac{C_{Be}}{C_{Ae}}$$

Rearranging, we get $$C_{Ae} - \frac{C_{Be}}{K_C} = 0$$

So, lets assume rate law as $-r_A = k_A\left(C_A - \frac{C_B}{K_C}\right)$

Also when $C_B = 0$, it satisfies the given rate law. Hence the proposed rate law is correct.

CDP3-C (b)

A + 2B → 2D

Rate law at low temperature: $-r_A = kC_A^{1/2}C_B$

Here, $K_C = \frac{C_{De}^{\ 2}}{C_{Ae}C_{Be}^{\ 2}}$

$$C_{Ae}C_{Be}^{\ 2} - \frac{C_{De}^{\ 2}}{K_C} = 0$$

$$-r_A = k_A\left(C_{Ae}C_{Be}^{\ 2} - \frac{C_{De}^{\ 2}}{K_C}\right)$$

But it does not satisfy the irreversible rate law at low temperatures.
Hence it is not correct
So, taking square root of K_C

$$\sqrt{K_C} = \frac{C_{De}}{C_{Ae}^{\ 1/2}C_{Be}}, \qquad C_{Ae}^{\ 1/2}C_{Be} - \frac{C_{De}}{\sqrt{K_C}} = 0$$

$$-r_A = k_A\left(C_{Ae}^{\ 1/2}C_{Be} - \frac{C_{De}}{\sqrt{K_C}}\right)$$

Which satisfies the irreversible rate law.
Hence it is the required rate law.

CDP3-C (c)

A + B → C + D

Irreversible rate law: $-r_A' = \frac{kP_AP_B}{1 + K_AP_A + K_BP_B}$

We know, $K_P = \frac{P_CP_D}{P_BP_A}$ or $P_BP_A - \frac{P_CP_D}{K_P} = 0$

Hence assume rate law as:

$$-r_A = \frac{k\left(P_AP_B - \frac{P_CP_D}{K_P}\right)}{1 + K_AP_A + K_BP_B + K_CP_C + K_DP_D}$$

Which satisfies both the above mentioned conditions.

CDP3-D

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

$Y_{NH_3,O} = 0.15$ P=8.2 atm T = 227°C = 500K

a) Assuming ideal gas law

$$C_{to} = \frac{n_{To}}{V_o} = \frac{P_o}{RT_o} = \frac{8.2\ atm}{0.082\ \frac{latm}{gmol°K}(500K)} = 0.2\ gmol/l$$

b) $C_{NH_3,O} = Y_{NH_3,O}\ C_{To} = (0.15)(0.2\ gmol/1) = 0.03\ gmol/1$

c) $NH_3 + \frac{5}{4}\ O_2 \longrightarrow NO + \frac{3}{2}\ H_2O$

Compound	Symbol	Initial	Change	Final
NH_3	A	0.15	$-0.15X$	$0.15(1-X)$
O_2	B	0.18	$-\frac{5}{4}(0.15X)$	$0.18-\frac{5}{4}(0.15X)$
NO	C	0	$+0.15X$	$0.15X$
H_2O	D	0	$+\frac{3}{2}(0.15X)$	$+\frac{3}{2}(0.15X)$
N_2	I	0.67	0	0.67
Total	T	1.00	$+ 1/4(0.15X)$	$1 + 1/4(0.15X)$

Initial $N_2 = 0.79(1-0.15) = 0.79(0.85) = 0.67$

Initial $O_2 = 0.85-0.67=0.18$

1) $P_i = y_i P = \frac{n_i}{n_T} P = 8.2\ atm\ (\frac{n_i}{1+[0.15/4]X})$

$$C_i = \frac{n_i}{V} = \frac{P_i}{RT} = \frac{n_i}{1 + 0.15/4\ X} \frac{8.2\ atm}{.082\ \frac{1\ atm}{gmol°K}(500K)} = 0.2\ \frac{gmol}{1}\ (\frac{n_i}{1 + 0.15/4\ X}$$

i	η_i	P_i (atm)	C_i
A	$0.15(1-X)$	$1.23\frac{1-X}{1+[0.15/4]X}$	$0.03\frac{1-X}{1+[0.15/4]X}$
B	$0.18-\frac{5}{4}(0.15X)$	$8.2(\frac{0.18-5/4(0.15X)}{1+[0.15/4]X})$	$(0\ 036-\frac{0.15}{4}X)/(1+\frac{0.15}{4}X)$
C	$0.15X$	$1.23\frac{X}{1+\left[\frac{0.15}{4}\right]X}$	$0.03X/1+\frac{0.15}{4}X$
D	$\frac{3}{2}(0.15X)$	$1.85\frac{X}{1+[0.15/4]X}$	$0.045/(1+\frac{0.15}{4}X)$
I	0.67	$5.49\frac{1}{1+[0.15/4]X}$	$0.133/(1+\frac{0.15}{4}X)$

check $P_{TOT} = \frac{1.23-1.23X+8.2(.18)-(8.2)(5/4)(0.15X)+1.23X+1.85X+5.49}{1+(0.15/4)X}$

$= \frac{8.2-0.313X}{1+(0.15/4)X} = 8.2$

$V = V_o\ (1+\frac{0.15}{4}X)$

2) Constant volume

$C_i = 0.2\ \eta_i$

$P_i = C_iRT = (0.082)(500)(0.2)\eta_i = 8.2\ \eta_i$

i	η_i	C_i	P_i
A	$0.15(1-X)$	$0.03\ (1-X)$	$1.23\ (1-X)$
B	$0.18-\frac{5}{4}(0.15X)$	$0.036-\frac{0.15}{4}X$	$8.2(0.18-\frac{5}{4}(0.15X)$
C	$0.15\ X$	$0.03\ X$	$1.23\ X$
D	$\frac{3}{2}(0.15X)$	$0.045\ X$	$1.85\ X$
I	0.67	0.133	5.49
		$0.199+0.008X$	$8.2-0.313\ X$

$= 0.2\ (1+\frac{0.15}{4}X)$

$P_{TOT} = 8.2 - 0.313\ X$ atm

3) Same at (1)

d) $4A+5B \rightarrow 4C+6D$

Mole balance for a PFR

$$\frac{dF_A}{dV} = -r_A$$

$$\frac{dF_b}{dV} = -r_B$$

$$\frac{dF_C}{dV} = -r_C$$

$$\frac{dF_D}{dV} = -r_D$$

Rate Law(assume elementary):

$$-r_A = kC_A^4 C_B^5$$

Combine with equation 3-40 and 3-48

$$\frac{dF_A}{dV} = k\left(\frac{P_{T0}}{RT_0}\right)^9\left(\frac{F_A}{F_A+F_B+F_C}\right)^4\left(\frac{F_B}{F_A+F_B+F_C}\right)^5$$

$$\frac{dF_B}{dV} = \frac{5}{4}k\left(\frac{P_{T0}}{RT_0}\right)^9\left(\frac{F_A}{F_A+F_B+F_C}\right)^4\left(\frac{F_B}{F_A+F_B+F_C}\right)^5$$

$$\frac{dF_C}{dV} = -k\left(\frac{P_{T0}}{RT_0}\right)^9\left(\frac{F_A}{F_A+F_B+F_C}\right)^4\left(\frac{F_B}{F_A+F_B+F_C}\right)^5$$

$$\frac{dF_D}{dV} = -k\left(\frac{P_{T0}}{RT_0}\right)^9\left(\frac{F_A}{F_A+F_B+F_C}\right)^4\left(\frac{F_B}{F_A+F_B+F_C}\right)^5$$

CDP3-E

$$A + 2B \longrightarrow C + D$$

a)

Species	Symbol	Initial moles	Change	Final moles	Concentration
Benzoyl chloride	A	N_{A0}	$-N_{A0}X$	$N_{A0}(1-X)$	$N_{A0}(1-X)/V$
Ammonia	B	$N_{A0}\theta_B$	$-2N_{A0}X$	$N_{A0}(\theta_B-2X)$	$N_{A0}(\theta_B-2X)/V$
Benzylamide	C	$N_{A0}\theta_C$	$N_{A0}X$	$N_{A0}(\theta_C+X)$	$N_{A0}(\theta_C+X)/V$
Ammonium Chloride	D	$N_{A0}\theta_D$	$N_{A0}X$	$N_{A0}(\theta_D+X)$	$N_{A0}(\theta_D+X)/V$

b) $C_{A0} = N_{A0}/V = 2$ gmol/l

$\theta_B = C_{B0}/C_{A0} = 6/2=3$

$$X = \frac{N_{A0} - N_A}{N_{A0}}$$

$\theta_C = \theta_D=0$

X=0.25

Final conc. of ammonia $= \frac{N_{A_0}}{V}(\theta_B-2X)=2(3-2(0.25))=5$gmol/l

Final conc. of benzylamide $= \frac{N_{A_0}}{V}(\theta_c+X) = 2\ (0 + 0.25) = 0.5$ gmol/l

c) Stoichiometric table for a flow system using ammonia as the basis

$$\frac{A}{2} + B \longrightarrow \frac{C}{2} + \frac{D}{2}$$

Species	Symbol	Entering	Change	Exit	Concentration
Ammonia	B	F_{B0}	$-F_{B0}X$	$F_{B0}(1-X)$	$F_{B0}(1-X)/v_o$
Benzo chloride	A	$\theta_A F_{B0}$	$-F_{B0}X/2$	$F_{B0}(\theta_A-X/2)$	$F_{B0}(\theta_B-X/2)/v_o$
Benzylamide	C	$\theta_C F_{B0}$	$F_{B0}X/2$	$F_{B0}(\theta_C+X/2)$	$F_{B0}(\theta_C+X/2)/v_o$
Ammonium Chloride	D	$\theta_D F_{B0}$	$F_{B0}X/2$	$F_{B0}(\theta_D+X/2)$	$F_{B0}(\theta_D+X/2)/v_o$

Table for the flow system using ammonia as the basis is different from the original in the following ways.

1) Molar flow rates considered rather than number of moles.

2) $\theta_i = F_{io}/F_{Bo}$, as opposed to N_{io}/N_{Ao}

3) Concentration found by dividing the exiting molar flow rate by the volumetric flow rate v_o.

CDP3-F

Given : A + B -> C taking place in a square duct.

$P_0 = 1$ atm. = constant

$k = 10^6$ ft^3/(lb.mole)(sec.)

$T = T_0 = 540°F = 1000°R$

$P_B^o = 0.25$ atm.

$F_{A0} = 1.5$ lb mole/sec.

(a) If B is at equilibrium in the gas phase throughout the reactor

$C_B = \frac{P_B^o}{RT}$ = constant. Since B maintains its equilibrium vapor pressure throughout the reactor, as soon as 1 molecule of B is consumed by the reaction, it is replaced by a molecule of B in the liquid. Hence, $\delta = 1 - 1 = 0$, $\varepsilon = Y_{A0}\delta$

$-r_A = k\, C_A\, C_B = k\, C_{BO}\, C_{AO}[1-X]$; Just inside the reactor,

$$C_{AO} = \frac{y_{AO} P_0}{RT} = \frac{(1-y_{BO})P_0}{RT}$$

$$\therefore\ -r_A = k\, C_A\, C_B = k\, y_{BO}[1-y_{BO}]\left[\frac{P_0}{RT}\right]^2 (1-X)$$

(b) At $X = 0.5$

$$-r_A = \frac{10^6 ft^3}{(1 lbmole)(sec)}\left[\frac{(.25\ atm)(.75\ atm)}{(.730\ \frac{atm\ ft^3}{lb\ mole\ ^\circ R} \times 1000^\circ R)^2}\right][0.5] = .174\ \frac{lbmole}{ft^3 sec.}$$

CDP3-G

a)

$$3\ Si\ HCl_3 + 3H_2 \rightarrow 2Si\ (S) + 7HCl + Si\ H_2\ Cl_2$$

Take $S_i\ HCl_3$ as basis

$$Si\ HCl_3 + H_2 \rightarrow \frac{2}{3}\ Si\ (s) + \frac{7}{3}\ HCl + \frac{1}{3}\ SiH_2Cl_2$$

Species	Symbol	Entering	Change	Leaving
$S_i\ HCl_3$ (g)	A	F_{AO}	$-F_{AO}X$	$F_A = F_{AO}(1-X)$
H_2 (g)	B	$F_{BO} = \theta_B F_{AO}$	$-F_{AO}X$	$F_B = F_{AO}(\theta_B - X)$
H_2HCl (g)	C	0	$+\frac{7}{3}F_{AO}X$	$F_C = \frac{7}{3}F_{AO}X$
$S_i\ H_2Cl_2$ (g)	D	0	$+\frac{1}{3}F_{AO}X$	$F_D = \frac{1}{3}F_{AO}X$
S_i (s)	S	0	$\frac{2}{3}F_{AO}X$	—

Assume isothermal and constant pressure. Neglect the vapor pressure of $S_i(s)$

$\theta_B = 1$ Stoichiometric feed

δ only involves the changes in gas phase

$$\varepsilon = y_{AO}\,\delta = \frac{1}{2}\left(\frac{1}{3} + \frac{7}{3} - 1 - 1\right)$$

$$\varepsilon = \frac{1}{2}\left(\frac{2}{3}\right) = \frac{1}{3}$$

$$C_{AO} = y_{AO}\frac{P_0}{R\,T_0} = \frac{1}{2}\left(\frac{2.0}{(0.082)(1327)}\right) \qquad C_{AO} = 0.0088 \text{ mol/dm}^3$$

$$C_A = \frac{F_A}{\upsilon} = C_{A0}\frac{(1 - X)}{(1 + \varepsilon X)} = \frac{0.0088\,(1 - X)}{1 + X/3}$$

$$C_B = \frac{F_B}{\upsilon} = C_A\frac{(\theta_B - X)}{(1 + \varepsilon X)} = \frac{0.0088\,(1 - X)}{1 + X/3}$$

$$C_C = \frac{F_C}{\upsilon} = \frac{7}{3}\frac{F_{A0}X}{\upsilon_0(1 + \varepsilon X)} = \frac{7}{3}C_{A0}\frac{X}{(1 + \varepsilon X)} = 0.021\frac{X}{(1 + X/3)}$$

$$C_D = \frac{F_D}{\upsilon} = \frac{1}{3}\frac{F_{A0}X}{\upsilon_0(1 + \varepsilon X)} = 0.0031\frac{X}{1 + X/3}$$

The solution to parts (b) and (c)

b) $2\,S_i HCl_3 + 2H_2 \rightarrow S_i(S) + 3HCl + S_i HCl_3$

and

c) $2\,S_i HCl_3 \rightarrow S_i + 2HCl + S_i HCl_4$

are similar to Part (a).

CDP3-H

$$4\,Cl_2 + CH_4 \longrightarrow CCl_4 + 4HCl$$

T = 75°C = 348 K P = 950 kPa = 9.39 atm

Cl_4 vapor pressure = 95 kPa = 0.94 atm = P_V

$$C_i = \frac{F_i}{v} = \frac{F_i}{v_o(1+\varepsilon X)} = \frac{F_i}{v_o}$$

So we can use the stoichiometric table, substituting C's for F's

i	F_i	C_i
A	$F_{AO}(1-X)$	$C_{AO}(1-X)$
B	$4F_{AO}(1-X)$	$4C_{AO}(1-X)$
C	$4F_{AO}X$	$4C_{AO}X$
D	$\frac{F_{AO}X}{5F_{AO}}$	$\frac{C_{AO}X}{5C_{AO}}$

where $C_{AO} = 0.0658$ gmol/l and $F_{AO} = 0.02631$ gmol/s

<u>After condensation</u>

$$v = v_o \frac{F_t}{F_{to}} = v_o \frac{F_{AO}(5-X)}{5F_{AO}(0.90)} = v_o \frac{5-X}{4.5}$$

$$C'_i = \frac{F_i}{v} = \frac{F_i}{v_o}\frac{(4.5)}{(5-X)}$$

Note: at $X = 0.5$ (beginning of condensation) $C_i = C'_i$

i	F_i	C_i
A	$5F_{A0}-F_{A0}X$	$C_{A0}(1-X)(4.5)/(5-X)$
B	$F_{A0}(5-X)$	$4C_{A0}(1-X)(4.5)/(5-X)$
C	$4F_{A0}X$	$4C_{A0}X(4.5)/(5-X)$
D	$0.1F_{A0}(5-X)/0.9$	$C_{A0}(5-X)(4.5)/(5-X)/9=0.5C_{A0}$
Total	$F_{A0}(5-X)+F_{A0}(5-X)/9$	$C_{A0}(5-X)^2/40.5$

where $F_{AO} = 0.02631$ gmol/S and $C_{AO} = 0.0658$ gmol/l

$$y_{DE} = \frac{P_V}{P} = \frac{95}{950} = 0.10$$

Stoich Table $CH_4 + 4Cl_2 \longrightarrow 4HCl + CCl_4$

Assume stoichiometric feed F_i

Species	Symbol	In	Change	Before Condensation $P_D < P_V$ remaining	After Condensation $P_D = P_V$ remaining
CH_4	A	F_{AO}	$-F_{AO}X$	$F_A = F_{AO}(1-X)$	$F_{AO}(1-X)$
Cl_2	B	$4F_{AO}$	$-4F_{AO}X$	$F_B = 4F_{AO}(1-X)$	$4F_{AO}(1-X)$
HCl_4	C	0	$+4F_{AO}X$	$F_C = 4F_{AO}X$	$4F_{AO}X$
CCl_4	D(g)	0	$+F_{AO}X$	$F_D = F_{AO}X$	$0.10F_T'$
	D(l)	0	—	—	—
	$F_{TO} = 5F_{AO}$			$F_T = 5F_{AO}$	$F_T' = 5F_{AO} - F_{AO}X + 0.10F_T'$
					$F_T' = \frac{F_{AO}(5-X)}{0.90}$

When condensation first begins $F_T = F_T'$

$$5F_{AO} = F_{AO}\frac{(5-X)}{0.90} \longrightarrow X_c = 0.50$$

Before Condensation

$$\varepsilon = y_{AO}\delta \qquad \delta = 0 \longrightarrow \varepsilon = 0$$

$\Delta T = \Delta P = 0 \longrightarrow$ Total concentration is constant

$$C_T = C_{To} = \frac{P_o}{RT_o} = \frac{9.39 \text{ atm}}{0.08205 \frac{\text{atm lit}}{\text{gmol K}} \times 348 \text{ K}} = 0.329 \frac{\text{gmol}}{\text{lit}}$$

$$C_{AO} = \frac{1}{5} C_{To} = \frac{0.329}{5} \text{ gmol/l} = 0.0658 \text{ gmol/l}$$

$$F_{AO} = C_{AO} v_o = (0.0658) \text{ gmol/l } (0.4) \text{ l/s} = 0.02631 \text{ gmol/s}$$

CDP3-I

$$C_2H_6(g) + 2Br_2(g) \longrightarrow C_2H_4Br_2(g,l) + 2HBr(g)$$

T + 200°C = 473 K P = 2500 kPa = 24.7 atm; $P_{V,C_2H_4Br_2}$ = 506.5 kPa

$$y_{DE} = \frac{P_v}{P} = \frac{506.5}{2500} = 0.203$$

Stoich table

$$C_2H_6(g) + 2\ Br_2(g) \longrightarrow 2\ HBr(g) + C_2H_4Br_2(g,l)$$

assume stoichiometric feed

Species	Symbol	In	Change	F_i before condensation P_D < P_V remaining	F'_i After condensation P_D = P_V remaining
C_2H_6	A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$	$F_{A0}(1-X)$
Br_2	B	$2F_{A0}$	$-2F_{A0}X$	$F_B = 2F_{A0}(1-X)$	$2F_{A0}(1-X$
HBr	C	0	$2F_{A0}X$	$F_C = 2F_{A0}X$	$2F_{A0}X$
$C_2H_4Br_2$	D(g)	0	$F_{A0}X$	$F_D = F_{A0}X$	$0.203F'_T$
	D(l)	0	-	-	-
		$F_{T0} = 3F_{A0}$		$F_T = 3F_{A0}$	$F'_T = 3F_{A0}-F_{A0}X+0.203F'_T$

When condensation first begins $F_T = F'_T$ $F_T' = \frac{F_{A0}(3-X)}{0.797}$

$$3F_{A0} = \frac{F_{A0}(3-X)}{0.797} \longrightarrow X_C = 0.609$$

Before condensation

$\varepsilon = y_{A0}\delta$ $\delta = 0$ $\longrightarrow \varepsilon = 0$

$\Delta T = \Delta P = 0$ So total concentration is constant

$$C_T = C_{To} = \frac{P_o}{RT_o} = \frac{24.7 \text{ atm}}{0.08205 \frac{\text{atm lit}}{\text{gmol K}} \times 473 \text{ K}} = 0.673 \text{ gmol/l}$$

$$C_{AO} = \frac{1}{3} C_{To} = \frac{0.673}{3} \text{ gmol/l} = 0.212 \text{ gmol/l}$$

i	F_i	C_i
A	$F_{A0(1-X)}$	$C_{A0}(1-X)(2.39)/(3-X)$
B	$2F_{A0}(1-X)$	$2C_{A0}(1-X)(2.39)/(3-X)$
C	$2F_{A0}X$	$2C_{A0}(X)(2.39)/(3-X)$
D	$F_{A0}(3-X)/3.93$	$C_{A0}(0.609)$
Total	$F_{A0}(3-X)/0.797$	

where $F_{AO} = 0.106$ gmol/s and $C_{AO} = 0.212$ gmol/l

X	F_A gmol/s	F_B gmol/s	F_C gmol/s	F_D gmol/s	F_T gmol/s	C_A gmol/l
X	$F_{AO}(1-X)$	$2F_{AO}(1-X)$	$2F_{AO}X$	$F_{AO}X$	$3F_{AO}$	$C_{AO}(1-X)$
	0.106	0.212	0	0	0.318	0.212
0.2	0.085	0.170	0.042	0.021	0.318	0.170
0.4	0.064	0.127	0.085	0.042	0.318	0.127
0.609	0.041	0.083	0.129	0.065	0.318	0.083
X	$F_{AO}(1-X)$	$2F_{AO}(1-X)$	$2F_{AO}X$	$F_{AO}\frac{(1-X)}{3.93}$	$F_{AO}\frac{(3-X)}{0.797}$	$C_{AO}\frac{(1-X)(2.39)}{(3-X)}$
0.609	0.041	0.083	0.129	0.065	0.318	0.083
0.8	0.021	0.042	0.170	0.059	0.293	0.039
1.0	0	0	0.212	0.054	0.266	0

C_B gmol/l	C_C gmol/l	C_D gmol/l
$2C_{AO}(1-X)$	$2C_{AO}X$	$C_{AO}X$
0.424	0	0
0.339	0.085	0.042
0.254	0.170	0.085
0.166	0.258	0.129
$2C_{AO}\frac{(1-X)(2.39)}{(3-X)}$	$2C_{AO}X\frac{(2.39)}{(3-X)}$	$C_{AO}(0.409)$
0.166	0.258	0.129
0.078	0.312	0.109
0	0.335	0.090

$$F_{AO} = C_{AO}\, v_o = (0.212)\ \text{gmol/l}\ (0.5)\ \text{l/s} = 0.106\ \text{gmol/s}$$

$$C_i = \frac{F_i}{v} = \frac{F_i}{v_o(1+\varepsilon X)} = \frac{F_i}{v_o}$$

So we can first use the stoichiometric table, substituting C's for F's

i	F_i	C_i
A	$F_{AO}(1-X)$	$C_{AO}(1-X)$
B	$2F_{AO}(1-X)$	$2C_{AO}(1-X)$
C	$2F_{AO}X$	$2C_{AO}X$
D	$F_{AO}X$	$C_{AO}X$
Total	$3F_{AO}$	$3C_{AO}$

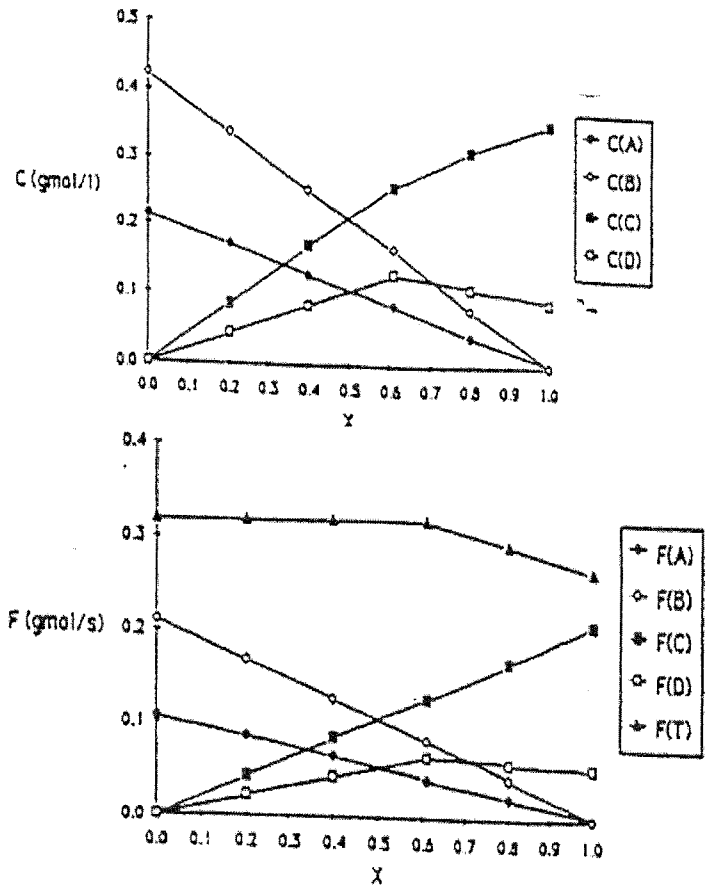
where $F_{AO} = 0.106$ gmol/s and $C_{AO} = 0.212$ gmol/s

After condensation

$$v = v_o \frac{F_t'}{F_{to}} = v_o \frac{F_{AO}}{3F_{AO}} \frac{(3-X)}{0.797} = v_o \frac{(3-X)}{2.39}$$

$$C_i' = \frac{F_i}{v} = \frac{F_i\ (2.39)}{v_o\ (3-X)}$$

Note that at X = 0.609 (beginning of condensation) $C_i = C_i'$



CDP3-J

Species	Symbol	Entering	Change	Leaving
SiH_4	A	F_{A0}	$-3F_{A0}$	$F_{A0}(1-X)$
NH_3	B	$F_{B0}=\theta_B F_{A0}$	$-4F_{A0}X$	$F_{A0}(\theta-4X/3$
Si_3N_4	C	0	$F_{A0}X$	$F_{A0}X/3$
H_2	D	0	$12F_{A0}X$	$4F_{A0}X$

$$\theta_B=\frac{F_{B0}}{F_{A0}}=1$$

$$y_{A0}=0.5$$

$$\varepsilon=y_{A0}\delta=0.5(1+12-3-4)=3$$

$$C_{A0}=y_{A0}C_{T0}=0.5\left(\frac{P_0}{RT_0}\right)=0.5\left(\frac{1Pa}{8314\frac{Pa*dm^3}{mol*k}*973K}\right)=6.18*10^{-8}$$

$$C_A=\frac{C_{A0}(1-X)}{1+\varepsilon X}=\frac{6.18*10^{-8}(1-X)}{1+3X}$$

$$C_B=\frac{1.68*10^{-8}\left(1-\frac{4X}{3}\right)}{1+3X}$$

$$C_C=\frac{2.06*10^{-8}X}{1+3X}$$

$$C_D=\frac{2.47*10^{-7}X}{1+3X}$$

$$C_{A0}=y_{A0}C_{T0}=0.5\left(\frac{P_0}{RT_0}\right)=0.5\left(\frac{1Pa}{8314\frac{Pa*dm^3}{mol*k}*973K}\right)=6.18*10^{-8}$$

$$C_A=\frac{C_{A0}(1-X)}{1+\varepsilon X}=\frac{6.18*10^{-8}(1-X)}{1+3X}$$

$$C_B=\frac{1.68*10^{-8}\left(1-\frac{4X}{3}\right)}{1+3X}$$

$$C_C=\frac{2.06*10^{-8}X}{1+3X}$$

$$C_D=\frac{2.47*10^{-7}X}{1+3X}$$

CDP3-K

$$CH_4(g) + 2\,Cl_2(g) \xrightarrow{h\nu} CH_2Cl_2(g,l) + 2HCl(g)$$

(a)

Component	Symbol	Initial moles	Change	Out
Cl2	A	1.0	-X	1-X
CH4	B	0.5	-0.5X	0.5(1-X)
CH2Cl2	C	0	+0.5X	0.5X
HCl	D	0	+X	X
Total	T	1.5		1.5

(b) $\delta = 1 + 2 - 1 - 2 = 0$; $y_{AO} = 1.0$

$\varepsilon = y_{AO}\,\delta = 0$

(c) System is gas phase until $P_c = 400$ mmHg

$$\frac{0.5X'}{1.5}(760) = 400$$

$\therefore X' = 1.5789 \longrightarrow CH_2Cl_2$ does not condense at 1 atm.

$$k = 0.2\left(\frac{dm^3}{gmole}\right)^2 \frac{1}{S} \longrightarrow \text{3rd order}$$

$$-r_A = k\,C_A^2\,C_B$$

$$C_A = C_{AO}(1-XA)$$

$$C_B = \frac{1}{2}C_{AO}(1-XA)$$

$$-r_A = \frac{1}{2}\,k\,C_{AO}^3(1-XA)^3$$

(d) $C_{AO} = y_{AO} \frac{P}{RT}$

$$C_{AO} = \frac{1}{1.5} = \frac{1}{0.08206} \quad \frac{1}{298.2} = 0.02724 \ \frac{\text{gmol}}{\text{dm}^3}$$

$$C_A = C_{AO} (1-X_A) = 0.02724 (1-0.6) = 0.01090 \ \frac{\text{gmol}}{\text{dm}^3}$$

(e) $-r_A = \frac{1}{2} k C_{AO}^3 (1-X_A)^3$

$$-r_A = \frac{1}{2} (0.2)^3 (0.02724)^3 (1-0.6)^3$$

$$-r_A = 1.297 \times 10^{-7} \ \frac{\text{gmol}}{\text{dm3 s}}$$

(f) $k = A \exp \{- \frac{E}{RT}\}$

$$A = 2 \times 10^{12} \ \frac{\text{dm}^6}{\text{s gmol}^2}$$

$$0.2 = 2 \times 10^{12} \exp \{\frac{- E}{(8.314)(298.2)}\} \quad \text{at } 25°C$$

$$E = 74212 \ \frac{J}{\text{gmol}}$$

(g) At 100°C = 373.2 °K

$$\frac{k_{100}}{k_{25}} = \exp \{- \frac{E}{R} (\frac{1}{373.2} - \frac{1}{298.2})\} = 409.8$$

$$k_{100°C} = 81.95 \ (\frac{\text{dm}^3}{\text{gmol}})^2 \frac{1}{S}$$

Solutions for Chapter 4 - Isothermal Reactor Design

P4-1 Individualized solution.

P4-2 (a)

Cooking food (effect of temperature), removing of stains with bleach (effect of bleach conc.), dissolution of sugar in coffee or tea.

P4-2 (b) Example 4-1

There would be no error! The initial liquid phase concentration remains the same.

P4-2 (c) Example 4-2

For 50% conversion, X = 0.5 and k = 0.311min^{-1}

$$F_{AO} = \frac{F_C}{X} = \frac{6.137}{0.5} = 12.27 lbmol/\min \qquad \text{Also, } v_{AO} = \frac{F_{AO}}{C_{AO}} = \frac{12.27 ft^3}{\min}$$

$v_o = v_{Ao} + v_{Bo} = 2v_{Ao}$ and also, $v_{Ao} = v_{Bo}$

$v_o = 24.52$ ft^3/min

Using Mole Balance,

$$V = \frac{v_o X}{k(1-X)} = \frac{24.52 \times 0.5}{0.311(0.5)} = 78.93$$

$$= 592 gal$$

This is less volume than Example 4-2 because the rate is higher.

P4-2 (d) Example 4-3

For P = 60atm,

$C_{AO} = 0.0415$ lbmol/ft^3 $\left(C_{AO} = \frac{y_{AO} P_O}{RT_O} = \frac{60}{0.73 \times 1980}\right)$

Using equation E-4-3.6, for X = 0.8

We see that the only thing that changes is C_{A0} and it increases by a factor of 10, therby decreasing the volume by a factor of 10.

$$V \propto \frac{1}{P}$$

P4-2 (e) Example 4-4

New $D_p = 3D_0/4$

Because the flow is turbulent

$$\beta_o \sim \frac{1}{D_p}$$

$$\beta_2 = \beta_1 \frac{D_{p2}}{D_{p1}} = 0.0775 \frac{1}{0.75} = 0.1033$$

$$y = \left(1 - \frac{2\beta L}{P_o}\right)^{\frac{1}{2}} = \left(1 - \frac{2 \cdot 0.103 \frac{atm}{ft} \cdot 60\,ft}{10\,atm}\right)^{\frac{1}{2}} = (-0.24)^{\frac{1}{2}}$$

Now $1 - \frac{2\beta_o L}{P_o} \leq 0$, so too much pressure drop P = 0 and the flow stops.

P4-2 (f) Example 4-5

For without pressure drop, conversion will remain same as example X = 0.82.
With Pressure drop,

$$\alpha_{new} = \frac{\alpha_o}{10} = 0.0037 kg^{-1}$$

For decrease in diameter,
$\beta_o = 2 \times 0.01244[266.9 \times 2 + 12920.8]$
$= 334.75 lb_f/ft^3 = 334.75(lb_f/ft^3) \times 1/144(ft^2/in^2) \times 1/14.7(atm/(lb_f/in^2)) = 0.15814 atm/ft$
$= 52.71$ kPa/m

For turbulent flow:

$$\beta \sim \frac{1}{D_P} \text{ and } \alpha \sim \frac{1}{P_0} \Rightarrow \alpha_2 = \alpha_1 \frac{P_{01}}{P_{02}} \frac{D_{p1}}{D_{p2}}$$

$$X = \frac{\frac{kC_{AO}W}{v_o}\left(1 - \frac{\alpha W}{2}\right)}{1 + \frac{kC_{AO}W}{v_o}\left(1 - \frac{\alpha W}{2}\right)} = \frac{4.6(0.949)}{1 + 4.6(0.949)}$$

X = 0.8136 – virtually the same

(2) Optimum diameter would be larger

$$\alpha = 0.037 \times \frac{52.71}{25.8} = 0.0756 kg^{-1}$$

if $D_{P2} = \frac{1}{2} D_{p1}$

$$\alpha_2 = \alpha_1 \frac{D_{p1}}{D_{p2}} = 2\alpha_1$$

$$1 - \frac{\alpha_2 W}{2} = 1 - \alpha_1 W = 1 - (0.037)(27.5) = -0.0175$$

Now 1-αW < 0, too much pressure drop due to higher superficial velocity.

P4-2 (g) Example 4-6

For turbulent flow

$$\alpha \sim \frac{1}{D_P} \quad \text{and} \quad \alpha \sim \frac{1}{P_0}$$

$$\alpha_2 = \alpha_1 \left(\frac{D_{P1}}{D_{P2}} \right) \left(\frac{P_{01}}{P_{02}} \right) = \alpha_1 \left(\frac{1}{\frac{1}{5}} \right) \left(\frac{1}{5} \right) = \alpha_1$$

Therefore there is no change.

P4-2 (h) Exmple 4-7

For pressure doubled and temperature decrease

$C_{TO} = 2*P_o/RT$ and T = 688K

See Polymath program P4-2-h.pol.

POLYMATH Results

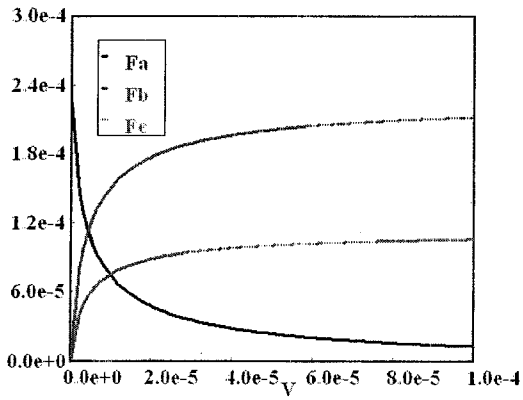
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	1.0E-04	1.0E-04
Fa	2.26E-04	1.363E-05	2.26E-04	1.363E-05
Fb	0	0	2.124E-04	2.124E-04
Fc	0	0	1.062E-04	1.062E-04
E	2.4E+04	2.4E+04	2.4E+04	2.4E+04
T	688	688	688	688
Cto	0.573773	0.573773	0.573773	0.573773
Ft	2.26E-04	2.26E-04	3.322E-04	3.322E-04
Ca	0.573773	0.0236075	0.573773	0.0236075
k	213.40078	213.40078	213.40078	213.40078
ra	-70.254837	-70.254837	-0.1189309	-0.1189309
Fao	2.26E-04	2.26E-04	2.26E-04	2.26E-04
rb	70.254837	0.1189309	70.254837	0.1189309
vo	3.939E-04	3.939E-04	3.939E-04	3.939E-04
rc	35.127419	0.0594654	35.127419	0.0594654
X	0	0	0.9395277	0.9395277
Tau	0	0	0.253044	0.253044
rateA	70.254837	0.1189309	70.254837	0.1189309

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Fa)/d(V) = ra
[2] d(Fb)/d(V) = rb
[3] d(Fc)/d(V) = rc

Explicit equations as entered by the user
[1] E = 24000
[2] T = 688
[3] Cto = 2*1641/8.314/T
[4] Ft = Fa+Fb+Fc
[5] Ca = Cto*Fa/Ft
[6] k = 0.29*exp(E/1.987*(1/500-1/T))
[7] ra = -k*Ca^2
[8] Fao = 0.000226
[9] rb = -ra
[10] vo = Fao/Cto
[11] rc = -ra/2
[12] X = 1-Fa/Fao
[13] Tau = V/vo
[14] rateA = -ra



P4-2 (i) Example 4-8 Individualized solution.

P4-2 (j) Example 4-9

Using trial and error, we get maximum feed rate of B = 0.0251dm^3/s to keep concentration of B 0.01mol/dm^3.

See Polymath program P4-2-j.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	500	500
ca	0.05	0.0063485	0.05	0.0063485
cb	0	0	0.009981	0.009981

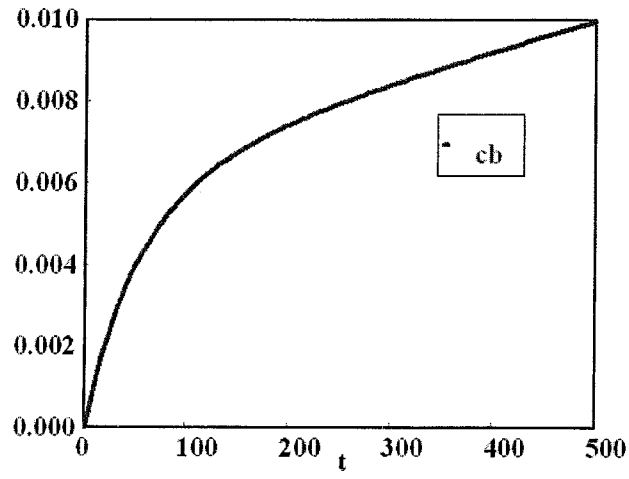
cc	0	0	0.0078965	0.0078965
cd	0	0	0.0078965	0.0078965
k	0.22	0.22	0.22	0.22
v00	0.0251	0.0251	0.0251	0.0251
cb0	0.025	0.025	0.025	0.025
v0	5	5	5	5
ca0	0.05	0.05	0.05	0.05
rate	0	0	3.91E-05	1.394E-05
v	5	5	17.55	17.55
x	0	0	0.5543321	0.5543321Differential

equations as entered by the user

[1] d(ca)/d(t) = -k*ca*cb-v00*ca/v
[2] d(cb)/d(t) = -k*ca*cb+v00*(cb0-cb)/v
[3] d(cc)/d(t) = k*ca*cb-v00*cc/v
[4] d(cd)/d(t) = k*ca*cb-v00*cd/v

Explicit equations as entered by the user

[1] k = .22
[2] v00 = 0.0251
[3] cb0 = 0.025
[4] v0 = 5
[5] ca0 = 0.05
[6] rate = k*ca*cb
[7] v = v0+v00*t
[8] x = (ca0*v0-ca*v)/(ca0*v0)



If the concentration of A is tripled the maximum feed rate becomes 0.064 dm^3/s

P4-2 (k through r) Individualized solution.

P4-3 Solution is in the decoding algorithm given with the modules.

P4-4

We have to find the time required to cook spaghetti in Cuzco, Peru.

Location	Elevation (km)	Pressure (mm Hg)	Boiling Point (°C)	Time (min)
Ann Arbor	0.21	739	99.2	15
Boulder	1.63	625	94.6	17
Cuzco	3.416	493	88.3	?

Assume reaction is zero order with respect to spaghetti conversion:

$$-r_A = k = Ae^{\frac{-E}{RT}} = -\frac{dC_A}{dt}$$

so that

$$-C\Big|_{C_{A0}}^{C_A} = \left(Ae^{\frac{-E}{RT}} \right) t$$

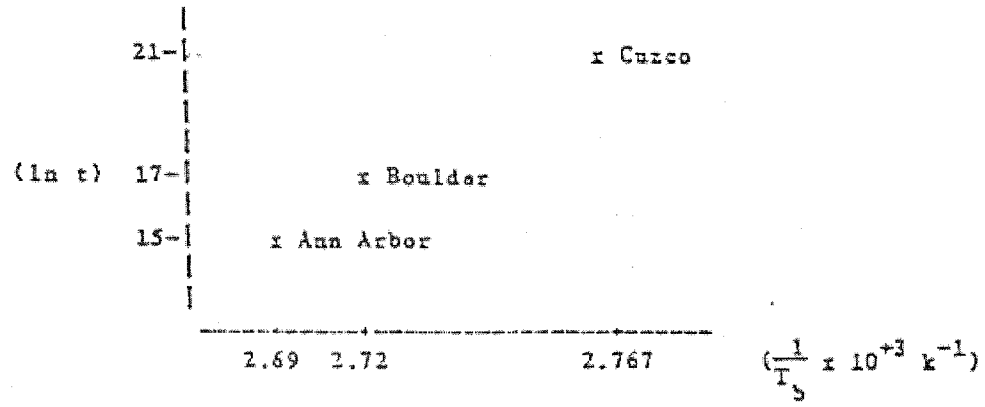
For complete conversion (i.e.: well cooked) $C_A = 0$ at time t.
Therefore

$$C_{A0} = tAe^{\frac{-E}{RT}}$$

$$\frac{C_{A0}}{A} = te^{\frac{-E}{RT}}$$

$$\ln\left(\frac{C_{A0}}{A}\right) = \ln k = \ln t - \frac{E}{R}\frac{1}{T_b}$$

Now, plot the natural log of the cooking time versus $1/T_b$ and get a linear relationship. Extrapolation to T_b = 88.3°C = 361.45 K yields t = 21 minutes.



P4-5 (a)

$A + B \Rightarrow C$ $C_{AO} = C_{BO} = 2$ mol/dm^3 $k_1 = 0.07$ dm^3/mol/min
$v_A = v_B = 5$ dm^3/min $E_A = 20{,}000$ cal/mol
$T_1 = 300$K

Rate Law: $r_A = -kC_AC_B$ $C_A = C_{AO}(1-X)$ $C_j = F_j/v_j$

CSTR V=200 dm^3 T=350 K

Using the Arrhenius equation at the CSTR temperature of 350K yields the new specific reaction rate.

$$k = 0.07\exp\frac{20{,}000}{1.987}\left(\frac{1}{300}-\frac{1}{350}\right)$$

$k = 8.45 \text{dm}^3/\text{mol} \cdot \text{min}$

CSTR Design Equation: $X = (V)(-r_A)/(F_{AO})$

$$X = \frac{V\left(kC_{A0}^2(1-X)^2\right)}{10}$$

$$X = \frac{(200dm^3)(8.45\frac{dm^3}{mol*\min})(1\frac{mol}{dm^3})^2(1-X)^2}{10\frac{mol}{\min}}$$

From the quadratic equation: X=0.925

PBR V=800 dm^3 T=300K

Design Equation:

$$F_{AO}\frac{dX}{dV} = -r_A$$

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} = \frac{kC_{AO}^2(1-X)^2}{F_{A0}}$$

$$dX = \frac{(0.07\frac{dm^3}{mol*\min})(1\frac{mol}{dm^3})^2(1-X)^2}{10\frac{mol}{\min}}dV$$

$$\frac{X}{1-X} = \frac{kC_{A0}^2V}{F_{A0}}$$

X=0.85

So, considering the above results, we will choose a CSTR.

P4-5 (b)

Batch Reactor V=200dm^3 N_{A0}=N_{B0}=200 moles X=0.90 Assume Isothermal

Design Equation:

$$t = N_{A0}\int_0^X \frac{dX}{-r_A V}$$

$$t = \frac{(200 moles)}{\left(8.45\frac{dm^3}{mol * \min}\right)\left(1\frac{mol}{dm^3}\right)^2 (200 dm^3)}\int_0^X \frac{dX}{(1-X)^2}$$

$$t = 1.06\min$$

P4-5 (c)

T=273K

Find the specific reaction rate at the new temperature of 273 K using the Arrhenius Equation.

$$k = 2.54\times10^{-3}$$

$$k = \frac{(200)(9)}{(2.54\times10^{-3})(200)} = 3543\min = 2.5\text{days}$$

P4-5 (d)

1) CSTR and PFR are connected in series:

$$X_{CSTR} = \frac{(200dm^3)(0.07dm^3/mol.\min)(1mol/dm^3)^2(1-X)^2}{10mol/\min}$$

Solving the quadratic equation, X_{CSTR} = 0.44

For PFR,

$$F_{A0}\frac{dX}{dV} = -r_A$$

$$dX = \frac{(0.07dm^3/mol/\min)C_{AO}(1-X)(1-X)^2}{10mole/\min}dV$$

$$\int_{0.44}^{X}\frac{dX}{(1-X)^3} = \frac{(0.07dm^3/mol/\min)(1mol/dm^3)^2(800dm^3)}{10mole/\min}$$

$$X = 0.736$$

2) when CSTR and PFR are connected in parallel,

$$X_{CSTR} = \frac{(200dm^3)(0.07dm^3/mol.\min)(1mol/dm^3)^2(1-X)^2}{5mol/\min.}$$

X_{CSTR} = 0.56

For PFR,

$$\int_0^X \frac{dX}{(1-X)^2} = \frac{(0.07 dm^3/mol.\min)(1 mol/dm^3)^2(800 dm^3)}{5 mol/\min}$$

$X_{PFR} = 0.92$

Hence, final conversion X = $\frac{0.56+0.92}{2}$ =0.74

P4-5 (e)

To process the same amount of species A, the batch reactor must handle

$$2M\left(\frac{5dm^3}{\min}\right)\left(\frac{60\min}{hr}\right)\left(\frac{24h}{day}\right) = 14400\frac{mol}{day}$$

If the reactants are in the same concentrations as in the flow reactors, then

$$V = \left(14400\frac{mol}{day}\right)\left(\frac{1dm^3}{mol}\right) = 14400\frac{dm^3}{day}$$

So the batch reactor must be able to process 14400 dm^3 every 24 hours.

Now we find the time required to reach 90% conversion. Assume the reaction temperature is 300K.

$$\frac{dX}{dt} = \frac{-r_A V}{N_{A0}} = \frac{kC_{A0}^2(1-X)V}{N_{A0}}$$

$$t_R = \frac{N_{A0}}{VkC_{A0}^2}\frac{X}{1-X}, \text{ and since } \frac{N_{A0}}{V} = C_{A0}$$

$$t_R = \frac{1}{kC_{A0}}\frac{X}{1-X} = \frac{1}{4.2\frac{dm^3}{mol\cdot hr} * 1\left(\frac{mol}{dm^3}\right)}\frac{0.9}{0.1} = 2.14hr$$

Assume that it takes three hours to fill, empty, and heat to the reaction temperature.

$t_f = 3$ hours

$t_{total} = t_R + t_f$

$t_{total} = 2.14$hours + 3 hours = 5.14 hours.

Therefore, we can run 4 batches in a day and the necessary reactor volume is

$$\frac{14400dm^3}{4} = 3600dm^3$$

Referring to Table 1-1 and noting that 3600 dm^3 is about 1000 gallons, we see that the price would be approximately $85,000 for the reactor.

P4-5 (f)

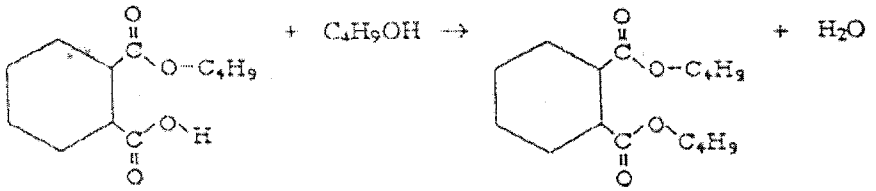
The points of the problem are:

1) To note the significant differences in processing times at different temperatures (i.e. compare part (b) and (c)).

2) That the reaction is so fast at 77°C that a batch reactor is not appropriate. One minute to react and 180 to fill and empty.

3) Not to be confused by irrelevant information. It does not matter if the reactor is red or black.

P4-6 (a)



Species	Symbol	Entering	Change	Leaving
MBP	A	F_{A0}	$-F_{A0}X$	$F_A=F_{A0}(1-X)$
butanol	B	$5F_{A0}$	$-F_{A0}X$	$F_B=F_{A0}(5-X)$
DBP	C	0	$F_{A0}X$	$F_C=F_{A0}X$
water	D	0	$F_{A0}X$	$F_D=F_{A0}X$

entering $F_{butanol} = 5\ F_{MBP,0}$

$-r_A = k\ C_A\ C_B$ elementary reaction

$-r_A = k\ (F_A/\upsilon)\ (F_A/\upsilon)$ for liquid systems

volumetric flow $\upsilon = \upsilon_0$

$$-r_A = k\ C_{AO}^2\ (1-X)\ (5-X)$$

$$V_{CSTR} = \frac{F_{A0}X}{-r_A} = \frac{F_C}{kC_{A0}^2(1-X)(5-X)}$$

$$\dot{m}_c = 4 \times 10^6 \frac{\text{lb}}{\text{yr}}, \quad F_C = 4 \times 10^6 \text{ lb/yr}, \quad 30\text{d/yr operation}$$

$$F_C = 4 \times 10^6 \frac{\text{lb}}{\text{yr}} \times \frac{1\text{ yr}}{30\text{d}} \frac{1\text{ d}}{24\text{ hr}} \times \frac{1\text{ lb mol}}{278\text{ lb}} = 20.0 \frac{\text{mol}}{\text{hr}}$$

$$V_{CSTR} = 1000 \text{ gal} \times \frac{1\text{ ft}^3}{7.48\text{ gal}} = 133.7 \text{ ft}^3$$

$$133.7 \text{ ft}^3 = \frac{20 \text{ lbmole/hr}}{1.2 \frac{\text{ft}^3}{\text{lbmole}\cdot\text{hr}} \left(\frac{0.2 \text{ lbmole}}{\text{ft}^3}\right)^2 (1-X)(5-X)}$$

$$X^2 - 6X + 1.89 = 0$$

$$X = 0.33$$

P4-6 (b)

To increase conversion, use PFR, higher temperature, or use better catalyst.

P4-6 (c)

MB $$V = \frac{F_{A0}X}{-r_A}$$

RL $$-r_A = kC_AC_B$$

S $$C_A = C_{A0}(1-X) \qquad C_B = C_{A0}(5-X) \qquad F_{A0} = \frac{1 \text{ lbmol}}{\text{min}} = \frac{60 \text{ lbmol}}{\text{hr}}$$

C $$V = \frac{F_{A0}X}{kC_{A0}^2(1-X)(5-X)}$$

E $$V = \frac{(60 \text{ lbmol/h})(.85)}{\left(\frac{1.2\text{ft}^3}{\text{lbmol}\cdot\text{h}}\right)\left(\frac{0.2\text{lbmol}}{\text{ft}^3}\right)^2 (1-.85)(5-.85)}$$

P4-6 (d)

PFR Design Equation

$$\frac{dX}{dV} = \frac{-r_a}{F_{A0}}$$

$$\frac{dX}{dV} = \frac{kC_{A0}^2(1-X)(5-X)}{F_{A0}}$$

$$V = 535 dm^3$$

P4-6 (e)

Mw (DBP) = 278 lb/lbmol V=1000gal = 133.7 ft³

therefore 14.4 X 10^3 lbmol of DBP need to be produced in 30 days

Mole balance:

$$t = N_{A0}\int_0^X \frac{dX}{-r_A V}$$

$$t = \frac{1}{kC_{A0}}\frac{1}{(5-1)}\ln\left(\frac{5-X}{5(1-X)}\right)$$

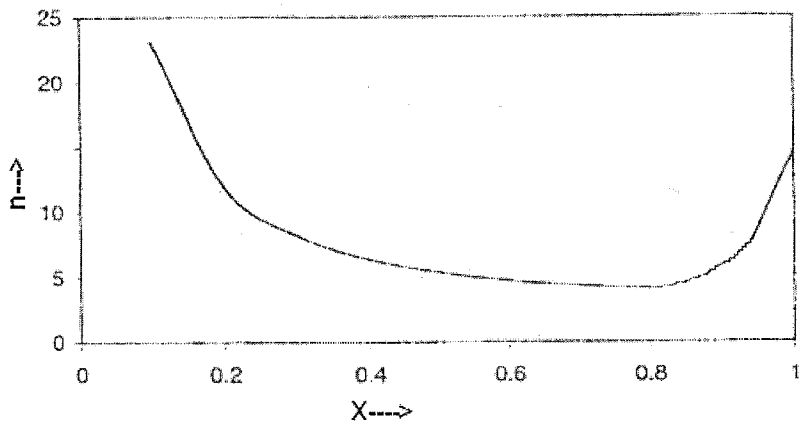
The above equation relates the reaction time for a batch and the conversion achieved during that batch. There is a trade-off between high conversion and few batches and low conversion but many batches per day. What conversion will result in the smallest number of reactors?

$$N_{A0} = 133.7\ \text{ft}^3 * C_{A0} \qquad C_{A0} = 0.2 lbmol/ft^3$$

$$\frac{Product}{reactor * day} = \frac{N_{A0}X * 24hr}{t_{batch}} = \frac{N_{A0}X24}{t_{rxn}+3} = \frac{N_{A0}X24}{\frac{1}{kC_{A0}}\ln\left(\frac{5-X}{5-5X}\right)+3} = f(X)$$

$$\frac{Moleproduct}{day} = \frac{4*10^6 lbs}{30 days}\frac{lbmol}{278 lb} = 480\frac{mol}{day}$$

$$n = \frac{480 mol/day}{f(X) mol/day/reactor}$$



The minimum occurs at X = 0.82 and corresponds to 4.192 or 5 reactors

P4-6 (f) Individualized solution

P4-6 (g) Individualized solution

P4-6 (h) Individualized solution

P4-7 (a)

Elementary gas phase reaction.

$A \rightarrow B + 2C$

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

$$-r_A = kC_A$$

$$C_A = C_{A0}\frac{(1-X)}{(1+\varepsilon X)} \qquad \varepsilon = y_{A1}\delta = (1)(2+1-1) = 2$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{10}{(0.082)(400)} = 0.3\frac{\text{mol}}{\text{dm}^3}$$

$$V = F_{A0}\int_0^x \frac{dX}{-r_A} = \frac{F_{A0}}{kC_{A0}}\int_0^x \frac{(1+\varepsilon X)}{(1-X)}dX$$

$$= \frac{F_{A0}}{kC_{A0}}\left[(1+\varepsilon)ln\frac{1}{1-X} - \varepsilon X\right]$$

$$= \left(\frac{(2.5\,\text{mol/min})}{(0.044\ \text{min}^{-1})(0.3\,\text{mol/dm}^3)}\right)\left((1+2)ln\frac{1}{1-.9} - 1.8\right)$$

$$= (189.4\ \text{dm}^3)(5.11)$$

$$V = 967\ \text{dm}^3$$

P4-7 (b)

$$V = \frac{F_{A0}X(1+\varepsilon X)}{C_{A0}k(1-X)}$$

$$k = 10^{-1}e^{\frac{85,000}{8.31}\left(\frac{1}{323}-\frac{1}{400}\right)} = 0.044$$

$$V = \frac{(2.5\,\text{mol/min})(0.9)(1+2(.9))}{(0.044\ \text{m}^{-1})(0.3\,\text{mol/dm}^3)(1-.9)} = 4772\ \text{dm}^3$$

P4-7 (c)

For $\alpha = 0.001\text{dm}^{-3}$

See Polymath program P4-7-c.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
v	0	0	500	500
x	0	0	0.656431	0.656431
y	1	0.1721111	1	0.1721111
Co	0.3	0.3	0.3	0.3
esp	2	2	2	2
alfa	0.001	0.001	0.001	0.001

C	0.3	0.0077768	0.3	0.0077768
k	0.044	0.044	0.044	0.044
r	-0.0132	-0.0132	-3.422E-04	-3.422E-04
fo	2.5	2.5	2.5	2.5

Differential equations as entered by the user

[1] d(x)/d(v) = -r/fo

[2] d(y)/d(v) = -alfa*(1+esp*x)/(2*y)

Explicit equations as entered by the user

[1] Co = 0.3

[2] esp = 2

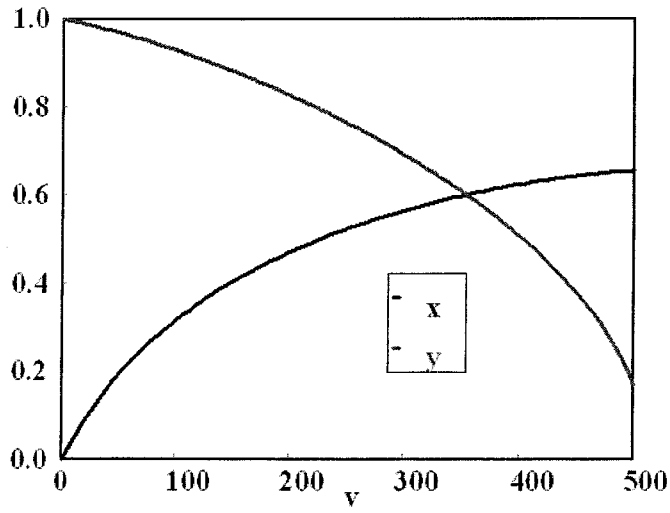
[3] alfa = 0.001

[4] C = Co*(1-x)*y/(1+esp*x)

[5] k = 0.044

[6] r = -k*C

[7] fo = 2.5



At V = 500,
x = 0.66, y = 0.17

P4-7 (d) Individualized solution

P4-7 (e)

$$A \leftrightarrow B + 2C$$

Rate Law: $-r_A = -k_f\left(C_A - C_B C_C^2/K_C\right) = 0$ (at equilibrium)

$K_C = 0.025$

Stoichiometry: $C_A = \frac{C_{Ao}(1-X)}{1+\varepsilon X}$, $C_B = \frac{C_{Ao}X}{1+\varepsilon X}$, $C_C = \frac{2C_{Ao}X}{1+\varepsilon X}$

$$K_C = \frac{C_B C_C^2}{C_A} = \left(\frac{C_{Ao}X}{1+\varepsilon X}\right)\left(\frac{2C_{Ao}X}{1+\varepsilon X}\right)^2\left(\frac{1+\varepsilon X}{C_{Ao}(1-X)}\right) = \frac{4C_{Ao}^2X^3}{(1+\varepsilon X)^2(1-X)}$$

$\varepsilon = 2$ and $C_{Ao} = 0.3$

$X_{eq} = 0.52$

$X = (0.90)X_{eq} = 0.47$

CSTR

$$-r_A = \frac{kC_{Ao}}{(1+\varepsilon X)}\left((1-X) - \frac{4C_{Ao}^2X^3}{(1+\varepsilon X)^2K_C}\right)$$

$$V = \frac{F_{Ao}X(1+\varepsilon X)}{kC_{Ao}\left((1-X) - \frac{4C_{Ao}^2X^3}{(1+\varepsilon X)^2K_C}\right)} = \frac{(2.5\ \text{mol/min})(0.47)(1+2(0.47))}{(0.044\ \text{min}^{-1})(0.3\ \text{mol/dm}^3)\left((1-0.47) - \frac{4(0.3\ \text{mol/dm}^3)^2(0.47)^3}{(1+2(0.47))^2 0.025}\right)}$$

$V = 1300\ \text{dm}^3$

PFR

$$F_{A_o}\frac{dX}{dV} = -r_A \quad \text{or} \quad \frac{dV}{dX} = \frac{F_{A_o}}{-r_A}$$

$$-r_A = \frac{kC_{A_o}}{(1+\varepsilon X)}\left((1-X) - \frac{4C_{A_o}^2X^3}{(1+\varepsilon X)^2K_C}\right)$$

Using these equations in Polymath we get the volume to be 290 dm^3.

P4-7 (f)

$A \Leftrightarrow B + 2C$

Rate Law: $-r_A = -k_f\left(C_A - C_BC_C^2/K_C\right) = 0$ (at equilibrium)

$K_C = 0.025$

Stoichiometry: $C_A = \frac{C_{A_o}(1-X)}{1+\varepsilon X}$, $C_B = \frac{C_{A_o}X}{1+\varepsilon X}$, $C_C = \frac{2C_{A_o}X}{1+\varepsilon X}$

$$K_C = \frac{C_BC_C^2}{C_A} = \left(\frac{C_{A_o}X}{1+\varepsilon X}\right)\left(\frac{2C_{A_o}X}{1+\varepsilon X}\right)^2\left(\frac{1+\varepsilon X}{C_{A_o}(1-X)}\right) = \frac{4C_{A_o}^2X^3}{(1+\varepsilon X)^2(1-X)}$$

$\varepsilon = 2$ and $C_{A_o} = 0.3$

$X_{eq} = 0.52$

$X = (0.90)X_{eq} = 0.47$

PFR

$$F_{A_o}\frac{dX}{dV} = -r_A \quad \text{or} \quad \frac{dV}{dX} = \frac{F_{A_o}}{-r_A}$$

$$-r_A = \frac{kC_{A_o}}{(1+\varepsilon X)}\left((1-X) - \frac{4C_{A_o}^2X^3}{(1+\varepsilon X)^2K_C}\right)$$

Using Polymath to solve the differential equation gives a volume of 290 dm^3
See Polymath program P4-7-f.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
X	0	0	0.47	0.47
V	0	0	290.23883	290.23883
Kc	0.025	0.025	0.025	0.025
Fao	2.5	2.5	2.5	2.5
Cao	0.3	0.3	0.3	0.3
k	0.044	0.044	0.044	0.044
e	2	2	2	2
ra	-0.0132	-0.0132	-9.391E-04	-9.391E-04

ODE Report (RKF45)

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

Explicit equations as entered by the user
[1] Kc = .025
[2] Fao = 2.5
[3] Cao = .3
[4] k = .044
[5] e = 2
[6] ra = -(k*Cao/(1+e*X))*((1-X)-(4*Cao^2*X^3)/((1+e*X)^2*Kc))

CSTR

$$-r_A = \frac{kC_{Ao}}{(1+\varepsilon X)}\left((1-X) - \frac{4C_{Ao}^2X^3}{(1+\varepsilon X)^2K_C}\right)$$

$$V = \frac{F_{Ao}X(1+\varepsilon X)}{kC_{Ao}\left((1-X) - \frac{4C_{Ao}^2X^3}{(1+\varepsilon X)^2K_C}\right)} = \frac{(2.5\ \text{mol/min})(0.47)(1+2(0.47))}{(0.044\ \text{min}^{-1})(0.3\ \text{mol/dm}^3)\left((1-0.47) - \frac{4(0.3\ \text{mol/dm}^3)^2(0.47)^3}{(1+2(0.47))^2 0.025}\right)}$$

$V = 1300\ \text{dm}^3$

PFR with pressure drop: Alter the Polymath equations from part (c).

See Polymath program P4-7-f-pressure.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
v	0	0	500	500
x	0	0	0.5077714	0.5077714
y	1	0.3181585	1	0.3181585
Kc	0.025	0.025	0.025	0.025
alfa	0.001	0.001	0.001	0.001
Cao	0.3	0.3	0.3	0.3
k	0.044	0.044	0.044	0.044
esp	2	2	2	2
fo	2.5	2.5	2.5	2.5
r	-0.0132	-0.0132	-1.846E-04	-1.846E-04

ODE Report (STIFF)

Differential equations as entered by the user
[1] d(x)/d(v) = -r/fo
[2] d(y)/d(v) = -alfa*(1+esp*x)/(2*y)

Explicit equations as entered by the user
[1] Kc = .025
[2] alfa = 0.001
[3] Cao = 0.3
[4] k = 0.044
[5] esp = 2
[6] fo = 2.5

[7] r = -(k*Cao/(1+esp*x))*(4*Cao^2*x^3/((1+esp*x)^2*Kc))

At V = 500 dm^3 X = 0.507 and y = 0.381

P4-7 (g)

Membrane reactor: $A \rightarrow B + 2C$

$C_A = C_O F_A/F_T$ $C_B = C_O F_B/F_T$ $C_C = C_O F_C/F_I$

$F_T = F_A + F_B + F_C$ and $-r_A = r_B = r_C/2$

Using polymath,

For PFR,

See Polymath program P4-7-g.pol.

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
v	0	0	1040	1040
Fa	2.5	1.3231889	2.5	1.3231889
Fb	0	0	0.3635477	0.0684325
Fc	0	0	2.3536223	2.3536223
Kc	0.025	0.025	0.025	0.025
Ft	2.5	2.5	3.7452437	3.7452437
Co	0.3	0.3	0.3	0.3
K	0.044	0.044	0.044	0.044
kc	0.08	0.08	0.08	0.08
ra	-0.0132	-0.0132	-3.827E-04	-3.827E-04
X	0	0	0.4707245	0.4707245

Differential equations as entered by the user

[1] d(Fa)/d(v) = ra

[2] d(Fb)/d(v) = -ra - kc*Co*Fb/Ft

[3] d(Fc)/d(v) = -2*ra

Explicit equations as entered by the user

[1] Kc = 0.025

[2] Ft = Fa+ Fb+ Fc

[3] Co = 0.3

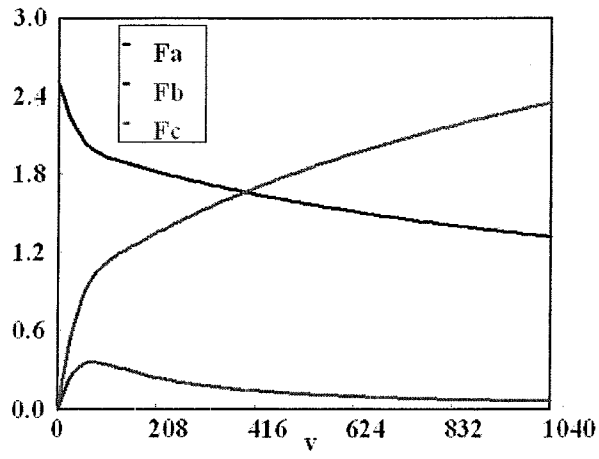
[4] K = 0.044

[5] kc = .08

[6] ra = - (K*Co)*(Fa/Ft- Co^2*Fb*Fc^2/(Kc*Ft^2))

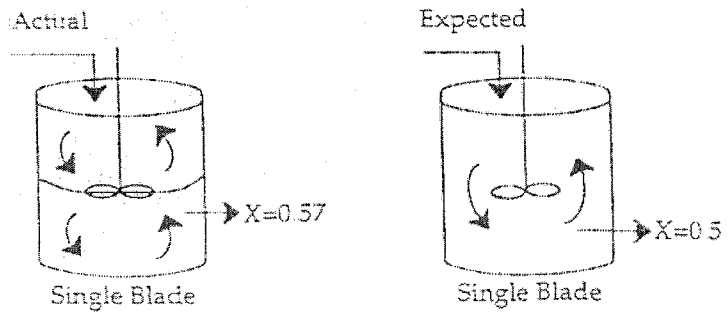
[7] X = 1 - Fa/2.5

Solving for when X = 0.47, we get V = 1040 dm^3



P4-8 (a)

The blades makes two equal volumes zones of 500gal each rather than one 'big' mixing zone of 1000gal.



Predicted

$$V = \frac{F_{A0}X}{C_{A0}^2 k(1-X)^2} = a\frac{X}{(1-X)^2}$$

$$[a] = \frac{F_{A0}}{C_{A0}^2 k} = \frac{\dfrac{\text{mol}}{\text{min}}}{\dfrac{\text{gal}}{\text{mol min}}\left(\dfrac{\text{mol}}{\text{gal}}\right)^2}$$

$$a = [\text{gal}]$$

$$1000\ \text{gal} = a\frac{X}{(1-X)^2} = a\frac{.5}{.25} = 2a$$

$$a = 500\ \text{gal}$$

$$1 - 3X_1 + X_1^2 = 0$$

$$X_1 = \frac{3\sqrt{9-4}}{2} = .38$$

Reactor 2

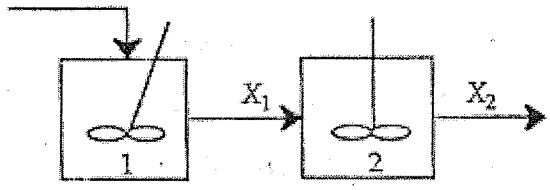
$$500 = \frac{500\ (X_2 - .38)}{(1-X_2)^2}$$

$$1 - 2X_2 + X_2^2 = X_2 - .38$$

$$X_2^2 - 3X + 1.38 = 0$$

$$X_2 = \frac{3 \pm \sqrt{9 - 4(1.38)}}{2} = .57$$

Measured



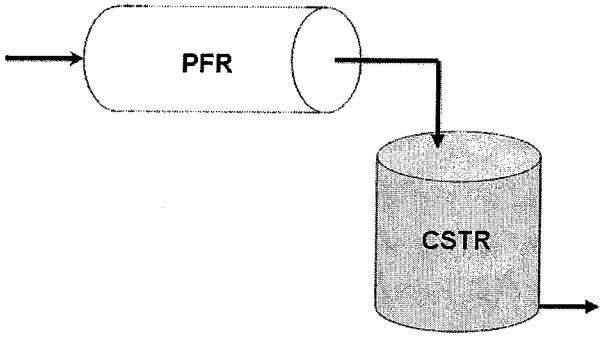
$$V = a\frac{X}{(1-X)^2} \quad \text{For Reactor 1}$$

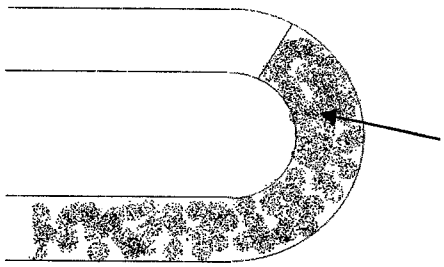
$$500\ \text{gal} = \frac{500\ \text{gal}\ X_1}{(1-X_1)^2}$$

$$1 - 2X_1 + X_1^2 = X_1$$

P4-8 (b)

A CSTR is been created at the bend due to backmixing, so the effective arrangement is a PFR is in series with a CSTR.





CSTR zone created due to backmixing

$A \rightarrow B$

$k = 5\ \text{min}^{-1}$ $\quad v_o = 5\ \text{dm}^3/\text{min}.$

$X_{expected} = 0.632 \quad X_{actual} = 0.586$

$$V = \int_0^X \frac{F_{AO}dX}{-r_A} = \frac{v_o}{k}\ln\left[\frac{1}{1-X_{Expected}}\right] = \frac{5}{5}\ln\left(\frac{1}{1-.632}\right) = 1.0$$

Now,

For PFR, $V_P = \ln\left(\frac{1}{1-X_1}\right)$ 1

For CSTR, $V_C = \frac{F_{AO}(X_{actual} - X_1)}{-r_A} = \frac{(X_{actual} - X_1)}{(1-X_{actual})}$ 2

Also, $\frac{V_P}{V} + \frac{V_C}{V} = 1$ 3

Solving 1, 2 and 3 by using polymath,

See Polymath program P4-8-b.pol.

POLYMATH Results

NLES Solution

Variable	Value	f(x)	Ini Guess
X1	0.350949	3.148E-10	0
Vc	0.567756	-3.297E-14	1
V	1		
X2	0.586		
Vp	0.432244		

NLES Report (safenewt)

Nonlinear equations

[1] f(X1) = ln(1/(1-X1)) -Vp = 0

[2] f(Vc) = (X2-X1)/(1-X2) - Vc = 0

Explicit equations

[1] V = 1

[2] X2 = .586

[3] Vp = V - Vc

$V_C = 0.57$ dm^3 ; $V_P = 0.43$ dm^3 ; $X_1 = 0.35$

P4-8 (c)

$C_{AO} = 2$ mol/dm^3

$A \rightarrow B$

Assuming 1st order reaction,

For CSTR, $\tau = \frac{C_{AO}X}{-r_A}$

$-r_A = kC_A = kC_{AO}(1-X)$

$\Rightarrow \tau k = \frac{X}{1-X} = \frac{0.4}{0.6} = 0.67$

For PFR, $V = F_{A0}\int_0^X \frac{dX}{kC_{A0}(1-X)}$, $\tau k = \int_0^X \frac{dX}{1-X}$

$\Rightarrow X_{PFR} = 1 - \exp(-\tau k) = 1\text{-}\exp(-0.67) = 0.486$

Now assuming 2nd order reaction,

For CSTR, Now, assuming 2nd order reaction,

For CSTR, $\tau = \dfrac{C_{AO}X}{-r_A}$

$$-r_A = kC_A^2 = kC_{AO}^2(1-X)^2$$

$$\Rightarrow \tau kC_{AO} = \frac{X}{(1-X)^2} = \frac{0.4}{0.6^2} = 1.111$$

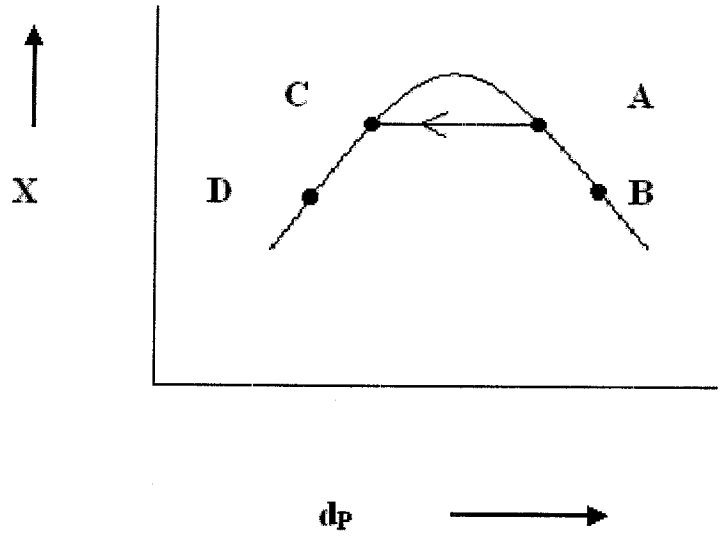
For PFR, $\tau = \dfrac{1}{kC_{AO}}\displaystyle\int_0^X \frac{dX}{(1-X)^2} = \frac{1}{kC_{AO}}\frac{X}{1-X}$

$$\Rightarrow X = 1 - \frac{1}{1+\tau kC_{AO}} = 1 - \frac{1}{2.111} = .526$$

So, while calculating PFR conversion they considered reaction to be 1st order. But actually it is a second order reaction.

P4-8 (d)

A graph between conversion and particle size is as follows: Originally we are at point **A** in graph, when particle size is decreased by 15%, we move to point **B,** which have same conversion as particle size at **A**. But when we decrease the particle size by 20%, we reach at point **C**, so a decrease in conversion is noticed. Also when we increase the particle size from position A, we reach at point **D,** again there is a decrease in the conversion.



P4-9

$$A \Leftrightarrow B$$

$T_o = 300K$ $K_{CO}(300K) = 3.0$ $V = 1000gal = 3785.4\ dm^3$

Mole balance: $V = \dfrac{F_{AO}X}{-r_A}$

Rate law: $$-r_A = k_O\left[C_A^2 - \frac{C_B^2}{K_C}\right]$$

Stoichiometry: $C_A = C_{AO}(1-X)$ and $C_B = C_{BO}X$

$$\Rightarrow \quad V = \frac{F_{AO}}{k_O C_{AO}^{\ 2}} \frac{X}{\left[(1-X)^2 - \frac{X^2}{K_C}\right]}$$

$$Z = \frac{F_{AO}}{k_O C_{AO}^{\ 2}} = \frac{V\left[(1-X)^2 - \frac{X^2}{K_C}\right]}{X} = \frac{3785.4}{0.4}\left[0.6^2 - \frac{0\,4^2}{3}\right]$$

$$Z = 2902.2 dm^3$$

Now using: $$V = \left(\frac{Z}{z}\right)\frac{X}{\left[(1-X)^2 - \frac{X^2}{K_C}\right]} \quad \Rightarrow \quad f(X) = 0 = V - \left(\frac{Z}{z}\right)\frac{X}{\left[(1-X)^2 - \frac{X^2}{K_C}\right]}$$

where $$z = \frac{k}{k_O} = \exp\left(\frac{E}{R}\left[\frac{1}{T_O} - \frac{1}{T}\right]\right)$$ and

$$K_C = K_{CO}\exp\left(\frac{\Delta H_{RX}}{R}\left[\frac{1}{T_O} - \frac{1}{T}\right]\right)$$

Solving using polymath to get a table of values of X Vs T.

See Polymath program P4-9 pol

POLYMATH Results

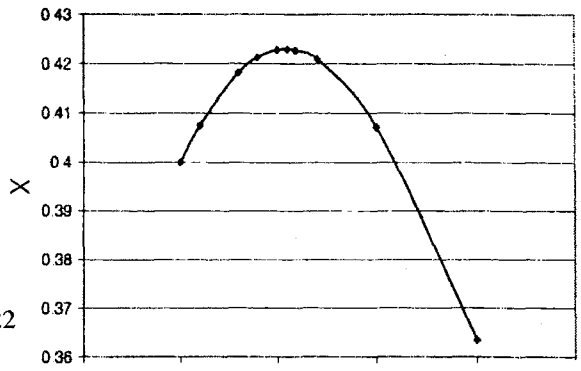
NLE Solution

Variable	Value	f(x)	Ini Guess
X	0.4229453	3.638E-12	0.5
To	300		
T	305.5		
z	2902.2		
V	3785.4		
E	1.5E+04		
R	2		
y	1.5684405		
Kco	3		
Hrx	-2 5E+04		
Kc	1 4169064		

NLE Report (safenewt)

Nonlinear equations

[1] f(X) = (z/y)*X/((1-X)^2 - X^2/Kc) -V = 0



Explicit equations
[1] To = 300
[2] T = 305.5
[3] z = 2902.2
[4] V = 3785.4
[5] E = 15000
[6] R = 2
[7] y = exp(E/R*(1/To-1/T))
[8] Kco = 3
[9] Hrx = -25000
[10] Kc = Kco*exp(Hrx/R*(1/To-1/T))

T(in K)	X
300	0.40
301	0.4075
303	0.4182
304	0.4213
305	0.4228
305.5	0.4229
305.9	0.4227
307	0.421
310	0.4072
315	0.3635

We get maximum X = 0.4229 at T = 305.5 K.

P4-10 (a)

For substrate:

Cell: $v_o C_C = r_g V$

$F_{SO} - F_S + r_s V = 0$

$$(C_{SO} - C_S)v_O = r_g V = VY_{S/C}\left[\frac{\mu_{max} C_S}{K_M + C_S} C_C\right]$$

P4-10 (b)

$$C_C = Y_{C/S}[C_{SO} - C_S]$$

$$(C_{SO} - C_S)v_O - VY_{S/C}\left[\frac{\mu_{MAX} C_S}{K_M + C_S} C_C\right] = 0$$

$$\Rightarrow \quad (C_{SO} - C_S)v_O - VY_{C/S}\left[\frac{\mu_{MAX} C_S}{K_M + C_S}\right](C_{SO} - C_S) = 0$$

$$(30 - C_S)5 - 25 \times 0.8 \times \left[\frac{0.5 \times C_S}{5 + C_S}\right](30 - C_S) = 0$$

Solving we get $C_S = 5.0$ g/dm^3 or 30 g/dm^3. if $C_S = C_{S0}$ no reaction has occurred so the only valid answer is $C_S = 0.5$ g/dm^3.

P4-10 (c)

$C_C = Y_{C/S}(C_{SO} - C_S)$
$= 0.8(30 - 5.0)$g/dm^3 = 20 g/dm^3.

P4-10 (d)

$v_{new} = v_o/2 = 2.5$ dm^3/h
Using equation from above, we get $C_S = 1.67$ g/dm^3 and $C_C = 22.67$ g/dm^3

P4-10 (e)

$V_{new} = V_o/3 = 25/3$ dm^3
Using equation from above, we get $C_S = 3.0$ g/dm^3 and $C_C = 21.6$ g/dm^3

P4-10 (f)

For batch reactor:

$C_{SO} = 30$ g/dm^3 $C_{CO} = 0.1$ g/dm^3
$C_C = C_{C0} + Y_{C/S}(C_{SO} - C_S)$
$V = 10$ dm^3

See Polymath program P4-10-f.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	15	15
Cs	30	0.0382152	30	0.0382152
Cso	30	30	30	30
Ycs	0.8	0.8	0.8	0.8
Km	5	5	5	5
Umax	0.5	0.5	0.5	0.5
Cco	0.1	0.1	0.1	0.1
Cc	0.1	0.1	24.069428	24.069428

rg	0.0428571	0.0428571	5.4444349	0.0912841
rs	-0.0535714	-6.8055436	-0.0535714	-0.1141052
negative_	0.0535714	0.0535714	6.8055436	0.1141052

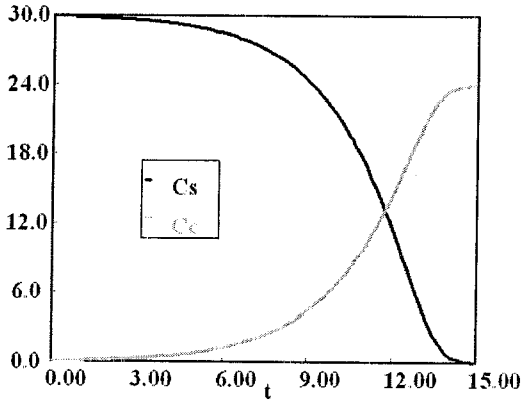
ODE Report (RKF45)

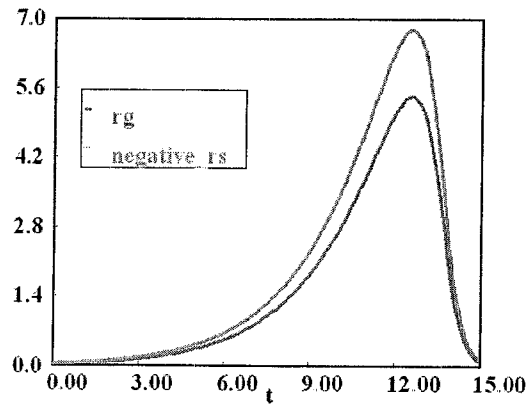
Differential equations as entered by the user

[1] d(Cs)/d(t) = rs

Explicit equations as entered by the user

[1] Cso = 30
[2] Ycs = 0.8
[3] Km = 5
[4] Umax = 0.5
[5] Cco = 0.1
[6] Cc = Cco+Ycs*(Cso-Cs)
[7] rg = (Umax*Cs/(Km+Cs))*Cc
[8] rs = -(1/Ycs)*rg
[9] negative_rs = -rs





P4-10 (g)

Graphs should look the same as part (f) since reactor volume is not in the design equations for a constant volume batch reactor.

P4-11

Gaseous reactant in a tubular reactor: A → B

$-r_A = kC_A$

$k = 0.0015\,\text{min}^{-1}$ at 80°F

$E = 25{,}000\dfrac{cal}{g\,mol}$ $\quad X = 0.90$ $\quad M_B = 1000\dfrac{lb}{hr}$

$MW_A = MW_B = 58\dfrac{lb}{lb\,mol}$ $\quad D_t = 1$ inch (I.D.) $\quad L = 10\,ft$

$P = 132\ psig = 146.7\ psia$ $\quad T = 260°F = 720°R$ $\quad n_t =$ number of tubes

$$F_B = \frac{1000\frac{lb}{hr}}{58\frac{lb}{lb\,mol}} = 17.21\frac{lb\,mol}{hr} \qquad F_{A0} = \frac{F_B}{X} = \frac{17.21\frac{lb\,mol}{hr}}{0.9} = 19.1\frac{lb\,mol}{hr}$$

For a plug flow reactor:

$$V = \frac{n_t \pi D_t^2 L}{4} = F_{A0}\int_0^{0.9}\frac{dX}{-r_A}$$

$$\delta = 1-1 = 0 \qquad y_A = 1.0 \qquad \varepsilon = y_A\delta = 0$$

$$-r_A = kC_{A0}(1-X) \qquad C_{A0} = \frac{P_A}{RT} = \frac{P}{RT}$$

$$V = F_{A0}\int_0^{0.9}\frac{dX}{-r_A} = F_{A0}\int_0^{0.9}\frac{dX}{kC_{A0}(1-X)} = \frac{F_{A0}}{kC_{A0}}\ln\left(\frac{1}{1-0.9}\right) = \frac{F_{A0}RT}{kP}\ln 10$$

At $T_2 = 260°F = 720°R$, with $k_1 = 0.0015\ min^{-1}$ at $T_1 = 80°F = 540°R$,

$$k_2 = k_1\exp\left(\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right) = 0.0015\exp\left(\frac{25000}{1.104}\left(\frac{1}{540}-\frac{1}{720}\right)\right) = 53.6\,min^{-1}$$

$$k_2 = 53.6\,min^{-1} = 3219\,hr^{-1}$$

$$V = \frac{F_{A0}RT}{kP}\ln 10 = \frac{\left(19.1\frac{lb\,mol}{hr}\right)\left(10.73\frac{ft^3\ psia}{lb\,mol\,°R}\right)(720°R)}{\left(3219\,hr^{-1}\right)(146.7\,psia)}\ln 10$$

$$V = 0.72\,ft^3$$

$$V = \frac{n_t \pi D_t^2 L}{4}$$

$$n_t = \frac{4V}{\pi D_t^2 L} = \frac{4\left(0.72\,ft^3\right)}{\pi\left(\frac{1}{12}\,ft\right)^2(10\,ft)} = 13.2$$

Therefore 14 pipes are necessary.

P4-12

A → B/2

Stoichiometry

$$\delta = \frac{1}{2} - 1 = -\frac{1}{2}$$

$$y_{A0} = \frac{F_{A0}}{F_{A0} + F_{B0} + F_{C0}} = \frac{1}{2}$$

$$\epsilon = y_{A0}\delta = -1/4$$

Mole Balance

$$V_{PFR} = F_{A0} \int_0^X \frac{dX}{-r_A}$$

Rate Law (elementary reaction)

$$-r_A = kC_A^2 = \frac{kC_{A0}^2(1-X)^2}{(1+\epsilon X)^2}$$

Combining

$$\frac{V_{PFR}kC_{A0}^2}{F_{A0}} = \int_0^X \frac{(1-X)^2}{(1+\epsilon X)^2} dX = 2\epsilon(1+\epsilon)ln(1-X) + \epsilon^2 X + \frac{(1+\epsilon)^2 X}{1-X}$$

(for the integration, refer Appendix A)
from the Ideal Gas assumption,

$$C_{AO} = y_{AO}C_{TO}$$

Substituting Eq.(5), X = 0.8 and ϵ = -1/4 to Eq. (4) yields,

$$\frac{V_{PFR}ky_{AO}^2C_{TO}^2}{F_{AO}} = 2(-1/4)(1-1/4)\ln(1-0.8) + (-1/4)^2 0.8 + \frac{(1-1/4)^2 0.8}{1-0.8} = 2.9 \quad \text{.....(6)}$$

Molar flow rate of A cut in half,

$$F'_{A0} = \frac{1}{2}F_{A0}$$

$$y'_{A0} = \frac{F'_{A0}}{F'_{A0} + F_{B0} + F_{C0}} = \frac{1}{3}$$

$$\epsilon' = y'_{A0}\delta = -1/6$$

From Eq. (4),

$$\frac{V_{PFR}kC'^2_{A0}}{F'_{A0}} = 2\epsilon'(1+\epsilon')ln(1-X') + \epsilon'^2 X' + \frac{(1+\epsilon')^2 X'}{1-X'}$$

$$\frac{V_{PFR}ky'^2_{AO}C'^2_{TO}}{F'^2_{AO}} =$$

$$2\epsilon'(1+\epsilon')ln(1-X') + \epsilon'^2X' + \frac{(1+\epsilon')^2X'}{1-X'}$$

$$\frac{8}{9}\frac{V_{PFR}ky_{AO}^2C_{TO}^2}{F_{AO}} = \frac{8}{9}(2.9) = 2.58 =$$

$$2(-1/6)(1-1/6)ln(1-X') + (-1/6)^2X' + \frac{(1-1/6)^2X'}{1-X'}$$

Polymath Non-Linear Equation Solver, $X' = 0.758$

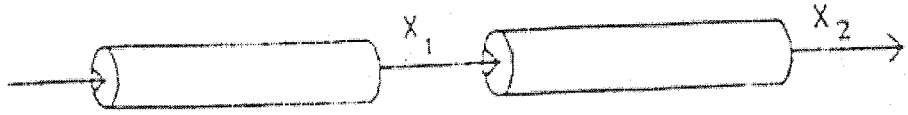
P4-13

Given: The metal catalyzed isomerization $A \Leftrightarrow B$, liquid phase reaction

$$-r_A = k_1\left(C_A - \frac{C_B}{K_{eq}}\right) \text{ with } K_{eq} = 5.8$$

For a plug flow reactor with $y_A = 1.0$, $X_1 = 0.55$

Case1: an identical plug flow reactor connected in series with the original reactor.



Since $y_A = 1.0$, $\theta_B = 0$. For a liquid phase reaction $C_A = C_{A0}(1-X)$ and $C_B = C_{A0}X$

$$-r_A = kC_{A0}\left((1-X) - \frac{X}{K_{eq}}\right)$$

For the first reactor,

$$V_1 = F_{A0}\int_0^{X_1}\frac{dX}{-r_A} = F_{A0}\int_0^{X_1}\frac{dX}{kC_{A0}\left((1-X)-\frac{X}{K_{eq}}\right)} \text{ or}$$

$$\frac{kC_{A0}V_1}{F_{A0}} = \int_0^{X_1}\frac{dX}{1-\left(1+\frac{1}{K_{eq}}\right)X} = -\frac{1}{1+\frac{1}{K_{eq}}}\ln\left[1-\left(1+\frac{1}{K_{eq}}\right)X\right]\Bigg|_0^{X_1}$$

$$\frac{kC_{A0}V_1}{F_{A0}} = -\frac{1}{1+\frac{1}{K_{eq}}}\ln\left[1-\left(1+\frac{1}{K_{eq}}\right)X_1\right] = -0.853\ln(.355) = 0.883$$

Take advantage of the fact that two PFR's in series is the same as one PFR with the volume of the two combined.

$V_F = V_1 + V_2 = 2V_1$ and at V_F $X = X_2$

$$\frac{kC_{A0}V_F}{F_{A0}} = \int_0^{X_F}\frac{dX}{1-\left(1+\frac{1}{K_{eq}}\right)X} = -\frac{1}{1+\frac{1}{K_{eq}}}\ln\left[1-\left(1+\frac{1}{K_{eq}}\right)X\right]\Bigg|_0^{X_F}$$

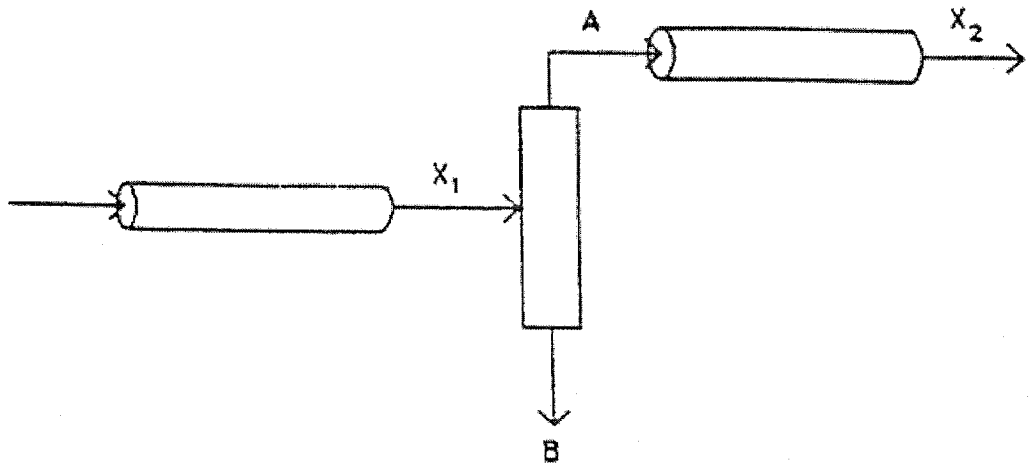
$$\frac{kC_{A0}V_F}{F_{A0}} = 2\frac{kC_{A0}V_1}{F_{A0}} = -\frac{1}{1+\frac{1}{K_{eq}}}\ln\left[1-\left(1+\frac{1}{K_{eq}}\right)X_2\right]$$

$$2\frac{kC_{A0}V_1}{F_{A0}} = 2(0.883) = 1.766$$

$$1.766 = -\frac{1}{1+\frac{1}{5.8}}\ln\left[1-\left(1+\frac{1}{5.8}\right)X_2\right]$$

$X_2 = 0.74$

Case 2: Products from 1st reactor are separated and pure A is fed to the second reactor,



The analysis for the first reactor is the same as for case 1.

$$\frac{kC_{A0}V_1}{F_{A0}} = -\frac{1}{1+\frac{1}{K_{eq}}}\ln\left[1-\left(1+\frac{1}{K_{eq}}\right)X_1\right]$$

By performing a material balance on the separator, $F_{A0,2} = F_{A0}(1-X_1)$

Since pure A enters both the first and second reactor $C_{A0,2} = C_{A0}$, $C_{B0,2} = 0$, $\theta_B = 0$

$C_A = C_{A0}(1 - X)$ $C_B = C_{A0}X$ for the second reactor

$$V_2 = F_{A0,2}\int_0^{X_2}\frac{dX}{-r_A} = \frac{F_{A0}(1-X)}{kC_{A0}}\int_0^{X_2}\frac{dX}{(1-X)-\frac{X}{K_{eq}}}$$

$$\frac{kC_{A0}V_2}{F_{A0}(1-X_1)} = -\frac{1}{1+\frac{1}{K_{eq}}}\ln\left[1-\left(1+\frac{1}{K_{eq}}\right)X_2\right]$$

and since $V_1 = V_2$

$$\frac{kC_{A0}V_2}{F_{A0}} = \frac{kC_{A0}V_1}{F_{A0}}$$

or

$$-\frac{1}{1+\frac{1}{K_{eq}}}\ln\left[1-\left(1+\frac{1}{K_{eq}}\right)X_1\right] = -\frac{1-X_1}{1+\frac{1}{K_{eq}}}\ln\left[1-\left(1+\frac{1}{K_{eq}}\right)X_2\right]$$

$$1-\left(1+\frac{1}{K_{eq}}\right)X_2 = \left[1-\left(1+\frac{1}{K_{eq}}\right)X_1\right]^{\frac{1}{1-X_1}}$$

$$X_2 = \frac{1-\left[1-\left(1+\frac{1}{K_{eq}}\right)X_1\right]^{\frac{1}{1-X_1}}}{1+\frac{1}{K_{eq}}} = \frac{1-(0.356)^{\frac{1}{0.45}}}{1.174} = 0.766$$

Overall conversion for this scheme:

$$\overline{X} = \frac{F_{A0}-F_{A0,2}(1-X_2)}{F_{A0}} = \frac{F_{A0}-F_{A0}(1-X_1)(1-X_2)}{F_{A0}} = 1-(1-X_1)(1-X_2)$$

$$\overline{X} = 0.895$$

P4-14

Given: Ortho- to meta- and para- isomerization of xylene.

$$M \xrightarrow{k_1} P$$
$$M \xrightarrow{k_2} O$$
$$O \longrightarrow P \text{ (neglect)}$$

Pressure = 300 psig
T = 750°F
V = 1000 ft^3 cat.

Assume that the reactions are irreversible and first order.
Then:

$$-r_M = k_1 C_M + k_2 C_M = k C_M$$
$$k = k_1 + k_2$$
$$\varepsilon = 0$$

Check to see what type of reactor is being used.
Case 1:

$$v_0 = 2500 \frac{gal}{hr} \qquad X = 0.37$$

Case 2:

$$v_0 = 1667 \frac{gal}{hr} \qquad X = 0.50$$

Assume plug flow reactor conditions:

$$F_{M0} dX = -r_M dV \quad \text{or}$$
$$V = F_{M0} \int_0^X \frac{dX}{-r_M}$$
$$V = \int_0^X \frac{C_{M0} v_0 dX}{-r_M} = v_0 \int_0^X \frac{dX}{k(1-X)} = \frac{v_0}{k} \ln(1-X)$$

C_{M0}, k, and V should be the same for Case 1 and Case 2.
Therefore,

$$(kV)_{Case1} = -(v_0)_{Case1} \ln(1 - X_{Case1}) = -2500 \frac{gal}{hr} \ln[1-0.37] = 1155 \frac{gal}{hr}$$
$$(kV)_{Case2} = -(v_0)_{Case1} \ln(1 - X_{Case2}) = -1667 \frac{gal}{hr} \ln[1-0.50] = 1155 \frac{gal}{hr}$$

The reactor appears to be plug flow since $(kV)_{Case\ 1} = (kV)_{Case\ 2}$

As a check, assume the reactor is a CSTR.

$$F_{M0} X = C_{M0} v_0 X = -r_M V$$

$$V = \frac{C_{M0}X}{-r_M}v_0 = \frac{v_0 X}{k(1-X)} \quad \text{or} \quad kV = \frac{v_0 X}{1-X}$$

Again kV should be the same for both Case 1 and Case 2.

$$(kV)_{Case1} = \frac{(v_0)_{Case1} X_{Case1}}{1-X_{Case1}} = \frac{2500\frac{gal}{hr}(0.37)}{1-0.37} = 1468\frac{gal}{hr}$$

$$(kV)_{Case2} = \frac{(v_0)_{Case2} X_{Case2}}{1-X_{Case2}} = \frac{1667\frac{gal}{hr}(0.50)}{1-0.50} = 1667\frac{gal}{hr}$$

kV is not the same for Case 1 and Case 2 using the CSTR assumption, therefore the reactor must be modeled as a plug flow reactor.

$$kV = 1155\frac{gal}{hr}$$

$$k = \frac{1155\frac{gal}{hr}}{1000\,ft^3\,cat.} = 1.55\frac{gal}{hr\,ft^3\,cat}$$

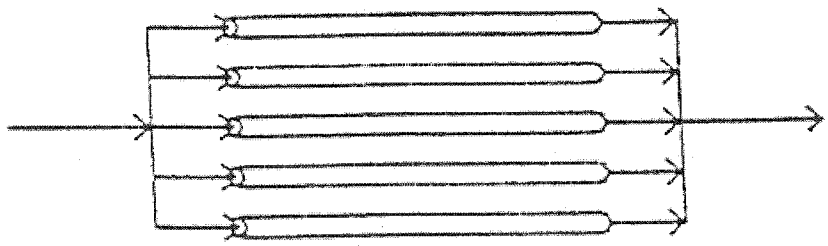
For the new plant, with $v_0 = 5500$ gal / hr, $X_F = 0.46$, the required catalyst volume is:

$$V = \frac{-v_0}{k}\ln(1-X_F) = \frac{-5500\frac{gal}{hr}}{1.155\frac{gal}{hr\,ft^3\,cat}}\ln(1-0.46) = 2931\,ft^3\,cat$$

This assumes that the same hydrodynamic conditions are present in the new reactor as in the old.

P4-15

A→ B in a tubular reactor



Tube dimensions: L = 40 ft, D = 0.75 in.
$n_t = 50$

$$V = \frac{n_t \pi D^2}{4}L = \frac{(50)\pi\left(\frac{0.75}{12}\right)^2}{4}40 = 6.14\,ft^3$$

$$F_{A0} = \frac{m_A}{MW_A} = \frac{500\frac{lb}{hr}}{73\frac{lb}{lb\,mol}} = 6.86\frac{lb\,mol}{hr}$$

$$V = F_{A0}\int_0^X \frac{dX}{-r_A}$$

$$-r_A = \frac{kC_{A0}(1-X)}{1+\varepsilon X} = kC_{A0}(1-X)$$

$$V = F_{A0}\int_0^X \frac{dX}{-r_A} = F_{A0}\int_0^X \frac{dX}{kC_{A0}(1-X)} = \frac{F_{A0}}{kC_{A0}}\ln\left(\frac{1}{1-X}\right)$$

with $C_{A0} = \frac{P}{RT} = \frac{y_{A0}P}{RT}$

$$V = \frac{F_{A0}RT}{ky_{A0}P}\ln\left(\frac{1}{1-X}\right) \text{ or } k = \frac{F_{A0}RT}{Vy_{A0}P}\ln\left(\frac{1}{1-X}\right)$$

Assume Arrhenius equation applies to the rate constant.

At $T_1 = 600°R$, $k_1 = 0.00152 = Ae^{\frac{-E}{RT_1}}$

At $T_2 = 760°R$, $k_2 = 0.0740 = Ae^{\frac{-E}{RT_2}}$

$$\frac{k_2}{k_1} = \exp\left[\frac{-E}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right]$$

$$\ln\frac{k_2}{k_1} = \frac{-E}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) = \frac{E}{R}\frac{T_2-T_1}{T_1T_2}$$

$$\frac{E}{R} = \frac{T_1T_2}{T_1-T_2}\ln\frac{k_2}{k_1} = \frac{(660)(760)}{100}\ln\frac{0.740}{0.00152} = 19{,}500°R$$

$$A = k_1\exp\left[\frac{E}{RT_1}\right]$$

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

From above we have

$$k = \frac{F_{A0}RT}{Vy_{A0}P}\ln\left(\frac{1}{1-X}\right)$$

so $\frac{F_{A0}RT}{Vy_{A0}P}\ln\left(\frac{1}{1-X}\right) = k_1\exp\left[-\frac{E}{R}\left(\frac{1}{T}-\frac{1}{T_1}\right)\right]$

Dividing both sides by T gives:

$$\frac{F_{A0}R}{Vy_{A0}P}\ln\left(\frac{1}{1-X}\right)=\frac{k_1\exp\left[-\frac{E}{R}\left(\frac{1}{T}-\frac{1}{T_1}\right)\right]}{T}$$

$$\frac{\left(6.86\frac{lb\,mol}{hr}\right)\left(10.73\frac{psia\,ft^3}{lb\,mol\,^\circ R}\right)}{\left(.00152\frac{}{\sec}\right)\left(3600\frac{\sec}{hr}\right)\left(6.14\,ft^3\right)\left(114.7\,psia\right)}\ln 5=\frac{\exp\left[-19500\left(\frac{1}{T}-\frac{1}{660^\circ R}\right)\right]}{T}$$

Evaluating and simplifying gives:

$$0.0308^\circ R^{-1}=\frac{\exp\left[-19500\left(\frac{1}{T}-\frac{1}{660^\circ R}\right)\right]}{T}$$

Solving for T gives:

T = 738°R = 278°F

P4-16

Reversible isomerization reaction

m-Xylene → p-Xylene

X_e is the equilibrium conversion.

Rate law: $$-r_m=k\left(C_m-\frac{C_p}{k_e}\right)$$

At equilibrium,

$-r_m = 0$ => $$C_m=\frac{C_p}{k_e}$$

$$C_{mo}\left(1-X_e\right)=\frac{C_{mo}X_e}{K_e}$$

$$K_e=\frac{X_e}{1-X_e}$$

$$1+\frac{1}{K_e}=\left(1+\frac{1-X_e}{X_e}\right)=\frac{X_e+1-X_e}{X_e}=\frac{1}{X_e}$$

$$-r_m=kC_{A0}\left(1-\frac{X}{X_e}\right)$$

P4-16 (a)

For batch reactor,

Mole balance: $$\frac{dX}{dt} = \frac{-r_m V}{N_{mO}} = \frac{kC_{A0}}{C_{A0}}\left(1 - \frac{X}{X_e}\right)$$

$$\tau = \frac{X_e}{k}\ln\left(\frac{X_e}{X_e - X}\right)$$

For PFR,

$$V = F_{AO}\int\frac{dX}{-r_m}$$

$$= \frac{v_o}{k}\int\frac{dX}{1-\left(1+\frac{1}{K_e}\right)X}$$

$$\tau_{PFR} = \frac{1}{k}\int\frac{dX}{1-\left(1+\frac{1}{K_e}\right)X}$$

$$\tau_{PFR} = \frac{X_e}{k}\ln\frac{X_e}{X_e - X}$$

P4-16 (b)

For CSTR,

$$V = \frac{F_{mo}X}{-r_m}$$

$$\tau_{CSTR} = \frac{X}{k\left[1-\left(1+\frac{1}{K_e}\right)X\right]}$$

Putting the value of K_e,

$$\tau_{CSTR} = \frac{X}{k}\left(\frac{X_e}{X_e - X}\right)$$

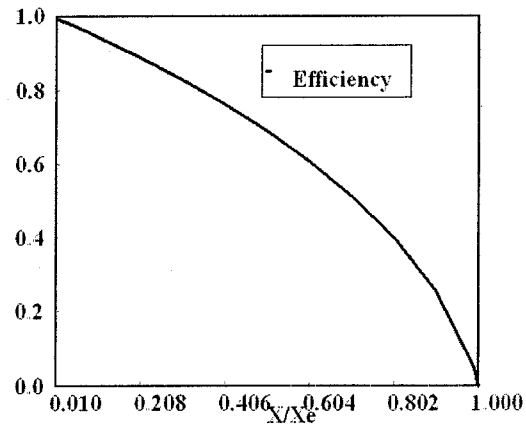
P4-16 (c)

Volume efficiency = $\eta_V = \frac{\tau_{PFR}}{\tau_{CSTR}} = \frac{\frac{X_e}{k}\ln\left(\frac{X_e}{X_e - X}\right)}{\frac{X_e}{k}\left(\frac{X}{X_e - X}\right)} = \frac{\ln\left(\frac{X_e}{X_e - X}\right)}{\left(\frac{X}{X_e - X}\right)} = \left(\frac{X_e - X}{X}\right)\ln\left(\frac{X_e}{X_e - X}\right)$

$$\eta_V = \frac{1-\left(\frac{X}{X_e}\right)}{\frac{X}{X_e}} \ln\left(\frac{1}{1-\frac{X}{X_e}}\right)$$

Following is the plot of volume efficiency as a function of the ratio (X/X_e),

See Polymath program P4-16-c.pol.



P4-16 (d)

Efficiency = V_{PFR} / V_{CSTR} = 1 from problem statement, which is not possible because conversion will not be the same for the CSTR's in series as for the PFR.

P4-17 (a)

$A \rightarrow \frac{1}{2} B$

$\varepsilon = -1/2$, $X = 0.3$, $W = 1$ kg, $y_{exit} = 0.25$

For PBR, $-r_A = kC_A^2$ and $C_A = \frac{C_O(1-X)y}{(1+\varepsilon X)}$

$$\frac{dX}{dW} = -\frac{r_A}{F_{AO}} = \frac{kC_O(1-X)^2 y^2}{v_o(1+\varepsilon X)^2} \qquad \text{let } z = \frac{kC_{Ao}}{v_o}$$

$$\frac{dX}{dW} = z\frac{(1-X)^2 y^2}{(1+\varepsilon X)^2} \qquad \text{and} \qquad \frac{dy}{dW} = -\frac{\alpha}{2y}(1+\varepsilon X)$$

Solving for z by trial and error in Polymath to match x and y at exit,

$X = 0.3$ $y_o = 1$ and $y_f = 5/20 = 0.25$

we get: $\alpha = 1.043$ kg^{-1} and $z = 0.7$ kg^{-1}

See Polymath program P4-17-a1.pol.

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
W	0	0	1	1
x	0	0	0.302004	0.302004
y	1	0.2521521	1	0.2521521
esp	-0.5	-0.5	-0.5	-0.5
alfa	1.043	1.043	1.043	1.043
Z	0.7	0.7	0.7	0.7

Differential equations as entered by the user
[1] d(x)/d(W) = Z*((1-x)*y/(1+esp*x))^2
[2] d(y)/d(W) = -alfa*(1+esp*x)/(2*y)

Explicit equations as entered by the user
[1] esp = -0.5
[2] alfa = 1.043
[3] Z = .7

Now for CSTR:

$$W = \frac{F_o X}{-r_A} = \frac{X(1+\varepsilon X)^2}{z(1-X)^2}$$

Solving we get for W = 1kg and z = 0.7 kg^{-1}

X = 0.40

See Polymath program P4-17-a2.pol.

POLYMATH Results
NLE Solution

Variable	Value	f(x)	Ini Guess
x	0.396566	-1.142E-13	0.5
W	1		
esp	-0.5		
Z	0.7		

NLE Report (fastnewt)

Nonlinear equations
[1] f(x) = W*Z*((1-x)/(1+esp*x))^2-x = 0

Explicit equations
[1] W = 1
[2] esp = -0.5
[3] Z = 0.7

P4-17 (b)

For turbulent flow:

$$\alpha = (\text{constant})\frac{G^2}{D_P} \qquad \therefore \frac{\alpha_2}{\alpha_1} = \left(\frac{G_2}{G_1}\right)^2\left(\frac{D_{P1}}{D_{P2}}\right) = \left(\frac{1}{4}\right)^2\left(\frac{1}{2}\right)$$

$$\alpha_2 = \frac{\alpha_1}{32} = 0.0326 \quad \text{and} \quad \frac{z_2}{z_1} = 4 \quad \Rightarrow \therefore z_2 = 4 \times 0.7 = 2.8$$

Now solving using polymath:

See Polymath program P4-17-b.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
w	0	0	1	1
x	0	0	0.8619056	0.8619056
y	1	0.9887079	1	0.9887079
esp	-0.5	-0.5	-0.5	-0.5
alfa	0.0326	0.0326	0.0326	0.0326
Z	2.8	2.8	2.8	2.8

ODE Report (STIFF)

Differential equations as entered by the user
[1] d(x)/d(w) = Z*((1-x)*y/(1+esp*x))^2
[2] d(y)/d(w) = -alfa*(1+esp*x)/(2*y)

Explicit equations as entered by the user
[1] esp = -0.5
[2] alfa = 0.0326
[3] Z = 2.8

So, conversion in PBR, X = 0.862

P4-17 (c) Individualized solution

P4-17 (d) Individualized solution

P4-18

Given a Fluidized Bed CSTR:

$$W = \frac{F_{A0}X}{-r'_A}, \quad -r'_A = kP_A$$

$$P_A = C_A RT = \frac{F_A}{\upsilon} RT = \frac{F_{A0}(1-X)RT}{\upsilon_0(1+\varepsilon X)\frac{P_0}{P}\frac{T}{T_0}} = \overbrace{C_{A0}RT_0}^{P_{A0}} \frac{1-X}{1+\varepsilon X}\left(\frac{P}{P_0}\right)$$

$\delta = 0 \therefore \varepsilon = 0$, then $P_A = P_{A0}(1-X)\frac{P}{P_0}$

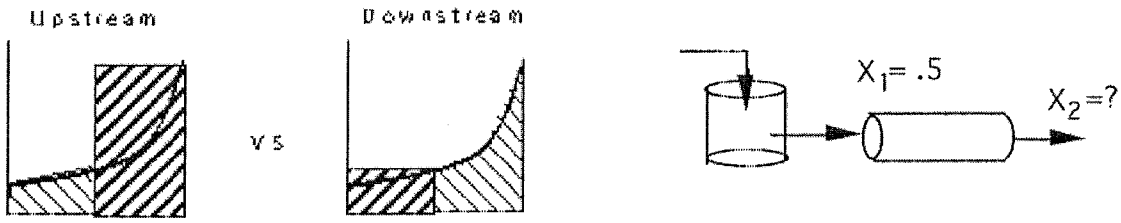
No pressure drop in the CSTR

$$P_A = P_{A0}(1-X) \qquad W = \frac{F_{A0}X}{kP_{A0}(1-X)},$$

k & F_{A0} unknown - group into a constant, use values from 1st case:

$$\frac{k}{F_{A0}} = \left(\frac{X}{1-X}\right)\frac{1}{P_{A0}W} = \frac{0.5}{0.5}\frac{1}{20(50)} \qquad \frac{k}{F_{A0}} = \frac{10^{-3}}{\text{atm kg cat}}$$

a) Put PFR downstream - less wasted volume



P4-18 (b)

b) PBR: $$F_{A0}\frac{dX}{dW} = -r'_A = kP_{A0}(1-X)\frac{P}{P_0} = kP_{A0}(1-X)(1-\alpha W)^{1/2} \text{ (since } \varepsilon = 0)$$

$$\frac{dX}{dW} = \frac{P_{A0}k}{F_{A0}}(1-X)(1-\alpha W)^{1/2}$$

$$\int_{X_1}^{X_2}\frac{dX}{1-X} = \frac{P_{A0}k}{F_{A0}}\int_0^W (1-\alpha W)^{1/2}dW$$

When $X = X_1$, $W = 0$

$$\ln\left[\frac{1-X_1}{1-X_2}\right] = \frac{kP_{A0}}{F_{A0}}\left(\frac{2}{3\alpha}\right)\left[1-(1-\alpha W)^{3/2}\right]$$

$$\ln\left[\frac{1-0.5}{1-X_2}\right] = \frac{10^{-3}}{\text{atm kg}}\ 20\text{atm}\left(\frac{2}{3\left(\frac{0.018}{\text{kg}}\right)}\right)\left[1-\left(1-0.018\text{kg}^{-1}\ 50\text{kg}\right)^{3/2}\right]$$

$$X_2 = 0.756$$

P4-18 (c)

c) $P = P_0(1-\alpha W)^{1/2} = 20\ \text{atm}\left(1-0.018\text{kg}^{-1}(50\text{kg})\right)^{1/2} = 6.3\ \text{atm}$

P4-18 (d)

For turbulent flow

$$\alpha_2 = \alpha_1\left(\frac{D_{P1}}{D_{P2}}\right)^2\left(\frac{A_{c1}}{A_{c2}}\right)^2 = \left(0.018kg^{-1}\right)\left(\frac{2}{1}\right)^2\left(\frac{1^2}{1.5^2}\right)^2 = 0.0142kg^{-1}$$

$P_{exit} = P_0(1-\alpha W)^{0.5} = (20\text{atm})(1\text{-}0.0142\text{kg}^{-1}(50\text{kg}))^{1/2} = 10.7\ \text{atm}$

$$\ln\left[\frac{1-0.5}{1-X_2}\right] = \frac{10^{-3}}{atmkg}20atm\left(\frac{2}{3\left(0.0142kg^{-1}\right)}\right)\left[1-\left(1-0.0142kg^{-1}(50kg)\right)^{3/2}\right]$$

$X_2 = 0.77$

P4-19

Production of phosgene in a microreactor.

$CO + Cl_2 \rightarrow COCl_2$ (Gas phase reaction)

$A + B \rightarrow C$

See Polymath program P4-19.pol.

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
W	0	0	3.5E-06	3.5E-06
X	0	0	0.7839904	0.7839904
y	1	0.3649802	1	0.3649802
e	-0.5	-0.5	-0.5	-0.5
FA0	2.0E-05	2.0E-05	2.0E-05	2.0E-05
FB0	2.0E-05	2.0E-05	2.0E-05	2.0E-05
Fa	2.0E-05	4.32E-06	2.0E-05	4.32E-06
Fb	2.0E-05	4.32E-06	2.0E-05	4.32E-06
v0	2.83E-07	2.83E-07	2.83E-07	2.83E-07
v	2.83E-07	2.444E-07	4.714E-07	4.714E-07
Fc	0	0	1.568E-05	1.568E-05
Ca	70.671378	9.1638708	70.671378	9.1638708
Cb	70.671378	9.1638708	70.671378	9.1638708
a	3.55E+05	3.55E+05	3.55E+05	3.55E+05
k	0.004	0.004	0.004	0.004
rA	-19.977775	-19.977775	-0.3359061	-0.3359061
Cc	0	0	53.532416	33.259571

ODE Report (RKF45)

Differential equations as entered by the user

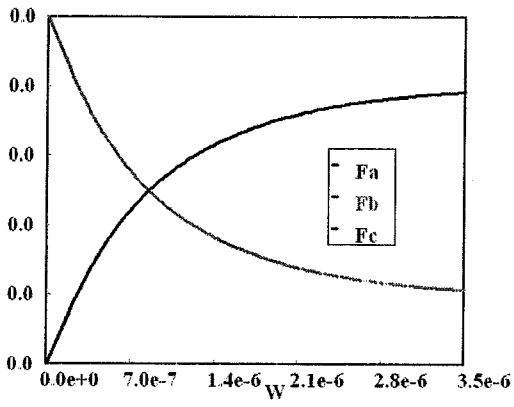
[1] d(X)/d(W) = -rA/FA0

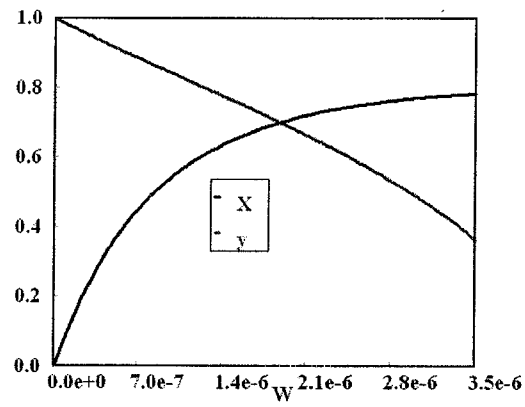
[2] d(y)/d(W) = -a*(1+e*X)/(2*y)

Explicit equations as entered by the user

[1] e = -.5
[2] FA0 = 2e-5
[3] FB0 = FA0
[4] Fa = FA0*(1-X)
[5] Fb = FB0-FA0*X
[6] v0 = 2.83e-7
[7] v = v0*(1+e*X)/y
[8] Fc = FA0*X
[9] Ca = Fa/v
[10] Cb = Fb/v
[11] a = 3.55e5
[12] k = .004
[13] rA = -k*Ca*Cb
[14] Cc = Fc/v

P4-19 (a)





P4-19 (b)

The outlet conversion of the reactor is 0.784

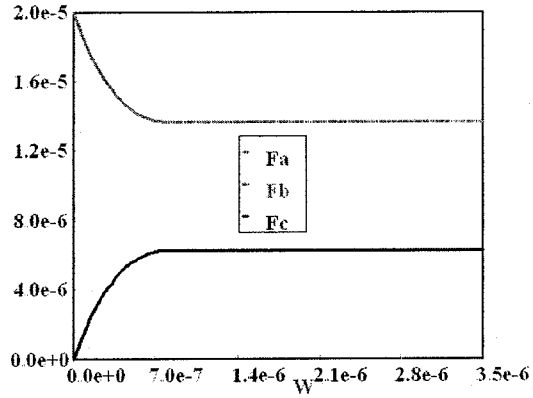
The yield is then MW*F_A*X = 99 g/mol * 2 e-5 mol/s * 0.784 = .00155 g/s = 48.95 g/ year.

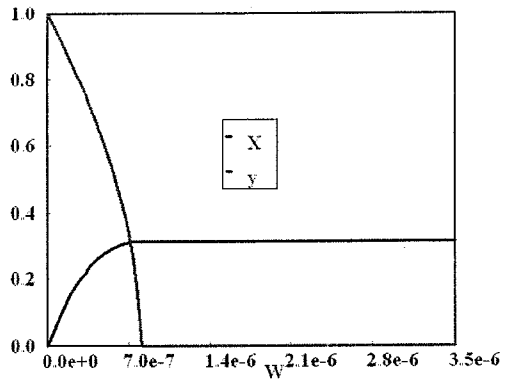
Therefore 10,000 kg/year / 48.95 kg/ year = 204 reactors are needed.

P4-19 (c)

Assuming laminar flow, $\alpha \sim D_p^{-2}$, therefore

$$\alpha_2 = \alpha_1 \frac{D_{P1}^2}{D_{P2}^2} = \left(3.55\times10^5 kg^{-1}\right)4 = 14.2\times10^5 kg^{-1}$$





P4-19 (d)

A lower conversion is reached due to equilibrium. Also, the reverse reaction begins to overtake the forward reaction near the exit of the reactor.

P4-19 (e) Individualized solution

P4-19 (f) Individualized solution

P4-19 (g) Individualized solution

P4-20 (a)

Mole Balance

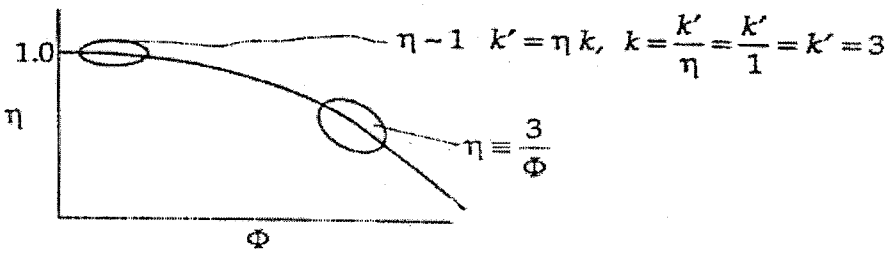
$$\frac{dX}{dW} = r'_A / F_{A0}$$

Rate Law

$$-r'_A = k' C_A^2$$

$$k' = k\,\eta = k\left[\frac{3}{\Phi^2}(\Phi \coth \Phi - 1)\right]$$

$$\Phi = c\,D_p$$



Large D_p $\quad cD_p \longrightarrow$ Increasing Particle Size

Then

$$\eta = \frac{3}{\Phi} = \frac{3}{cD_P}$$

when $D_p = 2$ mm, $K' = 0.06$, $\eta = \frac{k'}{k} = \frac{.06}{3} = 0.02$

$$0.02 = \frac{3}{c(2)}$$

$$c = 75$$

$$\boxed{\Phi = 75\, D_p}$$

For turbulent flow: $\alpha = \dfrac{2\beta}{P_o A_o \rho (1-\phi)}$ $\qquad \beta_o = \dfrac{G(1-\phi)}{g\rho_o D_o \phi^3}(1.75G)$

$$\Rightarrow \alpha = \frac{\text{constant}}{D_P}$$

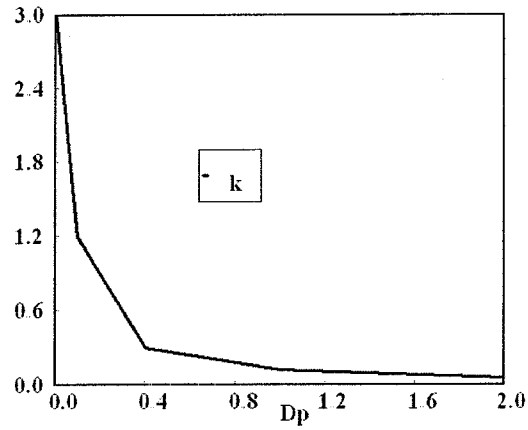
$$\alpha = \frac{\alpha_o D_{Po}}{D_{P1}}$$

$$\alpha_0 = \frac{2\beta_0}{A_C(1-\phi)\rho_C P_0} = \frac{2\left(0.001\dfrac{atm}{dm}\right)}{0.82126\, dm^2 (1-0.35)\left(2.35\dfrac{kg}{dm^3}\right)(20\, atm)}$$

$$\alpha_0 = 8.0 * 10^{-5} kg^{-1}$$

P4-20 (b)

See Polymath program P4-20-b.pol.



P4-20 (c)

Gas, $\varepsilon = 0$, $C_A = C_{A0}(1-X)y$

$$\frac{dy}{dW} = -\frac{\alpha}{2y}, \text{ where } \alpha = \alpha_1\left(\frac{D_{p1}}{D_p}\right)$$

$$\alpha_1 = \frac{2\beta_o}{P_o(1-\phi)\rho_c A_c} = \frac{2(10^{-3}\ \text{atm}\cdot\text{dm}^{-1})}{20\ \text{atm}(1-0.35)(2.65\ \text{kg/dm}^3)(0.82\ \text{din}^2)} = 7.08\times10^{-5}\ \text{kg}^{-1}$$

$$\frac{dX}{dW} = \left(\frac{k'C_A^2}{F_{A0}}\right)(1-X)^2y^2 \quad \text{and} \quad \frac{dy}{dW} = -\frac{\alpha}{2y}$$

$$k' = k\left[\frac{1}{\Phi^2}(\Phi\coth\Phi - 1)\right] \quad \text{where } k = 3 \text{ and } \Phi = 75D_p$$

$$\alpha = 7.08 * 10^{-5} kg\left(\frac{D_{p1}}{D_p}\right)$$

$D_{p1} = 1$, $C_{A0} = 0.207$, $F_{A0} = 5$
$W = 0$ $X = 0$ $y = 1.0$
$W_z = 100$
See POLYMATH program Vary D_p

See Polymath program P4-20-c.pol.

POLYMATH Results
Calculated values of the DEQ variables

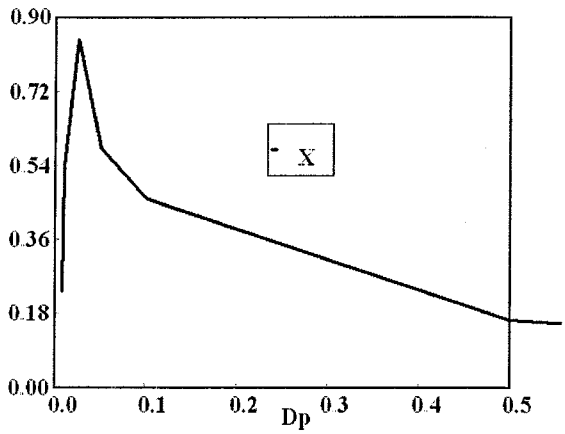
Variable	initial value	minimal value	maximal value	final value
w	0	0	100	100
X	0	0	0.5707526	0.5707526
y	1	0.2366432	1	0.2366432
Dp	0.0075	0.0075	0.0075	0.0075
Q	0.5625	0.5625	0.5625	0.5625
Fao	5	5	5	5

alpha	0.00944	0.00944	0.00944	0.00944
Cao	0.207	0.207	0.207	0.207
kprime	2.9385672	2.9385672	2.9385672	2.9385672
ra	-0.1259147	-0.1259147	-0.0012992	-0.0012992

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(X)/d(w) = -ra/Fao
[2] d(y)/d(w) = -alpha/2/y

Explicit equations as entered by the user
[1] Dp = .0075
[2] Q = 75*Dp
[3] Fao = 5
[4] alpha = .0000708/Dp
[5] Cao = .207
[6] kprime = 3*(3/Q^2)*(Q*coth(Q)-1)
[7] ra = -kprime*(Cao*(1-X)*y)^2



P4-20 (d) Individualized solution

P4-20 (e) Individualized solution

P4-20 (f) Individualized solution

P4-20 (g) Individualized solution

P4-20 (h) Individualized solution

P4-21 (a)

Assume constant volume batch reactor

Mole balance: $C_{A0}\frac{dX}{dt} = -r_A$

Rate law and stoichiometry: $-r_A = kC_A = kC_{A0}(1-X)$

Specific reaction rate: $k(25^\circ C) = 0.0022\,weeks^{-1}$

Combine:

$$t = C_{A0}\int_0^X \frac{dX}{kC_{A0}(1-X)} = \frac{-1}{k}\ln(1-X)$$

$$52.2\,weeks = \frac{-1}{0.0022\,weeks^{-1}}\ln(1-X)$$

$$X = 0.108$$

$C_A = C_{A0}(1-X)$ but since volume and molecular weight are constant the equation can be written as:

$m_A = m_{A0}(1-X)$

$$6500\,IU = m_{A0}(1-0.108)$$

$$m_{A0} = 7287\,IU$$

$$\%OU = \frac{C_{A0}-C_A}{C_A}*100 = \frac{7287-6500}{6500}*100 = 12.1\%$$

P4-21 (b)

10,000,000 lbs/yr = 4.58 * 10^9 g/yr of cereal
Serving size = 30g
Number of servings per year = 4.58 * 10^9 / 30 =1.51 * 10^9 servings/yr
Each serving uses an excess of 787 IU = 4.62 * 10^{-4} = 1.02 * 10^{-6} lb
Total excess per year = (1.51 * 10^8 servings/yr) * (1.02 * 10^{-6} lbs/serving) = 154.11 lb/yr
Total overuse cost = $100/lb * 154.11 lb/yr = $15411 / yr (trivial cost)

P4-21 (c)

If the nutrients are too expensive, it could be more economical to store the cereal at lower temperatures where nutrients degrade more slowly, therefore lowering the amount of overuse. The cost of this storage could prove to be the more expensive alternative. A cost analysis needs to be done to determine which situation would be optimal.

P4-21 (d)

$$k(40^\circ C) = 0.0048\,weeks^{-1}$$ 6 months = 26 weeks

$$t = C_{A0}\int_0^X \frac{dX}{kC_{A0}(1-X)} = \frac{-1}{k}\ln(1-X)$$

$$26 weeks = \frac{-1}{0.0048\,weeks^{-1}}\ln(1-X)$$

$$X = 0.12$$

$C_A = C_{A0}(1-X)$ but since volume and molecular weight are constant the equation can be written as:

$$m_A = m_{A0}(1-X)$$

$$6500\,IU = m_{A0}(1-0.12)$$

$$m_{A0} = 7386\,IU$$

$$\%OU = \frac{C_{A0}-C_A}{C_A}*100 = \frac{7386-6500}{6500}*100 = 13.6\%$$

P4-22 No solution necessary

P4-23

$CH_2OHCH_2Cl + NaHCO_3 \rightarrow (CH_2OH)_2 + NaCl + CO_2$

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

$F_{AO} = 0.1$ mol/min = 6 mol/hr

P4-23 (a)

Mole balance: $\dfrac{dC_A}{dt} = r + \dfrac{v_O}{V}(C_{AO} - C_A)$

$$\frac{dC_B}{dt} = r + \frac{v_O}{V}(-C_B) \qquad \frac{dC_C}{dt} = -r + \frac{v_O}{V}(-C_C)$$

Rate law: $r_A = -kC_AC_B$

$$V = V_O + v_Ot$$

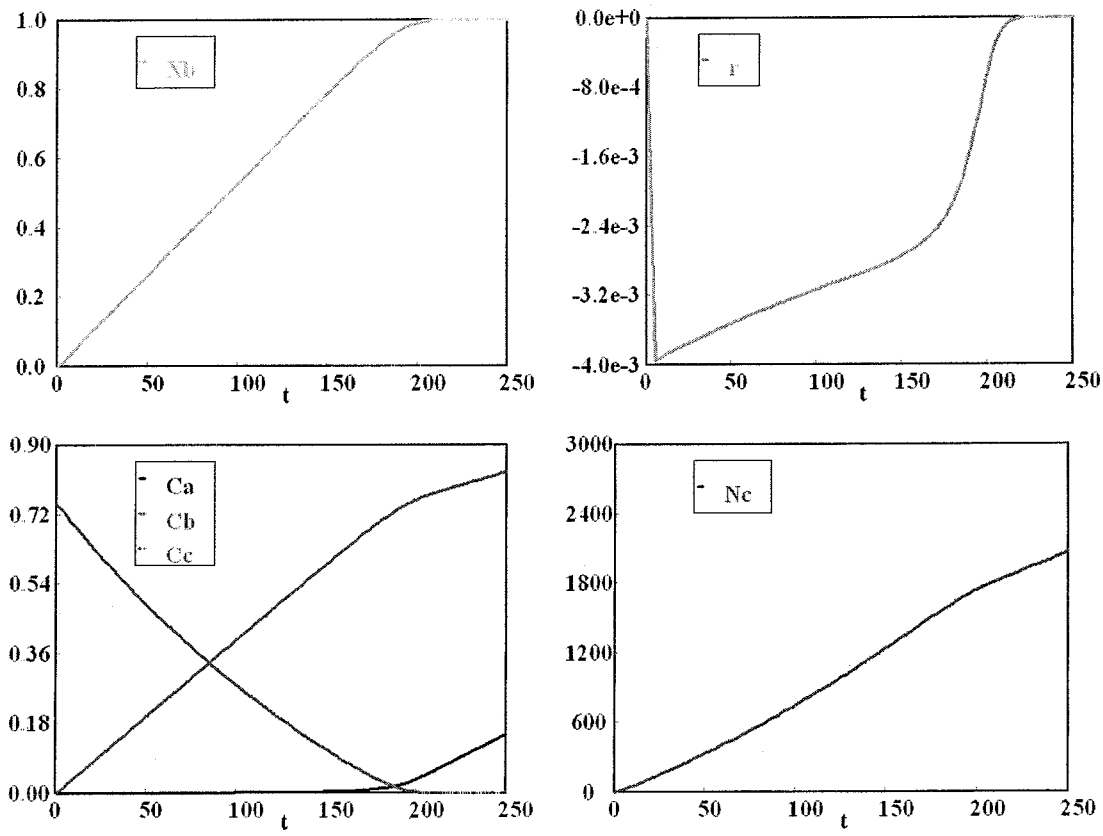
See Polymath program P4-23-a.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	250	250
Ca	0	0	0.15	0.15
Cb	0.75	1.395E-13	0.75	1.395E-13
Cc	0	0	0.829586	0.829586
Fao	6	6	6	6
Cao	1.5	1.5	1.5	1.5
k	5.1	5.1	5.1	5.1
Vo	1500	1500	1500	1500
vo	4	4	4	4
V	1500	1500	2500	2500
r	0	-0.0039398	0	-1.067E-13
Xb	0	0	1	1
Nc	0	0	2073.9649	2073.9649

ODE Report (RKF45)
Differential equations as entered by the user
[1] d(Ca)/d(t) = r+(vo/V)*(Cao-Ca)
[2] d(Cb)/d(t) = r+(vo/V)*(-Cb)
[3] d(Cc)/d(t) = -r+(vo/V)*Cc

Explicit equations as entered by the user
[1] Fao = 6
[2] Cao = 1.5
[3] k = 5.1
[4] Vo = 1500
[5] vo = Fao/Cao
[6] V = Vo+vo*t
[7] r = -k*Ca*Cb
[8] Xb = 1-Cb*V/(0.75*1500)
[9] Nc = Cc*V



P4-23 (b)

Taking average time for activities like charging, heating, cleaning = 4.5 hr
So, if there is one batch per day, the time for reaction = 24-4.5 hr = 19.5 hr

Since at the temperature at which we are operating the reactor no side reactions occur, the quickest way to run the reaction will be at the highest flow rate of A (2 mol/min or 120 mol/hour)

But at 19.5 hours and a flow rate of 120 mol/hr, 1560 dm^3 would be added to the reactor. Because the volume of the reactor is 2500 dm^3, and there is already 1500 dm^3 of B in the reactor, the reaction cannot not run for 19.5 hours at a flow rate of 120 mol/hr (2 mol/min)

Also, because there is 1500 dm^3 of B at a concentration of 0.75 M, there are only 1125 moles of B to react. This means about 750 dm^3 of 1.5 M A is all that can be reacted. More A may be added to the reactor to keep the reaction rate high as the concentration of B drops, but adding twice the necessary volume would be a waste of time and material (on top of being physically impossible!).

To add 1125 moles of A at a rate of 120 mol/min takes 9.375 hours. Using the Polymath code from part (a) and changing Fao to 120 and the time to 9.375 gives 1107 moles of C. Allowing the reaction to go for 9.5 hours results in 1115 moles of C and a reaction time of 10 hours gives 1124 moles of C.

Now consider multiple batches per day. If two batches are run, then there will be 9 hours of downtime, meaning that the time for the reaction will be 15 hours - split between the two batches, with a maximum

batch time of 10 hours. The following table shows the three possible times for reactions and the moles of C that are formed from the two batches.

Maximum Batch Time (hr)	Total Moles of C Formed
10	1723
9	1790
8	1795

So the best setup will be to run 2 batches per day. One batch will run for 8 hours and the second batch for 7 hours. Both will be run with a flow rate of 2 mol/min of A.

(If three batches are run there will be 13.5 hours of downtime and only 10.5 hours for the reaction. A maximum of 1257 moles of C can be formed if the time is split evenly for each batch (3.5 hours).)

See the Polymath code from part (a) and vary time and flow rate.

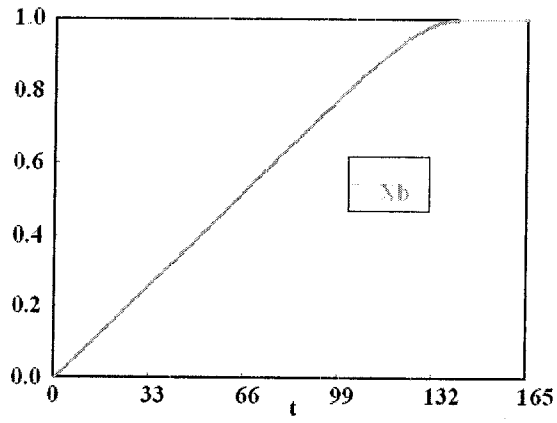
P4-23 (c)

F_{AO} = 0.15 mol/min = 9 mol /hr

vo = Fao/Ca = 9 mol/hr / 1.5 mol/dm^3 = 6 dm^3/hr

1000 dm^3 is needed to fill the reactor. At 6 dm^3/hr it will take 166.67 hours

Now solving using the code from part (a) with the changed equations:
See Polymath program P4-23-c.pol.



P4-23 (d) Individualized solution

P4-24

$$NaOH + CH_3COOC_2H_5 \longrightarrow CH_3COO^-Na^+ + C_2H_5OH$$

$$A + B \longrightarrow C + D$$

Mole balance: $\frac{dC_A}{dt} = r + \frac{v_O}{V}(C_{AO} - C_A)$

$$\frac{dC_B}{dt} = r + \frac{v_O}{V}(-C_B) \qquad \frac{dC_C}{dt} = -r + \frac{v_O}{V}(-C_C)$$

Rate law: $r_A = -kC_AC_B$

$$V = V_O + v_O t$$

$$k = k_0 \exp\left(\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right)$$

To produce 200 moles of D, 200 moles of A and 200 moles of B are needed. Because the concentration of A must be kept low, it makes sense to add A slowly to a large amount of B. Therefore, we will start with pure B in the reactor. To get 200 moles of B, we need to fill the reactor with at least 800 dm^3 of pure B. Assume it will take 6 hours to fill, heat, etc. the reactor. That leaves 18 hours to carry out the reaction. We will need to add 1000 dm^3 of A to get 200 moles in the reactor. We need to check to make sure the reactor can handle this volume if only 1 batch per day is to be used. Since we add 1800 dm^3 or 1.8 m^3 and the reactor has a volume of 4.42 m^3 we can safely carry out a single batch per day and achieve the necessary output of ethanol.

Now vary the initial amount of B in the reactor, the flow rate of A, and the temperature to find a solution that satisfies all the constraints. The program below shows one possible solution.

See Polymath program P4-24.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	6.5E+04	6.5E+04
Ca	0	0	0.1688083	0.1688083
Cb	0.25	0.0068364	0.25	0.0068364
Cc	0	0	0.0151725	0.0142903
Cd	0	0	0.0151725	0.0142903
ko	5.2E-05	5.2E-05	5.2E-05	5.2E-05
Fao	0.04	0.04	0.04	0.04
Cao	0.2	0.2	0.2	0.2
Vo	1200	1200	1200	1200
vo	0.2	0.2	0.2	0.2
T	308	308	308	308
k	1.224E-04	1.224E-04	1.224E-04	1.224E-04
ra	0	0	1.397E-06	1.412E-07
V	1200	1200	1.42E+04	1.42E+04
Nc	0	0	202.92284	202.92284

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Ca)/d(t) = -ra+(vo/V)*(Cao-Ca)
[2] d(Cb)/d(t) = -ra-(vo/V)*Cb
[3] d(Cc)/d(t) = ra-(vo/V)*Cc
[4] d(Cd)/d(t) = ra-(vo/V)*Cd

Explicit equations as entered by the user

```
[1] ko = 5.2e-5
[2] Fao = .04
[3] Cao = .2
[4] Vo = 1200
[5] vo = Fao/Cao
[6] T = 35+273
[7] k = ko*exp((42810/8.3144)*(1/293-1/T))
[8] ra = k*Ca*Cb
[9] V = Vo+vo*t
[10] Nc = Cc*V
```

P4-25 (a)

$$A \leftrightarrow B + 2C$$

To plot the flow rates down the reactor we need the differential mole balance for the three species, noting that BOTH A and B diffuse through the membrane

$$\frac{dF_A}{dV} = r_A - R_A$$

$$\frac{dF_B}{dV} = r_B - R_B$$

$$\frac{dF_C}{dV} = r_C$$

Next we express the rate law:
First-order reversible reaction

$$-r_A = k\left(C_A - \frac{C_B C_C^2}{K_C}\right) = k\left(\frac{C_{T0}F_A}{F_T} - \left(\frac{C_{T0}}{F_T}\right)^3\left(\frac{F_B F_C^2}{K_C}\right)\right)$$

Transport out the sides of the reactor:

$$R_A = k_A C_A = \frac{k_A C_{T0} F_A}{F_T}$$

$$R_B = k_B C_B = \frac{k_B C_{T0} F_B}{F_T}$$

Stoichiometery:

$-r_A = r_B = 1/2\ r_C$

Combine and solve in Polymath code:
See Polymath program P4-25-a.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
v	0	0	20	20
Fa	100	57.210025	100	57.210025
Fb	0	0	9.0599877	1.935926
Fc	0	0	61.916043	61.916043
Kc	0.01	0.01	0.01	0.01
Ft	100	100	122.2435	121.06199
Co	1	1	1	1
K	10	10	10	10
Kb	40	40	40	40
ra	-10	-10	-0.542836	-0.542836
Ka	1	1	1	1
Ra	1	0.472568	1	0.472568
Rb	0	0	2.9904791	0.6396478
Fao	100	100	100	100
X	0	0	0.4278998	0.4278998

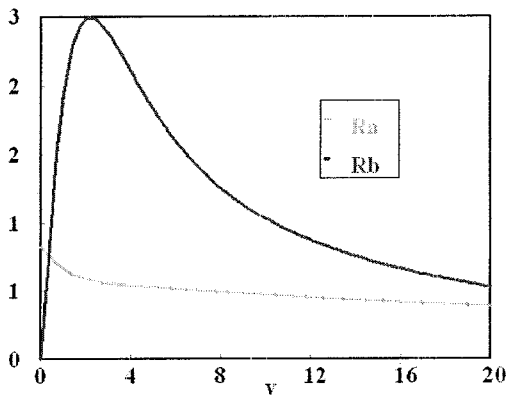
ODE Report (RKF45)

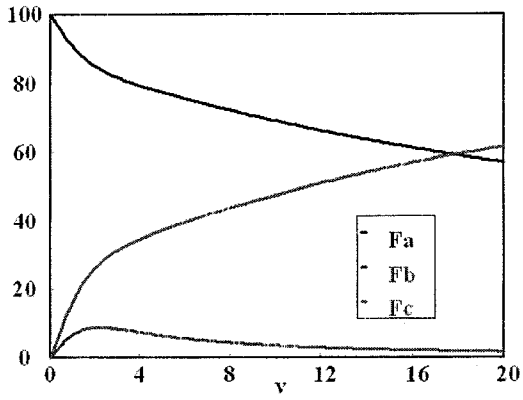
Differential equations as entered by the user

[1] d(Fa)/d(v) = ra - Ra
[2] d(Fb)/d(v) = -ra - Rb
[3] d(Fc)/d(v) = -2*ra

Explicit equations as entered by the user

[1] Kc = 0.01
[2] Ft = Fa+ Fb+ Fc
[3] Co = 1
[4] K = 10
[5] Kb = 40
[6] ra = - (K*Co/Ft)*(Fa- Co^2*Fb*Fc^2/(Kc*Ft^2))
[7] Ka = 1
[8] Ra = Ka*Co*Fa/Ft
[9] Rb = Kb*Co*Fb/Ft





P4-25 (b)

The setup is the same as in part (a) except there is no transport out the sides of the reactor.

See Polymath program P4-25-b.pol.

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
v	0	0	20	20
Fa	100	84.652698	100	84.652698
Fb	0	0	15.347302	15.347302
Fc	0	0	30.694604	30.694604
Kc	0.01	0.01	0.01	0.01
Ft	100	100	130.6946	130.6946
Co	1	1	1	1
K	10	10	10	10
ra	-10	-10	-3.598E-09	-3.598E-09
Fao	100	100	100	100
X	0	0	0.153473	0.153473

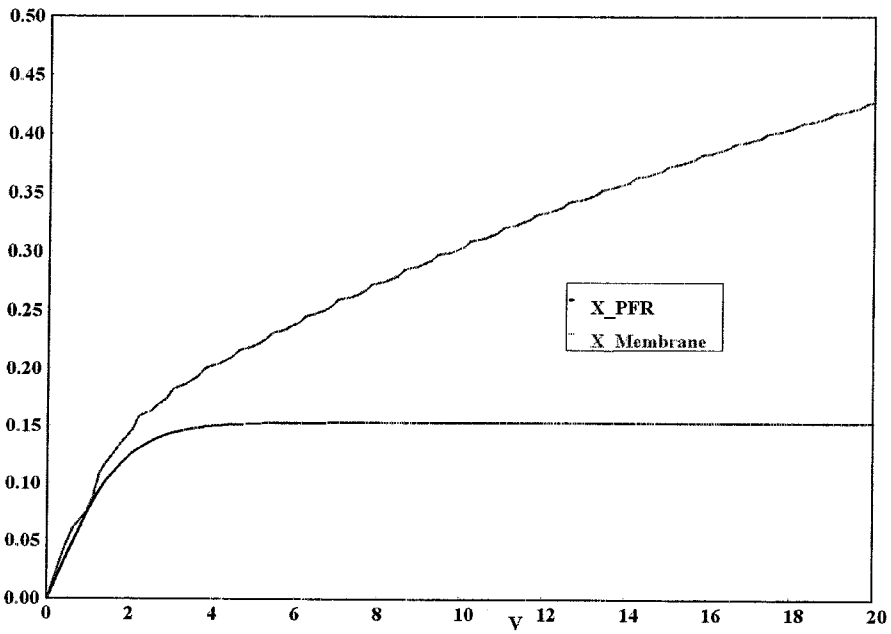
ODE Report (RKF45)

Differential equations as entered by the user

[1] d(Fa)/d(v) = ra
[2] d(Fb)/d(v) = -ra
[3] d(Fc)/d(v) = -2*ra

Explicit equations as entered by the user

[1] Kc = 0.01
[2] Ft = Fa+ Fb+ Fc
[3] Co = 1
[4] K = 10
[5] ra = - (K*Co/Ft)*(Fa- Co^2*Fb*Fc^2/(Kc*Ft^2))



P4-25 (c) Conversion would be greater if C were diffusing out.

P4-25 (d) Individualized solution

P4-26

$$CO + H_2O \leftrightarrow CO_2 + H_2$$
$$A + B \leftrightarrow C + D$$

Assuming catalyst distributed uniformly over the whole volume

Mole balance: $\frac{dF_A}{dW} = r \qquad \frac{dF_B}{dW} = r \qquad \frac{dF_C}{dW} = -r \qquad \frac{dF_D}{dW} = -r - R_{H_2}$

Rate law: $r = r_A = r_B = -r_C = -r_D = -k\left[C_A C_B - \frac{C_C C_D}{K_{eq}}\right]$

$$R_{H_2} = K_{H_2} C_D$$

Stoichiometry: $C_A = C_{TO}\frac{F_A}{F_T} \qquad C_B = C_{TO}\frac{F_B}{F_T} \qquad C_C = C_{TO}\frac{F_C}{F_T}$

$$C_D = C_{TO}\frac{F_D}{F_T}$$

$$F_T = F_A + F_B + F_C + F_D$$

Solving in polymath:

See Polymath program P4-26.pol.

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
W	0	0	100	100
Fa	2	0.7750721	2	0.7750721
Fb	2	0.7750721	2	0.7750721
Fc	0	0	1.2249279	1.2249279
Fd	0	0	0.7429617	0.5536716
Keq	1.44	1.44	1.44	1.44
Ft	4	3.3287437	4	3.3287437
Cto	0.4	0.4	0.4	0.4
Ca	0.2	0.0931369	0.2	0.0931369
Cb	0.2	0.0931369	0.2	0.0931369
Kh	0.1	0.1	0.1	0.1
Cc	0	0	0.147194	0.147194
Cd	0	0	0.0796999	0.0665322
Rh	0	0	0.00797	0.0066532
k	1.37	1.37	1.37	1.37
r	-0.0548	-0.0548	-0.002567	-0.002567

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(Fa)/d(W) = r
[2] d(Fb)/d(W) = r
[3] d(Fc)/d(W) = -r
[4] d(Fd)/d(W) = - r -Rh

Explicit equations as entered by the user

[1] Keq = 1.44
[2] Ft = Fa+Fb+Fc+Fd
[3] Cto = 0.4

```
[4]  Ca = Cto*Fa/Ft
[5]  Cb = Cto*Fb/Ft
[6]  Kh = 0.1
[7]  Cc = Cto*Fc/Ft
[8]  Cd = Cto*Fd/Ft
[9]  Rh = Kh*Cd
[10]  k = 1.37
[11]  r = -k*(Ca*Cb-Cc*Cd/Keq)
```

For 85% conversion, W = weight of catalyst = 430 kg

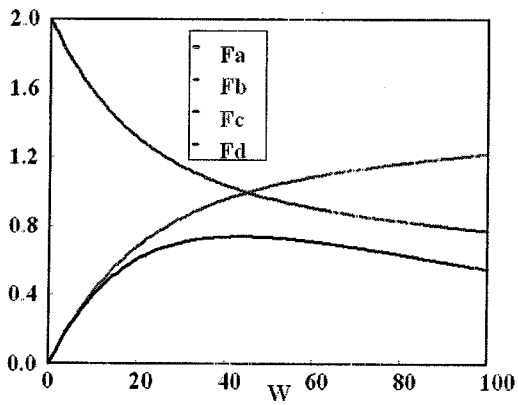
In a PFR no hydrogen escapes and the equilibrium conversion is reached.

$$K_{eq} = \frac{C_C C_D}{C_A C_B} = \frac{C_{A0}^2 X^2}{C_{A0}^2 (1-X)^2} = \frac{X^2}{(1-X)^2} = 1.44$$

solve this for X,

X = .5454
This is the maximum conversion that can be achieved in a normal PFR.

If feed rate is doubled, then the initial values of Fa and Fb are doubled. This results in a conversion of .459



P4-27 Individualized solution

P4-28 (a)

Assume isothermal and ε=0

therefore, $P = P_0 (1 - \alpha W)^{.5}$ $1=10 (1-.01\ g^{-1}W)^{.5}$

$W = 99g$

P4-28 (b)

$$\frac{dX}{dW} = \frac{-r_A}{F_{AO}}$$

$$\frac{P}{Po} = (1 - W\alpha)^5$$

$$-r_A = kC_A$$

$C_A = C_{AO}(1 - X)\ P/Po$

$C_A = C_{AO}(1 - X)(1 - 0.01\ W)^5$

Integrate from X=0 to X=.9

$$\frac{dX}{dW} = \frac{kC_{AO}(1-X)}{F_{AO}}(1-.01W)^5$$

$$W = 59.88g$$

First 5% conversion integrate from X=0 to X=.05

W=1.31 g

Last 5% conversion integrate from X=.85 to X=.90

W=10.85 g

P4-29 Individualized solution

P4-30 (a)

First order gas phase reaction,

$C_6H_5CH(CH_3)_2 \rightarrow C_6H_6 + C_3H_6$

$$y_{AO} = 1, \delta = 1 \Rightarrow \varepsilon = 1$$

$$y = \frac{P}{P_O}, a = \frac{kC_{AO}}{F_{AO}}$$

For a PBR:

$$\frac{dX}{dW} = \frac{a(1-X)}{(1+X)}y \quad \text{.....(1)}$$

$$\frac{dy}{dW} = -\frac{(1+X)}{2y}\alpha \quad \text{.....(2)}$$

X = 0.064 and y = 0.123,

Solving (1) and (2) by trial and error on polymath we get,

$\alpha = 0.000948$ (kg of catalyst)$^{-1}$

a = 0.000101 dm^{-3}

Now solve for a fluidized bed with 8000 kg of catalyst.

Mole balance: $W = \frac{F_{A0}X}{-r_A}$

Rate law: $-r_A = kC_A$

Stoichiometry: $C_A = C_{A0}\frac{1-X}{1+\varepsilon X}$

Combine: $W = \frac{X(1+\varepsilon X)}{a(1-X)} = 8000 = \frac{X(1+X)}{0.000101(1-X)}$

$X = 0.37$

P4-30 (b)

For a PBR:

$$\frac{dX}{dW} = \frac{a(1-X)}{(1+X)}y$$

$$\frac{dy}{dW} = -\frac{(1+X)}{2y}\alpha$$

where $a = \frac{kC_{AO}}{F_{AO}}$

From chapter 12 we see that k will increase as D_P decreases. We also know that for turbulent flow $\alpha \sim \frac{1}{D_P}$. This means that there are competing forces on conversion when D_P is changed.

We also know that alpha is dependant on the cross-sectional area of the pipe: $\alpha \sim \frac{1}{A_C}$

But alpha is also a function of superficial mass velocity (G). If the entering mass flow rate is held constant, then increasing pipe diameter (or cross-sectional area) will result in lower superficial mass velocity. The relationship is the following for turbulent flow:

$G \sim \frac{1}{A_C}$ and $\alpha \sim G^2$

therefore, $\alpha \sim \frac{1}{A_C^2}$.

If we combine both effects on alpha we get the following:

$$\alpha \sim \frac{1}{A_C}\frac{1}{A_C^2}$$

$$\alpha \sim \frac{1}{A_C^3}$$

So increasing pipe diameter will lower alpha and increase conversion and lower pressure drop.

For Laminar flow:

$$\alpha \sim \frac{1}{D_P^2}$$

so decreasing the particle diameter has a larger effect on alpha and will increase pressure drop resulting in a lower conversion.

For Laminar flow $\alpha \sim G$ and so $\alpha \sim \frac{1}{A_C^2}$.

This means increasing pipe diameter will have the same trends for pressure drop and conversion but will result in smaller changes.

P4-30 (c) Individualized Solution

P4-31 (a)

$\varepsilon = 0.33(1-3) = -0.666$ $P_{AO} = 0.333*10$ $F_{AO} = 13.33$ $K = 0.05$

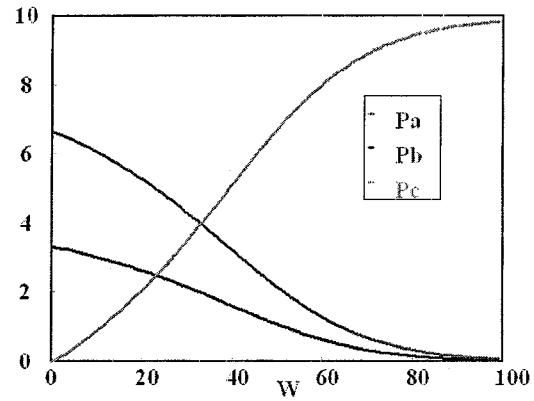
Mole balance: $dX/dW = -ra/Fao$

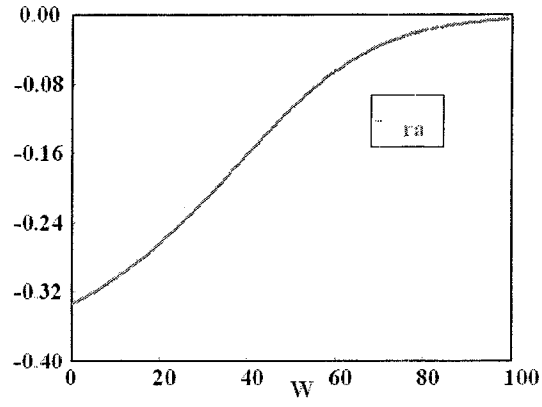
Rate law: $r_A = -KP_B$

$P_A = P_{AO}(1 - X)/(1 - 0.666X)$ $P_B = 2P_A$

$P_C = P_{AO}X/(1 - 0.666X)$

For $\alpha = 0$, $y = 1$(no pressure drop)





See Polymath program P4-31-a.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
W	0	0	100	100
X	0	0	0.995887	0.995887
K	0.05	0.05	0.05	0.05
Pao	3.33	3.33	3.33	3.33
Pa	3.33	0.0406732	3.33	0.0406732
Pb	6.66	0.0813464	6.66	0.0813464
Pc	0	0	9.8482838	9.8482838
Fao	13.33	13.33	13.33	13.33
ra	-0.333	-0.333	-0.0040673	-0.0040673

esp	-0.666	-0.666	-0.666	-0.666

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(X)/d(W) = -ra/Fao

Explicit equations as entered by the user

[1] K = 0.05
[2] Pao = 0.333*10
[3] Pa = Pao*(1 - X)/(1 - 0.666*X)
[4] Pb = 2*Pa
[5] Pc = Pao*X/(1 - 0.666*X)
[6] Fao = 13.33
[7] ra = -K*Pb
[8] esp = -0.666

For first 5% conversion weight required = W_1 = 2 kg
For last 5% conversion weight required = W_2 = 38 kg
Ratio = W_2/ W_1 = 19
Polymath solution (4-34 a)

P4-31 (b)

For $\alpha = 0.027\ kg^{-1}$,
Polymath code with pressure drop equation:
See Polymath program P4-31-b.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
w	0	0	30	30
X	0	0	0.4711039	0.4711039
y	1	0.1896048	1	0.1896048
K	0.05	0.05	0.05	0.05
Pao	3.33	3.33	3.33	3.33
Pa	3.33	0.4867002	3.33	0.4867002
Pb	6.66	0.9734003	6.66	0.9734003
Pc	0	0	1.0583913	0.4335164
Fao	13.33	13.33	13.33	13.33
ra	-0.333	-0.333	-0.04867	-0.04867
esp	-0.666	-0.666	-0.666	-0.666
alfa	0.027	0.027	0.027	0.027

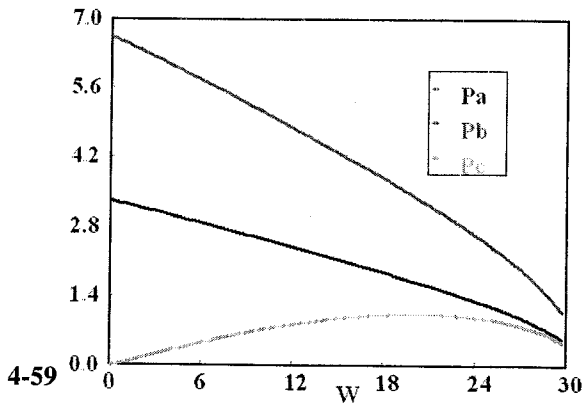
ODE Report (STIFF)

Differential equations as entered by the user

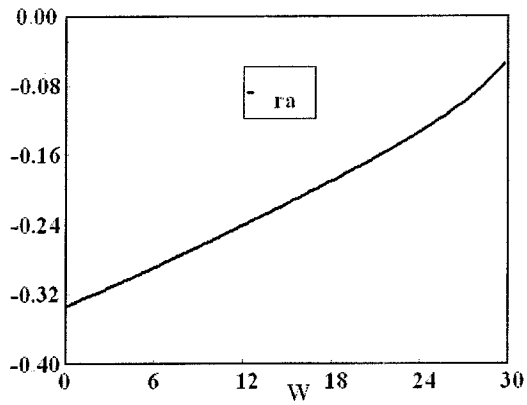
[1] d(X)/d(w) = -ra/Fao
[2] d(y)/d(w) = -alfa*(1 - esp*X)/(2*y)

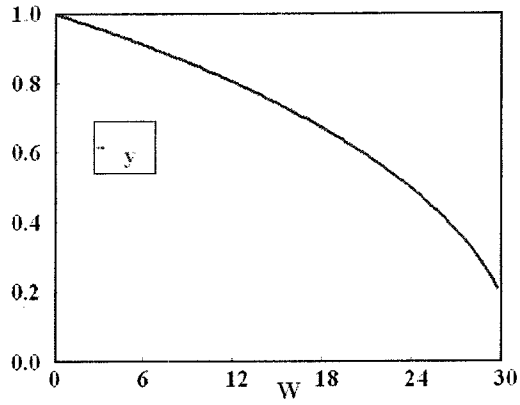
Explicit equations as entered by the user

[1] K = 0.05
[2] Pao = 0.333*10
[3] Pa = Pao*(1 - X)*y/(1 - 0.666*X)
[4] Pb = 2*Pa
[5] Pc = Pao*X*y/(1 - 0.666*X)
[6] Fao = 13.33



[7] ra = -K*Pb
[8] esp = -0.666
[9] alfa = 0.027





P4-31 (c)

1) For laminar flow:

Diameter of pipe = D and diameter of particle = D_P

Now $D_1/D_o = 3/2$ so $G_1 = 4/9G_o$

$\alpha = (\text{constant})(G/D_P^2)(1/A_C)$

So $\alpha = \alpha_O(G_1/G_o)(D_{P0}/D_{P1})^2(D_o/D_1)^2$

$= \alpha_O(4/9)(2/3)^2(2/3)^2 = 0.00237\ kg^{-1}$

Less pressure drop and more conversion for same weight of catalyst as in part (b).

2) For turbulent flow:

$\beta \propto G^2/D_P$

$\alpha = (\text{constant})(G^2/D_P)(1/A_C)$

So, $\alpha = \alpha_O(G_1/G_o)^2(D_{P0}/D_{P1})(D_o/D_1)^2$

$= \alpha_O(4/9)^2(2/3)(2/3)^2 = 0.0016\ kg^{-1}$

Again less pressure drop and more conversion for the same catalyst weight.

It is better to have a larger diameter pipe and a shorter reactor, assuming the flow remains the same as through the smaller pipe.

P4-32 (a)

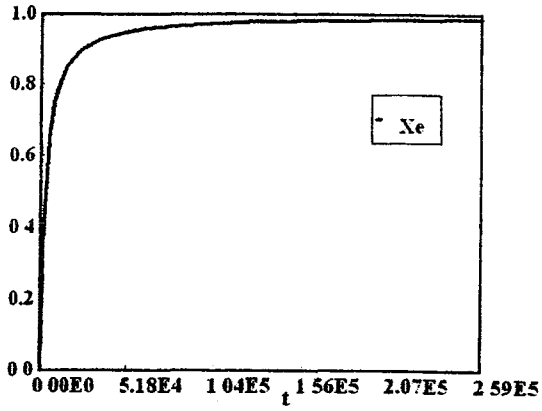
At equilibrium, r = 0 => $C_A C_B = \dfrac{C_C C_D}{K_C}$

$V = V_0 + v_o t$

$$C_A = \frac{N_{AO}(1-X)}{V} = \frac{C_{AO}(1-X)}{\dfrac{V}{V_o}} = \frac{C_{AO}(1-X)}{\left(1+\dfrac{v_o}{V_o}t\right)}$$

$$C_B = \frac{C_{BO}\frac{v_O}{V_O}t - C_{AO}X}{\left(1+\frac{v_o}{V_O}t\right)}$$

$$C_C = C_D = \frac{C_{AO}X}{\left(1+\frac{v_o}{V_O}t\right)}$$



$$\Rightarrow C_{AO}(1-X)\left(C_{BO}\frac{v_O}{V_O}t - C_{AO}X\right) = \frac{(C_{AO}X)^2}{K_C}$$

$$\Rightarrow t = \frac{V_O C_{AO}}{v_O C_{BO}}\left[\frac{X^2}{K_C(1-X)} + X\right]$$

Now solving in polymath,

See Polymath program P4-32-a.pol.

P4-32 (b)

See Polymath program P4-32-b.pol.

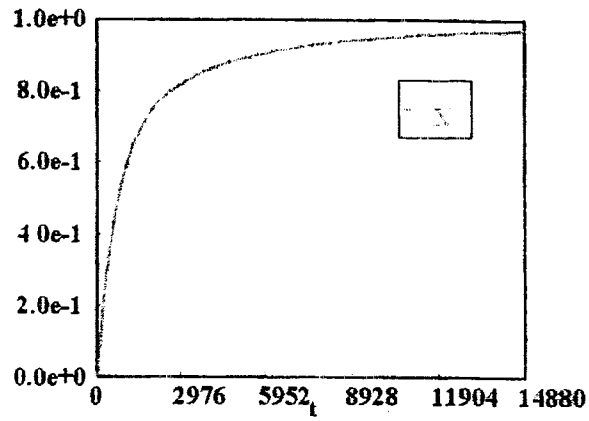
POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	1.5E+04	1.5E+04
Ca	7.72	0 2074331	7 72	0.2074331
Cb	10.93	7.6422086	10.93	9.51217
Cc	0	0	3.2877914	1.41783
Cd	0	0	3.2877914	1.41783
Kc	1.08	1.08	1 08	1 08
k	9.0E-05	9 0E-05	9.0E-05	9.0E-05
ra	-0.0075942	-0.0075942	-1.006E-05	-1.006E-05
vo	0.05	0.05	0.05	0.05
Vo	200	200	200	200
V	200	200	950	950
X	0	0	0.9731304	0.9731304

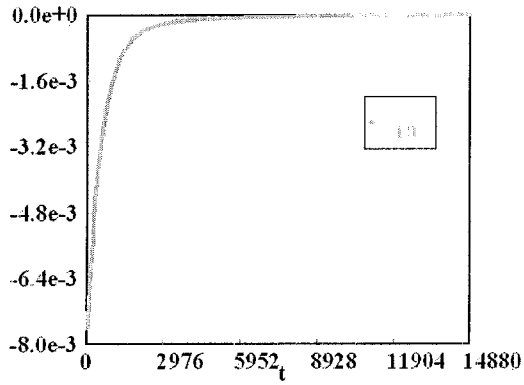
ODE Report (RKF45)

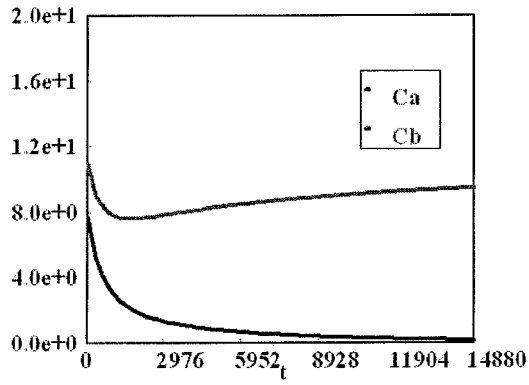
Differential equations as entered by the user



[1] d(Ca)/d(t) = ra - Ca*vo/V
[2] d(Cb)/d(t) = ra - vo/V*(Cb- 10.93)
[3] d(Cc)/d(t) = -ra - vo*Cc/V
[4] d(Cd)/d(t) = -ra - vo*Cd/V

Explicit equations as entered by the user
[1] Kc = 1.08
[2] k = 0.00009
[3] ra = -k*(Ca*Cb - Cc*Cd/Kc)
[4] vo = 0.05
[5] Vo = 200
[6] V = Vo + vo*t
[7] X = 1 - Ca/7.72

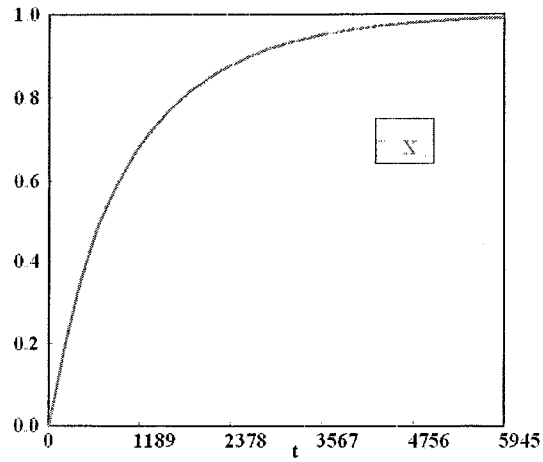




Polymath solution

P4-32 (c)

Change the value of v_o and C_{AO} in the Polymath program to see the changes.



P4-32 (d)

As ethanol evaporates as fast as it forms: $C_D = 0$
Now using part (b) remaining equations,
Polymath code:

See Polymath program P4-32-d.pol.

POLYMATH Results
Calculated values of the DEQ variables

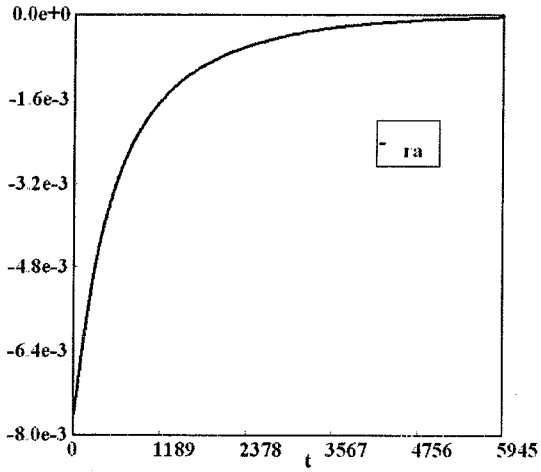
Variable	initial value	minimal value	maximal value	final value
t	0	0	6000	6000
Ca	7.72	0.0519348	7.72	0.0519348
Cb	10.93	6.9932872	10.93	7.8939348
k	9.0E-05	9.0E-05	9.0E-05	9.0E-05
ra	-0.0075942	-0.0075942	-3.69E-05	-3.69E-05
vo	0.05	0.05	0.05	0.05
Vo	200	200	200	200

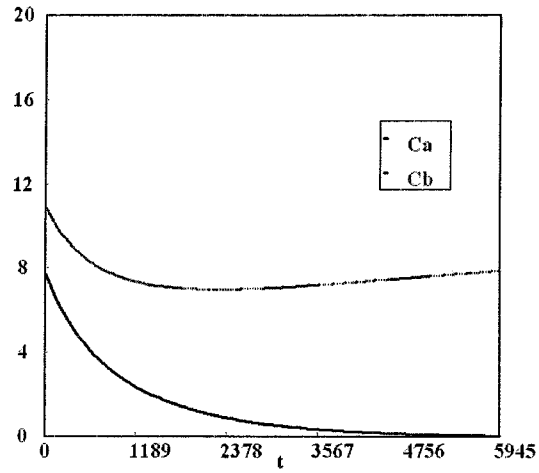
V	200	200	500	500
X	0	0	0.9932727	0.9932727

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Ca)/d(t) = ra - Ca*vo/V
[2] d(Cb)/d(t) = ra - vo/V*(Cb- 10.93)

Explicit equations as entered by the user
[1] k = 0.00009
[2] ra = -k*Ca*Cb
[3] vo = 0.05
[4] Vo = 200
[5] V = Vo + vo*t
[6] X = 1 - Ca/7.72





P4-32 (e) Individualized solution

P4-32 (f) Individualized solution

P4-33 (a)

Mole balance on reactor 1:

$$C_{A0}v_{A0} - C_{A1}v - r_{A1}V = \frac{dN_{A1}}{dt} \quad \text{with } v_{A0} = \frac{1}{2}v_0$$

$$\frac{C_{A0}}{2}v_0 - C_{A1}v - r_{A1}V = \frac{dN_{A1}}{dt}$$

Liquid phase reaction so V and v are constant.

$$\frac{C_{A0}}{2\tau} - \frac{C_{A1}}{\tau} - r_{A1} = \frac{dC_{A1}}{dt}$$

Mole balance on reactor 2:

$$C_{A1}v_0 - C_{A2}v_0 - r_{A2}V = \frac{dN_{A2}}{dt}$$

$$\frac{C_{A1}}{\tau} - \frac{C_{A2}}{\tau} - r_{A2} = \frac{dC_{A2}}{dt}$$

Mole balance for reactor 3 is similar to reactor 2:

$$C_{A2}v_0 - C_{A3}v_0 - r_{A3}V = \frac{dN_{A3}}{dt}$$

$$\frac{C_{A2}}{\tau} - \frac{C_{A3}}{\tau} - r_{A3} = \frac{dC_{A3}}{dt}$$

Rate law:

$$-r_{Ai} = kC_{Ai}C_{Bi}$$

Stoichiometry

For parts a, b, and c $C_{Ai} = C_{Bi}$

so that $-r_{Ai} = kC_{Ai}^2$

Combine:

$$\frac{C_{A0}}{2\tau} - \frac{C_{A1}}{\tau} - kC_{A1}^2 = \frac{dC_{A1}}{dt}$$

$$\frac{C_{A1}}{\tau} - \frac{C_{A2}}{\tau} - kC_{A2}^2 = \frac{dC_{A2}}{dt}$$

$$\frac{C_{A2}}{\tau} - \frac{C_{A3}}{\tau} - kC_{A3}^2 = \frac{dC_{A3}}{dt}$$

See Polymath program P4-33.pol.

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	100	100
Ca1	0	0	0.8284264	0.8284264
Ca2	0	0	0.7043757	0.7043757
Ca3	0	0	0.6109587	0.6109587
k	0.025	0.025	0.025	0.025
Cao	2	2	2	2
tau	10	10	10	10
X	1	0.3890413	1	0.3890413

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(Ca1)/d(t) = (Cao/2 -Ca1)/tau -k*Ca1^2
[2] d(Ca2)/d(t) = (Ca1 - Ca2)/tau -k*Ca2^2
[3] d(Ca3)/d(t) = (Ca2 - Ca3)/tau -k*Ca3^2

Explicit equations as entered by the user
[1] k = 0.025
[2] Cao = 2
[3] tau = 10
[4] X = 1 - 2*Ca3/Cao

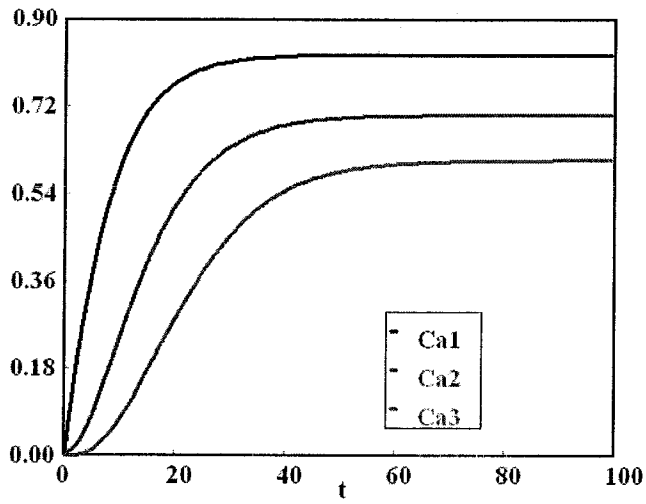
From Polymath, the steady state conversion of A is approximately 0.39

P4-33 (b)

99% of the steady state concentration of A (the concentration of A leaving the third reactor) is:
(0.99)(0.611) = 0.605
This occurs at t =

P4-33 (c)

The plot was generated from the Polymath program given above.



P4-33 (d)

We must reexamine the mole balance used in parts a-c. The flow rates have changed and so the mole balance on species A will change slightly. Because species B is added to two different reactors we will also need a mole balance for species B.

Mole balance on reactor 1 species A:

$$C_{A0}v_{A0} - C_{A1}v - r_{A1}V = \frac{dN_{A1}}{dt} \quad \text{with } v_{A0} = \frac{2}{3}v_0 \text{ and } v_0 = \frac{200}{15}$$

$$\frac{2C_{A0}}{3}v_0 - C_{A1}v - r_{A1}V = \frac{dN_{A1}}{dt}$$

Liquid phase reaction so V and v are constant.

$$\frac{C_{A0}}{2\tau} - \frac{C_{A1}}{\tau} - r_{A1} = \frac{dC_{A1}}{dt}$$

Mole balance on reactor 1 species B:

$$C_{B0}v_{B0} - C_{B1}v - r_{B1}V = \frac{dN_{B1}}{dt} \text{ and } v_{B0} = \frac{1}{3}v_0$$

Stoichiometry has not changed so that $-r_{Ai} = -r_{Bi}$ and it is a liquid phase reaction with V and v constant.

$$\frac{C_{B0}}{3\tau} - \frac{C_{B1}}{\tau} - r_{A1} = \frac{dC_{B1}}{dt}$$

Mole balance on reactor 2 species A:
We are adding more of the feed of species B into this reactor such that $v_2 = v_0 + v_{B0} = 20$

$$C_{A1}v_0 - C_{A2}v_2 - r_{A2}V = \frac{dN_{A2}}{dt}$$

$$\frac{C_{A1}}{\tau_1} - \frac{C_{A2}}{\tau_2} - r_{A2} = \frac{dC_{A2}}{dt} \text{ where } \tau_1 = \frac{V}{v_0} \text{ and } \tau_2 = \frac{V}{v_2}$$

Mole balance on reactor 2 species B:

$$C_{B1}v_0 + C_{B0}v_{B0} - C_{B2}v - r_{B2}V = \frac{dN_{B2}}{dt}$$

$$\frac{C_{B1}}{\tau_1} + \frac{C_{B0}v_{B0}}{V} - \frac{C_{B2}}{\tau_2} - r_{A2} = \frac{dC_{B2}}{dt}$$

Mole balance for reactor 3 species A:

$$C_{A2}v_2 - C_{A3}v_2 - r_{A3}V = \frac{dN_{A3}}{dt}$$

$$\frac{C_{A2}}{\tau_2} - \frac{C_{A3}}{\tau_2} - r_{A3} = \frac{dC_{A3}}{dt}$$

Mole balance for reactor 3 species B:

$$C_{B2}v_2 - C_{B3}v_2 - r_{A3}V = \frac{dN_{B3}}{dt}$$

$$\frac{C_{B2}}{\tau_2} - \frac{C_{B3}}{\tau_2} - r_{A3} = \frac{dC_{B3}}{dt}$$

Rate law:

$$-r_{Ai} = kC_{Ai}C_{Bi}$$

See Polymath program P4-33-d.pol.

POLYMATH Results
Calculated values of the DEQ variables

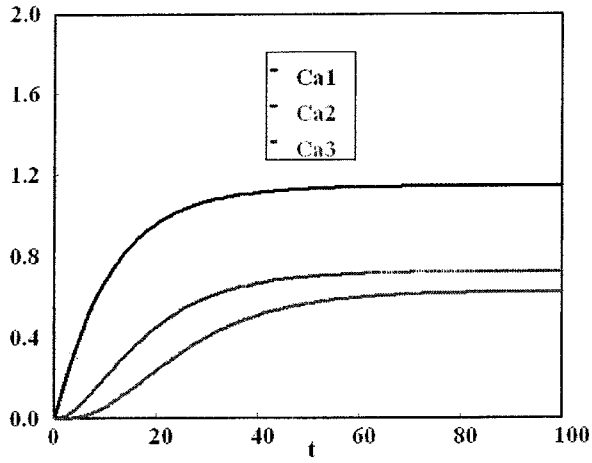
Variable	initial value	minimal value	maximal value	final value
t	0	0	100	100
Ca1	0	0	1.1484734	1.1484734
Ca2	0	0	0.7281523	0.7281523
Ca3	0	0	0.6278144	0.6278144
Cb1	0	0	0.4843801	0.4821755
Cb2	0	0	0.7349863	0.7291677
Cb3	0	0	0.6390576	0.6309679
k	0.025	0.025	0.025	0.025
Cao	2	2	2	2
tau	13.333333	13.333333	13.333333	13.333333
X	1	0.3721856	1	0.3721856
tau2	10	10	10	10
V	200	200	200	200
vbo	5	5	5	5

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Ca1)/d(t) = (2*Cao/3 -Ca1)/tau -k*Ca1*Cb1
[2] d(Ca2)/d(t) = Ca1/tau - Ca2/tau2 -k*Ca2*Cb2
[3] d(Ca3)/d(t) = (Ca2 - Ca3)/tau2 -k*Ca3*Cb3
[4] d(Cb1)/d(t) = (1*Cao/3-Cb1)/tau-k*Ca1*Cb1
[5] d(Cb2)/d(t) = Cb1/tau+Cao*vbo/V-Cb2/tau2-k*Ca2*Cb2
[6] d(Cb3)/d(t) = (Cb2-Cb3)/tau2-k*Ca3*Cb3

Explicit equations as entered by the user
[1] k = 0.025
[2] Cao = 2
[3] tau = 200/15
[4] X = 1 - 2*Ca3/Cao
[5] tau2 = 10
[6] V = 200
[7] vbo = 5

Equilibrium conversion is 0.372.
This conversion is reached at t = 85.3 minutes.



P4-33 (e) Individualized solution

CDP4-A

$$CH_3I + AgClO_4 \rightarrow CH_3ClO_4 + AgI$$

0.7 mol/l $CH_3I = C_{BO}$

0.5 mol/l $AgClO_4 = C_{AO}$

$V_o = 30\ dm^3$

$$r_{CH_3I} = -k\, C_{CH_3I}\, C^{3/2}_{AgClO_4}$$

$k = 0.00042\ (dm^3/mol)^{3/2}(sec)^{-1}$ T=298 K

X = 0.98

Let A = $AgClO_4$, B = CH_3I

$$t = N_{AO} \int_0^X \frac{dX}{-r_A V}$$

$V = V_0$ (liquid phase)

$$t = \frac{C_{AO}V_0}{V_0} \int_0^X \frac{dX}{k\, C_B C_A^{3/2}}$$

$$t = \frac{C_{AO}}{k} \int_0^X \frac{dX}{C_{AO}(7/5 - X)\, C_{AO}^{3/2}(1 - X)^{3/2}}$$

$$t = \frac{1}{k\, C_{AO}^{3/2}} \int_0^X \frac{dX}{(7/5 - X)(1 - X)^{3/2}}$$

Integration for X = 0.98, solved numerically

$$t = \frac{1}{0.00042\ (0.5)^{3/2}} \quad (24.18)$$

$t = 1.628 \times 10^5$ sec = 45.2 hr

CDP4-B

a)

Mole Balance : $$\frac{dN_A}{dt} = F_{A_0} - F_A + r_A V$$

$$V\frac{dC_A}{dt} = C_{A_0}v_0 - C_A v_0 - kC_A V$$

$$\frac{dC_A}{dt} = \frac{C_{A_0}v_0}{V} - \frac{C_A(v_0 + V)}{V}$$

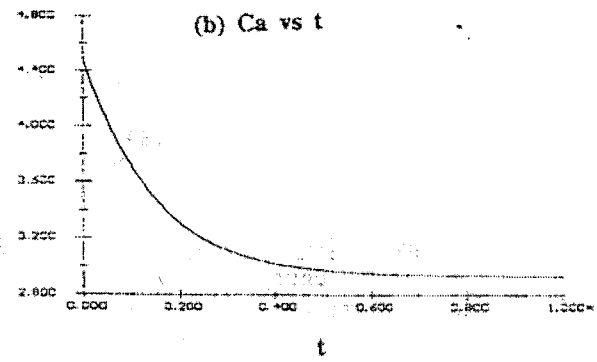
Use POLYMATH to plot C_A vs. t

Equations:

```
d(ca)/d(t)=(cao*vo/v)-(ca*(k*v+vo)/v)
cao=4.5
vo=70000
v=15000000
k=0.0025
```

$t_0 = 0$, $t_f = 1000$

Key: Ca



For steady-state:

$$t = 4.6\frac{\tau}{1 + \tau k} = 641 \text{ hrs}$$

$$C_A = \frac{C_{A_0}v_0}{kV + v_0} = 2.930 \text{ mg/dm}^3$$

99% of this is 2.906 mg/dm^3, which is below the standard of 3.0 mg/dm^3.

Polymath solution(Ans CDP4-B-a)

b)

Mole Balance : $$\frac{dN_A}{dt} = F_{A_0} - F_A + r_A V$$

$$\frac{dN_A}{dt} = C_{A_0}v_0 - C_A v_{out} - kC_A V$$

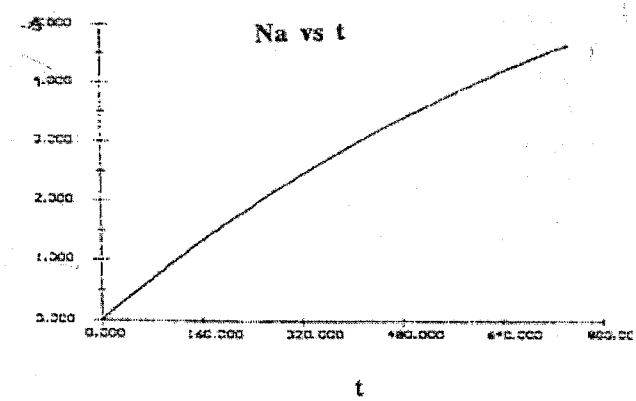
Use POLYMATH to generate plot of C_A and N_A vs. t.

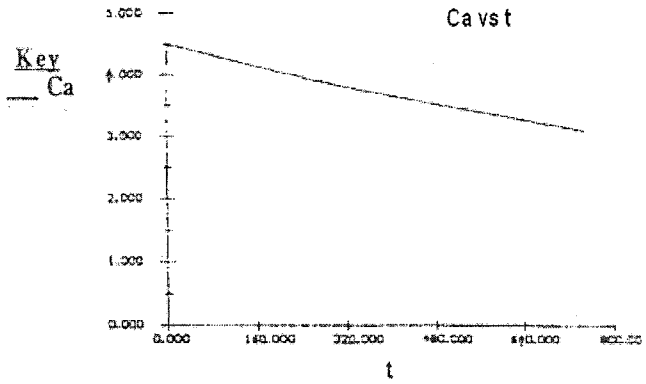
Equations:

```
d(na)/d(t)=cao*vo-ca*vout-k*ca
cao=4.5
vo=70000
vout=50000
k=0.0025
v=20000*t
ca=na/v
```

$t_0 = 1$, $t_f = 750$

Key: Na





Polymath solution(Ans CDP4-B-b)

c)

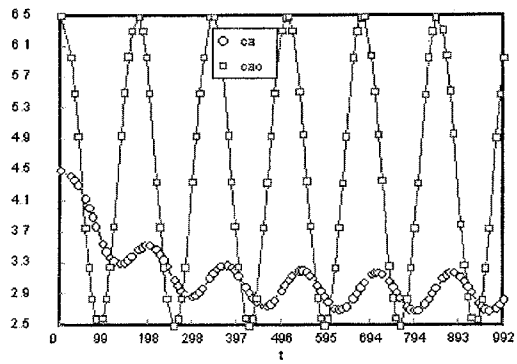
Use same equations as in part (a),

but change $C_{Ao} = 4.5$ to $C_{Ao} = 4.5 + 2.0\cos\left(\frac{\pi}{84}t\right)$

Equations:

```
d(ca)/d(t)=(cao*vo/v)-(ca*(k*v+vo)/v)
cao=4.5+2*cos(3.14159/84*t)
vo=70000
v=15000000
k=0.0025
```

$t_0 = 0, \quad t_f = 1000$

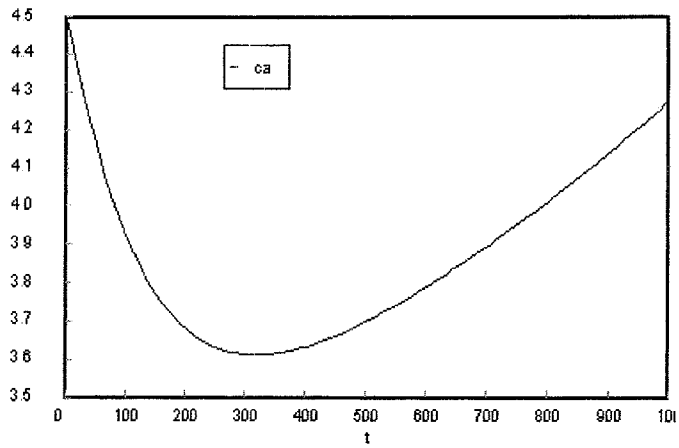


Polymath solution(Ans CDP4-B-c)

d) This part is almost same as part(b) with minor changes:
V = 15000000 – 10000t
v_o = 80000 and v_{out} = 70000

The reason the graph looks so different from(a) is that pure water is evaporated, but water with atrazine is coming in.

```
Polymath code:
d(ca)/dt=cao*vo/v)-
(ca(kv+vout)/v)
ca(0)=4.5          #
vo = 80000         #
v = 15000000 - 10000*t
k =   0.0025       #
cao =  4.5         #
vout = 70000       #
t(0)=0             #
t(f)=1000
```



CDP4-C

a)Find the number of moles of receptors:

$$1\times10^{6}\ \frac{\text{cells}}{\text{mL}} * 1\times10^{5}\ \frac{\text{receptors}}{\text{cell}} * \frac{1\text{ mole receptors}}{6.022\times10^{23}\text{ receptors}} * \frac{1000mL}{L} = 1.66\times10^{-10}\ \text{M}$$

$$1.66\times10^{-10}\frac{mol}{L} \div .01L = 1.66\times10^{-12} moles$$

Design equation:

$$N_{A0}\frac{dX}{dt} = -r_A$$

Rate Law:

$$-r_A = kC_AC_B$$

Stoichiometry:

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

$$C_B = C_{A0}(\theta_B - X)$$

Where:

Total number of moles:

$$1.66\times10^{-12} + 1\times10^{-9} = 1.002\times10^{-9}$$

hence:

$$y_A = \frac{1.66\times10^{-12}}{1.002\times10^{-9}} = 0.0017$$

$$y_B = \frac{1\times10^{-9}}{1.002\times10^{-9}} = 0.998$$

$$\theta_B = \frac{0.998}{0.0017} = 587$$

Combining and solving:

$$\frac{dX}{(1-X)(\theta_B - X)} = \frac{kC_{A0}^2 dt}{N_{A0}}$$

$$\frac{1}{\theta_B - 1}\ln\frac{\theta_{B-X}}{\theta_B(1-X)} = \frac{kC_{A0}^2 t}{N_{A0}}$$

$$t = 0.071\,\text{min}$$

b) Assume $C_B = C_{B0}$

Design Equation:

$$N_{A0}\frac{dX}{dt} = -r_A$$

Rate Law:

$$-r_A = kC_AC_B$$

Stoichiometry:

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

$$C_B = C_{B0}$$

Combine and solve:

$$\frac{dX}{1-X} = \frac{kC_{A0}C_{B0}dt}{N_{A0}}$$

$$\ln\frac{1}{1-X} = \frac{kC_{A0}C_{B0}t}{N_{A0}}$$

t=0.069 min

A very good approximation.

c) Design Equation:

$$N_{A0}\frac{dX}{dt} = -r_A$$

Rate Law:

$$-r_A = k_f C_A C_B - k_r C_C$$

Stoichiometry:

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

$$C_B = C_{B0}$$

$$C_C = C_{A0}X$$

Combine and solve:

$$N_{A0}\frac{dX}{dt} = k_f C_{A0}(1-X)C_{B0} - k_r C_{A0}X$$

$$\frac{dX}{k_f C_{A0}C_{B0} - k_f C_{A0}C_{B0} - k_r C_{A0}X} = \frac{dt}{N_{A0}}$$

$$\int_0^X \frac{dX}{k_f C_{B0} - X\left(k_f C_{B0} + k_r\right)} = \int_0^5 \frac{C_{A0}dt}{X}$$

$$\frac{1}{k_f C_{B0} + k_r}\ln\frac{k_f C_{B0}}{k_f C_{B0} - X\left(k_f C_{B0} + k_r\right)} = \frac{5C_{A0}}{N_{A0}}$$

$$\frac{1}{.1+.1}\ln\frac{.1}{.1-X(.1+.1)} = 500$$

$$X = 0.5$$

CDP4-D

Batch reaction: $2A + B \rightarrow 2C$

$k_1 = 1.98$ ft^3/lbmol.min, $k_2 = 9.2 \times 10^3$ (ft^3/lbmol)^2/min

V = 5 gal =0.67 ft^3, X = 0.65

$C_{A0} = 0.002$ lbmol/0.67ft^3 = 2.98×10^{-3} lbmol/ft^3

$C_{B0} = 0.0018$ lbmol/0.67ft^3 =2.69×10^{-3} lbmol/ft^3

Mole Balance: $$\frac{dN_A}{dt} = -r_A V$$

Rate law: $-r_A = k_1 C_A C_B + k_2 C_A C_B^2$

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

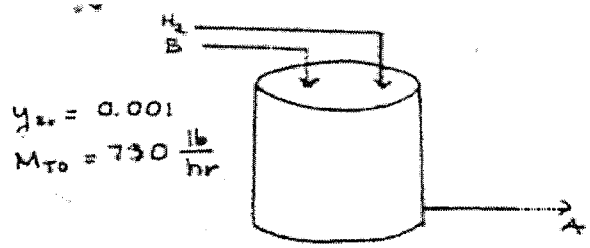
$C_B = C_{A0}(\theta_B - (b/a)X) = C_{A0}(0.9 - 0.5X)$

Combine:

$$C_{A0}\frac{dX}{dt} = C_{A0}{}^2(1-X)\left[k_1(0.9-0.5X)+k_2C_{A0}(1-X)(0.9-0.5X)^2\right]$$

Integrating between X=0 to X=0.65 for t = 0 to t = t gives
t = 24.1 min

CDP4-E



Finally

F_{AF}, F_{H_2f}

F_{BF} C_{BF} (etc)

$Y_{BF} = 10^{-5}$

V = 50 gal. liquid

T = 100°C = 373°K = 672°R

P = 500 psig

$-r_B = k\,C_{H_2}\,C_B$

Liquid feed is a mixture of A and B $y_{Ao} = 1 - y_{Bo} = 0.999$
Because of the low concentration of B in the feed, such properties as SG, the specific gravity, M_W, the molecular weight, and the solubility of H_2 are essentially that of component A. assume that any H_2 depleted via reaction is instantaneously replaced via absorption of H_2 gas over the liquid reacting mixture. Then at 500psig,

$$C_{H_2,f} = \left[\frac{5.0g}{1}\right] \times \left[\frac{1gmole}{2g}\right] \times \left[\frac{1\ lbmole}{454\ gmoles}\right] \times \left[\frac{3.785l}{gal}\right] = \frac{.0208lbmole}{gal}$$

$$F_{AO} \simeq F_{Af} \text{ because } y_B \ll 1 \ . \ F_{Af} = \frac{N_t}{(M_{WA})} = \frac{730\ lb/hr}{\frac{196\ lb}{lbmole}} = 3.72\ lbmole/hr$$

Assume that there is no volume change accompanying absorption of H_2: Then

$$\therefore v_o = \frac{M_t}{SG\ \rho_{H_2O}} = v = \text{constant, or}$$

$$v = \left[\frac{730\ lbA}{hr.}\right] \times \left[\frac{lb\ x\ H_2O}{.9801bA}\right] \times \frac{1\ ft^3}{62.41\ lb} \times \left[\frac{7.48\ gal}{ft^3}\right] = 89.3\ gal/hr.$$

$$C_{BO} = \frac{F_{BO}}{V_o} \simeq \frac{y_{BO}F_{TO}}{V_o} = \frac{(10^{-3})(3.72)lbmole/hr}{(89.3)gal/hr} = 4.17 \times 10^{-5} lbmole/gal$$

Using equation for a CSTR

$$V = \frac{F_{BO}X}{-r_B}$$

$$k = \frac{F_{BO}X}{V\ C_{BO}(1-X)C_{H_2,f}} = \frac{v_o\ X}{V(1-X)C_{H_2,f}}$$

$$k = \frac{(89.3\ gal/hr)(0.99)}{50\ gal\ \left(\frac{0.0208\ lbmol}{gal}\right)\ (0.01)}$$

$$k = 8.49 \times 10^3\ gal/(lbmole - hr)$$

With reactor at 300 psig, Henry's law is: $C_{H_2} \propto P$

$$\therefore C_{H_2}\ (300\ psig) = C_{H_2}\ (500\ psig) \times \left(\frac{300+14.7}{500+14.7}\right) = (.0208)\left[\frac{314.7}{514.7}\right] \frac{lbmole}{gal}$$

$$C_{H_2} = 0.0127\ lbmole/gal$$

Let conversion be X_2 when pressure = 300 psig

$$V = \frac{F_{BO}X_2}{k\ C_{BO}(1-X_2)CH_{2,300}} = \frac{v_o\ X_2}{k(1-X_2)C_{H_{2,300}}}$$

$$\frac{X_2}{1-X_2} = \frac{(50\ gal)(8.49x10^{3}\ gal/lbmol-hr)(0.0127\ lbmol/gal)}{89.3\ gal/hr}$$

$$F_{H_2,F} = C_{H_2,F}\, v_o = \left(\frac{.0127\ lbmole}{gal}\right)\left(\frac{89.4 gal}{hr}\right) = 1.134\ lbmole/hr$$

$$y_{BF} = \frac{F_{BO}\ (1-X_2)}{F_{H_2,F} + F_{TO}} = \frac{(3.72x10^{-3})\ (1-0.984)}{1-1.34+3.72} = 1.23x10^{-5}$$

CDP4-F

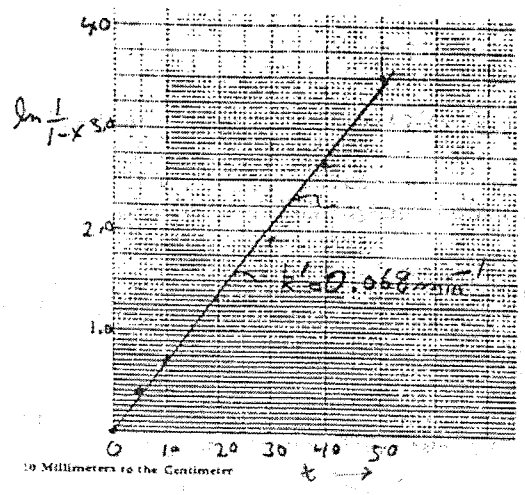
$$N_{A0}\frac{dX}{dt} = V\rho_C\left(-r'_A\right) = V\rho_C\, kC_A$$

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

$$\frac{dX}{dt} = \rho_C\, k\,(1-X)$$

$$\ln\frac{1}{1-X} = K\rho_C t$$

t	0	5	10	20	30	40	50
X	0	.3	.5	.73	.85	0.93	.97
$\ln\frac{1}{(1-X)}$	0	.36	.69	1.31	1.89	2.66	3.5



A plot $\ln\left(\frac{1}{(1-X)}\right)$ is linear wrt time so we conclude the reaction is first order in 5, 6 benzzzoquinoline with k'=0.068 min^{-1}

$$\ln\left[\frac{r_A(T_2)}{r_A(T_1)}\right] = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\ln 4 = \frac{E}{R}\left[\frac{1}{353} - \frac{1}{383}\right]$$

$$\frac{E}{R} = \frac{\ln 4}{\frac{30}{(353(383))}} = 6248\ ^\circ K$$

$$E = 12.414\ \frac{cal}{mol}$$

at 90°C = 363K

$$k(363) = \left[e^{6248\left(\frac{1}{373} - \frac{1}{363}\right)}\right] k(373)$$

$$k(363) = 0.63\ k(373)$$

$$k_2' = \frac{k_2}{k_1}\frac{\rho_{c2}}{\rho_{c1}} k_1' = (.63)(2)\, k_1' = 1.26\, k_1'$$

$$k_1' = 0.0857$$

$$\ln\frac{1}{1-X} = k't$$

$$X = 1 - e^{-k't}$$

τ	0	10	20	30	40	50
X	0	0.57	0.82	0.42	0.97	0.99

CDP4-G

Develop a design equation

Mole balance: $F_A(r) - F_A(r + \Delta r) + r_A(2\pi r \Delta r h) = 0$

$$\Rightarrow \frac{F_A(r)\ F_A(r+\Delta r)}{\Delta r} = r_A(2\pi r h) \quad \Rightarrow \frac{dF_A}{dr} = r_A(2\pi r h)$$

Rate law: $-r_A = k_1 C_A C_B$

Assuming θ_B=1 and $\varepsilon = 0$

Stoichiometry: $C_A = C_{A0}(1-X)$ and $C_B = C_{A0}(\theta_B - X) = C_{A0}(1-X)$

Also $F_A = F_{A0}(1-X)$ $\Rightarrow \frac{dF_A}{dr} = -F_{A0}\frac{dX}{dr} = r_A(2\pi r h)$

Combine: $\frac{dX}{dr} = \frac{2\pi rhkC_{A0}{}^2(1-X)^2}{F_{A0}} \Rightarrow \int_0^X \frac{dX}{(1-X)^2} = \int_{R_0}^r \frac{(2\pi kC_{A0}{}^2)rdr}{F_{A0}}$

By Integration we get: $\frac{X}{1-X} = \frac{k\pi hC_{A0}{}^2}{F_{A0}}(r^2 - R_o{}^2)$

$$\Rightarrow X = \frac{\frac{k\pi hC_{A0}{}^2}{F_{A0}}(r^2 - R_o{}^2)}{1+\frac{k\pi hC_{A0}{}^2}{F_{A0}}(r^2 - R_o{}^2)}$$

b) Now, with the pressure drop,
$C_A = C_B = C_{A0}(1-X)y$

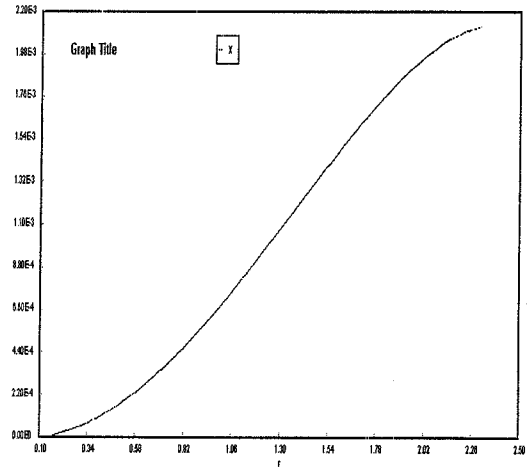
Hence, $-r_A = kC_{A0}{}^2(1-X)^2y^2 \Rightarrow$

$$\frac{dX}{dr} = \frac{2\pi rhkC_{A0}{}^2(1-X)^2y^2}{F_{A0}}$$

Where $y = (1-\alpha W)^{1/2}$ and

$$W = \rho_b\pi(r^2 - R_0{}^2)h$$

Using polymath, following graph is obtained:



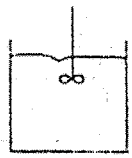
Differential equations
d(X)/d(r) = 2*3.1416*h*k*Cao^2/Fao*(1-X)^2*y^2*r
y = (1-alfa*W)^0.5
W = density*3.1416*h*(r^2- ro^2)
ro = 0.1
density = 2
Cao = 0.1
Fao = 10
k = 0.6
h = 0.4
alfa = 0.07
variable name : r
initial value : 0.1

c) Increasing the value of k increases conversion while decreasing it decreases the conversion. Increasing F_{A0} will decrease the conversion and decreasing it will increase the conversion. Increasing C_{A0} causes a dramatic increase of conversion. Similarly, decreasing C_{A0} results in a large decrease in conversion. Increasing the height will only slightly increase the conversion and decreasing the height causes a real small decrease in the conversion. Increasing R_0 decreases the volume of the reactor and hence decreases the conversion. Increasing R_L will increase the conversion as volume increases.

CDP4-H

Liquid phase reaction

$$A + B \longrightarrow C$$



well mixed
no inflow or outflow

BATCH

1. Mole balance on batch reactor

$$N_{AO}\frac{dX}{dt} = -r_A V$$

$$t = N_{AO}\int_0^X \frac{dX}{-r_A V}$$

2. Rate law

$$-r_A = k\,C_A C_B$$

3. Stoichiometry

liquid phase $V = V_o$ (batch) [if flow $\upsilon = \upsilon_o$]

$$C_A = \frac{N_A}{V} = \frac{N_A(1-X)}{V_O} = C_{Ao}(1-X)$$

$$C_B = \frac{N_B}{V} = \frac{N_{Ao}(\theta_B - \frac{b}{a}X)}{V_O} = C_{Ao}(1-X)$$

$$\theta_B = \frac{y_{Bo}}{y_{Ao}} = \frac{N_{Bo}}{N_{Ao}} = \frac{C_{Bo}}{C_{Ao}} = \frac{2}{2} = 1$$

4. Combine

$$-r_A = k\,C_{AO}^2(1-X)^2$$

$$t = N_{AO}\int_0^X \frac{dX}{-r_A V} = \frac{N_{AO}}{V_O}\int_0^X \frac{dX}{-r_A} = C_{AO}\int_0^X \frac{dX}{kC_{AO}^2(1-X)^2}$$

$$t = \frac{1}{k\,C_{AO}}\int_0^X \frac{dX}{(1-X)^2} = \frac{1}{k\,C_{AO}}\left[\frac{X}{1-X}\right]$$

Table of reaction integrals can be found in Appendix A-10,

a)

$$t = \frac{1}{(0.01\ dm^3/mol\ min)\ (2\ mol/dm^3)}\left[\frac{0.9}{1-0.9}\right], \quad t = 450\ min$$

1. Mole balance on CSTR

$$V = \frac{F_{AO}X}{-r_A}$$

2. Rate Law

$$-r_A = k\,C_A C_B$$

3. Stoichiometry

liquid phase $\upsilon = \upsilon_o$

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{Ao}\,(1-X)}{\upsilon_O} = C_{Ao}\,(1-X)$$

$$C_B = \frac{F_B}{\upsilon} = \frac{F_{Ao}\,(\theta_B - \frac{b}{a}X)}{\upsilon_O} = C_{Ao}\,(1-X)$$

4. Combine

$$V = \frac{F_{AO}X}{k\,C_{AO}^2(1-X)^2}$$

5. Parameter evaluation

$$V = \frac{10\ mol/min\ (0.9)}{(0.01\ dm^3/mol\ min)(2\ mol/dm^3)^2(1-0.9)^2}$$

b) $V = 22500\ dm^3$

1. Mole balance on PFR

$$F_{AO}\frac{dX}{dV} = -r_A$$

if no pressure or phase change (liquid phase) therefore

$$V = F_{AO}\int_0^X \frac{dX}{-r_A}$$

2. Rate law

$$-r_A = k\,C_A C_B$$

3. Stoichiometry

liquid phase $\upsilon = \upsilon_o$

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0} = C_{A0}(1-X)$$

$$C_B = \frac{F_B}{\upsilon} = \frac{F_{A0}\left(\theta_B - \frac{b}{a}X\right)}{\upsilon_0} = C_{A0}(1-X)$$

4. Combine

$$-r_A = k\,C_{A0}^2(1-X)^2$$

$$V = F_{A0}\int_0^x \frac{dV}{k\,C_{A0}^2(1-X)^2} = \frac{F_{A0}X}{k\,C_{A0}^2}\int_0^x \frac{dX}{(1-X)^2}$$

$$V = \frac{F_{A0}X}{k\,C_{A0}^2}\left[\frac{X}{1-X}\right]$$

5. Parameter evaluation

$$V = \frac{(10\ \text{mol/min})}{(.01\ \text{dm}^3/\text{mol min})(2\ \text{mol/dm}^3)^2}\,\frac{0.9}{1-0.9}$$

d) Solution similar to part (a) to (c)

e) $-r_A = k\left[C_A C_B - \frac{C_C}{K_C}\right]$ At equilibrium , $-r_A = 0$

$$K_C = \frac{C_{Ce}}{C_{Ae}\,C_{Be}} = \frac{C_{A0}X}{C_{A0}^2(1-X)^2} = \frac{X}{C_{A0}(1-X)^2}$$

$$K\,C_{A0} = \frac{2\text{dm}^3}{\text{mol}} \times \frac{2\text{mol}}{\text{dm}^3} = 4$$

$$1 - 2X + X^2 = \frac{X}{K\,C_{A0}} = \frac{X}{4}$$

$$X^2 - 2.25\,X + 1 = 0$$

$$X_e = 0.61$$

PFR

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} = kC_{A0}\left[C_{A0}(1-X)^2 - \frac{X}{K_C}\right] = kC_{A0}^2\left[(1-X)^2 - \frac{X}{K_C C_{A0}}\right]$$

$$= \frac{(.01)(2)^2}{10}\left[1-2X+X^2\,\frac{X}{4}\right]$$

$$V = 250\int_0^{.6} \frac{dX}{1 - 2.25X + X^2}$$

$$V = 250\,\frac{h}{3}[f(0) + 4f(.15) + 2f(.3) + 4f(.45) + f(.6)] =$$

$$250\,\frac{0.15}{3}[1 + 4(1.41) + 2(2.41) + 4(5.26) + 100]$$

$$V = 250\,\frac{h}{3}[f(0) + 4f(.15) + 2f(.3) + 4f(.45) + f(.6)]$$

$$= 250\,\frac{0.15}{3}[1 + 4(1.41) + 2(2.41) + 4(5.26) + 100]$$

$$= 1656\ \text{dm}^3$$

CDP4-I (a)

Benzene is A

$$-r_A = k_A\left(C_A^2 - \frac{C_B C_C}{K_C}\right)$$

for equilibrium $-r_A = 0 \quad \therefore \quad C_A^2 - \frac{C_B C_C}{K_C} = 0$

$$C_A^2 = \frac{C_B C_C}{K_C}$$

$$C_A = C_{Ao}(1-X) \quad C_B = \frac{C_{Ao}X}{2} \quad C_c = \frac{C_{Ao}X}{2}$$

$$C_{Ao}^2(1-X_c)^2 = \frac{C_{Ao}^2 X_c^{\,2}}{4K_c}$$

$$4K_c(1-X_c)^2 = X_c^{\,2}$$

$$4K_c - 8K_c X_c + 4K_c X_c^{\,2} = X_c^{\,2}$$

$$0.2X^2 - 2.4X_c + 1.2 = 0$$

$$X_c = 0.52$$

CDP4-I (b)

PFR

Design Equation: $V = F_{Ao}\int \frac{dX}{-r_A}$

Rate Law: $-r_A = k_A\left(C_A^2 - \frac{C_B C_C}{K_C}\right)$

Stoichiometry: $C_A = C_{Ao}(1-X) \quad C_B = \frac{C_{Ao}X}{2} \quad C_c = \frac{C_{Ao}X}{2}$

$$C_{Ao} = \frac{P}{RT} = \frac{5\,\text{atm}}{\left(0.73\frac{\text{ft}^3\cdot\text{atm}}{\text{lbmol}\cdot{}^\circ\text{R}}\right)(1859.67^\circ\text{R})} = 0.0037\frac{\text{lbmol}}{\text{ft}^3}$$

Combine : $$V = \frac{F_{Ao}}{kC_{Ao}^2}\int_0^X \frac{dX}{\left[(1-X)^2 - \frac{X^2}{4K_c}\right]}$$

$$V = \frac{(10\text{lbmol/min})(1\text{min/60s})}{(1800\text{ft}^3/\text{lbmol}\cdot\text{s})(0.0037)^2}\int_0^X \frac{dX}{\left[(1-X)^2 - 0.833X^2\right]}$$

$$V = 6.76\text{ft}^3\int_0^X \frac{dX}{\left[1-2X+0.167X^2\right]}$$

$$V = 6.76\left(\frac{1}{(0.617)(11.45-0.523)}\ln\left[\frac{0.523}{11.45}\left(\frac{X-11.45}{X-0.523}\right)\right]\right)$$

$$V = 13.5\text{ft}^3$$

CDP4-I (c)

CSTR

Design Equation : $$V = \frac{F_{Ao}X}{-r_A}$$

Rate Law : $$-r_A = k_A\left(C_A^2 - \frac{C_B C_C}{K_C}\right)$$

Stoichiometry : $$C_A = C_{Ao}(1-X) \quad C_B = \frac{C_{Ao}X}{2} \quad C_c = \frac{C_{Ao}X}{2}$$

Combine : $$V = \frac{F_{Ao}X}{k_A C_{Ao}^2\left[(1-X)^2 - \left(\frac{X^2}{4K_c}\right)\right]}$$

$$V = \frac{(10)(0.51)(1/60)}{(1800)(0.0037)^2\left[(1-0.51)^2 - \left(\frac{0.51^2}{4(0.3)}\right)\right]} = 147.73\,\text{ft}^3$$

CDP4-I (d)

Amount processed in CSTR :

$$(10\,\text{lbmol/min})(60\,\text{min/hr})(24\,\text{hr/day}) = 14{,}400\,\text{lbmol/day}$$

Batch

$$t = C_{Ao}\int\frac{dX}{-r_A} = \frac{C_{Ao}}{kC_{Ao}^2}\int\frac{dX}{\left[(1-X)^2 - \frac{X^2}{4K_c}\right]}$$

$$t = \frac{1}{kC_{Ao}}\left(\frac{1}{(0.167)(11.45-0.523)}\ln\left[\frac{0.523}{11.45}\left(\frac{X-11.45}{X-0.523}\right)\right]\right)$$

$$t = 0.30\,s$$

Taking into account the time it takes to clean the reactor and other down time assume that the total time per run is 4 hours. Assuming that the reactor can be used twenty-four hours a day there can be 6 runs per day.

$$\frac{14{,}400\ \text{lbmol/day}}{6\ \text{runs/day}} = 2400\ \text{lbmol/run}$$

$$t = \frac{N_{Ao}}{V}\int\frac{dX}{-r_A} \quad \therefore \quad V = \frac{N_{Ao}}{t}\int\frac{dX}{-r_A}$$

$$V = \frac{N_{Ao}}{t}\frac{1}{kC_{Ao}^2}\left(\frac{1}{(0.167)(11.45-0.523)}\ln\left[\frac{0.523}{11.45}\left(\frac{X-11.45}{X-0.523}\right)\right]\right)$$

$$V = \frac{2400}{(4)(1800)(0.0037)^2}\left(\frac{1}{(0.167)(11.45-0.523)}\ln\left[\frac{0.523}{11.45}\left(\frac{X-11.45}{X-0.523}\right)\right]\right)$$

$$V = 48{,}690\ ft^3$$

CDP4-I (e)

$E = 30{,}202$ btu/lbmol

for $X = 0$, $\quad -r_A = kC_{Ao}^2$

$$\frac{-r_{A(800)}}{-r_{A(1400)}} = \frac{k_{800}C_{Ao}^2}{k_{1400}C_{Ao}^2} = \frac{k_{800}}{k_{1400}} = \exp\frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\frac{-r_{A(800)}}{-r_{A(1400)}} = \exp\frac{30{,}202\ \text{btu/lbmol}}{1.987\ \text{btu/lbmol}\cdot{}^\circ R}\left(\frac{1}{1259.67^\circ R} - \frac{1}{1859.67^\circ R}\right)$$

$$\frac{-r_{A(800)}}{-r_{A(1400)}} = 49$$

CDP4-J

PBR

MB: $\frac{dX}{dW} = \frac{-r_A}{F_{AO}}$

Rate Law: $-r_A = k C_A$ $\qquad C_A = C_{AO}(1-X)$

Combine:

$$\int_0^{.141} \frac{dX}{1-X} = \left(\frac{kC_{AO}}{F_{AO}}\right)\int_0^{W} (1-W\alpha)^{1/2}\, dW$$

$$.152 = \left(\frac{kC_{AO}}{F_{AO}}\right)\int_0^{1000} (1-8x10^{-4}W)^{5}\, dW$$

$$\frac{kC_{AO}}{F_{AO}} = 2x10^{-4}$$

CSTR

MB: $W = \frac{F_{AO}X}{-r_A}$

Combine:

$$W = \frac{F_{AO}}{kC_{AO}}\frac{X}{(1-X)}$$

$$1000 = \frac{1}{2x10^{-4}}\frac{X}{(1-X)}$$

$$X = .18$$

b) We know, ε = 0, so

$$P = P_0(1-\alpha W)^{1/2} \Rightarrow 1 = 20(1-\alpha W)^{1/2}$$

=> α = 9.98 x 10^{-4}

c) For conversion to be maximum, α should be minimum

Also, we know that α is proportional to $\frac{G^2}{A_c D_P} = \frac{1}{D_{pipe}{}^6 D_p{}^2}$ for turbulent flow

And it is proportional to $\frac{G}{A_c D_p{}^2} = \frac{1}{D_{pipe}{}^4 D_p{}^2}$ for laminar flow

Hence for minimum α, D_p and D_{pipe} should be increased. **d)** Yes, we can increase D_p and decrease D_{pipe} (or vice versa) according to the above equation to get the same value of α.**e)**

For assumed turbulent flow,α is proportional to $\frac{1}{D_{pipe}{}^6 D_p{}^2}$

Now, $\frac{\alpha_1}{\alpha_2} = \frac{D_{pipe2}{}^6 D_{p2}{}^2}{D_{pipe1}{}^6 D_{p1}{}^2} = 1$

$\frac{D_{pipe1}}{D_{pipe2}} = \frac{4}{6}$ and D_{p1}= 0.5 cm

=>**D_{p2} = 0.044 cm**

f) We're given, $k \sim \frac{1}{D_p} \Rightarrow k_2 = k_1 \frac{D_{p1}}{D_{p2}}$

Hence $\frac{k_2}{k_1} = \frac{0.5}{0.044} = 11.4$

g) Rate law: $-r_A = kC_A$

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

Mole balance: $\frac{dX}{dW} = \frac{-r_A}{F_{A0}}$

Combining: $\frac{dX}{dW} = \frac{k_2 C_{A0}{}^2 (1-X)(1-\alpha_2 W)^{1/2}}{F_{A0}}$ (for ε = 0)

$\frac{k_2}{k_1} = 11.4$ and $\frac{C_{A0} k_1}{F_{A0}} = 2\times10^{-4}$ Integrating with limits: (X→0 to X; W→ 0 to 1000) => **X = 0.78**

CDP4-K

1. Mole Balance: $\frac{dX}{dz} = \frac{-r_A A_C}{F_{Ao}}$

2. Rate Law: $r_A = -k' C_A^2 \rho_C (1-\varphi)$

where k', ρ_C, and φ are unknown constants. They will be grouped into one unknown constant, k_o.

$$k_o = k' \rho_C (1-\varphi)$$

3. Stoichiometry: $C_A = C_{Ao} \frac{(1-X)}{(1+\varepsilon X)} y$

$$\varepsilon = y_{Ao}\delta = (1)(1+\tfrac{1}{2}-1) = \tfrac{1}{2}$$

4. Pressure Drop : $$\frac{dy}{dz} = -\frac{\beta_o}{P_o y}(1+\varepsilon X)$$

when neglecting the turbulent contribution to pressure drop, β_o is given by

$$\beta_o = G\left[\frac{150(1-\varphi)^2\mu}{\rho_o g_C D_p^2 \varphi^3}\right]$$

where all of the bracketed variables are unknown constants.

$$G = \frac{\dot{m}}{A_C}$$

The mass flow rate is also and unknown constant. Thus β_o can be written as a constant, B, over cross - sectional area.

$$\beta_o = \frac{B}{A_C} \quad \text{where} \quad B = \dot{m}\left[\frac{150(1-\varphi)^2\mu}{\rho_o g_C D_p^2 \varphi^3}\right]$$

Where B is a function of the mass flow rate, feed properties, and catalyst properties---all of which are constant for part (a). Note that all equations up to now apply to a tubular PBR and spherical PBR. To find B and k_o we must model the tubular PBR on POLYMATH by entering the above equations in addition to

$$A_C = \frac{\pi}{4}(20\,\text{dm})^2 = 314\,\text{dm}^2$$

B and k_o must be arbitrarily chosen at first. Then, depending on whether POLYMATH gives high or low values of y and X, one can converge on the true values of k_o and B. In order to do so efficiently, however, one must make use of the following trends: (Note that the following table is completely true only when $\varepsilon > 0$.)

a) From POLYMATH:
B=843
k=0.21
x=.67
P=yP_o=.973*1500=1459.5

Equations:

d(y)/d(z)=-beta/(po*y)*(1+eps*x)

d(x)/d(z)=-ra*Ac/Fao

po=1500

eps=0.5

Fao=950

R=10

Cao=0.4

k=0.21

B=843

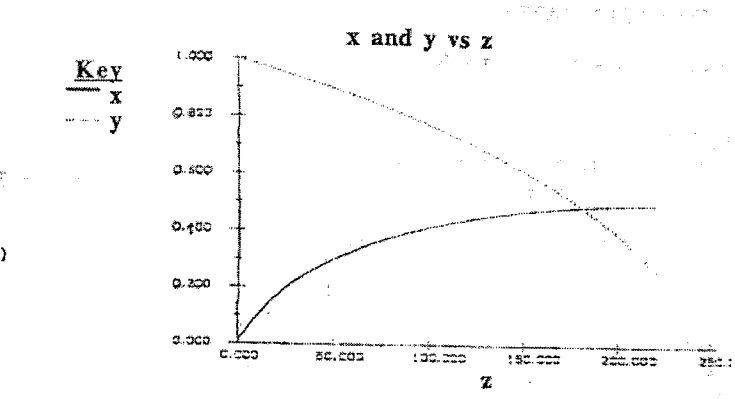
Ac=3.1416*(R**2)

Ca=Cao*y*(1-x)/(1+eps*x)

beta=B/Ac

ra=-k*Ca**2

$z_0 = 0, \quad z_f = 220$



Equations:

d(y)/d(z)=-beta/(po*y)*(1+eps*x)

d(x)/d(z)=-ra*Ac/Fao

po=1500

eps=0.5

Fao=950

R=26

Cao=0.4

k=0.21

B=843

L=24

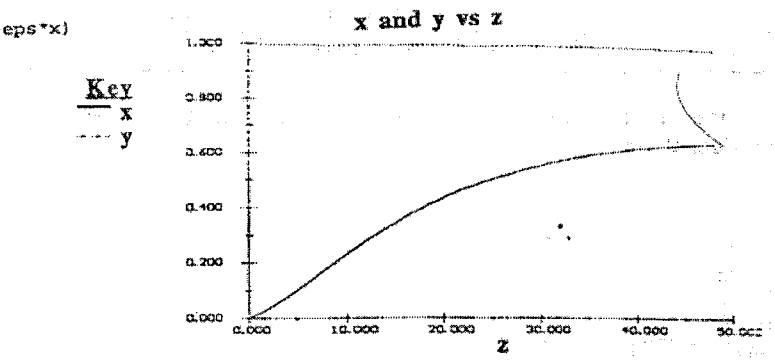
Ac=3.1416*(R**2-(z-L)**2)

Ca=Cao*y*(1-x)/(1+eps*x)

ra=-k*Ca**2

beta=B/Ac

$z_0 = 0, \quad z_f = 48$



b) From polymath: Maximum flow rate = 1750 mol/s

Equations:

d(y)/d(z)=-beta/(po*y)*(1+eps*x)

d(x)/d(z)=-ra*Ac/Fao

po=1500

eps=0.5

Fao=1750

R=26

Cao=0.4

k=0.21

B=843

L=24

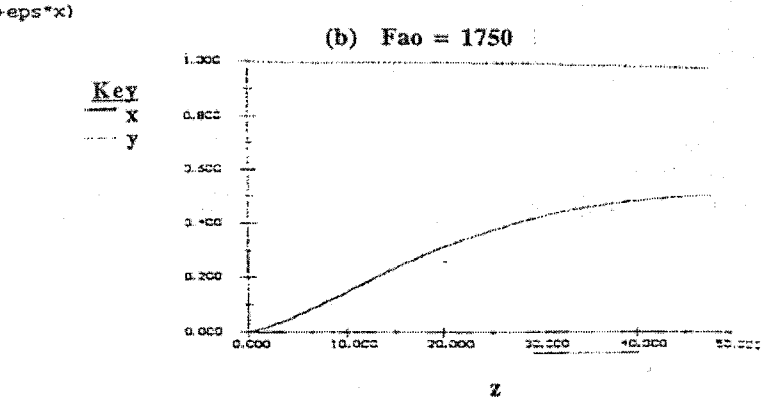
Ac=3.1416*(R**2-(z-L)**2)

Ca=Cao*y*(1-x)/(1+eps*x)

ra=-k*Ca**2

beta=B/Ac

$z_0 = 0, \quad z_f = 48$



c) From POLYMATH

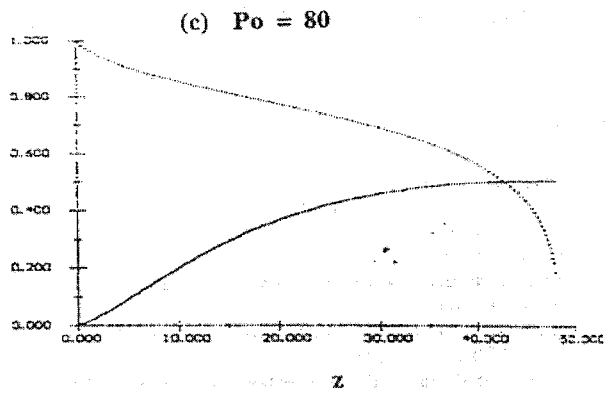
Minimum pressure=80 kPa

Equations:

```
d(y)/d(z)=-beta/(po*y)*(1+eps*x)
d(x)/d(z)=-ra*Ac/Fao
po=80
eps=0.5
Fao=950
R=26
Cao=0.4
k=0.21
B=843
L=24
Ac=3.1416*(R**2-(z-L)**2)
Ca=Cao*y*(1-x)/(1+eps*x)
ra=-k*Ca**2
beta=B/Ac
```

$z_0 = 0, \quad z_f = 48$

Key: x, y



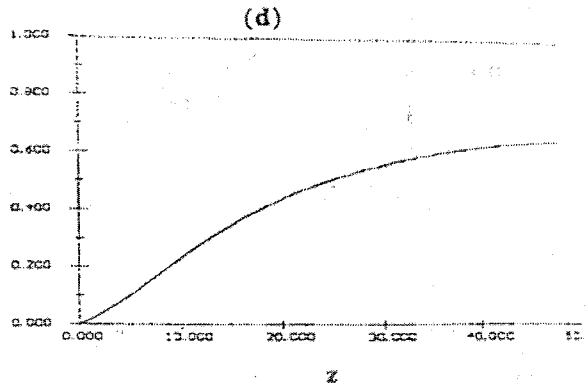
d) From POLYMATH:

Equations:

```
d(y)/d(z)=-beta/(po*y)*(1+eps*x)
d(x)/d(z)=-ra*Ac/Fao
po=1500
eps=0.5
Fao=950
R=26
Cao=0.4
k=0.21
B=843
L=24
Ac=3.1416*(R**2-(z-L)**2)
Ca=Cao*y*(1-x)/(1+eps*x)
ra=-k*Ca**2
beta=B/Ac
```

$z_0 = 0, \quad z_f = 48$

Key: x, y



CDP4-L

(a)

$$K_C = \frac{C_B}{C_A}$$

$$C_A = C_{Ao}(1-X) \ , \ C_B = C_{Ao}X$$

$$K_C = \frac{C_{Ao}X}{C_{Ao}(1-X)} = \frac{X}{1-X}$$

$$X_{eq} = \frac{K_C}{1+K_C} = \frac{0.5}{1+0.5} = 0.33$$

(b) For a conventional PFR:

$$F_{Ao}\frac{dX}{dV} = -r_A$$

$$-r_A = k(C_A - C_B/K_C) = kC_{Ao}((1-X) - X/K_C)$$

For the IMRCF:

$$\frac{dF_A}{dt} = r_A v_o$$

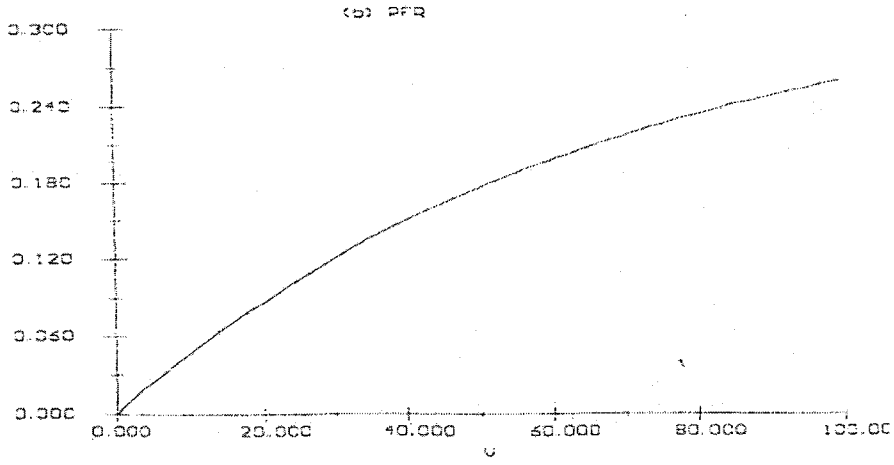
$$\frac{dF_B}{dt} = -r_A v_o - v_o k_C C_B$$

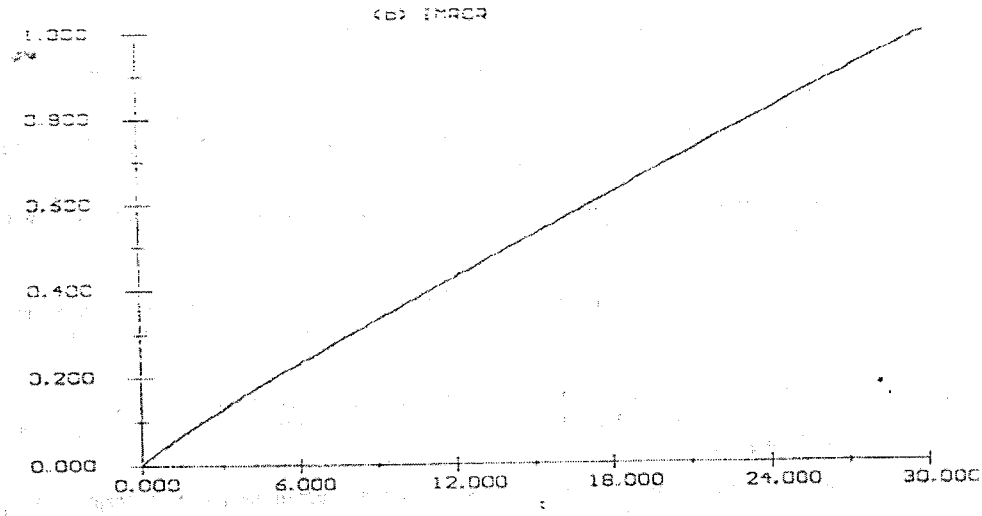
$$-r_A = k(C_A - C_B/K_C)$$

$$C_A = F_A/V \ , \ C_B = F_B/V$$

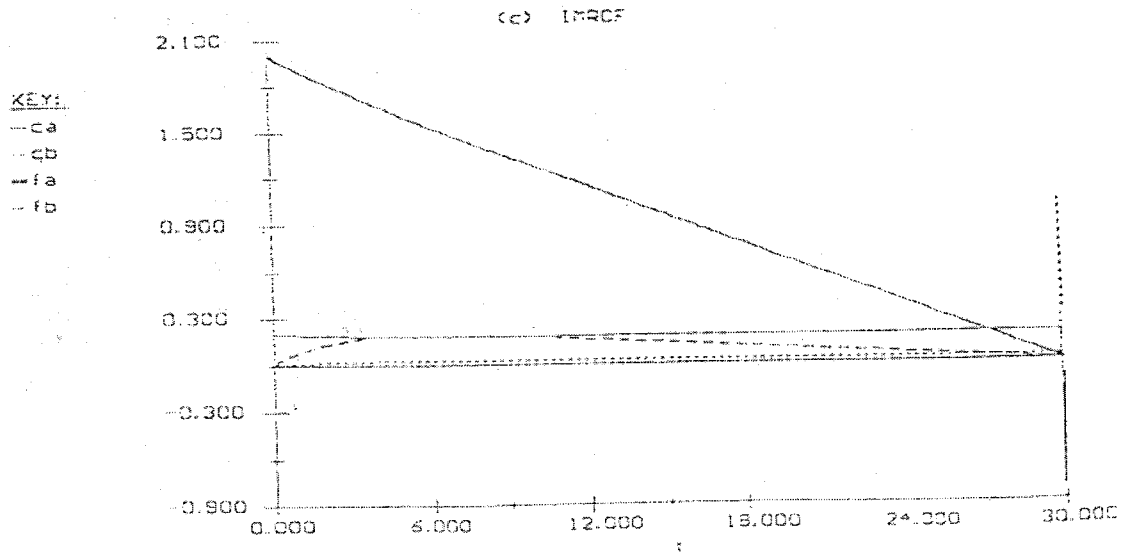
$$V = v_o\frac{(F_A + F_B)}{F_{Ao}}$$

Use these equations in POLYMATH to generate plots of the conversion profile.





(c) Use the same equations for the IMRCF in POLYMATH to generate the desired plot.



(d) By varying one parameter at a time we can see the effect of each:

Increasing the specific reaction rate causes changes in conversion. concentration, and molar flow rate to occur more quickly.

Lowering the transport coefficient (k_c) causes an increase in both C_B and F_B, which causes a decrease in conversion.

By raising the equilibrium constant (K_c), we cause a decrease in the molar flow rate of A and an increase in conversion.

(e) A significant increase in temperature for an exothermic reaction would drive the reaction in the reverse. This would cause a decrease in X and C_B and an increase in the C_A.

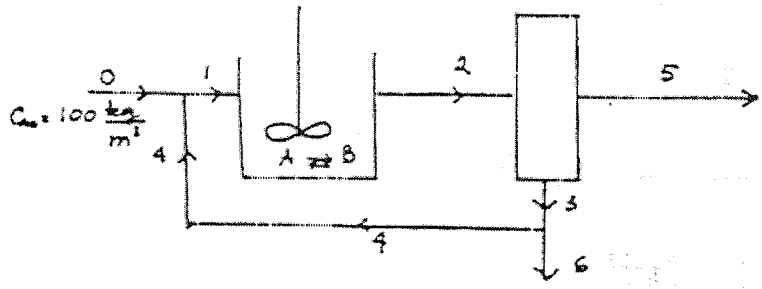
A significant decrease in temperature for an exothermic reaction would cause increase in the rate of the forward reaction. This would drive up X and C_B, while lowering C_A.

An increase in temperature would drive an endothermic reaction forward, raising X and C_B, while lowering C_A.

A decrease in temperature would cause an increase in the reverse reaction for an endothermic reaction. This would raise C_A, and lower both X and C_B.

CDP4-M No solution

CDP4-N



Note - A and B have the same molecular weight

$F_{A2} = F_{A3}$

$F_{A4} = y F_{A3}$

$F_{A1} = F_{AO} + y F_{A3}$

$F_{A2} = F_{A1}(1-X)$ where X is conversion defined with respect to F_{A1}

$F_{A5} = F_{B2}$ (by problem specification)

$F_{B1} = 0$ (by problem specification)

$F_{A1} = F_{AO} + y F_{A1}(1-X)$ have $F_{A1} = \frac{F_{AO}}{1-y(1-X)}$

Stoichiometric table

Inlet	Outlet
F_{A1}	$F_{A1}(1-X)$
$F_{B1}=0$	$F_{B1}+F_{A1}X = F_{A1}X$

Hence

$F_{B2} = F_{A1}X = \frac{F_{AO}X}{1-y(1-X)}$

Also

$v_1 = v_0 + v_4$

$v_2 = v_3 + v_5$

$v_1 = v_2$ (no volume change)

$C_{A1} = \frac{F_{A1}}{v_1} = 100$

$v_1 = \frac{F_{A1}}{C_{A1}} = \frac{F_{A1}}{100}$

CDP4-O No solution

Solution

$$A \xrightarrow{k_1} B \underset{k_3}{\overset{k_2}{\rightleftharpoons}} C$$

At equilibrium

$k_2 C_{Be} = k_3 C_{Ce}$

(a) $k_2 C_{B0} = k_3 C_{A0}$

$$\Rightarrow C_{B0} = \frac{k_3}{k_2} C_{A0} \quad \text{---------- (1)}$$

Initial Condition

$C_{B0} = C_{Be}$

$C_{A0} + \cancel{C_{B0}} + \underset{\rightarrow 0}{\cancel{C_{C0}}} = C_{Ae} + \underset{\rightarrow 0}{\cancel{C_{Be}}} + C_{Ce}$

$C_{Ce} = C_{A0}$

(b) $$\frac{dC_A}{dt} = -k_1 C_A \Rightarrow C_A = C_{A0}\, e^{-k_1 t}$$

$$\frac{dC_C}{dt} = +k_2 C_{B0} - k_3 C_C$$

C_{B0} is a constant

$$\Rightarrow C_C = \frac{k_2 C_{B0}}{k_3}\left[1 - e^{-k_3 t}\right]$$

$$\frac{dC_B}{dt} = -k_1 C_A - k_2 C_B + k_3 C_C$$

$$0 = k_1 C_{A0}\, e^{-k_1 t} - k_2 C_{B0} + k_2 C_{B0}\left[1 - e^{-k_3 t}\right]$$

From (1)

$$k_3\, e^{-k_3 t} = k_1\, e^{-k_1 t} \Rightarrow \boxed{k_1 = k_3}$$

(c) $$\frac{dC_A}{dt} = -k_1 C_A \Rightarrow C_A = C_{A0}\, e^{-k_1 t}$$

For a maxima in C_B,

$$\left.\frac{dC_B}{dt}\right|_{t=0} > 0 \Rightarrow \boxed{k_1 > k_3}$$

for a minima in C_B

$$\left.\frac{dC_B}{dt}\right|_{t=0} < 0 \Rightarrow \boxed{k_1 < k_3}$$

CDP4-Q

CDP4-R

CDP4-S

CDP4-T

CDP4-U

CDP4-V

Solutions for Chapter 5 – Collection and Analysis of Rate Data

P5-1 (a) Individualized solution
P5-1 (b) Individualized solution
P5-1 (c) Individualized solution
P5-1 (d) Individualized solution
P5-1 (e) Individualized solution
P5-1 (f) Individualized solution
P5-1 (g) Individualized solution

P5-1 (h) Example 5-1

The graphical method requires estimations of the area under and above curves on a plot as well as in reading the intersection of lines on the plot. This can lead to small inaccuracies in each data point.

The Finite differences method uses mathematical estimates to calculate the rate. It is only possible to use this when the time interval of each data point is uniform.

The graphical method uses polynomial regression to approximate C_A as a function of time. The derivative of the polynomial is then used to calculate the rate.

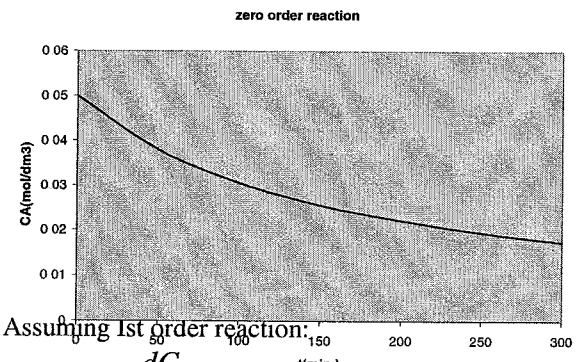
P5-1 (i) Example 5-2

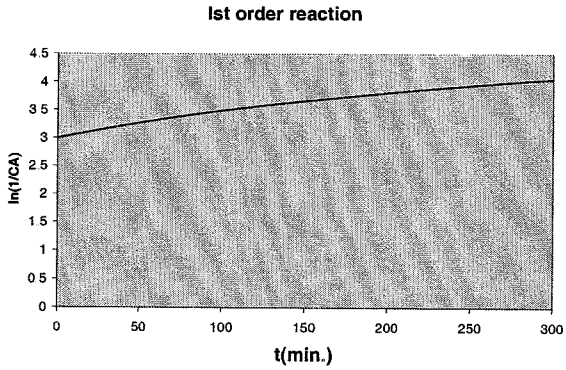
Assuming zero order reaction:

Rate law: $-\frac{dC_A}{dt} = k'$

$C_A = C_{AO} - k't$

t(min.)	0	50	100	150	200	250	300
C_A(mol/dm^3)	0.05	0.038	0.0306	0.0256	0.0222	0.0195	0.0174





Assuming Ist order reaction:

Rate law: $-\frac{dC_A}{dt} = k'C_A$

Or, $\ln(1/C_A) = k't + 3$

t(min.)	0	50	100	150	200	250	300
C_A(mol/dm^3)	0.05	0.38	0.0306	0.0256	0.0222	0.0195	0.0174

$\ln(1/C_A)$	3	3.27	3.49	3.66	3.81	3.94	4.05

Since none of these plots are straight lines, its is not Ist order reaction or second order reaction.

P5-1 (j) Example 5-3 Because when α is set equal to 2, the best value of k must be found.

P5-1 (k) Example 5-4

$C_{HCl,0}$ (mol/dm^3)	1.0	4.0	2.0	0.1	0.5
$-r''_{HCl,0}(mol/cm^2.s)\times10^7$	1.2	2.0	1.36	0.36	0.74

See Polymath program P5-1-k.pol.

POLYMATH Results
Nonlinear regression (L-M)

Model: r = k*(Ca^alfa)

Variable	Ini guess	Value	95% confidence
k	0.1	1.0672503	0.0898063
alfa	0.5	0.4461986	0.076408

Precision

R^2	= 0.9812838
R^2adj	= 0.9750451
Rmsd	= 0.0341709
Variance	= 0.0097304

Rate law: $-r'' = 1.1C_{HCl}^{0.44} mol/cm^2.s$

P5-1 (l) Example 5-5

rate law: $r_{CH_4} = kP_{CO}^{\alpha}P_{H_2}^{\beta}$

Regressing the data

r'(gmolCH_4/gcat.min)	P_{CO} (atm)	P_{H2} (atm)
5.2e-3	1	1
13.2e-3	1.8	1
30e-3	4.08	1
4.95e-3	1	0.1
7.42e-3	1	0.5
5.25e-3	1	4

See Polymath program P5-1-l.pol.

POLYMATH Results
Nonlinear regression (L-M)

Model: r = k*(PCO^alfa)*(PH2^beta)

Variable	Ini guess	Value	95% confidence
k	0.1	0.0060979	6.449E-04
alfa	1	1.1381455	0.0850634
beta	1	0.0103839	0.1951217

Precision

R^2	= 0.9869709

R^2adj = 0.9782849
Rmsd = 4.176E-04
Variance = 2.093E-06

Therefore order of reaction = 1.14
Again regressing the above data putting $\beta = 1$

POLYMATH Results
Nonlinear regression (L-M)
Model: r = k*(PCO^0.14)*(PH2)

Variable	Ini guess	Value	95% confidence
k	0.1	0.0040792	0.0076284

Precision
R^2 = -0.8194508
R^2adj = -0.8194508
Rmsd = 0.0049354
Variance = 1.754E-04

Therefore, k = 0.004 ($gmolCH_4/(gcat.min.atm^{1.14})$)

P5-2 Solution is in the decoding algorithm given with the modules.

P5-3 Individualized solution

P5-4 (a)

The kinetics of this deoxygenation of *hemoglobin* in blood was studied with the aid of a tubular reactor.

$$HbO_2 \rightarrow Hb + O_2$$

Rate law: $-r_A = k C_A^n$

Mole balance: $$F_{AO}\frac{dX}{dV} = kC_{AO}^n(1-X)^n$$

$dV = A_c dz$, where A_C is the tube cross sectional area

$$\frac{dX}{dz} = \frac{kC_{Ao}^n A_c}{F_{Ao}}(1-X)^n$$

$$\ln\left(\frac{dX}{dz}\right) = \ln a + n\ln(1-X)$$

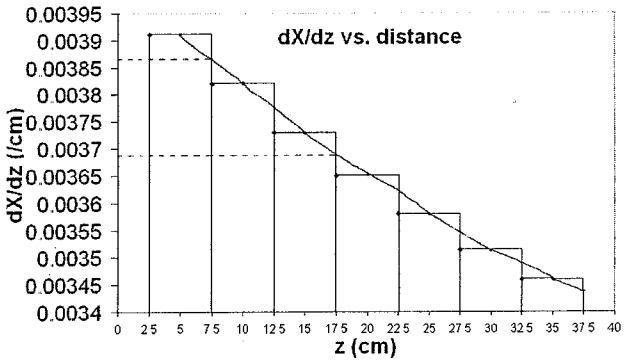
therefore,

$$where, a = \frac{kC_{Ao}^n A_c}{F_{Ao}}$$

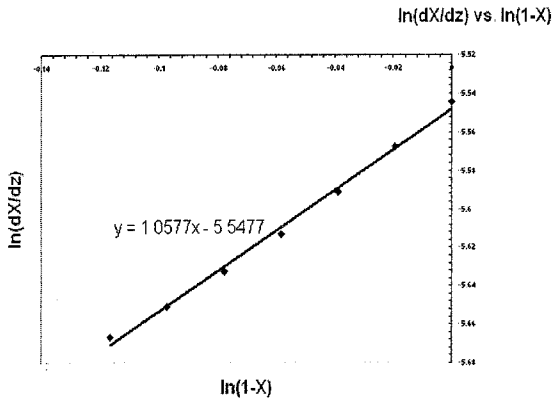
Electrode Position	1	2	3	4	5	6	7
Position (cm)	0	5	10	15	20	25	30
Δz (cm)	5	5	5	5	5	5	5
Conversion of HbO2 (X_A)	0.0000	0.0193	0.0382	0.0568	0.0748	0.0925	0.110
($1-X_A$)	1.0000	0.9807	0.9618	0.9432	0.9252	0.9075	0.8900
ΔX	-	0.0193	0.0189	0.0186	0.018	0.0177	0.0175
$\Delta X/\Delta z$ (cm^{-1})	-	0.00386	0.00378	0.00372	0.00360	0.00354	0.00350

Electrode Position	1	2	3	4	5	6	7
dX/dz (cm^{-1})	0.00386	0.00378	0.00368	0.00363	0.00355	0.0035	0.00345

A histogram plot of $\Delta X/\Delta z$ vs. z is then produced. The values of dX/dz are evaluated using equal-area graphical differentiation:



Using the values obtained above, a plot of $\ln(dX_A/dz)$ vs. $\ln(1-X_A)$ is produced and a line is fit to the data



$$\ln\left(\frac{dX}{dz}\right) = \ln a + n\ln(1-X)$$

$$where, a = \frac{kC_{Ao}^{n}A_c}{F_{Ao}}$$

$$\ln\left(\frac{dX}{dz}\right) = -5.5477 + 1.0577\ln(1-X)$$

n = 1

ln(a) = -5.5

a = exp(-5.5) = 4.1 x 10^{-3} *cm.*

Concentration of blood is 150g hemoglobin per liter of blood

Molecular weight of hemoglobin = 64500

Ac=0.0196cm

$$C_{Ao} = 2.3\times10^{-6} mol/cm^3$$

$$F_{Ao} = 45.7\times10^{-6} moles/s$$

$$k = \frac{F_{AO}a}{C_{AO}^{n}A_C} = \frac{45.7\times10^{-6} moles/s}{2.3\times10^{-6} moles/cm^3 \times 0.0196 cm^2}\left(4.1\times10^{-3} cm\right) = 4.1 s^{-1}$$

Hence rate law is,

$$-r_A = 4.1C_A\frac{mol}{dm^3 \bullet s}$$

P5-4 (b)

First we fit a polynomial to the data. Using Polymath we use regression to find an expression for X(z)

See Polymath program P5-4-b.pol.

POLYMATH Results
Polynomial Regression Report

Model: X = a0 + a1*z + a2*z^2 + a3*z^3 + a4*z^4 + a5*z^5 + a6*z^6

Variable	Value	95% confidence
a0	2.918E-14	0
a1	0.0040267	0
a2	-6.14E-05	0
a3	7.767E-06	0
a4	-5.0E-07	0
a5	1.467E-08	0
a6	-1.6E-10	0

General
Order of polynomial = 6
Regression including free parameter
Number of observations = 7

Statistics
R^2 = 1
R^2adj = 0
Rmsd = 1.669E-10
Variance = 1.0E+99

Next we differentiate our expression of X(z) to find dX/dz and knowing that

$$\ln\left(\frac{dX}{dz}\right) = \ln a + n\ln\left(1-X\right)$$

$$where, a = \frac{kC_{Ao}^{n}A_c}{F_{Ao}}$$

Linear regression of $\ln\left(\frac{dX}{dz}\right)$ as a function of $\ln\left(1-X\right)$ gives us similar vaules of slope and intercept as in the finite differences.

POLYMATH Results
Linear Regression Report

Model: ln(dxdz) = a0 + a1*ln(1-X)

Variable	Value	95% confidence
a0	-5.531947	0.0241574
a1	1.2824279	0.3446187

General
Regression including free parameter
Number of observations = 7

Statistics
R^2 = 0.9482059
R^2adj = 0.9378471
Rmsd = 0.0044015
Variance = 1.899E-04

n = 1.28

ln a = -5.53, a = 0.00396

$$k = \frac{F_{AO}a}{C_{AO}^{n}A_C} = \frac{45.7\times10^{-6}\,moles/s}{2.3\times10^{-6}\,moles/cm^3\times0.0196cm^2}\left(3.96\times10^{-3}cm\right) = 4.0s^{-1}$$

Hence rate law is,

$$-r_A = 4.0\,C_A^{1.28}\frac{mol}{dm^3\bullet s}$$

P5-5 (a)

Liquid phase irreversible reaction:

A → B + C ; C_{AO} = 2 mole/dm^3

$$\frac{C_{AO}-C_A}{\tau} = kC_A^{\alpha}$$

$$\ln\left(\frac{C_{AO}-C_A}{\tau}\right) = \ln k + \alpha \ln C_A$$

Space time (τ)min.	C_A(mol/dm^3)	ln(CA)	ln((CAO-CA)/τ)
15	1.5	0.40546511	-3.4011974
38	1.25	0.22314355	-3.9252682
100	1.0	0	-4.6051702
300	0.75	-0.28768207	-5.4806389
1200	0.5	-0.69314718	-6.6846117

By using linear regression in polymath:

See Polymath program P5-5-a.pol.

POLYMATH Results

Linear Regression Report

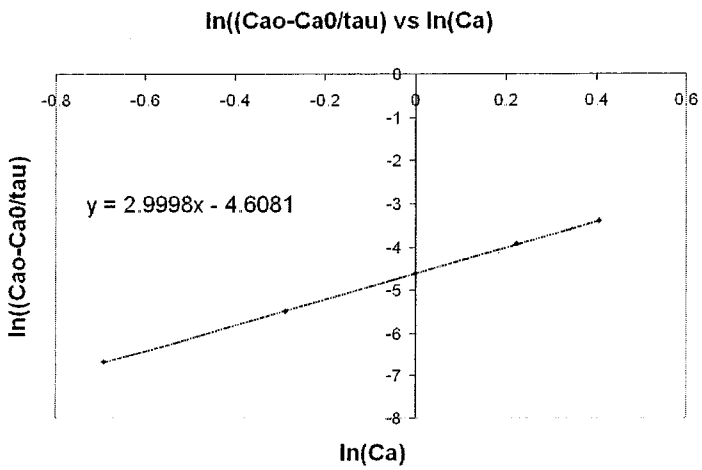
Model: y = a0 + a1*lnCa

$$\ln\left(\frac{C_{AO}-C_A}{\tau}\right) = \ln k + \alpha \ln C_A$$

Variable	Value	95% confidence
a0	-4.6080579	0.0162119
a1	2.9998151	0.0411145

Statistics

R^2 =	0.9999443
R^2adj =	0.9999258
Rmsd =	0.003883
Variance =	1.256E-04



Hence,

$\alpha = slope \equiv 3$

ln(k) = intercept = -4.6

therefore, k = 0.01 mole^{-2}min^{-1}

Rate law: $-\frac{dC_A}{dt} = 0.01C_A^3 mol/dm^3$ min

P5-5 (b) Individualized solution

P5-5 (c) Individualized solution

P5-6 (a)

Constant voume batch reactor: **A→ B +C**

Mole balance:

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

Integrating with initial condition when t = 0 and $C_A = C_{AO}$ for $\alpha \neq 1.0$

$$t = \frac{1}{k}\frac{C_{AO}^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1-\alpha)} = \frac{1}{k}\frac{(2)^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1-\alpha)}$$ .....substituting for initial concentration $C_{AO} = 2$ mol/dm^3.

t (min.)	C_A (mol/dm^3)
0	2
5	1.6
9	1.35
15	1.1
22	0.87
30	0.70
40	0.53
60	0.35

See Polymath program P5-6-a.pol.

POLYMATH Results

Nonlinear regression (L-M)

Model: t = (1/k)*((2^(1-alfa))-(Ca^(1-alfa)))/(1-alfa)

Variable	Ini guess	Value	95% confidence
k	0.1	0.0329798	3.628E-04
alfa	2	1.5151242	0.0433727

Precision

R^2 = 0.9997773

R^2adj = 0.9997327

Rmsd = 0.1007934

Variance = 0.0995612

K= 0.03 (mol/dm^3)$^{-0.5}$.s^{-1} and $\alpha = 1.5$

Hence , rate law is $-\frac{dC_A}{dt} = 0.03C_A^{1.5} mol/dm^3.s$

P5-6 (b) Individualized solution

P5-6 (c) Individualized solution

P5-6 (d) Individualized solution

P5-7 (a)

Liquid phase reaction of methanol and triphenyl in a batch rector.

$CH_3OH + (C_6H_5)_3CCl \rightarrow (C_6H_5)_3COCH_3 + HCl$

A + B → C + D

Using second set of data, when $C_{AO} = 0.01$ mol/dm^3 and $C_{BO} = 0.1$ mol/dm^3

t (h)	C_A(mol/dm^3)
0	0.1
1	0.0847
2	0.0735
5	0.0526
10	0.0357

Rate law:

$$-r_A = kC_A^m C_B^n$$

For table 2 data: $C_{AO} \ll C_{BO} \Rightarrow -r_A = k'C_A^m$ where $k' = kC_{BO}^n$

Using eqn 5-21, $t = \frac{1}{k'}\frac{C_{AO}^{(1-m)} - C_A^{(1-m)}}{(1-m)} = \frac{1}{k'}\frac{(0.01)^{(1-m)} - C_A^{(1-m)}}{(1-m)}$

See Polymath program P5-7-a-1.pol.

POLYMATH Results
Nonlinear regression (L-M)

Model: t = (1/k)*((0.1^(1-m))-(Ca^(1-m)))/(1-m)

Variable	Ini guess	Value	95% confidence
k	1	1.815656	0.0109025
m	2	2.0027694	0.0021115

Nonlinear regression settings
Max # iterations = 64

Precision
R^2 = 1
R^2adj = 0.9999999
Rmsd = 3.268E-04
Variance = 8.902E-07

Therefore, m = 2
For first set of data, equal molar feed => $C_A = C_B$
Hence, rate law becomes $-r_A = kC_A^2 C_B^n = kC_A^{(2+n)}$
Observation table 2: for C_{A0} =0.01 and C_{B0} = 0.1

t (h)	C_A(mol/dm^3)
0	1.0
0.278	0.95
1.389	0.816
2.78	0.707
8.33	0.50
16.66	0.37

$$t = \frac{1}{k}\frac{C_{AO}^{(1-(2+n))} - C_A^{(1-(2+n))}}{(1-(2+n))} = \frac{1}{k}\frac{(0.1)^{(-1-n)} - C_A^{(-1-n)}}{(-1-n))}$$

See Polymath program P5-7-a-2.pol.

POLYMATH Results
Nonlinear regression (L-M)

Model: t = (1^(-1-n)-Ca^(-1-n))/(k*(-1-n))

Variable	Ini guess	Value	95% confidence
n	3	0.8319298	0.0913065
k	2	0.1695108	0.0092096

Nonlinear regression settings
Max # iterations = 64

Precision

R^2	= 0.9999078
R^2adj	= 0.9998848
Rmsd	= 0.0233151
Variance	= 0.0048923

Therefore, n = 0.8

Hence rate law is: $-r_A = 0.17\, C_A^2\, C_B^{0.8}\, \frac{mol}{dm^3 h}$

P5-7 (b) Individualized solution

P5-8 (a)

At t = 0, there is only $(CH_3)_2O$. At t = ∞, there is no$(CH_3)_2O$. Since for every mole of $(CH_3)_2O$ consumed there are 3 moles of gas produced, the final pressure should be 3 times that of the initial pressure.

$P(\infty) = 3P_0$
$931 = 3P_0$
$P_0 \approx 310$ mm Hg

P5-8 (b)

Constant volume reactor at T = 504°C = 777 K
Data for the decomposition of dimethylether in a gas phase:

Time	0	390	777	1195	3155	∞
P_T(mm Hg)	312	408	488	562	799	931

$$(CH_3)_2O \rightarrow CH_4 + H_2 + CO$$

$y_{A0} = 1$

$\delta = 3 - 1 = 2$

$\varepsilon = \delta y_{A0} = 2$

$V = V_0\left(\frac{P_0}{P}\right)(1+\varepsilon X) = V_0$ because the volume is constant.

$P = P_0(1+\varepsilon X)$

at t = ∞, X = X_{AF} = 1

$$\frac{1}{V}\frac{dN_A}{dt} = -\frac{N_{A0}}{V_0}\frac{dX}{dt} = r_A$$

Assume $-r_A = kC_A$ (i.e. 1st order)

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

Then: $C_{A0}\frac{dX}{dt} = kC_{A0}(1-X)$

and $X = \frac{P-P_0}{\varepsilon P_0}$

Therefore: $\frac{dX}{dt} = \frac{1}{\varepsilon P_0}\frac{dP}{dt}$

$$\frac{1}{\varepsilon P_0}\frac{dP}{dt} = k\left[1-\frac{P-P_0}{\varepsilon P_0}\right] = \frac{k}{\varepsilon P_0}\left(\left[1+\varepsilon\right]P_0 - P\right)$$

or $\frac{dP}{dt} = k\left(\left[1+\varepsilon\right]P_0 - P\right)$

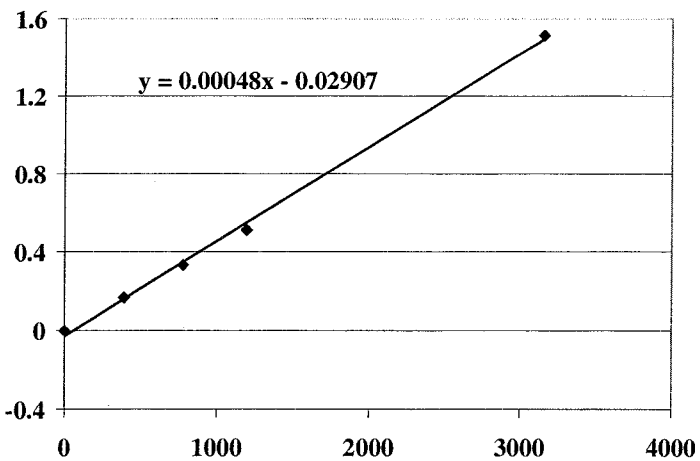
$$\int_{P_0}^{P}\frac{dP}{\left[1+\varepsilon\right]P_0 - P} = \int_0^t kdt$$

Integrating gives: $\ln\left[\frac{\varepsilon P_0}{(1+\varepsilon)P_0 - P}\right] = \ln\left[\frac{2P_0}{3P_0 - P}\right] = \ln\left[\frac{624}{936-P}\right] = kt$

Therefore, if a plot of $\ln\frac{624}{936-P}$ versus time is linear, the reaction is first order. From the figure below, we can see that the plot is linear with a slope of 0.00048.

Therefore the rate law is:

$$-r_A = 0.00048C_A$$



P5-8 (c) Individualized solution

P5-8 (d) The rate constant would increase with an increase in temperature. This would result in the pressure increasing faster and less time would be need to reach the end of the reaction. The opposite is true fro colder temperatures.

P5-9

Photochemical decay of bromine in bright sunlight:

t (min)	10	20	30	40	50	60
C_A (ppm)	2.45	1.74	1.23	0.88	0.62	0.44

P5-9 (a)

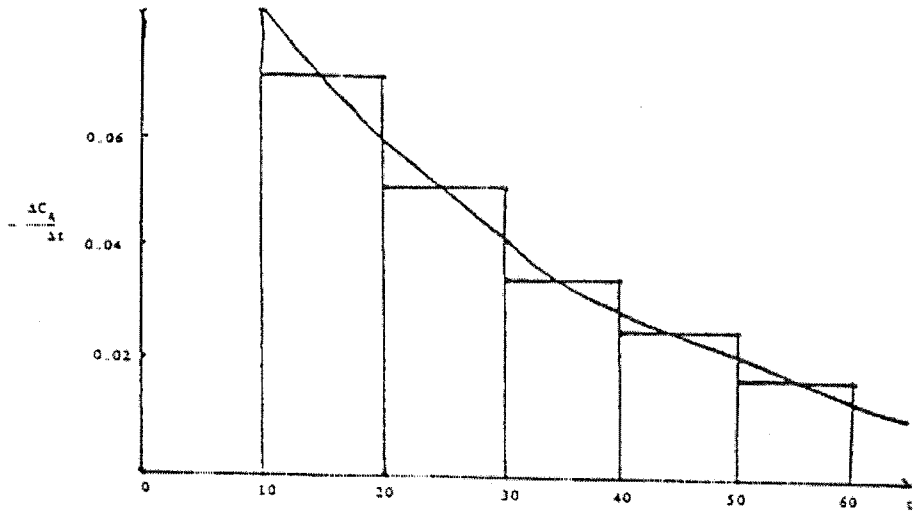
Mole balance: constant V

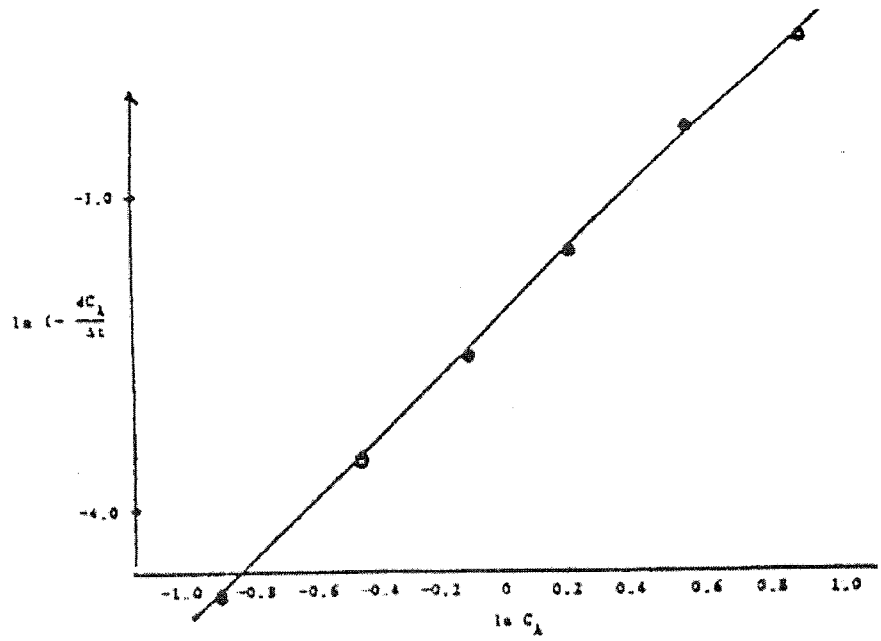
$$\frac{dC_A}{dt} = r_A = -kC_A^{\alpha}$$

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln(k) + \alpha \ln(C_A)$$

Differentiation

T (min)	10		20		30		40		50		60	
Δt (min)		10		10		10		10		10		10
C_A (ppm)	2.45		1.74		1.23		0.88		0.62		0.44	
ΔC_A (ppm)		-0.71		-0.51		-0.35		-0.26		-0.18		
$\frac{\Delta C_A}{\Delta t}\left(\frac{\text{ppm}}{\text{min}}\right)$		-0.071		-0.051		-0.035		-0.026		-0.018		





After plotting and differentiating by equal area

$-dC_A/dt$	0.082	0.061	0.042	0.030	0.0215	0.014
$\ln(-dC_A/dt)$	-2.501	-2.797	-3.170	-3.507	-3.840	-4.269
$\ln C_A$	0.896	0.554	0.207	-0.128	-0.478	-0.821

Using linear regression: $\alpha = 1.0$
$\ln k = -3.3864$
$k = 0.0344\ \text{min}^{-1}$

P5-9 (b)

$$\frac{dN_A}{dt} = Vr_A = F_B$$

$$r_A = -0.0344\frac{ppm}{\text{min}} = -0.0344\frac{mg}{l\ \text{min}} \quad \text{at } C_A = 1 \text{ ppm}$$

$$F_B = (25000\,gal)\left(0.0344\frac{mg}{l\ \text{min}}\right)\left(60\frac{\text{min}}{hr}\right)\left(\frac{1\,g}{1000\,mg}\right)\left(\frac{3.7851\,l}{1\,gal}\right)\left(\frac{1\,lbs}{453.6\,g}\right) = 0.426\frac{lbs}{hr}$$

P5-9 (c) Individualized solution

P5-10 (a)

Gas phase decomposition

A→ B +2C

Determine the reaction order and specific reaction rate for the reaction

Assume the rate law as: $\frac{dC_A}{dt} = -kC_A{}^n$

Integrating: $t = \frac{1}{k(n-1)}\left(\frac{1}{C_A{}^{n-1}} - \frac{1}{C_{A0}{}^{n-1}}\right)$

$t = t_{1/2}$ when $C_A = C_{A0}/2$

$$\Rightarrow \ln(t_{1/2}) = \ln\left(\frac{2^{n-1}-1}{(n-1)k}\right) + (1-n)\ln(C_{A0})$$

$\Rightarrow \ln(t) = a_0 + a_1 \ln(C_{A0})$

Run #	C_{A0} (gmol/lt)	t (min.)	ln t	ln C_{A0}
1	0.025	4.1	1.410987	-3.6888795
2	0.0133	7.7	2.0412203	-4.3199912
3	0.01	9.8	2.2823824	-4.6051702
4	0.05	1.96	0.67294447	-2.9957323
5	0.075	1.3	0.26236426	-2.5902672

See Polymath program P5-10-a.pol.

POLYMATH Results
Linear Regression Report

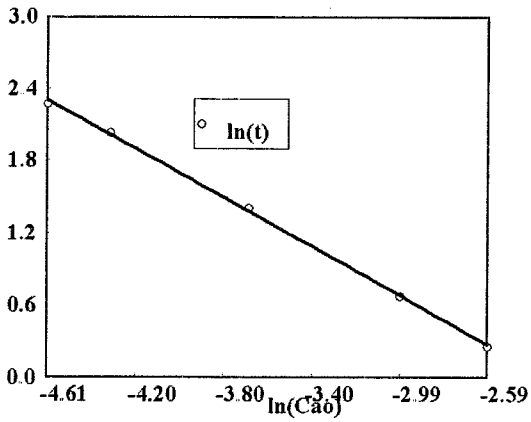
Model: lnt = a0 + a1*lnCa0

Variable	Value	95% confidence
a0	-2.3528748	0.1831062
a1	-1.0128699	0.0492329

General
Regression including free parameter
Number of observations = 5

Statistics

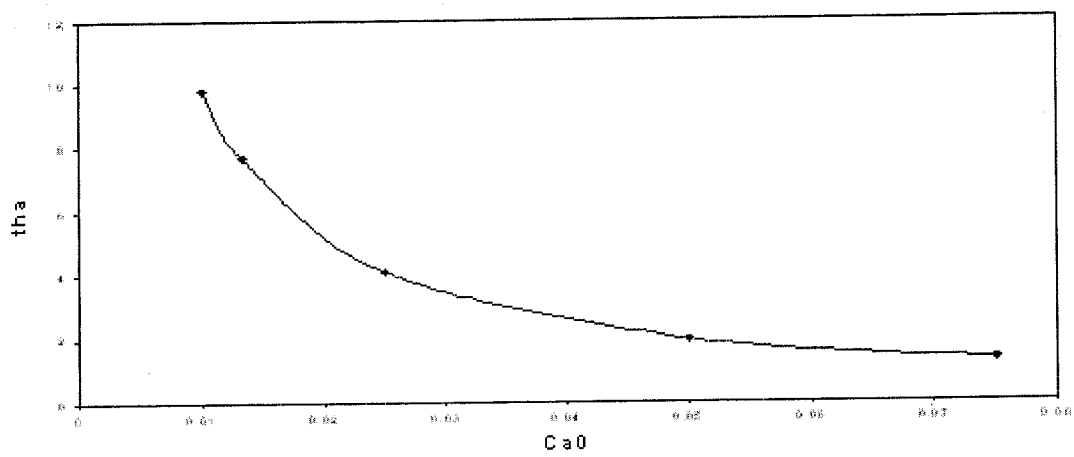
R^2 =	0.9993004
R^2adj =	0.9990673
Rmsd =	0.0091483
Variance =	6.974E-04



From linearization, n = 1- slope = 2.103 ≈ 2

$$k = \frac{(2^{\alpha-1}-1)e^{-\text{int}ercept}}{\alpha - 1} = 10.52 \frac{lt}{gmol.\min}$$

$$-\frac{dC_A}{dt} = 10.5 C_A{}^2 \, gmol/lt.\min$$



See Polymath program P5-10-a.pol.

POLYMATH Results
Nonlinear regression (L-M)

- **Model:** t = ((2^(a-1))-1)/(k*(a-1))*(1/Ca0^(a-1))

Variable	Ini guess	Value	95% confidence
a	2	1.9772287	0.093057
k	10.52	8.9909041	3.9974498

Precision

R^2	= 0.9986943
R^2adj	= 0.9982591
Rmsd	= 0.0531391
Variance	= 0.0235313

Rate law: $$-\frac{dC_A}{dt} = 9.0 C_A{}^2 \, gmol/lt.\min$$

P5-10 (b)

We know,

$$k = \frac{(2^{\alpha-1}-1)}{t_{1/2}(\alpha-1)}\left(\frac{1}{C_{A0}{}^{\alpha-1}}\right)$$

Solving for k at 110° C

$$k' = \frac{\left(2^{(2-1)}-1\right)}{2(2-1)}\left(\frac{1}{0.025^{(2-1)}}\right) = 20\frac{lt}{gmol.\min}$$

From these values, $$E = \frac{R\ln\frac{k_2}{k_1}}{\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} = \frac{\left(8.314\frac{J}{mol.K}\right)\ln\frac{20}{10.5}}{\left(\frac{1}{373K}-\frac{1}{383K}\right)} = 76.5 \text{ kJ/mol}$$

P5-11

O_3 + wall → loss of O_3 k_1
O_3 + alkene → products k_2
Rate law:

$$-r_{O_3} = \frac{dC_{O_3}}{dt} = k_1 + k_2 \frac{C_{Bu}}{C_{Oz}}$$

Using polymath nonlinear regression we can find the values of k1 and k2

Run #	ozone rate (mol/s.dm^3) Ozra	Ozone concentration (mol/s.dm^3) CO3	Butene concentration (mol/s.dm^3) Cbu
1	1.5e-7	0.01	1e-12
2	3.2e-7	0.02	1e-11
3	3.5e-7	0.015	1e-10
4	5.0e-7	0.005	1e-09
5	8.8e-7	0.001	1e-08
6	4.7e-7	0.018	1e-09

See Polymath program P5-11.pol.

POLYMATH Results
Nonlinear regression (L-M)

Model: Ozra = k1+k2*Cbu/CO3

Variable	Ini guess	Value	95% confidence
k1	2.0E-07	3.546E-07	4.872E-11
k2	0.1	0.0528758	1.193E-05

Nonlinear regression settings
Max # iterations = 300

Precision
R^2 = 0.7572693
R^2adj = 0.6965866
Rmsd = 4.531E-08
Variance = 1.848E-14

Rate law:

$$-r_{O_3} = \left(3.5\times10^{-7}\right) + \left(0.05\right)\frac{C_{Bu}}{C_{O_3}} mol/dm^3.s$$

P5-12

Given: Plot of percent decomposition of NO_2 vs V/F_{A0}

$$X = \frac{\%\text{ Decomposition of } NO_2}{100}$$

Assume that $-r_A = kC_A^n$

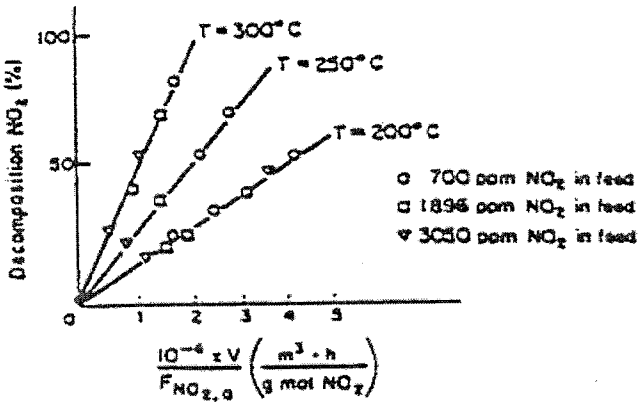
For a CSTR $V = \dfrac{F_{A0}X}{-r_A}$

or $\dfrac{V}{F_{A0}} = \dfrac{X}{-r_A} = \dfrac{X}{kC_A^n}$

with n = 0, $X = k\dfrac{V}{F_{A0}}$

X has a linear relationship with $\dfrac{V}{F_{A0}}$ as shown in the figure.

Therefore the reaction is zero order.



P5-13

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$

$$N_S = \text{moles of } SiO_2 = \frac{A_C \rho_S \delta}{MW_S}$$

A_C = cross-sectional area
ρ_S = silicon dioxide density
MW_S = molecular weight of silicon dioxide = 60.0
δ = depth of Si

$$N_F = \text{moles of HF} = \frac{w\rho V}{100\ MW_F}$$

w = weight percentage of HF in solution
ρ = density of solution
V = volume of solution
MW_F = molecular weight of HF = 20.0

Assume the rate law is $-r_S = kC_F^{\alpha}$

Mole balance: $\dfrac{dN_S}{dt} = r_S V$

$$-\frac{A_C \rho_S}{MW_S}\frac{d\delta}{dt} = k\left(\frac{wV}{100V\ MW_F}\right)^{\alpha} V$$

$$-\frac{d\delta}{dt} = \frac{kMW_S}{100^{\alpha} A_C \rho_S}\left(\frac{\rho}{MW_F}\right)^{\alpha} V w^{\alpha}$$

$$-\frac{d\delta}{dt} = \beta w^{\alpha} \text{ where } \beta = \frac{kMW_S}{100^{\alpha} A_C \rho_S}\left(\frac{\rho}{MW_F}\right)^{\alpha} V$$

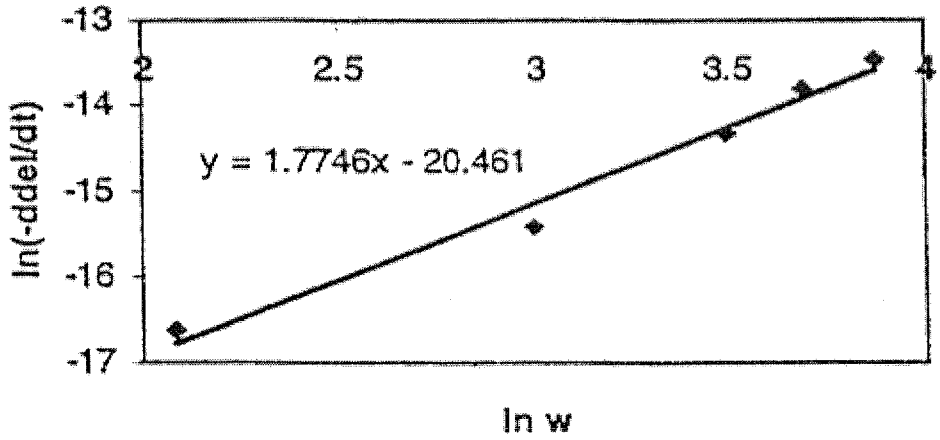
$$\ln\left(-\frac{d\delta}{dt}\right) = \ln\beta + \alpha \ln w$$

$\ln\left(-\frac{d\delta}{dt}\right)$	-16.629	-15.425	-14.32	-13.816	-13.479
ln w	2.079	2.996	3.497	3.689	3.871

where $\left(-\frac{d\delta}{dt}\right)$ is in $\frac{\text{m}}{\text{min}}$

From linear regression between $\ln\left(-\frac{d\delta}{dt}\right)$ and ln w we have:

slope = $\alpha = 1.775$
intercept = $\ln \beta = -20.462$ or $\beta = 1.2986 * 10^{-9}$



$$\beta = \frac{kMW_S}{100^{1.775} A_C \rho_S}\left(\frac{\rho}{MW_F}\right)^{1.775} V$$

$$A_C = \left(10 * 10^{-6} m\right)(10m)(2\,\text{sides})(1000\,\text{wafers}) = 0.2 m^2$$

$$MW_S = 60\frac{g}{gmol}$$

$$\rho_S = 2.32\frac{g}{ml} = 2.32 * 10^6 \frac{g}{m^3}$$

(Handbook of Chemistry and Physics, 57th ed., p.B-155)

$$\rho \approx 1\frac{g}{ml} = 10^6 \frac{g}{m^3}$$

$$MW_F = 20\frac{g}{gmol}$$

$$V = 0.5 dm^3 = 0.0005 m^3$$

$$\beta = 1.2986 * 10^{-9}$$

$$1.2986*10^{-9} = \left(\frac{10^6 \frac{g}{m^3}}{20\frac{g}{gmol}}\right)^{1.775} \frac{k\left(60\frac{g}{gmol}\right)}{\left(0.2m^2\right)\left(2.3*10^6\frac{g}{m^3}\right)(100)^{1.775}}\left(0.0005m^3\right)$$

$$k = 3.224*10^{-7}\left(\frac{m^3}{gmol}\right)^{0.775} \quad \text{min}^{-1}$$

Final concentration of HF $= \frac{5-2.316}{5}(0.2) = 0.107$ weight fraction = 10.7%

Initial concentration of HW = 0.2 (given) weight fraction = 20%

Mole balance for HF: $\frac{dN_F}{dt} = 6\frac{dN_S}{dt}$

$$-\frac{\rho V}{100MW_F}\frac{dw}{dt} = 6k\left(\frac{w\rho}{100\ MW_F}\right)^{\alpha} V \quad \text{where } \alpha = 1.775$$

$$-\int_{20}^{10.7}\frac{dw}{w^{1.775}} = 6k\left(\frac{\rho}{100MW_F}\right)^{0.775}\int_0^t dt$$

$$\frac{1}{0.775}\left(\frac{1}{w^{0.775}}\right)\Bigg|_{20}^{10.7} = 6\left(3.224*10^{-7}\right)\left(\frac{10^6}{20*100}\right)^{0.775} t$$

$$\frac{1}{0.775}\left(\frac{1}{10.7^{0.775}} - \frac{1}{20^{0.775}}\right) = 2.389*10^{-4}t$$

$t = 331$ min

P 5-14 (a)

A + 3B → C + 2D + E

Observation table for differential reactor:

Temperature(K)	Conc. Of A(mol/dm^3)	Conc. Of B(mol/dm^3)	Conc. Of C(mol/dm^3)	Rate (mol/dm^3.min)
323	0.10	0.10	0.002	0.001
333	0.10	0.10	0.006	0.003
343	0.05	0.10	0.008	0.004
353	0.10	0.05	0.02	0.01
363	0.20	0.01	0.02	0.01
363	0.01	0.01	0.01	0.005

Space time for differential reactor = 2 min

$$V = \frac{F_P}{-r_P} = \frac{v_0 C_P}{-r_P}$$

$$r_P = \frac{C_P}{\tau} = \frac{C_{C_2H_4}}{2}$$

Rate law:

$$r_C = Ae^{(-B/T)}C_A^{\alpha}C_B^{y}$$

$$\frac{C_C}{2} = Ae^{(-B/T)}C_A^{\alpha}C_B^{y}$$

Where, A is Arrhenius constant
B = activation energy/R
x is the order of reaction wrt A
y is order of reaction wrt B
C_A is the concentration of C_2H_4Br
C_B is the concentration of KI

Now using data for temperature 323K, 333K, and 363K, for finding the approximate value of B because, at these temperature, the concentration of A and B are the same. Using polymath, the rough value of B = 5500K

While using polymath for solving the rate law apart from guessing the initial values of n, m, and A , we change the value of B in the model to get the optimum solution. So after trial and error we got B = 6500K

See Polymath program P5-14-a.pol.

POLYMATH Results
Nonlinear regression (L-M)
Model: r = A*exp(-6500/T)*Ca^x*Cb^y

Variable	Ini guess	Value	95% confidence
A	3.6E+05	3.649E+06	2.928E+04
x	0.25	0.2508555	0.0032606
y	0.2	0.2963283	0.0020764

Precision

R^2	= 0.9323139
R^2adj	= 0.8871898
Rmsd	= 3.615E-04
Variance	= 1.568E-06

Hence, by nonlinear regression using polymath
A = 3.649E+06(mole/dm^3)$^{-2.6}$(1/s)
E = 6500R = 54.015 KJ/mol
x = 0.25
y = 0.30
hence,

$$r_C = 3.64E+06e^{(-54015/RT)}C_A^{0.25}C_B^{0.30} \text{ mole/dm}^3\text{.min}$$

P 5-14 (b) Individualized solution

P5-15 (a)

Model 1: Monod equation

$$\frac{dC_c}{dt} = r_g = \frac{\mu_{max} C_s C_c}{K_s + C_s}$$

See Polymath program P5-15-a.pol.

POLYMATH Results
Nonlinear regression (L-M)
Model: rg = (umax)*Cs*Cc/(Ks+Cs)

Variable	Ini guess	Value	95% confidence
umax	1	0.3284383	0.00686
Ks	1	1.694347	2.2930643

Precision

R^2	= 0.9999439
R^2adj	= 0.9999327
Rmsd	= 0.0038534
Variance	= 1.455E-04

$$r_g = \frac{0.033 C_S C_C}{1.69 + C_s} \text{ g/dm}^3\text{.h}$$

P5-15 (b)

Model 2: Tessier Equation

$$r_g = \mu_{max}\left[1 - \exp\left(-\frac{C_s}{k}\right)\right] C_C$$

See Polymath program P5-15-b.pol.

POLYMATH Results
Nonlinear regression (L-M)

Model: rg = umax*(1-exp(-Cs/k))*Cc

Variable	Ini guess	Value	95% confidence
umax	0.5	0.3258202	0.0034969
k	100	20.407487	5.7120407

Precision

R^2	= 0.9999454
R^2adj	= 0.9999345
Rmsd	= 0.0038004
Variance	= 1.415E-04

$$r_g = 0.33\left[1 - \exp\left(\frac{-C_S}{20.4}\right)\right] C_C \text{ g/dm}^3\text{.h}$$

P5-15 (c)

Model 3: Moser Equation

$$r_g = \frac{\mu_{max} C_C}{1 + k C_S^{-y}}$$

See Polymath program P5-15-c.pol.

POLYMATH Results
Nonlinear regression (L-M)

Model: rg = umax*Cc/(1+k*Cs^(-y))

Variable	Ini guess	Value	95% confidence
umax	0.3	0.3265614	6.984E-04
k	1.6	162.599	34.273983
y	1	2.0892232	0.0461489

Precision

R^2	= 0.9999447
R^2adj	= 0.999917
Rmsd	= 0.0038269
Variance	= 1.794E-04

$$r_g = \frac{0.33C_C}{1+162.6C_S^{(-2.1)}} \text{ g/dm}^3\text{.h}$$

P5-16

Thermal decomposition of isopropyl isocynate in a differential reactor.

Run	Rate (mol/s.dm^3)	Concentration (mol/dm^3)	Temperature -(K)
1	4.9 x 10^{-4}	0.2	700
2	1.1 x 10^{-4}	0.02	750
3	2.4 x 10^{-3}	0.05	800
4	2.2 x 10^{-2}	0.08	850
5	1.18 x 10^{-1}	0.1	900
6	1.82 x 10^{-2}	0.06	950

Rate law:

$$-r_A = Ae^{(-E/RT)}C_A^n$$

Where, A is Arrhenius constant
E is the activation energy
n is the order of reaction
C_A is the concentration of isopropyl isocynate

See Polymath program P5-16.pol.

POLYMATH Results
Nonlinear regression (L-M)

Model: rA = A*exp(-E/(8.314*T))*(CA)^n

Variable	Ini guess	Value	95% confidence
A	100	1.01E+04	327.35758
E	1000	5.805E+04	237.32096
n	1	1.7305416	0.0134196

Nonlinear regression settings
Max # iterations = 64

Precision

R^2	= 0.6690419
R^2adj	= 0.4484032
Rmsd	= 0.0097848

Variance = 0.0011489

Hence, by nonlinear regression using polymath
A = 10100 $(mole/dm^3)^{-2.6}(1/s)$
E = 58000 J/mol
n = 1.7
therefore,

$$-r_A = 10100\exp\left(\frac{-6976}{T}\right)C_A^{1.7}\ mole/dm^3.s$$

CDP5-A

Given the reaction $P + NH_2OH \rightarrow NH_2OHP$

where P is Penicillin and NH_2OHP is hydroxylamine acid (denoted by subscript HA)

Let A = Absorbency, then $C_{HA} = KA$ where K is some constant.

$C_P = C_{Po}(1-X)$ ($\varepsilon = 0$ for liquid phase reaction.)

$$C_{HA} = C_{Po}X = KA \quad \therefore \quad X = \frac{KA}{C_{Po}} \quad \text{when } X = 1 \text{ and } A = A_\infty$$

$$\text{At } t = \infty, \quad A_\infty = \frac{C_{Po}}{K} \quad \therefore \quad X = \frac{A}{A_\infty}$$

Assume reaction is irreversible: $-r_P = kC_P^a = kC_{Po}^a(1-X)^a$

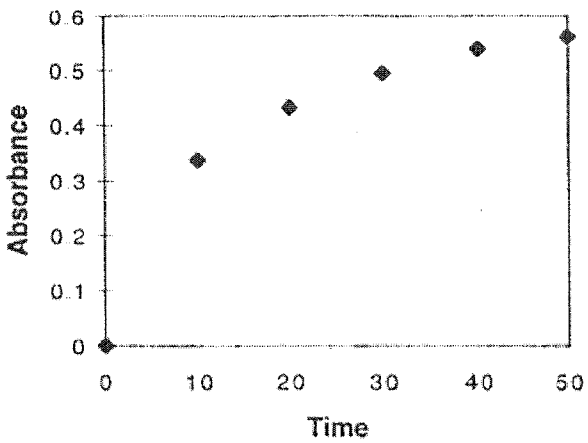
For a batch, constant volume reactor: $\frac{1}{V}\frac{dN_P}{dt} = \frac{dC_P}{dt} = r_P$

or $$\frac{dC_P}{dt} = C_{Po}\frac{dX}{dt} = -\frac{C_{Po}}{A_\infty}\frac{dA}{dt} = -kC_{Po}^a(1-X)^a = -kC_{Po}^a(1-A/A_\infty)^a$$

or $$\frac{dA}{dt} = k\left(\frac{C_{Po}}{A_\infty}\right)^{a-1}(A_\infty - A)^a = K(A_\infty - A)^a, \quad \text{where } K = k\left(\frac{C_{Po}}{A_\infty}\right)^{a-1}$$

Try integral analysis first. Assume that reaction is zero order:

Then $\frac{dA}{dt} = K$ or $\int_0^A dA = A = Kt$ a plot of A vs. t should be linear if reaction is zero order. From the plot below, it is evident that the reaction is not zero order:

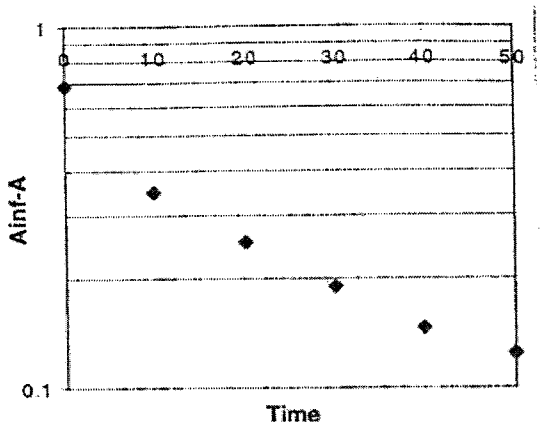


Next, assume that the reaction is first order:

$$\frac{dA}{dt} = K(A_\infty - A) \text{ or } \int_0^A \frac{dA}{(A_\infty - A)} = \int_0^t Kdt = \ln\frac{(A_\infty - A)}{A_\infty} = -Kt$$

$\therefore$ A plot of $(A_\infty - A)$ vs. t on semi - log paper should be linear.

Time	A	A_∞ - A
0	0	0.685
10	0.337	0.348
20	0.433	0.252
30	0.495	0.190
40	0.539	0.146
50	0.561	0.124
∞	0.685	0

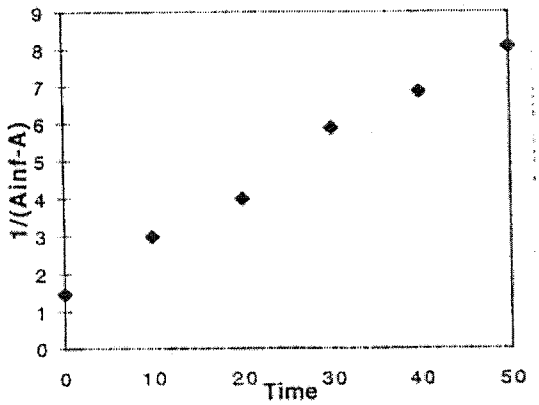


It is evident from the plot that the reaction is not first order. Try second order:

$$\frac{dA}{dt} = K(A_\infty - A)^2 \quad \therefore \quad \int_0^A \frac{dA}{(A_\infty - A)^2} = \frac{1}{(A_\infty - A)} - \frac{1}{A_\infty} = Kt$$

or $\frac{1}{(A_\infty - A)} = \frac{1}{A_\infty} + Kt$ $\therefore$ A plot of $\frac{1}{(A_\infty - A)}$ vs. t should be linear

Time	A	A_∞ - A
0	0	1.460
10	0.337	2.967
20	0.433	3.968
30	0.495	5.882
40	0.539	6.849
50	0.561	8.065



From the plot, it is evedent that linear relationship exists between ($1/A_\infty$ - A) and time; Therefore the reaction is second order.

CDP5-B

Determine the reaction order and specific rate constant for the isomerization reaction:

A→ B

Rate law:

$$-r_A = kC_A^{\alpha} = -\frac{dC_A}{dt}$$

Time (min)	C_A (mol/dm^3)	$-\Delta C_A/\Delta t$	$-dC_A/dt$
0	4		0.39
		0.37	
3	2.89		0.35
		0.32	
5	2.25		0.30
		0.267	
8	1.45		0.25
		0.225	
10	1		0.21
		0.175	
12	0.65		0.15
		0.133	
15	0.25		0.1
		0.072	
17.5	0.07		0.06

Plot of log $-dC_A/dt$ vs log C_A shows $\alpha = 0.5$

$$k_A = \frac{-\frac{dC_A}{dt}}{C_A^{0.5}} = \frac{.15}{0.65^{0.5}} = 0.19 \frac{mol^{0.5}}{dm^{1.5}\,\text{min}}$$

CDP5-C

Ethane hydrolysis over a commercial nickel catalyst in a stirred contained solid reactor.

$$H_2 + C_2H_6 \rightarrow 2CH_4$$

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

$$P_B = C_B RT = C_{A0} RT(\theta_B - X) = P_{A0}(\theta_B - X)$$

$$X = \frac{y_p F_{T0}}{2F_{A0}} = \frac{y_p}{2y_{A0}} = \frac{y_p(1+\theta_B)}{2}$$

$$-r'_A = -r'_B = \frac{F_{A0}X}{W} = \frac{F_p}{2W} = \frac{y_p F_{A0}}{2W}$$

$$-r'_A = kP_A^{\alpha} P_B^{\beta}$$

$$\ln(-r'_A) = \ln k + \alpha \ln P_A + \beta \ln P_B$$

- $y = A_0 + A_1X_1 + A_2X_2$

F_{T0}(gmol/h)	P_{A0}(atm)	P_{B0}(atm)	y_{CH4}	X	Q	P_A(atm)	P_B(atm)	$-r_A$(gmol/kg.h)
			0.0	0.0				
1.7	0.5	0.5	5	5	1	0.475	0.475	1.0625
			0.0	0.0				
1.2	0.5	0.5	7	7	1	0.465	0.465	1.05
			0.1	0.1				
0.6	0.5	0.5	6	6	1	0.42	0.42	1.2
			0.1					
0.3	0.4	0.6	6	0.2	1.5	0.32	0.52	0.6
0.75	0.6	0.6	0.1	0.1	1	0.54	0.54	0.9375
			0.0	0.0	0.6			
2.75	0.6	0.4	6	5	7	0.57	0.37	2.0625

POLYMATH Results

Nonlinear regression (L-M)

Model: ra = k*(Pa^alfa)*(Pb^beta)

Variable	Ini guess	Value	95% confidence

k	0.1	0.5068635	0.1124446
alfa	1	0.9828027	0.152574
beta	1	-1.9669749	0.1668241

Precision

R^2	= 0.999213
R^2adj	= 0.9986883
Rmsd	= 0.0051228
Variance	= 3.149E-04

k = 0.5 atm gmol/hr kg; $\alpha \equiv 1$; $\beta \equiv -2$

hence, the rate law is: $-r_A = 0.5\dfrac{P_A}{P_B^2}\ gmol/kg.hr$

CDP5-D

Since oxygen is found in excess, we assume that $-r_{NO}$ is dependent only on C_{NO}. This gives us a rate law of the form:

$$-r_{NO} = kC_{NO}^{\alpha}$$

From the units of the specific reaction rate, we assume that $\alpha = 3$. Now, using equation (5-18) from chapter 5, we can solve for the desired half-lives.

$$t_{1/2} = \frac{2^{\alpha-1}-1}{k(\alpha-1)}\left(\frac{1}{C_{NOo}^{\alpha-1}}\right) = \frac{2^{3-1}-1}{k(3-1)}\left(\frac{1}{C_{NOo}^{3-1}}\right) = \frac{2^2-1}{2k}\left(\frac{1}{C_{NOo}^2}\right)$$

(a) For $C_{NOo} = 3000$ppm:

$$t_{1/2} = \frac{3}{2\left(1.4\times10^{-9}\ \text{ppm}^{-2}/\text{min}\right)}\left(\frac{1}{(3000\ \text{ppm})^2}\right) = 119.05\ \text{min}$$

(b) For $C_{Noo} = 1$ ppm:

$$t_{1/2} = \frac{3}{2\left(1.4\times10^{-9}\ \text{ppm}^{-2}/\text{min}\right)}\left(\frac{1}{(1\ \text{ppm})^2}\right) = 1.071\times10^{9}\ \text{min}$$

CDP5-E

Given the data, postulate a rate law.

$$-r_A = kC_A^{\alpha}$$

Then write the design equation in terms of the data given, in this case volume and time.

$$C_A = N_A V$$

$$N_A = N_{A0}(1-X)$$

$$V = V_0(1+\varepsilon X)$$

$$X = \frac{V-V_0}{V_0\varepsilon}$$

$$C_A = \frac{1-\dfrac{V-V_0}{V_0\varepsilon}}{V}$$

Plug that into the design equation:

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

$$-\frac{d\left(\dfrac{1-\dfrac{V-V_0}{V_0\varepsilon}}{V}\right)}{dt} = k'\left(\frac{1-\dfrac{V-V_0}{V_0\varepsilon}}{V}\right)^{\alpha}$$

$$k' = k\left(N_{A0}^{\alpha-1}\right)$$

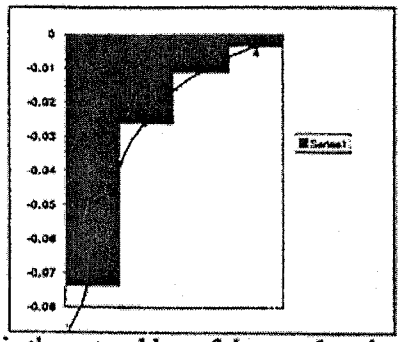
$$\ln-\frac{d\left(\dfrac{1-\dfrac{V-V_0}{V_0\varepsilon}}{V}\right)}{dt} = \alpha\ln\left(\frac{1-\dfrac{V-V_0}{V_0\varepsilon}}{V}\right) + \ln k'$$

$$k' = \frac{\dfrac{d\left(\dfrac{1-\dfrac{V-V_0}{V_0\varepsilon}}{V}\right)}{dt}}{\left(\dfrac{1-\dfrac{V-V_0}{V_0\varepsilon}}{V}\right)}$$

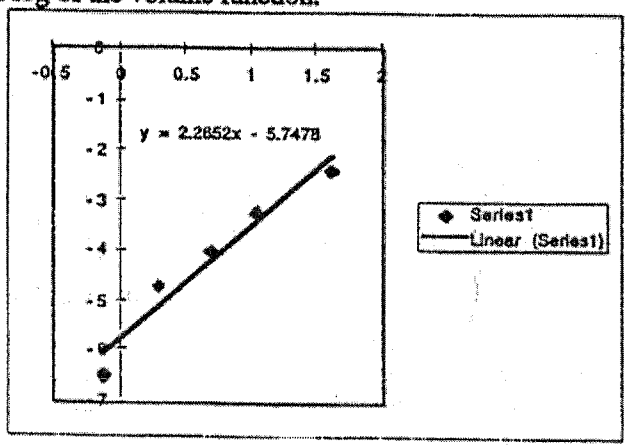
Now find the derivitive. To do that use the graphical method.

t	$(1-(V-V_0)/V_0\varepsilon)/V$	Δt	$\Delta 1-(V-V_0)/V_0\varepsilon)/V$	$\Delta 1-(V-V_0)/V_0\varepsilon)/V/\Delta t$	$d1-(V-V_0)/V_0\varepsilon)/V/dt$
0	5	30	-2.211	-0.0737	-0.09
30	2.789	30	-0.785	-0.0262	-0.04
60	2.003	60	-0.679	-0.011	-0.018
120	1.32	120	-0.448	-0.004	-0.009
240	0.88				-0.0015

The following graph is made.



Once that is done it is the natural log of those values is ready to be graphed. The following graph is the natural log of the derivitive of the volume function against the natural log of the volume function.



From the graph we see that α is 2. We can also find k:

$$k' = \frac{.09}{5} = .018$$

$$N_{A0} = y_{A0}N_{T0} = .85 * \frac{303.39 * .2}{8.314 * 313} = .020 moles$$

$$k = \frac{k'}{N_{A0}^{\alpha-1}} = \frac{.018}{.02^1} = .9$$

The following rate law is found:

$$-r_A = .9 * C_A^2$$

Now, to determine the volume of the CSTR we must use the design equation and stoichiometry:

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

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

$$C_{A0} = \frac{P_{A0}}{RT_0}$$

$$P_{A0} = y_{A0}P_0 = .6 * 1013.25kPa = 607.95$$

Combining these with the rate law just determined, the following volume is found.

$$V = \frac{F_{A0}X}{.9*\left[\frac{P_{A0}}{RT}(1-X)\right]^2} = \frac{16.67*.8}{.9*\left[\frac{607.95}{8.314*313}(1-.8)\right]^2} = 6787 dm^3$$

CDP5-F

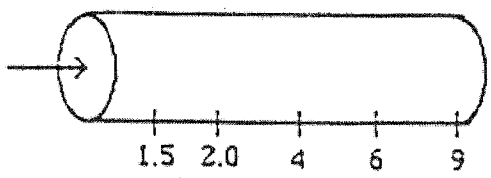
AsH_3 = 1.5	Z	P	$-\frac{dP}{dZ}$
	0	129	45.3
	1.5	70	28.63
	2.5	50	19.4
	4.0	30	9.5
	6.5	18	1.3
	9.0	16	(1.7)

AsH_3 = 3.0	Z	P	$-\frac{dP}{dZ}$
	0	129	90
	1.5	45	34.0
	2.5	22	15.4
	4.0	10	2.0

AsH_3 = 3.0	Z	P	$-\frac{dP}{dZ}$
	0	129	17.4
	1.5	95	15.0

PFR

$$A + B \rightleftarrows C$$



P_{A1} P_{A2} ... ...

Task 1. Rewrite the design equation (i.e., mole balance) in terms of the measurement variables. Recall $V = A_C Z$, then

$$\frac{dX}{dZ} = \frac{-r_A A_c}{F_{A0}}$$

For isothermal operation and no pressure drop.

$$C_A = C_{AO}\frac{(1-X)}{(1+\varepsilon X)}, \quad C_A = P_A/RT$$

$$P_A = P_{AO}\frac{(1-X)}{(1+\varepsilon X)}$$

$$(1+\varepsilon X)\,P_A = P_{AO}\,(1-X)$$

$$\boxed{X = \frac{1 - P_A/P_{AO}}{1 + \varepsilon X\, P_A/P_{AO}}}$$

$$\boxed{\frac{\dfrac{d[1 - P_A/P_{AO}]}{\left(1+\varepsilon\dfrac{P_A}{P_{AO}}\right)}}{dZ} = \frac{-r_A A_C}{F_{A0}}}$$

Now we have the differential mole balance in terms of the measured variables P_A and Z.

Postulate

$$-r_A = k\left[P_A^{\alpha} P_B^{\beta} - \frac{P_C^{\gamma}}{K_p}\right]$$

Task 2. Look for simplifications.

A) See if volume change can be neglected.

$$\varepsilon = y_{AS}\,\delta = \frac{0.129}{152}(-1) = \left(8 \times 10^{-4}\right) - 0$$

$\varepsilon \cong 0$ therefore neglect volume change.

Then: $$-\frac{dP_A}{dZ} = \overbrace{\frac{P_{A0}\,k\,A_C}{F_{A0}}}^{K'}\left[P_A^{\alpha} P_B^{\beta} - \frac{P_C^{\gamma}}{K_P}\right]$$

B) We see that for runs 1 and 3 where P_{AsH_3} = 1.5 and 3.0 torr, respectively, that most of the Et_3In is consumed, indicating the equilibrium is reasonably far to the right. Consequently, the reverse reaction is negligible in the first part of the reactor, i.e.,

$$-r_A = k' P_A^{\alpha} P_B^{\beta}$$

C) We also see that for runs 1 and 3 that B is in excess and that for excess B

$$-r_A = k' P_{B0}^{\beta} P_A^{\alpha} = k' P_A^{\alpha}$$

$$-\frac{dP_A}{dZ} = k'' P_A^{\alpha} \qquad \text{Algorithm}$$

Task 3. Calculate $\left(-\frac{\Delta P_A}{\Delta Z}\right)$ and plot vs Z to find $\left(-\frac{dP_A}{dZ}\right)$

Plot $\left(-\frac{dP_A}{dZ}\right)$ vs (PA) on log-log paper to find alpha.

Task 4. Take ratio of initial rates at $P_{AsH_3} = 3.0$ torr and $P_{AsH_3} = 1.5$ torr

$$\frac{\left(\frac{-dP_A}{dZ}_{02}\right)}{\left(\frac{-dP_A}{dZ}\right)_{01}} = \frac{k P_{A03} P_{B01}^{\beta}}{k P_{A01} P_{B01}^{\beta}} = \left(\frac{P_{B03}}{P_{B01}}\right)^{\beta}$$

$$\frac{90}{46} = \left(\frac{3}{1.5}\right)^{\beta}, \text{ Hence } \beta = .97 - 1.0$$

Therefore $-r_A = k\left[P_A P_B - \frac{P_C}{K_p}\right]$

We know $\gamma = 1$ because of thermodynamic consistency. i.e.

$$-r_A = 0 = k\left[P_{Ae} P_{Be} - \frac{P_{Ce}}{K_p}\right]$$

$$K_p = \frac{P_{Ce}}{P_{Ae} P_{Be}}$$

Task 5. Evaluate k' and K_p

From A_sH_3 of 3.0 torr we see equilibrium is reached at $P_{Ae} = .01$

$$P_{Ce} = 0.129 - 0.01 = .119$$

$$P_{Be} = 3.0 - .119 = 2.881$$

$$K_p = \frac{119}{(.01)(2.881)} = 4.13 \text{ torr}^{-1}$$

From initial rate

$$-\frac{dP_A}{dZ} = 90 \times 10^{-3} \frac{\text{torr}}{\text{cm}} = k' (.129 \text{ torr}) (3.0 \text{ torr})$$

$$k' = 0.23 (\text{torr cm})^{-1}$$

CDP5-G

From given data, find the rate law.
Given: Oxidation of propene to acrolein
Rate law:

$$r_A = kP_P^{\ a} P_{O_2}^{\ b}$$

$$\Delta W = 0.5\,\text{g}$$

Using Polymath non linear regression, the following results were obtained:

Nonlinear regression (L-M)

Model: ra = k*Pp^a*Po2^b

Variable	Ini guess	Value	95% confidence
k	5	0.006609	2.685E-05
a	1	0.9948724	0.0046367
b	1	0.2034299	0.001358

Precision

R^2	= 0.9999969
R^2adj	= 0.9999953
Rmsd	= 5.722E-07
Variance	= 4.011E-12

CDP5-H

1)

$$A \xrightarrow{k_A} \text{prod} \qquad -r_A = k_A C_A$$

$$B \xrightarrow{k_B} \text{prod} \qquad -r_B = k_B C_B$$

$$-r_I = k_A C_A + k_B C_B$$

$$-\frac{dC_I}{dt} = k_A C_{Ao}(1-X_A) + k_B C_{Bo}(1-X_B)$$

$$C_I(t) = C_A(t) + C_B(t) = C_{Ao}(1-X_A) + C_{Bo}(1-X_B)$$

$$C_I(t) = C_{Ao}(1 - X_A + \Theta_B - X_B) = C_{Ao}(1.75 - X_A - X_B)$$

$$\frac{dC_I}{dt} = C_{Ao}(k_A - k_A X_A + k_B \Theta_B - k_B X_B)$$

$$-\frac{dC_I}{dt} = C_{Ao}(k_A - k_A X_A + 0.75 k_B \Theta_B - k_B X_B)$$

II) $D \xrightarrow{k_D} \text{prod} \qquad -\frac{dC_{II}}{dt} = -r_{II} = k_D C_D^2 = k_D\, C_{DO}^2\, (1-X_D)^2$

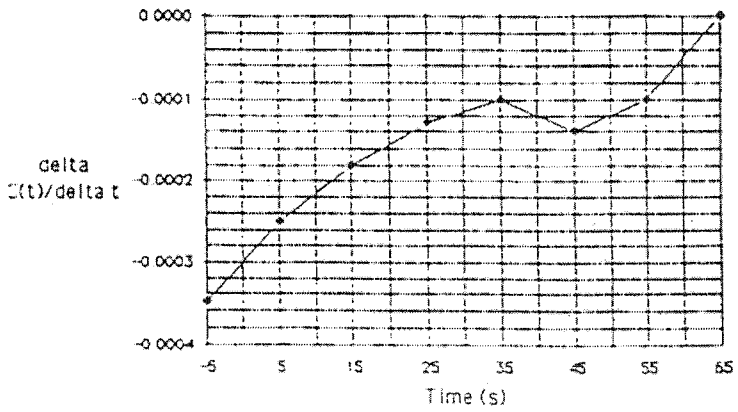
$$C_{II}(t) = C_D(t) = C_{DO}\,(1-X_{D_0})$$

So,

t(sec)	0	10	20	30	40	50	60
C(t) kmol/m^3	0.014	0.0115	0.0097	0.0084	0.0074	0.0060	0.0050
If $I_r = X_A + I_B$	0	0.313	0.538	0.700	0.825	1.00	1.125

If II, X_D	0	0.179	0.307	0.400	0.471	0.571	0.643
$\frac{\Delta C(t)}{\Delta(t)}$		-2.5×10^{-4}	-1.8×10^{-4}	-1.3×10^{-4}	-1×10^{-4}	-1.4×10^{-4}	-1×10^{-4}
$-\frac{dC(t)}{dt}$		$+2.7\times10^{-4}$	$+2.2\times10^{-4}$	$+1.6\times10^{-4}$	$+1.2\times10^{-4}$	$+1.2\times10^{-4}$	$+1.2\times10^{-4}$	$+0.8\times10^{-4}$
If II, $C_{Do}^2 (1-X_D)^2$	1.96×10^{-4}	1.321×10^{-4}	9.413×10^{-5}	7.06×10^{-5}	5.485×10^{-5}	3.61×10^{-5}	2.50×10^{-5}
k_D	1.378	1.665	1.700	1.701	2.188	3.327	3.203

If II were true, all k_D's should be the same —> II is not true



CDP5-I

(a) Experimental Plan to find the rate law for the hydrogenation of cyclopentane on a Pt/Al_2O_3 catalyst:

1. Since this is a stable catalyst we don't have to worry about catalyst decay and an Integral Reactor will be used.
2. Perform several different runs, holding C_{Ao} and W constant while F_{Ao} is varied from run to run.
3. Plot $X_{A,out}$ vs. W/F_{Ao} for all runs.
4. Fit a curve through all points which passes through the origin. The slope at any point is the reaction rate. Record the slope and corresponding C_{Ao} for many different X_A values. These data can be used to determine the rate law.

(b) Experimental Plan to find the rate law for the liquid-phase production of methyl bromide from an aqueous solution of methyl amine and bromine cyanide:

1. For a liquid-phase reaction without a catalyst, use a batch reactor.
2. While running the reaction record both C_A and C_B at equal time intervals
3. Repeat to ensure accurate data.

CDP5-I (c) No solution

CDP5-J No solution will be given.

CDP5-K No solution will be given.

Solutions for Chapter 6 – Multiple Reactions

P6-1 Individualized solution

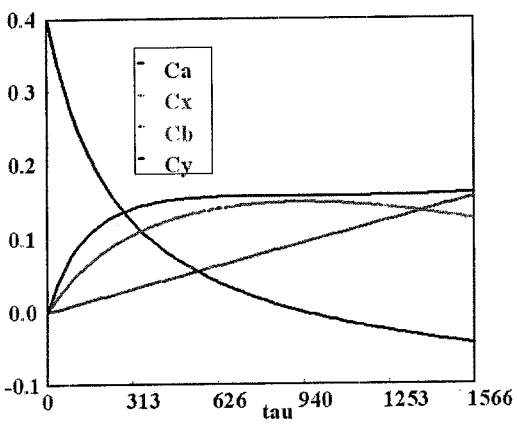
P6-2 (a) Example 6-2

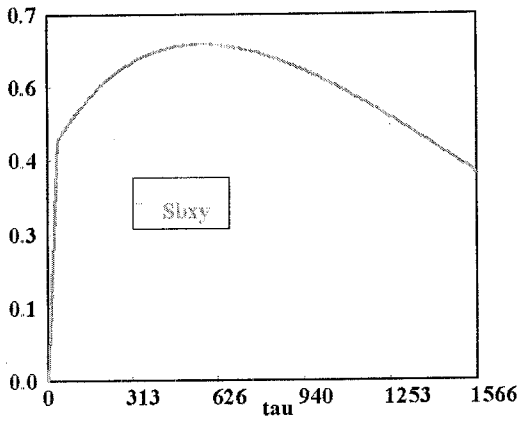
For PFR,

$$\frac{dC_A}{d\tau} = -k_1 - k_2 C_A - k_3 C_A^2 \qquad \frac{dC_X}{d\tau} = k_1$$

$$\frac{dC_B}{d\tau} = k_2 C_A \qquad \frac{dC_Y}{d\tau} = k_3 C_A^2$$

In PFR with V = 1566 dm^3 we get X = 1.0 and $S_{B/XY}$ = 0.394
also at V = 533 dm^3 $S_{B/XY}$ is at its maximum value of 0.625





See Polymath program P6-2-a.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
tau	0	0	1566	1566
Ca	0.4	-0.0439962	0.4	-0.0439962
Cx	1.0E-07	1.0E-07	0.1566001	0.1566001
Cb	0	0	0.1490534	0.1256308
Cy	1.0E-06	1.0E-06	0.1617665	0.1617665
Cao	0.4	0.4	0.4	0.4
X	0	0	1.1099906	1.1099906
k1	1.0E-04	1.0E-04	1.0E-04	1.0E-04
k2	0.0015	0.0015	0.0015	0.0015
k3	0.008	0.008	0.008	0.008
Sbxy	0	0	0.6436717	0.3946104

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Ca)/d(tau) = -k1-k2*Ca-k3*Ca^2
[2] d(Cx)/d(tau) = k1
[3] d(Cb)/d(tau) = k2*Ca
[4] d(Cy)/d(tau) = k3*Ca^2

Explicit equations as entered by the user
[1] Cao = 0.4
[2] X = 1-Ca/Cao
[3] k1 = 0.0001
[4] k2 = 0.0015
[5] k3 = 0.008
[6] Sbxy = Cb/(Cx+Cy)

(2) Pressure increased by a factor of 100.
Now $C_{A0} = P/RT = 0.4 \times 100 = 40$ mol/dm^3
For single CSTR, C_A^* does not change but

$$\tau = \frac{V}{v_O} = \frac{C_{AO} - C_A}{-r_A} = \frac{C_{AO} - C_A}{k_{1A} + k_{2A}C_A + k_{3A}C_A^2} = \frac{40 - 0.112}{0.0001 + 0.00168 + 0.0001}\,\text{sec}$$

$$\tau = 21217\,\text{sec}$$

P6-2 (b) Example 6-3

(a) CSTR: intense agitation is needed, good temperature control.

(b) PFR: High conversion attainable, temperature control is hard – non-exothermic reactions, selectivity not an issue

(c) Batch: High conversion required, expensive products

(d) and (e) Semibatch: Highly exothermic reactions, selectivity i.e. to keep a reactant concentration low, to control the conversion of a reactant.

(f) and (g) Tubular with side streams: selectivity i.e. to keep a reactant concentration high, to achieve higher conversion of a reactant.

(h) Series of CSTR's: To keep a reactant concentration high, easier temperature control than single CSTR.

(i) PFR with recycle: Low conversion to reuse reactants, gas reactants

(j) CSTR with recycle: Low conversions are achieved to reuse reactants, temperature control, liquid reactants

(k) Membrane Reactor: yield i.e. series reactions that eliminate a desired product

(l) Reactive Distillation: when one product is volatile and the other is not

P6-2 (c) Example 6-4

For $k_1 = k_2$, we get

$$C_A = C_{AO}\exp\left(-k_1\tau'\right) \quad \text{and} \quad \frac{dC_B}{d\tau'} + k_1C_B = k_1C_{AO}\exp\left(-k_1\tau'\right)$$

$$\Rightarrow \frac{d\left(C_B\exp\left(k_1\tau'\right)\right)}{d\tau'} = k_1C_{AO}$$

Now at $\tau' = 0$, $C_B = 0$ $\Rightarrow C_B = k_1C_{AO}\tau'\exp\left(-k_1\tau'\right)$

Optimum yield: $\frac{dC_B}{d\tau'} = 0 = k_1 C_{AO}\left[\exp\left(-k_1\tau'\right) - k_1\tau' \exp\left(-k_1\tau'\right)\right]$

$$\Rightarrow \tau'_{opt} = \frac{1}{k_1}$$

$$W_{opt} = \frac{vo}{k_1} \qquad \text{and} \qquad X_{opt} = 1 - \exp\left(-k_1\tau'\right) = 1 - e^{-1} = 0.632$$

For a CSTR:

$$W = \frac{F_{A0} - F_A}{-r'_A} = \frac{v_0\left(C_{A0} - C_A\right)}{-r'_A}$$

$$\tau' = \frac{C_{A0} - C_A}{-r'_A} = \frac{C_{A0} - C_A}{k_1 C_A}$$

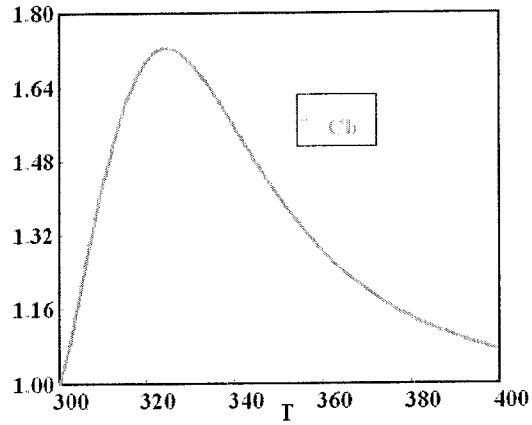
$$C_A = C_{A0}\left(\tau' k_1 + 1\right)$$

$$\tau' = \frac{C_{B0} - C_B}{-r'_B} = \frac{C_B}{-k_1 C_A + k_2 C_B} = \frac{C_B}{-k_1 C_{A0}\left(\tau' k_1 + 1\right) + k_2 C_B}$$

$$C_B = \frac{\tau' k_1 C_{A0}\left(\tau' k_1 + 1\right)}{\tau' k_2 + 1}$$

to find the maximum concentration of C, differentiate C_B with respect to τ' and set it equal to 0.

See Polymath program P6-2-c.pol.



$$\frac{dC_B}{d\tau'} = \frac{\tau'^2 k_1 + \tau'}{-k_2\left(\tau' k_2 + 1\right)} + 2\tau' k_1 + 1 = 0$$

simplifying we get

$$\tau'^2\left(2k_1k_2 - k_1\right) + \tau'\left(2k_1k_2 + k_2^2 - 1\right) + k_2 = 0$$

Then use the quadratic formula to solve for τ'.

(2) Operating temperature = 325 K

P6-2 (d) Example 6-5

$K_C = K_e = 0.25$

$$r_{2N_2} = k_{2N_2}\left[C_{NO}^2 - \frac{C_{N_2}C_{O_2}}{K_C}\right]$$

$$r_{NO} = -k_{1NO}C_{NH_3}C_{NO}^{1.5} - 2k_{2N_2}\left[C_{NO}^2 - \frac{C_{N_2}C_{O_2}}{K_C}\right]$$

$$r_{N_2} = \frac{5}{6}k_{1NO}C_{NH_3}C_{NO}^{1.5} + k_{2N_2}\left[C_{NO}^2 - \frac{C_{N_2}C_{O_2}}{K_C}\right] - \frac{1}{2}k_{3O_2}C_{N_2}C_{O_2}^2$$

$$r_{O_2} = k_{2N_2}\left[C_{NO}^2 - \frac{C_{N_2}C_{O_2}}{K_C}\right] - k_{3O_2}C_{N_2}C_{O_2}^2$$

P6-2 (e) Example 6-6

For liquid phase, $F_j = v_o C_j$

Equation (E 6-6.3): $$\frac{dF_{NO}}{dV} = v_O\frac{dC_{NO}}{dV} = -kC_{NH_3}C_{NO}^{1.5} - 2k_{2N_2}C_{NO}^2$$

$$\Rightarrow \frac{dC_{NO}}{d\tau} = -kC_{NH_3}C_{NO}^{1.5} - 2k_{2N_2}C_{NO}^2$$

Equation (E6-6.8): $$\frac{dF_{NO_2}}{dV} = v_O\frac{dC_{NO_2}}{dV} = k_{3O_2}C_{N_2}C_{O_2}^2$$

$$\Rightarrow \frac{dC_{NO_2}}{d\tau} = k_{3O_2}C_{N_2}C_{O_2}^2$$

P6-2 (f) Example 6-7

For equal molar feed in hydrogen and mesitylene.

$C_{HO} = y_{HO}C_{TO} = (0.5)(0.032)\text{lbmol/ft}^3 = 0.016\ \text{lbmol/ft}^3$

$C_{MO} = 0.016\ \text{lbmol/ft}^3$

Using equations from example, solving in Polymath,

we get

$\tau_{opt} = 0.38$ hr. At $\tau = 0.5$ hr all of the H_2 is reacted and only the decomposition of X takes place..

	Ex 6-7	This question
X_H	0.50	0.99
C_H	0.0105	0.00016
C_M	0.0027	0.0042
C_X	0.00507	0.0077
τ	0.2hr	0.38hr
$\bar{S}_{X/T}$	0.596	1.865

See Polymath program P6-2-f.pol.

POLYMATH Results

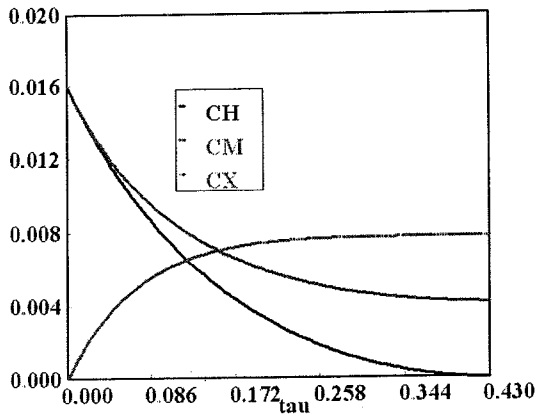
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
tau	0	0	0.43	0.43
CH	0.016	1.64E-06	0.016	1.64E-06
CM	0.016	0.0041405	0.016	0.0041405
CX	0	0	0.0077216	0.0077207
k1	55.2	55.2	55.2	55.2
k2	30.2	30.2	30.2	30.2
r1M	-0.1117169	-0.1117169	-2.927E-04	-2.927E-04
r2T	0	0	0.0159818	2.986E-04
r1H	-0.1117169	-0.1117169	-2.927E-04	-2.927E-04
r2H	0	-0.0159818	0	-2.986E-04
r1X	0.1117169	2.927E-04	0.1117169	2.927E-04
r2X	0	-0.0159818	0	-2.986E-04

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(CH)/d(tau) = r1H+r2H
[2] d(CM)/d(tau) = r1M
[3] d(CX)/d(tau) = r1X+r2X

Explicit equations as entered by the user
[1] k1 = 55.2
[2] k2 = 30.2
[3] r1M = -k1*CM*(CH^.5)
[4] r2T = k2*CX*(CH^.5)
[5] r1H = r1M
[6] r2H = -r2T
[7] r1X = -r1M
[8] r2X = -r2T



Increasing θ_H decreases τ_{opt} and $\tilde{S}_{X/T}$.

P6-2 (g) Example 6-8

Using equation from example 6-8:
Polymath code:

See Polymath program P6-2-g.pol.

POLYMATH Results
NLES Solution

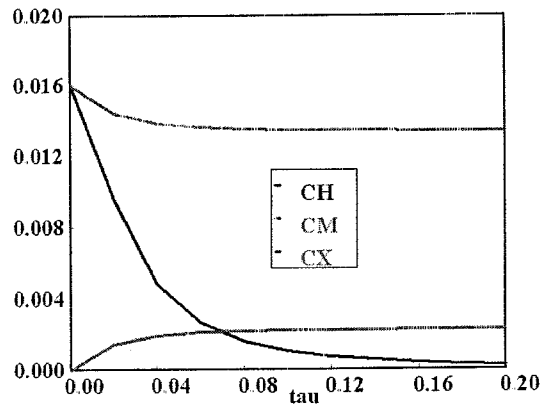
Variable	Value	f(x)	Ini Guess
CH	4.783E-05	-4.889E-11	1.0E-04
CM	0.0134353	-1.047E-11	0.013
CX	0.0023222	-9.771E-12	0.002
tau	0.5		
K1	55.2		
K2	30.2		
CHo	0.016		
CMo	0.016		

NLES Report (safenewt)

Nonlinear equations
[1] f(CH) = CH-CHo+K1*(CM*CH^.5+K2*CX*CH^.5)*tau = 0
[2] f(CM) = CM-CMo+K1*CM*CH^.5*tau = 0
[3] f(CX) = (K1*CM*CH^.5-K2*CX*CH^0.5)*tau-CX = 0

Explicit equations
[1] tau = 0.5
[2] K1 = 55.2
[3] K2 = 30.2
[4] CHo = 0.016
[5] CMo = 0.016

A plot using different values of τ is given.
For τ =0.5, the exit concentration are
$C_H = 4.8 \times 10^{-5}$ lbmol/ft^3 C_M =0.0134 lbmol/ft^3
C_X =0.00232 lbmol/ft^3



The yield of xylene from mesitylene based on molar flow rates exiting the CSTR for τ =0.5:

$$Y_{MX} = \frac{F_X}{F_{MO} - F_M} = \frac{C_X}{C_{MO} - C_M} = \frac{0.00232}{0.016 - 0.0134} = \frac{0.89 mole \cdot xylene \cdot produced}{mole \cdot mesitylene \cdot reacted}$$

The overall selectivity of xylene relative to toluene is:

$$\tilde{S}_{X/T} = \frac{F_X}{F_T} = \frac{8.3 mole \cdot xylene \cdot produced}{mole \cdot toluene \cdot produced}$$

	Ex 6-8	This Question
C_H	0.0089	4.8×10^{-5}
C_M	0.0029	0.0134
C_X	0.0033	0.00232
τ	0.5	0.5
Y_{MX}	0.41	0.89
$S_{X/T}$	0.7	8.3

P6-2 (h) Example 6-9

(1)

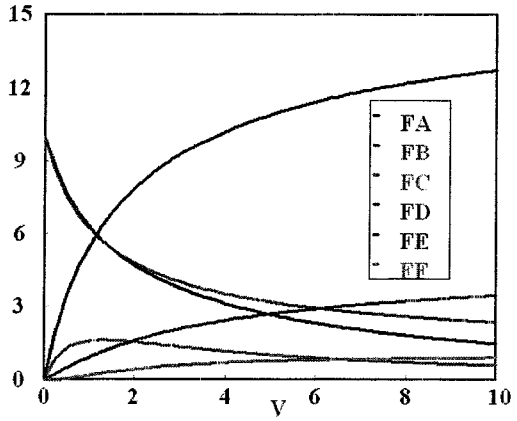
	$S_{D/U}$ Original Problem	$S_{D/U}$ P6-2 h
Membrane Reactor	2.58	1.01
PFR	0.666	0.208

Doubling the incoming flow rate of species B lowers the selectivity.

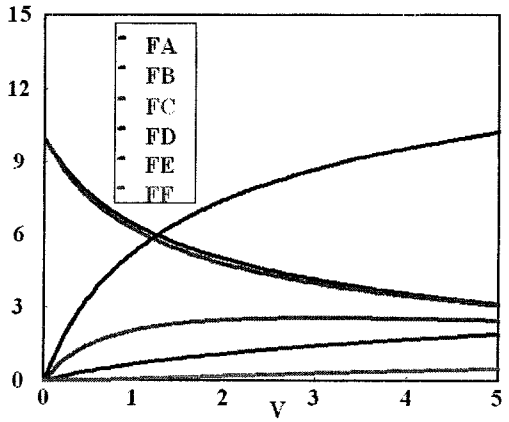
(2) The selectivity becomes 6.52 when the first reaction is changed to A+2B → D

P6-2 (i) Example 6-10

Original Case – Example 6-10



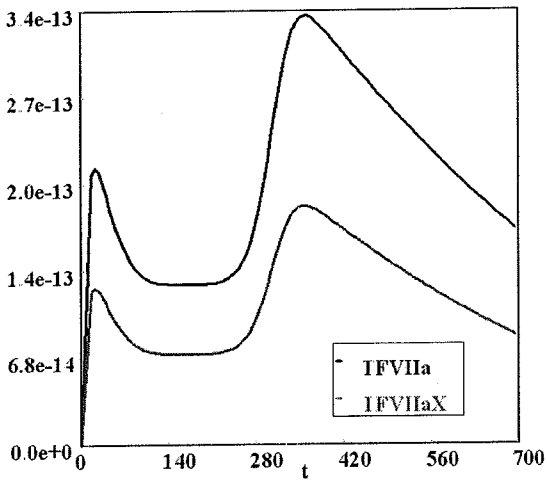
P6-2 i



The reaction does not go as far to completion when the changes are made. The exiting concentration of D, E, and F are lower, and A, B, and C are higher.

See Polymath program P6-2-i.pol.

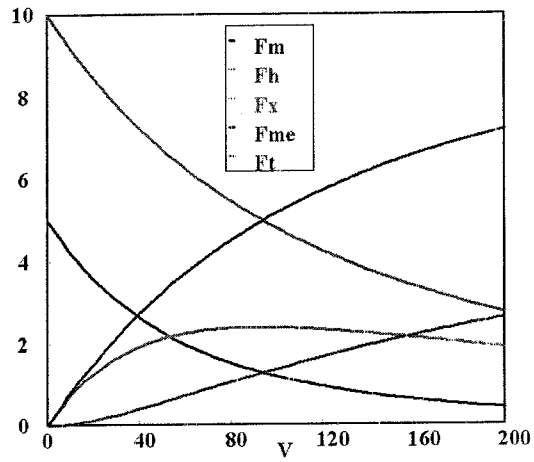
P6-2 (j)



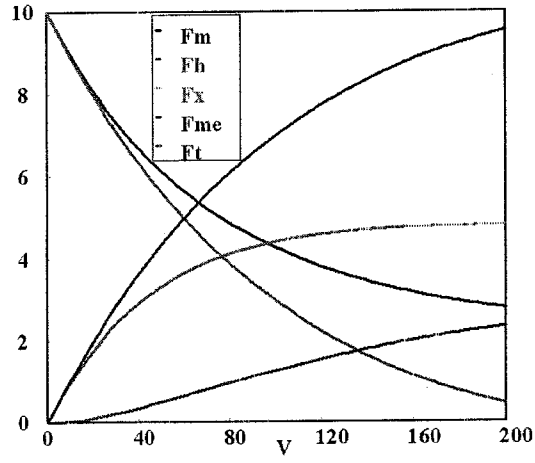
At the beginning, the reactants that are used to create TF-VIIa and TF-VIIaX are in high concentration. As the two components are created, the reactant concentration drops and equilibrium forces the production to slow. At the same time the reactions that consume the two components begin to accelerate and the concentration of TF-VIIa and TF-VIIaX decrease. As those reactions reach equilibrium, the reactions that are still producing the two components are still going and the concentration rises again. Finally the reactions that consume the two components lower the concentration as the products of those reactions are used up in other reactions.

P6-2 (k)

Base case



Equal-molar feed



Increasing y_{M0} will increase the production of m-xylene and methane, but will result in a large amount of un-reacted mesitylene.

P6-2 (l) Individualized solution

P6-3 Solution is in the decoding algorithm given with the modules (ICM problem)

P6-4 (a)

Assume that all the bites will deliver the standard volume of venom. This means that the initial concentration increases by 5e-9 M for every bite.

After 11 bites, no amount of antivenom can keep the number of free sites above 66 7% of total sites. This means that the initial concentration of venom would be 5 5e-8 M The best result occurs when a dose of antivenom such that the initial concentration of antivenom in the body is 5.7e-8 M, will result in a minimum of 66 48% free sites, which is below the allowable minimum.

See Polymath program P6-4-a.pol.

P6-4 (b)

The victim was bitten by a harmless snake and antivenom was injected. This means that the initial concentration of venom is 0. From the program below, we see that if an amount of antivenom such that the initial concentration in the blood is 7e-9 M, the patient will die.

See Polymath program P6-4-b.pol.

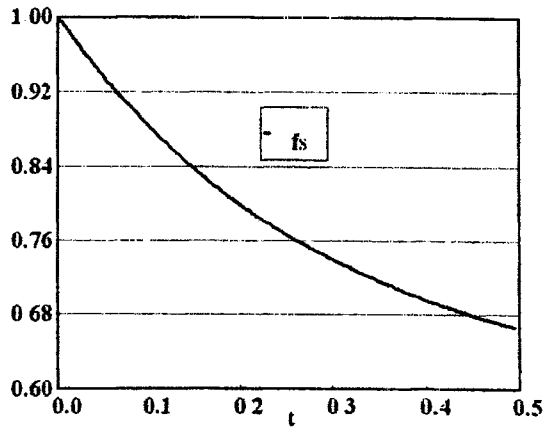
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	0 5	0.5
fsv	0	0	0	0
fs	1	0.6655661	1	0.6655661
Cv	0	0	0	0
Ca	7 0E-09	4 503E-09	7.0E-09	4.503E-09
fsa	0	0	0.3344339	0.3344339
Cp	0	0	0	0
kv	2 0E+08	2.0E+08	2.0E+08	2.0E+08
ksv	6.0E+08	6.0E+08	6.0E+08	6.0E+08
ka	2.0E+08	2 0E+08	2.0E+08	2.0E+08
kia	1	1	1	1
Cso	5.0E-09	5.0E-09	5 0E-09	5.0E-09
ksa	6.0E+08	6.0E+08	6 0E+08	6.0E+08
kp	1.2E+09	1.2E+09	1 2E+09	1.2E+09
kov	0	0	0	0
koa	0.3	0.3	0 3	0.3
kop	0 3	0.3	0.3	0 3
g	0	0	0	0
h	0	0	0	0
m	0	0	0	0
j	-2.1E-09	-2.1E-09	-1 351E-09	-1.351E-09

ODE Report (STIFF)

Differential equations as entered by the user
[1] d(fsv)/d(t) = kv * fs * Cv - ksv * fsv * Ca
[2] d(fs)/d(t) = -kv*fs*Cv - ka * fs * Ca + kia * fsa + g
[3] d(Cv)/d(t) = Cso * (-kv * fs * Cv - ksa * fsa * Cv) + h
[4] d(Ca)/d(t) = Cso*(-ka * fs * Ca + kia * fsa) + j
[5] d(fsa)/d(t) = ka * fs * Ca - kia * fsa - ksa * fsa * Cv
[6] d(Cp)/d(t) = Cso * (ksv * fsv * Ca + ksa * fsa * Cv) + m

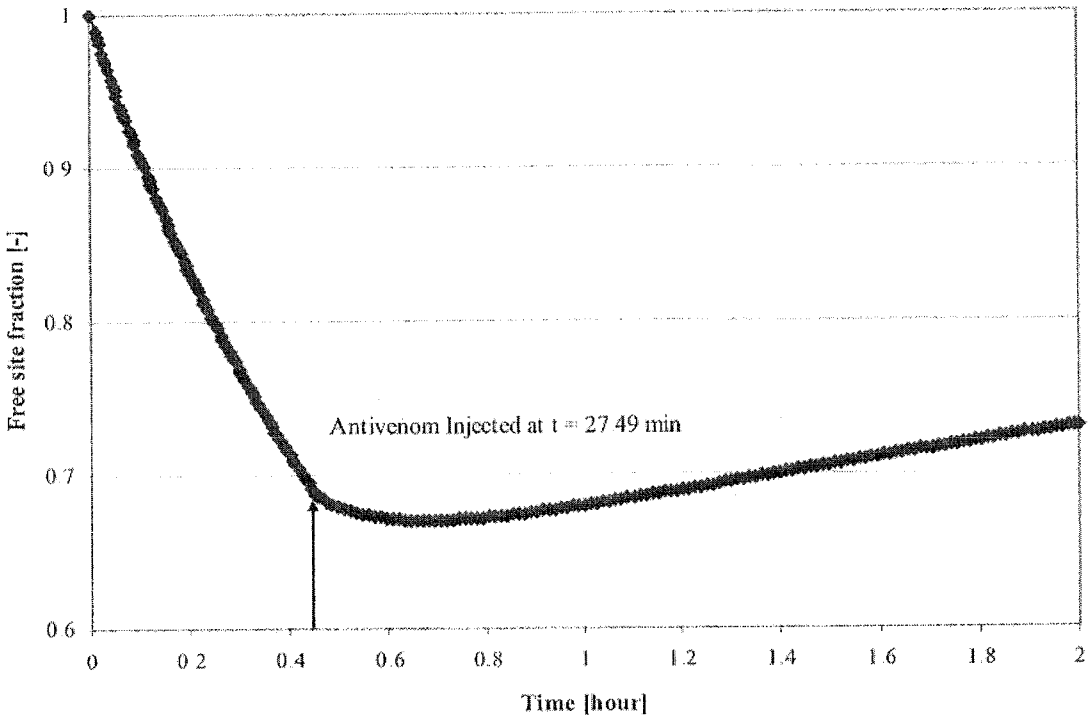
Explicit equations as entered by the user
[1] kv = 2e8
[2] ksv = 6e8
[3] ka = 2e8
[4] kia = 1
[5] Cso = 5e-9
[6] ksa = 6e8
[7] kp = 1 2e9



```
[8] kov = 0
[9] koa = 0.3
[10] kop = 0.3
[11] g = ksa * fsa * Cv + ksv * fsv * Ca
[12] h = -kp * Cv * Ca - kov * Cv
[13] m = kp * Cv * Ca - kop * Cp
[14] j = -Cso * ksv * fsv * Ca - kp * Cv * Ca - koa * Ca
```

P6-4 (c)

The latest time after being bitten that antivenom can successfully be administerd is 27.49 minutes. See the cobra web module on the CDROM/website for a more detailed solution to this problem



P6-4 (d) Individualized Solution

P6-5 (a)

Plot of C_A, C_D and C_U as a function of time (t):

See Polymath program P6-5-a.pol.

POLYMATH Results
Calculated values of the DEQ variables

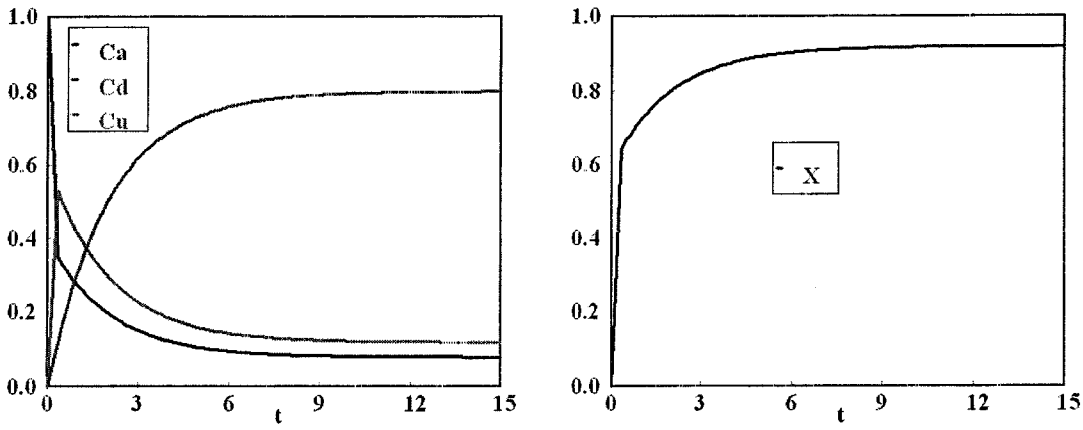
Variable	initial value	minimal value	maximal value	final value
t	0	0	15	15
Ca	1	0.0801802	1	0.0801802
Cd	0	0	0.7995475	0.7995475
Cu	0	0	0.5302179	0.1202723
k1	1	1	1	1

k2	100	100	100	100
K1a	10	10	10	10
K2a	1.5	1.5	1.5	1.5
Cao	1	1	1	1
X	0	0	0.9198198	0.9198198

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Ca)/d(t) = -(k1*(Ca-Cd/K1a)+k2*(Ca-Cu/K2a))
[2] d(Cd)/d(t) = k1*(Ca-Cd/K1a)
[3] d(Cu)/d(t) = k2*(Ca-Cu/K2a)

Explicit equations as entered by the user
[1] k1 = 1.0
[2] k2 = 100
[3] K1a = 10
[4] K2a = 1.5
[5] Cao = 1
[6] X = 1-Ca/Cao



To maximize C_D stop the reaction after a long time. The concentration of D only increases with time

P6-5 (b)

Conc. Of U is maximum at t = 0.31 min.(C_A = 0.53)

P6-5 (c)

Equilibrium concentrations:
C_{Ae} = 0.08 mol/dm^3
C_{De} = 0.8 mol/dm^3
C_{Ue} = 0.12 mol/dm^3

P6-5 (d)

See Polymath program P6-5-d.pol.

POLYMATH Results
NLES Solution

Variable	Value	f(x)	Ini Guess
Ca	0.0862762	-3.844E-14	1

Cd	0.7843289	-2.631E-14	0
Cu	0.1293949	6.478E-14	0
Ca0	1		
k1	1		
k2	100		
K1a	10		
K2a	1.5		
t	100		

NLES Report (safenewt)

Nonlinear equations
[1] f(Ca) = Ca0-t*(k1*(Ca-Cd/K1a)+k2*(Ca-Cu/K2a))-Ca = 0
[2] f(Cd) = t*k1*(Ca-Cd/K1a)-Cd = 0
[3] f(Cu) = t*(k2*(Ca-Cu/K2a))-Cu = 0

Explicit equations
[1] Ca0 = 1
[2] k1 = 1
[3] k2 = 100
[4] K1a = 10
[5] K2a = 1.5
[6] t = 100
[7] X = 1-Ca/Ca0

τ	1 min	10 min	100min
C_{Aexit}	0.295	0.133	0.0862
C_{Dexit}	0.2684	0.666	0.784
C_{Uexit}	0.436	0.199	0.129
X	0.705	0.867	0.914

P6-6 (a)

$A \rightarrow X$ $\qquad r_X = k_1 C_A^{1/2} \qquad k_1 = 0.004\left(\frac{mol}{dm^3}\right)^{1/2} \text{min}$

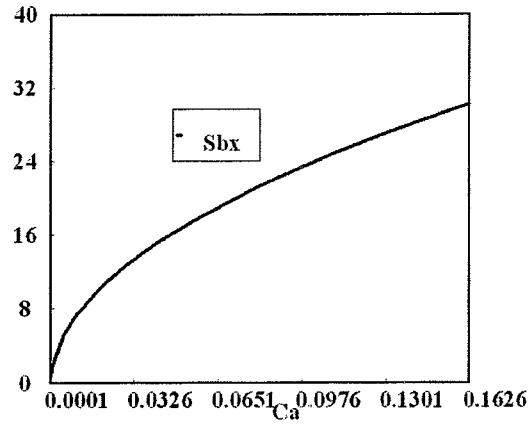
$A \rightarrow B$ $\qquad r_B = k_2 C_A \qquad k_2 = 0.3 \text{min}^{-1}$

$A \rightarrow Y$ $\qquad r_Y = k_3 C_A^{\,2} \qquad k_3 = 0.25 \frac{dm^3}{mol.\text{min}}$

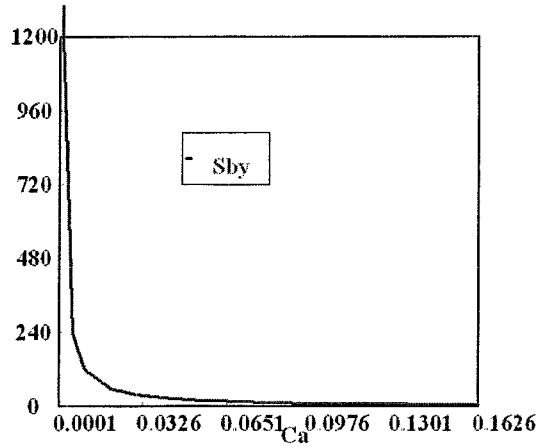
Sketch S_{BX}, S_{BY} and $S_{B/XY}$ as a function of C_A

See Polymath program P6-6-a.pol.

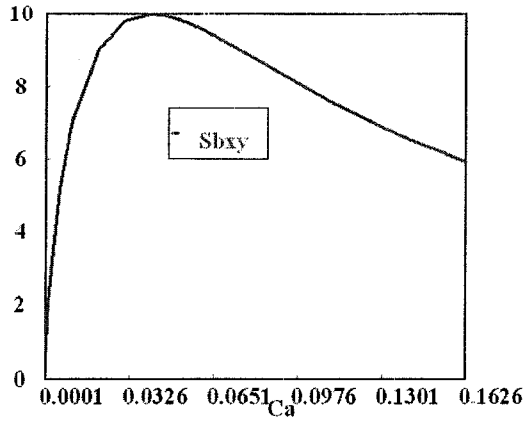
1) $S_{B/X} = \frac{r_B}{r_X} = \frac{k_2 C_A}{k_1 C_A^{1/2}} = \frac{k_2}{k_1} C_A^{1/2}$



2) $$S_{B/Y} = \frac{r_B}{r_Y} = \frac{k_2 C_A}{k_3 C_A^{\,2}} = \frac{k_2}{k_3 C_A}$$



3) $$S_{B/XY} = \frac{r_B}{r_X + r_Y} = \frac{k_2 C_A}{k_1 C_A^{\,1/2} + k_3 C_A^{\,2}}$$



P6-6 (b)

Volume of first reactor can be found as follows

We have to maximize $S_{B/XY}$
From the graph above, maximum value of $S_{BXY} = 10$ occurs at $C_A^* = 0.040$ mol/dm^3
So, a CSTR should be used with exit concentration C_A^*
Also, $C_{A0} = P_A/RT = 0.162$ mol/dm^3

And $-r_A = r_X + r_B + r_Y = (k_1 C_A^{1/2} + k_2 C_A + k_3 C_A^2)$

$$\Rightarrow V = \frac{v_0(C_{A0} - C_A^*)}{-r_A} = \frac{v_0(C_{A0} - C_A^*)}{(k_1(C_A^*)^{1/2} + k_2 C_A^* + k_3(C_A^*)^2)} = 92.4 dm^3$$

P6-6 (c)

Effluent concentrations:

We know, $\tau = 9.24$ min $\Rightarrow \tau = \frac{C_B}{r_B} = \frac{C_B}{k_2 C_A} \Rightarrow C_B^* = 0.11 \frac{mol}{dm^3}$

Similarly: $C_X^* = 0.007 \frac{mol}{dm^3}$ and $C_Y^* = 0.0037 \frac{mol}{dm^3}$

P6-6 (d)

Conversion of A in the first reactor:

$C_{A0} - C_A = C_{A0} X \Rightarrow X = 0.74$

P6-6 (e)

A CSTR followed by a PFR should be used.
Required conversion = 0.99

$\Rightarrow$ For PFR, Mole balance: $\frac{dV}{dX} = \frac{F_{A0}}{-r_A}$

$$\Rightarrow V = 10 \times 0.162 \times \int_{0.74}^{0.99} \frac{dX}{(k_1 C_A^{1/2} + k_2 C_A + k_3 C_A^2)} = 92.8 dm^3$$

P6-6 (f)

If we notice that E_2 is the smallest of the activation energies, we get a higher selectivity at lower temperatures. However, the tradeoff is that the reaction rate of species B, and therefore production of B, decrease as temperature drops. So we have to compromise between high selectivity and production. To do this we need expressions for k_1, k_2, and k_3 in terms of temperature. From the given data we know:

$$k_i = A_i \exp\left(\frac{-E_i}{1.98T}\right)$$

Since we have the constants given at T = 300 K, we can solve for A_i.

$$A_1 = \frac{.004}{\exp\left(\frac{-20000}{1.98(300)}\right)} = 1.49e12$$

$$A_2 = \frac{.3}{\exp\left(\frac{-10000}{1.98(300)}\right)} = 5.79e6$$

$$A_3 = \frac{.25}{\exp\left(\frac{-30000}{1.98(300)}\right)} = 1.798e21$$

Now we use a mole balance on species A

$$V = \frac{F_{A0} - F_A}{-r_A}$$

$$V = \frac{v(C_{A0} - C_A)}{-r_A}$$

$$\tau = \frac{C_{A0} - C_A}{-r_A} = \frac{C_{A0} - C_A}{k_1 C_A^{0.5} + k_2 C_A + k_3 C_A^2}$$

A mole balance on the other species gives us:

$$F_i = vC_i = r_i V$$

$$C_i = \tau r_i$$

Using these equations we can make a Polymath program and by varying the temperature, we can find a maximum value for C_B at T = 306 K. At this temperature the selectivity is only 5.9. This may result in too much of X and Y, but we know that the optimal temperature is not above 306 K. The optimal temperature will depend on the price of B and the cost of removing X and Y, but without actual data, we can only state for certain that the optimal temperature will be equal to or less than 306 K.

See Polymath program P6-6-f.pol.

POLYMATH Results
NLE Solution

Variable	Value	f(x)	Ini Guess
Ca	0.0170239	3.663E-10	0.05
T	306		
R	1.987		
k1	0.0077215		
k2	0.4168076		
Cao	0.1		
Cb	0.070957		
k3	0.6707505		
tau	10		
Cx	0.0100747		
Cy	0.0019439		
Sbxy	5.9039386		

NLE Report (safenewt)

Nonlinear equations
[1] f(Ca) = (Cao-Ca)/(k1*Ca^.5+k2*Ca+k3*Ca^2)-10 = 0

Explicit equations
[1] T = 306
[2] R = 1.987
[3] k1 = 1.49e12*exp(-20000/R/T)
[4] k2 = 5790000*exp(-10000/R/T)
[5] Cao = .1

[6] Cb = 10*k2*Ca
[7] k3 = 1.798e21*exp(-30000/R/T)
[8] tau = 10
[9] Cx = tau*k1*Ca^.5
[10] Cy = tau*k3*Ca^2
[11] Sbxy = Cb/(Cx+Cy)

P6-6 (g)

Concentration is proportional to pressure in a gas-phase system. Therefore:

$S_{B/XY} \sim \frac{P}{\sqrt{P} + P^2}$ which would suggest that a low pressure would be ideal. But as before the tradeoff is lower production of B. A moderate pressure would probably be best.

P6-7

US legal limit: 0.8 g/l
Sweden legal limit: 0.5 g/l

$A \xrightarrow{k1} B \xrightarrow{k2} C$

Where A is alcohol in the gastrointestinal tract and B is alcohol in the blood stream

$$\frac{dC_A}{dt} = -k_1 C_A$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2$$

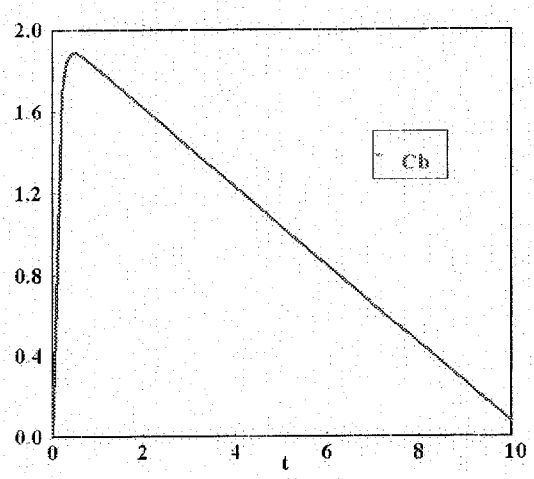
$$k_1 = 10\,hr^{-1}$$

$$k_2 = 0.192 \frac{g}{L\ hr}$$

Two tall martinis = 80 g of ethanol
Body fluid = 40 L

$$C_{A0} = \frac{80g}{40L} = 2\frac{g}{L}$$

Now we can put the equations into Polymath.
See Polymath program P6-7.pol.



POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	10	10
Ca	2	7.131E-44	2	7.131E-44
Cb	0	0	1.8901533	0.08
k1	10	10	10	10
k2	0.192	0.192	0.192	0.192

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Ca)/d(t) = -k1*Ca

[2] d(Cb)/d(t) = -k2+k1*Ca

Explicit equations as entered by the user
[1] k1 = 10
[2] k2 = 0.192

P6-7 (a)

In the US the legal limit it 0.8 g/L.
This occurs at t = 6.3 hours..

P6-7 (b)

In Sweden C_B = 0.5 g/l , t = 7.8 hrs.

P6-7 (c) In Russia C_B = 0.0 g/l, t = 10.5 hrs

P6-7 (d)

For this situation we will use the original Polymath code and change the initial concentration of A to 1 g/L. Then run the Program for 0.5 hours. This will give us the concentration of A and B at the time the second martini is ingested. This means that 1 g/l will be added to the final concentration of A after a half an hour.

At a half an hour C_A = 0.00674 g/L and C_B = 0.897 g/L. The Polymath code for after the second drink is shown below.

See Polymath program P6-7-d.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0.5	0.5	10	10
Ca	1.0067379	5.394E-42	1.0067379	5.394E-42
Cb	0.8972621	0.08	1.8069769	0.08
k1	10	10	10	10
k2	0.192	0.192	0.192	0.192

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Ca)/d(t) = -k1*Ca
[2] d(Cb)/d(t) = -k2+k1*Ca

Explicit equations as entered by the user
[1] k1 = 10
[2] k2 = 0.192

for the US t = 6.2 hours
Sweden: t = 7.8 hours
Russia: t =10.3 hours.

P6-7 (e)

The mole balance on A changes if the drinks are consumed at a continuous rate for the first hour. 80 g of ethanol are consumed in an hour so the mass flow rate in is 80 g/hr. Since volume is not changing the rate of change in concentration due to the incoming ethanol is 2 g/L/hr.

For the first hour the differential equation for C_A becomes:

$\frac{dC_A}{dt} = -k_1 C_A + 2t$ after that it reverts back to the original equations.

See Polymath program P6-7-e.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	11	11
Ca	0	0	0.1785514	6.217E-45
Cb	0	-1.1120027	0.7458176	-1.1120027
k1	10	10	10	10
k2	0.192	0.192	0.192	0.192

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Ca)/d(t) = if(t<1)then(-k1*Ca+2*t)else(-k1*Ca)
[2] d(Cb)/d(t) = -k2+k1*Ca

Explicit equations as entered by the user
[1] k1 = 10
[2] k2 = 0.192

US: C_B never rises above 0.8 g/L so the is no time that it would be illegal.
Sweden: t = 2.6 hours
Russia: t = 5.2 hours

P6-7 (f)

60 g of ethanol immediately → C_A = 1.5 g/L

C_B = 0.8 g/L at 0.0785 hours or 4.71 minutes.

So the person has about 4 minutes and 40 seconds to get to their destination.

P6-7 (g)

A heavy person will have more body fluid and so the initial concentration of C_A would be lower. This means a heavier person will reach the legal limit quicker. The opposite is true for a slimmer person. They will take longer to reach the legal limit, as their initial concentration will be higher.

P6-8 (a)

Let A be the tarzlon in the stomach and B be the tarzlon in the blood.

Mole Balances :

$$\frac{dC_A}{dt} = r_A$$

$$\frac{dC_B}{dt} = r_B$$

Rate Laws :

$$-r_A = k_1 C_A + k_2 C_A$$

$$r_B = k_1 C_A - k_3 - k_4 C_B$$

All k values are given in the proble m statement. It must be noted, however, that for $C_B < 0$, k_3 must be equal to 0.

These equations when entered in POLYMATH generate the following results:

See Polymath program P6-8-a.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	4	4
Ca	6.25	0.3111692	6.25	0.3111692
Cb	0	0	0.5977495	0.4057018
k1	0.15	0.15	0.15	0.15
k2	0.6	0.6	0.6	0.6
k4	0.2	0.2	0.2	0.2
k3	0.1	0.1	0.1	0.1

ODE Report (RKF45)

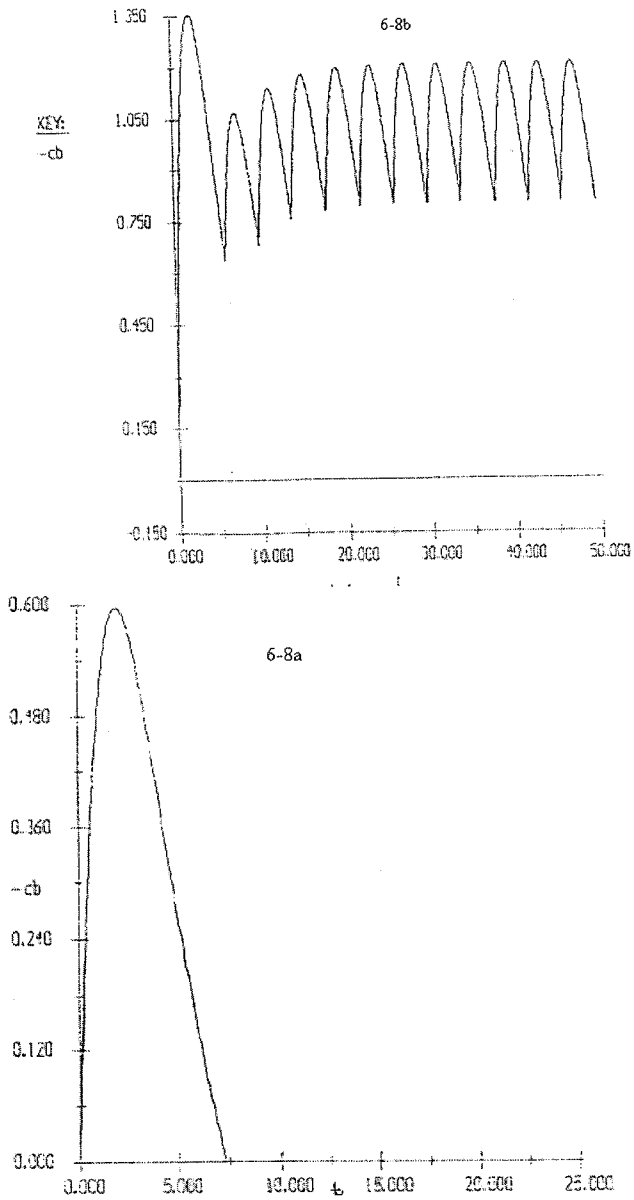
Differential equations as entered by the user
[1] d(Ca)/d(t) = -k1*Ca-k2*Ca
[2] d(Cb)/d(t) = k1*Ca-k3-k4*Cb

Explicit equations as entered by the user
[1] k1 = 0.15
[2] k2 = 0.6
[3] k4 = 0.2
[4] k3 = if(Cb<0)then (k1*Ca-k4*Cb) else (0.1)

P6-8 (b)

From the following graph generated using the above program in POLYMATH, we can see the proper doses of the drug:

1. First take two doses of the drug.
2. Six hours later take one dose.
3. Take one dose every four hours from then on.



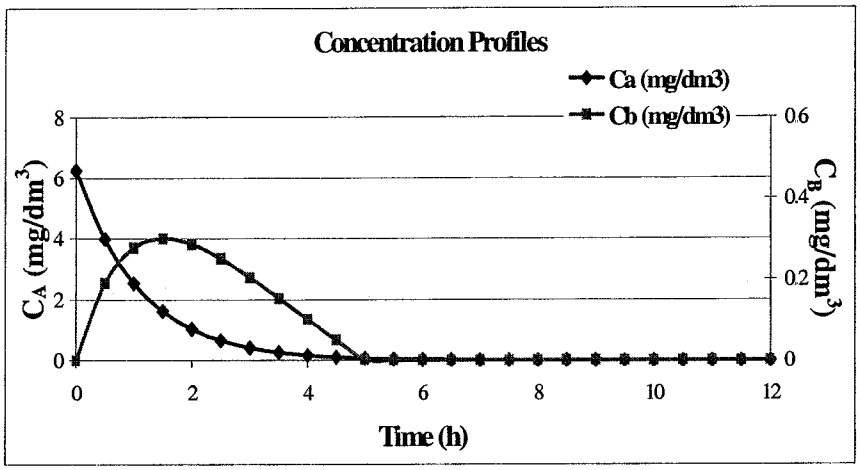
P6-8 (c)

If one takes initially two doses of Tarzlon, it is not recommended to take another dose within the first six hours. Doing so will result in build up of the drug in the bloodstream that can cause harmful effects.

P6-8 (d)

If the drug is taken on a full stomach most of it will not reach the wall at all. The processed food can also drag the drug to the intestines and may limit its effectiveness. This effect can be seen in the adsorption constant k_1 and elimination constant k_2 values. If k_1 decreases this means that the adsorption process is slow

and if k_2 increases means that the rate of elimination of Tarzlon increases. The next graph shows the concentration profiles for $k_1 = 0.10\ h^{-1}$ and $k_2 = 0.8\ h^{-1}$. Note that the maximum amount of the drug in the bloodstream is reduced by two.



Concentration profile for Tarzlon in the stomach (A) and bloodstream (B). The maximum amount of Tarzlon in the bloodstream is 0.3 mg/dm^3.

P6-9 (a)

Reactor selection

$A + B \rightarrow D \qquad r_D = -r_{1A} \qquad r_{1A} = 10\exp(-8000K/T)C_A C_B$

$A + B \rightarrow U \qquad r_U = -r_{2A} \qquad r_{2A} = 100\exp(-1000K/T)C_A^{1/2} C_B^{3/2}$

$$S_{DU} = \frac{r_D}{r_U} = \frac{10\exp(-8000K/T)C_A C_B}{100\exp(-1000K/T)C_A^{1/2} C_B^{3/2}} = \frac{\exp(-8000K/T)C_A^{1/2}}{10\exp(-1000K/T)C_B^{1/2}}$$

At T = 300K

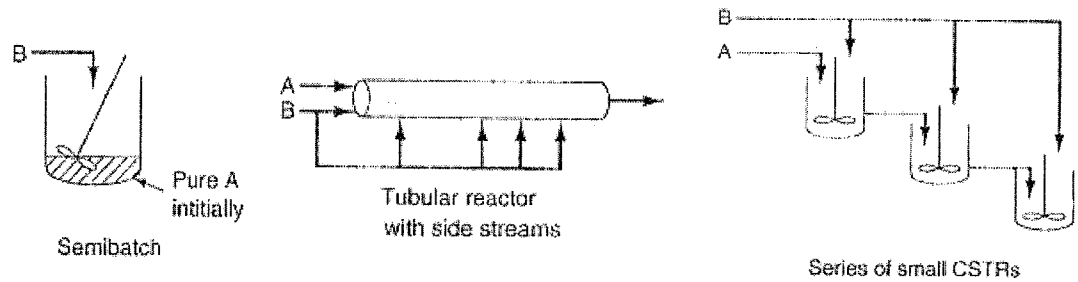
$k_1 = 2.62 \times 10^{-11}$ & $k_2 = 3.57$ $\qquad S_{D/U} = \dfrac{7.35\times10^{-12} C_A^{1/2}}{C_B^{1/2}}$

At T = 1000K

$k_1 = 3.35 \times 10^{-3}$ & $k_2 = 36.78$ $\qquad S_{D/U} = \dfrac{9.2\times10^{-5} C_A^{1/2}}{C_B^{1/2}}$

Hence In order to maximize S_{DU}, use higher concentrations of A and lower concentrations of B. This can be achieved using:

1) A semibatch reactor in which B is fed slowly into a large amount of A
2) A tubular reactor with side streams of B continually fed into the reactor
3) A series of small CSTR's with A fed only to the first reactor and small amounts of B fed to each reactor.



Also, since $E_D > E_U$, so the specific reaction rate for D increases much more rapidly with temperature. Consequently, the reaction system should be operated at highest possible temperature to maximize S_{DU}.

Note that the selectivity is extremely low, and the only way to increase it is to keep $\left(\frac{C_B}{C_A}\right)^{1/2} < 10^{-6}$ and add B drop by drop.

P6-9 (b)

$A + B \rightarrow D$ and $r_{1A} = 100\exp(-1000K/T)C_A C_B$

$A + B \rightarrow U$ and $r_{2A} = 10^6 \exp(-8000K/T)C_A C_B$

$$S_{DU} = \frac{r_D}{r_U} = \frac{100\exp(-1000K/T)C_A C_B}{10^6 \exp(-8000K/T)C_A C_B} = \frac{\exp(-1000K/T)}{10^4 \exp(-8000K/T)}$$

At T = 300K

$k_1 = 3.57$ & $k_2 = 2.623$ $S_{DU} = 1.14 \times 10^6$

At T = 1000K

$k_1 = 36.78$ & $k_2 = 3354.6$ $S_{DU} = 0.103$

Hence we should keep the temperature low to maximize S_{DU} but not so low that the desired reaction doesn't proceed to a significant extent.

P6-9 (c)

$A + B \rightarrow D$ and $r_{1A} = 10\exp(-8000K/T)C_A C_B$

$B + D \rightarrow U$ and $r_{2A} = 10^9 \exp(-10,000K/T)C_B C_D$

$$S_{DU} = \frac{r_{1A}}{r_{2A}} = \frac{10\exp(-8000K/T)C_A C_B}{10^9 \exp(-10000K/T)C_B C_D}$$

$$S_{DU} = \frac{\exp(-8000/T)C_A}{10^8 \exp(-10000/T)C_D}$$

Therefore the reaction should be run at a low temperature to maximize S_{DU}, but not too low to limit the production of desired product. The reaction should also take place in high concentration of A and the concentration of D should be limited by removing through a membrane or reactive distillation.

P6-9 (d)

$A \rightarrow D$ and $r_{1A} = 4280\exp(-12000K/T)C_A$

$D \rightarrow U_1$ and $r_{2D} = 10{,}100\exp(-15000K/T)C_D$

$A \rightarrow U_2$ and $r_{3A} = 26\exp(-10800\ K/T)C_A$

$$S_{D/U1U2} = \frac{r_D}{r_{U1} + r_{U2}} = \frac{4280\exp(-12000K/T)C_A - 10{,}100\exp(-15000K/T)C_D}{10{,}100\exp(-15000K/T)C_D + 26\exp(-10800K/T)C_A}$$

At T = 300K

$k_1 = 1.18 \times 10^{-14}$ & $k_2 = 1.94 \times 10^{-18}$ & $k_3 = 6.03 \times 10^{-15}$

If we keep $C_A > 1000C_D$

$$S_{D/U1U2} = \frac{1.18\times10^{-14}C_A - 1.94\times10^{-18}C_D}{1.94\times10^{-18}C_D + 6.03\times10^{-15}C_A} \approx \frac{1.18}{.603} = 1.96$$

At T = 1000K
$k_1 = 0.026$ & $k_2 = 3.1 \times 10^{-3}$ & $k_3 = 5.3 \times 10^{-4}$

If we keep $C_A > 1000C_D$

$$S_{D/U1U2} = \frac{0.026C_A - 3.1\times10^{-3}C_D}{3.1\times10^{-3}C_D + 5.3\times10^{-4}C_A} \approx \frac{.026}{.00053} = 49$$

Here, in order to lower U_1 use low temperature and high concentration of A
But low temperature and high concentration of A favours U_2
So, well have to optimize the temperature and concentration of A.
Membrane reactor in which D is diffusing out can be used.

P6-9 (e)

$A + B \rightarrow D$ and $r_{1A} = 10^9 \exp(-10000K/T)C_AC_B$

$D \rightarrow A + B$ and $r_{2D} = 20\exp(-2000\ K/T)C_D$

$A + B \rightarrow U$ and $r_{3A} = 10^3 \exp(-3000\ K/T)C_AC_B$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{10^9 \exp(-10000K/T)C_AC_B - 20\exp(-2000K/T)C_D}{10^3 \exp(-3000K/T)C_AC_B}$$

At T = 300K
$k_1 = 3.34 \times 10^{-6}$ & $k_2 = 0.025$ & $k_3 = 0.045$

The desired reaction lies very far to the left and C_D is probably present at very low concentrations so that:

$$S_{D/U} = \frac{3.34\times10^{-6}C_AC_B - 0.025C_D}{0.045C_AC_B} \approx \frac{0.000334}{4.5} = 0.000074$$

$$S_{D/U} \approx 0$$

At T = 1000K
$k_1 = 45399.9$ & $k_2 = 2.7$ & $k_3 = 49.7$

If we assume that $C_AC_B > 0.001C_D$ then,

$$S_{D/U} = \frac{45399.9C_AC_B - 2.7C_D}{49.7C_AC_B} \approx \frac{45399}{49.7} = 913$$

Here we need a high temperature for a lower reverse reaction of D and lower formation of U
Also we need to remove D as soon as it is formed so as to avoid the decomposition.

P6-9 (f)

$A + B \rightarrow D$ and $-r_{1A} = 10\exp(-8000K/T)C_AC_B$

$A \rightarrow U$ and $-r_{2A} = 26\exp(-10,800K/T)C_A$

$U \rightarrow A$ and $-r_{3U} = 1000\exp(-15,000K/T)C_U$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{10\exp(-8000K/T)C_AC_B}{26\exp(-10,800K/T)C_A - 1000\exp(-15,000K/T)C_U}$$

We want high concentrations of B and U in the reactor. Also low temperatures will help keep the selectivity high.

If we use pseudo equilibrium and set $-r_A = 0$.

$$-r_A = 10\exp\left(\frac{-8000}{T}\right)C_A C_B + 26\exp\left(\frac{-10800}{T}\right)C_A - 1000\exp\left(\frac{-15000}{T}\right)C_U = 0$$

$$\frac{C_A}{C_U} = \frac{10\exp\left(\frac{-8000}{T}\right)C_B + 26\exp\left(\frac{-10800}{T}\right)}{1000\exp\left(\frac{-15000}{T}\right)}$$

$$\frac{C_A}{C_U} = \frac{1}{100}\exp\left(\frac{7000}{T}\right)C_B + \frac{26}{1000}\exp\left(\frac{4200}{T}\right)$$

P6-9 (g)

$A + B \rightarrow D$ and $-r_{1A} = 800\exp(-8000K/T)C_A^{0.5}C_B$

$A + B \rightarrow U_1$ and $-r_{2B} = 10\exp(-300K/T)C_A C_B$

$D + B \rightarrow U_2$ and $-r_{3D} = 10^6\exp(-8000K/T)C_D C_B$

(1)

$$S_{D/U_1} = \frac{800\exp(-8000/T)C_A^{0.5}C_B}{10\exp(-300/T)C_A C_B} = \frac{80\exp(-8000/T)}{\exp(-300/T)C_A^{0.5}}$$

At T = 300

$$S_{D/U_1} = \frac{2.098*10^{-10}}{0.368C_A^{0.5}}$$

At T = 1000

$$S_{D/U_1} = \frac{29.43}{0.7408C_A^{0.5}}$$

To keep this selectivity high, low concentrations of A, and high temperatures should be used.

$$S_{D/U2} = \frac{800\exp(-8000/T)C_A^{0.5}C_B}{10^6\exp(-8000/T)C_D C_B} = \frac{800C_A^{0.5}}{10^6 C_D}$$

To keep this selectivity high, high concentrations of A and low concentrations of D should be used. Try to remove D with a membrane reactor or reactive distillation. The selectivity is not dependant on temperature.

To keep optimize the reaction, run it at a low temperature to maximized $S_{D/U1}$ in a membrane reactor that allows only D to diffuse out.

(2)

$$S_{D/U1U2} = \frac{800\exp(-8000/T)C_A^{0.5}C_B}{10\exp(-300/T)C_A C_B + 10^6\exp(-8000/T)C_D C_B}$$

$$S_{D/U1U2} = \frac{800\exp(-8000/T)C_A^{0.5}}{10\exp(-300/T)C_A + 10^6\exp(-8000/T)C_D}$$

At T = 300

$$S_{D/U1U2} = \frac{2.09*10^{-9}C_A^{0.5}}{3.67C_A + 2.62*10^{-6}C_D} \approx 0$$

At T = 1000 and very low concentrations of D

$$S_{D/U1U2} = \frac{0.268C_A^{0.5}}{7.408C_A + 335C_D} = \frac{.03617}{C_A^{0.5}}$$

If temperature is the only parameter that can be varied, then the highest temperature possible will result in the highest selectivity. Also removing D will help keep selectivity high.

P6-9 (h) No solution will be given

P6-9 (i)

$$\frac{r_D}{r_U} = \frac{\exp(-7000K/T)C_A^{1/2}}{10C_B^{1/2}}$$

$$\frac{dF_A}{dV} = r_A \qquad \frac{dF_B}{dV} = r_B + R_B$$

$$\frac{dF_U}{dV} = r_U \qquad \frac{dF_D}{dV} = r_D$$

$$R_B = \frac{F_{A0}}{V_T}$$

$$A + B \rightarrow D \qquad r_D = -r_{1A} \qquad r_{1A} = -10\exp(-8000K/T)C_AC_B$$

$$A + B \rightarrow U \qquad r_U = -r_{2A} \qquad r_{2A} = -100\exp(-1000K/T)C_A^{1/2}C_B^{3/2}$$

$$r_A = r_B = r_{1A} + r_{2A}$$

$$C_A = C_{T0}\frac{F_A}{F_T} \qquad C_B = C_{T0}\frac{F_B}{F_T}$$

$$C_{T0} = 0.4\frac{mol}{dm^3} \qquad v_0 = 10\frac{dm^3}{s}$$

$$F_{A0} = C_{T0}v_0$$

These equations are entered into Polymath and the plots below are for the membrane reactor. The code can be modified to compare with the PFR results.

See Polymath program P6-9-i.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	10	10
Fa	4	0.5141833	4	0.5141833
Fb	0	0	4.5141833	4.5141833
Fd	0	0	3.034E-06	3.034E-06
Fu	0	0	3.4858137	3.4858137
Cto	0.4	0.4	0.4	0.4
T	600	600	600	600
Ft	4	4	8.5141833	8.5141833
Cb	0	0	0.2120783	0.2120783
Ca	0.4	0.0241566	0.4	0.0241566

r1a	0	-4.575E-07	0	-8.297E-08
rd	0	0	4.575E-07	8.297E-08
r2a	0	-0.4461944	0	-0.2867066
ra	0	-0.4461948	0	-0.2867066
rb	0	-0.4461948	0	-0.2867066
ru	0	0	0.4461944	0.2867066
Vt	5	5	5	5
Fao	4	4	4	4
Rb	0.8	0.8	0.8	0.8
Sdu	5.423E+05	2.894E-07	5.423E+05	2.894E-07

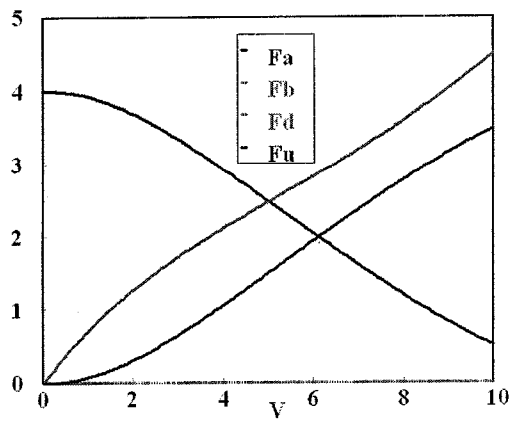
ODE Report (RKF45)

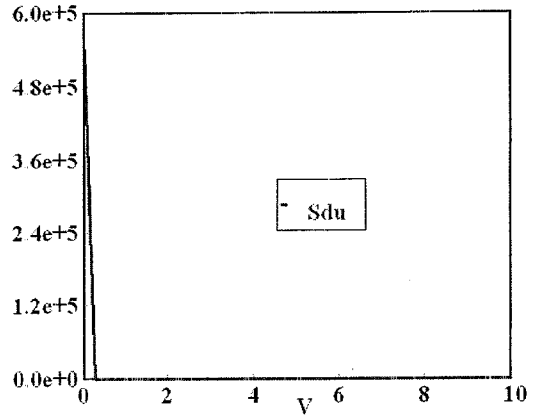
Differential equations as entered by the user

[1] d(Fa)/d(V) = ra
[2] d(Fb)/d(V) = rb+Rb
[3] d(Fd)/d(V) = rd
[4] d(Fu)/d(V) = ru

Explicit equations as entered by the user

[1] Cto = .4
[2] T = 600
[3] Ft = Fa+Fb+Fd+Fu
[4] Cb = Cto*Fb/Ft
[5] Ca = Cto*Fa/Ft
[6] r1a = -10*exp(-8000/T)*Ca*Cb
[7] rd = -r1a
[8] r2a = -100*exp(-1000/T)*Ca^.5*Cb^1.5
[9] ra = r1a+r2a
[10] rb = ra
[11] ru = -r2a
[12] Vt = 5
[13] Fao = 4
[14] Rb = Fao/Vt
[15] Sdu = exp(-7000/T)*Ca^.5/(10*Cb^.5+.00000000001)





P6-9 (j) No solution will be given

P6-9 (k) No solution will be given

P6-9 (l) No solution will be given

P6-10 (a)

Species A:

$$\frac{dC_A}{dt} = r_A$$

$$-r_A = k_1 C_A$$

Species B:

$$\frac{dC_B}{dt} = r_B$$

$$r_B = k_1 C_A - k_2 C_B$$

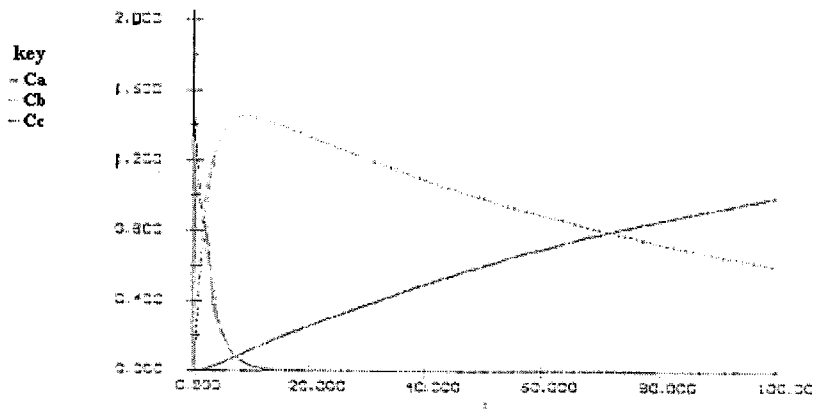
Species C:

$$\frac{dC_C}{dt} = r_C$$

$$r_C = k_2 C_B$$

Plugging into POLYMATH: gets the following.

Equations:	Variable	Initial value	Maximum value	Minimum value	Final value
d(ca)/d(t)=ra	t	0	100	0	100
d(cb)/d(t)=rb	ca	1.6	1.6	6.7898e-18	6.7898e-18
d(cc)/d(t)=rc	cb	0	1.4556	0	0.6037
k1=.4	cc	0	0.9963	0	0.9963
k2=.01	k1	0.4	0.4	0.4	0.4
ra=-k1*ca	k2	0.01	0.01	0.01	0.01
rc=k2*cb	ra	-0.64	-2.71592e-18	-0.64	-2.71592e-18
rb=k1*ca-k2*cb	rc	0	0.014556	0	0.006037
$t_0 = 0$, $t_f = 100$	rb	0.64	0.64	-0.0132417	-0.006037



P6-10 (b)

For CSTR, $\tau = 0.5h$

First calculate k_1 and k_2 :

$$k = k_0 \exp\left(\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right)$$

$$k_1 = 0.4 \exp\left(\frac{10{,}000}{R}\left(\frac{1}{373} - \frac{1}{T}\right)\right)$$

$$k_2 = 0.01\exp\left(\frac{20{,}000}{R}\left(\frac{1}{373}-\frac{1}{T}\right)\right)$$

See Polymath program P6-10-b.pol.

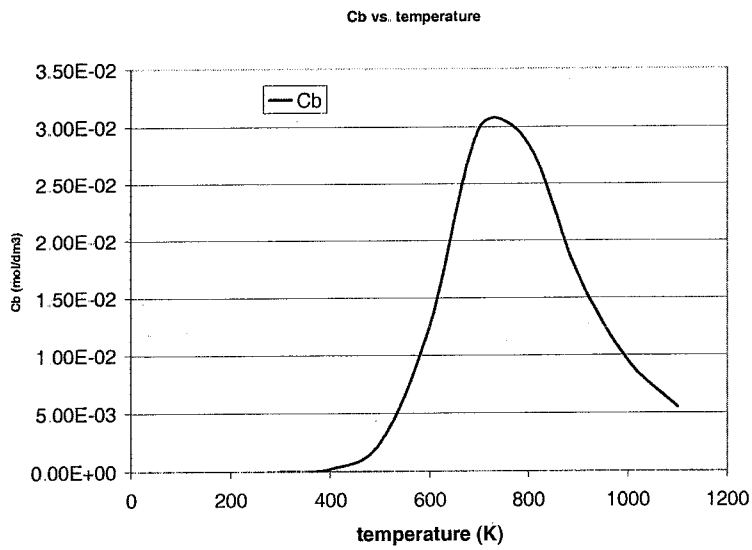
POLYMATH Results
NLES Solution

Variable	Value	f(x)	Ini Guess
Ca	1.5268515	-6.446E-13	1.5
Cb	0.0319385	7.28E-14	0
Cc	0.04121	0	0
tau	0.5		
T	760		
k1	0.0958161		
ra	-0.146297		
k2	2.580579		
rb	0.0638771		
rc	0.0824199		

NLES Report (safenewt)

Nonlinear equations
[1] f(Ca) = tau*(-ra)-(1.6-Ca) = 0
[2] f(Cb) = tau*(rb)-Cb = 0
[3] f(Cc) = tau*(rc)-Cc = 0

Explicit equations
[1] tau = .5
[2] T = 760
[3] k1 = 72*exp(-10000/(1.987*T))
[4] ra = -k1*Ca
[5] k2 = 1457152*exp(-20000/(1.987*T))
[6] rb = k1*Ca-k2*Cb
[7] rc = k2*Cb



- Therefore, C_B is maximum at T=760K.

P6-10 (c)

(c) Part is similar to part b except for two rate laws:

$$r_A = k_{-1}r * C_B - k_1 * C_A$$

$$r_B = k_1 * C_A - k_{-1} * C_B - k_2 * C_B$$

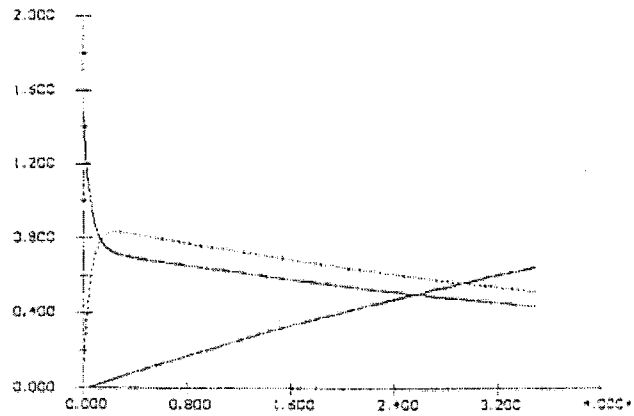
Using those rate laws inPOLYMATH produce the following:

Equations:

```
d(ca)/d(t)=ra
d(cb)/d(t)=rb
d(cc)/d(t)=rc
k1r=8.33e-5
k1f=.0001
k2=2.78e-6
rc=k2*cb
ra=k1r*cb-k1f*ca
rb=k1f*ca-k1r*cb-k2*cb
```

$t_0 = 0, \quad t_f = 350000$

Initial value
1.6
0
0



Variable	Initial value	Maximum value	Minimum value	Final value
t	0	350000	0	350000
ca	1.6	1.6	0.436316	0.436316
cb	0	0.833237	0	0.5159
cc	0	0.647784	0	0.647784
k1r	8.33e-05	8.33e-05	8.33e-05	8.33e-05
k1f	0.0001	0.0001	0.0001	0.0001
k2	2.78e-06	2.78e-06	2.78e-06	2.78e-06
rc	0	2.3164e-06	0	1.4342e-06
ra	-0.00016	-6.57168e-07	-0.00016	-6.57168e-07
rb	0.00016	0.00016	-1.20632e-06	-7.77034e-07

P6-10 (d)

This is similar to part d except for one rate law:

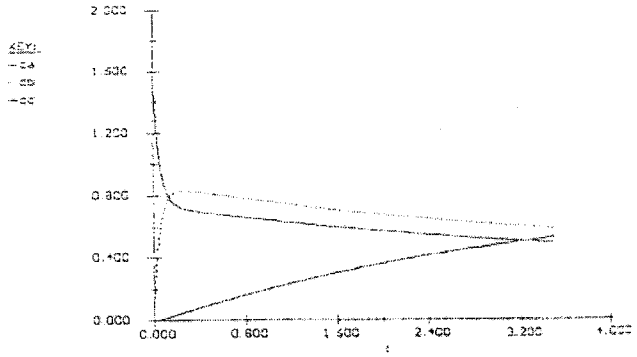
$$r_c = k_2 * C_B - k_{-2} * C_c$$

Using that in POLYMATH produces the following:

Equations:

d(ca)/d(t)=ra
d(cb)/d(t)=rb
d(cc)/d(t)=rc
k1r=8.33e-5
k1f=.0001
k2f=2.78e-6
k2r=1.39e-6
ra=k1r*cb-k1f*ca
rc=k2f*cb-k2r*cc
rb=k1f*ca-k1r*cb-k2f*cb+k2r*cc

$t_0 = 0, \quad t_f = 350000$



Variable	Initial value	Maximum value	Minimum value	Final value
t	0	350000	0	350000
ca	1.6	1.6	0.490306	0.490306
cb	0	0.833769	0	0.583662
cc	0	0.526032	0	0.526032
k1r	8.33e-05	8.33e-05	8.33e-05	8.33e-05
k1f	0.0001	0.0001	0.0001	0.0001
k2f	2.78e-06	2.78e-06	2.78e-06	2.78e-06
k2r	1.39e-06	1.39e-06	1.39e-06	1.39e-06
ra	-0.00016	-4.11573e-07	-0.00016	-4.11573e-07
rc	0	2.25569e-06	0	8.91396e-07
rb	0.00016	0.00016	-1.12493e-06	-4.79824e-07

P6-10 (e)

(e) When k1>100 and k2<0.1 the concentration of B immediately shoots up to 1.6 and then slowly comes back down, while CA drops off immediately and falls to zero. This is because the first reaction is so fast and the second reaction is slower with no reverse reactions.

When k2 = 1 then the concentration of B spikes again and remains high, while very little of C is formed. This is because after B is formed it will not got to C because the reverse reaction is faster.

When k-2 = 0.25, B shoots up, but does not stay as high because the second reverse reaction is a slightly slower than seen before, but still faster than the forward reaction.

P6-11 (a)

Intermediates (primary K-phthalates) are formed from the dissociation of K-benzoate with a $CdCl_2$ catalyst reacted with K-terephthalate in an autocatalytic reaction step:

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S \qquad \text{Series}$$

$$R + S \xrightarrow{k_3} 2S \qquad \text{Autocatalytic}$$

$$C_{AO} = \frac{P}{RT} = \frac{110kPa}{\left(8.314\frac{kPa.dm^3}{mol.K}\right)(683K)} = 0.02mol/dm^3$$

Maximum in R occurs at t = 880 sec. **See Polymath program** P6-11-a.pol.

POLYMATH Results

Variable	initial value	minimal value	maximal value	final value
t	0	0	1500	1500
A	0.02	0.003958	0.02	0.003958
R	0	0	0.0069892	0.005868
S	0	0	0.0100382	0.0100382
k1	0.00108	0.00108	0.00108	0.00108
k2	0.00119	0.00119	0.00119	0.00119
k3	0.00159	0.00159	0.00159	0.00159

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(A)/d(t) = -k1*A

[2] d(R)/d(t) = (k1*A)-(k2*R)-(k3*R*S)

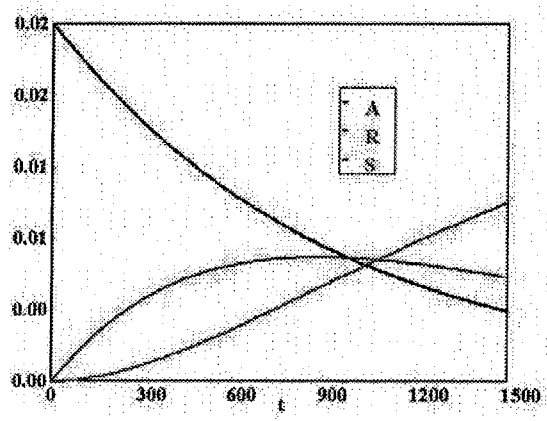
[3] d(S)/d(t) = (k2*R)-(k3*R*S)

Explicit equations as entered by the user

[1] k1 = 1.08e-3

[2] k2 = 1.19e-3

[3] k3 = 1.59e-3



P6-11 (b)

1) T = 703 K

C_{AO} = 0.019 mol/dm^3

$$k_1' = k_1 \exp\left(\frac{E_1}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)\right)$$

$$k_1' = (1.08\times10^{-3}s^{-1})\exp\left(\frac{(42600cal/mol)}{(1.987cal/mol.K)}\left(\frac{1}{683K} - \frac{1}{703K}\right)\right) = 2.64\times10^{-3}s^{-1}$$

Similarly,

$k_2' = 3.3\times10^{-3}s^{-1}$ and $k_3' = 3.1\times10^{-3}dm^3/mol.s$

Maxima in R occurs at around t =320 sec. **See Polymath program** P6-11-b1.pol.

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	1500	1500
A	0.019	3.622E-04	0.019	3.622E-04
R	0	0	0.0062169	8.856E-04
S	0	0	0.0174625	0.0174625
k1	0.00264	0.00264	0.00264	0.00264
k2	0.0033	0.0033	0.0033	0.0033
k3	0.0031	0.0031	0.0031	0.0031

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(A)/d(t) = -k1*A

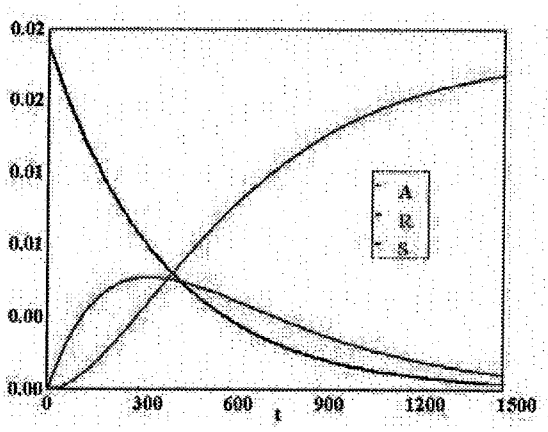
[2] d(R)/d(t) = (k1*A)-(k2*R)-(k3*R*S)

[3] d(S)/d(t) = (k2*R)-(k3*R*S)

Explicit equations as entered by the user

[1] k1 = 2.64e-3

[2] k2 = 3.3e-3



[3] k3 = 3.1e-3

2) T = 663 K
C_{AO} = 0.19 mol/dm^3

$$k_1' = (1.08\times10^{-3}s^{-1})\exp\left(\frac{(42600cal/mol)}{(1.987cal/mol.K)}\left(\frac{1}{683K}-\frac{1}{663K}\right)\right) = 0.42\times10^{-3}s^{-1}$$

$$k_2' = 0.4\times10^{-3}s^{-1}$$

$$k_3' = 0.78\times10^{-3}dm^3/mol.s$$

See Polymath program P6-11-b2.pol.

POLYMATH Results

Calculated values of the DEQ variables

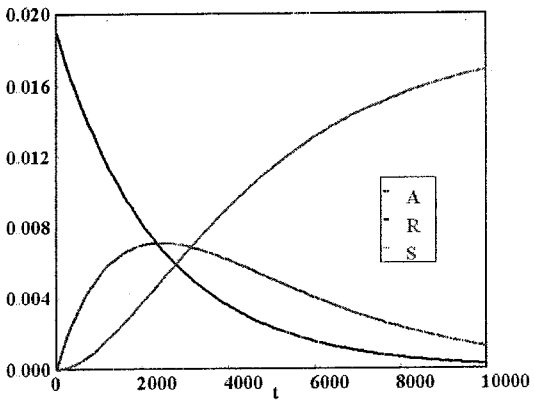
Variable	initial value	minimal value	maximal value	final value
t	0	0	10000	10000
A	0.019	2.849E-04	0.019	2.849E-04
R	0	0	0.0071414	0.0012573
S	0	0	0.016889	0.016889
k1	4.2E-04	4.2E-04	4.2E-04	4.2E-04
k2	4.0E-04	4.0E-04	4.0E-04	4.0E-04
k3	7.8E-04	7.8E-04	7.8E-04	7.8E-04

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(A)/d(t) = -k1*A
[2] d(R)/d(t) = (k1*A)-(k2*R)-(k3*R*S)
[3] d(S)/d(t) = (k2*R)-(k3*R*S)

Explicit equations as entered by the user
[1] k1 = 0.42e-3
[2] k2 = 0.4e-3
[3] k3 = 0.78e-3

Independent variable
variable name : t
initial value : 0
final value : 10000



Maxima in R occurs around t = 2500 sec.

P6-11 (c)

Use the Polymath program from part (a) and change the limits of integration to 0 to 1200. We get:

C_{Aexit} = 0.0055 mol/dm^3
C_{Rexit} = 0.0066 mol/dm^3

$C_{Sexit} = 0.0078$ mol/dm^3

P6-12 (a)

$$r_{1A} = -k_{1A}C_A = -(.07)(.1) = -0.07\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_{2A} = \frac{r_{2D}}{3} = \frac{(.3)(.51)^2(.1)}{3} = -0.0026\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_{3A} = 0 * r_{3E} = 0\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

P6-12 (b)

$$r_{1B} = \frac{-r_{1A}}{3} = \frac{(.7)(.1)}{3} = 0.023\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_{2B} = 0 * r_{2D} = 0\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_{3B} = 0 * r_{3E} = 0\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

P6-12 (c)

$$r_{1C} = \frac{-r_{1A}}{3} = \frac{(.7)(.1)}{3} = 0.023\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_{2C} = \frac{-2 * r_{2D}}{3} = \frac{-2(.3)(.51)^2(.1)}{3} = -0.0052\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_{3C} = -r_{3E} = -(.2)(.049)(.51) = -0.005\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

P6-12 (d)

$$r_{1D} = 0 * r_{1A} = 0\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_{2D} = (.3)(.51)^2(.1) = 0.0078\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_{3D} = \frac{-4r_{3E}}{3} = \frac{-4(.2)(.049)(.51)}{3} = -0.0067\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

P6-12 (e)

$$r_{1E} = 0 * r_{1A} = 0\frac{mol}{dm^3 \bullet s}$$

$$r_{2E} = 0 * r_{2D} = 0\frac{mol}{dm^3 \bullet s}$$

$$r_{3E} = (.2)(.049)(.51) = 0.005\frac{mol}{dm^3 \bullet s}$$

P6-12 (f)

$$r_A = -0.07 - 0.0026 = -0.0726\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_B = 0.023\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_C = 0.023 - 0.0052 - 0.005 = 0.0128\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_D = 0.0078 - 0.033 = 0.0011\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_E = 0.005\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

P6-12 (g)

$$V = \frac{F_{A0} - F_A}{-r_A}$$

$$= \frac{v_0(C_{A0} - C_A)}{-r_A}$$

$$= \frac{100(3 - 0.1)}{0.0726} = 4000\text{dm}^3$$

P6-12 (h)

Mole balance: $C_{AO} - C_A = (-r_A)\tau$

$$C_C = (r_C)\tau$$

$$C_D = (r_D)\tau$$

Rate law: $$r_A = -\left[k_{1A}C_A + \frac{1}{3}k_{2D}C_AC_C^2\right]$$

$$r_C = \left[\frac{1}{3}k_{1A}C_A - \frac{2}{3}k_{2D}C_AC_C^2 - k_{3E}C_CC_D\right]$$

$$r_D = \left[k_{2D}C_AC_C^2 - \frac{4}{3}k_{3E}C_CC_D\right]$$

Solving in polymath: $C_A = 0.0069M \quad C_B = 0.96M \quad C_C = 0.51M \quad C_D = 0.004M$

$S_{B/D} = r_B/r_D = 247 \qquad S_{B/C} = 1.88$

See Polymath program P6-12-h.pol.

POLYMATH Results
NLES Solution

Variable	Value	f(x)	Ini Guess
Ca	0.0068715	-2.904E-10	3
Cb	0.9620058	-1.332E-15	0
Cc	0.5097027	-1.67E-08	0
Cd	0.0038925	-2.391E-08	0
Ce	0.2380808	1.728E-08	0
kd	3		
ka	7		
rb	0.0160334		
ra	-0.0498855		
ke	2		
rc	0.008495		
rd	6.488E-05		
re	0.003968		
tau	60		
Cao	3		

NLES Report (safenewt)

Nonlinear equations
[1] f(Ca) = Cao-Ca+ra*tau = 0
[2] f(Cb) = Cb - rb*tau = 0
[3] f(Cc) = Cc-rc*tau = 0
[4] f(Cd) = Cd-rd*tau = 0
[5] f(Ce) = Ce - re*tau = 0

Explicit equations
[1] kd = 3
[2] ka = 7
[3] rb = ka*Ca/3
[4] ra = -(ka*Ca+kd/3*Ca*Cc^2)
[5] ke = 2
[6] rc = ka*Ca/3 - 2/3*kd*Ca*Cc^2 - ke*Cd*Cc
[7] rd = kd*Ca*Cc^2 - 4/3*ke*Cd*Cc
[8] re = ke*Cd*Cc
[9] tau = 60
[10] Cao = 3

P6-12 (i)

For PFR and gas phase:

Mole balance: $\frac{dF_A}{dV} = r_A \qquad \frac{dF_B}{dV} = r_B \qquad \frac{dF_C}{dV} = r_C \qquad \frac{dF_D}{dV} = r_D \qquad \frac{dF_E}{dV} = r_E$

Rate law:
$$r_A = -\left[k_{1A}C_A + \frac{1}{3}k_{2D}C_AC_C^2\right]$$
$$r_B = \left[\frac{1}{3}k_{1A}C_A\right]$$
$$r_C = \left[\frac{1}{3}k_{1A}C_A - \frac{2}{3}k_{2D}C_AC_C^2 - K_{3E}C_CC_D\right]$$
$$r_D = \left[k_{2D}C_AC_C^2 - \frac{4}{3}k_{3E}C_CC_D\right]$$
$$r_E = \left[k_{3E}C_CC_D\right]$$

Stoichiometry:
$$C_A = C_{TO}\frac{F_A}{F_T}y \qquad C_C = C_{TO}\frac{F_C}{F_T}y \qquad C_D = C_{TO}\frac{F_D}{F_T}y$$
$$F_T = F_A + F_B + F_C + F_D + F_E$$
$$\frac{dy}{dV} = \frac{-\alpha}{2y}\frac{F_T}{F_{TO}}$$

Plot of C_B and C_C are overlapping.

See Polymath program P6-12-i pol.

POLYMATH Results

Calculated values of the DEQ variables

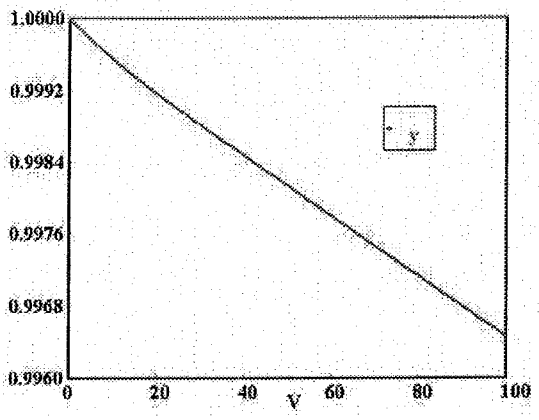
Variable	initial value	minimal value	maximal value	final value
V	0	0	100	100
Fa	20	9.147E-04	20	9.147E-04
Fb	0	0	6.6638171	6.6638171
Fc	0	0	6.6442656	6.6442167
Fd	0	0	0.0201258	0.0171261
Fe	0	0	0.0043322	0.0043322
y	1	0.9964621	1	0.9964621
Ft	20	13.330407	20	13.330407
Cto	0.2	0.2	0.2	0.2
Cc	0	0	0.0993605	0.0993325
ka	7	7	7	7
kd	3	3	3	3
ke	2	2	2	2
Ca	0.2	1.367E-05	0.2	1.367E-05
rb	0.4666667	3.191E-05	0.4666667	3.191E-05
ra	-1.4	-1.4	-9.586E-05	-9.586E-05
Cd	0	0	3.0E-04	2.56E-04
Fto	20	20	20	20
rc	0.4666667	-1.923E-05	0.4666667	-1.923E-05
rd	0	-7.012E-05	8.653E-04	-6.742E-05
re	0	0	5.908E-05	5.087E-05
alfa	1.0E-04	1.0E-04	1.0E-04	1.0E-04
X	0	0	0.9999543	0.9999543

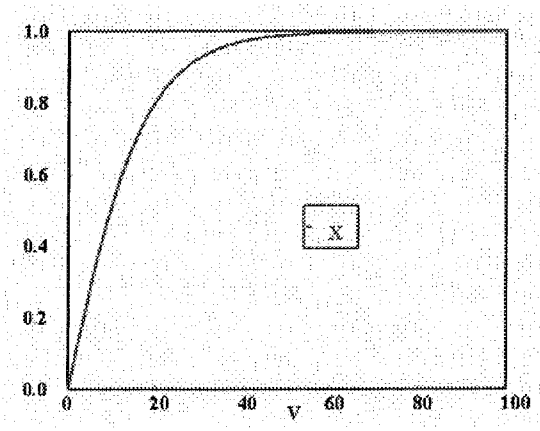
ODE Report (RKF45)

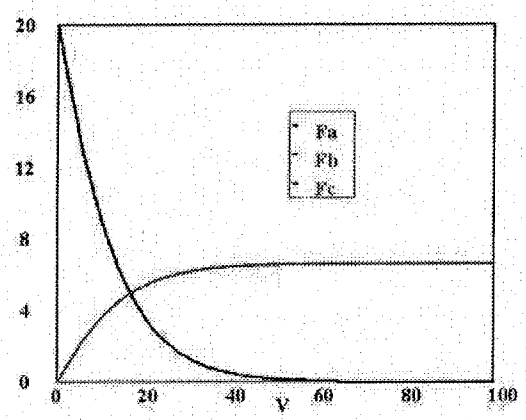
Differential equations as entered by the user
[1] d(Fa)/d(V) = ra
[2] d(Fb)/d(V) = rb
[3] d(Fc)/d(V) = rc
[4] d(Fd)/d(V) = rd
[5] d(Fe)/d(V) = re

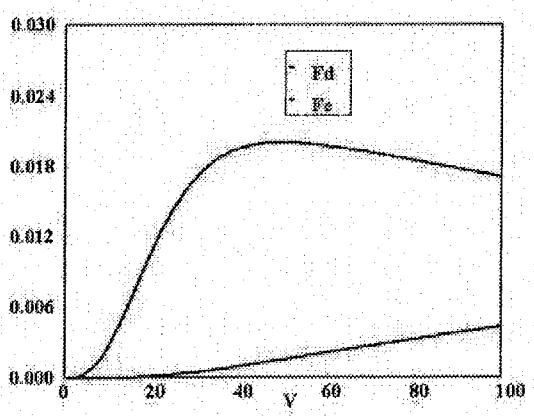
[6] d(y)/d(V) = -alfa*Ft/(2*y*Fto)

Explicit equations as entered by the user
[1] Ft = Fa+Fb+Fc+Fd+Fe
[2] Cto = 0.2
[3] Cc = Cto*Fc/Ft*y
[4] ka = 7
[5] kd = 3
[6] ke = 2
[7] Ca = Cto*Fa/Ft*y
[8] rb = ka*Ca/3
[9] ra = -(ka*Ca+kd/3*Ca*Cc^2)
[10] Cd = Cto*Fd/Ft*y
[11] Fto = 0.2*100
[12] rc = ka*Ca/3 - 2/3*kd*Ca*Cc^2 - ke*Cd*Cc
[13] rd = kd*Ca*Cc^2 - 4/3*ke*Cd*Cc
[14] re = ke*Cd*Cc
[15] alfa = 0.0001
[16] X = 1-Fa/20





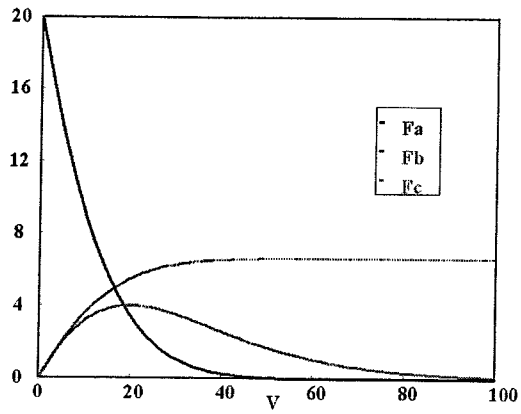


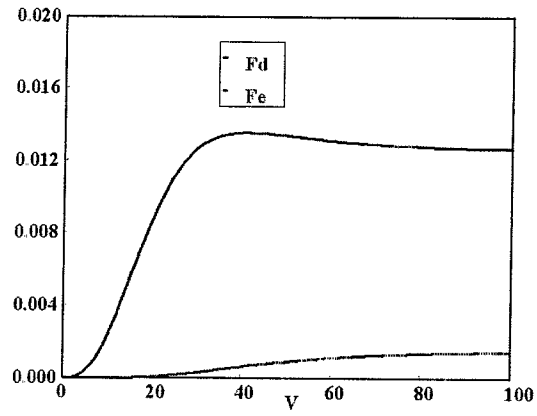


P6-12 (j) Changes in equation from part (i):

$$\frac{dF_C}{dV} = r_C - R_C \qquad R_C = k_{diffuse} C_C \qquad k_{diffuse} = 2\,\text{min}^{-1}$$

See Polymath program P6-12-j.pol.





P6-13 (a)

m-xylene → benzene + methane
A → B + M

m-xylene → p-xylene
A → P

See Polymath program P6-13-a.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	6000	6000
Fa	75	6.1072984	75	6.1072984
Fb	0	0	16.297198	16.297198
Fp	0	0	52.595503	52.595503
Fm	0	0	16.297198	16.297198
Fi	25	25	25	25
Ft	100	100	116.2972	116.2972
k1	0.22	0.22	0.22	0.22
k2	0.71	0.71	0.71	0.71
Cto	0.05	0.05	0.05	0.05
Ca	0.0375	0.0026257	0.0375	0.0026257
r1	-0.00825	-0.00825	-5.777E-04	-5.777E-04
Cb	0	0	0.0070067	0.0070067
r2	-0.026625	-0.026625	-0.0018643	-0.0018643
Cp	0	0	0.0226125	0.0226125
Spb	0	0	3.2272267	3.2272267
tau	0	0	3	3
Y	0	0	0.7634409	0.7634409
X	0	0	0.9185694	0.9185694

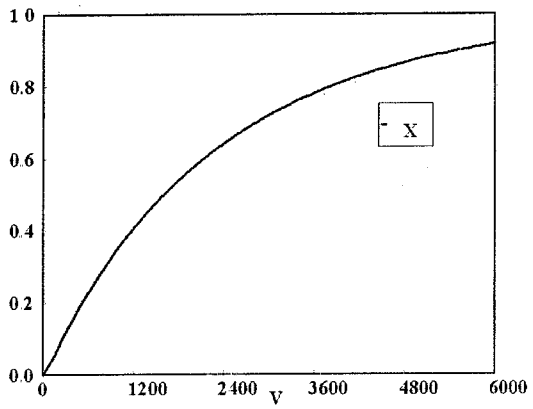
ODE Report (RKF45)

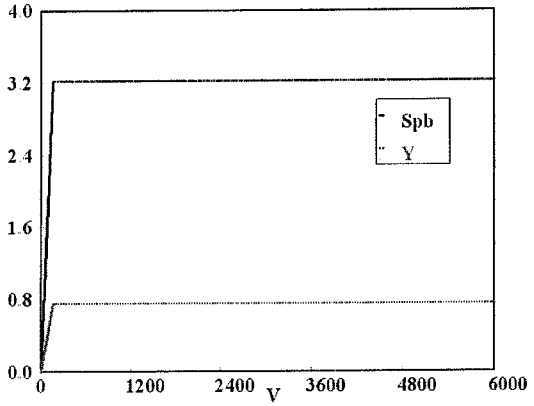
Differential equations as entered by the user
[1] d(Fa)/d(V) = r1+r2
[2] d(Fb)/d(V) = -r1
[3] d(Fp)/d(V) = -r2

Explicit equations as entered by the user
[1] Fm = Fb
[2] Fi = 25
[3] Ft = Fa+Fb+Fp+Fm+Fi
[4] k1 = .22

```
[5] k2 = .71
[6] Cto = .05
[7] Ca = Cto*Fa/Ft
[8] r1 = -k1*Ca
[9] Cb = Cto*Fb/Ft
[10] r2 = -k2*Ca
[11] Cp = Cto*Fp/Ft
[12] Spb = Cp/(Cb+.0000001)
[13] tau = V/2000
[14] Y = Fp/(75.00000001-Fa)
[15] X = (75-Fa)/75
```

a $\tau = 2.8$ is necessary to achieve 90% conversion





P6-13 (b)

CSTR

Mole Balances: $F_A = F_{Ao} + r_A V \quad F_B = r_B V \quad F_M = r_M V \quad F_P = r_P V$

Rate Laws: $r_A = -C_A(k_1 + k_2) \quad r_B = r_M = k_1 C_A \quad r_P = k_2 C_A$

$$k_1 = k_{1o}\exp\frac{-E_1}{R}\left(\frac{1}{T} - \frac{1}{946}\right) \qquad k_1 = k_{1o}\exp\frac{-E_1}{R}\left(\frac{1}{T} - \frac{1}{946}\right)$$

Using these equations and Polymath we find the optimal temperature is 1194 K. The maximum concentration of p-xylene is 0.013 mol/dm^3

See Polymath program P6-13-b.pol.

POLYMATH Results
NLES Solution

Variable	Value	f(x)	Ini Guess
Ca	0.012197	7.15E-11	0.0375
Cb	0.0122301	5.284E-12	0
Cm	0.0122301	5.284E-12	0
Cp	0.0130729	-3.069E-11	0
Cao	0.0375		
tau	0.5		
k1o	0.22		
E1	2.0E+04		
R	1.987		
k2o	0.71		
E2	10000		

Yp	0.5166557
T	1194
k1	2.0054175
rb	0.0244601
rm	0.0244601
k2	2.143628
rp	0.0261459
ra	-0.050606

NLES Report (safenewt)

Nonlinear equations
[1] f(Ca) = Ca-Cao-ra*tau = 0
[2] f(Cb) = Cb-rb*tau = 0
[3] f(Cm) = Cm-rm*tau = 0
[4] f(Cp) = Cp-rp*tau = 0

Explicit equations
[1] Cao = .0375
[2] tau = .5
[3] k1o = .22
[4] E1 = 20000
[5] R = 1.987
[6] k2o = .71
[7] E2 = 10000
[8] Yp = Cp/(.03750000001-Ca)
[9] T = 1194
[10] k1 = k1o*exp((E1/R)*(1/946-1/T))
[11] rb = k1*Ca
[12] rm = k1*Ca
[13] k2 = k2o*exp((E2/R)*(1/946-1/T))
[14] rp = k2*Ca
[15] ra = -k1*Ca-k2*Ca

P6-14(a)

$50dm^3$ PFR

Mole balance:

$$\frac{dC_A}{dV} = \frac{r_A}{v_0}, \qquad \frac{dC_B}{dV} = \frac{r_B}{v_0}$$
$$\frac{dC_C}{dV} = \frac{r_C}{v_0}, \qquad \frac{dC_D}{dV} = \frac{r_D}{v_0}$$
$$\frac{dC_E}{dV} = \frac{r_E}{v_0}, \qquad \frac{dC_F}{dV} = \frac{r_F}{v_0}$$

Rate laws:

$$
\begin{aligned}
r_A &= -r_{D1} - 3r_{E2} \\
r_B &= -2r_{D1} - r_{F3} \\
r_C &= r_{D1} + r_{E2} - 2r_{F3} \\
r_D &= r_{D1} - 2r_{E2} + r_{F3} \\
r_E &= r_{E2} \\
r_F &= r_{F3} \\
r_{D1} &= k_{D1} C_A C_B^2 \\
r_{E2} &= k_{E2} C_A C_D \\
r_{F3} &= k_{F3} C_B C_C^2
\end{aligned}
$$

The equation for the conversion of A is :

$$X = \frac{C_{A0} - C_A}{C_{A0}}$$

See Polymath program P6-14-a.pol.

POLYMATH Results
No Title 08-01-2005, Rev5.1.233

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	50	50
Fa	15	0.2090606	15	0.2090606
Fb	20	1.3440833	20	1.3440833
Fc	0	0	1.9655663	0.3535564
Fd	0	0	7.2554436	6.4570707
Fe	0	0	2.5920934	2.5920934
Ff	0	0	4.6265981	4.6265981
vo	10	10	10	10
Cao	1.5	1.5	1.5	1.5
Cbo	2	2	2	2
Ft	35	15.582463	35	15.582463
Cto	3.5	3.5	3.5	3.5
kd1	0.25	0.25	0.25	0.25
ke2	0.1	0.1	0.1	0.1
kf3	5	5	5	5
Cc	0	0	0.228291	0.0794128
Cd	0	0	1.4503322	1.4503322
Cb	2	0.3018965	2	0.3018965
Ca	1.5	0.0469574	1.5	0.0469574
rd1	1.5	0.0010699	1.5	0.0010699
re2	0	0	0.1004639	0.0068104
rf3	0	0	0.3632767	0.0095194
re	0	0	0.1004639	0.0068104
rf	0	0	0.3632767	0.0095194
rd	1.5	-0.042376	1.5	-0.0030314
ra	-1.5	-1.5	-0.0215011	-0.0215011
rb	-3	-3	-0.0116593	-0.0116593
rc	1.5	-0.0962952	1.5	-0.0111585

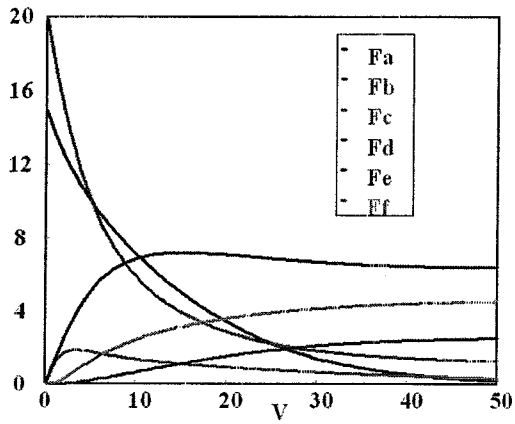
ODE Report (RKF45)

Differential equations as entered by the user

```
[1] d(Fa)/d(t) = ra
[2] d(Fb)/d(t) = rb
[3] d(Fc)/d(t) = rc
[4] d(Fd)/d(t) = rd
[5] d(Fe)/d(t) = re
[6] d(Ff)/d(t) = rf
```

Explicit equations as entered by the user

```
[1] vo = 10
[2] Cao = 1.5
[3] Cbo = 2
[4] Ft = Fa+Fb+Fc+Fd+Fe+Ff
[5] Cto = Cao+Cbo
[6] kd1 = 0.25
[7] ke2 = .1
[8] kf3 = 5
[9] Cc = Cto*Fc/Ft
[10] Cd = Cto*Fd/Ft
[11] Cb = Cto*Fb/Ft
[12] Ca = Cto*Fa/Ft
[13] rd1 = kd1*Ca*Cb^2
[14] re2 = ke2*Ca*Cd
[15] rf3 = kf3*Cb*Cc^2
[16] re = re2
[17] rf = rf3
[18] rd = rd1-2*re2+rf3
[19] ra = -rd1-3*re2
[20] rb = -2*rd1-rf3
[21] rc = rd1+re2-2*rf3
```



P6-14 (b)

(b) Determine the effluent concentration and conversion from a $50 dm^3$ CSTR.

Mole Balance:

$$\begin{aligned} F_{A0} - F_A &= -r_A V \\ F_{B0} - F_B &= -r_B V \\ F_C &= r_C V \\ F_D &= r_D V \end{aligned}$$

$$F_E = r_E V$$
$$F_F = r_F V$$

$\tau \equiv \frac{V}{v0}$, combining rate law and mole balance,

$$f(C_A) = C_A - C_{A0} - r_A\tau$$
$$f(C_B) = C_B - C_{B0} - r_B\tau$$
$$f(C_C) = -C_C + r_C\tau$$
$$f(C_D) = -C_D + r_D\tau$$
$$f(C_E) = -C_E + r_E\tau$$
$$f(C_F) = -C_F + r_F\tau$$

Polymath code,

```
f(ca)=ca-ca0-ra*tau
f(cb)=cb-cb0-rb*tau
f(cc)=rc*tau-cc
f(cd)=rd*tau-cd
f(ce)=tau*re-ce
f(cf)=tau*rf-cf
tau=V/vo
V=50
vo=10
ca0=1.5
cb0=2.0
rd1=kd1*ca*cb^2
re2=ke2*ca*cd
rf3=kf3*cb*cc^2
kd1=0.25
ke2=0.1
kf3=5
ra=-rd1-3*re2
rb=-2*rd1-rf3
rc=rd1+re2-2*rf3
rd=rd1-2*re2+rf3
re=re2
rf=rf3
ca(0)=1
cb(0)=1
cc(0)=1
cd(0)=1
ce(0)=1
cf(0)=1
```

(Ans) $C_A = 0.61, C_B = 0.79, C_C = 0.11, C_D = 0.45, C_E = 0.14, C_F = 0.25$

P6-14 (c)

(c) $V_0 = 40dm^3$ Semi-Batch reactor. (1) A is fed to B, (2) B is fed to A
(Case 1) A is fed to B,

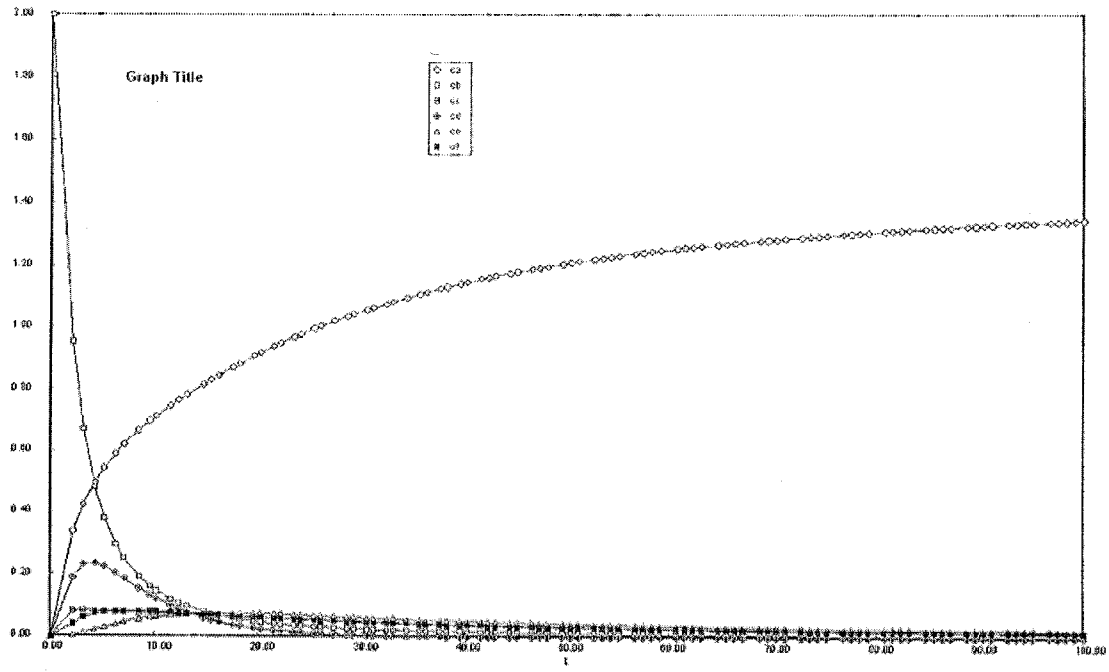
$$
\begin{aligned}
\frac{dC_A}{dt} &= r_A + v_0\frac{C_{A0} - C_A}{V} \\
\frac{dC_B}{dt} &= r_B - v_0\frac{C_B}{V} \\
\frac{dC_C}{dt} &= r_C - v_0\frac{C_C}{V} \\
\frac{dC_D}{dt} &= r_D - v_0\frac{C_D}{V} \\
\frac{dC_E}{dt} &= r_E - v_0\frac{C_E}{V} \\
\frac{dC_F}{dt} &= r_F - v_0\frac{C_F}{V} \\
X &= \frac{(C_{B0} - C_B)}{C_{B0}}
\end{aligned}
$$

and modifying corresponding polymath code.

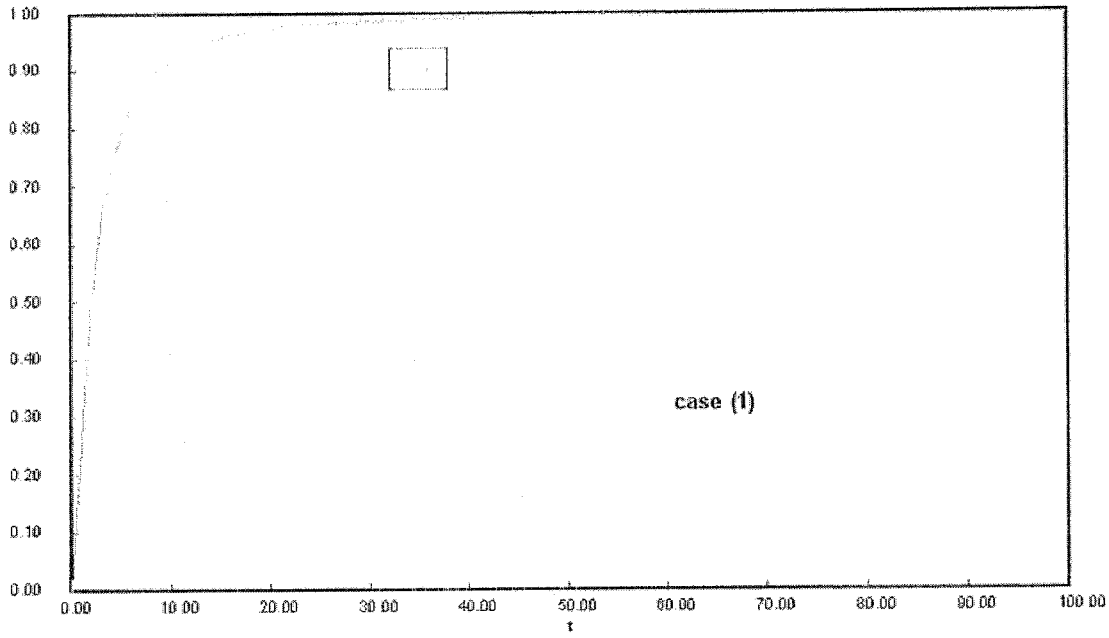
```
d(ca)/d(t)=ra-vo/V*ca
d(cb)/d(t)=rb+vo/V*(cb0-cb)
ca(0)=1.5
cb(0)=0
x=(ca0-ca)/ca0
```

Differences
(1) Because C_{B0} is higher than C_{A0} (i.e. 30% higher molar flow rate), case (2) reaches X = 1 in earlier time.
(2) With the same reason, case (2) produces D and F more
(3) With the same reason, C_B (in case 2) increases more drastically(excessively) than C_A (in case 1)

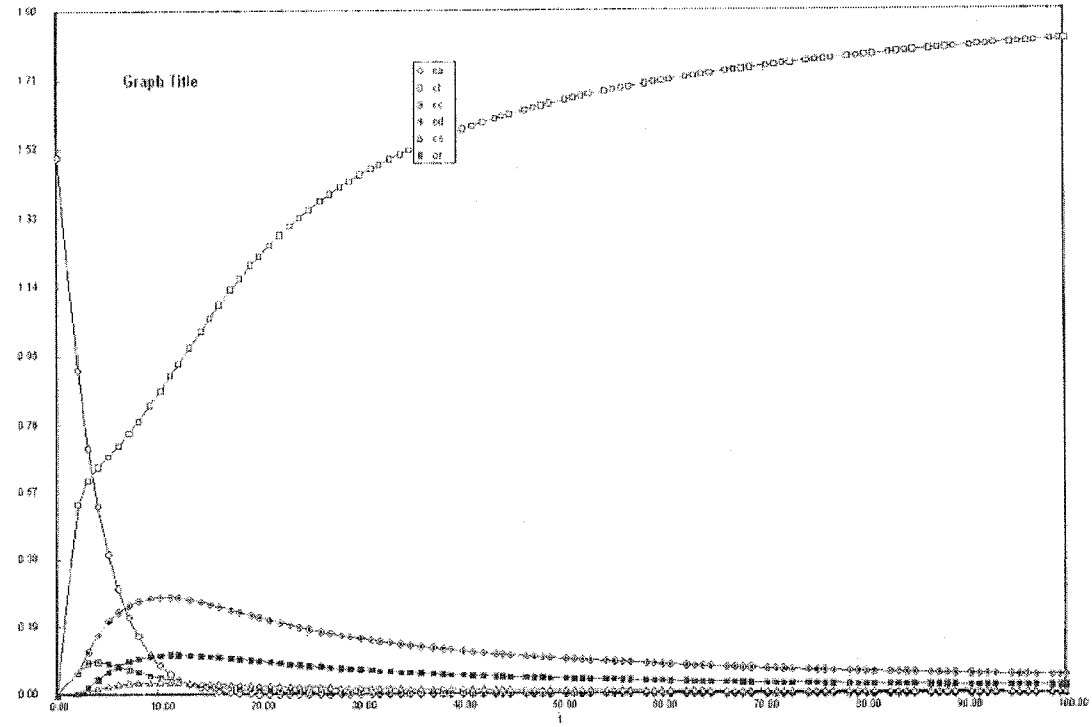
(c) case 1 concentration vs. time



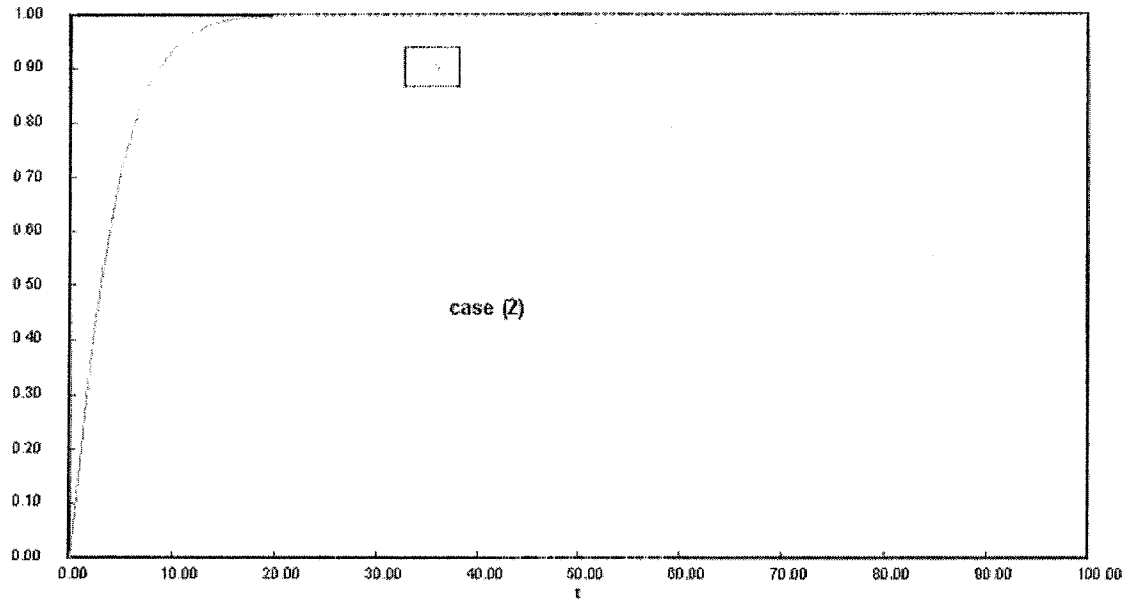
Case 1 conversion vs. time



Case 2 concentration vs. time



Case 2 conversion vs. time



P6-14 (d)

As θ_B increases the outlet concentration of species D and F increase, while the outlet concentrations of species A, C, and E decrease. When θ_B is large, reactions 1 and 3 are favored and when it is small the rate of reaction 2 will increase.

P6-14 (e)

When the appropriate changes to the Polymath code from part (a) are made we get the following.
See Polymath program P6-14-e.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	500	500
Fa	20	18.946536	20	18.946536
Fb	20	18.145647	20	18.145647
Fc	0	0	0.9342961	0.9342961
Fd	0	0	0.8454829	0.8454829
Fe	0	0	0.0445942	0.0445942
Ff	0	0	0.0149897	0.0149897
vo	100	100	100	100
Ft	40	38.931546	40	38.931546
Cto	0.4	0.4	0.4	0.4
kd1	0.25	0.25	0.25	0.25
ke2	0.1	0.1	0.1	0.1
kf3	5	5	5	5
Cc	0	0	0.0095994	0.0095994
Cd	0	0	0.0086869	0.0086869
Cb	0.2	0.1864364	0.2	0.1864364
Ca	0.2	0.1946651	0.2	0.1946651
rd1	0.002	0.0016916	0.002	0.0016916
re2	0	0	1.691E-04	1.691E-04
rf3	0	0	8.59E-05	8.59E-05
re	0	0	1.691E-04	1.691E-04
rf	0	0	8.59E-05	8.59E-05

rd	0.002	0.0014393	0.002	0.0014393
ra	-0.002	-0.0021989	-0.002	-0.0021989
rb	-0.004	-0.004	-0.003469	-0.003469
rc	0.002	0.0016889	0.002	0.0016889
Scd	1	1	1.1734311	1.1734311
Sef	0	0	83.266916	1.9686327

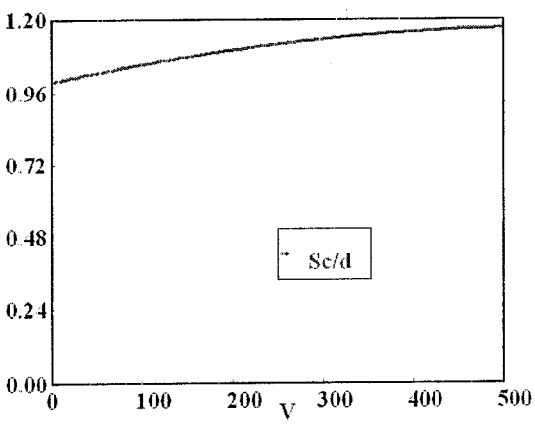
ODE Report (RKF45)

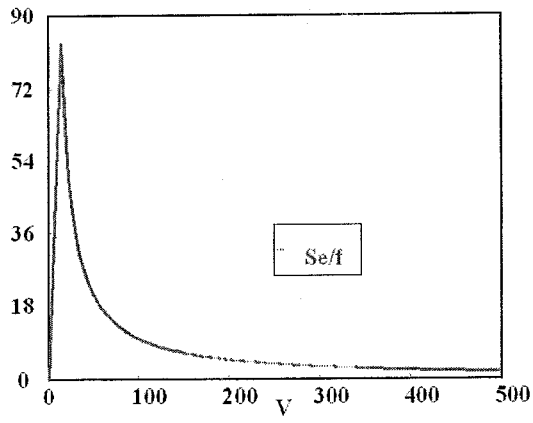
Differential equations as entered by the user

[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(Fe)/d(V) = re
[6] d(Ff)/d(V) = rf

Explicit equations as entered by the user

[1] vo = 100
[2] Ft = Fa+Fb+Fc+Fd+Fe+Ff
[3] Cto = .4
[4] kd1 = 0.25
[5] ke2 = .1
[6] kf3 = 5
[7] Cc = Cto*Fc/Ft
[8] Cd = Cto*Fd/Ft
[9] Cb = Cto*Fb/Ft
[10] Ca = Cto*Fa/Ft
[11] rd1 = kd1*Ca*Cb^2
[12] re2 = ke2*Ca*Cd
[13] rf3 = kf3*Cb*Cc^2
[14] re = re2
[15] rf = rf3
[16] rd = rd1-2*re2+rf3
[17] ra = -rd1-3*re2
[18] rb = -2*rd1-rf3
[19] rc = rd1+re2-2*rf3
[20] Scd = rc/(rd+.0000000001)
[21] Sef = re/(rf+.00000000001)

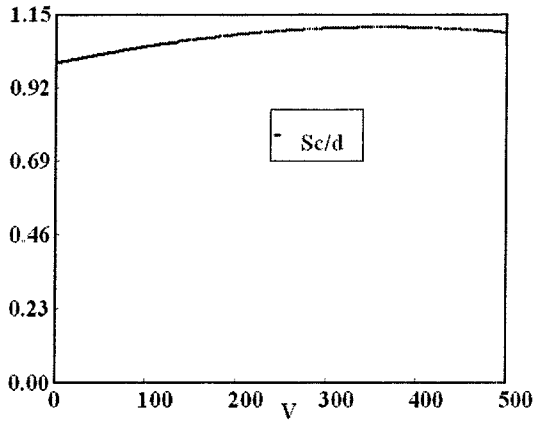


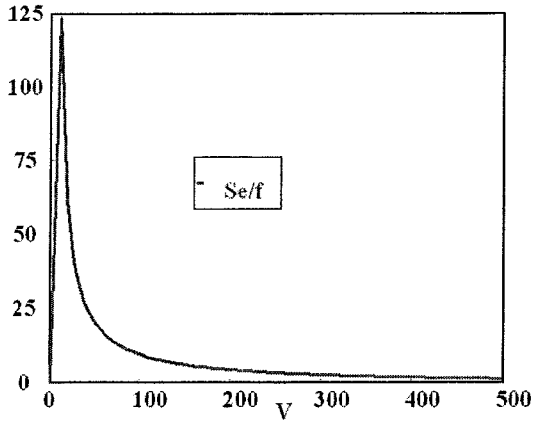


P6-14 (f)

The only change from part (e) is: $\frac{dF_D}{dV} = r_D - k_{cD} C_D$

See Polymath program P6-14-f.pol.



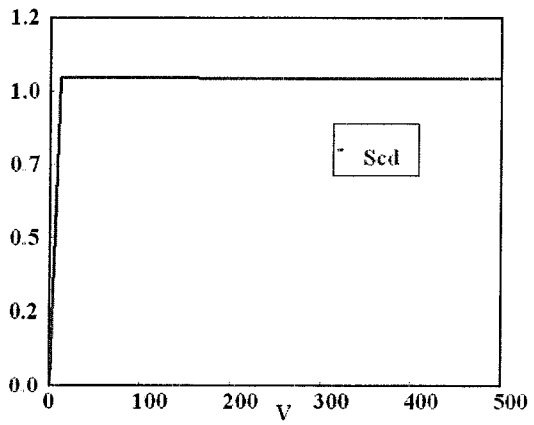


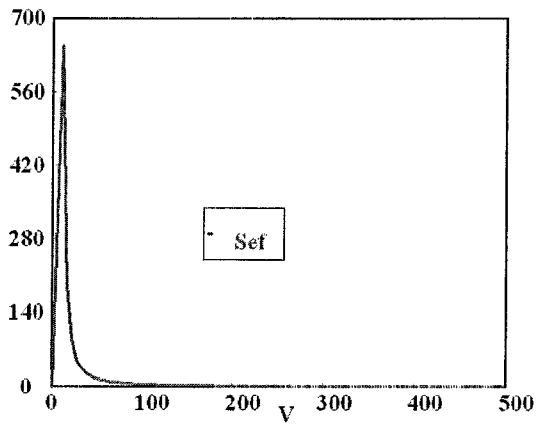
P6-14 (g)

The only change from part (e) is: $\frac{dF_B}{dV} = r_B - \frac{F_{B0}}{V_T}$

where $V_T = 500$ dm^3 and $F_{B0} = 20$ mol/min

See Polymath program P6-14-g.pol.





P6-15 (a)

(a) Enter the given program into POLYMATH. Equations for the concentrations must be added.

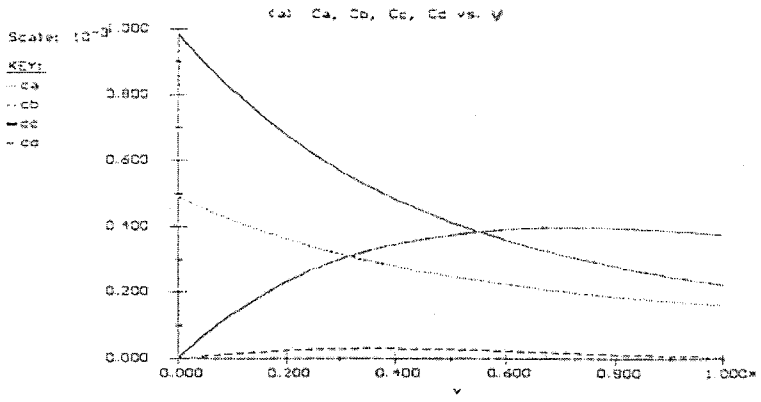
The following maximums can be seen in the graph given. (More exact values can be found in the corresponding table in POLYMATH.)

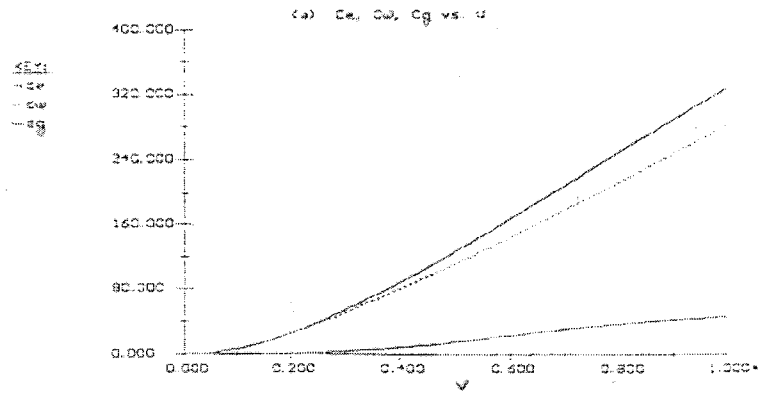
$C_{Cmax} = 0.0434$ and $C_{Dmax} = 0.0033$

Equations:	Initial value
d(fc)/d(v)=k1*(fa/ft)*(fb/ft)**(1/2)-k3*(fc/ft)+k4*(fw/ft)*(fd/ft)	0
d(fa)/d(v)=-k1*(fa/ft)*(fb/ft)**(1/2)-k2*(fa/ft)**2	9.83
d(fb)/d(v)=-k1/2*(fa/ft)*(fb/ft)**(1/2)	4.91
d(fw)/d(v)=k3*(fc/ft)-k4*(fw/ft)*(fd/ft)	0
d(fd)/d(v)=k2/2*(fa/ft)**2-k4*(fd/ft)*(fw/ft)	0
d(fe)/d(v)=k3*(fc/ft)	0
d(fg)/d(v)=k4*(fw/ft)*(fd/ft)	0

```
k1=0.04
ft=fa+fb+fc+fd+fe+fw+fg
k2=0.007
k3=0.014
k4=0.45
vo=100
cto=0.147
ca=cto*(fa/ft)
cb=cto*(fb/ft)
cc=cto*(fc/ft)
cd=cto*(fd/ft)
ce=cto*(fe/ft)
cw=cto*(fw/ft)
cg=cto*(fg/ft)
```

$v_0 = 0, \quad v_f = 1000$





P6-15 (b)

(b) Overall yield of HCOOH : $\tilde{Y}_C = \dfrac{F_C}{F_{Ao} - F_A}$

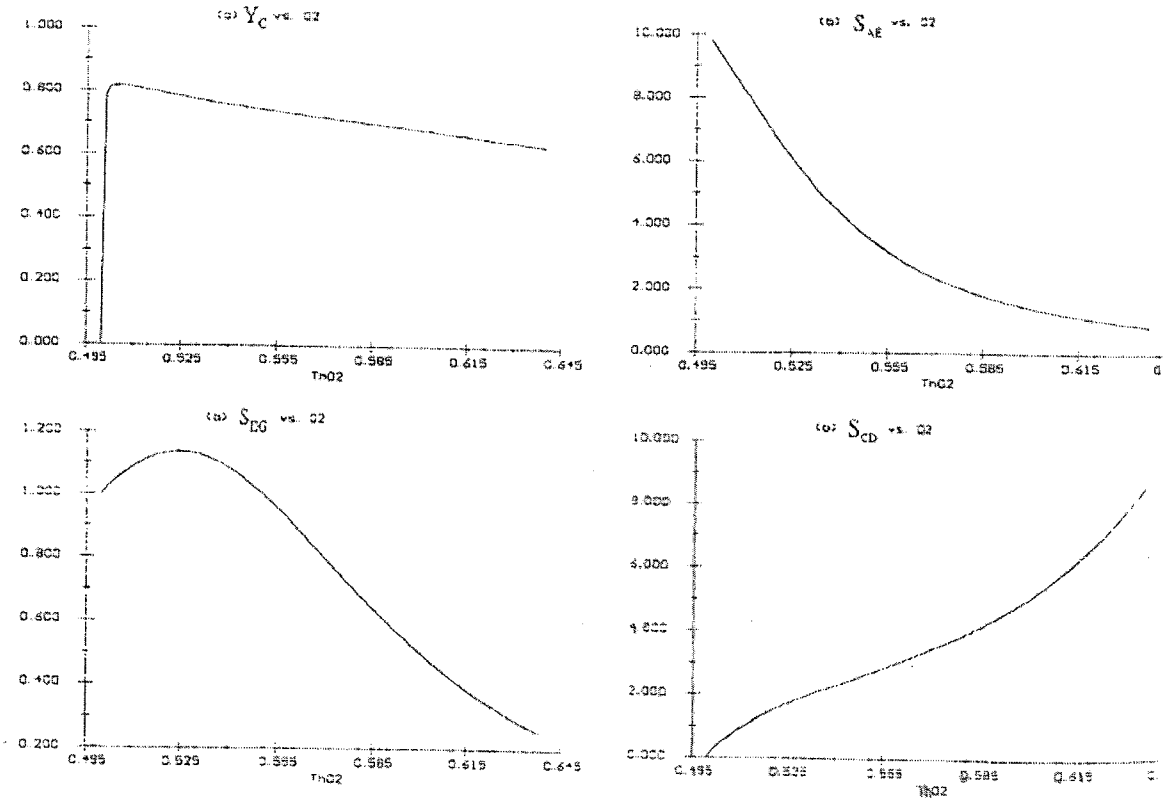
Selectivity of HCHO to CO : $\tilde{S}_{AE} = \dfrac{F_A}{F_E}$

Selectivity of $HCOOCH_3$ to CH_3OH : $\tilde{S}_{DG} = \dfrac{F_D}{F_G}$

Selectivity of HCOOH to $HCOOCH_3$: $\tilde{S}_{CD} = \dfrac{F_C}{F_D}$

$\Theta_{O_2} = \dfrac{C_B}{C_A}$

Add these equations to the previous program and use it to generate the desired plots.



P6-15 (c)

(c) Modify the original POLYMATH program by adding y to each of the concentration terms. Also add the following equation:

$$\frac{dy}{dV} = \frac{-\alpha}{2y}\left(\frac{F_T}{F_{To}}\right)$$

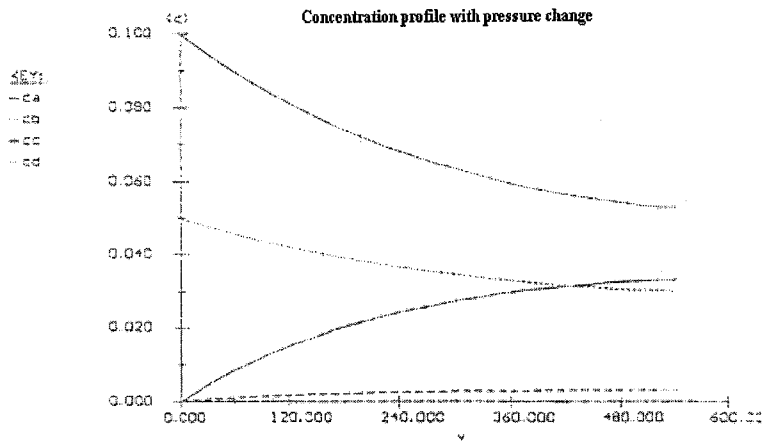
$\alpha = 0.002 \qquad F_{To} = 15$

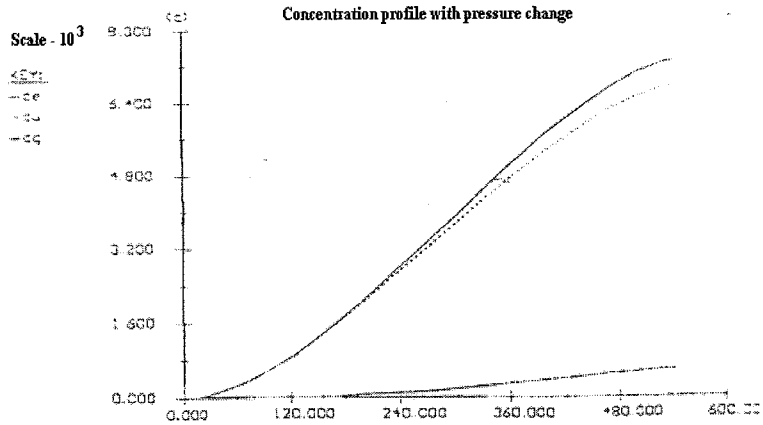
The graphs of concentration down the reactor are very similar to those generated in part (a). The only major difference is that with the change in pressure, the maximum reactor volume is significantly smaller.

Equations:	Initial value
d(fc)/d(v)=k1*(fa/ft)*(fb/ft)**(1/2)*y-k3*(fc/ft)*y+k4*(fw/ft)*(fd/ft)*y	0
d(fa)/d(v)=-k1*(fa/ft)*(fb/ft)**(1/2)*y-k2*(fa/ft)**2*y	10
d(fb)/d(v)=-k1/2*(fa/ft)*(fb/ft)**(1/2)*y	5
d(fw)/d(v)=k3*(fc/ft)*y-k4*(fw/ft)*(fd/ft)*y	0
d(fd)/d(v)=k2/2*(fa/ft)**2*y-k4*(fw/ft)*(fd/ft)*y	0
d(fe)/d(v)=k3*(fc/ft)*y	0
d(fg)/d(v)=k4*(fw/ft)*(fd/ft)*y	0
d(y)/d(v)=-0.002/2/y*(ft/fto)	1

```
k2=0.007
k1=0.04
ft=fa+fb+fc+fd+fe+fw+fg
k3=0.014
k4=0.45
vo=100
fto=15
ca=fa/vo
cb=fb/vo
cc=fc/vo
cd=fd/vo
ce=fe/vo
cw=fw/vo
cg=fg/vo
```

$v_0 = 0, \quad v_f = 1000$





P6-15 (d)

$$k_R = k_m \exp\left(\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right)$$

Substitute this equation in for all of the k values. Vary T and find out what temperature maximizes the yield of C.
The best temperature at which to run the reactor is 523 K or 250°C.

P6-16 (a)

(a)

Mole Balances: $\frac{dF_C}{dV} = r_C$ $\frac{dF_P}{dV} = r_P$ $\frac{dF_A}{dV} = r_A$ $\frac{dF_O}{dV} = r_O$

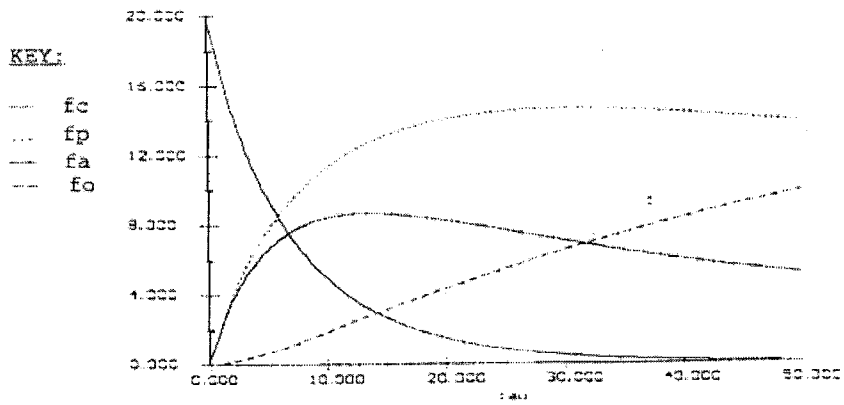
Rate Laws: $r_C = -k_1C_C - k_2C_C$ $r_P = k_1C_C - k_3C_P + k_4C_A$

$r_A = k_1C_C + k_3C_P - k_4C_A - k_5C_A$ $r_O = k_5C_A$

Stoichiometry: $C_C = C_{To}\left(\frac{F_C}{F_T}\right)$ $C_P = C_{To}\left(\frac{F_P}{F_T}\right)$ $C_A = C_{To}\left(\frac{F_A}{F_T}\right)$ $C_O = C_{To}\left(\frac{F_O}{F_T}\right)$

$F_T = F_C + F_P + F_A + F_O$

Use these equations in POLYMATH to generate a plot of the flow rates vs. τ.



P6-16 (b)

(b) For a CSTR

Mole Balances: $F_C = F_{Co} + r_C V$ $F_P = r_P V$ $F_A = r_A V$ $F_O = r_O V$

Rate Laws: $r_C = -k_1C_C - k_2C_C$ $r_P = k_1C_C - k_3C_P + k_4C_A$

$r_A = k_1C_C + k_3C_P - k_4C_A - k_5C_A$ $r_O = k_5C_A$

Stoichiometry: $F_C = v_o C_C \quad F_P = v_o C_P \quad F_A = v_o C_A \quad F_O = v_o C_O$

Combine: $f(C_C) = 0 = C_C - C_{Co} + (k_1 + k_2) C_C \tau$

$f(C_P) = 0 = C_P - (k_1 C_C - k_3 C_P + k_4 C_A)\tau$

$f(C_A) = 0 = C_A - (k_1 C_C - k_3 C_P - k_4 C_A - k_5 C_A)\tau$

$f(C_O) = 0 = C_O - k_5 C_A \tau$

Use these equations in POLYMATH to generate values for the flow rates at different values of τ. Use these values to generate the desired curve.

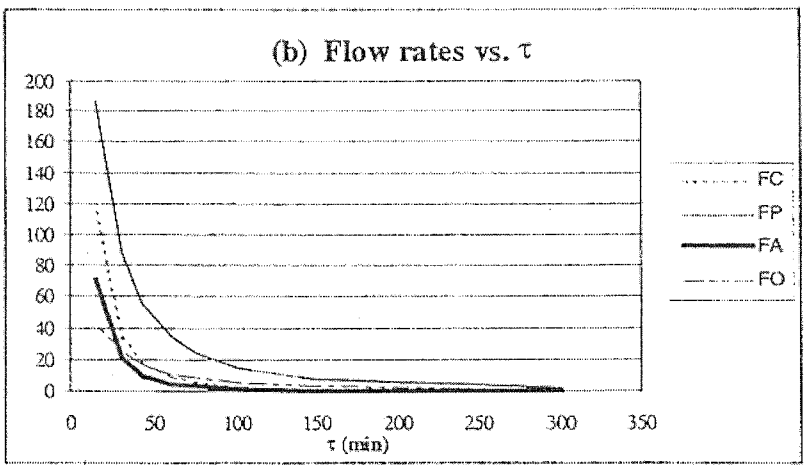
Equations:

```
f(cc)=cc-cco+(k1+k2)*cc*tau
f(cp)=cp-(k1*cc-k3*cp+k4*ca)*tau
f(ca)=ca-(k1*cc-k3*cp-k4*ca-k5*ca)*tau
f(co)=co-k5*ca*tau
cco=2
k1=0.12
k2=0.046
k3=0.02
k4=0.034
vo=10
k5=0.04
V=3000
fc=vo*cc
fp=vo*cp
fa=vo*ca
fo=vo*co
tau=V/vo
```

Initial value
2
0
0
0

Solution

Variable	Value	f()
cc	0.0393701	-8.945e-17
cp	0.211711	-1.078e-16
ca	0.00633865	-2.309e-15
co	0.0760638	-8.518e-18
cco	2	
k1	0.12	
k2	0.046	
k3	0.02	
k4	0.034	
vo	10	
k5	0.04	
V	3000	
fc	0.393701	
fp	2.11711	
fa	0.0633865	
fo	0.760638	
tau	300	



P6-16 (c) Individualized solution

P6-17 Individualized solution

P6-18 (a)

Blood coagulation living example
See Polymath program P6-18.pol

OLYMATH Results
Example CD Solved Problems - Blood Coagulation 08-25-2005, Rev5.1.233

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	700	700
TF	2.5E-11	8.24E-14	2.5E-11	8.24E-14
VII	1.0E-08	3.513E-10	1.0E-08	3.513E-10
TFVII	0	0	2.027E-11	5.71E-12
VIIa	1.0E-10	1.0E-10	9.724E-09	9.724E-09
TFVIIa	0	0	3.361E-13	1.665E-13
Xa	0	0	1.481E-09	1.481E-09
IIa	0	0	2.487E-07	1.846E-09
X	1.6E-07	1.426E-07	1.6E-07	1.426E-07
TFVIIaX	0	0	1.869E-13	8.423E-14
TFVIIaXa	0	0	5.673E-14	2.608E-14
IX	9.0E-08	8.994E-08	9.0E-08	8.994E-08
TFVIIaIX	0	0	7.2E-14	3.568E-14
IXa	0	0	3.579E-11	3.579E-11
II	1.4E-06	-3.41E-24	1.4E-06	-1.05E-25
VIII	7.0E-10	-2.024E-28	7.0E-10	-1.026E-38
VIIIa	0	0	5.352E-10	3.366E-11
IXaVIIIa	0	0	2.988E-12	2.873E-12
IXaVIIIaX	0	0	5.372E-12	4.995E-12
VIIIa1L	0	0	6.585E-10	6.585E-10
VIIIa2	0	0	6.585E-10	6.585E-10
V	2.0E-08	-1.55E-52	2.0E-08	2.793E-90
Va	0	0	1.943E-08	5.077E-09
XaVa	0	0	1.492E-08	1.492E-08
XaVaII	0	-3.938E-26	2.281E-10	-6.977E-27
mIIa	0	-8.77E-25	3.788E-07	1.663E-25
TFPI	2.5E-09	2.094E-09	2.5E-09	2.094E-09
XaTFPI	0	0	3.867E-10	3.867E-10
TFVIIaXaT	0	0	1.881E-11	1.881E-11
ATIII	3.4E-06	2.001E-06	3.4E-06	2.001E-06
XaATIII	0	0	6.073E-10	6.073E-10
mIIaATIII	0	0	8.247E-07	8.247E-07
IXaATIII	0	0	1.301E-11	1.301E-11
TFVIIIaAT	0	0	8.354E-14	8.354E-14
IIaATIII	0	0	5.734E-07	5.734E-07
k1	3.2E+06	3.2E+06	3.2E+06	3.2E+06
k2	0.0031	0.0031	0.0031	0.0031
k3	2.3E+07	2.3E+07	2.3E+07	2.3E+07
k4	0.0031	0.0031	0.0031	0.0031
k5	4.4E+05	4.4E+05	4.4E+05	4.4E+05
k6	1.3E+07	1.3E+07	1.3E+07	1.3E+07
k7	2.3E+04	2.3E+04	2.3E+04	2.3E+04
k8	2.5E+07	2.5E+07	2.5E+07	2.5E+07
k9	1.05	1.05	1.05	1.05
k10	6	6	6	6
k11	2.2E+07	2.2E+07	2.2E+07	2.2E+07
k12	19	19	19	19
k13	1.0E+07	1.0E+07	1.0E+07	1.0E+07
k14	2.4	2.4	2.4	2.4

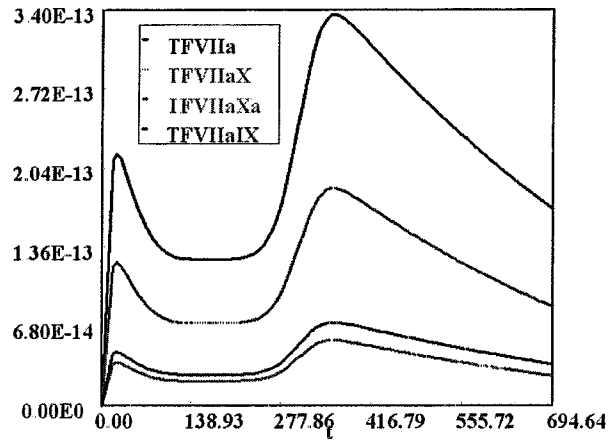
k15	1.8	1.8	1.8	1.8
k16	7500	7500	7500	7500
k17	2.0E+07	2.0E+07	2.0E+07	2.0E+07
k18	1.0E+07	1.0E+07	1.0E+07	1.0E+07
k19	0.005	0.005	0.005	0.005
k20	1.0E+08	1.0E+08	1.0E+08	1.0E+08
k21	0.001	0.001	0.001	0.001
k22	8.2	8.2	8.2	8.2
k23	0.006	0.006	0.006	0.006
k24	2.2E+04	2.2E+04	2.2E+04	2.2E+04
k25	0.001	0.001	0.001	0.001
k26	2.0E+07	2.0E+07	2.0E+07	2.0E+07
k27	4.0E+08	4.0E+08	4.0E+08	4.0E+08
k28	0.2	0.2	0.2	0.2
k29	1.0E+08	1.0E+08	1.0E+08	1.0E+08
k30	103	103	103	103
k31	63.5	63.5	63.5	63.5
k32	1.5E+07	1.5E+07	1.5E+07	1.5E+07
k33	9.0E+05	9.0E+05	9.0E+05	9.0E+05
k34	3.6E-04	3.6E-04	3.6E-04	3.6E-04
k35	3.2E+08	3.2E+08	3.2E+08	3.2E+08
k36	1.1E-04	1.1E-04	1.1E-04	1.1E-04
k37	5.0E+07	5.0E+07	5.0E+07	5.0E+07
k38	1500	1500	1500	1500
k39	7100	7100	7100	7100
k40	490	490	490	490
k41	7100	7100	7100	7100
k42	230	230	230	230
r1	8.0E-13	9.728E-17	8.0E-13	9.728E-17
r2	0	0	6.283E-14	1.782E-14
r3	5.75E-14	1.735E-14	5.75E-14	1.855E-14
r4	0	0	1.042E-15	5.189E-16
r5	0	0	9.923E-16	2.696E-17
r6	0	0	1.444E-11	6.953E-12
r7	0	0	4.073E-11	1.602E-14
r8	0	0	1.318E-12	5.971E-13
r9	0	0	1.962E-13	8.896E-14
r10	0	0	1.121E-12	5.083E-13
r11	0	0	5.381E-15	5.381E-15
r12	0	0	1.078E-12	4.982E-13
r13	0	0	3.024E-13	1.506E-13
r14	0	0	1.728E-13	8.609E-14
r15	0	0	1.296E-13	6.456E-14
r16	0	-1.6E-29	2.883E-13	4.511E-30
r17	0	-9.831E-28	1.159E-11	-4.231E-40
r18	0	0	4.674E-14	1.217E-14
r19	0	0	1.494E-14	1.439E-14
r20	0	0	4.406E-11	4.106E-11
r21	0	0	5.372E-15	5.006E-15
r22	0	0	4.405E-11	4.105E-11
r23	0	0	3.211E-12	2.044E-13
r24	0	0	9.527E-15	9.527E-15
r25	0	0	5.372E-15	5.006E-15
r26	0	-2.108E-52	3.312E-10	1.152E-91
r27	0	0	2.999E-09	2.999E-09
r28	0	0	2.974E-09	2.974E-09
r29	0	-3.763E-24	3.764E-08	6.12E-25
r30	0	-4.056E-24	2.35E-08	1.105E-24
r31	0	-2.5E-24	1.449E-08	6.81E-25
r32	0	-1.733E-25	7.132E-09	7.062E-26
r33	0	0	2.762E-12	2.762E-12
r34	0	0	1.372E-13	1.372E-13
r35	0	0	4.492E-14	1.762E-14
r36	0	0	2.065E-15	2.065E-15
r37	0	0	3.19E-15	3.19E-15
r38	0	0	4.387E-12	4.387E-12
r39	0	-1.248E-26	7.708E-09	4.499E-27

r40	0	0	3.502E-14	3.502E-14
r41	0	0	4.224E-09	2.704E-11
r42	0	0	1.78E-16	7.705E-17
Total	0	0	5.749E-07	1.903E-09

ODE Report (STIFF)

Differential equations as entered by the user

[1] d(TF)/d(t) = r2-r1-r3+r4
[2] d(VII)/d(t) = r2-r1-r6-r7-r5
[3] d(TFVII)/d(t) = r1-r2
[4] d(VIIa)/d(t) = -r3+r4+r5+r6+r7
[5] d(TFVIIa)/d(t) = r3-r4+r9-r8-r11+r12-r13+r14-r42-r37+r15
[6] d(Xa)/d(t) = r11+r12+r22-r27+r28-r33+r34-r38
[7] d(IIa)/d(t) = r16+r32-r41
[8] d(X)/d(t) = -r8+r9-r20+r21+r25
[9] d(TFVIIaX)/d(t) = r8-r9-r10
[10] d(TFVIIaXa)/d(t) = r10+r11-r12-r35+r36
[11] d(IX)/d(t) = r14-r13
[12] d(TFVIIaIX)/d(t) = r13-r14-r15
[13] d(IXa)/d(t) = r15-r18+r19+r25-r40
[14] d(II)/d(t) = r30-r29-r16
[15] d(VIII)/d(t) = -r17
[16] d(VIIIa)/d(t) = r17-r18+r19-r23+r24
[17] d(IXaVIIIa)/d(t) = -r20+r21+r22+r18-r19
[18] d(IXaVIIIaX)/d(t) = r20-r21-r22-r25
[19] d(VIIIa1L)/d(t) = r23-r24+r25
[20] d(VIIIa2)/d(t) = r23+r25-r24
[21] d(V)/d(t) = -r26
[22] d(Va)/d(t) = r26-r27+r28
[23] d(XaVa)/d(t) = r27-r28-r29+r30+r31
[24] d(XaVaII)/d(t) = r29-r30-r31
[25] d(mIIa)/d(t) = r31-r32-r39
[26] d(TFPI)/d(t) = r34-r33-r35+r36
[27] d(XaTFPI)/d(t) = r33-r34-r37
[28] d(TFVIIaXaTFPI)/d(t) = r35-r36+r37
[29] d(ATIII)/d(t) = -r38-r39-r40-r41-r42
[30] d(XaATIII)/d(t) = r38
[31] d(mIIaATIII)/d(t) = r39
[32] d(IXaATIII)/d(t) = r40
[33] d(TFVIIIaATIII)/d(t) = r42
[34] d(IIaATIII)/d(t) = r41



Explicit equations as entered by the user

[1] k1 = 3.2e6
[2] k2 = 3.1e-3
[3] k3 = 2.3e7
[4] k4 = 3.1e-3
[5] k5 = 4.4e5
[6] k6 = 1.3e7
[7] k7 = 2.3e4
[8] k8 = 2.5e7
[9] k9 = 1.05
[10] k10 = 6
[11] k11 = 2.2e7
[12] k12 = 19
[13] k13 = 1.0e7
[14] k14 = 2.4
[15] k15 = 1.8
[16] k16 = 7.5e3

```
[17] k17 = 2e7
[18] k18 = 1.0e7
[19] k19 = 5e-3
[20] k20 = 1e8
[21] k21 = 1e-3
[22] k22 = 8.2
[23] k23 = 6e-3
[24] k24 = 2.2e4
[25] k25 = 1e-3
[26] k26 = 2e7
[27] k27 = 4e8
[28] k28 = 0.2
[29] k29 = 1e8
[30] k30 = 103
[31] k31 = 63.5
[32] k32 = 1.5e7
[33] k33 = 9e5
[34] k34 = 3.6e-4
[35] k35 = 3.2e8
[36] k36 = 1.1e-4
[37] k37 = 5e7
[38] k38 = 1.5e3
[39] k39 = 7.1e3
[40] k40 = 4.9e2
[41] k41 = 7.1e3
[42] k42 = 2.3e2
[43] r1 = k1*TF*VII
[44] r2 = k2*TFVII
[45] r3 = k3*TF*VIIa
[46] r4 = k4*TFVIIa
[47] r5 = k5*TFVIIa*VII
[48] r6 = k6*Xa*VII
[49] r7 = k7*IIa*VII
[50] r8 = k8*TFVIIa*X
[51] r9 = k9*TFVIIaX
[52] r10 = k10*TFVIIaX
[53] r11 = k11*TFVIIa*Xa
[54] r12 = k12*TFVIIaXa
[55] r13 = k13*TFVIIa*IX
[56] r14 = k14*TFVIIaIX
[57] r15 = k15*TFVIIaIX
[58] r16 = k16*Xa*II
[59] r17 = k17*IIa*VIII
[60] r18 = k18*IXa*VIIIa
[61] r19 = k19*IXaVIIIa
[62] r20 = k20*IXaVIIIa*X
[63] r21 = k21*IXaVIIIaX
[64] r22 = k22*IXaVIIIaX
[65] r23 = k23*VIIIa
[66] r24 = k24*VIIIa1L*VIIIa2
[67] r25 = k25*IXaVIIIaX
[68] r26 = k26*IIa*V
[69] r27 = k27*Xa*Va
[70] r28 = k28*XaVa
[71] r29 = k29*XaVa*II
[72] r30 = k30*XaVaII
[73] r31 = k31*XaVaII
[74] r32 = k32*mIIa*XaVa
[75] r33 = k33*Xa*TFPI
[76] r34 = k34*XaTFPI
```

[77] r35 = k35*TFVIIaXa*TFPI
[78] r36 = k36*TFVIIaXaTFPI
[79] r37 = k37*TFVIIa*XaTFPI
[80] r38 = k38*Xa*ATIII
[81] r39 = k39*mIIa*ATIII
[82] r40 = k40*IXa*ATIII
[83] r41 = k41*IIa*ATIII
[84] r42 = k42*TFVIIa*ATIII
[85] Total = IIa+1.2*mIIa

P6-18 (b) No solution will be given

P6-19

(1) $C_2H_4 + 1/2O_2 \rightarrow C_2H_4O$ (2) $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

$E + 1/2O \rightarrow D$ $E + 3O \rightarrow 2U_1 + 2U_2$

$F_{IO} = 0.82F_{TO} = 0.007626$

P6-19 (a)

Selectivity of D over CO_2 $S = \dfrac{F_D}{F_{U1}}$

See Polymath program P6-19-a.pol.

POLYMATH Results

Variable	initial value	minimal value	maximal value	final value
W	0	0	2	2
Fe	5.58E-04	1.752E-10	5.58E-04	1.752E-10
Fo	0.001116	4.066E-05	0.001116	4.066E-05
Fd	0	0	2.395E-04	2.395E-04
Fu1	1.0E-07	1.0E-07	6.372E-04	6.372E-04
Fu2	0	0	6.371E-04	6.371E-04
Finert	0.007626	0.007626	0.007626	0.007626
Ft	0.0093001	0.0091804	0.0093001	0.0091804
K1	6.5	6.5	6.5	6.5
K2	4.33	4.33	4.33	4.33
Pto	2	2	2	2
Pe	0.1199987	3.817E-08	0.1199987	3.817E-08
Po	0.2399974	0.008858	0.2399974	0.008858
k1	0.15	0.15	0.15	0.15
k2	0.088	0.088	0.088	0.088
X	0	0	0.9999997	0.9999997
S	0	0	0.4101512	0.3758225
r1e	-0.0024829	-0.0024829	-3.692E-10	-3.692E-10
r2e	-0.0029803	-0.0029803	-8.136E-10	-8.136E-10

Differential equations as entered by the user
[1] d(Fe)/d(W) = r1e+r2e
[2] d(Fo)/d(W) = 1/2*r1e + 3*r2e
[3] d(Fd)/d(W) = -r1e
[4] d(Fu1)/d(W) = -2*r2e
[5] d(Fu2)/d(W) = -2*r2e

Explicit equations as entered by the user
[1] Finert = 0.007626
[2] Ft = Fe+Fo+Fd+Fu1+Fu2+Finert
[3] K1 = 6.5

```
[4] K2 = 4.33
[5] Pto = 2
[6] Pe = Pto*Fe/Ft
[7] Po = (Pto*Fo/Ft)
[8] k1 = 0.15
[9] k2 = 0.088
[10] X = 1 - Fe/0.000558
[11] S = Fd/Fu1
[12] r1e = -k1*Pe*Po^0.58/(1+K1*Pe)^2
[13] r2e = -k2*Pe*Po^0.3/(1+K2*Pe)^2
```

X = 0.999 and S = 0.376(mol of ethylene oxide)/(mole of carbon dioxide)

P6-19 (b)

Changes in equation from part (a):

$$\frac{dF_O}{dW} = \frac{1}{2}r_{1E} + 3r_{2E} + R_O \qquad \text{and} \quad F_O(o) = 0$$

$$R_O = \frac{0.12 \times 0.0093}{W} = \frac{0.001116}{2}\frac{mol}{kg.s}$$

From Polymath program: X = 0.71

S = 0.04 (mol of ethylene oxide)/(mole of carbon dioxide)

See Polymath program P6-19-b.pol

P6-19 (c)

Changes in equation from part (a):

$$\frac{dF_E}{dW} = r_{1E} + r_{2E} + R_E \qquad \text{and} \quad F_E(o) = 0$$

$$R_E = \frac{0.06 \times 0.0093}{W} = \frac{0.000558}{2}\frac{mol}{kg.s}$$

From Polymath program: X = 0.96

S = 0.41(mol of ethylene oxide)/(mole of carbon dioxide)

See Polymath program P6-19-c.pol

P6-19 (d) No solution will be given.

P6-20

Solved on web

Go to http://www.wits.ac.za/fac/engineering/procmat/ARHomepage/frame.htm

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P6-21 (a)

Isothermal gas phase reaction in a membrane reactor packed with catalyst.

A ←→ B + C $\qquad r'_{1C} = k_{1C}\left[C_A - \frac{C_B C_C}{K_{1C}}\right]$

A → D $\qquad r'_{2D} = k_{2D}C_A$

2C + D → 2E $\qquad r'_{3E} = k_{3E}C_C^2 C_D$

$$C_{AO} = \frac{P}{RT} = \frac{24.6atm}{\left(0.082dm^3atm/mol.K\right)(500K)} = 0.6mol/dm^3$$

See Polymath program P6-21-a.pol

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
W	0	0	100	100
Fa	10	0.349438	10	0.349438
Fb	0	0	3.2375418	0.4443151
Fc	0	0	4.9873025	4.8617029
Fd	0	0	2.7304877	2.7304877
Fe	0	0	1.3722476	1.3722476
y	1	0.3404952	1	0.3404952
k2d	0.4	0.4	0.4	0.4
K1c	0.2	0.2	0.2	0.2
Ft	10	9.7581913	13.220737	9.7581913
Cto	0.6	0.6	0.6	0.6
Cb	0	0	0.1403618	0.0093022
Ca	0.6	0.0073158	0.6	0.0073158
Cd	0	0	0.1019635	0.0571654
Cc	0	0	0.2117037	0.1017844
kb	1	1	1	1
k1c	2	2	2	2
r2d	0.24	0.0029263	0.24	0.0029263
k3e	5	5	5	5
r1c	1.2	0.0051635	1.2	0.0051635
ra	-1.44	-1.44	-0.0080898	-0.0080898
r3e	0	0	0.0216828	0.0029612
rd	0.24	0.0014457	0.24	0.0014457
rb	1.2	0.0051635	1.2	0.0051635
rc	1.2	-0.0042625	1.2	0.0022023
re	0	0	0.0216828	0.0029612
Ce	0	0	0.0398819	0.0287293
alfa	0.008	0.008	0.008	0.008
Fto	10	10	10	10

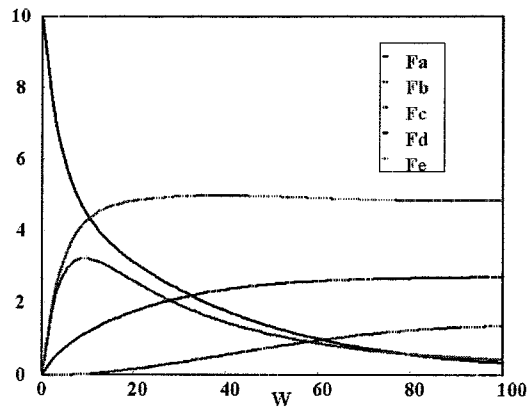
ODE Report (RKF45)

Differential equations as entered by the user

[1] d(Fa)/d(W) = ra
[2] d(Fb)/d(W) = rb-(kb*Cb)
[3] d(Fc)/d(W) = rc
[4] d(Fd)/d(W) = rd
[5] d(Fe)/d(W) = re
[6] d(y)/d(W) = -alfa*Ft/(2*Fto*y)

Explicit equations as entered by the user

[1] k2d = 0.4
[2] K1c = 0.2
[3] Ft = Fa+Fb+Fc+Fd+Fe [4] Cto = 0.6
[5] Cb = Cto*(Fb/Ft)*y
[6] Ca = Cto*(Fa/Ft)*y
[7] Cd = Cto*(Fd/Ft)*y
[8] Cc = Cto*(Fc/Ft)*y
[9] kb = 1
[10] k1c = 2
[11] r2d = k2d*Ca
[12] k3e = 5
[13] r1c = k1c*(Ca-(Cb*Cc/K1c))
[14] ra = -r1c-r2d



```
[15] r3e = k3e*(Cc^2)*Cd
[16] rd = r2d-(r3e/2)
[17] rb = r1c
[18] rc = r1c-r3e
[19] re = r3e
[20] Ce = Cto*(Fe/Ft)*y
[21] alfa = 0.008
[22] Fto = 10
```

P6-21 (b)

The interesting concentrations here are species C and D, both of which go through a maximum. Species C goes through a maximum for two reasons: (1) it is an intermediate product which is formed and then consumed, and (2) there is pressure drop along the length of the reactor and as pressure drops, so does concentration.

The concentration of species D goes through a maximum because of reason (2) above. Species D is formed but then the pressure drops, which causes the concentration to fall.

P6-21 (c) Individualized Solution

P6-22 (a) What factors influence the amplitude and frequency of the oscillation reaction?
Ans: k and the initial conditions

P6-22 (b) Oscillations eventually cease because the C_A is decreasing and becomes the limiting factor.

P6-22 (ac) Observation 1: τ_1 and τ_2 decreased
Observation 2: τ_{P1} increased
Observation 3: τ_{P2} decreased

Now, $\tau_1 = \frac{1}{\varepsilon}\ln\left(\frac{\mu_0}{\mu_1^*}\right)$ and $\tau_2 = \frac{1}{\varepsilon}\ln\left(\frac{\mu_0}{\mu_2^*}\right)$

$$\tau_{P1} = \frac{2\pi}{(\mu_1^{*2} + K_U)^{1/2}} \text{ and } \tau_{P2} = \frac{2\pi}{(\mu_2^{*2} + K_U)^{1/2}}$$

$$\varepsilon = \frac{k_0}{k_2},\ \mu_{1,2}^* = \left[\frac{(1-2K_U) \pm \sqrt{1-8K_U}}{2}\right]^{1/2}$$

From observation 2 and 3, we get
Decreasing μ_1^* and increasing μ_2^* => $K_U = (k_U/k_2)$ will increase
Also, from observation 1, ε increased => k_0/k_2 should be increased
Now, P → A $\quad k = k_0$ .....(1)
A → B $\quad k = k_U$ ..... (2)
A+2B → 3B $\quad k = k_1$ .....(3)
B → C $\quad k = k_2$ .....(4)
Hence the reaction (1) and (2) are more temperature sensitive than reaction (4)

P6-22 (d) Individualized solution

P6-23 Individualized solution

CDP6-24

$\upsilon_0 C_{A0} - \upsilon_0 C_A + r_A W = 0$

$-\upsilon_0 C_B + r_B W = 0$

$-\upsilon_0 C_C + r_C W = 0$

$-\upsilon_0 C_D + r_D W = 0$

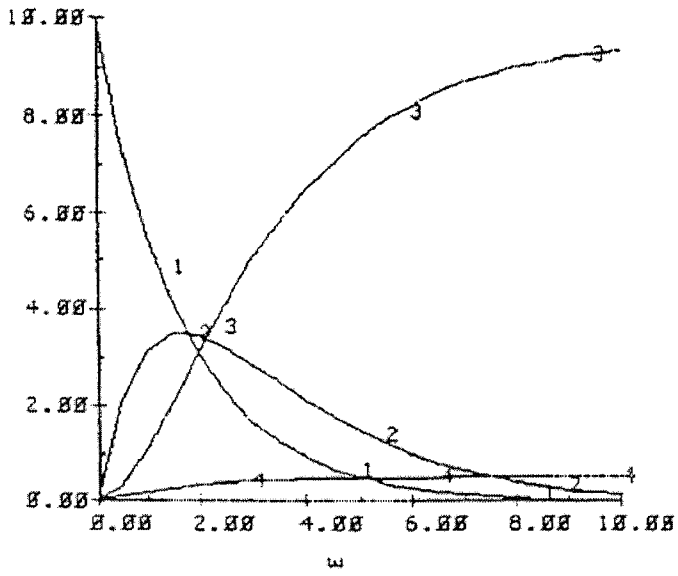
$r_A = -k_1 C_A - k_3 C_A$

$r_B = k_1 C_A - k_2 C_B$

$r_C = k_2 C_B$

$r_D = k_3 C_A$

KEY:
1 - ca
2 - cb
3 - cc
4 - cd



CDP6-25 (a)

PFR:

Mole balance:

$$\frac{dC_M}{d\tau} = r_M$$

$$\frac{dC_H}{d\tau} = r_H$$

$$\frac{dC_X}{d\tau} = r_X$$

$$\frac{dC_{Me}}{d\tau} = r_{Me}$$

$$\frac{dC_T}{d\tau} = r_T$$

$$\frac{dC_B}{d\tau} = r_B$$

Rate laws

$$r_M = -k_1 C_M C_H^{0.5}$$

$$r_H = r_M - k_2 C_X C_H^{0.5} - r_B$$

$$r_X = -r_M - k_2 C_X C_H^{0.5}$$

$$r_{Me} = -r_M + k_2 C_X C_H^{0.5} + r_B$$

$$r_T = k_2 C_X C_H^{0.5} - r_B$$

$$r_B = k_3 C_T C_H^{0.5}$$

$C_{H0} = 0.021$
$C_{M0} = 0.0105$
$\tau = .5$
Plugging those into POLYMATH gets the following:

CSTR:

Mole balance:

$$F_{H0} - F_H = (-r_{1H} - r_{2H} - r_{3H})V$$

$$F_{M0} - F_M = -r_{1M}V$$

$$F_X = (r_{1X} + r_{2X})V$$

$$F_T = (r_{2T} + r_{3T})V$$

$$F_{Me} = (r_{1Me} + r_{2Me} + r_{3Me})V$$

$$F_B = r_{3B}$$

Rate Law:

$$-r_{1M} = -r_{1H} = r_{1X} = r_{1Me} = k_1 C_H^{0.5} C_M$$

$$-r_{2H} = -r_{2X} = r_{2T} = r_{2Me} = k_2 C_H^{0.5} C_X$$

$$-r_{3H} = -r_{3T} = r_{3B} = r_{3Me} = k_3 C_H^{0.5} C_T$$

Stoichiometry:

$$F_H = v_0 C_H$$

$$F_M = v_0 C_M$$

$$F_X = v_0 C_X$$

$$F_T = v_0 C_T$$

$$F_{Me} = v_0 C_{Me} = v_0 (C_{H0} - C_H)$$

$$F_B = v_0 C_B = v_0 \left[(C_{M0} - C_M) - C_X - C_T \right]$$

Combining all of these:

$$C_{H0} - C_H = \left(k_1 C_H^{0.5} C_M + k_2 C_H^{0.5} C_X + k_3 C_H^{0.5} C_T \right) \tau$$

$$C_{M0} - C_M = k_1 C_H^{0.5} C_M \tau$$

$$C_X = \left(k_1 C_H^{0.5} C_M - k_2 C_H^{0.5} C_X \right) \tau$$

$$C_T = \left(k_2 C_X C_H^{0.5} - k_3 C_H^{0.5} C_X \right) \tau$$

$$C_{Me} = C_{H0} - C_H$$

$$C_B = \left(C_{M0} - C_M \right) - C_X - C_T$$

The following is the POLYMATH program and the summary table showing all of the concentrations.

Equations:

```
f(ch)=ch-cho+(k1*ch^.5*cm-k2*ch^.5*cx+k3*ct*ch^.5)*tau
f(cm)=cm-cmo+k1*ch^.5*cm*tau
f(cx)=(k1*ch^.5*cm-k2*ch^.5*cx)*tau-cx
f(ct)=(k2*ch^.5*cx-k3*ct*ch^.5)*tau-ct
cho=.021
k1=55.2
k2=30.2
k3=11.2
tau=.51
cmo=.0105
cme=cho-ch
cb=(cmo-cm)-cx-ct
```

Solution

Variable	Value	f()
ch	0.00776519	2.993e-15
cm	0.00301658	1.463e-14
cx	0.00317467	2.79e-14
ct	0.00286611	-1.495e-14
cho	0.021	
k1	55.2	
k2	30.2	
k3	11.2	
tau	0.51	
cmo	0.0105	
cme	0.0132348	
cb	0.00144264	

The conversion of Hydrogen and Mesitylene are then:

$$X_H = \frac{C_{H0} - C_H}{C_{H0}} = \frac{0.021 - 0.0078}{0.021} = 0.63$$

$$X_M = \frac{C_{M0} - C_M}{C_{M0}} = \frac{0.0105 - 0.0030}{0.0105} = .71$$

$C_H = 0.0078$ lb mol/ft^3 $C_M = 0.0030$ lb mol/ft^3 $C_X = 0.0032$ lb mol/ft^3
$C_T = 0.0029$ lb mol/ft^3 $C_{mc} = 0.013$ lb mol/ft^3 $C_B = 0.0014$ lb mol/ft^3

CDP6-25 (b)

When θM is reduced to 1.5, it now takes a τ of 0.24 h to achieve a maximum of xylene. Increasing θM to 10 now requires a τ of only 0.08 h

CDP6-25 (c)

To find out the reactor schemes needed, use the attainable region to get these graphs

Using a PFR would maximize C_x. If we used a ratio of mesitylene to hydrogen of 10, then we would only have to have a τ of .08 hours. So our voulme of the reactor would be only 38.08 ft^3. So our entering concentraions would be .0105 lb mol/ft^3 of Hydrogen and .105 lb mol/ft^3 of Mesitylene.

CDP6-25 (d)

First find the proportionality constants of the rate constants using the Arrhenius equation.

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

$$55.2 = A_1 e^{-(20000/(1.987*833.3))}$$

$$A_1 = 9.72 \times 10^8$$

$$30.2 = A_2 e^{-(10000/(1.987*833.3))}$$

$$A_2 = 12674$$

$$11.2 = A_3 e^{-(30000/(1.987*833.3))}$$

$$A_3 = 8.28 \times 10^8$$

Once that is done, by trial and error come up with the temperature where $\tilde{S}_{XT} = \tilde{S}_{TB}$ and the answer is then 862K or 1551.6°R.

Equations:	Initial value
d(cm)/d(t)=rm	0.0105
d(ch)/d(t)=rh	0.021
d(cx)/d(t)=rx	0
d(cme)/d(t)=rme	0
d(ct)/d(t)=rt	0
d(cb)/d(t)=rb	0

rm=-55.2*cm*ch^.5

rb=11.2*ct*ch^.5

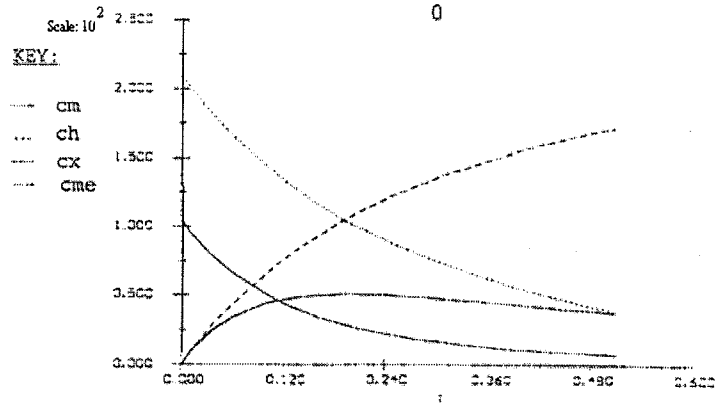
rx=-rm-30.2*cx*ch^.5

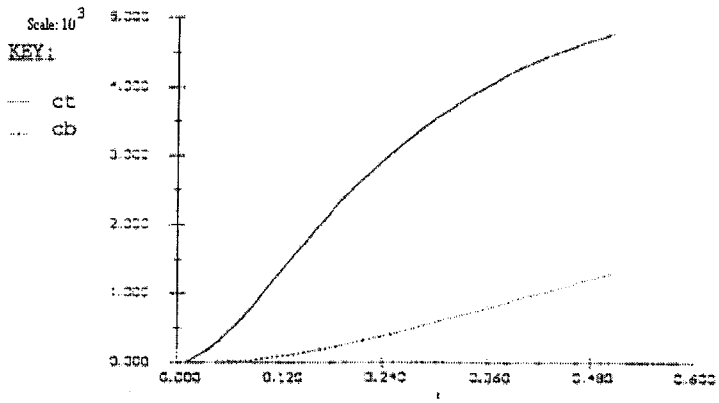
rt=30.2*cx*ch^.5-rb

rh=rm-30.2*cx*ch^.5-rb

rme=-rm+30.2*cx*ch^.5+rb

$t_0 = 0, \quad t_f = 0.51$





Variable	Initial value	Maximum value	Minimum value	Final value
t	0	0.51	0	0.51
cm	0.0105	0.0105	0.000699836	0.000699836
ch	0.021	0.021	0.00381847	0.00381847
cx	0	0.00506614	0	0.00372332
cme	0	0.0171815	0	0.0171815
ct	0	0.00477233	0	0.00477233
cb	0	0.00130452	0	0.00130452
rm	-0.083992	-0.00238715	-0.083992	-0.00238715
rb	0	0.00352127	0	0.00330288
rx	0.083992	0.083992	-0.00523484	-0.0045612
rt	0	0.0146868	0	0.00364547
rh	-0.083992	-0.0126384	-0.083992	-0.0126384
rme	0.083992	0.083992	0.0126384	0.0126384

The maximum concentration of xylene occurs at $\tau = 0.19$ h.

CDP6-26 (a)

Start with the mole balances:

$$\frac{dF_{11}}{dV} = r_{11} \qquad \frac{dF_{10}}{dV} = r_{10} \qquad \frac{dF_9}{dV} = r_9 \qquad \frac{dF_8}{dV} = r_9$$

$$\frac{dF_7}{dV} = r_7 \qquad \frac{dF_6}{dV} = r_6 \qquad \frac{dF_H}{dV} = r_H$$

Then the rate laws:

$$r_{11} = -k_1 C_H^5 C_{11}$$

$$r_{10} = k_1 C_H^5 C_{11} - k_2 C_H^5 C_{10}$$

$$r_9 = k_2 C_H^5 C_{10} - k_3 C_H^5 C_9$$

$$r_8 = k_3 C_H^5 C_9 - k_4 C_H^5 C_8$$

$$r_7 = k_4 C_H^5 C_8 - k_5 C_H^5 C_7$$

$$r_6 = k_5 C_H^5 C_7$$

$$r_H = k_1 C_H^5 C_{11} + k_2 C_H^5 C_{10} + k_3 C_H^5 C_9 + k_4 C_H^5 C_8 + k_5 C_H^5 C_7$$

Finally ,the stoichiometry:

$$F = C \cdot v_o$$

Putting all of those together and put it into POLYMATH and get the following program and answers.

```
d(c11)/d(V) =  r1/vo                  # c11(0)=0.137

d(c9)/d(V) = (-r2+r3)/vo              # c9(0)=0

d(c10)/d(V) = (-r1+r2)/vo             # c10(0)=0

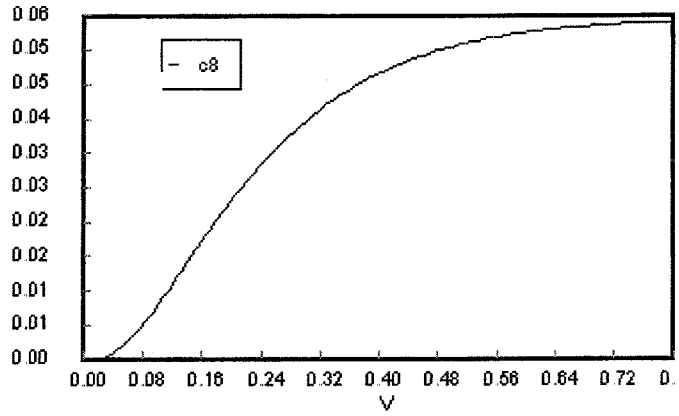
d(c8)/d(V) = (-r3+r4)/vo              # c8(0)=0

d(c7)/d(V) = (-r4+r5)/vo              # c7(0)=0

d(c6)/d(V) = -r5/vo                   # c6(0)=0

d(ch)/d(V) = (r1+r2+r3+r4+r5)/vo      # ch(0)=0.389

S9o = c9/(c10+c8+c7+c6+0.0000001)     #
S87 = c8/(c7+0.0000001) #
S89 = c8/(c9+0.0000001) #
S910= c9/(c10+0.0000001)#
k1 = k5*17.6          # k2 = k5*10
k3 = k5*4.4           # k4 = k5*2.7
vo = 1                # k5 = 2.1
r1 = -k1*ch^0.5*c11 #
r2 = -k2*ch^0.5*c10 #
r3 = -k3*ch^0.5*c9  #
r4 = -k4*ch^0.5*c8  #
r5 = -k5*ch^0.5*c7  #
X = 1-c11/c11o        # c11o = 0.1
V(0)=0                # V(f)=0.8
```

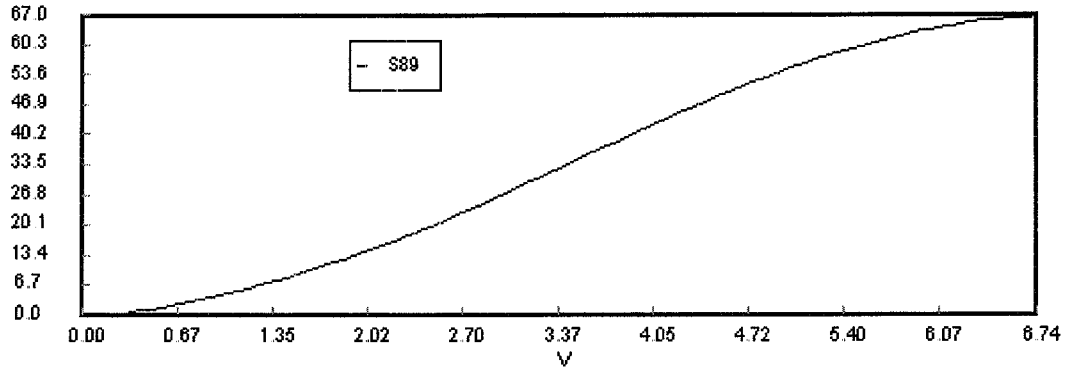


∴ The ratio of hydrogen to pentamethylbenzene is 2.83 and the volume is 0.8 m^3.

Polymath solution

CDP6-26 (b)

The polymath program is the same as the first, we see that the value of c11(o)=0.092 and ch(o)=0.434 and the ratio now becomes 4.8 to 1 and the volume increase to 6.8 m^3 to maximize S_{89}. To maximize S_{87} it follows that the volume would be smaller because earlier the reaction ends the less C_7 is formed.



CDP6-26 (c) Individualized solution

CDP6-27

Equations:	Initial value
f(fh)=(-rh)*V-fho+fh	1e-09
f(fc)=rc*V-fc	8
f(fca)=rca*V-fca	0.5

```
V=1000
fho=10000
fb=4320
fbo=7200
k1=2.7
K1=.0264
k2=.07
K2=.04
T=403
Pbo=1400
R=8.309
Pb=Pbo*.6
vo=2.41e7/Pbo
Ph=fh*8.309*403/vo
y=fc/(fbo-fb)
Pc=fc*8.309*T/vo
Pho=fho*R*T/vo
rb=-(k1*K1*Pb*Ph^.5)/(1+K1*Pb)
rca=k2*K2*Pc*Ph/(1+K2*Pc)
rh=(rb)-k2*K2*Pc*Ph/(1+K2*Pc)
rc=-(rb)-k2*K2*Pc*Ph/(1+K2*Pc)
```

Variable	Value	f()
fh	63.5619	5.826e-13
fc	8232.08	1.847e-12
fca	852.181	2.842e-14
V	1000	
fho	10000	
fb	4320	
fbo	7200	
k1	2.7	
K1	0.0264	
k2	0.07	
K2	0.04	
T	403	
Pbo	1400	
R	8.309	
Pb	840	
vo	17214.3	
Ph	12.3641	
y	2.85836	
Pc	1601.31	

Variable	Value
Pho	1945.2
rb	-9.08426
rca	0.852181
rh	-9.93644
rc	8.23208

The highest yield occurs at pressures: P_{BO} = 1400 kPa
P_{HO} = 1945.2 kPa

CDP6-28

(a)

Mole Balances:

$$\frac{dF_A}{dV} = r_{1A} + r_{2A} \qquad \frac{dF_B}{dV} = 2r_{1A} - r_{2A} - r_{3C} \qquad \frac{dF_C}{dV} = -r_{1A} + r_{3C}$$

$$\frac{dF_D}{dV} = r_{2A} \qquad \frac{dF_E}{dV} = -r_{2A} \qquad \frac{dF_G}{dV} = -r_{3C}$$

Rate Laws:

$$-r_{1A} = k_1\left(C_A C_B^2 - C_C/K_1\right)$$

$$-r_{2A} = k_2\left(C_A C_D - C_E C_B/K_2\right)$$

$$-r_{3C} = k_3 C_C$$

Stoichiometry:

$$C_i = C_{To}\left(\frac{F_i}{F_T}\right)\left(\frac{T_o}{T}\right)$$

$$F_T = F_A + F_B + F_C + F_D + F_E + F_G$$

$$C_{To} = \frac{P_o}{RT_o}$$

Use these equations in POLYMATH. Vary P_o and T_o to find the optimal conditions. We determine these to be:

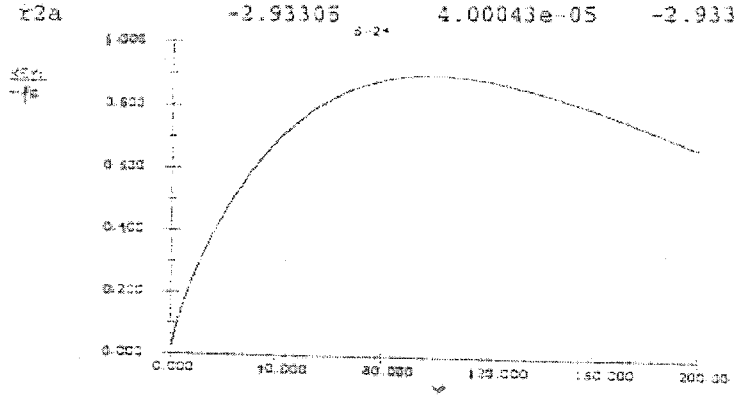
$$T_o = 315.8 \text{ K} \qquad P_o = 160 \text{ atm} \qquad V = 100 \text{ dm}^3$$

Equations:	Initial value
d(fe)/d(v)=-r2a	6
d(fb)/d(v)=2*r1a-r2a-r3c	14
d(fa)/d(v)=r1a+r2a	5
d(fc)/d(v)=-r1a-r3c	0
d(fg)/d(v)=-r3c	0
d(fd)/d(v)=r2a	4

```
ft=fa+fb+fc+fd+fe+fg
To=315.8
Po=160
T=To
k1=.933*exp((2.5*(31400/1.987*(1/330-1/T))))
K1=131567*(0.00198*T)^2*exp(30620/1.987*(1/T-1/298))
k2=.636*exp(18000/1.987*(1/300-1/T))
K2=103943*exp(9834/1.987*(1/T-1/298))
k3=.244*exp(1.5*28956/1.987*(1/325-1/T))
Cto=Po/(.082*To)
ca=Cto*(fa/ft)*(To/T)
cb=Cto*(fb/ft)*(To/T)
cc=Cto*(fc/ft)*(To/T)
cd=Cto*(fd/ft)*(To/T)
ce=Cto*(fe/ft)*(To/T)
r3c=-k3*cc
r1a=-k1*(ca*cb^2-cc/K1)
r2a=-k2*(ca*cd-ce/K2)
```

$v_0 = 0, \quad v_f = 200$

Variable	Initial value	Maximum value	Minimum value	Final value
v	0	200	0	200
fe	6	9.99892	6	9.99558
fb	14	17.3038	14	15.4939
fa	6	6	0.184792	0.184792
fc	0	0.907053	0	0.682081
fg	0	1.13754	0	1.13754
fd	4	4	0.0010827	0.00441766
ft	30	30	27.4837	27.4983
To	315.8	315.8	315.8	315.8
Po	160	160	160	160
T	315.8	315.8	315.8	315.8
k1	0.00428571	0.00428571	0.00428571	0.00428571
K1	2791.12	2791.12	2791.12	2791.12
k2	2.88122	2.88122	2.88122	2.88122
K2	40761.5	40761.5	40761.5	40761.5
k3	0.0343899	0.0343899	0.0343899	0.0343899
Cto	6.17866	6.17866	6.17866	6.17866
ca	1.23573	1.23573	0.0415214	0.0415214
cb	2.88337	3.63472	2.88337	3.48136
cc	0	0.202498	0	0.153258
cd	0.823821	0.823821	0.000236662	0.000992615
ce	1.23573	2.24735	1.23573	2.24593
r3c	-0	-0	-0.00696389	-0.00527054
r1a	-0.0440299	-0.00215647	-0.0440299	-0.00215647
r2a	-2.93305	4.00043e-05	-2.93305	4.00043e-05



Methanol Synthesis

V	Fc
0	0
20	0.44820445
40	0.68570232
60	0.82334782
80	0.8904273
100	0.90829749
120	0.89276842
140	0.85543262
160	0.80470055
180	0.74660073
200	0.6853895

(b) Use the same POLYMATH program as above and vary the ratio of entering reactants. The optimal ratio would be :

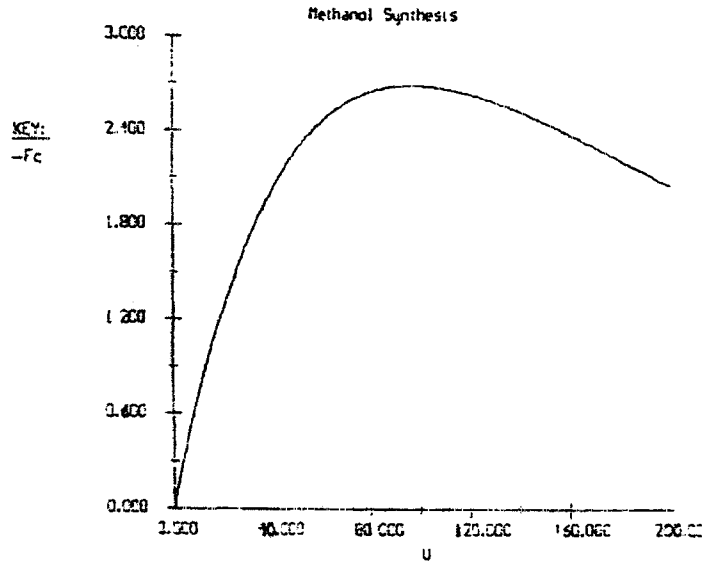
$\frac{8}{15}$ hydrogen gas, $\frac{4}{15}$ carbon monoxide, and $\frac{1}{5}$ carbon dioxide

These results are similar to those in part (a) in that the optimal volume is still 100 dm^3, and the concentration profile is very similar in shape. The primary difference is that the F_C values are more than doubled.

Methanol Synthesis

Equations:	Initial value
d(Fa)/d(V)=r1a+r2a	8
d(Fb)/d(V)=2*r1a-r2a-r3c	16
d(Fc)/d(V)=-r1a+r3c	0
d(Fe)/d(V)=-r2a	6
d(Fg)/d(V)=-r3c	0
d(Fd)/d(V)=r2a	0

```
Ft=Fa+Fb+Fc+Fd+Fe+Fg
To=315.8
Po=160
T=To
```




```
k1=.933*exp((2.5*(31400/1.987*(1/330-1/T))))
K1=131667*(0.00198*T)^2*exp(30620/1.987*(1/T-1/298))
k2=0.636*exp(18000/1.987*(1/300-1/T))
K2=103943*exp(9834/1.987*(1/T-1/298))
k3=0.244*exp(1.5*28956/1.987*(1/325-1/T))
Cto=Po/(.082*To)
Ca=Cto*(Fa/Ft)*(To/T)
Cb=Cto*(Fb/Ft)*(To/T)
Cc=Cto*(Fc/Ft)*(To/T)
Cd=Cto*(Fd/Ft)*(To/T)
Ce=Cto*(Fe/Ft)*(To/T)
r3c=-k3*Cc
r1a=-k1*(Ca*Cb^2-Cc/K1)
r2a=-k2*(Ca*Cd-Ce*Cb/K2)
```

$V_0 = 0.$ $V_f = 200$

Methanol Synthesis

Variable	Initial value	Maximum value	Minimum value	Final value
V	0	200	0	200
Fa	8	8	1.94105	1.94105
Fb	16	16	7.88738	7.88738
Fc	0	2.6816	0	2.05199
Fe	6	6	5.99941	5.99941
Fg	0	4.00756	0	4.00756
Fd	0	0.000590838	0	0.000590838
Ft	30	30	21.8885	21.8885
To	315.8	315.8	315.8	315.8
Po	160	160	160	160
T	315.8	315.8	315.8	315.8
k1	0.00428571	0.00428571	0.00428571	0.00428571
K1	2791.12	2791.12	2791.12	2791.12
k2	2.88122	2.88122	2.88122	2.88122
K2	40761.5	40761.5	40761.5	40761.5
k3	0.0343899	0.0343899	0.0343899	0.0343899
Cto	6.17866	6.17866	6.17866	6.17866
Ca	1.64764	1.64764	0.547917	0.547917
Cb	3.29528	3.29528	2.22658	2.22658
Cc	0	0.724199	0	0.579233
Cd	0	0.000156781	0	0.000156781
Ce	1.23573	1.59351	1.23573	1.59351
r3c	-0	-0	-0.024912	-0.0139193
r1a	-0.075678	-0.0116408	-0.076878	-0.0116408

Methanol Synthesis

V	Fc
0	0
20	1.2448568
40	2.0129151
60	2.4406221
80	2.6366715
100	2.680932
120	2.6292203
140	2.5193659
160	2.376518
180	2.2171669
200	2.0519865

CDP6-29 No solution will be given

CDP6-A

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

$C + B \rightarrow E + D$

First, find τ. To do this use the original design equation for a CSTR:

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

Then since $F_{A0} = C_{A0}v_0$ and $\tau = V/v_0$ then the design equation becomes:

$$\tau = \frac{C_{A0}X}{-r_A}$$

Using the rate law and stoichiometry we find:

$$-r_A = k_1 C_{A0}(1-X)$$

Combining all these and solving for τ when $X = .3$, $C_{A0} = .1$ and $k_1 = .412$

$$\tau = \frac{C_{A0}X}{k_1 C_{A0}(1-X)} = \frac{.1*.3}{.412*.1*.7} = 1.04\text{h}$$

Once that has been calculated, redo all the mole balances:

$$C_{A0} - C_A = -r_A\tau$$

$$C_{B0} - C_B = -r_B\tau$$

$$C_C = r_C\tau$$

$$C_D = r_D\tau$$

$$C_E = r_E \tau$$

Then do the rate laws:

$$-r_A = k_1 C_A$$
$$-r_B = k_1 C_A + k_2 C_C$$
$$r_C = k_1 C_A - k_2 C_C$$
$$r_D = k_1 C_A + k_2 C_C$$
$$r_E = k_2 C_C$$

Combining and rearranging into a function:

$$f(C_A) = 0 = C_A - C_{A0} + k_1 C_A \tau$$
$$f(C_B) = 0 = C_B - C_{B0} + (k_1 C_A + k_2 C_C)\tau$$
$$f(C_C) = 0 = (k_1 C_A - k_2 C_C)\tau - C_C$$
$$f(C_D) = 0 = (k_1 C_A + k_2 C_C)\tau - C_D$$
$$f(C_E) = 0 = k_2 C_C \tau - C_E$$

Plug those into POLYMATH:

6-F

Equations:

```
f(ca)=ca-cao+k1*ca*tau
f(cb)=cb-cbo+(k1*ca+k2*cc)*tau
f(cc)=(k1*ca-k2*cc)*tau-cc
f(cd)=(k1*ca+k2*cc)*tau-cd
f(ce)=k2*cc*tau-ce
cao=.1
k1=.412
tau=1.04
cbo=.14
k2=.055
```

Solution

Variable	Value	f()
ca	0.0700045	3.361e-15
cb	0.108382	4.023e-11
cc	0.0283726	9.472e-13
cd	0.0316184	-9.405e-13
ce	0.00162291	1.579e-11
cao	0.1	
k1	0.412	
tau	1.04	
cbo	0.14	
k2	0.055	

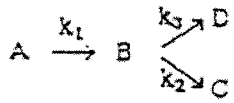
$C_c = .028$ need $F_{C0} = 10$

$$v_0 = \frac{F_C}{C_C} = \frac{10}{.028} = 357 gal/h$$

$$V = \tau v_0 = 1.04 * 357 = 371.3 gal$$

b)No solution will be given.

CDP6-B



Batch reactor: $y_{A0} = 1$

(a) $k_1 = 0.01\ \text{sec}^{-1}$, $t = 1.5\ \text{min} = 90\ \text{s}$

$$A \rightarrow B \qquad -r_A = k_1 C_A$$

$$N_{A0}\frac{dX}{dt} = -r_A V$$

$$C_{A0}\frac{dX}{dt} = k_1 C_A = k_1 C_{A0}(1-X)$$

$$\int_0^{X_1} \frac{dX}{1-X} = \int_0^t k_1\, dt$$

$$\ln\left(\frac{1}{1-X_1}\right) = k_1 t$$

$$\frac{1}{1-X_1} = e^{k_1 t}$$

$$X_1 = 1 - e^{-k_1 t}$$

$$C_A = C_{A0}(1-X_1) = C_{A0}\, e^{-k_1 t}$$

$$\frac{C_A}{C_{A0}} = e^{-k_1 t} = e^{-(0.01)(90)} = 0.41$$

(b) $A \rightarrow B \qquad r_{B1} = -r_A = k_1 C_A \qquad X_1$

$B \rightarrow C \qquad r_C = k_2 C_B \qquad X_2$

$B \rightarrow D \qquad r_D = k_3 C_B \qquad X_3$

$$-r_B = -r_{B1} + r_C + r_D = -k_1 C_A + k_2 C_B + k_3 C_B$$

$$\frac{-dC_B}{dt} = -k_1 C_{A0}\, e^{-k_1 t} + (k_2 + k_3) C_B$$

$$\frac{-dC_B}{dt} = -(0.01)(0.2)\, e^{-0.01t} + (0.003 + 0.002) C_B$$

$$\frac{-dC_B}{dt} = -0.002\left[1 - e^{-0.01t}\right] + 0.005\, C_B$$

Using a Runge-Kutta Gill numerical solution, we find that, for $t = 2\ \text{min} = 120\ \text{s}$, $C_B =$ $0.136\ \text{gmol/dm}^3$.

(c) $$\frac{dC_C}{dt} = r_C = k_2 C_B \ ; \ \frac{dC_C}{dt} = k_2 C_B \ ; \ C_C = k_2 \int_0^t C_B\, dt$$

From the solution in part (b), we have values of C_B at intervals as small as 5 sec, so we can use Simpson's rule to obtain C_C:

$t = 1\ \text{min} = 60\ \text{sec}$.

$$C_C = 0.003\left(\frac{15}{3}\right)[0 + 4(0.0449) + 2(0.0782) + 4(0.102) + 0.1183]$$

$$C_C = 0.0129\ \text{gmol/dm}^3$$

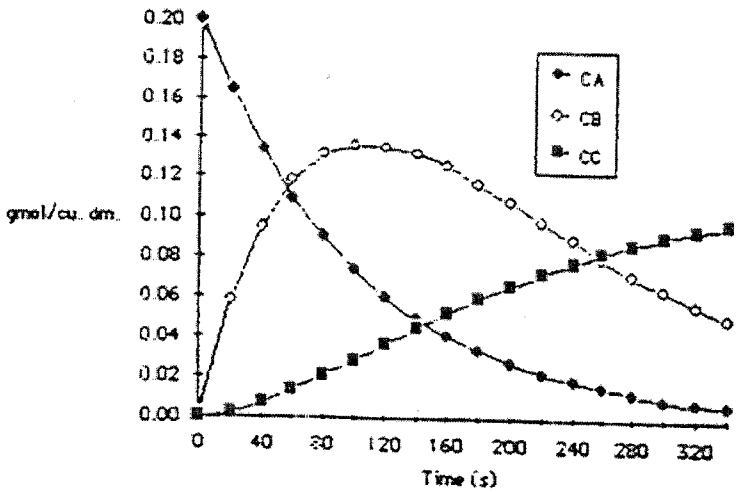
t = 2 min = 120 sec

$$C_C = 0.003\left(\frac{30}{3}\right)[0 + 4(0.0782) + 2(0.1183) + 4(0.134) + 0.1355]$$

$$C_C = 0.0366 \text{ gmol/dm}^3$$

(d)

T	C_A	C_B	C_C	C_D
0	0.2	0	0	0
20	0.164	0.0572	0.0018	0.0012
40	0.134	0.0950	0.0065	0.0043
60	0.108	0.118	0.0129	0.0086
80	0.0899	0.131	0.0205	0.0136
100	0.0736	0.136	0.0285	0.0190
120	0.0602	0.135	0.0366	0.0244
140	0.0493	0.131	0.0447	0.0298
160	0.0404	0.125	0.0523	0.0349
180	0.0331	0.116	0.0595	0.0392
200	0.0271	0.107	0.0662	0.0442
220	0.0222	0.0982	0.0724	0.0482
240	0.0181	0.0890	0.0779	0.0520
260	0.0149	0.0801	0.0829	0.0553
280	0.0122	0.0717	0.0874	0.0583
300	0.00996	0.0638	0.0914	0.0609
320	0.0082	0.0566	0.0949	0.0632
340	0.0067	0.0499	0.0979	0.0635



The concentration of B is highest at t = 100 sec, where its value is 0.1363 gmol/dm^3

(e)

Balance on A:

$$F_{A0} - F_A + r_A V = 0$$

$$\upsilon C_{A0} - \upsilon C_A - k_1 C_A V = 0$$

$$C_{A0} - C_A - k_1 C_A \tau = 0$$

$$C_{A0} - C_A (1 + k_1 \tau) = 0$$

$$\frac{C_A}{C_{A0}} = \frac{1}{(1 + k_1 \tau)}$$

Balance on B:

$$F_{B0} - F_B + r_B V = 0$$

$$-\upsilon C_B + (k_1 C_A - k_2 C_B - k_3 C_B) V = 0$$

$$-C_B + k_1 C_A \tau - k_2 C_B \tau - k_3 C_B \tau = 0$$

$$C_B (1 + k_2 \tau + k_3 \tau) = k_1 \tau C_A$$

$$C_A = \frac{C_B (1 + k_2 \tau + k_3 \tau)}{k_1 \tau}$$

$$\frac{C_A}{C_{A0}} = \frac{1}{1 + k_1 \tau} = \frac{C_B (1 + k_2 \tau + k_3 \tau)}{C_{A0} k_1 \tau}$$

$$\frac{C_B}{C_{A0}} = \frac{k_1 \tau}{(1 + k_1 \tau)(1 + k_2 \tau + k_3 \tau)}$$

τ(s)	10	50	100	150	200	300	500
C_B/C_{A0}	0.08	0.26	0.33	0.34	0.33	0.3	0.23

$C_{B,max}$ occurs at $\tau = 150\ \Delta$

$$\therefore F_B = \upsilon C_B = \left(20 \frac{dm^3}{min}\right)(150\ \Delta)\left(\frac{min}{60\ sec.}\right) = 50\ dm^3/min$$

CDP6-C

First, find the values for k.

$$k_1 = 2989e^{(-10.87/(.001987*700))} = 1.2$$

$$k_2 = 9466e^{(-15.11/(.001987*700))} = .18$$

$$k_3 = 11127e^{(-15.06/(.001987*700))} = .22$$

In this problem
Isobutylene = I
Methacrolein = M
CO_2 = D
CO = C
Oxygen = O

The mole balances for these species are as follows:

$$F_{I0} - F_I = (-r_{1I} - r_{2I} - r_{3I})V$$

$$F_M = r_{1M} V$$

$$F_D = r_{2D} V$$

$$F_C = r_{3D} V$$

Oxygen is in excess so we will assume that $F_o = F_{o0}$.
The rate laws for these reactions are as follows:

$$-r_{1I} = -r_{1O} = r_{1M} = k_1 C_I C_{O0}$$

$$-r_{2I} = \frac{-4r_{2O}}{25} = \frac{1}{4} r_{2D} = k_2 C_I C_{O0}$$

$$-r_{3I} = \frac{4r_{3O}}{-17} = \frac{1}{4}r_{3C} = k_3 C_I C_{OO}$$

Combine all of these and come up with the following:

$$C_{IO} - C_I = (k_1 C_I C_{OO} + k_2 C_I C_{OO} + k_3 C_I C_{OO})\tau$$

$$C_{OO} - C_O = (k_1 C_I C_{OO} + \frac{25}{4} k_2 C_I C_{OO} + \frac{17}{4} k_3 C_I C_{OO})\tau$$

$$C_M = k_1 C_I C_{OO} \tau$$

$$C_D = 4 * k_2 C_I C_{OO} \tau$$

$$C_C = 4 * k_3 C_I C_{OO} \tau$$

Before plugging into POLYMATH, evaluate the parameters and derive equations for conversion.

$$C_T = \frac{p}{RT} = \frac{2}{.082 * 700} = 0.034$$

$$C_{IO} = y_{AO} C_T = .1 * .034 = 0.0034$$

$$C_{OO} = 0.031$$

$$X_I = \frac{C_{IO} - C_I}{C_{IO}}$$

$$X_{1I} = \frac{C_M}{C_{IO}}$$

$$X_{2I} = \frac{C_D}{4C_{IO}}$$

$$X_{3I} = X_I - X_{1I} - X_{2I}$$

Then plug into POLYMATH to get the following:

Equations:	Initial value
f(ci)=ci-cio+(k1*ci*coo+k2*ci*coo+k3*ci*coo)*tau	0.001
f(cm)=k1*ci*coo*tau-cm	0.001
f(cd)=4*k2*ci*coo*tau-cd	0.004
f(cc)=4*ci*coo*tau-cc	0.004
f(co)=co-coo+(k1*ci*coo+25/4*k2*ci*coo+17/2*k3*ci*coo)*tau	0.01
cio=.0034	
k1=1.2	
coo=.031	
k2=.18	
k3=.22	
tau=10	
x1=cm/cio	
x2=.25*cd/cio	
x=(cio-ci)/ci	
x3=x-x1-x2	

Solution

Variable	Value	f()
ci	0.00227273	-1.775e-12
cm	0.000845455	1.011e-12
cd	0.000507273	-1.381e-12
cc	0.00281818	3.835e-13
cio	0.0034	
k1	1.2	
coo	0.031	
k2	0.18	
k3	0.22	
tau	10	
x1	0.248663	
x2	0.0372995	
x	0.496	
x3	0.210037	

$X_I = 0.496 \quad X_{II} = 0.25 \quad X_{2I} = 0.037 \quad X_{3I} = 0.21$

CDP6-D

$A \rightarrow B \qquad -r_A = k_1 C_A ; k_1 = 10 \sec^{-1}$

$C \rightarrow D + E \qquad -r_C = k_2 ; k_2 = 0.03 \frac{lbmol}{ft^3 \sec}$

$F_T = 10$ lbmol/sec

$$\frac{dF_a}{dV} = r_A = -k_1 C_A$$

$$F_A = C_A v_0$$

$$C_{T0} = \frac{0.5}{0.73 * 900} = 7.61 * 10^{-6}$$

$$\therefore v_0 = 13140$$

$$V = 1005 ft^3$$

See POLYMATH solution below

Equations:	Initial value
d(fa)/d(V)=ra	5
d(fc)/d(V)=rc	5
d(fb)/d(V)=-ra	0
d(fd)/d(V)=-rc	0
d(fe)/d(V)=-rc	0
k1=10	
k2=.03	

```
ft=fa+fc+fb+fd+fe
fao=5
cto=5/(900*.73)
fto=1.0
rc=-k2
x=(fao-fa)/fao
avo=fto/cto
ca=cto*(fa/ft)
ra=-k1*ca
```

Variable	Initial value	Maximum value	Minimum value	Final value
V	0	105	0	105
fa	5	5	2.49621	2.49621
fc	5	5	1.85	1.85
fb	0	2.50379	0	2.50379
fd	0	3.15	0	3.15
fe	0	3.15	0	3.15
k1	10	10	10	10
k2	0.03	0.03	0.03	0.03
ft	10	13.15	10	13.15
fao	5	5	5	5
cto	0.00761035	0.00761035	0.00761035	0.00761035
fto	10	10	10	10
rc	-0.03	-0.03	-0.03	-0.03
x	0	0.500758	0	0.500758
avo	1314	1314	1314	1314
ca	0.00380518	0.00380518	0.00144464	0.00144464

CDP6-E

a) Using the equation for the equilibrium constants:

$$K_{c1} = \frac{C_C C_D}{C_A C_B} \qquad K_{c2} = \frac{C_X C_Y}{C_C C_B}$$

We can come up with the equations for C_A, C_D, and C_X.

$$C_A = \frac{C_C C_D}{K_{c1} C_B}$$

$$C_D = \frac{K_{c1} C_A C_B}{C_C}$$

$$C_X = \frac{K_{c2} C_C C_B}{C_Y}$$

The rest can be found with stoichiometry.

$$C_Y = C_X$$

$$C_B = C_{B0} - C_D - C_Y$$

$$C_C = C_{A0} - C_A - C_X$$

POLYMATH

6-5 a

Equations:

```
f(ca)=ca-cc*cd/(K1*cb)
f(cd)=cd-K1*ca*cb/cc
f(cx)=cx-K2*cc*cb/cy
K1=4
K2=1
cy=cx
cbo=1.5
cao=1.5
cc=cao-ca-cx
x=(cao-ca)/cao
cb=cbo-cd-cy
```

6-5 a

Solution

Variable	Value	f()
ca	0.0306182	3.049e-19
cd	0.109652	-1.084e-18
cx	0.714386	-1.105e-16
K1	4	
K2	1	
cy	0.714386	
cbo	1.5	
cao	1.5	
cc	0.754995	
x	0.979588	
cb	0.675961	

$C_A = 0.0306$ $C_B = 0.68$ $C_C = 0.75$ $C_D = 0.11$

$C_X = 0.71$ $C_Y = 0.71$

We also find that X = 0.98

b) With the new equation we must find the new equilibrium equations.

$$C_Z = K_{c3} C_A C_X$$

$$C_Y = \frac{K_{c2} C_C C_B}{C_X}$$

$$C_D = \frac{K_{c1} C_A C_B}{C_C}$$

The rest are the same except for:

$$C_X = C_Y - C_Z$$

$$C_A = C_{A0} - C_D - C_Z$$

Equations:

```
f(cz)=cz-k3*ca*cx
f(cy)=cy-k2*cc*cb/cx
f(cd)=cd-k1*ca*cb/cc
k3=5
cx=cy-cz
k2=1.51
k1=2.63
cao=1.5
cbo=1.5
sdz=cd/cz
syz=cy/cz
ca=cao-cd-cz
cb=cbo-cd-cy
cc=cao-ca-cx
scx=cc/cx
```

Variable	Value	f()
cz	0.990725	1.092e-13
cy	1.07384	1.144e-12
cd	0.268101	-2.607e-15
cx	0.0831135	
cao	1.5	
cbo	1.5	
T	300	
sdz	0.270611	
syz	1.08389	
k3	49.4255	
ca	0.241174	
k2	0.480271	
cb	0.15806	
k1	8.26888	
x	0.839217	
cc	1.17571	
scx	14.1453	

We find that

$C_Z = 0.65$ $C_Y = 0.91$ $C_D = 0.37$ $C_X = 0.27$

$C_A = 0.48$ $C_B = 0.22$ $C_C = 0.76$

$X = 0.68$

$S_{CX} = 2.8$ $S_{DZ} = 0.57$ $S_{YZ} = 1.41$

c) When the temperature is raised from 300 K to 500 K, S_{CX} goes down, S_{DZ} goes up and S_{YZ} goes up.

d) First find the proportionality constants from the Arrhenius equation.

$$0.002 = A_1 e^{-(10000/1.987*300)}$$

$$A_1 = 38603$$

$$0.06 = A_2 e^{-(20000/1.987*300)}$$

$$A_2 = 2.24 \times 10^{13}$$

$$0.3 = A_3 e^{-(30000/1.987*300)}$$

$$A_3 = 2.16 \times 10^{21}$$

Once those are known, come up with equations for the equations in terms of space-time τ.

$$\tau = \frac{C_{A0} - C_A}{k_1 + k_2 C_A + k_3 C_A^2}$$

$$\tau k_1 + \tau k_2 C_A + \tau k_3 C_A^2 - C_{A0} + C_A = 0$$

$$C_A = \frac{-(\tau k_2 + 1) + \sqrt{(\tau k_2 + 1)^2 - 4(\tau k_3)(\tau k_1 - C_{A0})}}{2\tau k_3}$$

$$\tau = \frac{-C_X}{-k_1} \qquad \tau = \frac{-C_B}{k_2 C_A} \qquad \tau = \frac{-C_Y}{-k_3 C_A^2}$$

$$C_X = k_1 \tau \qquad C_B = k_2 \tau C_A \qquad C_Y = k_3 \tau C_A^2$$

Use EXCEL solver in order to find the temperature that maximizes C_B

T	Ca
312.5336841	0.016513937
k1	Cx
0.003919233	0.039192325
k2	Cb
0.230891512	0.038129279
k3	Cy
2.260443602	0.006164458

CDP6-F (a)

Mole balances:

$dF_A/dV = -r_D-r_U$
$dF_D/dV = r_D$
$dF_U/dV = r_U$
Rate laws:

$r_D = k_1 C_A^2$ $\quad k_1 = 15\ ft^3/lbmol.s$

$r_U = k_2 C_A$ $\quad k_2 = 0.015\ s^{-1}$

Stoichiometry: $C_A = C_{To}(F_A/F_T)$, $\quad F_T = F_A + F_D + F_U$

Cost = $60F_B - 15F_C - 10F_{AO}$

Using these equations in polymath to find the necessary volume to maximize Cost:

$V = 1425\ ft^3$

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	2000	2000
fu	0	0	0.0237312	0.0237312
fa	0.06705	0.0018652	0.06705	0.0018652
fd	0	0	0.0414537	0.0414537
k1	15	15	15	15
k2	0.015	0.015	0.015	0.015
fao	0.06705	0.06705	0.06705	0.06705
ft	0.06705	0.06705	0.06705	0.06705
cao	0.00447	0.00447	0.00447	0.00447
ca	0.00447	1.243E-04	0.00447	1.243E-04
Cost	-0.6705	-0.6705	1.46684	1.4607519
rd	2.997E-04	2.319E-07	2.997E-04	2.319E-07
ru	6.705E-05	1.865E-06	6.705E-05	1.865E-06

ODE Report (RKF45)

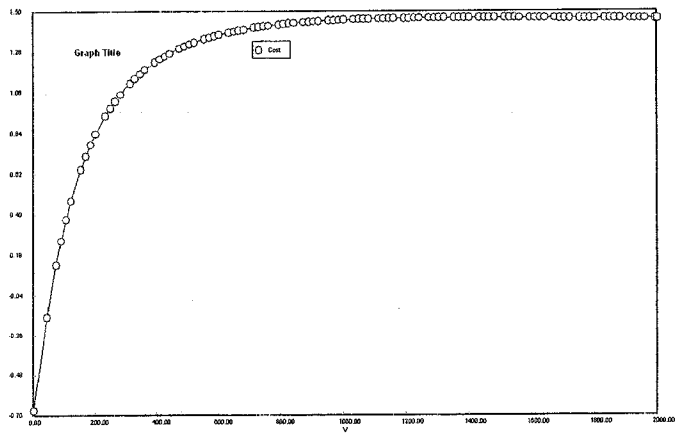
Differential equations as entered by the user

[1] d(fu)/d(V) = ru
[2] d(fa)/d(V) = -ru-rd
[3] d(fd)/d(V) = rd

Explicit equations as entered by the user

[1] k1 = 15
[2] k2 = 0.015
[3] fao = 0.06705
[4] ft = fu+fa+fd
[5] cao = 0.00447
[6] ca = cao*(fa/ft)
[7] Cost = (60*fd-15*fu-10*fao)
[8] rd = k1*(ca^2)
[9] ru = k2*ca

Independent variable
variable name : V
initial value : 0
final value : 2000



CDP6-F (b)

Mole balances:

$F_A = F_{Ao} + r_A V$ $\quad F_D = r_D V$ $\quad F_U = r_U V$

Rate laws: $r_A = -r_D - r_U$ $\quad r_D = k_1 C_A^2$ $\quad r_U = k_2 C_A$

$$k_i = k_{io} \exp\left(\frac{E_i}{R}\right)\left(\frac{1}{T} - \frac{1}{919.67}\right) \qquad F_i = v_o C_i$$

Cost = $v_o(60F_B - 15F_C - 10F_{AO})$

Use these equations in Polymath and vary T from 860 ° R to 1160 ° R and find maximum value of cost.

Cost steadily rises with temperature and reaches a maximum at 970 °R(510.33 °F).

POLYMATH Results

NLES Solution

Variable	Value	f(x)	Ini Guess
ca	0.0023213	5.354E-08	0.00447
cd	0.0016225	-5.354E-08	0
cu	5.262E-04	-2.76E-15	0
cao	0.00447		
E1	10000		
R	1.987		
T	970		
k2o	0.015		
E2	2.0E+04		
k1o	15		
vo	15		
V	400		
tau	26.666667		
cost	0.6713603		
k1	11.292187		
k2	0.0085009		
rd	6.085E-05		
ru	1.973E-05		
ra	-8.058E-05		

NLES Report (safenewt)

Nonlinear equations

[1] f(ca) = ca-cao-ra*tau = 0
[2] f(cd) = cd-rd*tau = 0
[3] f(cu) = cu-ru*tau = 0

Explicit equations

[1] cao = 0.00447
[2] E1 = 10000
[3] R = 1.987
[4] T = 970
[5] k2o = 0.015
[6] E2 = 20000
[7] k1o = 15
[8] vo = 15
[9] V = 400
[10] tau = V/vo
[11] cost = vo*(60*cd-15*cu-10*cao)
[12] k1 = k1o*exp((E1/R)*(1/T-1/919.67))
[13] k2 = k2o*exp((E2/R)*(1/T-1/919.67))
[14] rd = k1*(ca^2)
[15] ru = k2*ca
[16] ra = -k1*(ca^2)-k2*ca

CDP6-G 3

Mole Balances : $\frac{dC_A}{dt} = r_A \qquad \frac{dC_B}{dt} = r_B \qquad \frac{dC_C}{dt} = r_C$

$\frac{dC_E}{dt} = r_E \qquad \frac{dC_F}{dt} = r_F$

Rate Laws : $r_A = -r_1 - r_2 - r_4 \qquad r_B = -r_1 \qquad r_C = r_1 - r_2 - r_3$

$r_E = r_3 - r_4 \qquad r_F = r_2 + r_4$

$r_1 = \frac{wk_1 C_A C_B}{1 + K_A C_A} \qquad r_2 = \frac{wk_2 C_A C_C}{1 + K_A C_A}$

$r_3 = wk_3 C_C \qquad r_4 = \frac{wk_4 C_A C_E}{1 + K_A C_A}$

Stoichiometry : $C_{Bo} = 0.54 \text{ kmol/dm}^3 = 540 \text{ mol/dm}^3$

from Henry's Law :

$C_{Ao} = 5.9 \text{ MPa}\left(0.058 \text{ kmol/m}^3 \cdot \text{MPa}\right) = 0.3422 \text{ mol/dm}^3$

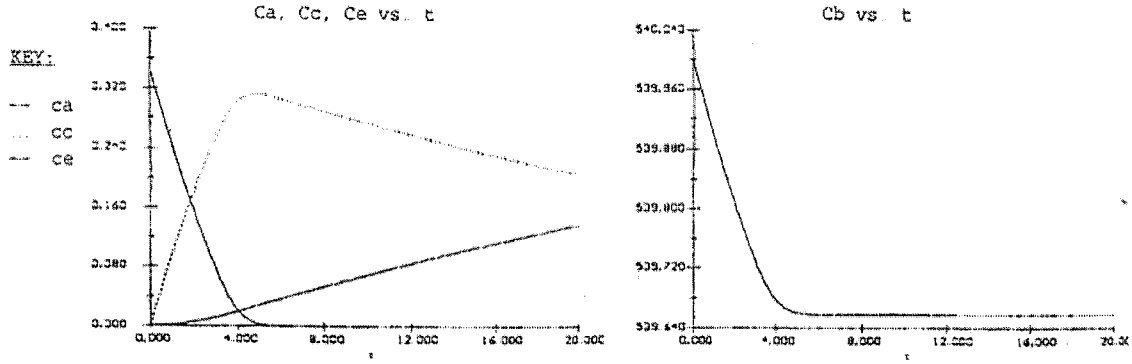
Use these equations in the following POLYMATH program to generate graphs of C_A, C_B, C_C, C_E, and C_F as a function of time.

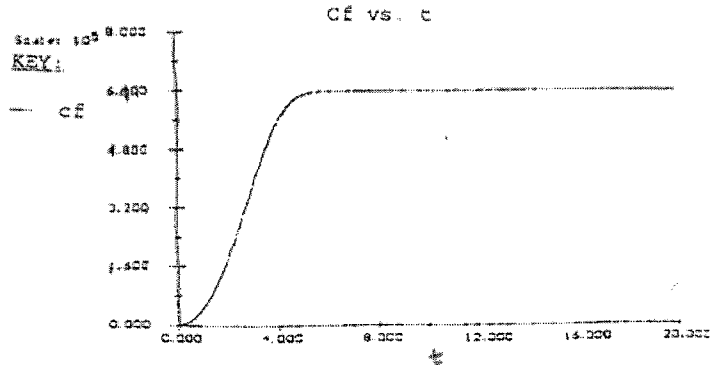
Equations:	Initial value
d(ca)/d(t)=ra	0.3422
d(cb)/d(t)=rb	540
d(cc)/d(t)=rc	0
d(ce)/d(t)=re	0
d(cf)/d(t)=rf	0

```
w=10
k1=0.000468
Ka=22.76
k2=0.000227
k4=0.00147
k3=0.00282
r3=w*k3*cc
r1=w*k1*ca*cb/(1+Ka*ca)
r2=w*k2*ca*cc/(1+Ka*ca)
r4=w*k4*ca*ce/(1+Ka*ca)
rb=-r1
re=r3-r4
rf=r2+r4
ra=-r1-r2-r4
rc=r1-r2-r3
```

$t_0 = 0, \quad t_f = 20$

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	20	0	20
ca	0.3422	0.3422	9.18517e-20	9.18517e-20
cb	540	540	539.658	539.658
cc	0	0.311641	0	0.205675
ce	0	0.136398	0	0.136398
cf	0	6.37928e-05	0	6.37928e-05
w	10	10	10	10
k1	0.000468	0.000468	0.000468	0.000468
Ka	22.76	22.76	22.76	22.76
k2	0.000227	0.000227	0.000227	0.000227
k4	0.00147	0.00147	0.00147	0.00147
k3	0.00282	0.00282	0.00282	0.00282
r3	0	0.00878827	0	0.00580002
r1	0.0984025	0.0984025	2.31981e-19	2.31981e-19
r2	0	1.621e-05	0	4.28838e-23
r4	0	4.96363e-06	0	1.84167e-22
rb	-0.0984025	-2.31981e-19	-0.0984025	-2.31981e-19
re	0	0.00878695	0	0.00580002
rf	0	2.07778e-05	0	2.27051e-22
ra	-0.0984025	-2.32208e-19	-0.0984025	-2.32208e-19
rc	0.0984025	0.0984025	-0.00834598	-0.00580002





CDP6-H

The equilibrium constant for the reaction

$$\text{tr-OL} \rightleftarrows \text{cs-OL}$$

can be estimated as a function of temperature from the mole fraction data below 100°C.

$$K_p = \frac{y_{cs}}{y_{tr}}$$

$$\frac{d \ln K_p}{d(1/T)} = \frac{\Delta H_R}{R}$$

T	323	375
y_{tr}	.8	.75
y_{cs}	.2	.25
K_p	.25	.33
ln K_p	-1.39	-1.11
1000/T	3.09	2.68

$$\frac{-1.39 - (-1.11)}{3.09 - 2.68} \times 1000 = -683 = \frac{\Delta H_R}{R}$$

$$\Delta H = -1.357 \frac{\text{cal}}{\text{mol}}$$

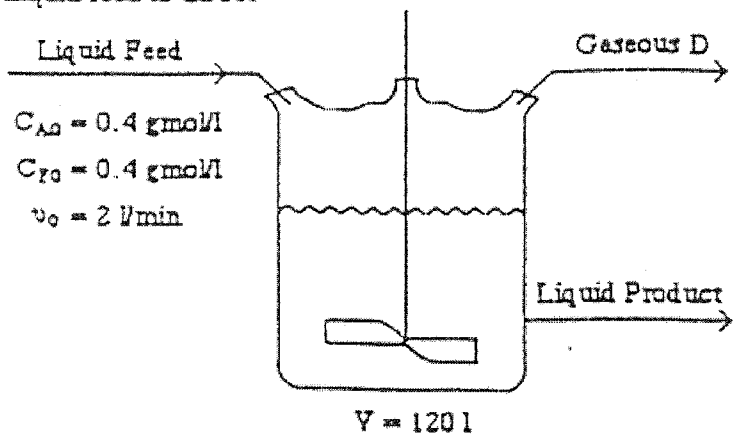
CDP6-I 2, 9-17

CDP6-J

CDP6-K 2, 9-13

CDP6-L

Given: Liquid feed to CSTR



$\varepsilon = 0$

With the following reaction sequence

$A \xrightarrow{k_1} C$ $\quad -r_1 = k_1 C_A \quad k_1 = 0.01\ min^{-1}$

$A \xrightarrow{k_2} B$ $\quad -r_2 = k_2 C_A \quad k_2 = 0.02\ min^{-1}$

$B \xrightarrow{k_3} C$ $\quad -r_3 = k_3 C_B \quad k_3 = 0.07\ min^{-1}$

$F \xrightarrow{k_4} B + D\uparrow$ $\quad -r_4 = k_4 C_F^2 \quad k_4 = 0.50\ l/gmol - min$

(a) Since C is an end product formed through intermediate B by either $A \xrightarrow{k_2} B \xrightarrow{k_3} C$ or $F \xrightarrow{k_4} B + D\uparrow \xrightarrow{k_3} C$, or directly from $A \xrightarrow{k_1} C$, the maximum concentration of C occurs when all A and F have been converted to C : $C_{max} = C_{A0} + C_{F0}$, (with $\varepsilon = 0$).

(b) Both A and F are only decomposed by the above scheme:

Balance on A : $\upsilon_0 C_{A0} - \upsilon_0 C_A = (-r_A) V = (-r_1 - r_2) V = (k_1 + k_2) C_A V$

$$\frac{C_{A0} - C_A}{C_A} = (k_1 + k_2)\frac{V}{\upsilon_0} = (k_1 + k_2)\tau$$

$$\text{or } C_A = \frac{C_{A0}}{1 + (k_1 + k_2)\tau} = \frac{0.4\ gmol/l}{1 + (0.01 + 0.02)\ min^{-1}\left(\frac{120\ l}{2\ l/min}\right)} = \frac{0.4\ gmol/l}{1 + (0.03)\ (60)}$$

$C_A = 0.143\ gmol/l$

Balance on F : $\upsilon_0 C_{F0} - \upsilon_0 C_F = (-r_F) V = k_4 C_F^2 V$

$$k_4 \tau C_F^2 + C_F - C_{F0} = 0 \quad \text{where } \tau = \frac{V}{\upsilon_0} = 60\ min$$

Solving we get: $C_F = 0.1 gmol/l$

Balance for B: $0 - v_o C_B = (-r_B)V = (k_3 C_B - k_2 C_A + k_4 C_F^2)V$

$$C_B = \frac{(k_2 C_A + k_4 C_F^2)\tau}{1 + k_3\tau} = \frac{(0.01\,min^{-1} \times 0.143\,gmol/l + 0.5\,l.mol^{-1}\,min^{-1}\,0.1\,gmol/l^2)60\,min}{1 + 0.07\,min^{-1}\,60\,min}$$

$$C_B = 0.0907\,gmol/l$$

Balance for C: $0 - v_o C_c = (-r_c)V = (-k_3 C_B - k_1 C_A)V$

$$C_C = (k_3 C_B + k_1 C_A)\tau = (0.07\,min^{-1} \times 0.0907\,gmol/l + 0.01\,min^{-1} \times 0.143\,gmol/l)60\,min$$

$$C_C = 0.467\,gmol/l$$

Mole fraction of C $= \dfrac{C_C}{C_A + C_B + C_C + C_F} = \dfrac{0.467}{0.143 + 0.09 + 0.467 + 0.1} = \dfrac{0.467}{0.8} = 0.583$

CDP6-M

4A + 5B → 4C + 6D $\quad -r_{1A} = k_{1A} C_A C_B^2$

2A +1.5B → E + 3D $\quad -r_{2A} = k_{2A} C_A C_B$

2C + B → 2F $\quad -r_{3B} = k_{3B} C_C^2 C_B$

4A + 6C → 5E + 6D $\quad -r_{4C} = k_{4C} C_C C_A^{2/3}$

Rate laws:

$-r_A = r_{1A} + r_{2A} + (2/3)r_{4C}$ $\qquad -r_B = 1.25r_{1A} + 0.75r_{2A} + r_{3B}$

$-r_C = -r_{1A} + 2r_{3B} + r_{4C}$ $\qquad -r_D = -1.5r_{1A} - 1.5r_{2A} - r_{4C}$

$-r_E = -0.5r_{2A} - (5/6)r_{4C}$ $\qquad -r_F = -2r_{3B}$

Using these equations inpolymath to find the exiting molar flow rates.

POLYMATH Results

NLES Report (safenewt)

Nonlinear equations

[1] f(ca) = vo*ca-fao-ra*W = 0
[2] f(cb) = vo*cb-fbo-rb*W = 0
[3] f(cc) = vo*cc-rc*W = 0
[4] f(cd) = vo*cd-rd*W = 0
[5] f(ce) = vo*ce-re*W = 0
[6] f(cf) = vo*cf-rf*W = 0

Explicit equations

[1] vo = 10
[2] fao = 10
[3] W = 3
[4] fbo = 10
[5] rho = 0.0012
[6] k1 = 5
[7] k2 = 2
[8] k3 = 10
[9] k4 = 5
[10] fa = vo*ca
[11] fb = vo*cb
[12] fc = vo*cc
[13] fd = vo*cd
[14] fe = vo*ce
[15] ff = vo*cf
[16] r1 = rho*k1*ca*(cb^2)
[17] r2 = rho*k2*ca*cb
[18] r3 = rho*k3*cb*(cc^2)
[19] r4 = rho*k4*cc*(ca^(2/3))
[20] rf = 2*r3
[21] re = 0.5*r2+(5/6)*r4
[22] ra = -r1+r2-(2/3)*r4
[23] rb = -1.25*r1-0.75*r2-r3
[24] rc = r1-2*r3-r4
[25] rd = 1.5*r1+1.5*r2+r4

NLES Solution

Variable	Value	f(x)	Ini Guess
ca	0.998927	-1.056E-15	1
cb	0.997227	1.082E-15	1
cc	0.0017849	-1.422E-16	0
cd	0.0037612	-1.041E-16	0
ce	3.613E-04	-1.735E-18	0
cf	1.285E-12	1.254E-13	0
vo	10		
fao	10		
W	3		
fbo	10		
rho	0.0012		
k1	5		
k2	2		
k3	10		
k4	5		
fa	9.98927		
fb	9.9722697		
fc	0.0178487		
fd	0.0376119		
fe	0.0036129		
ff	1.285E-11		
r1	0.0059604		
r2	0.0023908		
r3	3.812E-08		
r4	1.07E-05		
rf	7.625E-08		
re	0.0012043		
ra	-0.0035767		
rb	-0.0092436		
rc	0.0059496		
rd	0.0125374		

(b) $\tilde{Y}_{AE} = \dfrac{F_E}{F_{Ao} - F_A} = \dfrac{3.6\times10^{-3}}{10-9.989} = 0.336$

$\tilde{Y}_{BF} = \dfrac{F_F}{F_{Bo} - F_B} = \dfrac{2.29\times10^{-7}}{10-9.973} = 8.25\times10^{-6}$

$\tilde{Y}_{AC} = \dfrac{F_C}{F_{Ao} - F_A} = \dfrac{0.0178}{10-9.989} = 1.663$

CDP6-N 3, 6-21

CDP6-O 3, 6-25

Solutions for Chapter 7 – Reaction Mechanisms, Pathways, Bioreactions and Bioreactors

P7-1 (a) Example 7-1

The graph of I_o/I will remain same if CS_2 concentration changes. If concentration of M increases the slope of line will decrease.

P7-1 (b) Example 7-2

For t = 0 to t = 0.35 sec, PSSH is not valid as steady state not reached.
And at low temperature PSSH results show greatest disparity.

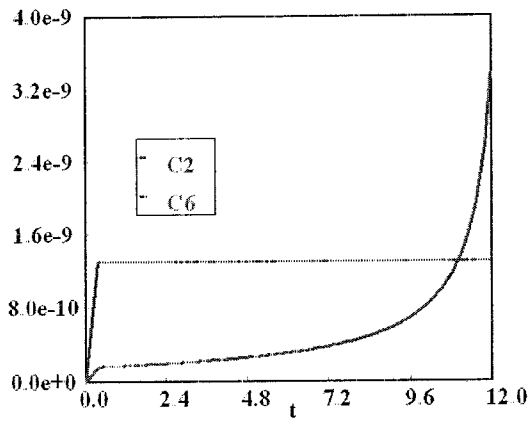
See Polymath program P7-1-b.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	12	12
C1	0.1	2.109E-04	0.1	2.109E-04
C2	0	0	1.311E-09	1.311E-09
C6	0	0	3.602E-09	3.602E-09
C4	0	0	2.665E-07	1.276E-08
C7	0	0	0.0979179	0.0979179
C3	0	0	0.0012475	0.0012475
C5	0	0	0.0979179	0.0979179
C8	0	0	6.237E-04	6.237E-04
CP5	0	0	0.0979123	0.0979123
CP1	0.1	2.166E-04	0.1	2.166E-04
k5	3.98E+09	3.98E+09	3.98E+09	3.98E+09
T	1000	1000	1000	1000
k1	0.0014964	0.0014964	0.0014964	0.0014964
k2	2.283E+06	2.283E+06	2.283E+06	2.283E+06
k4	9.53E+08	9.53E+08	9.53E+08	9.53E+08
k3	5.71E+04	5.71E+04	5.71E+04	5.71E+04

ODE Report (STIFF)

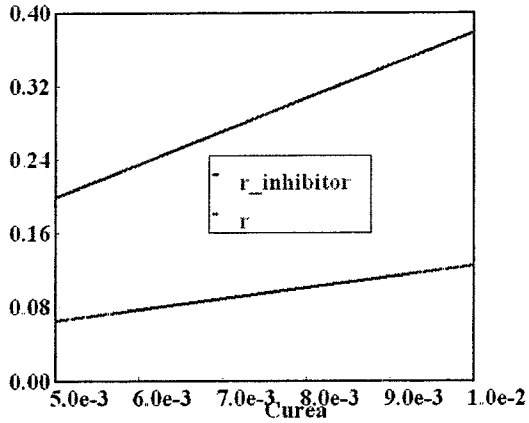
Differential equations as entered by the user
[1] d(C1)/d(t) = -k1*C1-k2*C1*C2-k4*C1*C6
[2] d(C2)/d(t) = 2*k1*C1-k2*C1*C2
[3] d(C6)/d(t) = k3*C4-k4*C6*C1
[4] d(C4)/d(t) = k2*C1*C2-k3*C4+k4*C6*C1-k5*C4^2
[5] d(C7)/d(t) = k4*C1*C6
[6] d(C3)/d(t) = k2*C1*C2
[7] d(C5)/d(t) = k3*C4
[8] d(C8)/d(t) = 0.5*k5*C4^2
[9] d(CP5)/d(t) = k3*(2*k1/k5)^0.5*CP1^0.5
[10] d(CP1)/d(t) = -k1*CP1-2*k1*CP1-(k3*(2*k1/k5)^0.5)*(CP1^0.5)



P7-1 (c) Example 7-3

The inhibitor shows competitive inhibition.

See Polymath program P7-1-c.pol.



P7-1 (d) Example 7-4

1)Now $C_{urea} = 0.001 mol/dm^3$ and t = 10 min = 600 sec.

$$t = \frac{k_M}{V_{MAX}} \ln\left(\frac{1}{1-X}\right) + \frac{C_{urea} X}{V_{MAX}}$$

$$600\,\text{sec} = \frac{0.0266 mol/dm^3}{0.000266 mol/s.dm^3} \ln\left(\frac{1}{1-X}\right) + \frac{(0.001 mol/dm^3)X}{0.000266 mol/s.dm^3}$$

Solving, we get X = 0.9974.

2) For CSTR, $\tau = t = 461.7\,\text{sec}$

$$\tau = \frac{C_{urea} X}{-r_{urea}} \qquad -r_{urea} = \frac{V_{MAX} C_{urea}}{K_M + C_{urea}}$$

$$-r_{urea} = \frac{C_{urea} X}{\tau}$$

$$\Rightarrow \frac{0.000266 mol/s.dm^3 \times 0.1 mol/dm^3 (1-X)}{0.0266 mol/dm^3 + 0.1 mol/dm^3 (1-X)} = \frac{(0.1 mol/dm^3)X}{461.7\,\text{sec}}$$

Solving, we get X = 0.675

See Polymath program P7-1-c.pol.

POLYMATH Results
NLE Solution

Variable	Value	f(x)	Ini Guess
X	0.6751896	-8.062E-10	0.5

NLE Report (safenewt)

Nonlinear equations
[1] f(X) = 0.0000266*(1-X)/(0.0266+0.1*(1-X))-0.1*X/461.7 = 0

3) For PFR,

$$\tau = \int_{C_{ures}}^{C_O} \frac{dC_{urea}}{-r} \qquad \text{and } C_{urea} = C_{urea0}(1-X)$$

$$\Rightarrow \qquad \tau = \frac{k_M}{V_{MAX}} \ln\left(\frac{1}{1-X}\right) + \frac{C_{urea} X}{V_{MAX}}$$

Same as batch reactor, but t replaced by τ X = 0.8

P7-1 (e) Example 7-5

$$Y_{S/P} = \frac{-\Delta C_S}{\Delta C_P} = \frac{-(238.7 - 245)}{5.03 - 2.14} = 2.18 g/g$$

$$Y_{P/S} = \frac{1}{Y_{S/P}} = \frac{1}{2.18} = 0.46 g/g$$

$$Y_{S/C+P} = \frac{1}{Y_{C+P/S}} = \frac{1}{0.075 + 0.46} = 1.87 g/g$$

Yes there is disparity as substrate is also used in maintenance.

P7-1 (f) Example 7-6

1) if we go for 24 hrs, fermentation will stop at 13.2 hrs as $C_P = C_P^*$.

See Polymath program P7-1-f-1.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	13.2	13.2
Cc	1	1	16.558613	16.550651
Cs	250	39.292786	250	39.292786
Cp	0	0	92.981376	92.981376
rd	0.01	0.01	0.16559	0.1655065
Ysc	12.5	12.5	12.5	12.5
Ypc	5.6	5.6	5.6	5.6
Ks	1.7	1.7	1.7	1.7
m	0.03	0.03	0.03	0.03
umax	0.33	0.33	0.33	0.33
rsm	0.03	0.03	0.4967701	0.4965195
kobs	0.33	0.0039386	0.33	0.0039386
rg	0.3277712	0.0624825	2.1455962	0.0624825

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Cc)/d(t) = rg-rd
[2] d(Cs)/d(t) = Ysc*(-rg)-rsm
[3] d(Cp)/d(t) = rg*Ypc

Explicit equations as entered by the user
[1] rd = Cc*0.01
[2] Ysc = 1/0.08
[3] Ypc = 5.6
[4] Ks = 1.7
[5] m = 0.03
[6] umax = 0.33
[7] rsm = m*Cc
[8] kobs = (umax*(1-Cp/93)^0.52)
[9] rg = kobs*Cc*Cs/(Ks+Cs)

2)Semi-Batch reactor:

See Polymath program P7-1-f-2.pol.

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	24	24
Cc	1.0E-04	1.0E-04	0.0474697	0.0474697
Cs	1.0E-04	1.0E-04	12.206266	12.206266
Cp	0	0	0.2748298	0.2748298
rd	1.0E-06	1.0E-06	4.747E-04	4.747E-04
Ysc	12.5	12.5	12.5	12.5
Ypc	5.6	5.6	5.6	5.6
Ks	1.7	1.7	1.7	1.7
m	0.03	0.03	0.03	0.03
umax	0.33	0.33	0.33	0.33
rsm	3.0E-06	3.0E-06	0.0014241	0.0014241
kobs	0.33	0.3294925	0.33	0.3294925
rg	1.941E-09	1.941E-09	0.0137289	0.0137289
Cso	5	5	5	5
vo	0.5	0.5	0.5	0.5
Vo	1	1	1	1
V	1	1	13	13

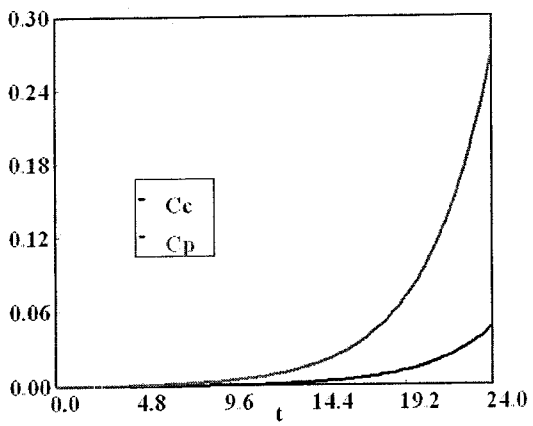
ODE Report (RKF45)

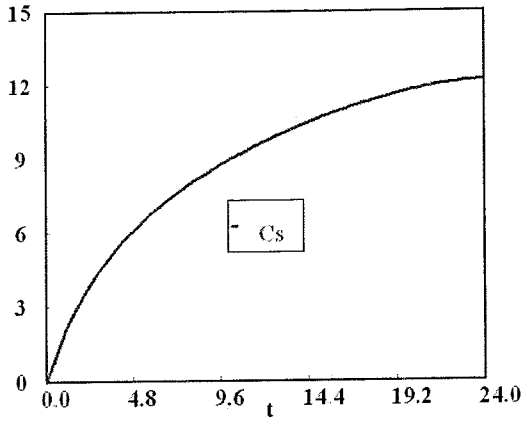
Differential equations as entered by the user

[1] d(Cc)/d(t) = rg-rd
[2] d(Cs)/d(t) = vo*Cso/V + Ysc*(-rg)-rsm
[3] d(Cp)/d(t) = rg*Ypc

Explicit equations as entered by the user

[1] rd = Cc*0.01
[2] Ysc = 1/0.08
[3] Ypc = 5.6
[4] Ks = 1.7
[5] m = 0.03
[6] umax = 0.33
[7] rsm = m*Cc
[8] kobs = (umax*(1-Cp/93)^0.52)
[9] rg = kobs*Cc*Cs/(Ks+Cs)
[10] Cso = 5
[11] vo = 0.5
[12] Vo = 1
[13] V = Vo+vo*t





3)Changes from part(2) $r_g = \mu_{max}\left(1-\frac{C_P}{C_P^*}\right)^{0.52} \frac{C_C C_S}{K_S + C_S + \frac{C_S^2}{K_I}}$

See Polymath program P7-1-f-3.pol.

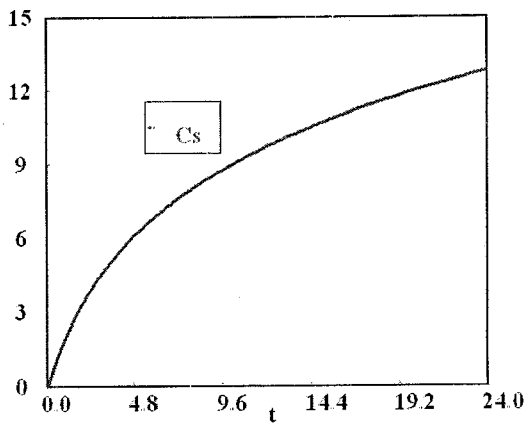
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	24	24
Cc	1.0E-04	1.0E-04	1.514E-04	1.514E-04
Cs	1.0E-04	1.0E-04	12.823709	12.823709
Cp	0	0	4.669E-04	4.669E-04
rd	1.0E-06	1.0E-06	1.514E-06	1.514E-06
Ysc	12.5	12.5	12.5	12.5
Ypc	5.6	5.6	5.6	5.6
Ks	1.7	1.7	1.7	1.7
m	0.03	0.03	0.03	0.03
umax	0.33	0.33	0.33	0.33
rsm	3.0E-06	3.0E-06	4.541E-06	4.541E-06
kobs	0.33	0.3299991	0.33	0.3299991
Ki	0.7	0.7	0.7	0.7
Cso	5	5	5	5
vo	0.5	0.5	0.5	0.5
Vo	1	1	1	1
V	1	1	13	13
rg	1.941E-09	1.941E-09	8.215E-06	2.568E-06

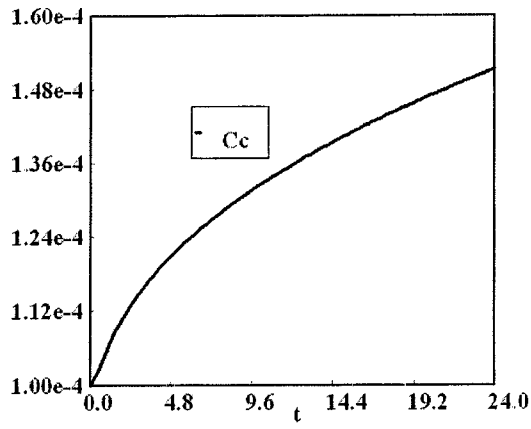
ODE Report (RKF45)

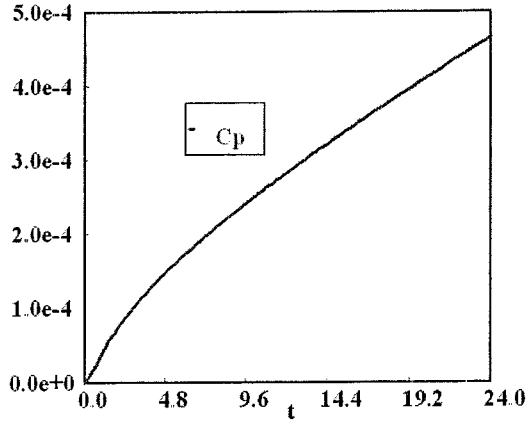
Differential equations as entered by the user
[1] d(Cc)/d(t) = rg-rd
[2] d(Cs)/d(t) = vo*Cso/V + Ysc*(-rg)-rsm
[3] d(Cp)/d(t) = rg*Ypc

Explicit equations as entered by the user
[1] rd = Cc*0.01
[2] Ysc = 1/0.08
[3] Ypc = 5.6
[4] Ks = 1.7
[5] m = 0.03
[6] umax = 0.33
[7] rsm = m*Cc

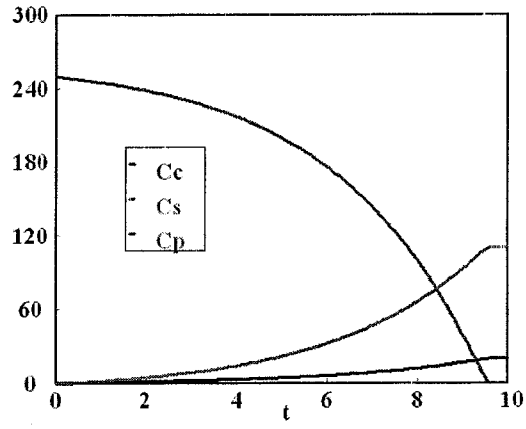


```
[8] kobs = (umax*(1-Cp/93)^0.52)
[9] Ki = 0.7
[10] Cso = 5
[11] vo = 0.5
[12] Vo = 1
[13] V = Vo+vo*t
[14] rg = kobs*Cc*Cs/(Ks+Cs+Cs^2/Ki)
```





4)After 9.67 hrs, $C_S = 0$.



P7-1 (g) Individualized solution

P7-1 (h) Individualized solution

P7-1 (i) Individualized solution

P7-1 (j) Individualized solution

P7-1 (k) Individualized solution

P7-1 (l) Individualized solution

P7-1 (m) Individualized solution

P7-1 (n) Individualized solution

P7-2 Solution is in the decoding algorithm given with the modules.

P7-3

Burning:

$$O_2 \xrightarrow{k_1} 2O\cdot$$

$$O\cdot + H_2O \xrightarrow{k_2} 2OH\cdot$$

$$CO\cdot + OH\cdot \xrightarrow{k_3} CO_2 + H\cdot$$

$$H\cdot + O_2 \xrightarrow{k_4} OH\cdot + O\cdot$$

Burning of Model Compound

$$HCl + H\cdot \xrightarrow{k_5} H_2 + Cl\cdot$$

$$H\cdot + Cl\cdot \xrightarrow{k_6} HCl$$

Retardation

$$\boxed{-r_{CO} = r_{CO_2} = k_3(CO)(OH\cdot)}$$

$$r_{O\cdot} = 0 = 2k_1(O_2) - k_2(O\cdot)(H_2O) + k_4(H\cdot)(O_2)$$

then

$$(O\cdot) = \frac{2k_1(O_2) + k_4(H\cdot)(O_2)}{k_2(H_2O)}$$

$$r_{OH\cdot} = 0 = 2k_2(O\cdot)(H_2O) - k_3(CO)(OH\cdot) + k_4(H\cdot)(O_2)$$

then

$$(OH\cdot) = \frac{2k_2(O\cdot)(H_2O) + k_4(H\cdot)(O_2)}{k_3(CO)}$$

substituting for $(O\cdot)$

$$(OH\cdot) = \frac{2k_2(H_2O)\dfrac{2k_1(O_2) + k_4(H\cdot)(O_2)}{k_2(H_2O)} + k_4(H\cdot)(O_2)}{k_3(CO)}$$

$$(OH\cdot) = \frac{4k_1(O_2) + 3k_4(H\cdot)(O_2)}{k_3(CO)}$$

$$-r_{CO} = r_{CO_2} = k_3(CO)(OH\cdot)$$

$$-r_{CO} = 4k_1(O_2) + 3k_4(H\cdot)(O_2)$$

$$-r_{H\cdot} = k_3(CO)(OH\cdot) - k_4(H\cdot)(O_2) - k_5(HCl)(H\cdot) - k_6(Cl\cdot)(H\cdot)$$

$$-r_{Cl\cdot} = 0 = k_5(HCl)(H\cdot) - k_6(Cl\cdot)(H\cdot)$$

$$Cl\cdot = \frac{k_5 (HCl)}{k_6}$$

$$r_{H\cdot} = 4k_1 (O_2) + 3k_4 (H\cdot)(O_2) - k_4 (H\cdot)(O_2) - 2k_5 (HCl)(H\cdot)$$

$$\boxed{r_{H\cdot} = 4k_1 (O_2) + 2[k_4 (O_2) - k_5 (HCl)](H\cdot)}$$

$$r_{H\cdot} = a + b(H\cdot)$$

Constant Volume

$$e^{-bt}\frac{dC_H}{dt} - C_H \cdot *b * e^{-bt} = ae^{-bt} \qquad \frac{dC_H}{dt} = a + bC_H$$

Using the integrating factor

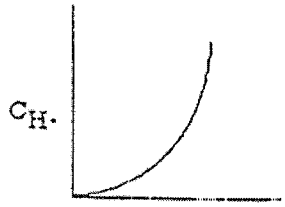
$$\frac{d(e^{-bt}C_{H\cdot})}{dt} = a\, e^{-bt}$$

$$C_{H\cdot} = -\frac{a}{b} + K_1 e^{bt}$$

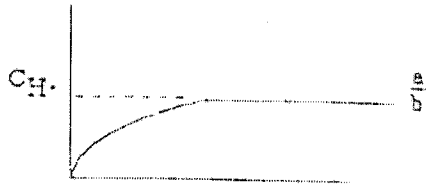
$t = 0 \quad C_{H\cdot} = 0 \quad$ therefore $K_1 = \frac{a}{b}$

$$\boxed{C_{H\cdot} = \frac{a}{b}\left[e^{bt} - 1\right]}$$

If $k_4 (O_2) > k_5 (HCl)$, then "b" is positive



If $k_5 (HCl) > k_4 (O_2)$, then "b" is negative



$$\frac{dC_{CO}}{dt} = r_{CO} = -\left[4k_1(O_2) + 3k_4(H\cdot)(O_2)\right]$$

$$= -a - p(C_{H\cdot})$$

$$= -a - p\left[\frac{a}{b}e^{bt} - 1\right]$$

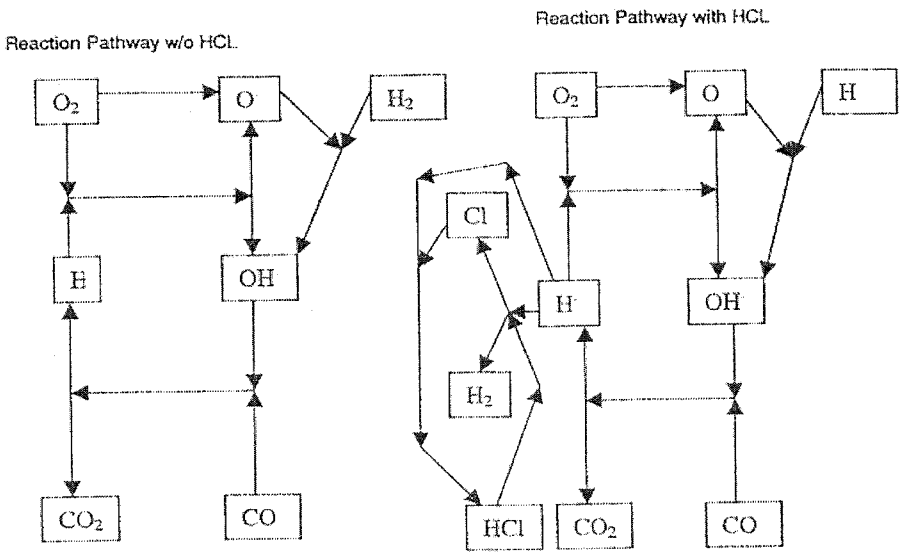
$$p(C_H) = 3k_4(O_2)C_H$$

$$p = 3k_4(O_2)$$

$$a = 4k_1(O_2)$$

$t = 0 \quad C_{CO} = C_{CO,0}$

$$\boxed{C_{CO} = C_{CO,0} - at - p\frac{a}{b^2}e^{bt} + pt}$$



P7-3 (d) Individualized solution

P7-3 (e) Individualized solution

P7-4

The reaction sequence is:

$$CH_3CHO \xrightarrow{k_1} CH_3\cdot + CHO\cdot$$

$$CH_3\cdot + CH_3CHO \xrightarrow{k_2} CH_3\cdot + CO + CH_4$$

$$CHO\cdot + CH_3CHO \xrightarrow{k_3} CH_3\cdot + 2CO + H_2$$

$$2CH_3\cdot \xrightarrow{k_4} C_2H_6$$

$r_1 = k_1 C_{AC}$

$r_2 = k_2 C_{AC} C_{CH_3\cdot}$

$r_3 = k_3 C_{CHO\cdot} C_{AC}$

$r_4 = k_4 C^2_{CH_3\cdot}$

$$-r_{AC} = r_1 + r_2 + r_3 = k_1 C_{AC} + k_2 C_{AC} C_{CH_3\cdot} + k_3 C_{AC} C_{CHO\cdot}$$

$$= C_{AC}\left[k_1 + k_2 C_{CH_3\cdot} + k_3 C^2_{CHO\cdot}\right] \quad (1)$$

Active intermediates: $CH_3\cdot$, $CHO\cdot$

$$-r_{CH_3} = -r_1 + r_2 - r_3 + \frac{1}{2} r_4 = 0$$

$$= -k_1 C_{AC} + k_2 C_{AC} C_{CH_3\cdot} - k_3 C_{CHO\cdot} C_{AC} - k_2 C_{AC} C_{CH_3} + \frac{1}{2} k_4 C^2_{CH_3\cdot}$$

$$= -k_1 C_{AC} + k_2 C_{AC} C_{CH_3\cdot} - k_3 C_{CHO\cdot} C_{AC} + \frac{1}{2} k_4 C^2_{CH_3\cdot} \quad (2)$$

$$-r_{CHO\cdot} = -r_1 + r_3 = -k_1 C_{AC} + k_3 C_{CHO\cdot} C_{AC} = 0$$

$$\text{or} \quad C_{CHO\cdot} = \frac{k_1}{k_3} \quad (3)$$

Substituting (3) in (2) gives:

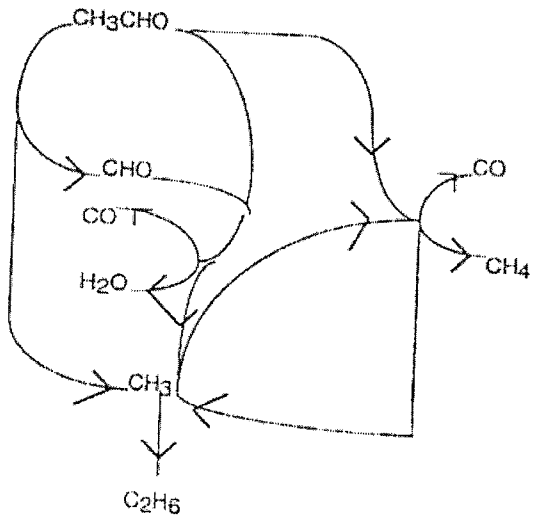
$$\frac{k_4 C^2_{H_3\cdot}}{2} = k_1 C_{AC} + k_3 C_{CHO\cdot} C_{AC} = k_1 C_{AC} + k_1 C_{AC} = 2k_1 C_{AC}$$

$$\text{or} \quad C_{CH_3\cdot} = 2(C_{AC})^{1/2}\left(\frac{k_1}{k_4}\right)^{1/2}$$

$$-r_{AC} = C_{AC}\left[k_1 + 2k_2\left(\frac{k_1}{k_4}\right)^{\frac{1}{2}}(C_{AC})^{\frac{1}{2}} + \frac{k_1^2}{k_3}\right]$$

$$= k_1 C_{AC}\left[1 + \frac{2k_2}{\sqrt{k_1 k_4}}\sqrt{C_{AC}} + \frac{k_1}{k_3}\right]$$

With $\frac{k_2}{\sqrt{k_1 k_4}} >> 1$ or $C_{AC} >> 1$, $-r_{AC} \propto (C_{AC})^{3/2}$ as suggested by equation (7-2).



P7-4 (d) Individualized solution

P7-4 (e) Individualized solution

P7-5 (a)

Gas phase reaction

$$2NO + O_2 \xrightarrow{k_2} 2NO_2$$

with third order kinetics and an apparent negative activation energy. Consider the following mechanism, in which NO_3 is an active intermediate.

$$NO + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} NO_3 \qquad r_1 = k_1[NO][O_2] - k_{-1}[NO_3]$$

$$NO_3 + NO \xrightarrow{k_2} 2NO_2 \qquad r_2 = k_2[NO][NO_3]$$

$$-r_{NO} = -r_1 - r_2$$

$$= -k_1[NO][O_2] + k_{-1}[NO_3] - k_2[NO][NO_3]$$

$$r_{NO_3} = r_1 - r_2$$

$$= k_1[NO][O_2] - k_{-1}[NO_3] - k_2[NO][NO_3]$$

$$[NO_3] = \frac{k_1[NO][O_2]}{k_{-1} + k_2[NO]}$$

$$-r_{NO} = -k_1[NO][O_2] + (k_{-1} - k_2[NO])\frac{k_1[NO][O_2]}{k_{-1} + k_2[NO]}$$

$$= \frac{-k_1k_2[NO]^2[O_2] - k_1k_2[NO]^2[O_2]}{k_{-1} + k_2[NO]}$$

$$= \frac{-2k_1k_2[NO]^2[O_2]}{k_{-1} + k_2[NO]}$$

$$k_{-1} >> k_2[NO]$$

$$-r_{NO} = \frac{2k_1k_2}{k_{-1}}[NO]^2[O_2]$$

For the overall activation energy to be negative,

$$-(E_1 + E_2) + E_{-1} = E_{ov} < 0$$

$$\Rightarrow E_{-1} < (E_1 + E_2)$$

As long as all energies are positive values.

P7-5 (b)

$$Cl_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2Cl$$

$$Cl + CO \underset{k_4}{\overset{k_3}{\rightleftarrows}} COCl$$

$$COCl + Cl_2 \xrightarrow{k_5} COCl_2 + Cl$$

$$r_{COCl} = 0 = k_3(Cl)(CO) - k_4(COCl) - k_5(COCl)(Cl_2)$$

$$(COCl) = \frac{k_3(Cl)(CO)}{k_4 + k_5(Cl_2)}$$

$$r_{COCl_2} = k_5(COCl)(Cl_2) = \frac{k_1 k_3(CO)(Cl)(Cl_2)}{k_4 + k_5(Cl_2)}$$

$$r_{Cl} = 0 = k_1(Cl_2) - k_2(Cl)^2 - k_3(Cl)(CO) + k_4(COCl) + k_5(COCl)(Cl_2)$$

add r_{COCl} to r_{Cl}

$$r_{Cl} + r_{COCl} = 0 + 0 = k_1(Cl_2) - k_2(Cl)^2$$

$$(Cl)^2 = \frac{k_1}{k_2}(Cl_2)$$

$$(Cl) = \sqrt{\frac{k_1}{k_2}(Cl_2)}$$

$$r_{COCl_2} = \frac{k_1 k_3(CO)\frac{k_1}{k_2}(Cl_2)^{0.5}(Cl_2)}{k_4 + k_5(Cl_2)} = \frac{k_1 k_3 \frac{k_1}{k_2}(CO)(Cl_2)^{\frac{3}{2}}}{k_4 + k_5(Cl_2)}$$

$$k_4 >> k_5(Cl_2)$$

$$r_{COCl_2} = \frac{k_1^2 k_3}{k_2 k_4}(CO)(Cl_2)^{\frac{3}{2}}$$

P7-5 (c) Individualized solution

P7-5 (d) Individualized solution

P7-6 (a)

$$NO_2 + h\nu \xrightarrow{K_1} NO + O$$

$$O_2 + O + M \xrightarrow{K_2} O_3 + M$$

$$O_3 + NO \xrightarrow{K_3} NO_2 + O_2$$

Using PSSH,

$$r_O = 0 = k_1 C_{NO_2} - k_2 C_{O_2} C_O C_M \qquad \Rightarrow \qquad C_O C_M = \frac{k_1 C_{NO_2}}{k_2 C_{O_2}}$$

$$r_{O_3} = 0 = k_2 C_{O_2} C_O C_M - k_3 C_{O_3} C_{NO} \quad \Rightarrow \quad C_{O_3} = \frac{k_2 C_{O_2} C_O C_M}{k_3 C_{NO}} = \frac{k_1 C_{NO_2}}{k_3 C_{NO}}$$

P7-6 (b)

$$\frac{dC_{O_3}}{dt} = k_2 C_{O_2} C_O C_M - k_3 C_{O_3} C_{NO} \qquad \frac{dC_{NO_2}}{dt} = -k_1 C_{NO_2} + k_3 C_{O_3} C_{NO}$$

$$\frac{dC_{NO}}{dt} = k_1 C_{NO_2} - k_3 C_{O_3} C_{NO} \qquad \frac{dC_{O_2}}{dt} = -k_2 C_{O_2} C_O C_M + k_3 C_{O_3} C_{NO}$$

$$\frac{dC_O}{dt} = k_1 C_{NO_2} - k_2 C_{O_2} C_O C_M$$

P7-6 (c)

$$-r_{O_3} = \left[\frac{k[O_3]^2[M]}{[O_2][M] + k^1[O_3]}\right]$$

O_2, M and O_3 appear in the denominator, active species suggested is O.

Applying rule 3 of table 7-1 to O_2 and O_3:

$$O_3 + O \rightarrow 2O_2$$

$$O_2 + O \rightarrow O_3$$

O_3 and M appear in the numerator. Applying rule 1 of Table 7-1 to O_3: $O_3 \rightarrow O_2 + O$

If the second and third equations are combined, and M is added to each side of the equation:

$$M + O_3 \underset{k3}{\overset{k1}{\rightleftharpoons}} O_2 + O + M$$

$$O_3 + O \xrightarrow{k3} 2O_2$$

A mechanism is proposed which satisfies all the rules of thumb:

$$r_{O_3} = -r_1 + r_2 - r_3 = -k_1[M][O_3] + k_2[O_2][O][M] - k_3[O][O_3] = 0$$

$$r_O = r_1 - r_2 - r_3 = k_1[M][O_3] - k_2[O_2][O][M] - k_3[O][O_3] = 0$$

$$[O] = \frac{k_1[M][O_3]}{k_2[O_2][M] + k_3[O_3]}$$

Then $r_{O_3} = -k_1[M][O_3] + \dfrac{k_1 k_2[M]^2[O_3][O_2] - k_1 k_3[M][O_3]^2}{k_2[O_2][M] + k_3[O_3]}$

$$r_{O_3} = \frac{-k_1 k_2[M]^2[O_3][O_2] + k_1 k_2[M]^2[O_3][O_2] - 2k_1 k_3[M][O_3]^2}{k_2[O_2][M] + k_3[O_3]}$$

$$r_{O_3} = \frac{\frac{2k_1 k_3}{k_2}[M][O_3]^2}{[O_2][M] + \frac{k_3}{k_2}[O_3]} \quad \text{with } k = \frac{2k_1 k_3}{k_2} \text{ and } k^1 = \frac{k_3}{k_2}$$

P7-6 (d) Individualized solution

P7-6 (e) Individualized solution

P7-7(a)

LOW TEMPERATURES - NO ANTIOXIDANT

$$\frac{d[I\bullet]}{dt} = r_i = 2k_0[I_2] - k_i[I\bullet][RH] \qquad (A)$$

$$\frac{d[RH]}{dt} = -k_i[I\bullet][RH] - k_{P_2}[RO_2\bullet][RH] \qquad (B)$$

$$\frac{d[RO_2\bullet]}{dt} = k_{P_1}[R\bullet][O_2] - k_{P_2}[RO_2\bullet][RH] - k_t[RO_2\bullet]^2 \qquad (C)$$

$$\frac{d[R\bullet]}{dt} = k_i[RH][I\bullet] - k_{P_1}[R\bullet][O_2] + k_{P_2}[RO_2\bullet][RH] \qquad (D)$$

PSSA .... $\frac{d[RADICALS]}{dt} = 0$

$$(A) = 0 \quad r_i = 0 \quad \boxed{[I\bullet] = \frac{2k_0[I_2]}{k_i[RH]}}$$

$$\frac{d[R\bullet]}{dt} = 0 = k_i[RH][I\bullet] - k_{P1}[R\bullet][O_2] + k_{P_2}[RO_2\bullet][RH]$$

$$\uparrow$$

$$\boxed{\frac{2k_0[I_2]}{k_i[RH]}}$$

$$\boxed{[R\bullet] = \frac{2k_0[I_2] + k_{P_2}[RO_2\bullet][RH]}{k_{P_1}[O_2]}}$$: still need to eliminate $[RO_2\bullet]$

$$\frac{d[RO_2\bullet]}{dt} = 0 = k_{P_1}[R\bullet][O_2] - k_{P_2}[RO_2\bullet][RH] - k_t[RO_2\bullet]^2$$

Substitute for $[R\bullet]$:

$$2k_0[I_2] - k_t[RO_2\bullet]^2 = 0$$

$$\boxed{[RO_2\bullet] = \sqrt{\frac{2k_0}{k_t}[I_2]}}$$

Now substitute the expressions for the radicals into $\frac{d[RH]}{dt}$ the expression for the degradation of the oil.

$$\frac{d[RH]}{dt} = -k_i\left[\frac{2k_0[I_2]}{k_i[RH]}\right][RH] - k_{P_2}\left[\frac{2k_0[I_2]}{k_t}\right]^{1/2}[RH]$$

$$\downarrow$$

$$[I\bullet]$$

$$= 2k_0[I_2] - \left[\frac{2k_{P_2}^2[k_0]}{k_t}\right]^{1/2}[I_2]^{1/2}[RH]$$

ODE to be solved- low temperatures, no antioxidant:

$$\boxed{-\frac{d[RH]}{dt} = 2k_0[I_2] + \left[\frac{2k_{P_2}^2[k_0]}{k_t}\right]^{1/2}[I_2]^{1/2}[RH]}$$

P7-7(b)

Low temperatures with anti-oxidant

$$\frac{d[R\bullet]}{dt} = k_i[RH][I\bullet] - k_{P_1}[R\bullet][O_2] + k_{P_2}[RO_2\bullet][RH] \text{ (same)}$$

$$\frac{d[A\bullet]}{dt} = k_{A1}[AH][RO_2\bullet] - k_{A2}[A\bullet][RO_2\bullet]$$

$$\frac{d[RH]}{dt} = -k_i[I\bullet][RH] - k_{P_2}[RO_2\bullet][RH]$$

Apply PSSH:

$$\frac{d[I\bullet]}{dt} = 0 \qquad \boxed{[I\bullet] = \frac{2k_0[I_2]}{k_i[RH]}}$$

$$\frac{d[A\bullet]}{dt} = 0 \Rightarrow \boxed{[A\bullet] = \frac{k_{A1}[AH]}{k_{A2}}}$$

$$\frac{d[R\bullet]}{dt} = 0 \qquad \boxed{[R\bullet] = \frac{2k_0[I_2] + k_{P_2}[RO_2\bullet][RH]}{k_{P_1}[O_2]}}$$

$$\frac{d[RO_2\bullet]}{dt} \equiv 0 \quad 2k_0[I_2] - k_t[RO_2\bullet]^2 - 2(k_{A1}[AH][RO_2\bullet])$$

$$\therefore -k_t[RO_2\bullet]^2 - 2k_{A1}[AH][RO_2\bullet] + 2k_0[I_2] = 0$$

$$k_t[RO_2\bullet]^2 + (2k_{A1}[AH])[RO_2\bullet] - 2k_0[I_2] = 0 \qquad \text{Quadradtic in } [RO_2\bullet]$$

$$\boxed{[RO_2\bullet] = \frac{-2k_{A1}[AH] \pm \sqrt{(2k_{A1}[AH])^2 + 8k_t k_0[I_2]}}{2k_t}} \qquad [RO_2\bullet] \text{ MUST be positive}$$

Now (FINALLY!), let's substitute into $\frac{d[RH]}{dt}$:

$$\frac{d[RH]}{dt} = -k_i[I\bullet][RH] - k_{P_2}[RO_2\bullet][RH]$$

$$\frac{d[AH]}{dt} = -k_{A1}[AH][RO_2\bullet] = -k_{A1}[AH]\frac{-2k_{A1}[AH] + \sqrt{(2k_{A1}[AH])^2 + 8k_t k_0[I_2]}}{2k_t}$$

$$\frac{d[RH]}{dt} = -2k_0[I_2] - k_{P_2}[RH]\frac{-2k_{A1}[AH] + \sqrt{(2k_{A1}[AH])^2 + 8k_t k_0[I_2]}}{2k_t}$$

P7-7(c)

If the radicals are formed at a constant rate, then the differential equation for the concentration of the radicals becomes:

$$\frac{d[I\bullet]}{dt} = k_0 - k_i[I\bullet][RH] = 0$$

and $[I\bullet] = \frac{k_0}{k_i[RH]}$

The substitution in the differential equation for R· also changes. Now the equation is:

$$\frac{d[R\bullet]}{dt} = k_i[I\bullet][RH] - k_{P1}[R\bullet][O_2] + k_{P2}[RO_2\bullet][RH] = 0$$

and solving and substituting gives: $[R\bullet] = \frac{k_0 + k_{P2}[RO_2\bullet][RH]}{k_{P1}[O_2]}$

Now we have to look at the balance for RO_2·.

$$\frac{d[RO_2\bullet]}{dt} = k_{P1}[R\bullet][O_2] - k_P[RO_2\bullet][RH] - k_t[RO_2\bullet]^2 = 0$$

and if we substitute in our expression for [R·] we get

$0 = k_0 - k_t[RO_2\bullet]^2$ which we can solve for [RO_2·].

$$[RO_2\bullet] = \sqrt{\frac{k_0}{k_t}}$$

Now we are ready to look at the equation for the motor oil.

$$\frac{d[RH\bullet]}{dt} = -k_i[I\bullet][RH] - k_{P2}[RO_2\bullet][RH]$$

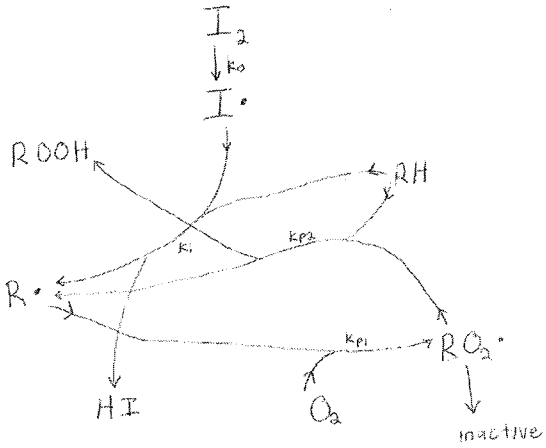
and making the necessary substitutions, the rate law for the degradation of the motor oil is:

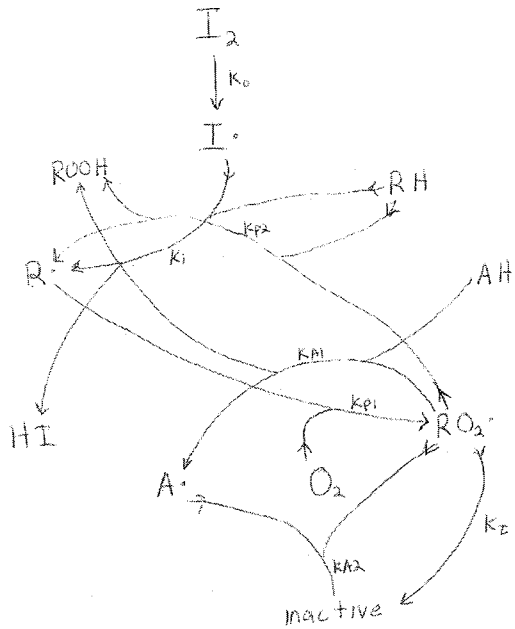
$$\frac{d[RH\bullet]}{dt} = r_{RH} = -k_0 - k_{P2}\sqrt{\frac{k_0}{k_t}}[RH]$$

P7-7(d)

Without antioxidants

With antioxidants





P7-7 (e) Individualized solution

P7-7 (f) Individualized solution

P7-7 (g) Individualized solution

P7-8 (a)

Given: Illness mechanism

$H \xrightarrow{k_1} I$	$r_1 = k_1[H]$	(Healthy person gets ill)
$I + H \xrightarrow{k_2} 2I$	$r_2 = k_2[H][I]$	(healthy person contracts disease from ill person)
$I \xrightarrow{k_3} H$	$r_3 = k_3[I]$	(Ill person gets well)
$I \xrightarrow{k_4} D$	$r_4 = k_4[I]$	(Ill person dies)

$r_D = k_4[I]$

Applying pseudo steady state hypothesis to I: $r_I = r_1 + r_2 - r_3 - r_4 = 0$

or $k_1[H] + k_2[H][I] - k_3[I] - k_4[I] = 0$ or $[I] = \dfrac{k_1[H]}{(k_3 + k_4) - k_2[H]}$

$\therefore\ r_D = \dfrac{k_1 k_4[H]}{k_3 + k_4 - k_2[H]}$

P7-8 (b)

at $[H] = \dfrac{k_3 + k_4}{k_2}$ the death rate becomes infinite.

P7-8 (c)

It is enlightening to calculate r_H:

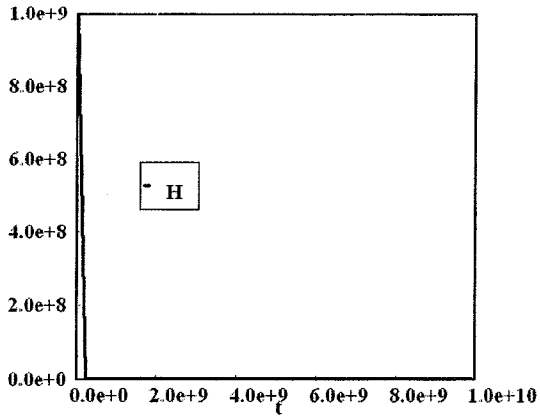
$$r_H = -r_1 - r_2 + r_3 = -k_1[H] - k_2[H][I] + k_3[I] = -k_1[H] - (k_2[H] - k_3)[I]$$

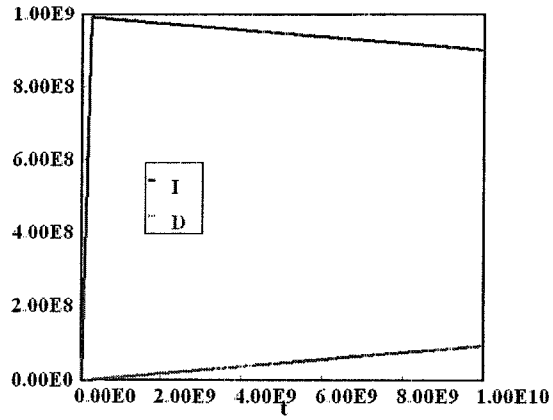
$$r_H = \frac{-k_1 k_4[H]}{(k_3 + k_4 - k_2[H])} = -r_D < 0$$

This expression states that for every person who is ill and dies, a healthy person becomes ill. For the population as a whole, "illness is but a 'way station' on the road to 'death'." Note further that $r_H < 0$, and therefore the population will die off eventually. Initially, the death rate will be slow, until $[H] \to (k_3 + k_4)/k_2$. The model neglects the possibility of birth. In practice, it would appear to be useful in describing epidemic-like diseases, which occur over a short time so that the birth rate can be neglected.

P7-8 (d)

See Polymath program P7-8-d.pol.





Everyone becomes ill rather quickly, and the rate at which an ill person recovers to a healthy person is much slower than the rate at which a healthy person becomes ill. Eventually everyone is ill and people start dying.

P7-8 (e) Individualized solution

P7-8 (f) Individualized solution

P7-9 (a)

Starting with the design equation for a batch reactor

$$\frac{dC_P}{dt} = r_P$$

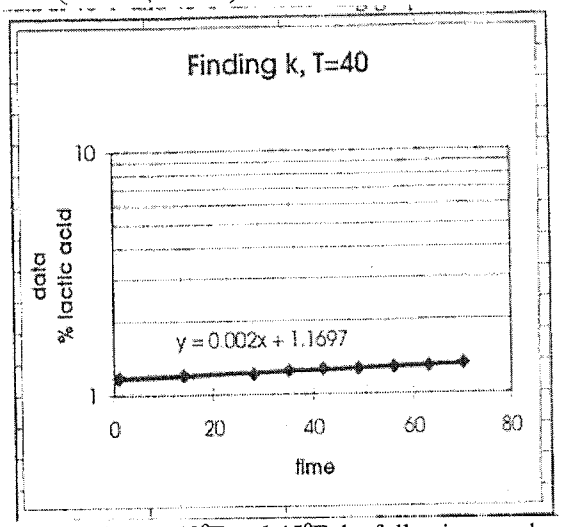
$$r_P = kC$$

$$C = (C_{SO} - C_P)\left(1 - \frac{C_P}{1.4}\right)$$

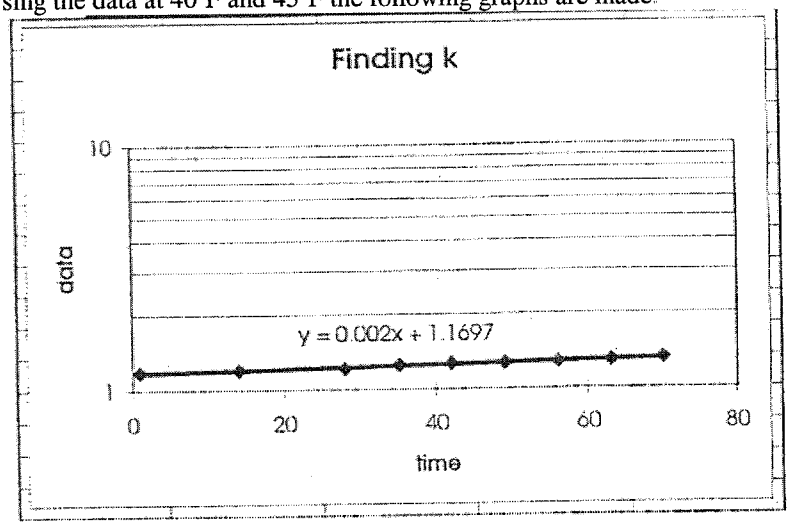
$$\frac{dC_p}{dt} = k\left[C_{SO} - C_p\right]\left[1 - \frac{C_p}{1.4}\right]$$

integrating

$$\ln\left(.933\frac{C_p - 1.5}{C_p - 1.4}\right) = 7.14kt + C$$



Using the data at 40°F and 45°F the following graphs are made.



from these: $k_{40} = 2.8*10^{-4}$ $C_{40} = 1.1697$

$k_{45} = 8.26*10^{-4}$ $C_{45} = 1.1883$

The activation energy then is:

$$\ln\left(.933\frac{C_p - 1.5}{C_p - 1.4}\right) = 7.14kt + C$$

$$E = -\frac{R\ln(k_2/k_1)}{1/T_2 - 1/T_1} = 108120\frac{Btu}{mol}$$

P7-9 (b)

$$k_{38} = k_{45}10\text{^}\left(\frac{-E}{2.3R}\left(\frac{1}{497} - \frac{1}{504}\right)\right) = 1.8*10^{-4}$$

Using interpolation, C = 1.18086

Using the same equation used on the graphs we can solve for t when $C_p = 1.1$

t = 49 days.

P7-9 (c)

$$k_{77} = k_{45}10\text{^}\left(\frac{-E}{2.3R}\left(\frac{1}{536} - \frac{1}{504}\right)\right) = .0023$$

C = 1.211

t = 2 days

P7-9 (d)

The data appears that it may fit the Monod equation for substrate consumption at the stationary phase.

P7-9 (e) Individualized solution

P7-9 (f) Individualized solution

P7-10 (a)

$E + S \xrightarrow{k1} E\bullet S$ $\qquad$ $E\bullet S \xrightarrow{k2} E + S$

$E\bullet S \xrightarrow{k3} P + S$ $\qquad$ $P + S \xrightarrow{k4} E\bullet S$

$$r_{E\bullet S} = k_1(E)(S) - k_2(E\bullet S) - k_3(E\bullet S) + k_4(P)(S)$$

since S is not consumed: $S_T = S + E\bullet S$ or $S = S_T - E\bullet S$

$$r_{E\bullet S} = k_1(E)\left[(S_T) - (E\bullet S)\right] - k_2(E\bullet S) - k_3(E\bullet S) + k_4(P)\left[(S_T) - (E\bullet S)\right]$$

$$(E\bullet S) = \frac{k_1(E)(S_T) + k_4(P)(S_T)}{k_1(E) + k_2 + k_3 + k_4(P)}$$

$$-r_E = k_1(E)(S) - k_2(E\bullet S)$$

$$-r_E = k_1(E)(S_T)\left[1 - \frac{k_1(E) + k_4(P)}{k_1(E) + k_2 + k_3 + k_4(P)}\right] - \frac{k_1k_2(E)(S_T) + k_2k_4(P)(S_T)}{k_1(E) + k_2 + k_3 + k_4(P)}$$

P7-10 (b)

$E + S \xrightarrow{k1} E\bullet S$ $\qquad$ $E\bullet S \xrightarrow{k2} E + S$

$E\bullet S \xrightarrow{k3} E\bullet P$ $\qquad$ $E\bullet P \xrightarrow{k4} E\bullet S$

$E\bullet P \xrightarrow{k_5} P + E$

$$r_{E\bullet P} = 0 = k_3(E\bullet S) - k_4(E\bullet P) - k_5(E\bullet P)$$

$$(E\bullet P) = \frac{k_3(E\bullet S)}{k_4 + k_5}$$

$$r_{E\bullet S} = k_1(E)(S) - k_2(E\bullet S) - k_3(E\bullet S) + k_4(E\bullet P)$$

since E is not consumed: $E_T = E + E\bullet S + E\bullet P$ or $E = E_T - E\bullet S - E\bullet P$

$$E = E_T - E\bullet S - \left(\frac{k_3}{k_4 + k_5}\right)E\bullet S \qquad E = E_T - E\bullet S\left(1 + \frac{k_3}{k_4 + k_5}\right)$$

Insert this into the equation for $r_{E\bullet S}$ and solve for the concentration of the intermediate:

$$(E\bullet S) = \frac{k_1(S)(E_T)}{\left[1 + \frac{k_3}{k_4 + k_5}\right]k_1(S) + k_2 + k_3 - \frac{k_4 k_3}{k_4 + k_5}}$$

$$r_P = k_5(E\bullet P) = \frac{k_3 k_5(E\bullet S)}{k_4 + k_5}$$

$$r_P = \frac{k_1 k_3 k_5(S)(E_T)}{[k_3 + k_4 + k_5]k_1(S) + k_2 k_4 + k_3 k_5}$$

P7-10 (c) No solution will be given

P7-10 (d)

$$E + S_1 \underset{k_2}{\overset{k_1}{\rightleftarrows}} E\bullet S_1$$

$$E\bullet S_1 + S_2 \underset{k_4}{\overset{k_3}{\rightleftarrows}} E\bullet S_1 S_2$$

$$E\bullet S_1 S_2 \xrightarrow{k_5} P + E$$

(1) $r_{E\bullet S_1} = 0 = k_1(E)(S_1) - k_2(E\bullet S) - k_3(E\bullet S)(S_2) + k_4(E\bullet S_1 S_2)$

(2) $r_{E\bullet S_1 S_2} = 0 = k_3(E\bullet S)(S_2) - k_4(E\bullet S_1 S_2) - k_5(E\bullet S_1 S_2)$

If we add these two rates we get:

(3) $r_{E\bullet S_1} + r_{E\bullet S_1 S_2} = 0 = k_1(E)(S) - k_2(E\bullet S) - k_5(E\bullet S_1 S_2)$

From equation (2) we get $(E\bullet S_1 S_2) = \frac{k_3(E\bullet S)(S_2)}{k_4 + k_5}$

Plug this into equation 3 and we get:

$$(E\bullet S_1)=\frac{k_1(E)(S_1)}{k_2+\dfrac{k_3(S_2)}{k_4+k_5}}$$

$$(E\bullet S_1S_2)=\frac{k_3(S_2)k_1(E)(S_1)}{(k_4+k_5)\left(k_2+\dfrac{k_3(S_2)}{k_4+k_5}\right)}=\frac{k_1k_3(E)(S_1)(S_2)}{k_2k_4+k_5k_2+k_3(S_2)}$$

$$r_P=k_5(E\bullet S_1S_2)=\frac{k_1k_2k_5(S_1)(S_2)(E)}{k_2k_4+k_2k_5+k_3(S_2)}$$

$$(E_T)=(E)+(E\bullet S)+(E\bullet S_1S_2)$$

$$(E_T)=(E)\left[1+\frac{k_1(S_1)}{k_2+\dfrac{k_3(S_2)}{k_4+k_5}}+\frac{k_1k_3(S_1)(S_2)}{k_2k_4+k_5k_2+k_3(S_2)}\right]$$

$$r_P=\frac{k_1k_2k_5(S_1)(S_2)(E_T)}{k_2k_4+k_2k_5+k_3(S_2)\left[1+\dfrac{k_1(S_1)}{k_2+\dfrac{k_3(S_2)}{k_4+k_5}}+\dfrac{k_1k_3(S_1)(S_2)}{k_2k_4+k_5k_2+k_3(S_2)}\right]}$$

P7-10 (e)

$$E+S\underset{k_2}{\overset{k_1}{\rightleftarrows}}(E\bullet S)_1$$

$$(E\bullet S)_1\underset{k_4}{\overset{k_3}{\rightleftarrows}}(E\bullet S)_2+P_1$$

$$(E\bullet S)_2\xrightarrow{k_5}P_2+E$$

(1) $r_{(E\bullet S)_1}=0=k_1(E)(S)-k_2(E\bullet S)_1-k_3(E\bullet S)_1+k_4(E\bullet S)_2(P_1)$

(2) $r_{(E\bullet S)_2}=0=k_3(E\bullet S)_1-k_4(E\bullet S)_2(P)_1-k_5(E\bullet S)_2$

$$(E\bullet S)_2=\frac{k_3(E\bullet S)_1}{k_4(P_1)+k_5}$$

Add (1) and (2) to get $r_{(E\bullet S)_1}+r_{(E\bullet S)_2}=0=k_1(E)(S)-k_2(E\bullet S)_1-k_5(E\bullet S)_2$

$$(E\bullet S)_1=\frac{k_1(E)(S)}{k_2+\dfrac{k_5k_3}{k_5+k_4(P_1)}}$$

$$(E\bullet S)_2 = \left(\frac{k_3(E\bullet S)_1}{k_4(P_1)+k_5}\right)\left(\frac{k_1(E)(S)}{k_2+\frac{k_5k_3}{k_5+k_4(P_1)}}\right)$$

$$(E\bullet S)_2 = \frac{k_3k_1(E)(S)}{k_2k_4(P_1)+k_2k_5+k_5k_3}$$

$$r_{P_2} = k_5(E\bullet S)_2 = \frac{k_1k_3k_5(E)(S)}{k_2k_4(P_1)+k_2k_5+k_5k_3}$$

$$(E_T) = (E)+(E\bullet S)_1+(E\bullet S)_2$$

$$(E_T) = (E)\left[1+\frac{k_1(S)}{k_2+\frac{k_5k_3}{k_5+k_4(P_1)}}+\frac{k_3k_1(S)}{k_2k_4(P_1)+k_2k_5+k_5k_3}\right]$$

$$r_{P_2} = \frac{k_1k_3k_5(E_T)(S)}{\left(k_2k_4(P_1)+k_2k_5+k_5k_3\right)\left[1+\frac{k_1(S)}{k_2+\frac{k_5k_3}{k_5+k_4(P_1)}}+\frac{k_3k_1(S)}{k_2k_4(P_1)+k_2k_5+k_5k_3}\right]}$$

P7-10 (f)

$$E+S \underset{k_2}{\overset{k_1}{\rightleftarrows}} E\bullet S \xrightarrow{k_3} P$$

$$E+P \underset{k_5}{\overset{k_4}{\rightleftarrows}} E\bullet P$$

$$E\bullet S+P \underset{k_7}{\overset{k_6}{\rightleftarrows}} E\bullet S\bullet P$$

$$E\bullet P+S \underset{k_9}{\overset{k_8}{\rightleftarrows}} E\bullet S\bullet P$$

$$r_P = k_3(E\bullet S)$$

(1) $r_{(E\bullet S)} = 0 = k_1(E)(S)-k_2(E\bullet S)-k_3(E\bullet S)+k_6(E\bullet S)(P)+k_7(E\bullet S\bullet P)$

(2) $r_{(E\bullet P)} = 0 = k_4(E)(P)-k_5(E\bullet P)-k_8(E\bullet P)(S)+k_9(E\bullet S\bullet P)$

(3) $r_{(E\bullet S\bullet P)} = 0 = k_6(E\bullet S)(P)-k_7(E\bullet S\bullet P)+k_8(E\bullet P)(S)-k_9(E\bullet S\bullet P)$

(2) + (3): $r_{(E\bullet P)}+r_{(E\bullet S\bullet P)} = 0 = k_4(E)(P)-k_5(E\bullet P)+k_6(E\bullet S)(P)-k_7(E\bullet S\bullet P)$

now add (1) to this:

$$r_{(E\bullet S)}+r_{(E\bullet P)}+r_{(E\bullet S\bullet P)}=0=k_1(E)(S)-k_2(E\bullet S)-k_3(E\bullet S)+k_4(E)(P)-k_5(E\bullet P)$$

$$(E\bullet S)=\frac{k_1(E)(S)+k_4(E)(P)-k_5(E\bullet P)}{k_2+k_3}$$

$$(E\bullet P)=\frac{k_4(E)(P)+k_9(E\bullet S\bullet P)}{k_5+k_8(S)}$$

$$(E\bullet S\bullet P)=\frac{k_6(E\bullet S)(P)+k_8(E\bullet P)(S)}{k_7+k_9}$$

$$(E\bullet P)=\frac{k_4(E)(P)+k_9\left(\dfrac{k_6(E\bullet S)(P)+k_8(E\bullet P)(S)}{k_7+k_9}\right)}{k_5+k_8(S)}$$

$$(E\bullet P)=\frac{k_7k_4(E)(P)+k_9k_4(E)(P)+k_9k_6(E\bullet S)(P)+k_8(E\bullet P)(S)}{k_5+k_8(S)}$$

$$(E\bullet P)=\frac{k_7k_4(E)(P)+k_9k_4(E)(P)+k_9k_6(E\bullet S)(P)}{k_5}$$

$$(E\bullet S)=\frac{k_1(E)(S)+k_4(E)(P)-k_5\left(\dfrac{k_7k_4(E)(P)+k_9k_4(E)(P)+k_9k_6(E\bullet S)(P)}{k_5}\right)}{k_2+k_3}$$

$$(E\bullet S)=\frac{k_1(E)(S)+k_4(E)(P)-k_7k_4(E)(P)+k_9k_4(E)(P)}{k_2+k_3-k_6k_9(P)}$$

$$r_P=k_3(E\bullet S)=k_3(E)\frac{k_1(S)+k_4(P)-k_7k_4(P)+k_9k_4(P)}{k_2+k_3-k_6k_9(P)}$$

$$(E_T)=(E)+(E\bullet S)+(E\bullet P)+(E\bullet S\bullet P)$$

$$(E_T)=(E)+\frac{k_1(E)(S)+k_4(E)(P)-k_7k_4(E)(P)+k_9k_4(E)(P)}{k_2+k_3-k_6k_9(P)}$$

$$+\frac{k_7k_4(E)(P)+k_9k_4(E)(P)+k_9k_6\left(\dfrac{k_1(E)(S)+k_4(E)(P)-k_7k_4(E)(P)+k_9k_4(E)(P)}{k_2+k_3-k_6k_9(P)}\right)(P)}{k_5}$$

$$+\frac{k_6\left(\dfrac{k_1(E)(S)+k_4(E)(P)-k_7k_4(E)(P)+k_9k_4(E)(P)}{k_2+k_3-k_6k_9(P)}\right)(P)}{k_7+k_9}$$

$$k_8\left(\frac{\left(\frac{k_7k_4(E)(P)+k_9k_4(E)(P)+k_9k_6\left(\frac{k_1(E)(S)+k_4(E)(P)-k_7k_4(E)(P)+k_9k_4(E)(P)}{k_2+k_3-k_6k_9(P)}\right)(P)}{k_5}\right)(S)}{k_1+k_9}\right)$$

all of the terms in the numerator have (E) in it and so the (E) can be factored out and an expression for (E) in terms of (E_T), (P), and (S) can be made and plugged back into the equation for r_P.

P7-10 (g)

$$E+S\underset{k_2}{\overset{k_1}{\rightleftarrows}}E\bullet S\overset{k_3}{\rightarrow}P$$

$$E+P\underset{k_5}{\overset{k_4}{\rightleftarrows}}E\bullet P$$

$$r_{(E\bullet S)}=0=k_1(E)(S)-k_2(E\bullet S)-k_3(E\bullet S)$$

$$(E\bullet S)=\frac{k_1(S)(E)}{k_2+k_3}$$

$$r_{(E\bullet P)}=0=k_4(E)(P)-k_5(E\bullet P)$$

$$(E\bullet P)=\frac{k_4(E)(P)}{k_5}$$

$$r_P=k_3(E\bullet S)-k_4(E)(P)+k_5(E\bullet P)$$

$$r_P=\frac{k_1k_3(S)(E)}{k_2+k_3}--k_4(E)(P)+k_4(E)(P)$$

$$r_P=\frac{k_1k_3(S)(E)}{k_2+k_3}$$

$$(E_T)=(E)+(E\bullet S)+(E\bullet P)$$

$$(E_T)=(E)+\frac{k_1(S)(E)}{k_2+k_3}+\frac{k_4(E)(P)}{k_5}$$

$$(E_T)=(E)\left[1+\frac{k_1(S)}{k_2+k_3}+\frac{k_4(P)}{k_5}\right]$$

$$r_P=\frac{k_1k_3(S)(E_T)}{(k_2+k_3)\left[1+\frac{k_1(S)}{k_2+k_3}+\frac{k_4(P)}{k_5}\right]}$$

$$r_P=\frac{k_3(S)(E_T)}{\left(\frac{k_2+k_3}{k_1}+(S)+\frac{k_4(k_2+k_3)(P)}{k_1k_5}\right)}$$

$$r_P = \frac{V_{max}(S)}{K_M + (S) + K_P(P)}$$

P7-10 (h) No solution will be given

P7-10 (i) No solution will be given

P7-10 (j) No solution will be given

P7-10 (k) No solution will be given

P7-11 (a)

The enzyme catalyzed reaction of the decomposition of hydrogen peroxide. For a batch reactor:

$$\frac{1}{V}\frac{dN_S}{dt} = \frac{dC_S}{dt} = r_S = \frac{-V_{max}C_S}{K_m + C_S} \quad \text{at } t = 0,\ C_S = C_{So}$$

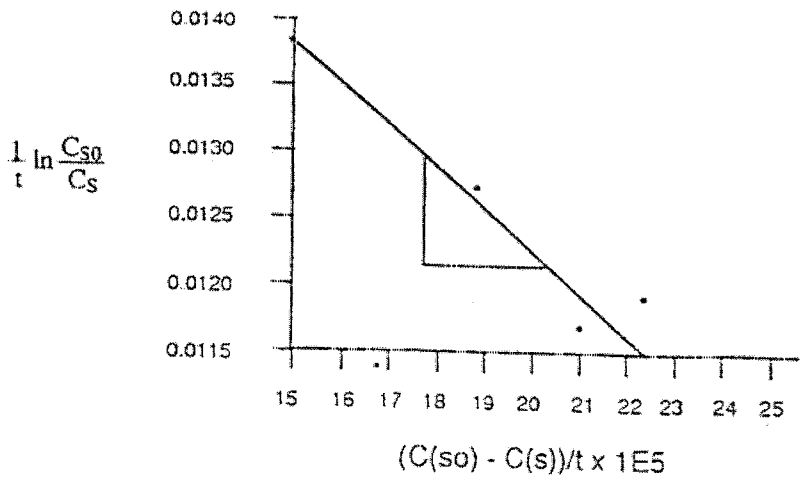
Rearranging and integrating:

$$\int_{C_{So}}^{C_S}\left[\frac{K_m}{C_S} + 1\right]dC_S = -\int_0^t V_{max}\,dt = K_m \ln\frac{C_S}{C_{So}} + C_S - C_{So} = -V_{max}\,t$$

$$\text{or } \frac{1}{t}\ln\frac{C_{So}}{C_S} = -\frac{C_{So} - C_S}{K_m\,t} + \frac{V_{max}}{K_m}$$

A plot of $\frac{1}{t}\ln\frac{C_{So}}{C_S}$ vs $\frac{C_{So} - C_S}{t}$ should be linear with slope $-\frac{1}{K_m}$

t	C_S	$\frac{C_{So}}{C_S}$	$\frac{1}{t}\ln\frac{C_{So}}{C_S}$	$C_{So} - C_S$	$\frac{C_{So} - C_S}{t}$
0	.0200	1.0	-	.0000	-
10	.01775	1.1268	.01193	.00225	.000225
20	.0158	1.2654	.01179	.0042	.00021
50	.0106	1.8867	.01270	.0094	.000188
100	.0050	4.0000	.01386	.0150	.00015



From the graph, slope $= \dfrac{.013 - .012}{(17.5 - 20.6)\times 10^{-5}}\left\{\dfrac{\text{min}^{-1}}{\text{g mol } 1\text{ min}^{-1}}\right\}$

$$= \frac{-.001}{-3.1\times 10^{-5}}\left\{\frac{1}{\text{g mol}}\right\} = \frac{1}{k_m}$$

$$K_m = .0310 \text{ g mol / l}$$

$$\text{At } \frac{1}{t}\ln\frac{C_{S0}}{C_S} = \frac{.031}{\text{min}}, \quad \frac{C_{S0}-C_S}{t} = \frac{1.75\times 10^{-4}\ \text{g mol}}{\text{l-min}}$$

$$\therefore \frac{V_{max}}{K_m} = \frac{1}{t}\ln\frac{C_{S0}}{C_S} + \frac{C_{S0}-C_S}{K_m t} = .013\ \text{min}^{-1} + \frac{1.75\times 10^{-4}}{.0310}\frac{\text{g mol/l-min}}{\text{g mol/l}}$$

$$\frac{V_{max}}{K_m} = \left(.013 + 5.64\times 10^{-3}\right)\text{min}^{-1} = .01865\ \text{min}^{-1}$$

$$V_{max} = \left(.01865\times \text{min}^{-1}\right)\left(.0310\ \frac{\text{g mol}}{\text{l}}\right) = 5.78\times 10^{-4}\ \frac{\text{g mol}}{\text{l-min}}$$

P7-11 (b)

$V_{max} \propto [E_t]$. If the enzyme concentration is increased by a factor of three, then

$$V_{max} = 3\left(5.78*10^{-4}\ \frac{gmol}{l*\text{min}}\right) = 17.34*10^{-4}\ \frac{gmol}{L*\text{min}}$$

$$k_m \ln\frac{C_S}{C_{SO}} + C_S - C_{SO} = -17.34*10^{-4}\ \frac{gmol}{L*\text{min}}*20\ \text{min} = -34.7*10^{-4}\ \frac{gmol}{L}$$

This equation should be solved by trial and error. Rearranging,

$$\ln\frac{C_S}{C_{S0}} = \frac{C_{S0}-C_S-.0347}{K_m}$$

$$\therefore\ C_S = C_{S0}\exp\left[\frac{C_{S0}-C_S-.0347}{K_m}\right] = .02\exp\left[\frac{-.0147-C_S}{.0310}\right]$$

Assume a C_S, calculate a new one from the RHS of the above equation.

Assume C_S	New C_S	% difference
0.015	0.0077	94.8
0.0077	0.0097	20.6
0.0097	0.0091	6.6
0.0091	0.0093	2.2
0.0093	0.0092	1.1
0.0092	0.0092	0

P7-11 (c) Individualized solution

P7-11 (d) Individualized solution

P7-12 (a)

Given the reaction sequence:

$$E + S \Leftrightarrow E \cdot S$$

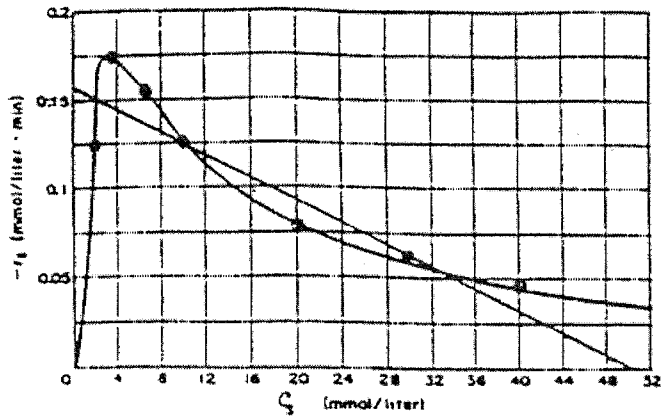
$$E \cdot S + S \Leftrightarrow S \cdot E \cdot S$$

$$E \cdot S \Leftrightarrow E + P$$

The plot of $-r_s$ vs C_s is shown below.

the mechanism for the above reaction is:

$-r_s = \dfrac{k C_s E_t}{1 + K_1 C_s + K_2 C_s^2}$; For $C_s << 1$: $-r_s \approx k C_s E_t$ in qualitative agreement with the graph at low values of C_s. For $C_s >> 1$: $-r_s = \dfrac{k E_t}{K_2 C_s}$. This is also in agreement with the graph.



$$\text{At} \frac{\partial(-r_s)}{\partial C_s} = \frac{k E_t}{1 + K_1 C_s + K_2 C_s^2} \cdot \frac{k C_s E_t [K_1 + 2K_2 C_s]}{(1 + K_1 C_s + K_2 C_s^2)^2} = \frac{k E_t (1 - K_2 C_s^2)}{(1 + K_1 C_s + K_2 C_s^2)^2} = 0$$

$$\text{or } C_s^2 = \frac{1}{K_2} \text{ with: } \frac{\partial^2(-r_s)}{\partial C_s^2} = \frac{-2k E_t C_s K_2}{(1 + K_1 C_s + K_2 C_s^2)^2} - \frac{2k E_t (1 - K_2 C_s^2)(K_1 + 2K_2 C_s)}{(1 + K_1 C_s + K_2 C_s^2)^3}$$

$$\frac{\partial^2(-r_s)}{\partial C_s^2} = \frac{2k E_t [-3K_2 C_s - K_1 + K_2 C_s^3]}{(1 + K_1 C_s + K_2 C_s^2)^3} \text{ with } C_s^2 = \frac{1}{\sqrt{K_2}}, \text{ the numerator becomes}$$

$$2k E_t \left[- K_1 - 3\sqrt{K_2} + \frac{1}{\sqrt{K_2}} \right] < 0 \therefore (-r_s) \text{ goes through a maximum.}$$

This observation also agrees with the above graph

P7-12 (b)

For a CSTR operating with V = 1000 l ; υ_0 = 3.2 l/min

$$\upsilon_0[C_{A0} - C_A] = -r_A V \text{ or } -r_A = \frac{C_{A0} - C_A}{\tau} ; \tau = \frac{V}{\upsilon_0} = \frac{1000}{3.2} = 313 \text{ min.}$$

with C_{A0} = 50 m moles/l , $-r_A = \frac{50 - C_A}{313}$; this (linear) equation is plotted on the accompanying graph, the equation intersects the $(-r_s)$ vs C_s curve from the rate of reaction at

$$C_s = 34 \frac{\text{m moles}}{\text{l}} , -r_s = 0.052 \frac{\text{m moles}}{\text{min - l}} ; C_s = 9.4 \frac{\text{m moles}}{\text{l}} ,$$

$$-r_s = 0.132 \frac{\text{m moles}}{\text{min - l}} ; C_s = 2.1 \frac{\text{m moles}}{\text{l}} , -r_s = 0.154 \frac{\text{m moles}}{\text{min - l}} .$$

Stability of points: assume that a perturbation $\theta_S = C_{S0} - \overline{C}_S$ occurs where the overbar designates the steady-state condition. Material balance for any time:

$$V \frac{dC_S}{dt} = r_S V + C_{S0} \upsilon_0 - C_S \upsilon_0$$

$$\text{or } \tau \frac{dC_S}{dt} = r_S \tau + C_{S0} - C_S$$

at steady state

$$0 = \bar{r}_S \tau + \overline{C}_{S0} + \overline{C}_S$$

Combining

$$\tau \frac{d\theta_S}{dt} = (r_S - \bar{r}_S)\tau + \theta_{S0} - \theta_S$$

Using a Taylor series expansion about $\overline{C}_S$ to linearize $r_S - \bar{r}_S$:

$$r_S - \bar{r}_S = \left(\frac{\partial r_S}{\partial C_S}\right)_{\overline{C}_S} (C_S - \overline{C}_S) = \left(\frac{\partial r_S}{\partial C_S}\right)_{\overline{C}_S} \theta_S \text{ and substituting}$$

$$\tau \frac{d\theta_S}{dt} = \left[\left(\frac{\partial r_S}{\partial C_S}\right)_{\overline{C}_S} \tau - 1\right] \theta_S + \theta_{S0} \quad \text{at } t = 0 , \theta_S = 0$$

For this solution of the above equation to be stable:

$$\left(\frac{\partial r_S}{\partial C_S}\right)_{\overline{C}_S} \tau - 1 < 0 \text{ or } \left(\frac{\partial r_S}{\partial C_S}\right)_{\overline{C}_S} \tau < 1 \text{ or } \left(\frac{\partial -r_S}{\partial C_S}\right)_{\overline{C}_S} \tau > -1$$

At C_s = 2.1 m moles/l, $-r_s$ = 0.154 m moles/ l -min, the slope of the reaction rate curve is positive. Therefore, this operating point is stable. For the other two points, the stability may be examined by estimating the derivative graphically:

$$\text{At } C_S = 9.4 \text{ m moles/l} , \left(\frac{\partial(-r_S)}{\partial C_S}\right)_{\overline{C}_S = 9.4} \cong \frac{\Delta -r_S}{\Delta C_S} = \frac{0.1425 - 0.1275}{8 - 10} = -\frac{0.150}{2} \text{ min}^{-1}$$

$$\left(\frac{\partial(-r_S)}{\partial C_S}\right)_{\overline{C}_S} \tau = \left(-\frac{0.150}{2} \text{ min}^{-1}\right)(313 \text{ min}) = -2.4 < -1$$

$\therefore$ the point $C_S = 9.4$, $-r_S = 0.132$ is unstable.

At $C_S = 2.1$ m moles/l, $\left(\frac{\partial(-r_S)}{\partial C_S}\right)_{\overline{C}_S = 2.1} \equiv \frac{\Delta(-r_S)}{\Delta C_S} = \frac{0.0675 - 0.018}{24 - 44} = -\frac{0.0495}{20}$ min^{-1}

$\left(\frac{\partial(-r_S)}{\partial C_S}\right)_{\overline{C}_S} \tau = \left(-\frac{0.0495}{2}\ \text{min}^{-1}\right)(313\ \text{min}) = -0.775 > -1$; stable

At $C_S = 5.1$ m moles/l, $-r_S = 0.154 \frac{\text{m moles}}{\text{l - min}}$ appears to be stable, but more accurate calculation of $\left(\frac{\partial(-r_S)}{\partial C_S}\right)$ is necessary to establish this conclusion definitively.

$$X = \frac{C_{S0} - C_S}{C_{S0}} = \frac{50 - 2.1}{50} = .958$$

P7-12 (c)

$$-r_S = \frac{kC_S E_T}{1 + K_1 C_s + K_2 C_S^2}$$

If E_T is reduced by 33%, $-r_S$ will also decrease by 33%. From the original plot, we see that if the curve $-r_S$ is decreased by 33%, the straight line from the CSTR calculation will cross the curve only once at approximately $C_S = 40$ mmol/L

X = 0.2

P7-12 (d) Individualized solution

P7-12 (e) Individualized solution

P7-13 (a)

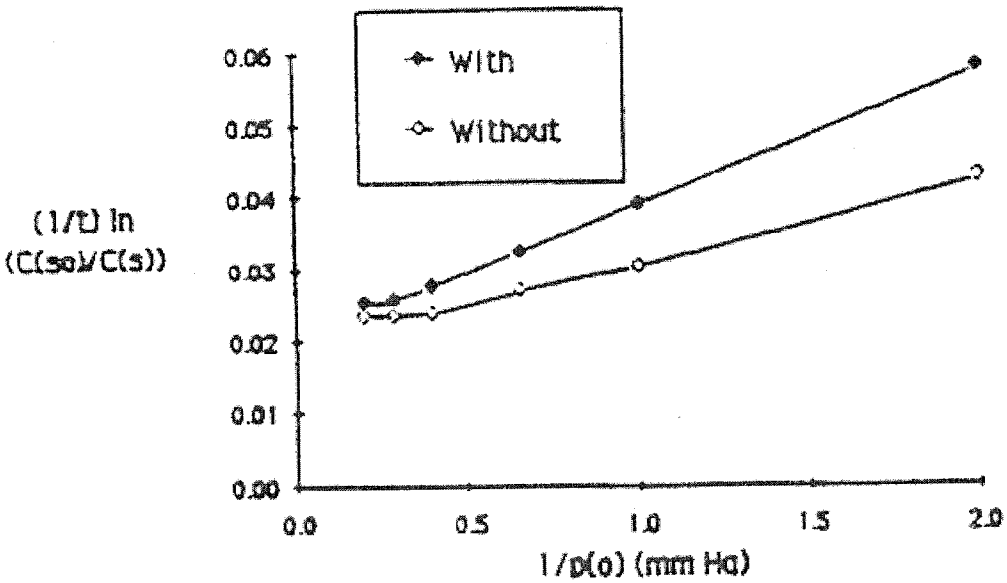
Data on Baker's Yeast at 23.4 °C

P_{O_2}	Q_{O_2} no sulfanilamide	Q_{O_2} 20 mg sulfanilamide/ml added to medium	$\frac{1}{Q_{O_2}}$ no sulfanilamide	$\frac{1}{P_{O_2}}$	$\frac{1}{Q_{O_2}}$ 20 mg sulfanilamide/ml added to medium
0.0	0.0	0.0	-	-	-
0.5	23.5	17.4	.0425	2.0	.0575
1.0	33.0	25.6	.0303	1.0	.0391
1.5	37.5	30.8	.02666	.66	.03246
2.5	42.0	36.4	.0238	.40	.02747
3.5	43.0	39.6	.0233	.285	.0253
5.0	43.0	40.0	.0233	.200	.0250

$r_p = \frac{K E_t S}{K_m + S} = \frac{V_{max} S}{K_m + S}$, where in this problem, Q_{O_2} = oxygen uptake in microliters of O_2 per hour per mg of cells = r_p, and O_2 is the substrate.

$$\therefore \frac{1}{r_p} = \frac{K_m}{V_{max} S} + \frac{1}{V_{max}} = \frac{K_m}{V_{max}}\left(\frac{1}{P_{O_2}}\right) + \frac{1}{V_{max}} = \frac{1}{Q_{O_2}}$$

Plot of $\frac{1}{Q_{O_2}}$ versus $\frac{1}{P_{O_2}}$ will have a slope of $\frac{K_m}{V_{max}}$ and an intercept of $\bar{\upsilon}_n$



From the graph, slope $= \frac{.0305 - .014}{1} = .0165$ Intercept = 0.019

$$\therefore V_{max} = 52.63 \frac{\text{ml } O_2}{\text{hr mg cells}}$$

Km = 0.0165 Vmax = (0.0165)(52.63) = 0.8684 mmHg

P7-13 (b)

Now, with competitive inhibition: $E + S \Leftrightarrow E \cdot S$

$I + E \Leftrightarrow I \cdot E$

$E \cdot S \Leftrightarrow P + E$

Rate law becomes: $r_p = \frac{V_{max} S}{S + K_m\left(1 + \frac{I}{K_I}\right)}$ or $\frac{1}{r_p} = \frac{K_m\left(1 + \frac{I}{K_I}\right)}{V_{max}}\left(\frac{1}{S}\right) + \frac{1}{V_{max}}$

In this case, the slope is : $\frac{K_m\left(1 + \frac{I}{K_I}\right)}{V_{max}}$ while the intercept is the same as in case (a)

For the case of uncompetitive inhibition: $E + S \Leftrightarrow E \cdot S$

$E \cdot S + I \Leftrightarrow I \cdot E \cdot S$

$E \cdot S \Leftrightarrow P + E$

Rate law becomes: $r_p = \dfrac{S\,V_{max}}{K_m + S\left(1 + \dfrac{I}{K_I}\right)}$ or $\dfrac{1}{r_p} = \dfrac{K_m}{V_{max}}\left(\dfrac{1}{S}\right) + \dfrac{1 + \dfrac{I}{K_I}}{V_{max}}$

In this case, the slope is the same, but the intercept is $\dfrac{1 + \dfrac{I}{K_I}}{V_{max}}$

And for the case of non-competitive inhibition: $E + I \Leftrightarrow E \cdot I$

$E \cdot I + S \Leftrightarrow I \cdot E \cdot S$

$E + S \Leftrightarrow E \cdot S$

$I \cdot E \cdot S \Leftrightarrow E \cdot S + I$

$E \cdot S \Leftrightarrow P + E$

$r_p = \dfrac{V_{max}\,S}{(S + K_m)\left(1 + \dfrac{I}{K_I}\right)}$ or $\dfrac{1}{r_p} = \dfrac{1 + \dfrac{I}{K_I}}{V_{max}} + \dfrac{1 + \dfrac{I}{K_I}}{V_{max}}\left(\dfrac{1}{S}\right)$

In this case both the slope and intercept change. Plotting the data of $\frac{1}{P_{O_2}}$ in mmHg versus $\frac{1}{Q_{O_2}}$ with sulfanilamide on the same plot as was plotted the data for the case with no sulfanilamide, it is seen that the slopes are different, but the intercept is the same. Therefore the inhibition is comparative.

P7-13 (c) Individualized solution

P7-13 (d) Individualized solution

P7-14

For No Inhibition, using regression,

Equation model: $\dfrac{1}{-r_s} = a0 + a1\left(\dfrac{1}{S}\right)$

a0 = 0.008 a1 = 0.0266

For Maltose,

Equation model: $\dfrac{1}{-r_s} = a0 + a1\left(\dfrac{1}{S}\right)$

a0 = 0.0098 a1 = 0.33

For α-dextran,

Equation model: $\frac{1}{-r_s} = a0 + a1\left(\frac{1}{S}\right)$

a0 = 0.008 a1 = 0.0377

$\Rightarrow$ Maltose show non-competitive inhibition as slope and intercept, both changing compared to no inhibition case.

$\Rightarrow$ α-dextran show competitive inhibition as intercept same but slope increases compared to no inhibition case.

P7-15

$$r_P = k(EHS)$$

$$(EHS) = K_M (EH)(S)$$

$$r_P = kK_M (EH)(S)$$

$$(EH_2^+) = K_2 (H^+)(EH)$$

$$(EH) = K_1 (H^+)(E^-)$$

$$(E^-) = \frac{(EH)}{K_1 (H^+)}$$

$$(E_T) = (E^-) + (EH) + (EH_2^+)$$

$$(E_T) = \frac{(EH)}{K_1 (H^+)} + (EH) + K_2 (H^+)(EH)$$

$$(EH) = \frac{(E_T)}{1 + \frac{1}{K_1 (H^+)} + K_2 (H^+)}$$

Now plug the value of (EH) into r_P

$$r_P = kK_M (EH)(S) = \frac{kK_M (E_T) K_1 (H^+)(S)}{1 + K_1 (H^+) + K_1 K_2 (H^+)^2}$$

At very low concentrations of H^+ (high pH) r_p approaches 0 and at very high concentrations of H^+ (low pH) r_P also approaches 0. Only at moderate concentrations of H^+ (and therefore pH) is the rate much greater than zero. This explains the shape of the figure.

P7-15 (a) Individualized solution

P7-15 (b) Individualized solution

P7-16 (a)

For batch reaction,

$$\frac{dC_S}{dt} = r_S \qquad r_S = -\frac{\mu_{max} C_S C_C}{K_M + C_S} \qquad \& \qquad r_C = -Y_{C/S} r_S$$

$$C_C = C_{CO} + Y_{C/S}(C_{SO} - C_S)$$

See Polymath program P7-16-a.pol.

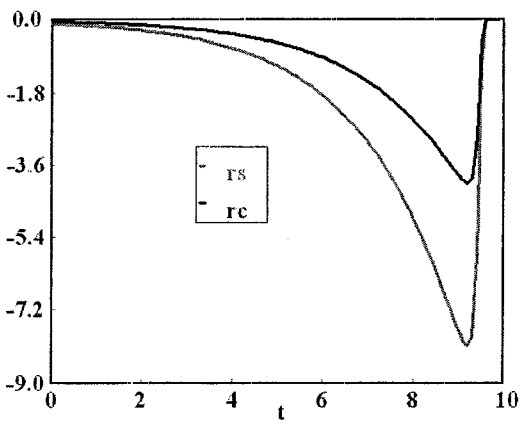
POLYMATH Results
Calculated values of the DEQ variables

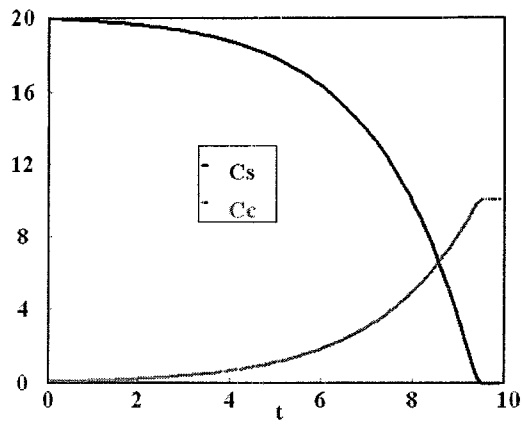
Variable	initial value	minimal value	maximal value	final value
t	0	0	10	10
Cs	20	6.301E-11	20	6.301E-11
Cso	20	20	20	20
Km	0.25	0.25	0.25	0.25
Ycs	0.5	0.5	0.5	0.5
Cco	0.1	0.1	0.1	0.1
Cc	0.1	0.1	10.1	10.1
umax	1	1	1	1
rs	-0.0987654	-8.0781496	-2.546E-09	-2.546E-09
rc	0.0493827	1.273E-09	4.0390748	1.273E-09

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Cs)/d(t) = rs

Explicit equations as entered by the user
[1] Cso = 20
[2] Km = 0.25
[3] Ycs = 0.5
[4] Cco = 0.1
[5] Cc = Cco+Ycs*(Cso-Cs)
[6] umax = 1
[7] rs = -umax*Cs*Cc/(Km+Cs)
[8] rc = -Ycs*rs





P7-16 (b)

For logistic growth law:

$$\frac{dC_C}{dt} = r_g \qquad r_g = \mu_{max}\left(1 - \frac{C_C}{C_\infty}\right)C_C$$

See Polymath program P7-16-b.pol.

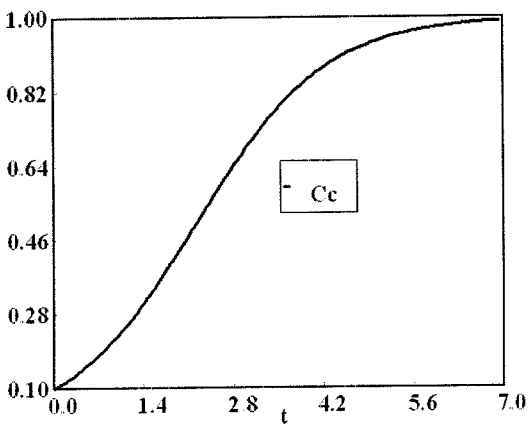
POLYMATH Results
Calculated values of the DEQ variables

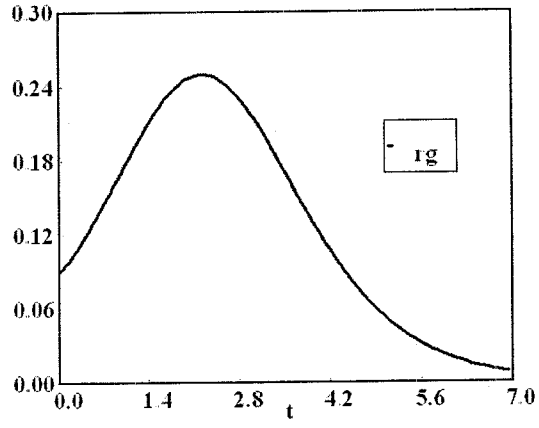
Variable	initial value	minimal value	maximal value	final value
t	0	0	7	7
Cc	0.1	0.1	0.9918599	0.9918599
umax	1	1	1	1
Coo	1	1	1	1
rg	0.09	0.0080739	0.2499857	0.0080739

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Cc)/d(t) = rg

Explicit equations as entered by the user
[1] umax = 1
[2] Coo = 1
[3] rg = umax*(1-Cc/Coo)*Cc





For part(a), $C_\infty = Y_{C/S}C_{SO} + C_{CO} = (0.5)(20)g/dm^3 + 0.1g/dm^3 = 10.1g/dm^3$

P7-16 (c)

For CSTR,

$$r_g = -Y_{C/S}r_S = \frac{Y_{C/S}\mu_{\max}C_S C_C}{K_M + C_S}$$

Dilution rate at which washout occurs = $\frac{Y_{C/S}\mu_{\max}C_{SO}}{K_M + C_{SO}} = \frac{0.5\times 1hr^{-1}\times 20g/dm^3}{0.25g/dm^3 + 20g/dm^3} = 0.494hr^{-1}$

P7-16 (d)

$$D_{\max\,prod} = Y_{C/S}\mu_{\max}\left[1-\sqrt{\frac{K_M}{K_M + C_{SO}}}\right] = 0.5\times 1hr^{-1}\times\left[1-\sqrt{\frac{0.25g/dm^3}{0.25g/dm^3 + 20g/dm^3}}\right]$$

$$D_{\max\,prod} = 0.44hr^{-1}$$

$$C_C = \left(\frac{Y_{C/S}(C_{SO}+K_M)}{Y_{C/S}\mu_{\max}-D}\right)\left(\frac{Y_{C/S}\mu_{\max}C_{SO}}{K_M+C_{SO}}-D\right)$$

$$C_C = \left(\frac{0.5(20+0.25)g/dm^3}{0.5\times 1hr^{-1}-0.44hr^{-1}}\right)\left(\frac{0.5\times 1hr^{-1}\times 20g/dm^3}{20.25g/dm^3}-0.44hr^{-1}\right)=9.08g/dm^3$$

$$C_S = \frac{DK_M}{Y_{C/S}\mu_{\max}-D}=1.83g/dm^3$$

$$C_P = Y_{P/C}C_C = 0.15\times 9.08g/dm^3 = 1.362g/dm^3$$

$$-r_S = \frac{\mu_{\max}C_SC_C}{K_M+C_S}=\frac{1\times 1.83g/dm^3\times 9.08g/dm^3}{0.25g/dm^3+1.83g/dm^3}=7.99g/dm^3.hr$$

P7-16 (e)

If $r_d = k_dC_C$

$$\dot{m} = C_Cv_O = (r_g - r_d)V$$

Divide by C_CV, $$D=\frac{(r_g-r_d)}{C_C}=\frac{(Y_{C/S}\mu_{\max}C_S)}{K_M+C_S}-k_d$$

$$\Rightarrow \quad C_S=\frac{(D+k_d)K_M}{Y_{C/S}\mu_{\max}-D}$$

Now $$-r_S = Y_{S/C}r_g \quad \Rightarrow \quad D(C_{SO}-C_S)=Y_{S/C}(DC_C+r_d)$$

$$C_C=\frac{Y_{C/S}D(C_{SO}-C_S)}{D+k_d}$$

For dilution rate at which wash out occur, $C_C = 0$

$$\Rightarrow \quad C_{SO} = C_S$$

$$\Rightarrow \quad C_{SO}=\frac{(D+k_d)K_M}{Y_{C/S}\mu_{\max}-D}$$

$$D_{MAX}=\frac{Y_{C/S}\mu_{\max}C_{SO}-k_dK_M}{C_{SO}+K_M}=\frac{0.5\times 1hr^{-1}\times 20g/dm^3-0.02hr^{-1}\times 0.25g/dm^3}{20g/dm^3+0.25g/dm^3}=0.493hr^{-1}$$

There is not much change in Dilution rate while considering cell death to one where cell death is neglected.

$$DC_C=\frac{Y_{C/S}D^2(C_{SO}-C_S)}{D+k_d} \qquad C_S=\frac{(D+k_d)K_M}{Y_{C/S}\mu_{\max}-D}$$

Now For $D_{\max\ prod}$, $$\frac{d(DC_C)}{dD}=0$$

$$D_{\max\ prod} = 0.446\ hr^{-1}$$

P7-16 (f)

Now $-r_m = mC_C$

$$DC_C = r_g \qquad \& \qquad D(C_{SO}-C_S)=-r_S-r_m$$

$$\dot{m} = C_Cv_O = (r_g)V = \mu C_CV$$

Divide by $C_C V$, $D = \mu = \dfrac{(Y_{C/S}\mu_{\max} C_S)}{K_M + C_S}$

Solving $\Rightarrow$ $C_S = \dfrac{DK_M}{Y_{C/S}\mu_{\max} - D}$

Now $-r_S = Y_{S/C} r_g$ $\Rightarrow$ $D(C_{SO} - C_S) - mC_C = Y_{S/C}(DC_C)$

$$C_C = \frac{[D(C_{SO} - C_S)]}{Y_{C/S}D + m}$$

For dilution rate at which wash out occur, $C_C = 0$

$\Rightarrow$ $C_{SO} = C_S$, $C_S = \dfrac{DK_M}{Y_{C/S}\mu_{\max} - D}$

$\Rightarrow$ $C_{SO} = \dfrac{DK_M}{Y_{C/S}\mu_{\max} - D}$

$\Rightarrow$ $D_{MAX} = \dfrac{Y_{C/S}\mu_{\max} C_{SO}}{C_{SO} + K_M} = \dfrac{0.5 \times 1 hr^{-1} \times 20 g/dm^3}{20 g/dm^3 + 0.25 g/dm^3} = 0.494 hr^{-1}$

Now For $D_{\max\ prod}$, $\dfrac{d(DC_C)}{dD} = 0$

$D_{\max\ prod}$ = 0.4763 hr^{-1}

P7-16 (g) Individualized solution

P7-16 (h) Individualized solution

P7-17

Tessier Equation,

$$r_g = \mu_{\max}\left(1 - e^{-C_S/k}\right)C_C$$

(a) For batch reaction,

$$\frac{dC_S}{dt} = r_S, \qquad -r_S = Y_{S/C} r_C, \qquad r_g = \mu_{\max}\left(1 - e^{-C_S/k}\right)C_C$$

$$C_C = C_{CO} + Y_{C/S}(C_{SO} - C_S)$$

See Polymath program P7-17-a.pol.

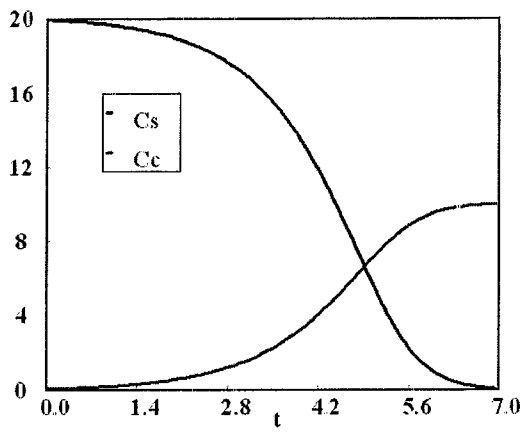
POLYMATH Results
Calculated values of the DEQ variables

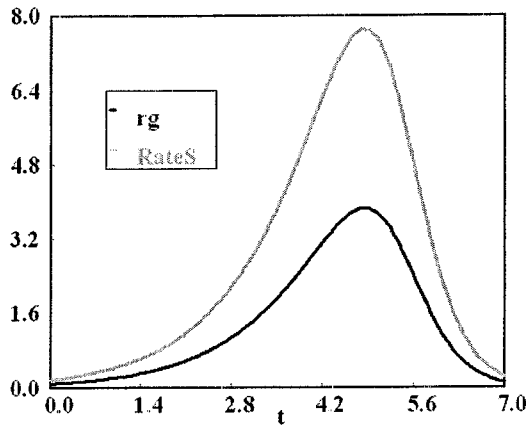
Variable	initial value	minimal value	maximal value	final value
t	0	0	7	7
Cs	20	0.0852675	20	0.0852675
Cco	0.1	0.1	0.1	0.1
Ycs	0.5	0.5	0.5	0.5
Cso	20	20	20	20
Cc	0.1	0.1	10.057366	10.057366
k	8	8	8	8
umax	1	1	1	1
Ysc	2	2	2	2
rg	0.0917915	0.0917915	3.8563479	0.1066265
rs	-0.183583	-7.7126957	-0.183583	-0.213253
RateS	0.183583	0.183583	7.7126957	0.213253

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Cs)/d(t) = rs

Explicit equations as entered by the user
[1] Cco = 0.1
[2] Ycs = 0.5
[3] Cso = 20
[4] Cc = Cco+Ycs*(Cso-Cs)
[5] k = 8
[6] umax = 1
[7] Ysc = 2
[8] rg = umax*(1-exp(-Cs/k))*Cc
[9] rs = -Ysc*rg
[10] RateS = -rs





(c) $DC_C = r_g \qquad D(C_{SO} - C_S) = r_S \qquad r_g = \mu C_C \qquad \mu = \mu_{\max}\left(1 - e^{-C_S/k}\right)$

$\dot{m} = C_C v_O = (r_g)V = \mu C_C V$

Divide by $C_C V$, $D = \mu = \mu_{\max}\left(1 - e^{-C_S/k}\right)$

$$C_S = -k \ln\left(1 - \frac{D}{\mu_{\max}}\right)$$

Now $-r_S = Y_{S/C} r_g \qquad C_C = Y_{C/S}(C_{SO} - C_S)$

For dilution rate at which wash out occur, $C_C = 0$

$$\Rightarrow \quad C_{SO} = C_S = -k \ln\left(1 - \frac{D}{\mu_{\max}}\right)$$

$$\Rightarrow \quad D_{MAX} = \mu_{\max}\left(1 - e^{-C_{S0}/k}\right) = 1hr^{-1}\left(1 - e^{-20g/dm^3/8g/dm^{\#}}\right) = 0.918hr^{-1}$$

(d) $DC_C = DY_{C/S}(C_{SO} - C_S) \qquad C_S = -k \ln\left(1 - \frac{D}{\mu_{\max}}\right)$

$$DC_C = DY_{C/S}\left(C_{SO} + k \ln\left(1 - \frac{D}{\mu_{\max}}\right)\right)$$

Now For $D_{max\ prod}$, $\dfrac{d(DC_C)}{dD} = 0$

$D_{max\ prod} = 0.628\ hr^{-1}$

P7-17 (a) Individualized solution

P7-17 (b) Individualized solution

P7-18 (a)

$r_g = \mu C_C$ $\qquad \mu = \dfrac{\mu_{max} C_S}{K_M + C_S}$

For CSTR, $DC_C = r_g$ $\qquad D(C_{SO} - C_S) = -r_S$ $\qquad -r_S = Y_{S/C} r_g$

$C_S = C_{SO}(1 - X) = 10g/dm^3(1 - 0.9) = 1g/dm^3$ $\qquad D = {}^{v_O}/_{V}$

$C_C = Y_{C/S}(C_{SO} - C_S) = 0.5(10 - 1)g/dm^3 = 4.5g/dm^3$

$$DC_C = r_g = \frac{\mu_{max} C_S C_C}{K_M + C_S}$$

$$\Rightarrow \quad \frac{v_O}{V} 4.5g/dm^3 = \frac{0.8hr^{-1} \times 1g/dm^3 \times 4.5g/dm^3}{(4+1)g/dm^3}$$

$$V = 6250dm^3$$

P7-18 (b)

Flow of cells out = Flow of cells in

$F_C = v_0 C_C$

Cell Balance: $F_C + r_g V - F_C = V \dfrac{dC_C}{dt}$

$$\frac{dC_C}{dt} = r_g$$

Substrate Balance: $\dfrac{dC_S}{dt} = v_0 C_{S0} - v_0 C_S - Y_{S/C} r_g$

$$r_g = \frac{\mu_{max} C_S C_C}{K_M + C_S}$$

This would result in the Cell concentration growing exponentially. This is not realistic as at some point there will be too many cells to fit into a finite sized reactor. Either a cell death rate must be included or the cells cannot be recycled.

P7-18 (c)

Two CSTR's

For 1st CSTR,

V = 5000dm^3, $DC_C = r_g$ $\qquad D(C_{SO} - C_S) = -r_S$

$$-r_S = Y_{S/C} r_g \qquad r_g = \frac{\mu_{max} C_S}{K_M + C_S} C_C \qquad D = {}^{v_O}\!/_{V}$$

See Polymath program P7-18-c-1cstr.pol.

POLYMATH Results
NLES Solution

Variable	Value	f(x)	Ini Guess
Cc	4.3333333	9.878E-12	4
Cs	1.3333333	1.976E-11	5
umax	0.8		
Km	4		
Csoo	10		
Cso	10		
Ysc	2		
rg	0.8666667		
rs	-1.7333333		
V	5000		
vo	1000		
D	0.2		
X	0.8666667		
Cco	4.33		

NLES Report (safenewt)

Nonlinear equations
[1] f(Cc) = D*(Cc)-rg = 0
[2] f(Cs) = D*(Cso-Cs)+rs = 0

Explicit equations
[1] umax = 0.8
[2] Km = 4
[3] Csoo = 10
[4] Cso = 10
[5] Ysc = 2
[6] rg = umax*Cs*Cc/(Km+Cs)
[7] rs = -Ysc*rg
[8] V = 5000
[9] vo = 1000
[10] D = vo/V
[11] X = 1-Cs/Csoo
[12] Cco = 4.33

$C_{C1} = 4.33$ g/dm^3 X = 0.867
$C_{S1} = 1.33$ g/dm^3 $C_{P1} = Y_{P/C} C_{C1} = 0.866$ g/dm^3

For 2nd CSTR, $D(C_{C2} - C_{C1}) = r_g$ $D(C_{S1} - C_S) = -r_S$

See Polymath program P7-18-c-2cstr.pol.

POLYMATH Results
NLES Solution

Variable	Value	f(x)	Ini Guess
Cc	4.9334151	3.004E-10	4
Cs	0.1261699	6.008E-10	5
umax	0.8		
Km	4		
Csoo	10		
Cs1	1.333		

Ysc	2
rg	0.120683
rs	-0.241366
V	5000
vo	1000
D	0.2
X	0.987383
Cc1	4.33

NLES Report (safenewt)

Nonlinear equations
[1] f(Cc) = D*(Cc-Cc1)-rg = 0
[2] f(Cs) = D*(Cs1-Cs)+rs = 0

Explicit equations
[1] umax = 0.8
[2] Km = 4
[3] Csoo = 10
[4] Cs1 = 1.333
[5] Ysc = 2
[6] rg = umax*Cs*Cc/(Km+Cs)
[7] rs = -Ysc*rg
[8] V = 5000
[9] vo = 1000
[10] D = vo/V
[11] X = 1-Cs/Csoo
[12] Cc1 = 4.33

$C_{C2} = 4.933\ g/dm^3$ $\quad X = 0.987$
$C_{S2} = 1.26\ g/dm^3$ $\quad C_{P1} = Y_{P/C}C_{C1} = 0.9866\ g/dm^3$

P7-18 (d)

For washout dilution rate, $C_C = 0$

$$\Rightarrow \quad D_{max} = \frac{\mu_{max} C_{SO}}{K_M + C_{SO}} = \frac{0.8hr^{-1} \times 10g/dm^3}{4g/dm^3 + 10g/dm^3} = 0.57hr^{-1}$$

$$D_{MAX\ PROD} = \mu_{max}\left[1 - \sqrt{\frac{K_M}{K_M + C_{SO}}}\right] = 0.8hr^{-1}\left[1 - \sqrt{\frac{4g/dm^3}{4g/dm^3 + 10g/dm^3}}\right] = 0.37hr^{-1}$$

Production rate = $C_C v_O(24hr) = 4.85\ g/dm^3$ x1000dm^3/hrx24hr = 116472.56g/day

P7-18 (e)

For batch reactor,

V = 500dm^3, $\quad \frac{dC_C}{dt} = r_g \qquad \frac{dC_S}{dt} = r_S$

$C_{CO} = 0.5\ g/dm^3 \quad C_{SO} = 10 g/dm^3$

$$-r_S = Y_{S/C} r_g \qquad r_g = \frac{\mu_{max} C_S}{K_M + C_S} C_C$$

See Polymath program P7-18-e.pol.

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	6	6
Cc	0.5	0.5	5.4291422	5.4291422
Cs	10	0.1417155	10	0.1417155
Km	4	4	4	4
Ysc	2	2	2	2
umax	0.8	0.8	0.8	0.8
rg	0.2857143	0.1486135	1.403203	0.1486135
rs	-0.5714286	-2.8064061	-0.2972271	-0.2972271

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Cc)/d(t) = rg
[2] d(Cs)/d(t) = rs

Explicit equations as entered by the user
[1] Km = 4
[2] Ysc = 2
[3] umax = 0.8
[4] rg = umax*Cs*Cc/(Km+Cs)
[5] rs = -Ysc*rg

For t = 6hrs, $C_C = 5.43 g/dm^3$.
So we will have 3 cycle of (6+2)hrs each in 2 batch reactors of $V = 500dm^3$.
Product rate = C_C x no. of cycle x no. of reactors x V = 5.43 g/dm^3 x 3 x 2 x 500dm^3
= 16290g/day.

P7-18 (g) Individualized solution

P7-18 (f) Individualized solution

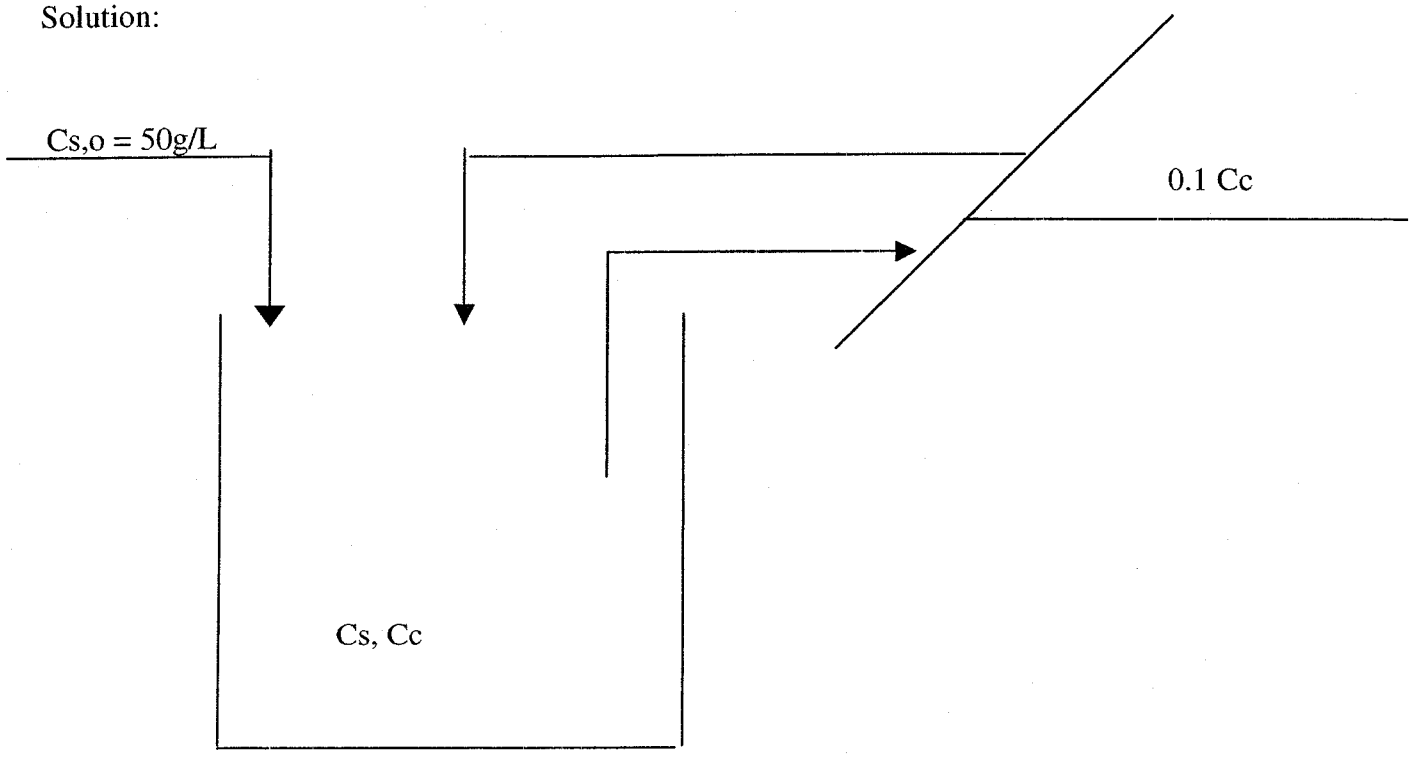
Fogler 7-19 Solution

Problem Statement:

Lactic acid is produced by a Lactobacillus species cultured in a CSTR. To increase the cell concentration and production rate, most of the cells in the reactor outlet are recycled to the CSTR, such that the cell concentration in the product stream is 10 % of cell concentration in the reactor. Find the optimum dilution rate that will maximize the rate of lactic acid production in the reactor. How does this optimum dilution rate change if the exit cell concentration fraction is changed? [$r_p = (\alpha \mu + \beta)Cc$]

$\mu_{max} = 0.5$ h-1, $K_s = 2.0$ g/L, $\alpha = 0.2$ g/g, $C_{s,0} = 50$ g/L
$\beta = 0.1$g/g.h, $Y_{x/s} = 0.2$ g/g, $Y_{p/s} = 0.3$ g/g

Solution:



A steady state material balance on the Bioreactor (including the recycle device) gives:

	Accumulation =	inlet -	outlet +	generation	
Cells:	0 =	0	$- D*0.1 * Cc +$	$\mu*Cc$	(7.19.1)
Substrate:	0 =	$D *C_{S0}$	$- D * C_S$	$-\mu*Cc/Y_{x/s} - r_P/Y_{p/s}$	(7.19.2)
Product:	0 =	0	$- D * C_P$ +		(7.19.3)

From equation (7.19.1) :

$$\frac{\mu_{max} C_S}{K_S + C_S} = \mu = 0.1 * D \quad \Rightarrow \quad C_S = \frac{0.1 * D * K_S}{\mu_{max} - 0.1 * D} \qquad (7.19.4)$$

From equation (7.19.2): $C_C = \dfrac{D*(C_{S,0} - C_S)}{\left(\dfrac{\mu}{Y_{X/S}} + \dfrac{\alpha\mu + \beta}{Y_{P/S}}\right)} = \dfrac{D*(C_{S,0} - C_S)}{\left(\dfrac{0.1*D}{Y_{X/S}} + \dfrac{\alpha*0.1*D + \beta}{Y_{P/S}}\right)}$

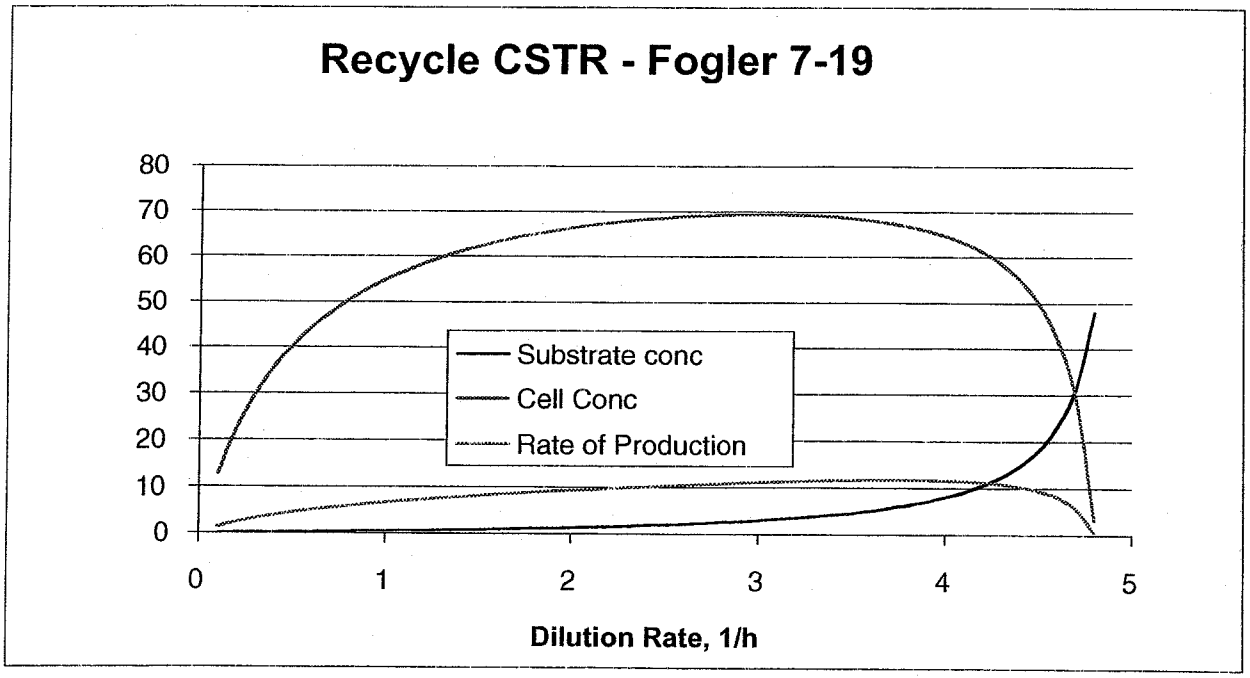
(7.19.5)

Rate of production $r_p = (\alpha\,\mu + \beta)Cc =$

$$\frac{(\alpha * 0.1 * D + \beta) * D * \left(C_{S,0} - \dfrac{0.1 * D * K_S}{\mu_{max} - 0.1 * D}\right)}{\left(\dfrac{0.1 * D}{Y_{X/S}} + \dfrac{\alpha * 0.1 * D + \beta}{Y_{P/S}}\right)} \qquad (7.19.6)$$

Differentiating equation (7.19.6) w.r.t. the dilution rate D, one can determine the optimum dilution rate that will maximize the rate of production.

For the given parameter values in the problem statement, the substrate and cell concentrations and the rate of lactic acid production can be calculated from the above equations and plotted versus the dilution rate. The optimum dilution rate = 3.765 hr^{-1}.



P7-20 (a)

$X_1 + S \rightarrow \text{More } X_1 + P_1$

$X_2 + X_1 \rightarrow \text{More } X_2 + P_2$

For CSTR,

$$\frac{dC_S}{dt} = D(C_{SO} - C_S) - Y_{S/X_1} r_{gX_1} \qquad \frac{dC_{X_1}}{dt} = D(-C_{X_1}) + r_{gX_1} - Y_{X_1/X_{21}} r_{gX_2}$$

$$\frac{dC_{X_2}}{dt} = D(-C_{X_2}) + r_{gX_2}$$

$$r_{gX_1} = \mu_1 C_{X_1} \qquad r_{gX_2} = \mu_2 C_{X_2}$$

See Polymath program P7-20-a.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	1	1

Cs	10	1.2366496	10	1.2366496
Cx1	25	25	25.791753	25.456756
Cx2	7	7	7.2791882	7.2791882
Km1	10	10	10	10
Km2	10	10	10	10
u1max	0.5	0.5	0.5	0.5
u2max	0.11	0.11	0.11	0.11
rgx1	6.25	1.4008218	6.25	1.4008218
rgx2	0.55	0.55	0.5748833	0.5748833
Yx1s	0.14	0.14	0.14	0.14
Ysx1	7.1428571	7.1428571	7.1428571	7.1428571
Yx2x1	0.5	0.5	0.5	0.5
Yx1x2	2	2	2	2
Cso	250	250	250	250
D	0.04	0.04	0.04	0.04

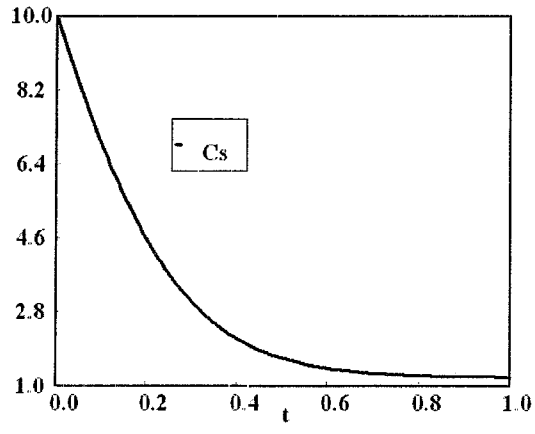
ODE Report (RKF45)

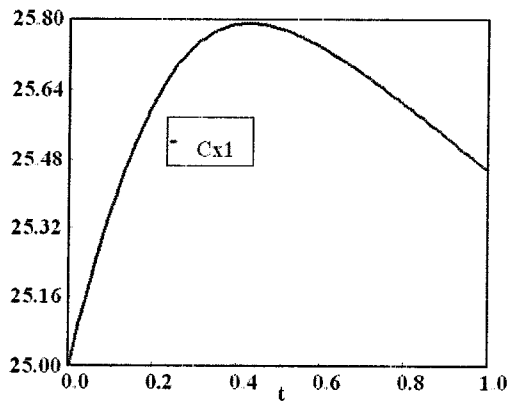
Differential equations as entered by the user

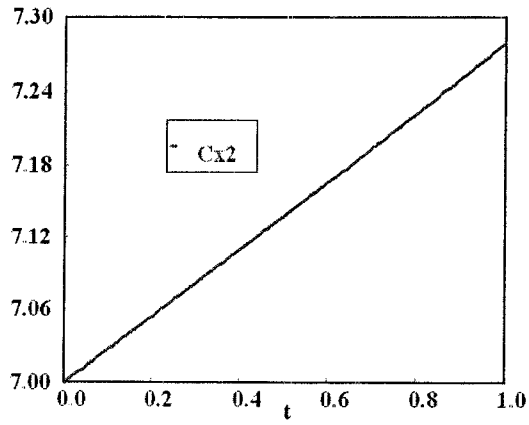
[1] d(Cs)/d(t) = D*(Cso-Cs)-Ysx1*rgx1
[2] d(Cx1)/d(t) = D*(-Cx1)+rgx1-Yx1x2*rgx2
[3] d(Cx2)/d(t) = D*(-Cx2)+rgx2

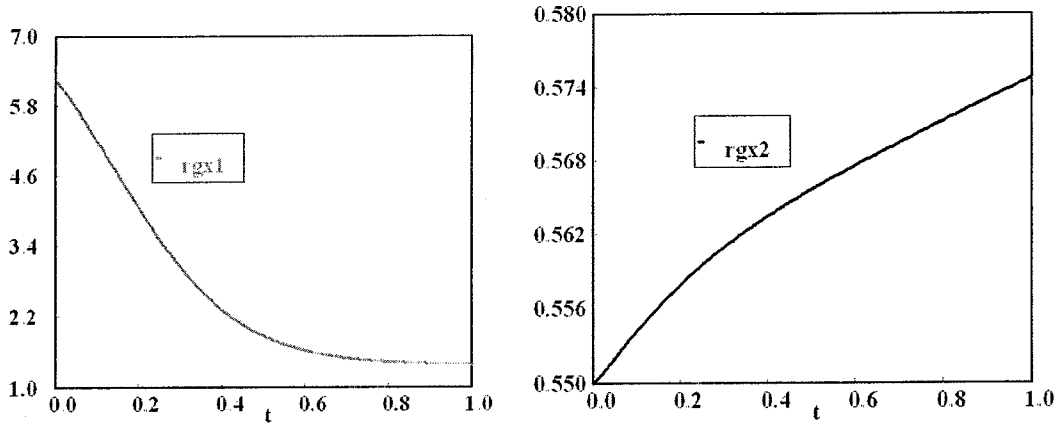
Explicit equations as entered by the user

[1] Km1 = 10
[2] Km2 = 10
[3] u1max = 0.5
[4] u2max = 0.11
[5] rgx1 = u1max*Cs*Cx1/(Km1+Cs)
[6] rgx2 = u2max*Cx1*Cx2/(Km2+Cx1)
[7] Yx1s = 0.14
[8] Ysx1 = 1/Yx1s
[9] Yx2x1 = 0.5
[10] Yx1x2 = 1/Yx2x1
[11] Cso = 250
[12] D = 0.04









P7-20 (b) When we increase D, C_S increases, C_{X1} decreases, and C_{X2} has very little decrease.

P7-20 (c) When C_{SO} decreased, C_S and C_{X1} both decreases, C_{X2} has no noticeable change.
When C_{Si} increased, C_{X1} increases, C_{X2} has no noticeable change for large t

P7-20 (d) Individualized solution

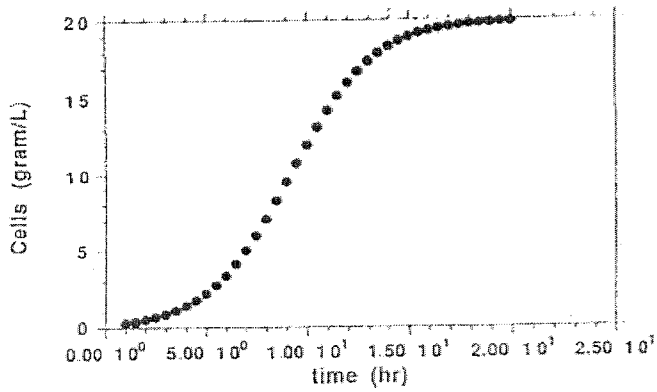
P7-20 (e) Individualized solution

P7-21 (a and b)

Run #1 No Yeast Extract
#2 Yeast Extract

The percent volume of the growth product H_2S collected above the broth was reported as a function of time:

cell + nutrient $\longrightarrow$ more cells + product



(a and b)

$C_X = C_{X0}\, e^{\mu(t - t_{lag})}$
or $C_X = C_{X0}\, e^{\mu t}\, e^{-\mu t_{lag}}$

curve fit exponential curve:

$X = A\, e^{kt}$

where $A = C_{X0} e^{-\mu t_{lag}}$

$$t_{lag} = \ln \frac{\left(\frac{C_{X0}}{A}\right)}{\mu}$$

Run 1 (between 15, 20, 30 hrs)

$\mu_{max} = 0.2125\ hr^{-1}$

$A = 7492.6$

$t_{log} = \ln\left(\frac{2.7 \times 10^4}{7492.6}\right) = 0.21252$

$t_{lag} = 6.0\ hr$

Run 2 (points 10, 15, 20 hrs)

$\mu_{max} = 0.3124\ hr^{-1}$

$A = 5571.7$

$t_{lag} = 5.1\ hr$

P7-21 (c)

Stationary

$t_{stationary}$ between

Time	45 to 55	25 to 15
length of time	10 hr	20 hr

P7-21 (d) Production starts at the end of the exponential (for both runs)

P7-21 (e)

$$\frac{dC_C}{dt} = D(C_{C0} - C_C) + \mu C_C = 0$$

$D(C_{C0} - C_C) + \mu C_C = 0$ $\qquad C_C = 0$

$-D C_C + \mu C_C = 0$

$C_C = 0$ or $D = \mu$ wash out occurs when $D > \mu_{max}$

P7-21 (f) Individualized solution

P7-21 (g) Individualized solution

P7-22 (a)

$$\frac{dC_C}{dt} = D(C_{C_{IN}} - C_C) + r_g$$

$\frac{dC_C}{dt} = 0 \qquad C_{C_{IN}} = 0$

$0 = -DC_C + r_g$

$C_{S0} = 30$

$\mu_{max} = 1.5\ hr^{-1}$

$C_{S_{IN}} = C_{C0} = 0.5\ g/dm^3$

$K_i = 50\ g/dm^3$

$K_S = 1\ g/dm^3$

$D = 0.75$

$Y_{C/S} = 0.08$

$$0 = -DC_C + \left(\frac{\mu_{max} C_S C_C}{K_S + C_S \left(1 + \frac{C_S}{K_I}\right)} \right)$$

$$\boxed{D = \left(\frac{\mu_{max} C_S}{K_S + C_S \left(1 + \frac{C_S}{K_I}\right)} \right)} \qquad D = \left(\frac{1.5\, C_S}{1 + C_S \left(1 + \frac{C_S}{8}\right)} \right)$$

$\boxed{C_S = C_{S0} - y_{S/X} C_C}$ by definition

$$y_{S/X} = \frac{1}{y_{S/X}} = \frac{1}{0.08} = 12.5$$

$$C_C = \frac{C_{S0} - C_S}{y_{S/X}} = \frac{C_{S0}}{12.5}$$

$$D = \left(\frac{\mu_{max} C_S}{K_S + C_S \left(1 + \frac{C_S}{K_I}\right)} \right) \qquad C_C = y_{C/S} (C_{S0} - C_S)$$

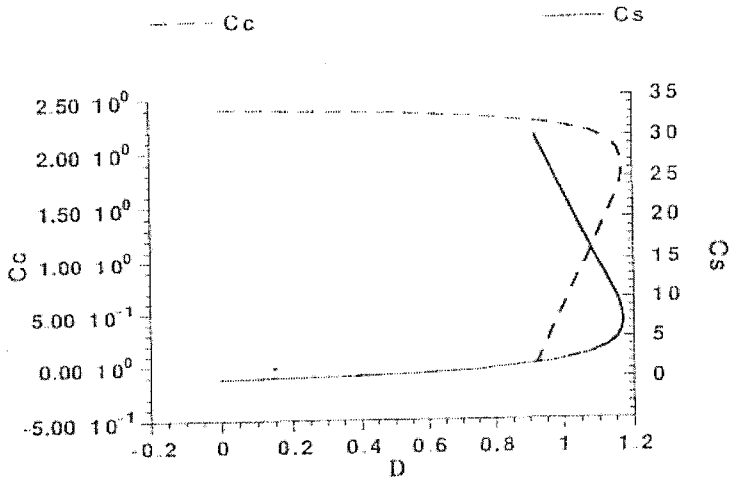
pick C_S, calculate D and C_C

$C_{S0} = 30.0\ g/dm^3$

$$D = \left(\frac{1.5\, C_S}{1 + C_S \left(1 + \frac{C_S}{8}\right)} \right) \qquad C_C = (30.0 - C_S)(0.08)$$

For $D = 0.876 hr^{-1}$ ($C_S = 2.5 g/dm^3$), production rate is maximum

P7-22 (c)



For $D = 0.27 hr^{-1}$, $C_C = 0$ if $C_{CO} = 0.5\ g/dm^3$.
For $D = 0.314 hr^{-1}$, $C_C = 0$ if $C_{CO} = 0\ g/dm^3$.
And for maximum production rate, $D = 0.876 hr^{-1}$.

P7-22 (d)

For batch reactor,

$$\frac{dC_C}{dt} = r_g \qquad \frac{dC_S}{dt} = -Y_{S/C} r_g \qquad r_g = \frac{\mu_{max} C_S C_C}{K_S + C_S(1 + C_S / K_I)}$$

See Polymath program P7-22-d.pol.

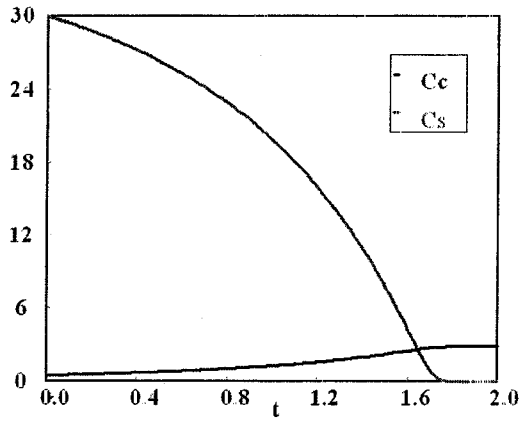
POLYMATH Results
Calculated values of the DEQ variables

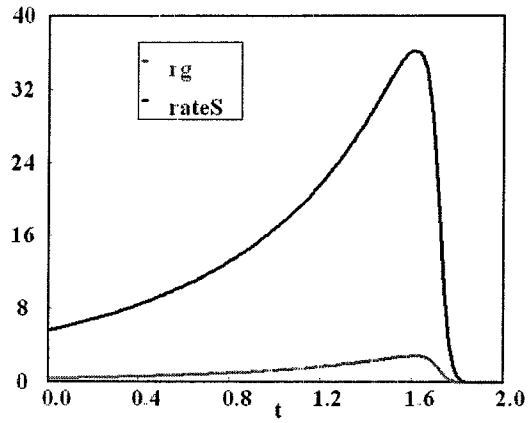
Variable	initial value	minimal value	maximal value	final value
t	0	0	2	2
Cc	0.5	0.5	2.9	2.9
Cs	30	2.01E-07	30	2.01E-07
Ki	50	50	50	50
umax	1.5	1.5	1.5	1.5
Ks	1	1	1	1
rg	0.4591837	8.744E-07	2.9019168	8.744E-07
Ycs	0.08	0.08	0.08	0.08
Ysc	12.5	12.5	12.5	12.5
rateS	5.7397959	1.093E-05	36.27396	1.093E-05

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Cc)/d(t) = rg
[2] d(Cs)/d(t) = -Ysc*rg

Explicit equations as entered by the user
[1] Ki = 50
[2] umax = 1.5
[3] Ks = 1
[4] rg = umax*Cs*Cc/(Ks+Cs*(1+Cs/Ki))
[5] Ycs = 0.08
[6] Ysc = 1/Ycs
[7] rateS = Ysc*rg





P7-22 (e)

For semi-batch reactor,

$$\frac{dC_C}{dt} = r_g - \frac{v_O C_C}{V} \qquad \frac{dC_S}{dt} = -Y_{S/C} r_g + \frac{v_O (C_{Sin} - C_S)}{V}$$

$$r_g = \frac{\mu_{max} C_S C_C}{K_S + C_S(1 + C_S / K_I)} \qquad V = V_O + v_O t$$

See Polymath program P7-22-e.pol.

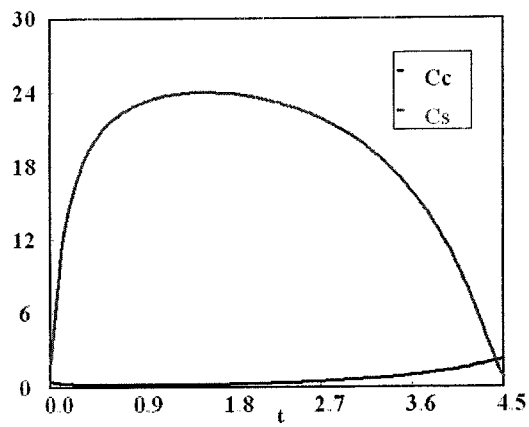
POLYMATH Results
Calculated values of the DEQ variables

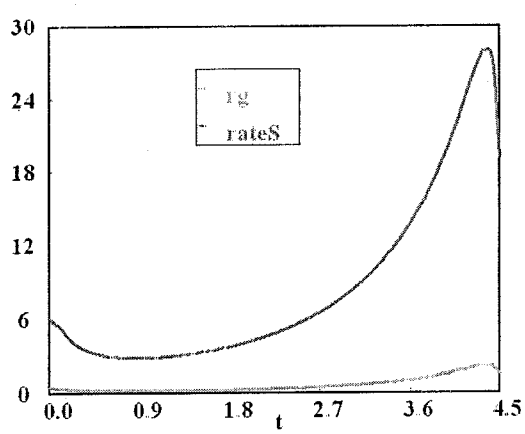
Variable	initial value	minimal value	maximal value	final value
t	0	0	4.5	4.5
Cc	0.5	0.2329971	2.2593341	2.2593341
Cs	2	0.8327919	24.016878	0.8327919
Ki	50	50	50	50
vo	50	50	50	50
Vo	10	10	10	10
V	10	10	235	235
Csin	30	30	30	30
umax	1.5	1.5	1.5	1.5
Ks	1	1	1	1
rg	0.487013	0.2329022	2.2464622	1.5283423
Ycs	0.08	0.08	0.08	0.08
Ysc	12.5	12.5	12.5	12.5
rateS	6.0876623	2.9112771	28.080778	19.104279
VCc	5	5	530.94351	530.94351

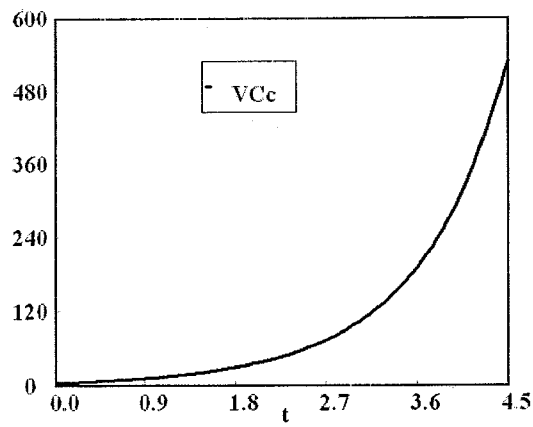
ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Cc)/d(t) = rg-vo*Cc/V
[2] d(Cs)/d(t) = -Ysc*rg+vo*(Csin-Cs)/V

Explicit equations as entered by the user
[1] Ki = 50
[2] vo = 50
[3] Vo = 10
[4] V = Vo+vo*t
[5] Csin = 30
[6] umax = 1.5
[7] Ks = 1
[8] rg = umax*Cs*Cc/(Ks+Cs*(1+Cs/Ki))
[9] Ycs = 0.08
[10] Ysc = 1/Ycs
[11] rateS = Ysc*rg
[12] VCc = V*Cc







P7-22 (f) Individualized solution

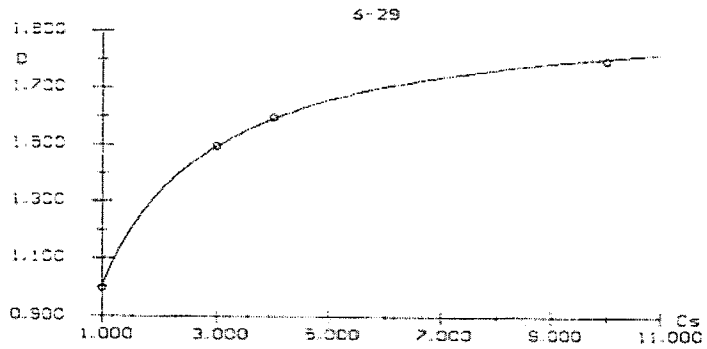
P7-22 (g) Individualized solution

P7-23 (a)

Fit the data to the equation:

$$D = \frac{C_S \mu}{K_S + C_S}$$

Using POLYMATH, find the values for μ_{max} and K_S. They are 1.98 and 0.97 respectively.



P7-23 (b)

Using this equation, solve for $Y_{C/S}$:

$$C_C = \frac{Y_{C/S}(C_{So} + K_S)}{\mu_{max} - D}\left(\frac{\mu_{max} C_{So}}{K_S + C_{So}} - D\right)$$

With the given information $Y_{C/S} = 0.099$, therefore, $Y_{S/C}$ is equal to the inverse of that, 10.075.

P7-24 No solution will be given.

P7-25 No solution will be given

P7-26 See Professional Reference Shelf 7.5 on the website for a sample solution.

CDP7-A No solution will be given.

CDP7-B

Given the following reaction scheme:

$$I^- + OCl^- \rightarrow OI^- + Cl^-$$

with the following rate law: $r_{OI^-} = \frac{kC_{I^-} C_{OCl^-}}{C_{OH^-}}$

Active intermediates assumed to be HOCl and HOI.
From table I, the first rule of thumb suggests:

$$OH^- + HOCl \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} OCl^- + H_2O \;,\; -r_1 = k_1 C_{OH^-} C_{HOCl} - k_{-1} C_{OCl^-} C_{H_2O}$$

$$OH^- + HOI \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} OI^- + H_2O \;,\; -r_2 = k_2 C_{OH^-} C_{HOI} - k_{-2} C_{OI^-} C_{H_2O}$$

The third rule of thumb suggests that the reverse reactions occur. A chain propagation step, involving the conversion of one intermediate into the other might tie in both the reactions above.

$$I^- + HOCl \overset{k_3}{\rightarrow} HOI + Cl^- \;,\; -r_3 = k_3 C_{I^-} C_{HOCl}$$

This step makes the overall reaction sequence $I^- + OCl^- \rightarrow OI^- + Cl^-$ possible:

$$-r_{OI} = r_2 = k_{-2} C_{OI^-} C_{H_2O} - k_2 C_{HO^-} C_{HOI}$$

$$-r_{HOI} = -r_2 + r_3 = k_2 C_{OH^-} C_{HOI} - k_{-2} C_{OI^-} C_{H_2O} - k_3 C_{I^-} C_{HOCl} = 0$$

$$k_3 C_{I^-} C_{HOCl} = k_2 C_{OH^-} C_{HOI} - k_{-2} C_{OI^-} C_{H_2O} = -r_{OI}$$

$$-r_{HOCl} = -r_1 - r_3 = k_1 C_{OH^-} C_{HOCl} - k_{-1} C_{OCl^-} C_{H_2O} + k_3 C_{I^-} C_{HOCl} = 0$$

or $[k_1 C_{OH^-} + k_3 C_{I^-}] C_{HOCl} = k_{-1} C_{OCl^-} C_{H_2O}$; i.e., $C_{HOCl} = \frac{k_{-1} C_{OCl^-} C_{H_2O}}{k_1 C_{OH^-} + k_3 C_{I^-}}$

Then: $-r_{OI} = \frac{k_{-1} k_3 C_{I^-} C_{OCl^-} C_{H_2O}}{k_1 C_{OH^-} + k_3 C_{I^-}}$ is close; with $k_1 >> k_3$

$$-r_{OI} = \frac{KC_{I^-} C_{OCl^-}}{C_{OH^-}} \text{ where } K = \frac{k_{-1} k_3}{k_1}$$

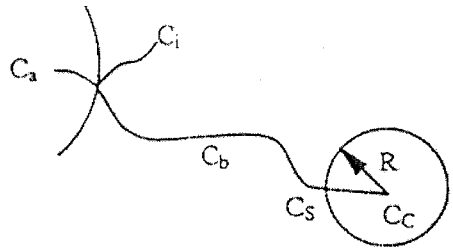
An alternative approach assumes that reaction 1 quickly attains equilibrium, then:

$$C_{HOCl} = \frac{k_{-1} C_{OCl^-} C_{H_2O}}{k_1 C_{OH^-}}$$

Then $-r_{OI} = k_3 C_{I^-} C_{HOCl} = \left[\frac{k_3 k_{-1} C_{H_2O}}{k_1}\right] \frac{C_{I^-} C_{OCl^-}}{C_{OH^-}}$

These two approaches are basically equivalent

CDP7-C



(a) Assumptions:

- Transfer rate from bubble bulk to fluid interface is not rate limiting, i.e., C_i is the equilibrium oxygen concentration.
- System is at pseudo steady-state with regard to the particle size, i.e., particle growth is slow compared to oxygen transfer.
- Rate of oxygen consumption is directly proportional to the cell growth rate:

$$r_{O_2} = \frac{1}{y_{O_2}} r_C \quad \text{where } y_{O_2} = \text{yield of cells on oxygen} \left\{\frac{\text{g cells}}{\text{mmole } O_2}\right\}$$

This implies that any oxygen utilization required to maintain the cells is negligible, and there is no significant metabolic product being synthesized.

Oxygen balance:
$$R_{O_2} = k_l a_b (C_i - C_b)$$
$$= k_l a_b C_C (C_b - C_s)$$
$$= \frac{\eta}{y_{O_2}} k C_S C_C$$

where:

$k_l a_b$ = overall mass transfer resistance from the bubble to the bulk.

a_C = surface area per gram of cells

k = mass transfer of cells on O_2

y_{O_2} = yield of cells on O_2

Rearrange O_2 balances:

$$\frac{R_{O_2}}{k_l a_b} = C_i - C_b \qquad (1)$$

$$\frac{R_{O_2}}{k_C a_C C_C} = C_b - C_s \qquad (2)$$

$$\frac{y_{O_2} R_{O_2}}{\eta k C_C} = C_s \qquad (3)$$

Add equations 1, 2 and 3

$$\frac{C_i}{R_{O_2}} = \frac{1}{k_l a_b} + \frac{1}{C_C}\left(\frac{1}{k_C a_C} + \frac{y_{O_2}}{\eta k}\right) \qquad (4)$$

(1) When oxygen consumption by the cells is slow, the process is reaction rate limited.
Thus $\eta \rightarrow 1$ and: $\frac{C_i}{R_{O_2}} = \frac{1}{k_l a_b} + \frac{y_{O_2}}{C_C k}$

(2) When oxygen consumption is much faster than mass transfer, the mass transfer becomes the limiting factor. $\frac{C_i}{R_{O_2}} = \frac{1}{k_l a_b} + \frac{1}{k_C a_C C_C}$

(b) To increase the growth rate, you could:

- Increase $k_l\, a_b$ by increasing fermentor agitation.
- Increase the concentration of cells (since this is an autocatalytic reaction)
- Increase clump surface area and the effectiveness factor by decreasing the particle size (also by increasing fermentor agitation).

(c) $R_C = y_{O_2} R_{O_2}$ From equation (4), have:

$$\frac{R_C}{C_i} = y_{O_2}\left[\frac{1}{k_l\, a_b} + \frac{1}{C_C}\left(\frac{1}{k_C\, a_C} + \frac{y_{O_2}}{\eta k}\right)\right]^{-1}$$

$$= y_{O_2} C_C\left[\frac{C_C}{k_l\, a_b} + \frac{1}{k_C\, a_C} + \frac{y_{O_2}}{\eta k}\right]^{-1}$$

$$\int_{C_{C0}}^{C_C} \frac{1}{y_{O_2} C_C\, C_i}\left[\frac{C_C}{k_l\, a_b} + \frac{1}{k_C\, a_C} + \frac{y_{O_2}}{\eta k}\right] dC_C = \int_0^t dt$$

$$\frac{C_C - C_{C0}}{k_l\, a_b} + \left(\frac{1}{k_C\, a_C} + \frac{y_{O_2}}{\eta k}\right) \ln \frac{C_C}{C_{C0}} = y_{O_2} C_i t$$

(d) Assumptions:

- There is a constant number of particles
- Each pellet is roughly spherical and has constant density.

We do not know which resistances are controlling, so we know there are no reaction limitations, but may be either internal or external diffusion limitations.

$$R_C = y_{O_2} C_i\left[\frac{1}{k_l\, a_b} + \frac{1}{C_C}\left(\frac{1}{k_C\, a_C} + \frac{y_{O_2}}{\eta k}\right)\right]^{-1}$$

As particle growth increases, k_C, a_C and η will change as functions of the particle diameter.

Thus need to find particle diameter as a function of C_C

$C_C = n\rho_C V_C$ where n = number concentration of particles (1/l)

$V_C = \frac{\pi}{6} d_p^3$ ρ_C = the density of the particles (g/l)

$d_p^3 = \frac{6C_C}{\pi n\, \rho_C}$ V_C = particle volume (l)

Internal diffusional resistance can be modeled as:

$$\frac{1}{\eta k} = \alpha_1 d_p$$

External diffusional resistance with or without shear is:

$$\frac{1}{k_C\, a_C} = \alpha_2 d_p^b \qquad 1.5 \le b \le 2$$

$$R_C = y_{O_2} C_i\left[\frac{1}{k_l\, a_b} + \frac{1}{C_C}\left(\alpha_1 d_p + y_{O_2} \alpha_2 d_p^b\right)\right]^{-1}$$

$$R_C = y_{O_2} C_i\left[\frac{1}{k_l\, a_b} + \frac{1}{C_C}\left(\alpha_1' C_C^{1/3} + \alpha_2 C_C^{b/3}\right)\right]^{-1}$$

where $\alpha_1 = \alpha_1 \frac{6}{\pi n\, \rho_C}$ and $\alpha_2 = \alpha_2 \frac{6 y_{O_2}}{\pi n\, \rho_C}$

Dropping the primes and simplifying:

$$R_C = y_{O_2} C_i\left[\frac{1}{k_l\, a_b} + \alpha_1 C_C^{2/3} + \alpha_2 C_C^{b/3-1}\right]^{-1}$$

$$\int_{C_{C0}}^{C_C} \left[\frac{1}{k_l a_b} + \alpha_1 C_C^{-2/3} + \alpha_2 C_C^{b/3-1}\right] dC_C = \int_0^t y_{O_2} C_i \, dt$$

$$\frac{C_C - C_{C0}}{k_l a_b} + 3\alpha_1 \left(C_C^{1/3} - C_{C0}^{1/3}\right) + \frac{3\alpha_2}{b}\left(C_C^{b/3} - C_{C0}^{b/3}\right) = y_{O_2} C_i \, t$$

(e) From part (c), we have:

$$\frac{C_C - C_{C0}}{k_l a_b} + \left(\frac{1}{k_C a_C} + \frac{y_{O_2}}{\eta k}\right) \ln \frac{C_C}{C_{C0}} = y_{O_2} C_i \, t$$

For a vigorously stirred fermentor, assume that fluid shear is sufficiently high, that transport to the edge of the floc is negligible[1]:

$$\frac{1}{k_C a_C} \rightarrow 0$$

The mass transfer resistance from air bubble to bulk liquid depends on the fermentor design, air flow rate, agitation rate and a number of other factors. For a 10 l laboratory scale fermentor, $k_l a_b$ was found to be ~ 150 $\frac{\text{m Mole}}{\text{l hr atm}}$ during the growth phase of the fermentation.[2]

Dividing through by Henry's low constant:

$$k_l a_b = \left(150 \frac{\text{m Mole}}{\text{l hr atm}}\right)\left(0.88 \frac{\text{atm l}}{\text{m Mole}}\right)\left(\frac{1 \text{ hr}}{3600 \text{ s}}\right)$$

$$= 3.67 \times 10^{-2} \text{ s}^{-1}$$

Effectiveness factor: Microbial growth on multiple substrates (here oxygen and glucose) is typically modelled using Monod type kinetics:

$$\mu (\text{hr}^{-1}) = \mu m \left(\frac{C_N}{K_N + C_N}\right)\left(\frac{C_0}{K_0 + C_0}\right)$$

$$R_C = \mu C_C$$

By representing the reaction as first-order with respect to oxygen, we are essentially assuming a low oxygen concentration, relative to the intrinsic rate parameter, K_0:

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By representing the reaction as first-order with respect to oxygen, we are essentially assuming a low oxygen concentration, relative to the intrinsic rate parameter, K_0:

For a first-order reaction, the effectiveness factor is:

$$\eta = \frac{3}{\phi^2}(\phi \cosh \phi - 1)$$

$$\eta = 0.45$$

Reaction rate constant:

$$k = \frac{\mu_{max}}{K_s} = \frac{8.3 \times 10^{-5} \text{ s}^{-1}}{3.2 \times 10^{-4} \frac{\text{gO}_2}{\text{l}}} = 0.26 \frac{\text{l}}{\text{gO}_2 \text{ s}}$$

Finally, assume an initial cell concentration of 0.25 g cell/l, the cell concentration equation now becomes:

$$\frac{(C_C - 0.25)\frac{\text{g cell}}{\text{l}}}{3.67 \times 10^{-2} \text{ s}^{-1}} + \left[\frac{1.5 \frac{\text{g cell}}{\text{gO}_2}}{(0.45)\left(0.26 \frac{\text{l}}{\text{gO}_2 \text{ s}}\right)}\right] \ln 4C_C = \left(1.5 \frac{\text{g cell}}{\text{gO}_2}\right)\left(7.7 \times 10^{-3} \frac{\text{g O}_2}{\text{l}}\right) t$$

$$27.25 (C_C - 0.25) + 12.8 \ln 4C_C = 0.012 t$$

Clearly, mass transfer from the gas to the liquid phase and internal diffusion play important roles in determining the cell growth rate.

Cell mas vs time. Start at 0.25 g/l

t (hr)	C_C (g/l)	t (hr)	C_C (g/l)
0	0.25	8	11.15
1	1.13	9	12.67
2	2.37	10	14.21
3	3.74	11	15.74
4	5.17	12	17.28
5	6.64	0.5	0.62
6	8.13	1.5	1.72
7	9.63		

From the graph it can be seen that growth starts out exponentially and becomes linear as the fermentation becomes limited by gas-liquid mass transfer.

Sensitivity analysis:

The gas-liquid mass transfer coefficient is related to the agitation rate to the 0.95 power[3]: $k_l a_b \propto N^{0.95}$

What is the effect of increasing the agitation by 50%?

$$k_l a_2 = k_l a_1 (1.5^{0.95})$$

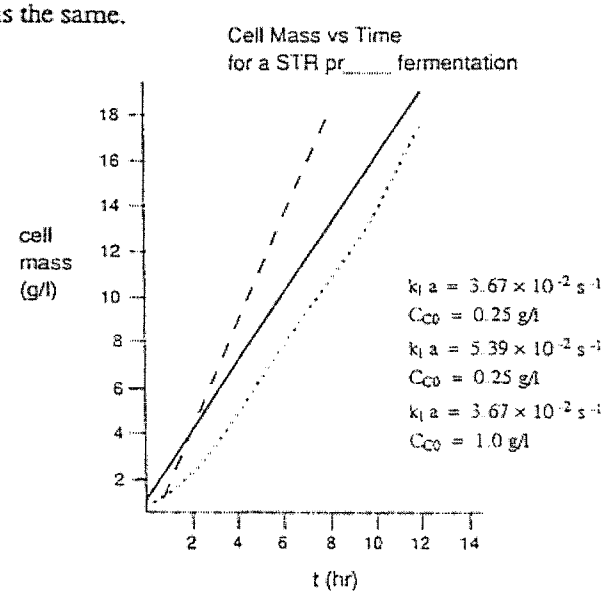
$$= (3.67 \times 10^{-2})\, s^{-1} (1.5^{0.95})$$

$$= (5.39 \times 10^{-2})\, s^{-1} \qquad \text{(see graph)}$$

Since cell growth has an exponential portion, another way to increase the growth rate would be to increase the innocuous size, C_{C0}. What happens when C_{C0} is quadrupled?

$$C_{C0} = 1.0 \text{ g/l} \qquad \text{(see graph)}$$

From the results shown in the graph, a relatively small increase in the agitation rate leads to a significant increase in the cell growth rate, while an increase in innoculum size means that the fermentation reaches a gas-liquid transfer-limited state more quickly, but the growth rate remains the same.



References:

(1) James E. Bailey and David F. Ollis, Biochemical Engineering Fundamentals, (NY: McGraw-Hill, 1977), Chapters 7 and 8.

(2) G.F. Payne, PhD Thesis, University of Michigan, (1983).

(3) D.I.C. Wang, et. al., Fermentation and Enzyme Technology, (NY: John Wiley & Sons, 1979), Chapter 9.

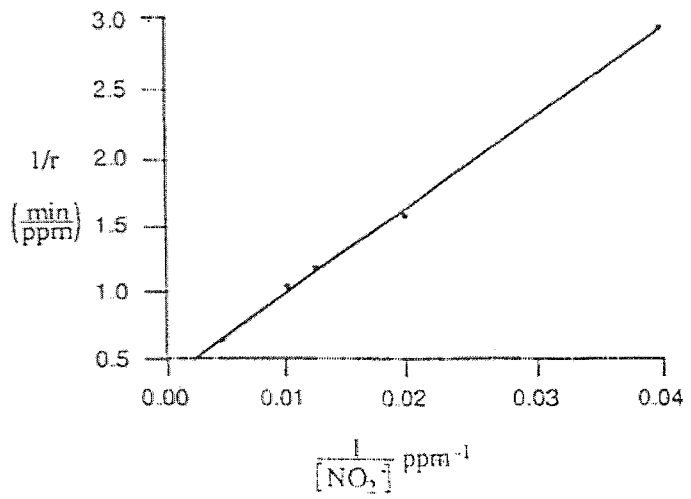
CDP7-D No solution will be given.

CDP7-E

Since the denitrification follows Michaelis-Menton kinetics, first determine V_{max} and K_m from Lineweaver Burk plot.

Initial $[NO_2^-]$ (ppm)	$\frac{1}{[NO_2^-]}$	Time for 50.6° reduction, (min)	Rate of reaction r, (ppm/min)	1/r
25	.04	35	.357	2.800
50	.02	38	.658	1.520
75	.013	44	.852	1.173
100	.010	50	1.000	1.000
200 (given)	.005	66 (given)	1.515	0.660

where the rate of reaction is found by the ratio: $\frac{\text{initial}\,[NO_2^-]/2}{\text{time for 50\% reduction}}$



Lineweaver Burk: $\frac{1}{r} = \left(\frac{K_m}{V_{max}}\right)\frac{1}{S} + \frac{1}{V_{max}}$ where $S^* = [NO_2^-]$

From the plot, $V_{max} = \frac{1}{\text{intercept}} = 2.73 \frac{\text{ppm}}{\text{min}}$

$$\therefore K_m = 165 \text{ ppm}$$

Next, need conversion as a function of time.

Design equation: $N_{S0} \frac{dX}{dt} = -r_S V$

Rate Law: $-r_S = \frac{V_{max} S}{K_m + S}$

Stoichiometry: $S = S_0 (1 - X)$

Combining: $S_0 \frac{dX}{dt} = V_{max} S_0 \left[\frac{1 - X}{K_m + S_0 (1 - X)}\right]$

$$\int_0^X \frac{K_m + S_0 (1 - X)}{(1 - X)} dX = V_{max} \int_0^t dt$$

$$\therefore K_m \ln\left(\frac{1}{1 - X}\right) + S_0 X = V_{max} t$$

Finally, $V_{max} t = S_0 X - K_m \ln (1 - X)$
Know V_{max}, K_m, $t = 68$ hrs $= 4080$ min

$$S_0 = 0.25 \left(\frac{\text{mol}}{\text{l}}\right)\left(46 \frac{\text{g}}{\text{mol}}\right)\left(\frac{1000 \text{ mg}}{\text{g}}\right)\left(\frac{1 \text{ ppm}}{\text{mg/l}}\right) = 11{,}500 \text{ ppm}$$

Iteration to find the conversion obtained after 68 hrs gives: $X = 0.930$
The $[NO_2^-]$ level is: $(1 - 0.930)(11{,}500 \text{ ppm}) = 805$ ppm
Since t, K_m, and S_0 are fixed by the system, the change must be made in V_{max}.

Desired conversion: $X = 1 - \frac{500}{11{,}500} = .9565$

$$\therefore \text{Desired } V_{max} = \frac{11{,}500 (.9565) - 165 \ln (1 - .9565)}{4080} = 2.823 \frac{\text{ppm}}{\text{min}}$$

Since $V_{max} \alpha [E_t]$, increasing the concentration of whole cells in the emulsion will increase

$$V_{max} : \left(\frac{2.823}{273}\right) 50 \frac{\text{mg cells}}{\text{ml emulsion}} = 51.7 \frac{\text{mg cells}}{\text{ml emulsion}}.$$

Therefore, increasing the cell loading to $52 \frac{\text{mg cells}}{\text{ml emulsion}}$ would results in a level of $[NO_2^-] <$ 500 ppm after 68 hours.

CDP7-F No solution will be given.

CDP7-G

Mole balances in a CSTR

$$DC_{S0} - DC_S + r_S = 0$$

$$-DC_p - r_p = 0$$

$$C_{S0} - C_S = \frac{r_p}{D}$$

$$C_p = \frac{r_p}{D}$$

the rate law as given is:

$$r_p = -r_S$$

$$r_p = \frac{V_{max} C_S}{K_S + C_S}\left(1 - \frac{C_p}{C_p^*}\right)$$

Plugging those into POLYMATH and using different values of D and C_c, come up with the following:

Using a volume of 200 dm^3 and a cell concentration of 50, get the best production of the L-malic acid.

Equations:

```
f(cs)=cs-cso+rp/D
f(cp)=cp-rp/D
cso=2
D=50
cc=50
vmax=76
km=.048
cpstar=1.69
rp=vmax*cs/(km+cs)*(1-cp/cpstar)*cc
```

Initial value

4	
2	

Solution

Variable	Value	f()
cs	0.351657	3.222e-15
cp	1.64834	-3.277e-15
cso	2	
D	50	
cc	50	
vmax	76	
km	0.048	
cpstar	1.69	
rp	82.4171	

CDP7-H

Michaelis-Menton Kinetics:

$$-r_s = \frac{V_{max} C_S}{K_m + C_S}$$

$$K_m = 6.2 \times 10^{-2} \text{ ml/ml} = 6.2\%$$

$$V_{max} = 5.6 \frac{\mu\text{mol}}{\text{ml} \cdot \text{min}} \qquad E = 40 \text{ mg}$$

Mole Balance:

$$-\frac{dC_S}{dt} = \frac{V_{max} C_{S\%}}{K_m + C_{S\%}}$$

$$C_{S\%} = C_{So\%}(1 - X) \quad \Rightarrow \quad x = \frac{1.4 - 0.2}{1.4} = 0.86$$

Where $C_{s\%}$ is the percent of fish oil.
For most oils:

$$C_T = \frac{\text{density}}{MW} = \frac{0.9}{300} = 3 \times 10^{-3} \text{ mol/ml} = 3 \times 10^3 \, \mu\text{mol/ml}$$

$$C_S = C_T C_{S\%}$$

$$\Rightarrow \int_{1.4}^{0.2} \frac{K_m + C_{S\%}}{C_{S\%}} dC_{S\%} = \int_0^t \frac{V_{max}}{C_T} dt = \int_0^t \frac{5.6 \times 10^{-3}}{3} dt$$

$$\Rightarrow K_m \ln\left(\frac{1.4}{0.2}\right) + (1.4 - 0.2) = \frac{5.6 \times 10^{-3}}{3} t$$

$$\Rightarrow t = \frac{6.2 \ln(7) + 1.2}{5.6 \times 10^{-3}/3} \text{ min} = 7106 \text{ min} = 118.4 \text{ hrs}$$

CDP7-I No solution will be given.

CDP7-J

(a) No solution will be given.

(b)

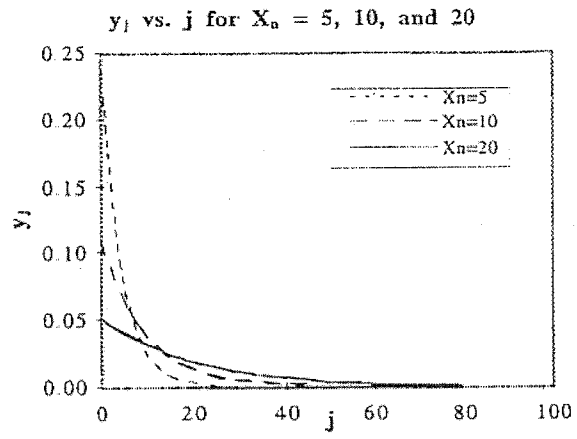
$$y_j = (1 - p)p^{j-1} \qquad w_j = j(1 - p)^2 p^{j-1}$$

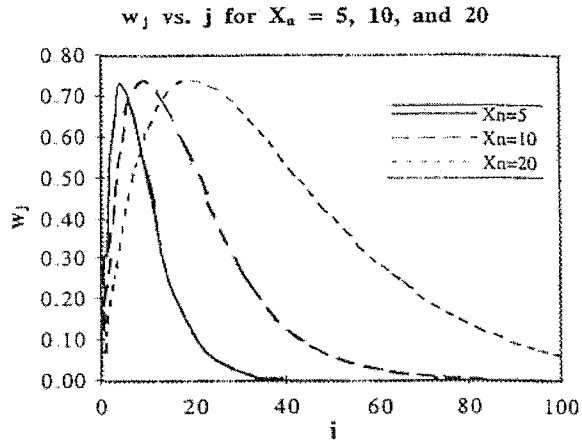
$$X_n = \frac{1}{1 - p} \qquad \text{For } X_n = 5: \quad p = 0.80$$

$$X_n = 10: \quad p = 0.90$$

$$X_n = 20: \quad p = 0.95$$

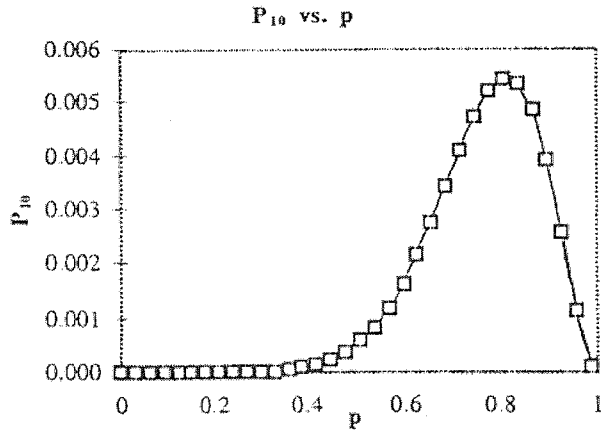
Use these equations to generate the desired graphs:





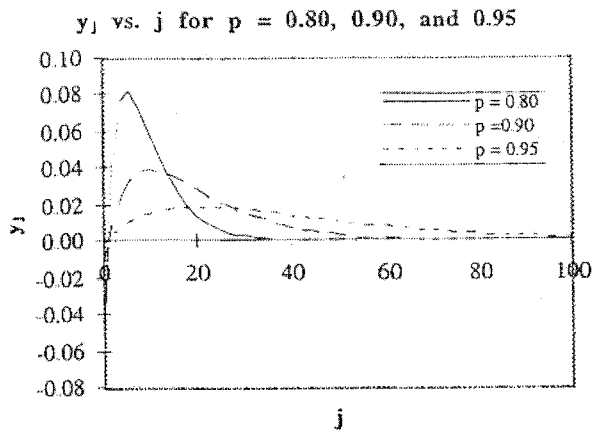
$$P_j = M_o(1-p)^2 p^{j-1} = M_o(1-p)^2 p^9$$

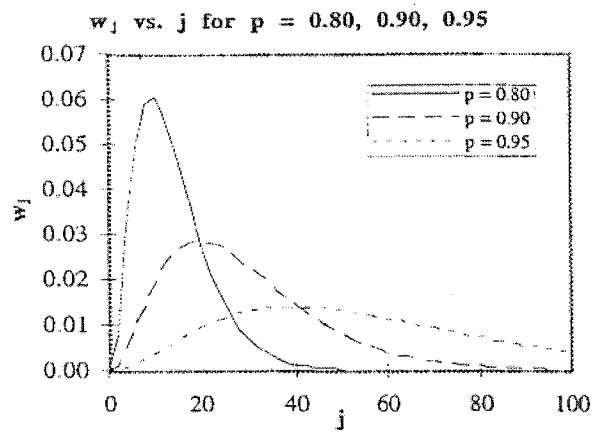
Use the above equation to generate a graph of P_{10} vs. p:



(c) $y_j = (j-1)(1-p)^2 p^{j-2}$ $w_j = \frac{1}{2} j(1-p)^3 (j-1) p^{j-2}$

Use these equations to generate graphs of y_j and w_j vs. j.





(d) $\overline{M}_n = \mu_n M_M = \dfrac{M_M}{1-p}$

$$\overline{M}_w = \mu_w M_M = M_M \frac{1+p}{1-p}$$

$$D = \frac{\mu_w}{\mu_n} = \left(\frac{1+p}{1-p}\right)(1-p) = 1+p$$

We must find the value of p.

$$\ln \frac{M}{M_o} = \left(\frac{8k_p^2 f I_{2o}}{k_o k_t}\right)^{1/2}\left[\exp\left(\frac{-k_o t}{2}\right) - 1\right] = -0.067$$

$$M = 2.803$$

$$I_2 = I_{2o}\exp(-k_o t) = (0.001)\exp\left[\left(-1.4\times10^{-3}\right)(14{,}400)\right] = 2.794\times10^{-9}$$

$$p = \beta = \frac{k_p M}{k_p M + k_m M + k_c C + k_s S + \sqrt{2k_t k_o f(I_2)}} = 0.99991$$

This can then be used to calculate the desired values:

$$\overline{M}_n = \frac{104}{1-0.99991} = 1.155\times10^6$$

(e) Mole fraction of polystyrene of chain length 10 (y_{10}).

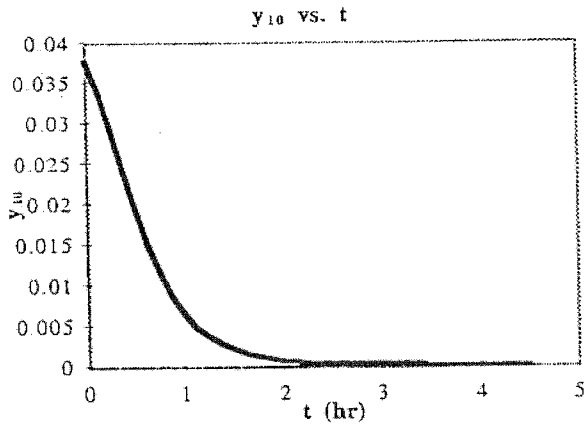
$$I_2 = I_{2o}\exp(-k_o t)$$

$$M = M_o \exp\left[\left(\frac{8k_p^2 f I_{2o}}{k_o k_t}\right)^{1/2}\left(\exp\left(\frac{-k_o t}{2}\right) - 1\right)\right]$$

$$p = \beta = \frac{k_p M}{k_p M + k_m M + k_s S + \sqrt{2k_t k_o f(I_2)}}$$

$$y_n = (1-p)p^{n-1} \qquad n = 10$$

Use the above equations to plot y_n vs.t::



CDP7-K

Reaction

$$R_j + I \xrightarrow{k_a} P_j$$

(a) and (b)

$$\overline{X}_N = \frac{-r_M}{\sum r_j} = \left(\frac{\sum r_j}{-r_M}\right)^{-1}$$

$$\sum r_j = r_i + \sum\left(k_p M\left(R_j - R_{j-1}\right) + \left(k_a + k_d\right)R_j \sum R_i k_M M R_j + k_c C R_j + k_s S R_j + k_a I R_j\right)$$

Let $\sum R_j = R^*$

$$\sum r_j = r_i + R^*\left(k_m M + k_s S + k_a I\right)$$

$$\overline{X}_N = \left[\frac{r_i + R^*\left(k_m M + k_s S + k_a I\right)}{k_p M R^*}\right]^{-1} = \left[\frac{r_i}{-r_M} + \frac{k_m}{k_p} + \frac{k_s S}{k_p M} + \frac{k_a I}{k_p M}\right]^{-1}$$

$$\overline{X}_N = \left[\frac{r_i}{r_p} + \frac{k_m}{k_p} + \frac{k_s S}{k_p M} + \frac{k_a I}{k_p M}\right]^{-1} = \left[\left(\frac{f k_0 k_i}{k_p^2}\right)^{\frac{1}{2}} \frac{I^{\frac{1}{2}}}{M} + \frac{k_m}{k_p} + \frac{k_s S}{k_p M} + \frac{k_a I}{k_p M}\right]^{-1}$$

(c) From the above derivation we know that

$$\frac{1}{\overline{X}_N} = \frac{r_i}{r_p} + \frac{k_m}{k_p} + \frac{k_s S}{k_p M} + \frac{k_a I}{k_p M}$$

Neglecting the solvent term and rearranging yields:

$$\frac{1}{\overline{X}_N} = \frac{r_i}{-r_M} + \frac{k_m}{k_p} + \frac{k_a I}{k_p M} = \frac{r_i\left(-r_M\right)}{\left(-r_M\right)^2} + \frac{k_m}{k_p} + \frac{k_a I}{k_p M}$$

Substituting in for $-r_M$ and r_i and simplifying:

$$\frac{1}{\overline{X}_N} = \frac{2k_o f(I_2)/M(-r_M)}{k_p^2(2k_o f(I_2)/k_t)} + \frac{k_m}{k_p} + \frac{k_0 I}{k_p M}$$

$$\frac{1}{\overline{X}_N} = \frac{k_t(-r_M)}{k_p^2(M)} + \frac{k_m}{k_p} + \frac{k_0 I}{k_p M}$$

(d) To determine rate law parameters experimentally from a CSTR both the final X_N value and the final concentrations of M and I must be recorded. These data can be used in the above equation to find values for the parameters.

(e) An increase in temperature would cause an increase in all three primary steps of free-radical polymerization (initiation, propagation, and termination). By looking at the overall rate law:

$$r_M = k_p M\sqrt{\frac{2k_o(I_2)f}{k_t}}$$

it can be seem that the greatest effect of temperature would be on propagation. Overall, there would be an increase in monomer disappearance and an increase in polymerization.

CDP7-L

a) PFR:

$$\frac{dM}{d\tau} = r_M \qquad \frac{dI_2}{d\tau} = r_{I_2}$$

$$r_M = -k_p M\sqrt{\frac{2k_o I_2 f}{k_t}} \qquad r_{I_2} = -k_0 I_2$$

Plug those into POLYMATH to get this graph.

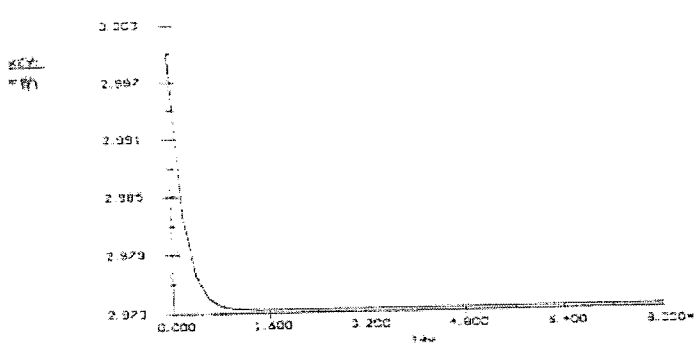
Equations:

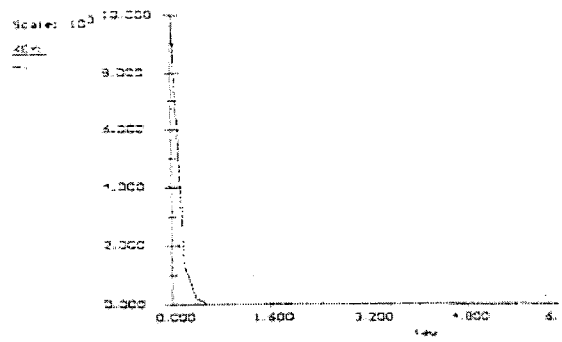
```
d(m)/d(tau)=rm
d(i)/d(tau)=ri
kp=10
ko=1e-3
f=.5
kt=5e7
ri=-ko*i
rm=-kp*m*sqrt(2*ko*i*f/kt)
```

$tau_0 = 0, \quad tau_f = 79998$

Initial value
3
0.01

Variable	Initial value	Maximum value	Minimum value	Final value
tau	0	79998	0	79998
m	3	3	2.97329	2.97329
i	0.01	0.01	5.06171e-38	5.06171e-38
kp	10	10	10	10
ko	0.001	0.001	0.001	0.001
f	0.5	0.5	0.5	0.5
kt	5e+07	5e+07	5e+07	5e+07
ri	-1e-05	-5.06171e-41	-1e-05	-5.06171e-41
rm	-1.34164e-05	-2.99158e-23	-1.34164e-05	-2.99158e-23



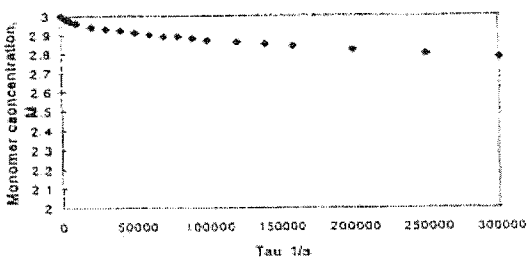


CSTR:

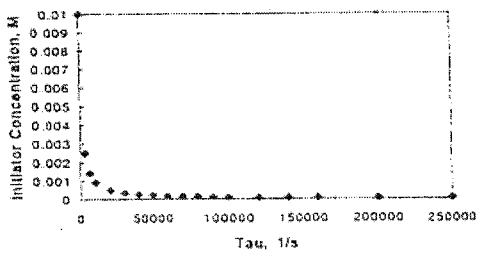
$$M_0 - M = -r_M * \tau \qquad I_{20} - I_2 = -r_{I_2} * \tau$$

The rate laws are the same so again using POLYMATH the following graphs are generated.

Monomer vs space time CSTR



Initiator Concentration vs Space Time CSTR



Equations:	Initial value
f(m)=m-mo-rm*tau	2.5
f(i)=i-io-ri*tau	0.001

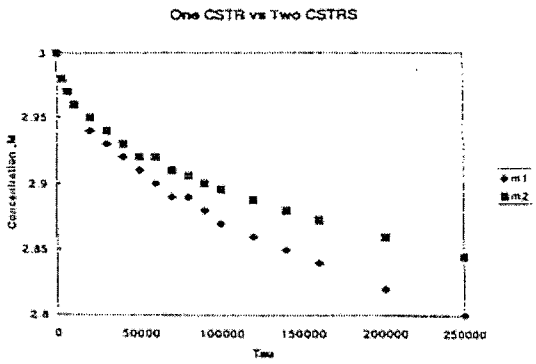
```
mo=3
tau=Sell
io=.01
kp=10
ko=1e-3
f=.5
kt=5e7
ri=-ko*i
rm=-kp*m*sqrt(2*ko*i*f/kt)
```

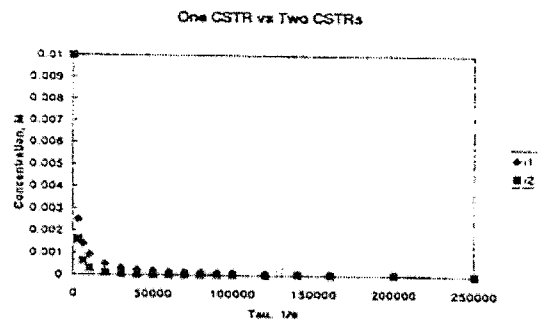
b) For two CSTRs, the design equations change just a bit.

$$M_0 - M_1 = -r_{M_1} * \frac{\tau}{2} \qquad I_{20} - I_{21} = -r_{I_{21}} * \frac{\tau}{2}$$

$$M_1 - M_2 = -r_{M_2} * \frac{\tau}{2} \qquad I_{21} - I_{22} = -r_{I_{22}} * \frac{\tau}{2}$$

The rate laws are the same with the exception that instead of just I_2 or M, I_{21}, I_{22}, M_1, or M_2 are used depending on which reactor they came from and the following graphs are generated.





c) Making k_p bigger causes I_2 to decrease rapidly and M does not get formed as much. Increasing k_p causes M to decrease slightly, but not by that much. Increasing k_i, causes M not to decrease by very much staying very close to 3.

CDP7-M No solution will be given

CDP7-N

$$I + M \xrightarrow{k_i} R_1$$

$$R_j + M \xrightarrow{k_p} R_{j+1}$$

$$-r_I = k_i MI$$

a) Balance on I

$$\tau = \frac{I_o - I}{-r_I} = \frac{I_0 - I}{k_i MI}$$

$$\Rightarrow I = \frac{I_0}{1 + \tau k_i M}$$

$$-r_M = k_i MI + k_p M \sum_{j=1}^{\infty} R_j$$

$$\text{As} \sum_{j=1}^{\infty} R_j = I_o - I$$

$$-r_M = k_i MI + k_p M(I_0 - I)$$

Balance on M:

$$\tau = \frac{M_0 - M}{-r_M} = \frac{M_0 - M}{k_i MI + k_p M(I_0 - I)}$$

$$\Rightarrow \tau k_i MI + \tau k_p M(I_0 - I) = M_0 - M$$

$$\Rightarrow \frac{\tau k_i MI_0}{1 + \tau k_i M} + \frac{\tau k_p I_0 M(\tau k_i M)}{1 + \tau k_i M} = M_0 - M$$

$$\Rightarrow \tau k_i I_0 M + \tau^2 k_p k_i I_0 M^2 = (M_0 - M)(1 + \tau k_i M)$$

$$\Rightarrow \tau k_i (1 + \tau k_p I_0) M^2 + (1 + \tau k_i I_0 - \tau k_i M_0) M - M_0 = 0$$

$$\Rightarrow M = \frac{-(1 + \tau k_i I_0 - \tau k_i M_0) + \sqrt{(1 + \tau k_i I_0 - \tau k_i M_0)^2 + 4 * \tau k_i (1 + \tau k_p I_0) M_0}}{2\tau k_i (1 + \tau k_p I_0)}$$

b) $-r_{R_1} = -k_i MI + k_p MR_1$

Balance on R_1

$$\tau = \frac{0 - R_1}{-k_i MI + k_p MR_1} \Rightarrow R_1 = I\left(\frac{\tau k_i M}{1 + \tau k_p M}\right)$$

$-r_{R_2} = -k_p MR_1 + k_p MR_2$

Balance on R_2

$$\tau = \frac{0 - R_2}{-k_p MR_1 + k_p MR_2} \Rightarrow R_2 = R_1\left(\frac{\tau k_p M}{1 + \tau k_p M}\right)$$

Similarly,

$$R_3 = R_2\left(\frac{\tau k_p M}{1 + k_p M\tau}\right)$$

$$R_j = R_1\left(\frac{\tau k_p M}{1 + \tau k_p M}\right)^{j-1}$$

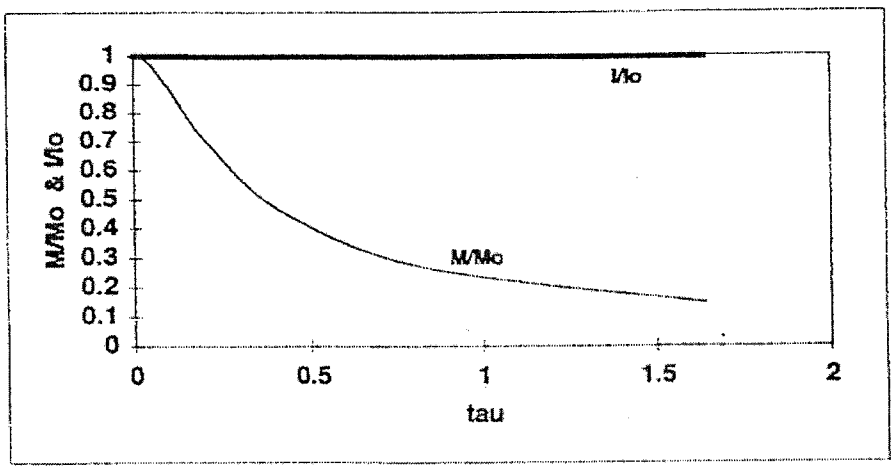
$$R_j = I\left(\frac{\tau k_p M}{1 + \tau k_p M}\right)\left(\frac{\tau k_p M}{1 + \tau k_p M}\right)^{j-1}$$

$$R_j = \frac{I(\tau k_p M)}{\tau k_p M}\left(\frac{\tau k_p M}{1 + \tau k_p M}\right)^{j}$$

$$R_j = \frac{I_0}{1 + \tau k_i M}\frac{k_i}{k_p}\left(\frac{\tau k_p M}{1 + \tau k_p M}\right)^{j}$$

c) Initiation Rate constant $k_i << k_p$ propagation rate constant
Hence, nearly no change in the concentration of Initiator (I).

Mo	1
Io	1
ki	0.015
kp	1000



d)

$$\lambda_0 = \sum_{j=1}^{\infty} R_j = I_0 - I = \frac{\tau k_i M I_0}{1 + \tau k_i M}$$

$$\lambda_1 = \sum_{j=1}^{\infty} jR_j = \frac{I_0}{1 + \tau k_i M} \frac{k_i}{k_p} \sum_{j=1}^{\infty} j \left(\frac{\tau k_p M}{1 + k_p M} \right)^j$$

$$= \frac{I_0}{1 + \tau k_i M} \frac{k_i}{k_p} \left\{ \frac{\left[\tau k_p M / \left(1 + \tau k_p M \right) \right]}{\left[1 - \frac{\tau k_p M}{\left(1 + \tau k_p M \right)} \right]^2} \right\}$$

$$\text{As} \sum_{j=1}^{\infty} jx^j = \frac{x}{(1-x)^2}$$

$$\lambda_1 = \frac{\tau k_i M I_0}{1 + \tau k_i M} \left(1 + k_p M \right)$$

$$\lambda_2 = \sum_{j=1}^{\infty} j^2 R_j = \frac{I_0}{1 + \tau k_i M} \frac{k_i}{k_p} \sum_{j=1}^{\infty} j^2 \left(\frac{\tau k_p M}{1 + \tau k_p M} \right)^j$$

$$= \frac{I_0}{1 + \tau k_i M} \frac{k_i}{k_p} \left\{ \frac{\left(\frac{\tau k_p M}{1 + \tau k_p M} \right) \left(1 + \frac{\tau k_p M}{1 + \tau k_p M} \right)}{\left(1 - \frac{\tau k_p M}{1 + \tau k_p M} \right)^3} \right\}$$

$$As \sum_{j=1}^{\infty} j^2 x^j = \frac{x(1+x)}{(1-x)^3}$$

$$\Rightarrow \lambda_2 = \frac{\tau k_i M I_0}{1+\tau k_i M}\left(1+\tau k_p M\right)\left(1+2\tau k_p M\right)$$

$$\boxed{\begin{aligned} \mu_n &= \frac{\lambda_1}{\lambda_0} = \left(1+\tau k_p M\right) \\ \mu_W &= \frac{\lambda_2}{\lambda_1} = \left(1+2\tau k_p M\right) \\ D &= \frac{\mu_W}{\mu_n} = \frac{1+2\tau k_p M}{1+\tau k_p M} \end{aligned}}$$

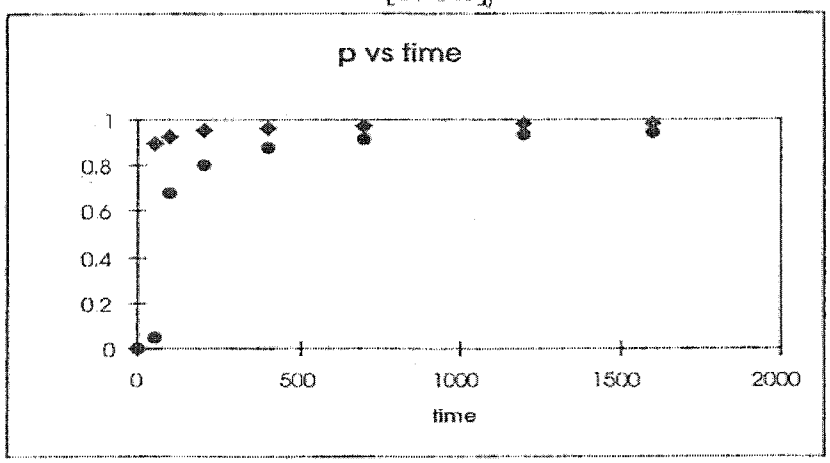
CDP7-O

a)With the reaction self catalyzed the mole balance and rate law becomes:

$$-\frac{d[COOH]}{dt} = k[COOH]^3$$

We can then get [COOH] as a function of time. The following graph shows both the given values of p and the calculated value as a function of time where

$$p = \frac{[COOH]_0 - [COOH]}{[COOH]_0}$$



It appears to follow this above 500 min.

b) The new mole balance and rate law is:

$$-\frac{d[COOH]}{dt} = k[COOH][OH][H^+]$$

$$[OH] = [COOH]$$

$$COOH \rightleftharpoons COO^- + H^+$$

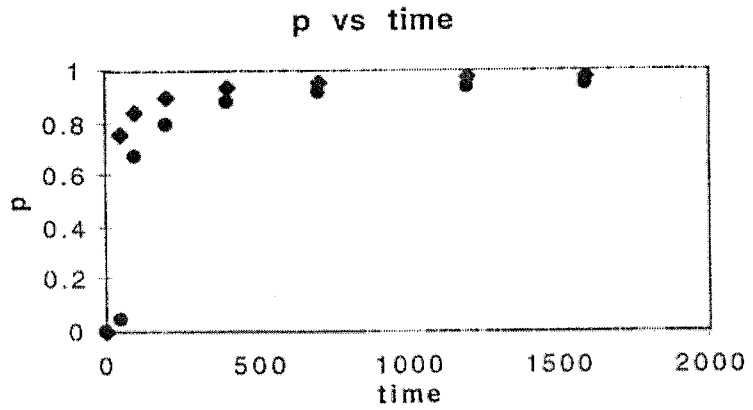
$$K_{eq} = \frac{[COO^-][H^+]}{[COOH]}$$

$$[COO^-] = [H^+]$$

$$[H^+]^2 = K_{eq}[COOH]$$

$$-\frac{d[COOH]}{dt} = k[COOH]^{3/2}$$

Solving for [COOH] as a function of time gives the following graph:



It follows the data above 200 min.

c) This mechanism can be made to fit either rate law, depending on whether HA dissociates before or after the first reaction.

CDP7-P

CDP7-Q

$$I + M \xrightarrow{k_0} R_1$$

$$R_j + M \xrightarrow{k_p} R_{j+1}$$

$$-\frac{dI}{dt} = k_0 MI = \left(k_p M\right)\frac{k_0 I}{k_p}$$

$$-\frac{dI}{k_p M dt} = \frac{k_0}{k_p} I$$

$$d\theta = k_p M dt$$

$$\frac{dI}{d\theta} = -\frac{k_0}{k_p} I \Rightarrow I = I_0 e^{-\frac{k_0}{k_p}\theta}$$

$$\frac{dR_1}{dt} = -k_0 MI + k_p MR_1$$

$$\frac{dR_1}{d\theta} = \frac{k_0}{k_p} I_0 e^{\left(-\frac{k_0}{k_p}\right)\theta} - R_1$$

$$\frac{d\left(e^{\theta} R_1\right)}{d\theta} = \frac{k_0}{k_p} I_0 e^{\left(1-\frac{k_0}{k_p}\right)\theta}$$

$$\Rightarrow R_1 = \frac{k_0}{k_p}\frac{I}{\left(1-\frac{k_0}{k_p}\right)}\left[e^{-\frac{k_0}{k_p}\theta} - e^{-\theta}\right]$$

$$-\frac{dR_2}{dt} = -k_p MR_1 + k_p MR_2$$

$$\Rightarrow \frac{dR_2}{d\theta} = R_1 - R_2$$

$$\Rightarrow \frac{d\left(e^{\theta} R_2\right)}{d\theta} = e^{\theta} R_1 = \frac{k_0 I_0}{k_p - k_0}\left[e^{\left(1-\frac{k_0}{k_p}\right)\theta} - 1\right]$$

$$\Rightarrow R_2 = \frac{k_0 I_0}{k_p\left(1-\frac{k_0}{k_p}\right)^2}\left[e^{-\frac{k_0}{k_p}\theta} - e^{-\theta}\right] - \frac{k_0 I_0 \theta e^{-\frac{k_0}{k_p}}}{k_p - k_0}$$

$$\frac{dR_3}{d\theta} = R_2 - R_3$$

$$\Rightarrow \frac{d\left(e^{\theta} R_3\right)}{d\theta} = \frac{k_0 I_0}{k_p\left(1-\frac{k_0}{k_p}\right)^2}\left[e^{\left(1-\frac{k_0}{k_p}\right)\theta} - 1\right] - \frac{k_0 I_0 \theta}{k_p\left(1-\frac{k_0}{k_p}\right)}$$

$$\Rightarrow R_3 = \frac{k_0 I_0}{k_p\left(1-\frac{k_0}{k_p}\right)^3}\left[e^{-\frac{k_0}{k_p}\theta} - e^{-\theta}\right] - \frac{k_0 I_0}{k_p\left(1-\frac{k_0}{k_p}\right)^2}\theta e^{-\theta} - \frac{k_0 I_0}{k_p\left(1-\frac{k_0}{k_p}\right)^2}\frac{\theta^2 e^{-\theta}}{2}$$

$$\Rightarrow R_j = \frac{k_0 I_0}{k_p\left(1-\frac{k_0}{k_p}\right)}\left[\frac{e^{-\frac{k_0}{k_p}\theta} - e^{-\theta}}{\left(1-\frac{k_0}{k_p}\right)^{j-1}} - \sum_{i=1}^{j-1}\frac{\theta^i e^{-\theta}}{(i)!\left(1-\frac{k_0}{k_p}\right)^{j-1}}\right]$$

For j>1

CDP7-R

$$I + M \xrightarrow{k_0} R_1$$

$$R_j + M \xrightarrow{k_p} R_{j+1}$$

$$\tau = \frac{I_0 - I}{k_0 M I}$$

$$\theta' = k_p M \tau$$

$$\theta' = \frac{k_p (I_0 - I)}{k_0 I}$$

$$I = \frac{k_p I_0}{k_0 \theta' + k_p}$$

$$\tau = \frac{M_0 - M}{k_p M I_0}$$

$$M = \frac{M_0}{k_p I_0 \tau + 1}$$

$$\theta' = \frac{k_p M_0 \tau}{k_p I_0 \tau + 1}$$

$$\tau = \frac{R_1}{k_0 M I - k_p M R_1}$$

$$R_1 = \frac{k_0 I \theta'}{k_p (1 + \theta')}$$

$$\tau = \frac{R_2}{k_p M R_1 - k_p M R_2}$$

$$R_2 = \frac{R_1 \theta'}{1 + \theta'} = \frac{k_0 k_p I_0 \theta'^2}{k_p (1 + \theta')^2 (k_0 \theta' + k_p)} = \frac{k_0 I_0 \theta'^2}{(1 + \theta')^2 (k_0 \theta' + k_p)}$$

$$R_j = \frac{k_0 I_0 \left(\frac{k_p M_0 \tau}{k_p I_0 \tau + 1} \right)^j}{(k_0 \theta' + k_p) \left(1 + \frac{k_p M_0 \tau}{k_p I_0 \tau + 1} \right)^j}$$

Fogler 7-24 Solution

Problem Statement:

In biotechnology industry, *E. coli* is grown aerobically to highest possible concentrations in batch or fed-batch reactors to maximize production of an intracellular protein product. To avoid substrate inhibition, glucose concentration in the initial culture medium is restricted to 100 grams/liter in the initial charge of 80 liter culture medium in a 100 liter capacity bioreactor. After much of this glucose is consumed, a concentrated glucose feed (500 g/l) will be fed into the reactor at a constant volumetric feed rate of 1.0 liter/hour. When the dissolved oxygen concentration in the culture medium falls below a critical value of 0.5 mg/liter, acetic acid is produced in a growth-associated mode with an α of 0.1 g acet/g cellmass. The by-product acetic acid inhibits cell growth linearly, with the toxic concentration (no cell growth) at C_P^* of10 g/liter. Find the optimum volumetric flow rate that will maximize the overall rate of cell mass production when the bioreactor is filled up and if the feed is turned on after glucose falls below 10 g/l. Inoculum concentration is 1 g cells/liter.

Additional parameters:

$\mu_{max} = 1.2\ hr^{-1}$, $K_G = 1.0$ g/l , $K_O = 1$ mg/l, $Y_{x/s} = 0.5$ g/g, $Y_{p/s} = 0.3$ g/g, $q_{o/x} = 1000$ mg/g

Oxygen mass transfer rate $k_La = 500\ hr^{-1}$, Saturation oxygen concentration $C_{O2}^* = 7.5$ mg/liter

$$r_g = \left(\frac{\mu_{max} C_S}{K_S + C_S}\right)\left(\frac{C_{O_2}}{K_{O_2} + C_{O_2}}\right)\left(1 - \frac{C_P}{C_P^*}\right)C_C$$

$$\frac{dC_{O_2}}{dt} = k_L a\left(C_{O_2}^* - C_{O_2}\right) - q_{O_2/C} r_g$$

Increase the value of mass transfer rate (up to 1000) or the saturation oxygen concentration (up to 40 mg/liter) to see if higher cell densities can be obtained in the fed-batch reacator.

(a) list ways you can work this problem incorrectly.
(b) How could you make this problem more difficult?

(Contibuted by Prof. D. S. Kompala, University of Colorado)

Solution:

This problem is solved numerically in three parts, using the following equations on Berkeley Madonna package:

The first time period covers the simple batch culture, when glucose and dissolved oxygen are being consumed for cell growth.

```
METHOD Stiff

STARTTIME = 0
STOPTIME = 3.4
DT = 0.02

INIT G =100
INIT X = 1.0
INIT O = 7.5
INIT P = 0

mumax = 1.2
KG = 1.0
KO = 1.0
Yxs = 0.5
Yps = 0.3
q = 1000
kLa = 1000
alpha = 0

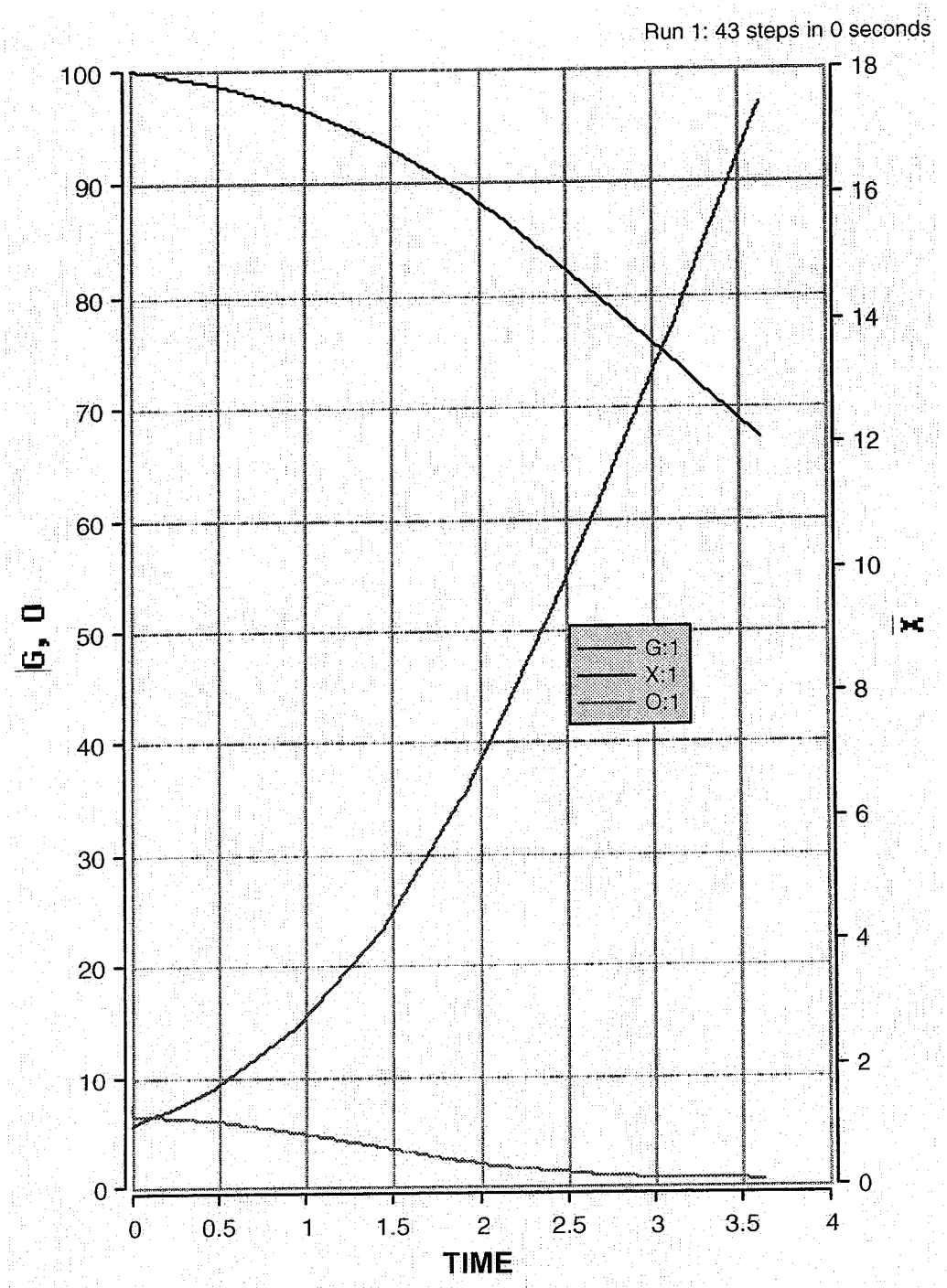
SATG = G/(KG+G)
SATO = O/(KO+O)
SATP = 1.0 - (P/10)

mux = mumax * SATG*SATO*SATP*X

d/dt(X) = mux
d/dt(G) = - mux/Yxs
d/dt(O) = kLa*(7.5 - O) - q*mux
d/dt(P) = alpha*mux
```

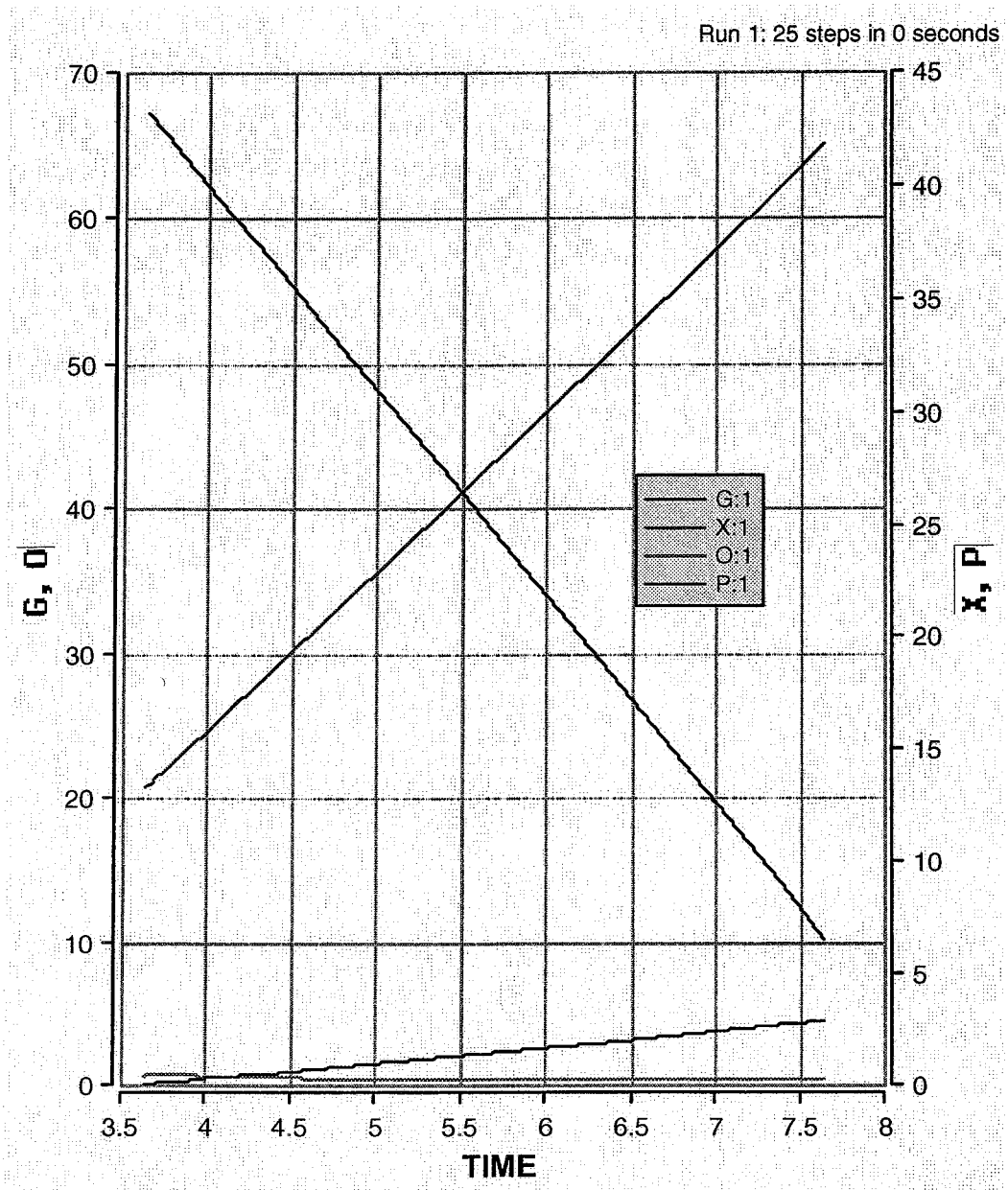
The numerical simulation results shown below identifies the time at which the dissolved oxygen concentration falls below the critical value of 0.5 mg/liter, triggering the formation of the by-product acetic acid.

From the simulation results, we find that the dissolved oxygen concentration falls below the critical values of 0.5 mg/l at the batch culture time of 3.64 hours. At that time, the glucose concentration has fallen to 67.1 g/l and cell mass concentration has growth to 17.45 g/l. The by-product acetic acid concentration remains zero through the early batch culture, as the dissolved oxygen concentration is above the critical level throughout this time. In the program above, the parameter alpha is set to zero to ensure that no acetic acid is produced.



In the second part of the batch culture, acetic acid is getting produced and glucose is still above its set point of 10 g/l, when the concentrated glucose feed is added to the bioreactor.

The program equations are given above slightly modified to change the alpha value to the given value of 0.1 g acetic acid/g g cell mass and integrated from the end of first part of batch culture.



From the simulation results, we see that glucose concentration reaches the predetermined value of 10 g/l (for turning on the feed) at 7.65 hours of batch culture. At that time, the cell mass concentration has reached 41.02 g/l and the by-product acetic acid concentration has reached 2.85 g/l. Using these values as the initial conditions for the third part of culture, a glucose feed is added and the balance equations are therefore modified to include the dilution of all bioreactor contents with the fresh nutrient medium. The modified program equations are shown below:

METHOD Stiff

STARTTIME = 7.65
STOPTIME = 209.5
DT = 0.02

INIT G =10.0364
INIT X = 41.8957
INIT O = 0.1978
INIT P = 2.85834
INIT V = 80

mumax = 1.2
KG = 1.0
KO = 1.0
Yxs = 0.5
Yps = 0.3
q = 1000
kLa = 1000
alpha = 0.1
vin = 0.1

SATG = G/(KG+G)
SATO = O/(KO+O)
SATP = 1.0 - (P/10)

mux = mumax * SATG*SATO*SATP*X

d/dt(X) = mux - X*vin/V
d/dt(G) = - mux/Yxs +(vin/V)*(500 - G)
d/dt(O) = kLa*(7.5 - O) - q*mux
d/dt(P) = alpha*mux - P*vin/V
d/dt(V) = vin

The constant value for vin, the volumetric feed rate can be systematically varied to find the highest cell mass concentration, when the reactor volume gets filled, i.e. becomes 100 liters. Simulation results for different vin values are tabulated below:

vin	time, hrs	Volume	X cell concent
0.05	407.8	100	87.53
0.1	208	100	87.58
0.2	107.7	100	87.6
0.3	75.3	100	87.5
0.4	57.4	100	87.3

0.5	47.7	100	87.5
0.6	41	100	87.6
0.7	36.2	100	87.5

It is clear from these simulation results that volumetric feed rate does not make a strong difference in the final cell mass concentration. The time for filling up the reactor volume to 100 liter is of course strong affected by the volumetric feed rate

It is expected if the k_La is smaller, then the acetic acid production will be higher. In that case, the volumetric feed rate will have a significant effect on the maximum cell mass concentration achieved in the fed batch reactor.

These simulations nevertheless provide a useful introduction to the concepts of fed-batch culture.

Solutions for Chapter 8 – Steady-State Nonisothermal Reactor Design

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P8-1 Individualized solution

P8-2 (a) Example 8-1

For CSTR

$$V = \frac{F_{A0}X}{-r_A} = \frac{X}{\upsilon_0 k(1-X)}$$

$$X = \frac{\tau k}{1+\tau k} = \frac{\tau A e^{-E/RT}}{1+Ae^{-E/RT}}$$

One equation, two unknowns

Adiabatic energy balance

$$T = T_0 - \frac{\Delta H_{Rx} X}{C_{P_A}}$$

In two equations and two unknowns

In Polymath form the solution

$$f(X) = X - \frac{\tau A e^{-E/RT}}{1+Ae^{-E/RT}}$$

$$f(T) = T_0 - \frac{\Delta H_{Rx} X}{C_{P_A}}$$

Enter X, A, E, R, C_{P_A}, T_0 and ΔH_{Rx} to find τ and from that you can find V.

P8-2 (b) Example 8-2

Helium would have no effect on calculation

$$\%\text{Error} = \frac{-\Delta C_P (T - T_R)}{-\left[\Delta H^\circ_{Rx} + \Delta C_P (T - T_R)\right]}$$

$$= \frac{1270}{23{,}210} \times 100 = 5.47\%$$

P8-2 (c) Example 8-3

(a) $V = 0.8\ m^3$

See Polymath program P8-2-c.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	0.8	0.8
X	0	0	0.5403882	0.5403882
Cao	9.3	9.3	9.3	9.3
Fao	146.7	146.7	146.7	146.7
T	340	340	363.39881	363.39881
Kc	2.8783812	2.4595708	2.8783812	2.4595708
k	8.5452686	8.5452686	38.191248	38.191248
Xe	0.7421605	0.7109468	0.7421605	0.7109468
ra	-79.470998	-110.4184	-79.470998	-85.208593
rate	79.470998	79.470998	110.4184	85.208593

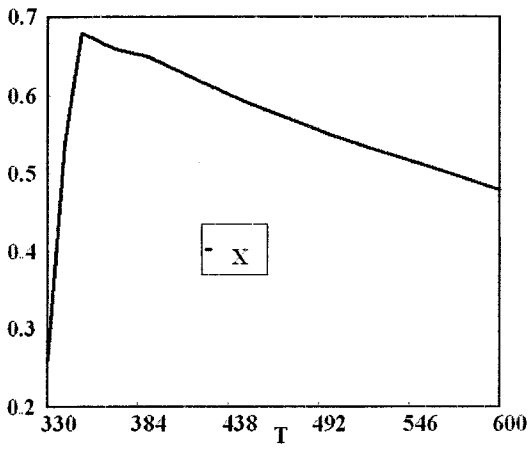
ODE Report (RKF45)

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

Explicit equations as entered by the user
[1] Cao = 9.3
[2] Fao = .9*163
[3] T = 340+43.3*X
[4] Kc = 3.03*exp(-830.3*((T-333)/(T*333)))
[5] k = 31.1*exp(7906*(T-360)/(T*360))
[6] Xe = Kc/(1+Kc)
[7] ra = -k*Cao*(1-(1+1/Kc)*X)
[8] rate = -ra

PFR

T	330	340	350	370	390	420	450	500	600
X	0.26	0.54	0.68	0.66	0.65	0.62	0.59	0.55	0.48



CSTR has the same trend.

P8-2 (d) Example 8-4

Counter-Current: Guess T_a at V = 0 to be 330 and it will give an entering coolant temperature of 310 K.

See Polymath program P8-2-d.pol.

POLYMATH Results
No Title 08-17-2005, Rev5.1.233

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	5	5
X	0	0	0.7797801	0.7797801
T	310	310	344.71423	310.83085
Ta	330.7	310.16835	335.79958	310.16835
Cao	9.3	9.3	9.3	9.3
Fao	14.67	14.67	14.67	14.67
Kc	3.6518653	2.7812058	3.6518653	3.6255777
k	0.9004084	0.9004084	11.763976	0.9639302
Xe	0.7850325	0.7355341	0.7850325	0.7838108
ra	-8.3737978	-27.114595	-0.0460999	-0.0460999
dHrx	-6900	-6900	-6900	-6900
Ua	5000	5000	5000	5000
Cpo	159	159	159	159
rate	8.3737978	0.0460999	27.114595	0.0460999
m	50	50	50	50
Cpc	75	75	75	75

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(X)/d(V) = -ra/Fao
[2] d(T)/d(V) = ((ra*dHrx)-Ua*(T-Ta))/Cpo/Fao
[3] d(Ta)/d(V) = -Ua*(T-Ta)/m/Cpc

Explicit equations as entered by the user
[1] Cao = 9.3
[2] Fao = .9*163*.1
[3] Kc = 3.03*exp(-830.3*((T-333)/(T*330)))
[4] k = 31.1*exp(7906*(T-360)/(T*360))
[5] Xe = Kc/(1+Kc)
[6] ra = -k*Cao*(1-(1+1/Kc)*X)
[7] dHrx = -6900
[8] Ua = 5000
[9] Cpo = 159
[10] rate = -ra
[11] m = 50
[12] Cpc = 75

P8-2 (e) Example 8-5

At V = 0, T_a = 995.15 and gives a counter current entering temperature of 1250 K.
See Polymath program P8-2-e.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	0.001	0.001
X	0	0	0.3512403	0.3512403
T	1035	972.39417	1035	1034.4748
Ta	995.15	986.00676	1249.999	1249.999
Fao	0.0376	0.0376	0.0376	0.0376
Cpa	163	163	163	163
delCp	-9	-9	-9	-9
Cao	18.8	18.8	18.8	18.8
To	1035	1035	1035	1035

dHrx	7.414E+04	7.414E+04	7.47E+04	7.414E+04
ra	-67.304	-67.304	-6.3363798	-31.792345
Ua	1.65E+04	1.65E+04	1.65E+04	1.65E+04
mc	0.111	0.111	0.111	0.111
Cpc	34.5	34.5	34.5	34.5

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(X)/d(V) = -ra/Fao
[2] d(T)/d(V) = (Ua*(Ta-T)+ra*dHrx)/(Fao*(Cpa+X*delCp))
[3] d(Ta)/d(V) = -Ua*(T-Ta)/mc/Cpc

Explicit equations as entered by the user
[1] Fao = .0376
[2] Cpa = 163
[3] delCp = -9
[4] Cao = 18.8
[5] To = 1035
[6] dHrx = 80770+delCp*(T-298)
[7] ra = -Cao*3.58*exp(34222*(1/To-1/T))*(1-X)*(To/T)/(1+X)
[8] Ua = 16500
[9] mc = .111
[10] Cpc = 34.5

(b) P8-2 (f) Example 8-6

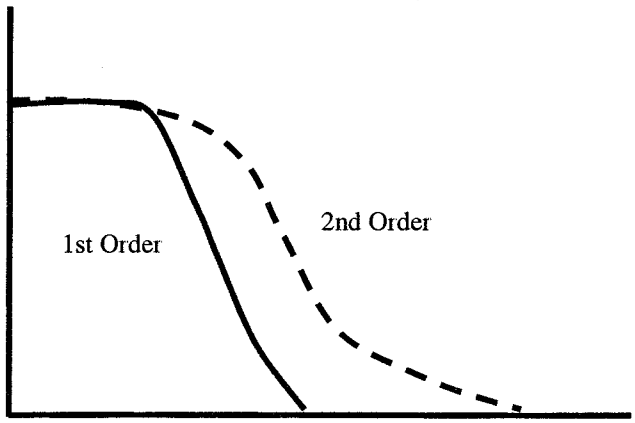
Energy balance will remain the same

$$X_{EB} = 2\times10^{-3}(T-300)$$

for $2A \rightarrow 2B$

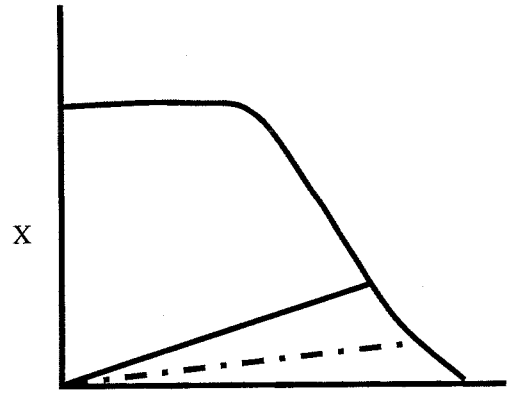
$$K = \frac{C_B^2}{C_A^2} = \frac{X^2}{(1-X)^2}$$

$$X_e = \frac{\sqrt{K_e}}{1+\sqrt{K_e}}$$



(c) P8-2 (g) Example 8-7

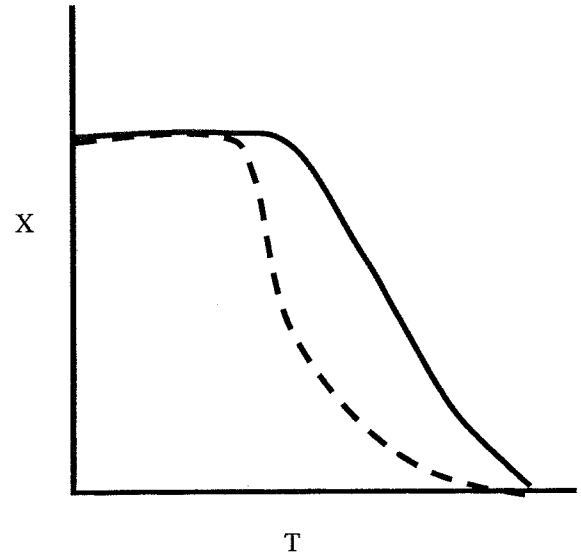
Both X_e and X_{EB} will change. The slope of energy balance will decrease by a factor of 3.



Also X_e will be more temperature sensitive

$$K_e = K_e \exp \frac{\Delta H_{Rx}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)$$

The dotted line in the plot below shows an increase in $-\Delta H_{Rx}$



•

(d) P8-2 (h) Example 8-8

(1) C_{A0} will decrease but this will have no effect

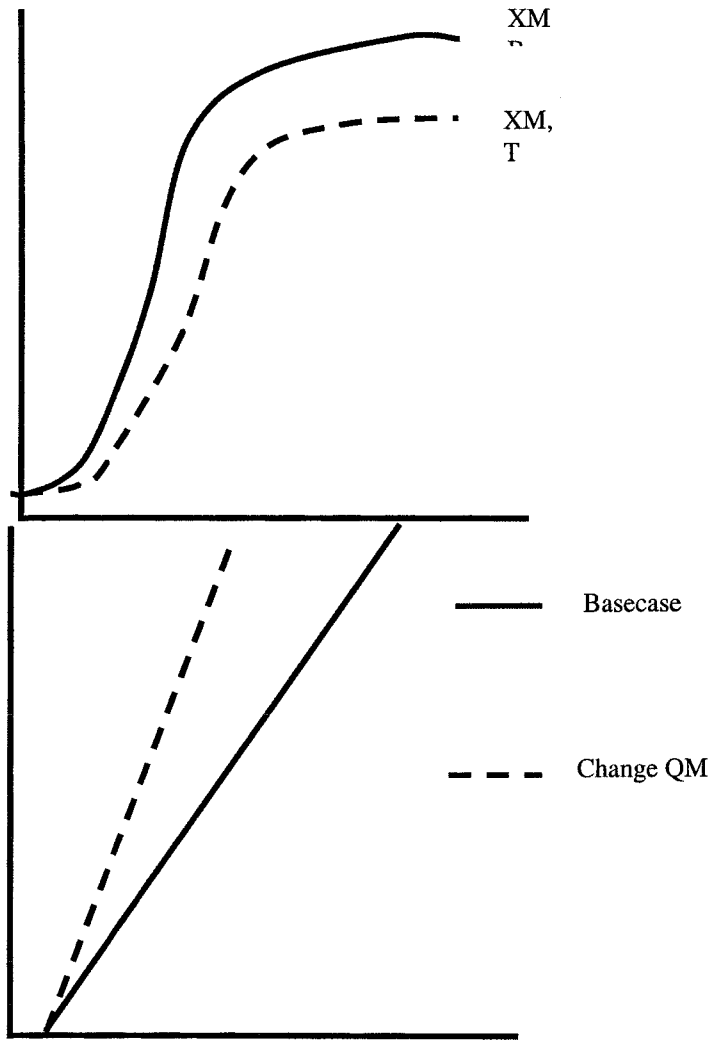
(2) τ will decrease

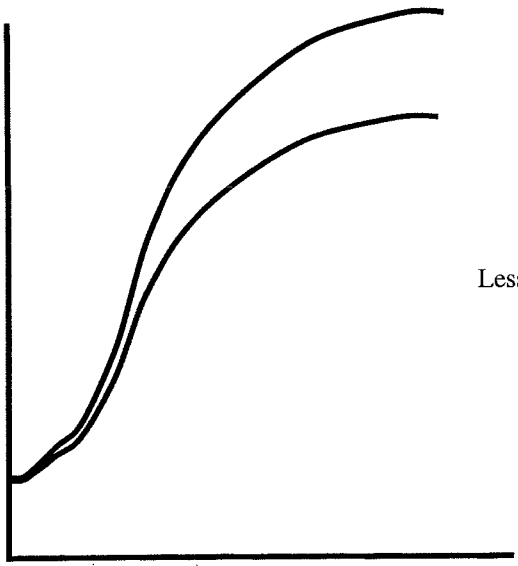
$$\tau = \frac{401.1 \text{ ft}^3}{466.1 \text{ ft}^3/\text{s}}$$

(3) In the energy balance the slope of the energy balance of X vs. T will be greater

$$\sum \Theta_i C_{P_C} = 35 + (18.65)(18) + 4 \times (1.67)(19.5) = 35 + 335.7 + 130.2$$

$$= 501 \frac{BTU}{kmol°R}$$





Less Conversions

P8-2 (i) Example 8-9

Change $C_P = 29$ and $-\Delta H = 38700$

POLYMATH Results
NLES Solution

Variable	Value	f(x)	Ini Guess
X	0.7109354	2.444E-11	0.367
T	593.6885	1.2E-09	564
tau	0.1229		
A	1.696E+13		
E	3.24E+04		
R	1.987		
k	20.01167		

NLES Report (safenewt)

Nonlinear equations
[1] f(X) = X-(397.3*(T-535)+92.9*(T-545))/(38700+7*(T-528)) = 0
[2] f(T) = X-tau*k/(1+tau*k) = 0

Explicit equations
[1] tau = 0.1229
[2] A = 16.96*10^12
[3] E = 32400
[4] R = 1.987
[5] k = A*exp(-E/(R*T))

Vary the heat exchanger area to find the effect on conversion.

P8-2 (j)

$\alpha = 1.05\ dm^3$
See Polymath program P8-2-j.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	1	1
Fa	100	2.738E-06	100	2.738E-06
Fb	0	0	55.04326	55.04326
Fc	0	0	22.478369	22.478369
T	423	423	812.19122	722.08816
y	1	0.3120454	1	0.3120454
k1a	482.8247	482.8247	4.484E+04	2.426E+04
k2a	553.05566	553.05566	1.48E+07	3.716E+06
Cto	0.1	0.1	0.1	0.1
Ft	100	77.521631	100	77.521631
To	423	423	423	423
Ca	0.1	2.069E-09	0.1	2.069E-09
Cb	0	0	0.0415941	0.0415941
Cc	0	0	0.016986	0.016986
r1a	-48.28247	-373.39077	-5.019E-05	-5.019E-05
r2a	-5.5305566	-848.11153	-1.591E-11	-1.591E-11
Fto	100	100	100	100
alpha	1.05	1.05	1.05	1.05

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Fa)/d(V) = r1a+r2a
[2] d(Fb)/d(V) = -r1a
[3] d(Fc)/d(V) = -r2a/2
[4] d(T)/d(V) = (4000*(373-T)+(-r1a)*20000+(-r2a)*60000)/(90*Fa+90*Fb+180*Fc)
[5] d(y)/d(V) = -alpha/2/y*(Ft/Fto)

Explicit equations as entered by the user
[1] k1a = 10*exp(4000*(1/300-1/T))
[2] k2a = 0.09*exp(9000*(1/300-1/T))
[3] Cto = 0.1
[4] Ft = Fa+Fb+Fc
[5] To = 423
[6] Ca = Cto*(Fa/Ft)*(To/T)
[7] Cb = Cto*(Fb/Ft)*(To/T)
[8] Cc = Cto*(Fc/Ft)*(To/T)
[9] r1a = -k1a*Ca
[10] r2a = -k2a*Ca^2
[11] Fto = 100
[12] alpha = 1.05

(e) P8-2 (k) Example 8-11

Vary UA

$$UA = 70{,}000 \ J/m^3 \bullet s \bullet K$$

only the lower steady state exists at T = 318 K $S_{BC} = 0.05$

$$UA = 60{,}000 \ J/m^3 \bullet s \bullet K$$

only three steady states exist T = 318, 380 (about) and 408 (about) depending how you read the intersection on the graph.

$$UA = 700 \ J/m^3 \bullet s \bullet K$$

only three steady states T = 300 (about), T = 350 (about) and one are a very high temperature off the scale of the R (T) and G(T) plot.

In all cases S_{BC} remains low at 0.05, meaning that the reaction has neared completion to form species C therefore reactor is too large.

Vary T_0

$T_0 = 275$, very little effect.

Vary τ

$\tau = 0.001$ only the lower steady state at T = 316 about and other off scale $S_{BC} = 0.05$

z = 0.0001 only are steady state at T = 316 and others off scale $S_{BC} = 0.05$

$\tau = 0.00001$, $S_{BC} = 5$

However, the upper steady state is off the graph and needs to be studied

(f) P8-2 (l) Example PRS P8-4.1

$$\alpha \sim \frac{1}{d_P P_0}$$

$$\alpha_2 = \alpha_1 \frac{d_{P_1} P_{0_1}}{d_{P_2} P_{0_2}} = \left(\frac{1}{(1/2)} \frac{1}{(2)} \right) = 1$$

No effect for turbulent flow if both d_P and P changed at the same time.

P8-2 (m) Example T8-3

$m_c = 200$ g/s

See Polymath program P8-2-m.pol.

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
W	0	0	4500	4500
Ta	320	320	334.77131	334.77131
y	1	0.3044056	1	0.3044056
T	330	330	385.31436	338.18498
X	0	0	0.5645069	0.5645069
alpha	2.0E-04	2.0E-04	2.0E-04	2.0E-04
To	350	350	350	350
Uarho	0.5	0.5	0.5	0.5
Mc	200	200	200	200
Cpmc	18	18	18	18
Hr	-2.0E+04	-2.0E+04	-2.0E+04	-2.0E+04
Fao	5	5	5	5
thetaI	1	1	1	1
CpI	40	40	40	40
CpA	20	20	20	20
thetaB	1	1	1	1
CpB	20	20	20	20
Cto	0.3	0.3	0.3	0.3
Ea	2.5E+04	2.5E+04	2.5E+04	2.5E+04
Kc	66.01082	0.8247864	66.01082	31.551036
ka	0.046809	0.046809	11.205249	0.1177827
yao	0.3333333	0.3333333	0.3333333	0.3333333
xe	0.8024634	0.3122841	0.8024634	0.7374305
Cao	0.1	0.1	0.1	0.1
sumcp	80	80	80	80
Ca	0.1060606	0.0137198	0.1060606	0.0137198
Cb	0.1060606	0.0137198	0.1060606	0.0137198
Cc	0	0	0.0724316	0.0355685
ra	-5.265E-04	-0.0143957	-1.745E-05	-1.745E-05

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Ta)/d(W) = Uarho*(T-Ta)/(Mc*Cpmc)
[2] d(y)/d(W) = -alpha/2*(T/To)/y
[3] d(T)/d(W) = (Uarho*(Ta-T)+(-ra)*(-Hr))/(Fao*sumcp)
[4] d(X)/d(W) = -ra/Fao

Explicit equations as entered by the user
[1] alpha = .0002
[2] To = 350
[3] Uarho = 0.5
[4] Mc = 200
[5] Cpmc = 18
[6] Hr = -20000
[7] Fao = 5
[8] thetaI = 1
[9] CpI = 40
[10] CpA = 20
[11] thetaB = 1
[12] CpB = 20
[13] Cto = 0.3
[14] Ea = 25000
[15] Kc = 1000*(exp(Hr/1.987*(1/303-1/T)))
[16] ka = .004*exp(Ea/1.987*(1/310-1/T))
[17] yao = 1/(1+thetaB+thetaI)
[18] xe = Kc^0.5/(2+Kc^0.5)
[19] Cao = yao*Cto
[20] sumcp = (thetaI*CpI+CpA+thetaB*CpB)
[21] Ca = Cao*(1-X)*y*To/T
[22] Cb = Cao*(1-X)*y*To/T
[23] Cc = Cao*2*X*y*To/T
[24] ra = -ka*(Ca*Cb-Cc^2/Kc)

P8-2 (n)

(1) The concentration of A near the wall is lower than in the center because the velocity profile is parabolic. This means near the walls the velocity is much lower and therefore the time space near the wall is much larger than in the center. This means the reaction has longer to take place and conversion will be higher near the wall. Thus the concentration is lower.

Below is the FEMLAB solution.

1. Parameters in simulation on the tubular reactor from Example 8-12 (First Order reaction):

Reaction: $A + B \rightarrow C$

A- propylene oxide; B- water; C- propylene glycol

(1) operating parameters

Reactants

- Feed rate of A $F_{A0} = 0.1$ mol/s
- Inlet flow rate of A $v_{A0} = \dfrac{F_{A0} M_A}{\rho_A} = \dfrac{0.1 \times 58.1 \times 10^{-3}}{830} = 7 \times 10^{-6}$ m^3/s

- Inlet flow rate of B $v_{B0} = 2.5 \times 2 \times v_{A0} = 35 \times 10^{-6}$ m^3/s
- Inlet total flowrate $v_0 = 2v_{A0} + v_{B0} = 14 \times 10^{-6} + 35 \times 10^{-6} = 49 \times 10^{-6}$ m^3/s
- Inlet concentration of A $C_{A0} = \frac{F_{A0}}{v_0} = \frac{0.1}{49 \times 10^{-6}} = 2040.8$ mol/m^3
- Inlet concentration of B $C_{B0} = \frac{F_{B0}}{v_0} = \frac{v_{B0}\rho_B}{M_B v_0} = \frac{35 \times 10^{-6} \times 1000}{18 \times 10^{-3} \times 49 \times 10^{-6}} = 39682.5$ mol/m^3
- Inlet temperature of the reactant $T_0 = 312K$
- Coolant flowrate, $m_J = 0.01$ kg/s
- Inlet temperature of the coolant, $Ta_0 = 298$ K

(2) properties of reactants

- Heat of reaction, ΔH_{Rx}, dHrx = -525676+286098+154911.6=-84666.4 J/mol
- Activation energy, $E = 75362$ J/mol
- Pre-exponential factor, A = 16.96×1012 /3600 1/s
- Specific reaction rate $k_0 = 1.28/3600$ 1/s @300K
- Reaction rate $k = k_0 \exp\left[\frac{E}{R}(\frac{1}{T_0} - \frac{1}{T})\right]$ or $k = A\exp\left[-\frac{E}{RT}\right]$
- Gas constant, $R = 8.314$ J/mol·K
- Rate law $-r_A = kC_A$
- Thermal conductivity of the reaction mixture, $ke = 0.559$ W/m·K
- Average density of the reaction mixture, ρ, rho = 1000 kg/m^3
- Heat capacity of the reaction mixture, $Cp = 4180$ J/kg·K
- Diffusivity of all species, $Diff = 10^{-9}$ m^2/s

(3) properties of coolant

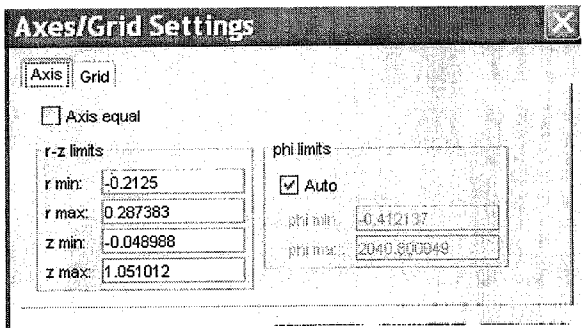
- Overall heat transfer coefficient, $U_k = 1300$ J/m^2·s·K
- Heat capacity of the coolant, $Cp_J = 4180$ J/kg·K

2. Size of the Tubular Reactor

- Reactor radius, $Ra = 0.1$ m
- Reactor length, $L = 1.0$ m

2. Femlab screen shots

(1) Domain

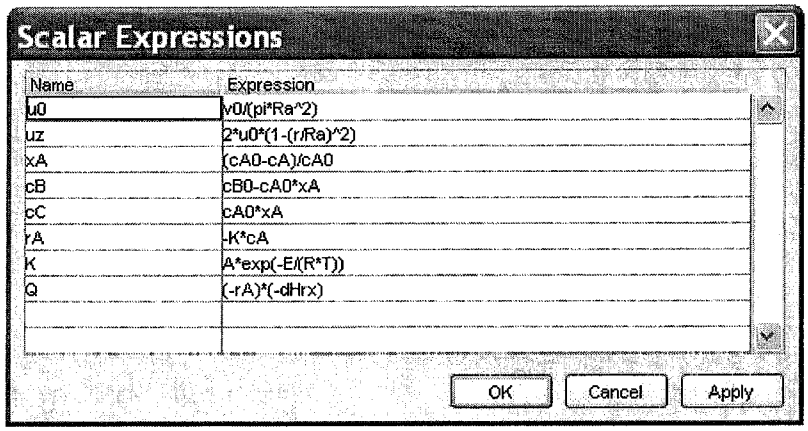


(2) Constants and scalar expressions

- Constants

Name	Expression	Value
Diff	1e-9	1e-9
E	75362	75362
A	16.96e12/3600	4.711111e9
R	8.314	8.314
T0	312	312
v0	49e-6	4.9e-5
cA0	2040.8	2040.8
cB0	39682.5	39682.5
Ra	0.1	0.1
dHrx	-84666.4	-84666.4
ke	0.559	0.559
rho	1000	1000
Cp	4180	4180
Uk	1300	1300
Ta0	273	273
CpJ	4180	4180
mJ	0.01	0.01

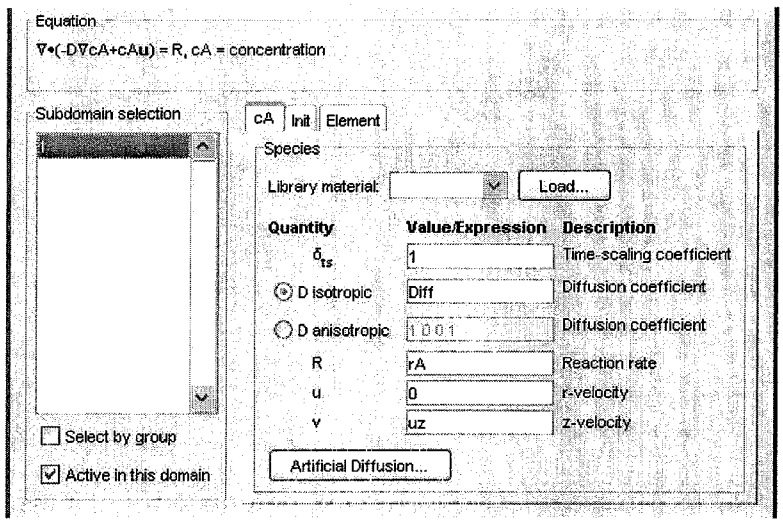
- Scalar expressions



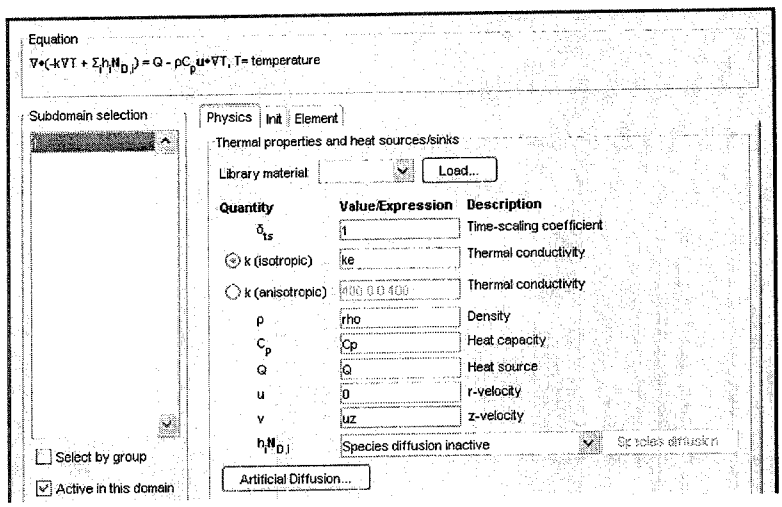
(3) Subdomain Settings

- Physics

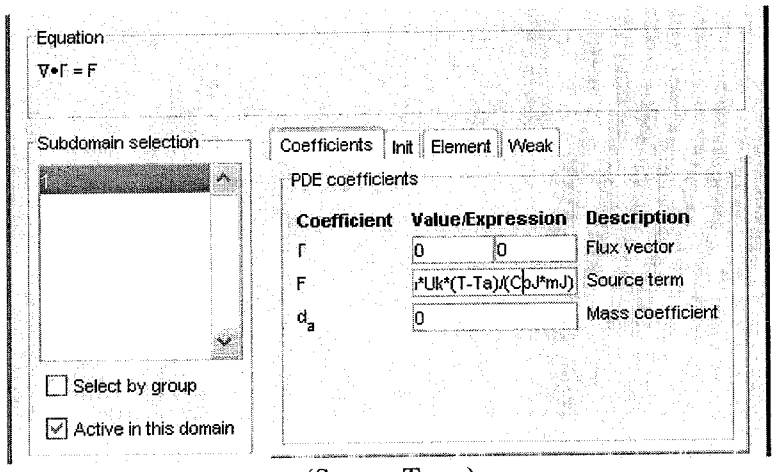
(mass balance)



(Energy balance)



(Cooling Jacket)



(Source Term)

F = Taz-2*pi*Ra*Uk*(T-Ta)/(CpJ*mJ)

- Initial values

(Mass balance) cA(t0) = cA0

(Energy Balance) T(t0) = T0

(Cooling Jacket) Ta(t0) = Ta0

- Boundary Conditions

@ r = 0, Axial symmetry

@ inlet, cA = cA0 (for mass balance)

T = T0 (for energy balance)

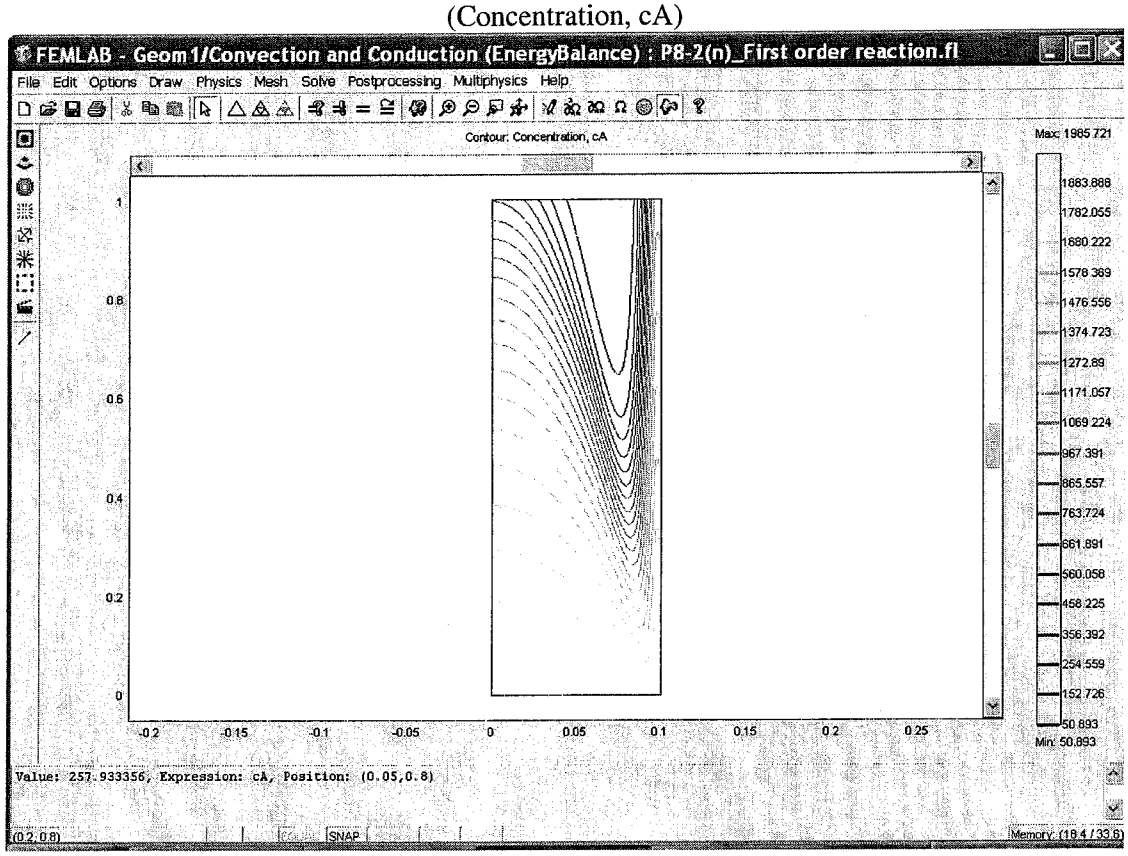
@ outlet, Convective flux

@ wall, Insulation/Symmetry (for mass balance)

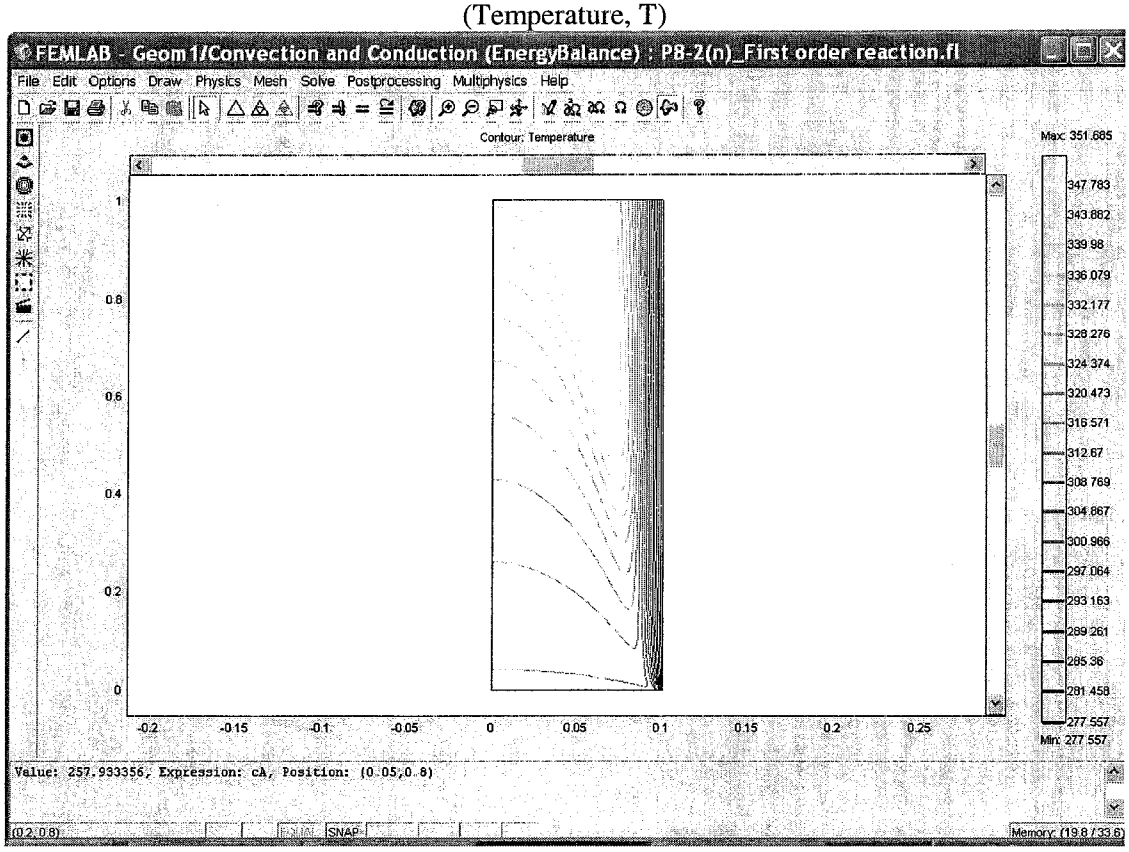
q0 = -Uk*(T-Ta0) (for energy balance)

(4) Results

(Concentration, cA)

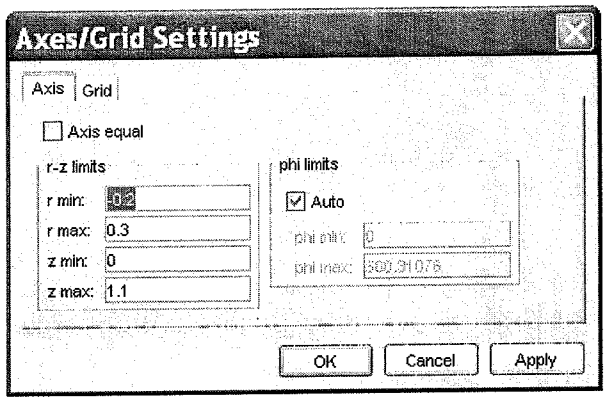


(Temperature, T)



Second order reaction

[1] Domain



[2] Constants & Scalar expressions

(1) Constants

Name	Expression	Value
Diff	1e-9	1e-9
E	95238	95238
A	1.1e8	1.1e8
R	8.314	8.314
T0	320	320
v0	0.0005	5e-4
cA0	500	500
cB0	500	500
Ra	0.1	0.1
rhoCat	1500	1500
dHrx	-83680	-83680
Keq0	1000	1000
ke	0.559*10	5.59
rho	1000	1000
Cp	4180	4180
Uk	1300	1300
Ta0	298	298
CpJ	4180	4180
mJ	0.01*10	0.1

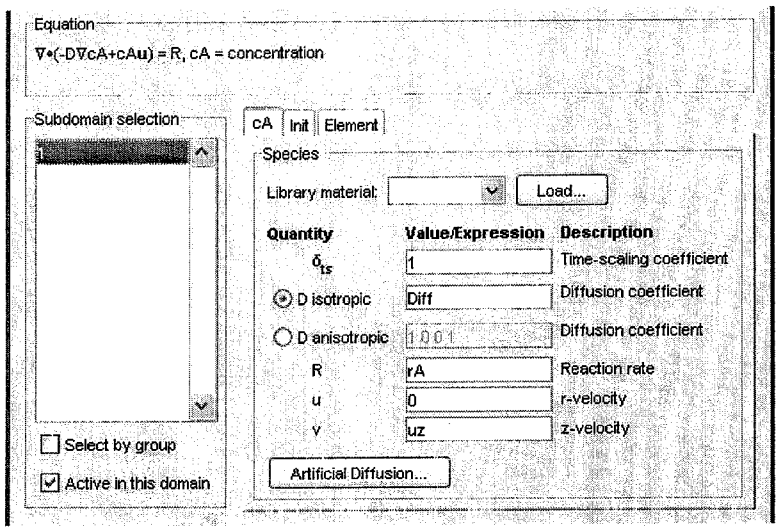
(2) Scalar expressions

Name	Expression
u0	v0/(pi*Ra^2)
uz	2*u0*(1-(r/Ra).^2)
xA	(cA0-cA)/cA0
cB	cB0-cA0*xA
cC	2*cA0*xA
rA	-A*exp(-E/R/T)*rhoCat*(cA.*cB-cC/Keq)
Keq	Keq0*exp(dHrx/R*(1/303-1/T))
Q	(-rA)*(-dHrx)

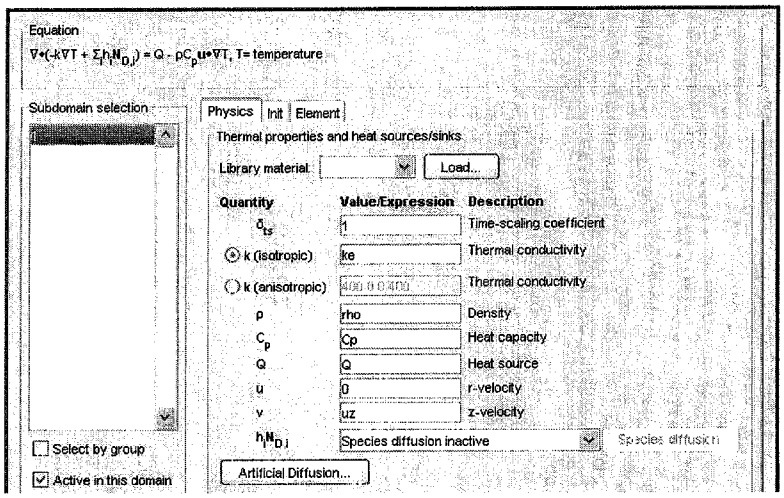
[3] Subdomain Settings

(1) Physics

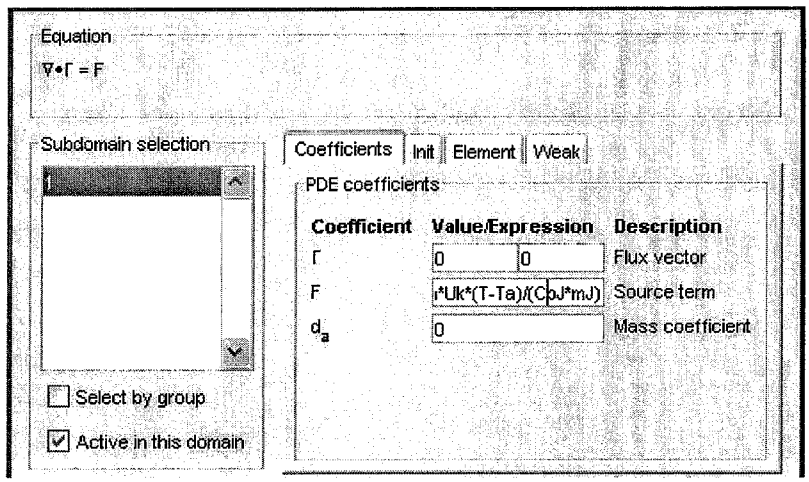
(Mass balance)



(Energy balance)



(Cooling Jacket)



(Source Term)

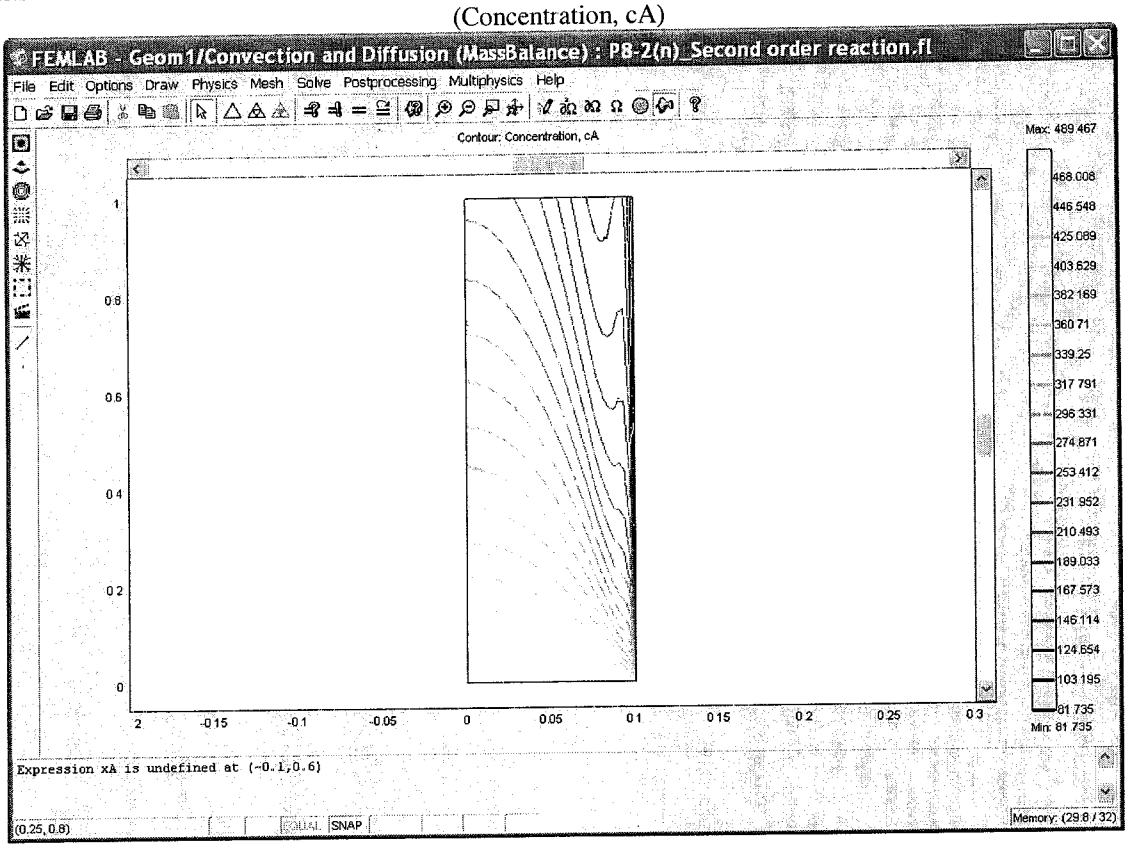
F = Taz-2*pi*Ra*Uk*(T-Ta)/(CpJ*mJ)

(2) Initial values
(Mass balance) cA(t0) = cA0
(Energy Balance) T(t0) = T0
(Cooling Jacket) Ta(t0) = Ta0

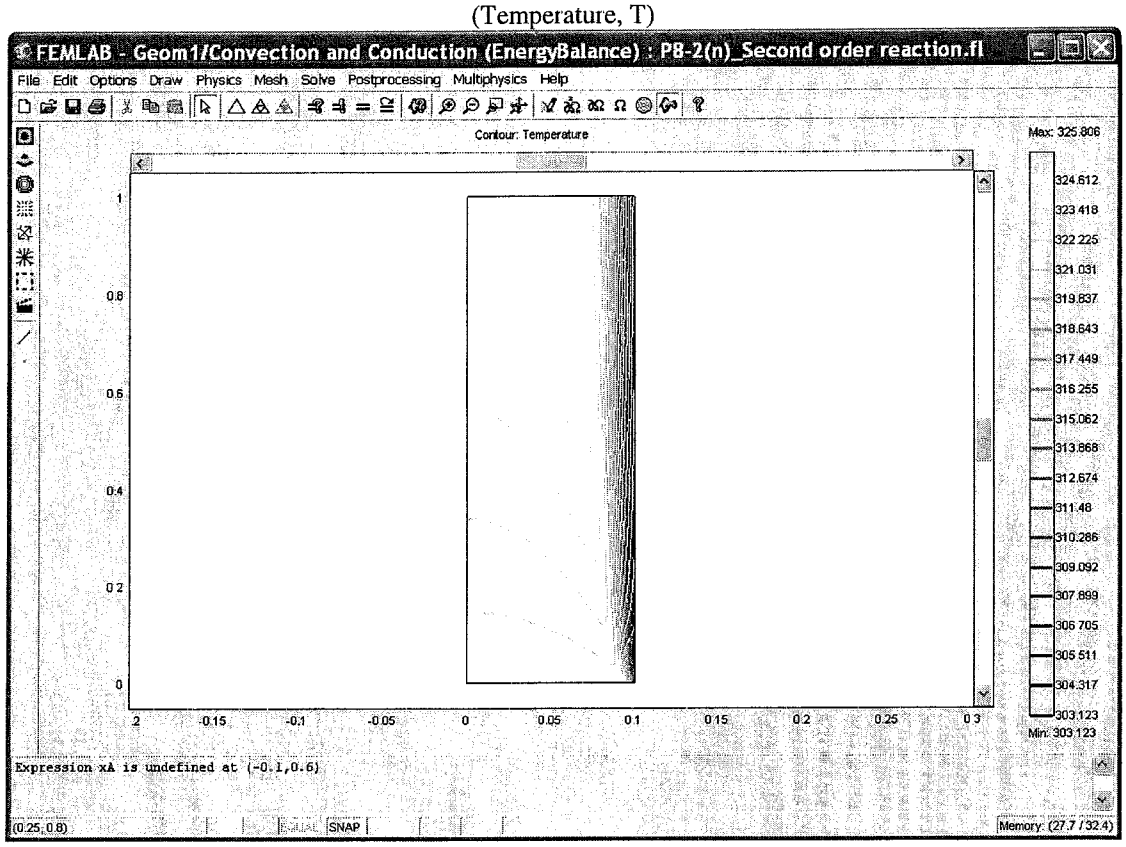
(3) Boundary Values
@ r = 0, Axial symmetry
@ inlet, cA = cA0 (for mass balance)
T = T0 (for energy balance)
@ outlet, Convective flux
@ wall, Insulation/Symmetry (for mass balance)
q0 = -Uk*(T-Ta0) (for energy balance)

[4] Results

(Concentration, cA)



(Temperature, T)



P8-2 (o) Individualized solution

P8-3 Solution is in the decoding algorithm available in the beginning of this manual.

P8-4

Find the reactor temperature at steady state (prior to shutdown)

Let M = mass of the NH_4NO_3 in reactor.

F_{A0} = lbs/hr of NH_4NO_3 fed to the reactor.

Mass balance: $F_{A0} - F_{A0}(1-X) = -r_A V = kM$

$$X = \frac{k(T)M}{F_{A0}}$$

Energy Balance:

$$-F_{A0}\sum\theta_i[H_{i0} - H_i(T)] + F_{A0}X\Delta H_{Rxn}(T) + F_{A0}(1-X)\Delta H_{VA} = 0$$

Where $H_i(T)$ is the enthalpy of i at the temperature of the reaction, ΔH_{VA} is the heat of vaporization of A, and $\Delta H_{Rxn}(T)$ is the heat of reaction at the outlet temperature.

$$NH_4NO(l) \rightarrow 2H_2O(g) + N_2O(g)$$

$$A \rightarrow 2B + C$$

The last term $F_{A0}(1-X)\Delta H_{VA}$ accounts for the unreacted NH_4NO_3, which exits as vapor rather than the liquid. Now, we can make some substitutions

$$\theta_B = \frac{.17}{.83}, \theta_A = 1, \theta_C = 0$$

Heat capacity of A is given, and the enthalpy change for water $200°F(l) \rightarrow 500°F(g)$ is also given. So, after dividing by F_{AO}, we obtain

$$C_{pA}(T-200) + \theta_B[H_B(500°F) + C_{ps}(T-500)] + \Delta H_{Rxn}X + (1-X)\Delta H_{VA} = 0$$

The previous equation assumes that the heat capacities are constant over a reasonable temperature range.

the phase change $NH_4NO(aq) \rightarrow NH_4NO(l)$ is isenthalpic.

In addition, we must account for the effect of the temperature dependence of ΔH_{Rxn}.

$$\Delta H_{Rxn}(T) = \Delta H_{Rxn}(T_R) + (T-T_R)[\frac{44}{80}C_{ps} - C_{pA}] = \Delta H_{Rxn}(Tr) + (T-Tr)\Delta C_P$$

Let $\Delta H_{Rxn} = H_B(500) - H_B(200)$, we have

$$C_{PA}(T-200) + \theta_B(\Delta H_W + C_{PS}(T-500) + X[\Delta H_{Rxn} + \Delta C_p(T-500)] + (1-X)\Delta H_{VA} = 0$$

$$or, T[C_{pA} + \theta_B C_{ps}] + [-C_{pA}(200) + \theta_B(\Delta H_w - 500C_{ps})] + X[\Delta H_{Rxn} + \Delta C_p(T-500)] + (1-X)\Delta H_{VA} = 0$$

Numerical Substitution with

K(560) = 5.03 and k(510) = .53

$$\ln(\frac{k_2}{k_1}) = -\frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Rightarrow \frac{E}{R} = -\ln(\frac{k_2}{k_1})\left(\frac{1}{T_2} - \frac{1}{T_1}\right)^{-1} = 44499$$

$$A_0 = k_1 \exp(\frac{E}{RT_1}) = 4.51424 \times 10^{19}$$

$$C_{pA} = .38\frac{Btu}{lb.R}; C_{ps} = .466$$

(P = 1 atm over 450 - 500°F Himmelblau)

$$C_{pc} = .2521\frac{Btu}{lb.R}$$ (Himmelblau, App E, over 230-265°C)

$$\theta_B = \frac{.17}{.83} = .205$$

$$\Delta H_W = 1034\frac{Btu}{lb}.03$$

$$F_{A0} = 257.3\frac{\text{lb } NH_4NO_3}{hr}$$

$$\Delta C_P = \frac{44.02}{80.05}(.2521) + \frac{36.03}{80.05}(.466) - .38 = -.0316\frac{Btu}{lb.R}$$

$$\Delta H_{Rxn} = C_{pA}(410 - T)$$

Substituting all these into the mass and energy balances:

Mass balance: $X = \dfrac{4.51\times10^{19}\exp\left(\dfrac{-44499}{T+459.67}\right)M}{257.3}$

Energy balance:

$$0 = .48T + 88.21 + X(-320.20 - .03T) + (1 - X)(155.80 - .38T)$$

Assume X = .96 and M=500. Then, from mass balance,

T = 510°F

P8-5

$$A + B \rightarrow 2C$$

	A	B	C
$F_{io}\left(\frac{lb-mole}{hr}\right)$	10	10	0.0
T_{io}(F)	80	80	-
$C_{Pio}\left(\frac{Btu}{lb\ mole°F}\right)$	51	44	47.5
$MW,\left(\frac{lb}{lb\ mol}\right)$	128	94	222
$\rho_{i,}\left(\frac{lb}{ft^3}\right)$	63	67.2	65

$$\Delta H_R = 20{,}000\frac{Btu}{lb\ mol\ A},$$

Energy balance with work term included is:

$$\frac{\dot{Q}-\dot{W}_S}{F_{A0}} - X_A \Delta H_R = \sum \theta_i \tilde{C}_{Pi}[T-T_o]$$

$$\theta_A = 1, \theta_B = \frac{F_{B0}}{F_{A0}} = \frac{10}{10} = 1, X_{AF} = 1$$

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

Substituting into energy balance,

$$UA(T_S - T) - W_S - F_{A0}\Delta H_R X_{AF} = F_{A0}\left[C_{pA} + C_{pB}\right][T - T_0]$$

$$\Rightarrow UA(T_S - T) - W_S - F_{A0}\Delta H_R = \left\{F_{A0}\left[C_{pA} + C_{pB}\right] + UA\right\}[T - T_0]$$

$$T = T_0 + \frac{UA(T_S - T) - W_S - F_{A0}\Delta H_R}{F_{A0}\left[C_{pA} + C_{pB}\right] + UA}$$

$$-W_s = 63525 \frac{Btu}{hr}$$

$$\therefore T = 199°F$$

P8-6

$$A + B \rightarrow C$$

Since the feed is equimolar, $C_{A0} = C_{B0} = .1$ mols/dm^3

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

$$C_B = C_{B0}(1\text{-}X)$$

Adiabatic:

$$T = T_0 + \frac{X[-\Delta H_R(T_0)]}{\sum \phi_i \tilde{C}_{P_i} + X\Delta\tilde{C}_P}$$

$$\Delta C_P = C_{pC} - C_{pB} - C_{pA} = 30 - 15 - 15 = 0$$

$$\Delta H_R(T) = H_C - H_B - H_A = \text{-41000-(-15000-(-20000)} = \text{-6000 cal/mol A}$$

$$\sum \theta_i \tilde{C}_i = C_{pA} + \theta_B C_{pB} = 15 + 15 = 30 \frac{cal}{mol\ K}$$

$$T = 300 + \frac{6000X}{30} = 300 + 200X$$

$$-r_A = k C_{A0}^2 (1-X)^2 = .01k(1-X)^2$$

P8-6 (a)

$$V_{PFR} = F_{A0} \int \frac{dX}{-r_A}$$

$$V_{CSTR} = \frac{F_{A0}X}{-r_A}$$

For the PFR, $F_{A0} = C_{A0}v_0 = (.1)(2) = .2$ mols/dm^3

See Polymath program P8-6-a.pol.

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	X	0	0	0.85	0.85
2	V	0	0	308.2917	308.2917
3	Ca0	0.1	0.1	0.1	0.1
4	Fa0	0.2	0.2	0.2	0.2
5	T	300.	300.	470.	470.
6	k	0.01	0.01	4.150375	4.150375
7	ra	-0.0001	-0.0018941	-0.0001	-0.0009338

Differential equations

1 d(V)/d(X) = -Fa0 / ra

Explicit equations

1 Ca0 = .1

2 Fa0 = .2

3 T = 300 + 200 * X

4 k = .01*exp((10000 / 2) * (1 / 300 - 1 / T))

5 ra = -k * (Ca0 ^ 2) * ((1 - X) ^ 2)

$V = 308.2917 \text{dm}^3$

For the CSTR,

$X = .85$, $T = 300+(200)(85) = 470$ K.

$k = 4.31$ (Using T = 470K in the formula).

$-r_A = .000971$ mol/dm^3/s

$$V = \frac{F_{A0}X}{-r_A} = \frac{.1\times2\times.85}{9.71\times10^{-4}} = 175 \text{ dm}^3$$

The reason for this difference is that the temperature and hence the rate of reaction remains constant throughout the entire CSTR (equal to the outlet conditions), while for a PFR, the rate increases gradually with temperature from the inlet to the outlet, so the rate of increases with length.

P8-6 (b)

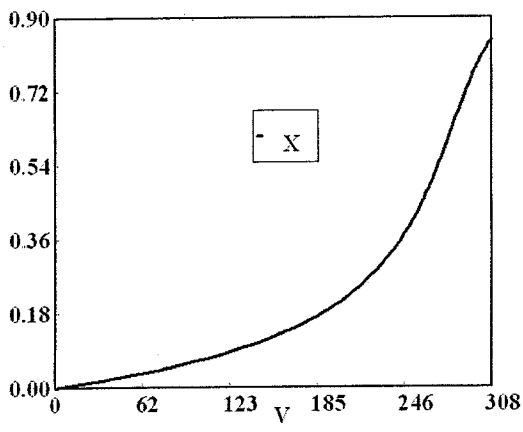
$$T = T_0 + \frac{X[-\Delta H_R]}{\sum \theta_i C_{P_i}}$$

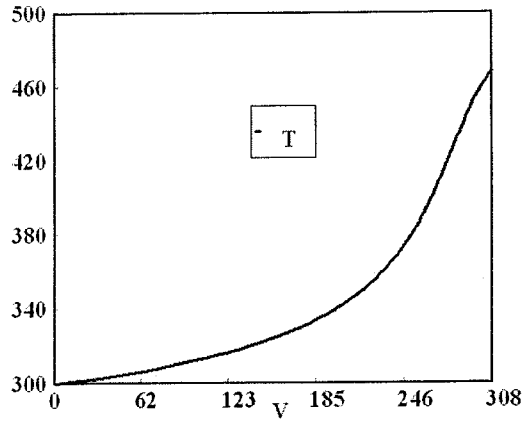
For boiling temp of 550 k,

$550 = T_0 + 200$

$T_0 = 350$K

P8-6 (c)





P8-6 (d)

$$V_{CSTR} = \frac{F_{A0} X}{-r_A}$$

$$\Rightarrow X = \frac{V_{CSTR}}{F_{A0}}(-r_A)$$

For V = 500 dm^3, F_{A0}=.2

$$-r_A = k C_{A0}^2 (1-X)^2 = .01k(1-X)^2$$

$$T = 300 + 200X$$

Now use Polymath to solve the non-linear equations.

See Polymath program P8-6-d-1.pol.

Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	T	484.4136	0	480.
2	X	0.9220681	-2.041E-09	0.9

	Variable	Value
1	k	6.072856
2	ra	0.0003688

Nonlinear equations

1 f(T) = 300 + 200 * X - T = 0

2 f(X) = 500 - .2 * X / ra = 0

Explicit equations

1 k = .01 * exp(10000 / 1.98 * (1 / 300 - 1 / T))

2 ra = 0.01 * k * (1 - X) ^ 2

Hence, X = .922 and T = 484.41 K

For the conversion in two CSTR's of 250 dm^3 each,
For the first CSTR, using the earlier program and V = 250 dm^3,

Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	T	476.482	1.137E-13	480.
2	X	0.88241	-5.803E-09	0.9

	Variable	Value
1	k	5.105278
2	ra	0.0007059

Nonlinear equations

1 f(T) = 300 + 200 * X - T = 0

2 f(X) = 250 - .2 * X / ra = 0

Explicit equations

1 k = .01 * exp(10000 / 1.98 * (1 / 300 - 1 / T))

2 ra = 0.01 * k * (1 - X) ^ 2

T = 476.48 ad X = .8824
Hence, in the second reactor,

$$V_{CSTR} = \frac{F_{A0}(X - X_1)}{-r_A}$$

$$\Rightarrow X = \frac{V_{CSTR}}{F_{A0}}(-r_A) + X_1$$

$$T = T_{out,CSTR1} + 200(X - X_1)$$

See Polymath program P8-6-d-2.pol.

Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	T	493.8738	0	480.
2	X	0.9693688	-1.359E-09	0.8824

	Variable	Value
1	k	7.415252
2	ra	6.958E-05

3	X1	0.8824

Nonlinear equations

1 f(T) = 476.48 + 200 * (X - X1) - T = 0

2 f(X) = 250 - .2 * (X - X1) / ra = 0

Explicit equations

1 k = .01 * exp(10000 / 1.98 * (1 / 300 - 1 / T))

2 ra = 0.01 * k * (1 - X) ^ 2

3 X1 = .8824

Hence, final X = .9694

P8-6 (e) Individualized solution

P8-6 (f) Individualized solution

P8-7 (a)

For reversible reaction, the rate law becomes

$$-r_A = k\left(C_A C_B - \frac{C_C}{K_C}\right)$$

$$X_e = \frac{K_e}{1+K_e}$$

$$T = 300 + 200\,X$$

$$k = k(300)\exp\left(\frac{E}{R}\left(\frac{1}{300} - \frac{1}{T}\right)\right)$$

$$K_C = K_C(450)\exp\left[\frac{\Delta H_{Rxn}}{R}\left(\frac{1}{450} - \frac{1}{T}\right)\right]$$

Stoichiometry:

$$C_C = C_{A0}X$$

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

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

See Polymath program P8-7-a.pol.

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	V	0	0	10.	10.
2	X	0	0	0.0050806	0.0050806

3	T	300.	300.	301.0161	301.0161
4	Fa0	0.2	0.2	0.2	0.2
5	Kc	0.3567399	0.3567399	0.3689877	0.3689877
6	k	0.01	0.01	0.0105787	0.0105787
7	Ca0	0.1	0.1	0.1	0.1
8	ra	-0.0001	-0.0001033	-0.0001	-0.0001033
9	Xe	0.2629391	0.2629391	0.2695332	0.2695332

Differential equations

1 d(X)/d(V) = -ra / Fa0

Explicit equations

1 T = 300 + 200 * X

2 Fa0 = .2

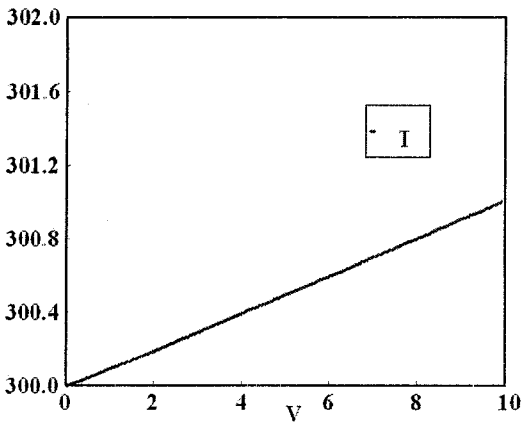
3 Kc = 10 * exp(6000 / 2 * (1 / 450 - 1 / T))

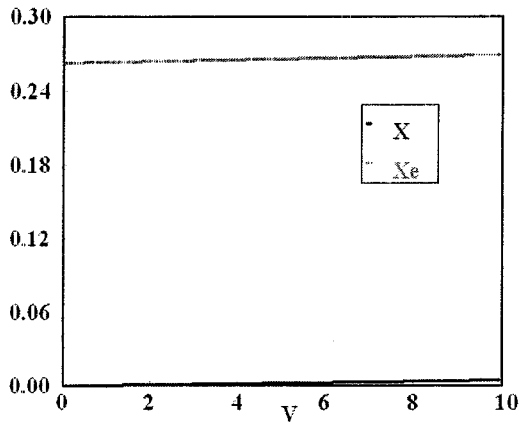
4 k = .01 * exp((10000 / 2) * (1 / 300 - 1 / T))

5 Ca0 = .1

6 ra = -k * (Ca0 ^ 2) * ((1 - X) ^ 2 - X / Kc)

7 Xe = Kc / (1 + Kc)





P8-7 (b)

When heat exchanger is added, the energy balance can be written as

$$\frac{dT}{dV}=\frac{Ua(T_a-T)+(-r_A)\left[-\Delta H_{Rxn}(T)\right]}{F_{A0}(\sum\theta_i C_{pi}+\Delta\hat{C}_P)}$$

So with $\Delta\hat{C}_P=0$, $\sum\theta_i C_{pi}=30$, ΔH_{Rxn} = -6000 cal/mol

$$\frac{dT}{dV}=\frac{Ua(T_a-T)+(-r_A)[6000]}{F_{A0}(30)}$$

Where Ua = 20 cal/m^3/s/K, T_a = 450 K

•

See Polymath program P8-7-b.pol.

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	V	0	0	10.	10.
2	X	0	0	0.5717112	0.5717112
3	T	450.	450.	463.9974	452.3087
4	Ca0	0.1	0.1	0.1	0.1
5	Fa0	0.2	0.2	0.2	0.2
6	Kc	10.	10.	12.22765	10.34614
7	k	2.586706	2.586706	3.616753	2.737647
8	ra	-0.0258671	-0.027946	-0.0035089	-0.0035089
9	Xe	0.9090909	0.9090909	0.9244008	0.9118643
10	UA	10.	10.	10.	10.
11	Ta	450.	450.	450.	450.
12	A	10.	10.	10.	10.

Differential equations

1 d(X)/d(V) = -ra / Fa0

2 d(T)/d(V) = (UA * (Ta - T) + (-ra) * 6000) / 30 / Fa0

Explicit equations

1 Ca0 = .1

2 Fa0 = .2

3 Kc = 10 * exp(6000 / 2 * (1 / 450 - 1 / T))

4 k = .01 * exp((10000 / 2) * (1 / 300 - 1 / T))

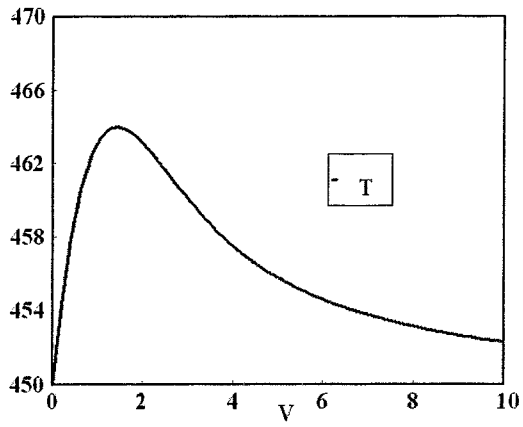
5 ra = -k * (Ca0 ^ 2) * ((1 - X) ^ 2 - X / Kc)

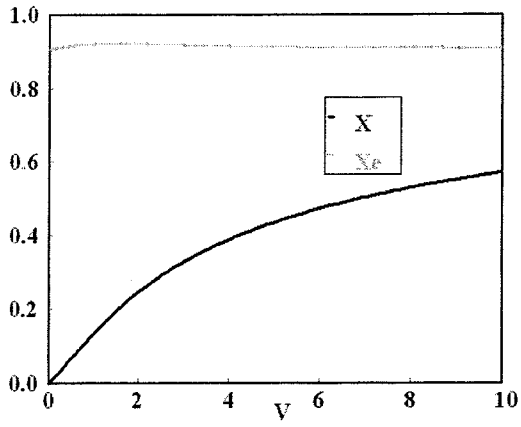
6 Xe = Kc / (1 + Kc)

7 UA = 10

8 Ta = 450

9 A = 10





P8-7 (c)

For a co-current heat exchanger,

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

C_{pC} = 1cal/g/K, T_{a1}=450 K, $\dot{m} = 50\frac{g}{\text{sec}}$

See Polymath program P8-7-c.pol.

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	V	0	0	10.	10.
2	X	0	0	0.575571	0.575571
3	T	450.	450.	465.3828	452.5192
4	Ca0	0.1	0.1	0.1	0.1
5	Fa0	0.2	0.2	0.2	0.2
6	Kc	10.	10.	12.46524	10.37812
7	Cpc	1.	1.	1.	1.
8	k	2.586706	2.586706	3.734633	2.751765
9	ra	-0.0258671	-0.0281568	-0.0034309	-0.0034309
10	Xe	0.9090909	0.9090909	0.9257347	0.912112
11	UA	10.	10.	10.	10.
12	Ta	450.	450.	450.	450.
13	A	10.	10.	10.	10.
14	mc	50.	50.	50.	50.
15	Q	0	-139.4201	0	-22.83309

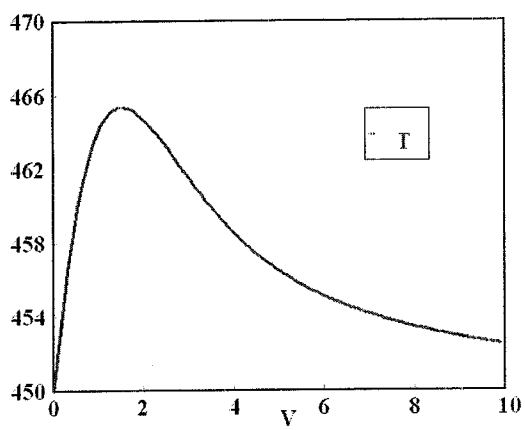
Differential equations

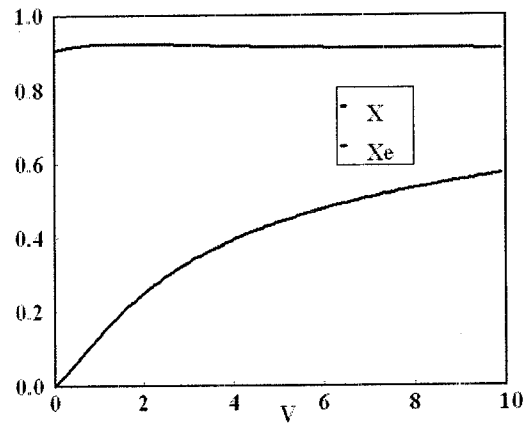
1 d(X)/d(V) = -ra / Fa0

2 d(T)/d(V) = (Q + (-ra) * 6000) / 30 / Fa0

Explicit equations

1 Ca0 = .1
2 Fa0 = .2
3 Kc = 10 * exp(6000 / 2 * (1 / 450 - 1 / T))
4 Cpc = 1
5 k = .01 * exp((10000 / 2) * (1 / 300 - 1 / T))
6 ra = -k * (Ca0 ^ 2) * ((1 - X) ^ 2 - X / Kc)
7 Xe = Kc / (1 + Kc)
8 UA = 10
9 Ta = 450
10 A = 10
11 mc = 50
12 Q = mc * Cpc * (Ta - T) * (1 - exp(-UA / mc / Cpc))





Next increase the coolant flow rate and run the same program to compare results.

P8-7 (d)

For counter-current flow,

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

See Polymath program P8-7-d.pol.

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	V	0	0	10.	10.
2	X	0	0	0.5395082	0.5395082
3	T	450.	450.	451.6471	450.2745

4	Ca0	0.1	0.1	0.1	0.1
5	Fa0	0.2	0.2	0.2	0.2
6	Kc	10.	10.	10.24606	10.04072
7	Cpc	1.	1.	1.	1.
8	k	2.586706	2.586706	2.693657	2.604286
9	ra	-0.0258671	-0.0260956	-0.0041231	-0.0041231
10	Xe	0.9090909	0.9090909	0.91108	0.9094262
11	UA	10.	10.	10.	10.
12	Ta	450.	450.	450.	450.
13	A	10.	10.	10.	10.
14	mc	50.	50.	50.	50.
15	Q	0	-149.7577	0	-24.96003

Differential equations

1 d(X)/d(V) = -ra / Fa0

2 d(T)/d(V) = (Q + (-ra) * 6000) / 30 / Fa0

Explicit equations

1 Ca0 = .1

2 Fa0 = .2

3 Kc = 10 * exp(6000 / 2 * (1 / 450 - 1 / T))

4 Cpc = 1

5 k = .01 * exp((10000 / 2) * (1 / 300 - 1 / T))

6 ra = -k * (Ca0 ^ 2) * ((1 - X) ^ 2 - X / Kc)

7 Xe = Kc / (1 + Kc)

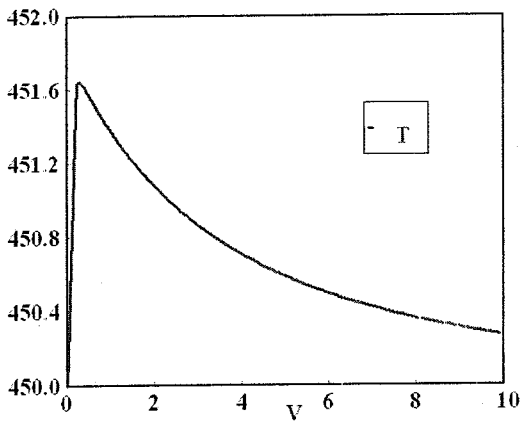
8 UA = 10

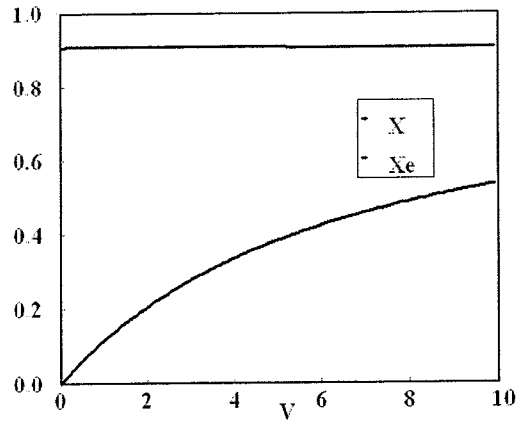
9 Ta = 450

10 A = 10

11 mc = 50

12 Q = mc * Cpc * (Ta - T) * (1 + exp(-UA / mc / Cpc))





P8-7 (e)

We see that it is better to use a counter-current coolant flow as in this case we achieve the maximum equilibrium conversion using a lesser volume of the PFR.

P8-7 (f)

If the reaction is irreversible but endothermic, we have

$-r_A = k\,C_{A0}^2(1-X)^2 = .01k(1-X)^2$ as obtained in the earlier problem.

$\Delta H_{Rxn} = 6000 cal/mol$

For co-current flow of coolant,

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

See Polymath program P8-7-f-co.pol.

we use 8- 7f cocurrent.pol

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	V	0	0	10.	10.
2	X	0	0	0.5227896	0.5227896
3	T	450.	439.9908	450.	446.1887
4	Ca0	0.1	0.1	0.1	0.1
5	Fa0	0.2	0.2	0.2	0.2
6	Cpc	1.	1.	1.	1.
7	k	2.586706	2.008972	2.586706	2.352492
8	ra	-0.0258671	-0.0258671	-0.0053573	-0.0053573
9	UA	10.	10.	10.	10.
10	Ta	450.	450.	450.	450.
11	mc	50.	50.	50.	50.

12	Q	0	0	90.71779	34.54357

Differential equations

1 d(X)/d(V) = -ra / Fa0

2 d(T)/d(V) = (Q + (-ra) * (-6000)) / 30 / Fa0

Explicit equations

1 Ca0 = .1

2 Fa0 = .2

3 Cpc = 1

4 k = .01 * exp((10000 / 2) * (1 / 300 - 1 / T))

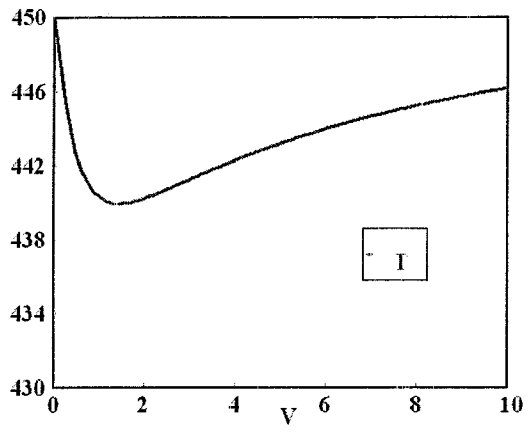
5 ra = -k * (Ca0 ^ 2) * ((1 - X) ^ 2)

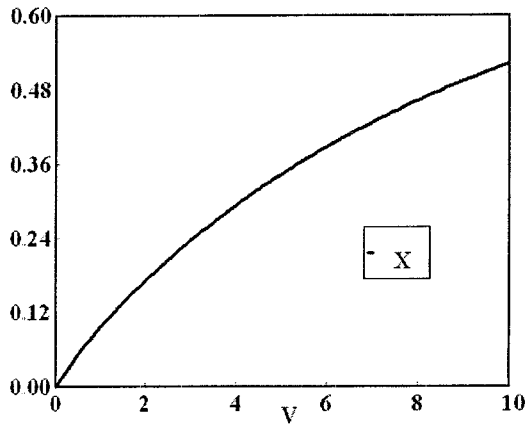
6 UA = 10

7 Ta = 450

8 mc = 50

9 Q = mc * Cpc * (Ta - T) * (1 - exp(-UA / mc / Cpc))





For counter-current flow,

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

See Polymath program P8-7-f-counter.pol.

POLYMATH program 8- 7f countercurrent.pol

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	V	0	0	10.	10.
2	X	0	0	0.5594826	0.5594826
3	T	450.	448.4634	450.	449.669

4	Ca0	0.1	0.1	0.1	0.1
5	Fa0	0.2	0.2	0.2	0.2
6	Cpc	1.	1.	1.	1.
7	k	2.586706	2.4901	2.586706	2.565639
8	ra	-0.0258671	-0.0258671	-0.0049788	-0.0049788
9	UA	10.	10.	10.	10.
10	Ta	450.	450.	450.	450.
11	mc	50.	50.	50.	50.
12	Q	0	0	139.7022	30.09601

Differential equations

1 d(X)/d(V) = -ra / Fa0

2 d(T)/d(V) = (Q + (-ra) * (-6000)) / 30 / Fa0

Explicit equations

1 Ca0 = .1

2 Fa0 = .2

3 Cpc = 1

4 k = .01 * exp((10000 / 2) * (1 / 300 - 1 / T))

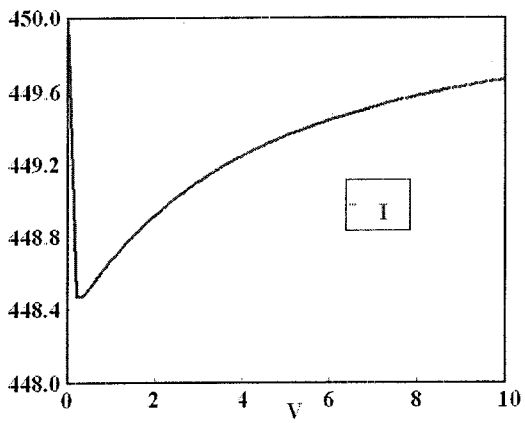
5 ra = -k * (Ca0 ^ 2) * ((1 - X) ^ 2)

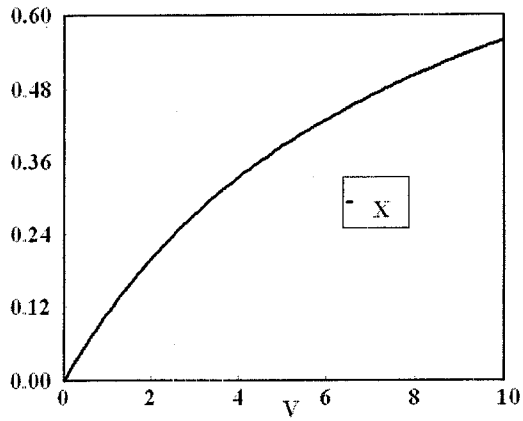
6 UA = 10

7 Ta = 450

8 mc = 50

9 Q = mc * Cpc * (Ta - T) * (1 + exp(-UA / mc / Cpc))





P8-7 (g)

For a runaway reaction, the following must be true:

$$T_r - T_C > \frac{RT_r^2}{E}$$

and $T_C = \frac{T_0 + \kappa T_a}{1+\kappa} = \frac{300+3*450}{1+3} = 412.5$

So if we plug this value into the original equation we get:

$\frac{1.987}{10000} T_r^2 - T_r + 450 > 0$

$T_r = 499$ K

P8-8 (a)

$$A + B \rightarrow C$$

Species Balance:

$$\frac{dX}{dW} = -\frac{r_A'}{F_{A0}}$$

$$v_0 = 20\, dm^3 / s$$

$$P_0 = 10\, atm$$

Stoichiometry:

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

$$\Rightarrow C_A = C_{A0}\left(\frac{1-X}{1+X}\right)\frac{T}{T_0}$$

Rate Law is:

$$-r_A = kC_A, with\ k = 0.133 \exp\left[\frac{E}{R}\left(\frac{1}{450} - \frac{1}{T}\right)\right]$$

$$E = 31400$$

$$\Delta H_{Rxn} = -20{,}000\, J / mol$$

Energy Balance:

$$T = T_0 + \frac{X[-\Delta H_R(T_0)]}{\sum \theta_i \tilde{C}_{P_i} + X\Delta\tilde{C}_P}$$

$$\Delta C_P = 15 + 24 - 40 = 0$$

$$T = 450 + \frac{20{,}000\, X}{40} = 450 + 500X$$

See Polymath program P8-8-a.pol.

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	X	0	0	0.8	0.8
2	W	0	0	43.13711	43.13711

3	T	450.	450.	850.	850.
4	v0	20.	20.	20.	20.
5	T0	450.	450.	450.	450.
6	k	0.133	0.133	6.904332	6.904332

Differential equations

1 d(W)/d(X) = v0 * (1 + X) * T / k / (1 - X) / T0

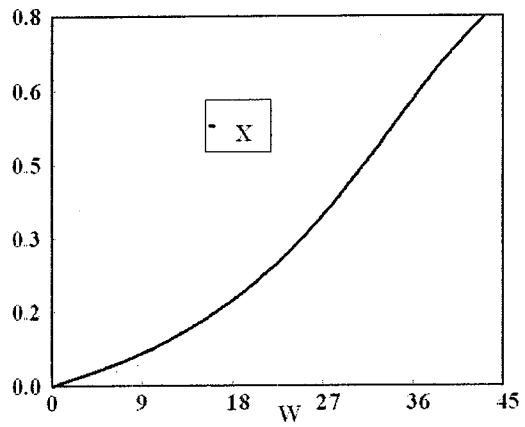
Explicit equations

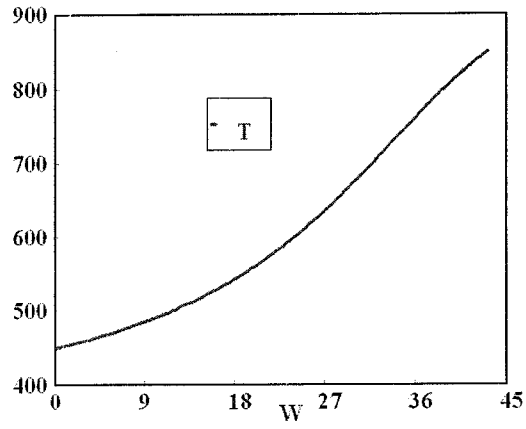
1 T = 450 + 500 * X

2 v0 = 20

3 T0 = 450

4 k = .133 * exp(31400 / 8.314 * (1 / T0 - 1 / T))





P8-8 (b)

Species Balance for CSTR:

$$W_{CSTR} = \frac{F_{A0} X}{-r'_A}$$

$$T = 450 + 500\,X = 450 + 500(.8) = 850\,K$$

$$k = .133 \exp\left[\frac{31400}{8.314}\left(\frac{1}{450} - \frac{1}{850}\right)\right] = 6.9$$

$$W_{CSTR} = 39.42\,kg$$

P8-8 (c) Individualized solution

P8-8 (d)

For pressure drop, an extra equation is added

$$\frac{dP}{dW} = -\frac{\alpha}{2}\left(\frac{T}{T_0}\right)\frac{P_0}{(P/P_0)}(1+\varepsilon X)$$

$$C_A = C_{A0}\left(\frac{1-X}{1+X}\right)\frac{T}{T_0}\frac{P}{P_0}$$

See Polymath program P8-8-d.pol.

Using POLYMATH program CRE_8_8d.pol
For $\alpha = .019$

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	W	0	0	0.8	0.8
2	X	0	0	0.0544753	0.0544753
3	P	1.013E+06	1.002E+06	1.013E+06	1.002E+06
4	T	450.	450.	850.	850.
5	v0	20.	20.	20.	20.
6	T0	450.	450.	450.	450.
7	k	0.133	0.133	6.904332	6.904332
8	P0	1.013E+06	1.013E+06	1.013E+06	1.013E+06
9	alpha	0.019	0.019	0.019	0.019

Differential equations

1 d(X)/d(W) = k / v0 * (1 - X) / (1 + X) * T0 / T * P / P0

2 d(P)/d(W) = -alpha / 2 * (T / T0) * P0 ^ 2 / P * (1 + X)

Explicit equations

1 T = 450 + 500 * W

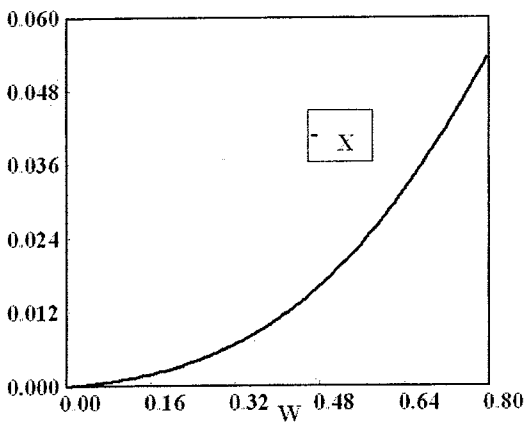
2 v0 = 20

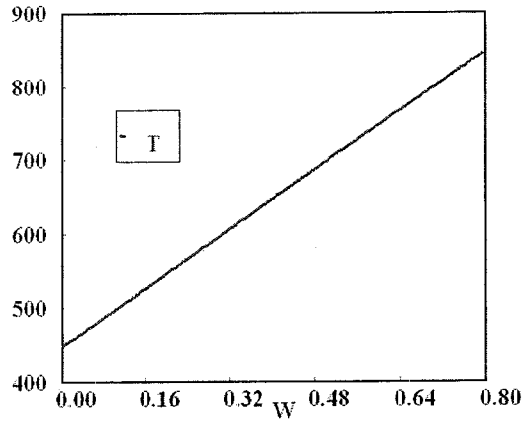
3 T0 = 450

4 k = .133 * exp(31400 / 8.314 * (1 / T0 - 1 / T))

5 P0 = 1013250

6 alpha = .019





•

P8-9 (a)

We use the same equations as problem P8-8, except that the energy balance changes as:

$$\frac{dT}{dW} = \frac{\frac{Ua}{\rho}(T_a - T) + (-r_A')(-\Delta H_{Rxn})}{F_{A0}C_{pA}}$$

Where $-\Delta H_{Rxn}$ = 20,000 J/mol, T_a=323 K, C_{pA}=40 J/mol/K

See Polymath program P8-9-a.pol.

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	W	0	0	50.	50.
2	X	0	0	0.1376181	0.1376181
3	T	450.	381.1888	450.	381.1888
4	T0	450.	450.	450.	450.
5	v0	20.	20.	20.	20.
6	k	0.133	0.0292331	0.133	0.0292331
7	Uarho	0.08	0.08	0.08	0.08
8	Ta	293.	293.	293.	293.
9	P0	1.013E+06	1.013E+06	1.013E+06	1.013E+06
10	CA0	270.8283	270.8283	270.8283	270.8283
11	CA	270.8283	242.3648	270.8283	242.3648
12	rA	-36.02017	-36.02017	-7.085084	-7.085084

Differential equations

1 d(X)/d(W) = k * (1 - X) / (1 + X) * T0 / T / v0

2 d(T)/d(W) = (Uarho * (Ta - T) + rA * 20000) / v0 / CA0 / 40

Explicit equations

1 T0 = 450

2 v0 = 20

3 k = 0.133 * exp(31400 / 8.314 * (1 / T0 - 1 / T))

4 Uarho = 0.08

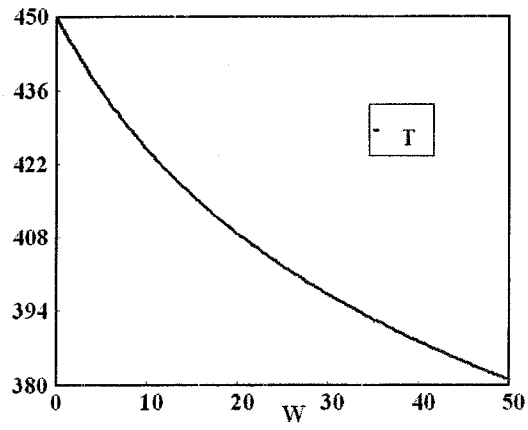
5 Ta = 293

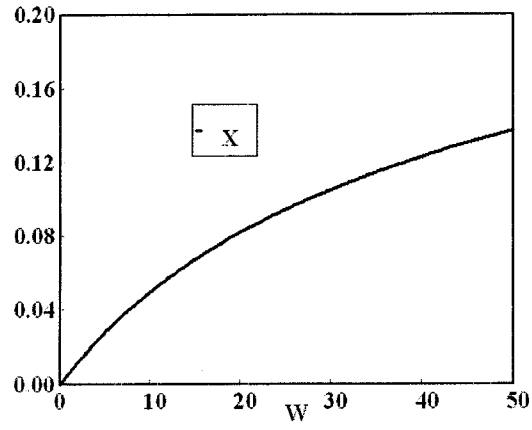
6 P0 = 1013250

7 CA0 = P0 / 8.314 / T0

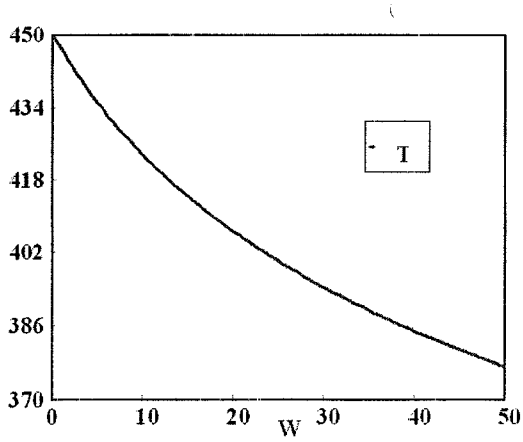
8 CA = CA0 * (1 - X) / (1 + X) * T0 / T

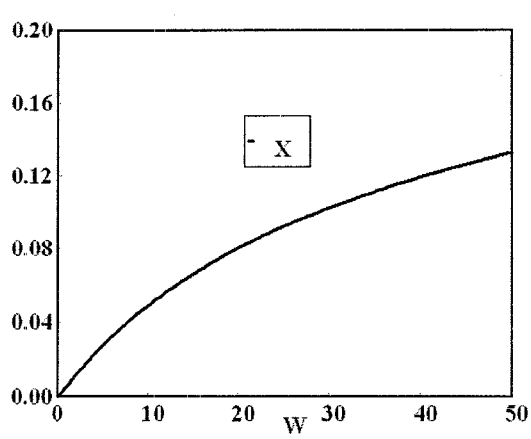
9 rA = -k * CA





If $\frac{UA}{\rho_b}$ was increased by a factor of 3000, we use the same program with the new value. The profiles are in the graphs below.



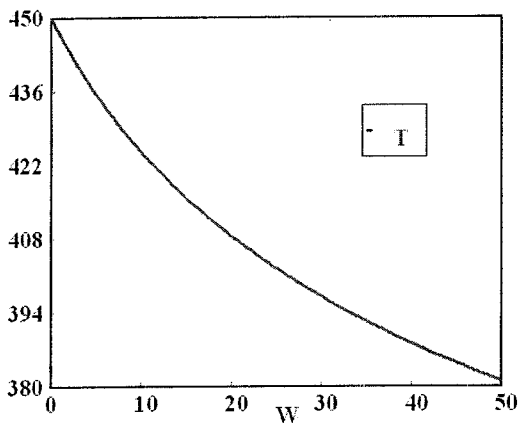


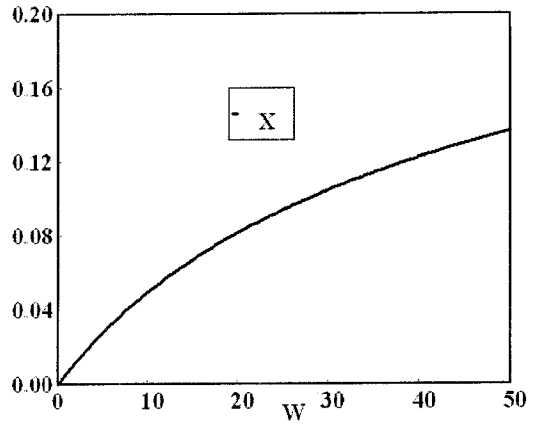
P8-9 (b)

For non-constant jacket temperature, the equation for incorporating the flow needs to be introduced.
co-current:

T_{a0} = 50 °C

$$\frac{dT_a}{dW} = \frac{\frac{Ua}{\rho}(T - T_a)}{\dot{m}_C C_{pC}}$$

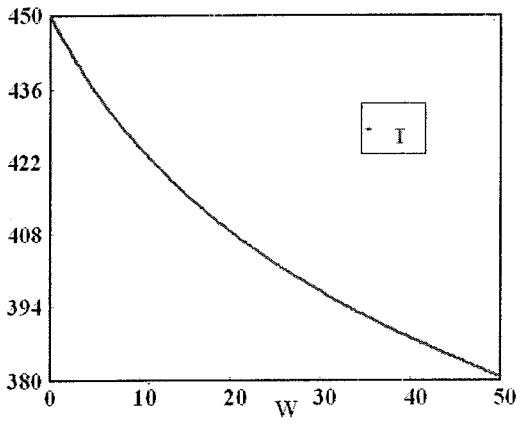


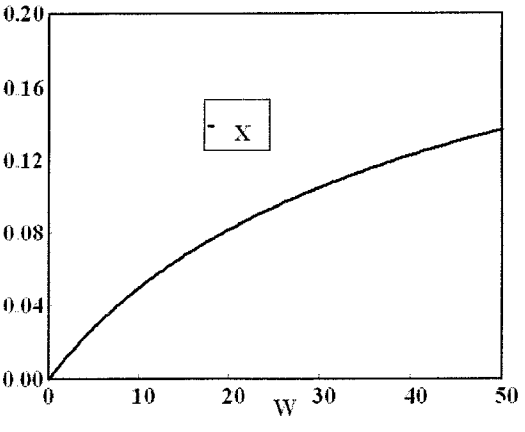


countercurrent:

$$\frac{dT_a}{dW} = -\frac{\frac{Ua}{\rho}(T - T_a)}{\dot{m}_C C_{pC}}$$

T_{af} = 50 °C
guess and check T_{a0} until T_a = 323 K at W = 50
T_{a0} = 438.8 K





P8-9 (c)

For a fluidized CSTR with W = 80 kg, UA = 500 J/s/K,

Species balance: $X_{MB} = \frac{\tau k}{1+\tau k}, \tau = \frac{\frac{W}{\rho_b} C_{A0}}{F_{A0}}$

Energy balance: $X_{EB} = \frac{\frac{UA}{\rho_b}\frac{(T-T_a)}{F_{A0}} + C_{pA}(T-T_0)}{-\Delta H_{Rxn}}$

$X_{EB} = X_{MB}$

Solving, X = .95, T = 323 K

P8-9 (d)

For a reversible reaction, we have all the previous equations, but the rate law is modified as:

$$-r_A = k_f C_A - k_r C_B C_C$$

$$C_B = C_C = C_{A0}\frac{X}{1+X}\frac{T_0}{T}$$

Plugging the equation for k_r, and solving using POLYMATH program, we get the plots. Only the co-current program and plots are shown.

See Polymath program P8-9-d.pol.

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	W	0	0	80.	80.
2	X	0	0	0.057593	0.057593
3	T	450.	420.7523	450.	420.7523
4	Ta	323.	323.	426.1627	420.7565
5	T0	450.	450.	450.	450.
6	v0	20.	20.	20.	20.
7	k	0.133	0.0742131	0.133	0.0742131
8	Uarho	240.	240.	240.	240.
9	P0	1.013E+06	1.013E+06	1.013E+06	1.013E+06
10	CA0	270.8283	270.8283	270.8283	270.8283
11	CA	270.8283	258.1071	270.8283	258.1071
12	kr	0.2	0.076962	0.2	0.076962
13	CC	0	0	15.77362	15.77362
14	CB	0	0	15.77362	15.77362
15	rA	-36.02017	-36.02017	-0.0062421	-0.0062421

Differential equations

1 d(X)/d(W) = -rA / v0 / CA0

2 d(T)/d(W) = (Uarho * (Ta - T) + rA * 20000) / v0 / CA0 / 40

3 d(Ta)/d(W) = Uarho * (T - Ta) / .2 / 5000

+ sign = cocurrent, -ve sign = countercurrent in RHS of eqn.

Explicit equations

1 T0 = 450

2 v0 = 20

3 k = 0.133 * exp(31400 / 8.314 * (1 / T0 - 1 / T))

4 Uarho = .08 * 3000

5 P0 = 1013250

6 CA0 = P0 / 8.314 / T0

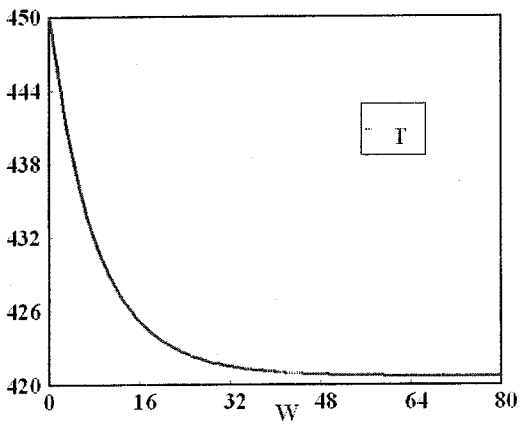
7 CA = CA0 * (1 - X) / (1 + X) * T0 / T

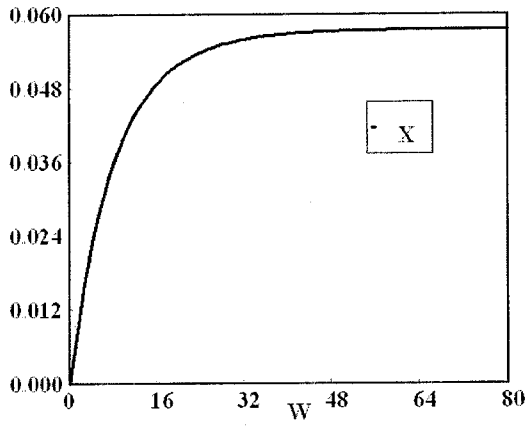
8 kr = 0.2 * exp(51400 / 8.314 * (1 / T0 - 1 / T))

9 CC = CA0 * X / (1 + X) * T0 / T

10 CB = CA0 * X / (1 + X) * T0 / T

11 rA = -(k * CA - kr * CB * CC)





P8-9 (e) Individualized solution

P8-10 (a)

$$A \rightarrow B + C$$

$$C_A = C_T \frac{F_A}{F_I}$$

$$\theta_I = \frac{F_I}{F_A}$$

$$C_T = C_A + C_I$$

$$F_T = F_A + F_I$$

•

$$C_{A01} = (C_{A0} + C_{I0})\frac{F_{A0}}{F_{A0} + F_{I0}}$$

$$C_{A01} = \frac{C_{A0} + C_{I0}}{\theta_I + 1}$$

P8-10 (b)

Mole balance:

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

Rate law: $-r_A = kC_A$

Stoichiometry: $C_A = C_{A01}\frac{1-X}{1+\varepsilon X}\frac{T_0}{T}$

$$\varepsilon = y_{A0}\delta$$

$$\delta = 1+1-1 = 1$$

$$y_{A0} = \frac{F_{A0}}{F_{T0}} = \frac{F_{A0}}{F_{A0} + F_{i0}} = \frac{1}{1+\theta_i}$$

$$\varepsilon = \frac{1}{1+\theta_i}$$

$$T = \frac{-X\Delta H_{RX} + (C_{PA} + \theta_i C_{Pi})T_0}{C_{PA} + \theta_i C_{Pi}}$$

Enter these equations into Polymath

See Polymath program P8-10-b.pol.

POLYMATH Results
Calculated values of the DEQ variables

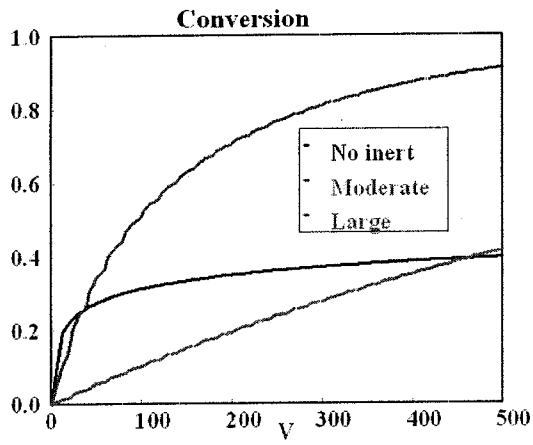
Variable	initial value	minimal value	maximal value	final value
V	0	0	500	500
X	0	0	0.417064	0.417064
Cao	0.0221729	0.0221729	0.0221729	0.0221729
Cio	0.0221729	0.0221729	0.0221729	0.0221729
theta	100	100	100	100
Fao	10	10	10	10
Cao1	4.391E-04	4.391E-04	4.391E-04	4.391E-04
e	0.009901	0.009901	0.009901	0.009901
To	1100	1100	1100	1100
dHrx	8.0E+04	8.0E+04	8.0E+04	8.0E+04
Cpa	170	170	170	170
Cpi	200	200	200	200
T	1100	1098.3458	1100	1098.3458
k	25.256686	24.100568	25.256686	24.100568
ra	-0.0110894	-0.0110894	-0.0061524	-0.0061524

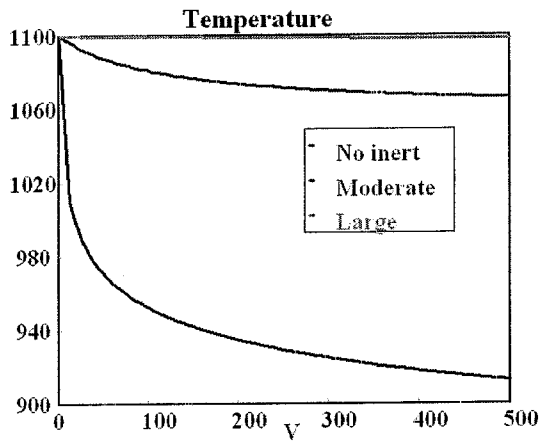
ODE Report (RKF45)

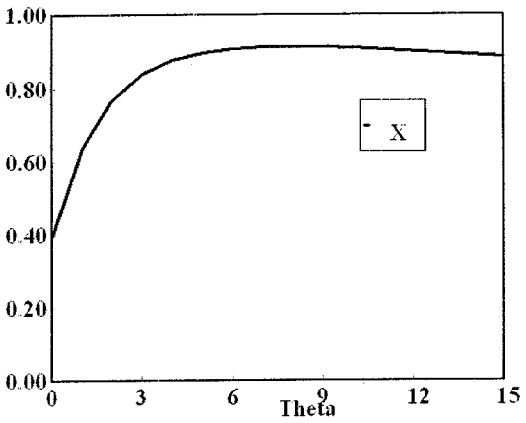
Differential equations as entered by the user
[1] d(X)/d(V) = -ra/Fao

Explicit equations as entered by the user

```
[1] Cao = 2/.082/1100
[2] Cio = Cao
[3] theta = 100
[4] Fao = 10
[5] Cao1 = (Cao+Cio)/(theta+1)
[6] e = 1/(1+theta)
[7] To = 1100
[8] dHrx = 80000
[9] Cpa = 170
[10] Cpi = 200
[11] T = (X*(-dHrx)+(Cpa+theta*Cpi)*To)/(Cpa+theta*Cpi)
[12] k = exp(34.34-34222/T)
[13] ra = -k*Cao1*(1-X)*To/(1+e*X)/T
```







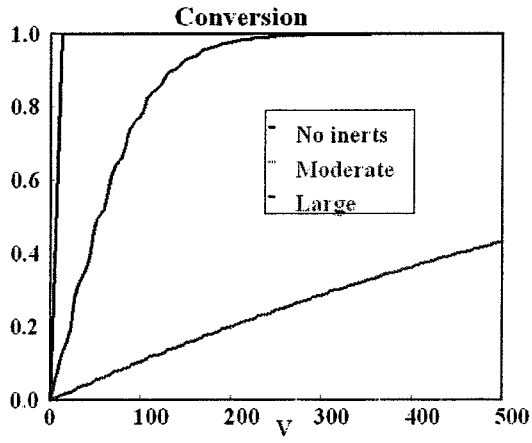
P8-10 (c)

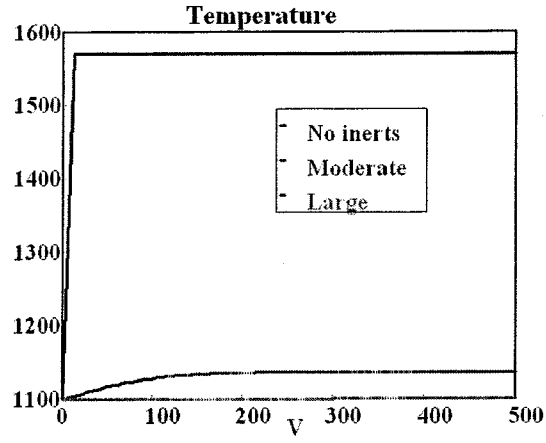
There is a maximum at $\theta = 8$. This is because when θ is small, adding inerts keeps the temperature low to favor the endothermic reaction. As θ increases beyond 8, there is so much more inert than reactants that the rate law becomes the limiting factor.

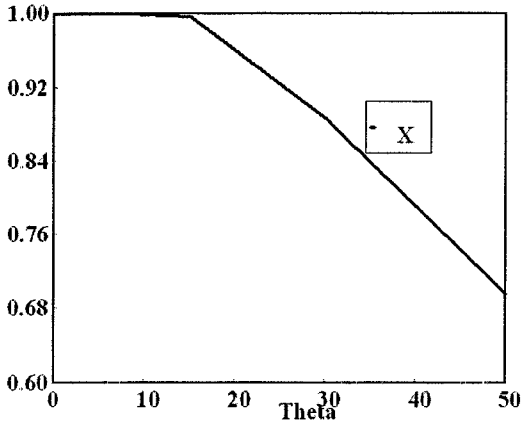
P8-10 (d)

The only change to the Polymath code from part (b) is that the heat of reaction changes sign. The new code is not shown, but the plots are below.

See Polymath program P8-10-d.pol.







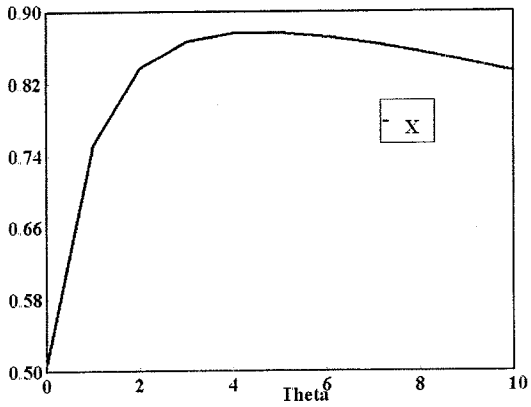
The maximum conversion occurs at low values of theta ($\theta < 8$) because the reaction is now exothermic. This means heat is generated during the reaction and there is no advantage to adding inerts as there was in the endothermic case.

P8-10 (e)

We need to alter the equations from part (c) such that $-r_A = kC_A^2$ and $C_{A0} = 1$

A plot of conversion versus theta shows a maximum at about $\theta = 5$.

See Polymath program P8-10-e.pol.



P8-10 (f)

We need to alter the equations from part (c) such that $-r_A = k\left[C_A - \frac{C_B C_C}{K_C}\right]$

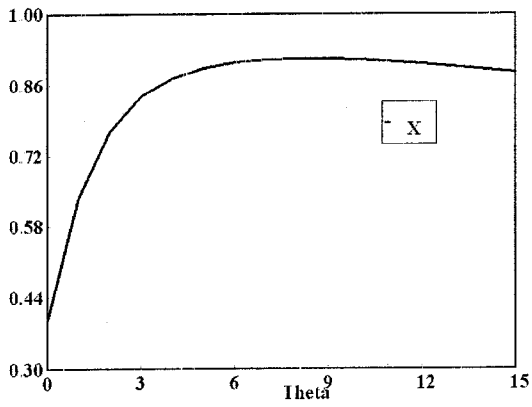
We already know that $C_A = C_{A0}\frac{1-X}{1+\varepsilon X}\frac{T_0}{T}$. Now weed need expressions for C_B and C_C. From stoichiometry we can see that $C_B = C_C$. In terms of C_{A0} we find that:

$$C_B = C_C = C_{A0}\frac{X}{1+\varepsilon X}\frac{T_0}{T}$$

We also need an equation for K_C: $K_C = K_{C1}\exp\left[\frac{\Delta H_{RX}}{R}\left(\frac{1}{T_1}-\frac{1}{T}\right)\right] = 2\exp\left[\frac{80000}{8.314}\left(\frac{1}{1100}-\frac{1}{T}\right)\right]$

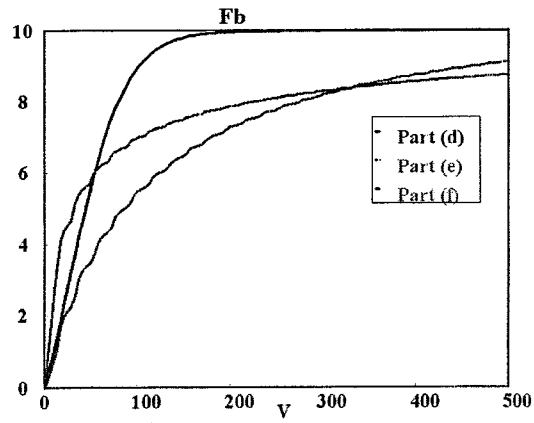
When we enter these inot Polymath we find that the maximumn conversion is achieved at approximately $\theta = 8$.

See Polymath program P8-10-f.pol.



P8-10 (g)

See Polymath program P8-10-g.pol.



P8-11 (a)

Start with the complete energy balance:

$$\frac{d\hat{E}}{dt} = \dot{Q} - \dot{W}_S - \Sigma E_i F_i\big|_{in} - \Sigma E_i F_i\big|_{out}$$

The following simplifications can be made:
It is steady state.
In part a, there is no heat taken away or added
There is no shaft work

That leaves us with

$$0 = -\Sigma E_i F_i\big|_{in} - \Sigma E_i F_i\big|_{out}$$

Evaluating energy terms:

In: $H_{A0}F_{A0} + H_{B0}F_{B0} + H_{C0}F_{C0}$

Out: $H_A(F_A + R_A V) + H_B(F_B + R_B V) + H_C(F_C + R_C V)$

Simplifying,

$$H_A(F_A + R_A V) + H_B(F_B + R_B V) + H_C(F_C + R_C V) - H_{A0}F_{A0} - H_{B0}F_{B0} - H_{C0}F_{C0} = 0$$

If only C is diffusing out of the reactor we get:

$$H_A F_A + H_B F_B + H_C\left(F_B + R_B V\right) - H_{A0}F_{A0} - H_{B0}F_{B0} - H_{C0}F_{C0} = 0$$

Now we evaluate F_i

$$F_A = F_{A0} - F_{A0}X$$

$$F_B = F_{B0} + F_{A0}X$$

$$F_C = F_{C0} + F_{A0}X - R_C V$$

Inserting these into our equation gives:

$$H_A F_{A0} - H_A F_{A0}X + H_B F_{B0} + H_B F_{A0}X + H_C F_{C0} + H_C F_{A0}X - H_{A0}F_{A0} - H_{B0}F_{B0} - H_{C0}F_{C0} = 0$$

and note that $F_{B0} = F_{C0} = 0$

$H_A F_{A0} - H_A F_{A0}X + H_B F_{A0}X + H_C F_{A0}X - H_{A0}F_{A0} = 0$ and combining and substituting terms gives:

$$F_{A0}\left(H_A - H_{A0}\right) + F_{A0}X\Delta H_{RX} = 0$$

$$F_{A0}C_{PA}\left(T-T_0\right)+F_{A0}X\Delta H_{RX}=0$$

Differentiating with respect to V with $\Delta C_P = 0$

$$F_{A0}C_p\frac{dT}{dV}+F_{A0}\frac{dX}{dV}\left(\Delta H_{Rx}(T)\right)=0$$

$$\frac{dT}{dV}=\frac{(r_A)\left[\Delta H_{Rx}(T)\right]}{\Sigma\theta_i C_p}$$

Combine that with the mole balance and rate law:

$$\frac{dF_A}{dV}=r_A \quad \frac{dF_B}{dV}=-r_A \quad \frac{dF_C}{dV}=-r_A-k_C C_C$$

$$-r_A=kC_A$$

$$C_A=C_{T0}\frac{F_A}{F_T}\frac{T_0}{T} \quad C_B=C_{T0}\frac{F_B}{F_T}\frac{T_0}{T} \quad C_C=C_{T0}\frac{F_C}{F_T}\frac{T_0}{T}$$

For kc = 10

See Polymath program P8-11-a.pol.

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	V	0	0	50.	50.
2	Fc	0	0	0.0012968	0.0005261
3	Fb	0	0	0.1978837	0.1978837
4	Fa	5.42	5.222116	5.42	5.222116
5	T	450.	450.	548.9418	548.9418
6	Ft	5.42	5.42	5.421297	5.420526
7	dHrx	-2.0E+04	-2.0E+04	-2.0E+04	-2.0E+04
8	k	0.133	0.133	0.6036997	0.6036997
9	kc	10.	10.	10.	10.
10	Cto	2.710027	2.710027	2.710027	2.710027
11	Ca	2.710027	2.610831	2.710027	2.610831
12	Kc	0.0006905	0.0002635	0.0006905	0.0002635
13	Cc	0	0	0.0006482	0.000263
14	Cb	2.710027	2.610831	2.710027	2.610831
15	ra	-0.3604336	-0.3604336	-0.0026249	-0.0026249
16	Cpa	40.	40.	40.	40.

Differential equations

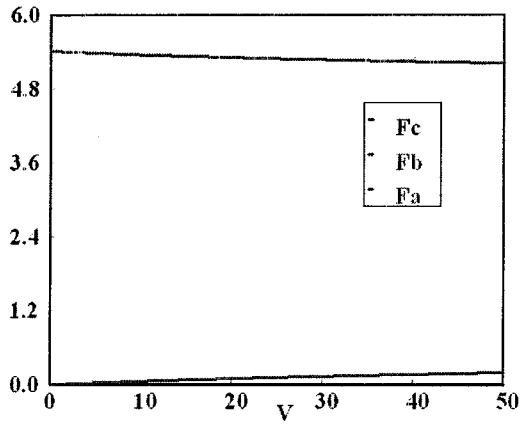
1 d(Fc)/d(V) = -ra - kc * Cc

2 d(Fb)/d(V) = -ra

3 d(Fa)/d(V) = ra
4 d(T)/d(V) = ra * dHrx / Cpa

Explicit equations

1 Ft = Fa + Fb + Fc
2 dHrx = -20000
3 k = .133 * exp((31400 / 8.314) * (1 / 450 - 1 / T))
4 kc = 10
5 Cto = 100 / .082 / 450
6 Ca = Cto * Fa / Ft
7 Kc = .01 * exp((dHrx / 8.314) * (1 / 300 - 1 / T))
8 Cc = Cto * Fc / Ft
9 Cb = Cto * Fa / Ft
10 ra = -k * (Ca - Cb * Cc / Kc)
11 Cpa = 40



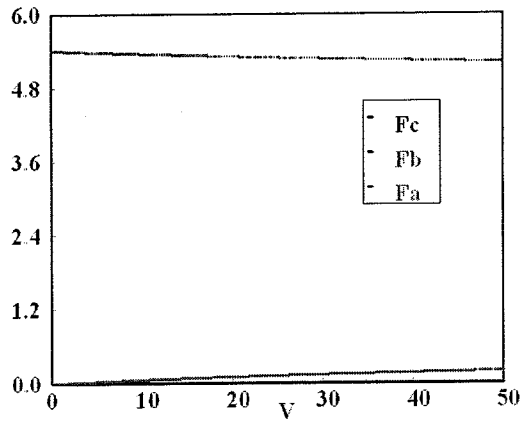
vary kc to see how the concentration profiles change.

P8-11 (b)

Now, the hear balance equation needs to be modified.

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + F_{A0}(r_A)\left[\Delta H_{Rx}(T)\right]}{F_{A0}\Sigma\theta_i C_p}$$

See Polymath program P8-11-b.pol.



P8-12(a)

To find the necessary heat removal, we start with the isothermal case of the energy balance

$$\frac{\dot{Q}}{F_{A0}} - \frac{\dot{W}_S}{F_{A0}} - X\left[\Delta H_{RX} + \Delta C_P\left(T - T_R\right)\right] = \sum \theta_i C_{Pi}\left(T - T_0\right)$$

Because there is no shaft work $W_S = 0$.

$\Delta C_P = 60 - 25 - 35 = 0$

And for isothermal operation $T = T_0$

If we simplify the energy balance using this information we get:

$$\frac{\dot{Q}}{F_{A0}} - X\Delta H_{RX} = 0$$

or $\dot{Q} = F_{A0} X \Delta H_{RX} = C_{A0} v X \Delta H_{RX}$

We now know everything except the heat of reaction to solve for the heat removed term. To find the heat of reaction consider the adiabatic case:

$\Delta C_P = 60 - 25 - 35 = 0$

$Q = 0$ and $W_S = 0$

$-X\Delta H_{RX} = \sum \theta_i C_{Pi}\left(T - T_0\right)$

Because feed is equal molar in A and B, $\theta_B = 1$

$-X\Delta H_{RX} = \left(C_{PA} + C_{PB}\right)\left(T - T_0\right)$

$$\Delta H_{RX} = \frac{(25+35)(350-300)}{-0.4} = -7500\frac{kJ}{mol}$$

Now go back to the isothermal case:

$$\dot{Q} = C_{A0} v X \Delta H_{RX} = \left(1000\frac{mol}{m^3}\right)\left(.5\frac{m^3}{\min}\right)(0.2)\left(-7500\frac{kJ}{mol}\right)$$

$$\dot{Q} = -750000\frac{kJ}{\min}$$

P8-12(b)

We start with the energy balance for the second CSTR (already simplified):

$$\frac{UA}{F_{A0}}(T_a - T) - (X_2 - X_1)\Delta H_{RX} = (C_{PA} + C_{PB})(T - T_0)$$

This equation has two unknowns (T and X_2) and so we need another equation.
Now wee need the mole balance for the second reactor

$$V_2 = \frac{F_{A0}(X_2 - X_1)}{-r_{A2}} = \frac{F_{A0}(X_2 - X_1)}{kC_{A0}^2(1 - X_2)^2}$$

This equation also brings in another unknown: k. We know that the specific reaction rate is dependant on temperature and if we have the activation energy, we can make an implicit equation for k as a function of T. To calculate the activation energy we will use the isothermal and adiabatic information for reactor 1 and the mole balance for reactor 1.

$$V_1 = \frac{F_{A0}X_1}{kC_{A0}^2(1 - X_1)^2}$$

$$k = \frac{F_{A0}X}{VC_{A0}^2(1 - X)^2} = \frac{vX}{VC_{A0}(1 - X)^2}$$

Solving for k at 300 and 350 K gives:
k(300 K) = 0.00015625
k(350 K) = 0.0005555

If we plug these numbers into the Arrhenius equation we get

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$ we get E/R = 2664.

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

If we use a nonlinear equation solver to solve the energy balance and mole balance for reactor 2 we find that the exit concentration is 0.423.

See Polymath program P8-12-b.pol.

POLYMATH Results
NLES Solution

Variable	Value	f(x)	Ini Guess
T	327.68712	-2.274E-13	340
X2	0.4214731	-6.666E-12	0.4
UA	4		

Ta	350
vo	0.5
X1	0.2
dHrx	-7500
To	300
V	1
k	3.309E-04
Cao	1000
Fao	500
ra	-110.73657

NLES Report (safenewt)

Nonlinear equations
[1] f(T) = (UA)*(Ta-T)/Fao-(X2-X1)*dHrx-60*(T-To) = 0
[2] f(X2) = V-Fao*(X2-X1)/(-ra) = 0

Explicit equations
[1] UA = 4
[2] Ta = 350
[3] vo = 0.5
[4] X1 = 0.2
[5] dHrx = -7500
[6] To = 300
[7] V = 1
[8] k = .00015625*exp(2663.8*(1/300-1/T))
[9] Cao = 1000
[10] Fao = Cao*vo
[11] ra = -k*Cao^2*(1-X2)^2

P8-12(c)

Now we need the differential form of the energy balance

$$\frac{dT}{dV} = \frac{Ua(T_a - T) - r_A \Delta H_{RX}}{F_{A0} \sum \theta_i C_{Pi}} = \frac{Ua(T_a - T) - r_A \Delta H_{RX}}{F_{A0}(C_{PA} + C_{PB})}$$

we also need the mole balance for a PFR. For this case it simplifies to:

$$\frac{dC_A}{dt} = \frac{dC_B}{dt} = -r_A$$

with $-r_A = kC_A C_B$ and we can use the same equation for k as in part (b).

When we put these equations into Polymath we get an outlet conversion of X = 0.33

See Polymath program P8-12-c.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	1	1
T	300	283.98681	300	283.98681
X	0.2	0.2	0.3281298	0.3281298
Cao	1000	1000	1000	1000
Ua	10	10	10	10
Ta	300	300	300	300
dHrx	-7500	-7500	-7500	-7500
Cb	800	671.87016	800	671.87016

v	0.5	0.5	0.5	0.5
Fao	500	500	500	500
Cpa	25	25	25	25
Cpb	35	35	35	35
k	1.563E-04	9.47E-05	1.563E-04	9.47E-05
Ca	800	671.87016	800	671.87016
ra	-100	-100	-42.749596	-42.749596

ODE Report (RKF45)

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

Explicit equations as entered by the user
[1] Cao = 1000
[2] Ua = 10
[3] Ta = 300
[4] dHrx = -7500
[5] Cb = Cao*(1-X)
[6] v = 0.5
[7] Fao = Cao*v
[8] Cpa = 25
[9] Cpb = 35
[10] k = 0.00015625*exp(2664*(1/300-1/T))
[11] Ca = Cao*(1-X)
[12] ra = -k*Ca*Cb

P8-12(d)

In this case we need to replace the rate law we used in part (c)

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

We also need an equation to calculate K_c at different temperatures.

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

be careful of the units when entering K_{c1} into Polymath. Also note that the initial temperature is different than in part (c)

We get an outlet conversion of X = 0.48

See Polymath program P8-12-d.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	1	1
T	350	314.93211	350	314.93211
X	0.2	0.2	0.4804694	0.4804694
R	0.0083144	0.0083144	0.0083144	0.0083144
Ua	10	10	10	10
Ta	300	300	300	300
dHrx	-7500	-7500	-7500	-7500
Cao	1000	1000	1000	1000

y	0.5	0.5	0.5	0.5
Fao	500	500	500	500
Cpa	25	25	25	25
Cpb	35	35	35	35
k	5.556E-04	2.381E-04	5.556E-04	2.381E-04
Ca	800	519.53058	800	519.53058
Cb	800	519.53058	800	519.53058
Cc	200	200	480.46942	480.46942
Kc	0.002	0.002	8.63E+121	8.63E+121
ra	-300.01803	-335.38132	-64.253241	-64.253241

ODE Report (RKF45)

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

Explicit equations as entered by the user
[1] R = 8.3144/1000
[2] Ua = 10
[3] Ta = 300
[4] dHrx = -7500
[5] Cao = 1000
[6] v = 0.5
[7] Fao = Cao*v
[8] Cpa = 25
[9] Cpb = 35
[10] k = 0.00015625*exp(2664*(1/300-1/T))
[11] Ca = Cao*(1-X)
[12] Cb = Cao*(1-X)
[13] Cc = Cao*X
[14] Kc = .002*exp((dHrx/R)*(1/350-1/T))
[15] ra = -k*(Ca*Cb-Cc/Kc)

P8-12(e) Individualized solution

P8-12(f)

For the gas phase the only the stoichiometry changes.

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

and $\varepsilon = y_{A0}\delta = 0.5(1-1-1) = -0.5$

From Polymath we see the exiting conversion is X = 0.365

See Polymath program P8-12-f.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	1	1
T	300	279.3717	300	279.3717
X	0.2	0.2	0.3650575	0.3650575
To	300	300	300	300
Ua	10	10	10	10
Ta	300	300	300	300

dHrx	-7500	-7500	-7500	-7500
Cao	1000	1000	1000	1000
vo	0.5	0.5	0.5	0.5
Fao	500	500	500	500
Cpa	25	25	25	25
Cpb	35	35	35	35
k	1.563E-04	8.111E-05	1.563E-04	8.111E-05
e	-0.5	-0.5	-0.5	-0.5
Ca	888.88889	834.06666	888.88889	834.06666
Cb	888.88889	834.06666	888.88889	834.06666
ra	-123.45679	-123.45679	-56.423752	-56.423752

ODE Report (RKF45)

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

Explicit equations as entered by the user
[1] To = 300
[2] Ua = 10
[3] Ta = 300
[4] dHrx = -7500
[5] Cao = 1000
[6] vo = 0.5
[7] Fao = Cao*vo
[8] Cpa = 25
[9] Cpb = 35
[10] k = 0.00015625*exp(2664*(1/300-1/T))
[11] e = -.5
[12] Ca = Cao*(1-X)*To/(1+e*X)/T
[13] Cb = Ca
[14] ra = -k*Ca*Cb

P8-13

$$K_C = \frac{C_C C_D}{C_A C_B} = \frac{X_e^2}{(1-X_e)^2}$$

$$\Rightarrow X_e = \frac{\sqrt{K_C}}{1+\sqrt{K_C}}$$

$$T = T_0 - \frac{\Delta H_R X}{C_{P_A} + C_{P_B}} = 300 - \frac{(-30000)}{(25+25)} X = 300 + 600X$$

See Polymath program P8-13.pol.

Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	Xe	0.9997644	3.518E-11	0.5 (0 < Xe < 1.)

	Variable	Value
1	T	300.

2	Kc	1.8E+07

Nonlinear equations

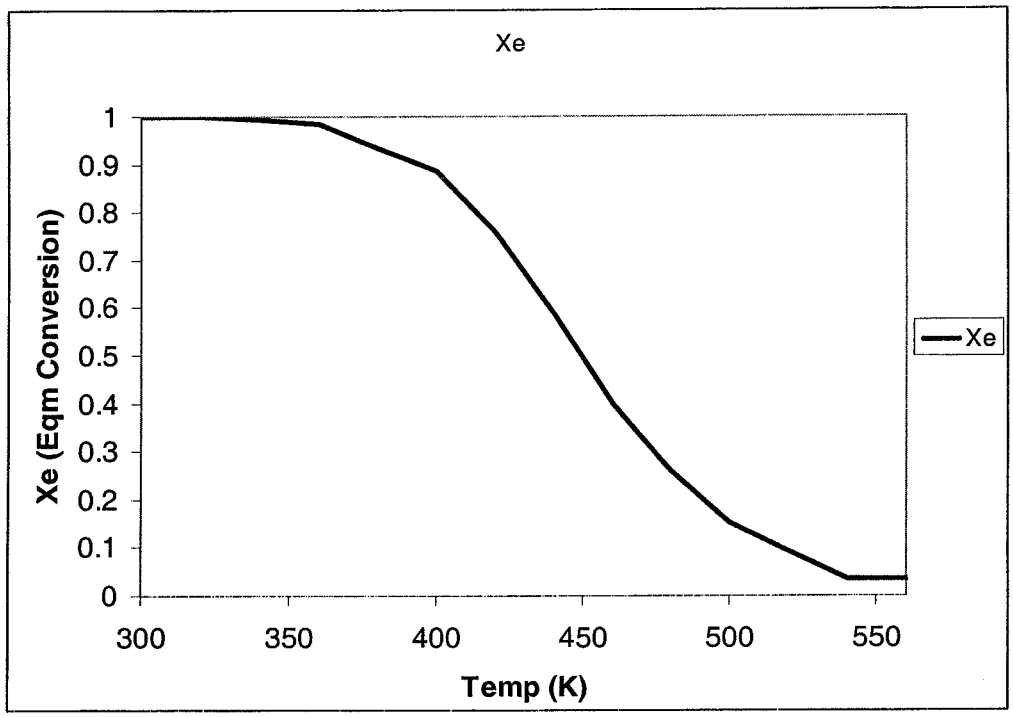
1 f(Xe) = Xe - (1 - Xe) * Kc ^ 0.5 = 0

Explicit equations

1 T = 300

2 Kc = 500000 * exp(-30000 / 1.987 * (1 / 323 - 1 / T))

T	X
300	1
320	0.999
340	0.995
360	0.984
380	0.935
400	0.887
420	0.76
440	0.585
460	0.4
480	0.26
500	0.1529
520	0.091
540	0.035
560	0.035



P8-14

For first reactor,

$$K_C = \frac{X_{e1}}{1 - X_{e1}} \text{ or } X_{e1} = \frac{K_C}{1 + K_C}$$

For second reactor

$$K_C = \frac{\theta_{B2+} X_{e2}}{1 - X_{e2}} or X_{e2} = \frac{K_C - \theta_{B2}}{1 + K_C}$$

For 3rd reactor

$$K_C = \frac{\theta_{B3+} X_{e3}}{1 - X_{e3}} or X_{e3} = \frac{K_C - \theta_{B3}}{1 + K_C}$$

1st reactor: in first reaction $X_e = 0.3$

So, $F_B = F_{A01}(.3)$

2nd reactor: Moles of A entering the 2nd reactor: $F_{A02} = 2F_{A01} - F_{A01}(.3) = 1.7F_{A01}$

$$\theta_{B2} = \frac{.2F_{A01}}{1.7F_{A0}} = .12$$

$$-F_{A02}\Sigma C_{P_i}\theta_i (T - T_0) + F_{A02} X (-\Delta H_R) = 0$$

$$X = \frac{(C_{pA} + \theta_B C_{pB})(T - T_0)}{-\Delta H_R}$$

Slope is now negative

3rd reactor:

$X_{e2} = 0.3$

Say $\theta_B = (.2F_{A01}) + .3F_{A02} = F_{A01}(.2 + .3\times 1.8)$

$F_{A03} = F_{A01} + F_{A02}(1 - X_{e2}) = F_{A01} + 1.8F_{A01}(1 - X_{e2}) = 1 + 1.8(1 - .3)F_{A01}$

$F_{A03} = 2.26F_{A01}$

Feed to the reactor 3:

$(2F_{A01}) + .3F_{A02} = F_{A01}(.2 + .3\times 1.8) = 0.7F_{A01}$

$$\theta_{B3} = \frac{.74}{2.26}$$

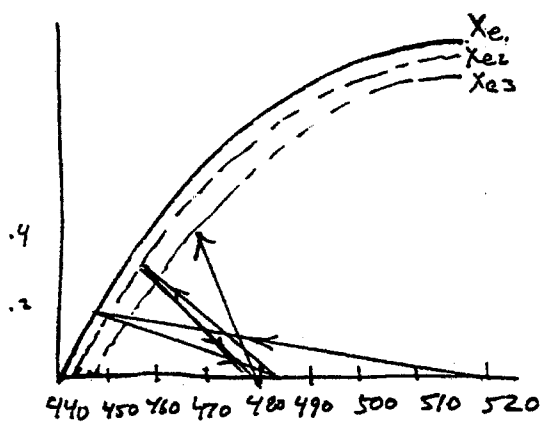
Feed Temperature to the reactor 2 is (520+450)/2 = 485 K

Feed Temperature to reactor 3 is 480 K

$X_{final} = .4$

Moles of B = $.2F_{A01} + .3F_{Ao2} + .4F_{A03} = F_{A01}(.2 + .54 + (.4)(2.26)) = 1.64\ F_{A01}$

$X = F_B/3F_{A01} = .54$



P8-14 (b)

The same setup and equations can be used as in part (a). The entering temperature for reactor 1 is now 450 K and the outlet is 520 K. When the two streams are joined prior to entering reactor 2 the temperature is (520+450)/2 = 485 K

Say that the outlet temperature for reactor 2 is 510 K. Then the entering temperature for reactor 3 would be (510+510+450)/3 = 490 K

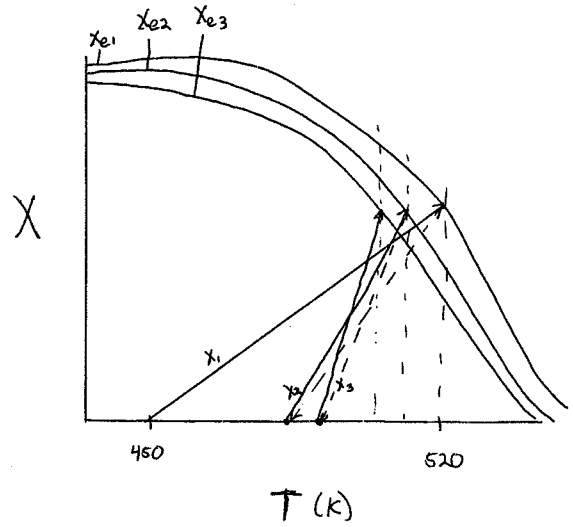
For any reactor j,

$$-F_{A0j}\Sigma C_{P_i}\theta_i(T - T_0) + F_{A0j}X(-\Delta H_R) = 0$$

$$X = \frac{(C_{pA} + \theta_B C_{pB})(T - T_0)}{-\Delta H_R}$$

and θ_B for reactor 1 = 0. For reactor 2, $\theta_B > 0$. This means that the slope of the conversion line from the energy balance is larger for reactor 2 than reactor 1. And similarly θ_B for reactor 3 > θ_B for reactor 2. So the line for conversion in reactor 3 will be steeper than that of reactor 2. The mass

balance equations are the same as in part (b) and so the plot of equilibrium conversion will decrease from reactor 1 to reactor 2, and, likewise, from reactor 2 to reactor 3.



P8-15 (a)

Substrate → More cells + Product

S → C + P

$G(T) = X^* - \Delta H_{RX}$

To solve for G(T) we need X as a function of temperature, which we get by solving the mass balance equation.

$$V = \frac{F_{A0}X}{-r_A} = \frac{F_{S0}X}{-r_S} \quad \text{and since } -r_S = \frac{r_g}{Y_{c/s}} \text{ then,}$$

$$V = \frac{Y_{c/s}F_{S0}X}{r_g}$$

$$r_g = \mu C_C \text{ and } \mu = \mu(T)\frac{C_S}{K_S + C_S}$$

$$\text{where } \mu(T) = \mu_{1\max}\left[\frac{0.0038 * T \exp\left(21.6 - \frac{6700}{T}\right)}{1 + \exp\left(153 - \frac{48000}{T}\right)}\right]$$

if we combine these equations we get:

$$V = \frac{Y_{c/s}F_{S0}X}{\frac{\mu(T)C_C C_S}{K_S + C_S}}$$

$$V = \frac{Y_{c/s} F_{S0} X \left(K_S + C_S\right)}{\mu(T) C_C C_S}$$

$$C_S = C_{S0}\left(1 - X\right) \text{ and } C_C = C_{S0} Y_{c/s} X$$

$$V = \frac{Y_{c/s} F_{S0} X \left(K_S + C_{S0}\left(1 - X\right)\right)}{\mu(T) C_{S0} Y_{c/s} X C_{S0}\left(1 - X\right)}$$

Canceling and combining gives:

$$V = \frac{F_{S0}\left(K_S + C_{S0}\left(1 - X\right)\right)}{\mu(T) C_{S0}^2\left(1 - X\right)}$$

Now solve this expression for X:

$$X = 1 - \frac{F_{S0} K_S}{\mu(T) V C_{S0}^2 - F_{S0} C_{S0}}$$

Now that we have X as a function of T, we can plot G(T).

To get R(T) we must calculate the heat removed which is the sum of the heat absorbed by reactants to get to the reaction temperature and the heat removed from any heat exchangers.

The heat gained by the reactants = $C_{P0}\left(T - T_0\right)$

The heat removed by the heat exchanger = $UA(T-T_a)/F_{S0}$

$$R(T) = C_{PS}\left(T - T_0\right) + \frac{UA}{F_{S0}}\left(T - T_a\right)$$

Now enter the equations into polymath and specify all other constants. The adiabatic case is shown below. The non-adiabatic case would be with explicit equation [12] as A = 1.1.

See Polymath program P8-15-a.pol.

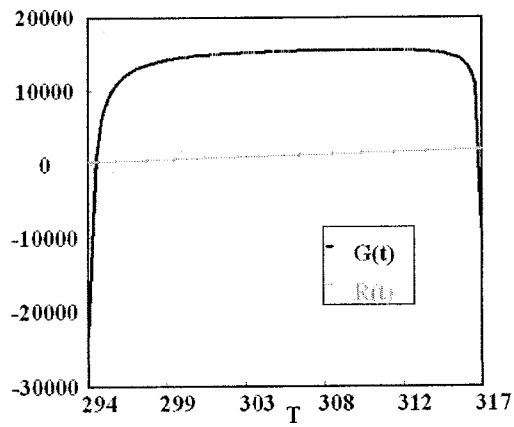
Differential equations as entered by the user

[1] d(T)/d(t) = 1

Explicit equations as entered by the user

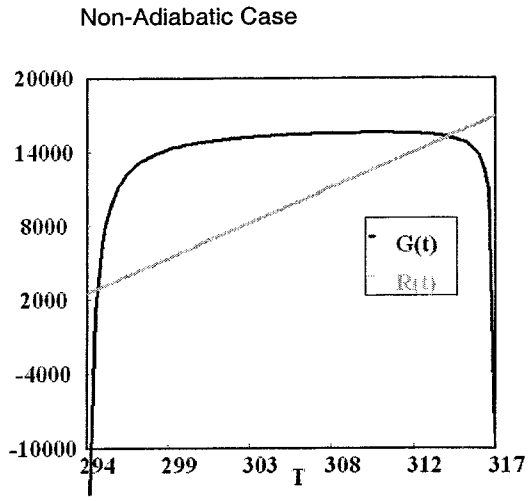
[1] mumax = .5
[2] Ycs = .8
[3] vo = 1
[4] Ta = 290
[5] mu = mumax*(.0038*T*exp(21.6-6700/T))/(1+exp(153-48000/T))
[6] Ks = 5
[7] V = 6
[8] Cso = 100
[9] Fso = vo*Cso
[10] Cps = 74

Adiabatic Case



```
[11] dH = -20000
[12] UA = 0*300
[13] kappa = UA/(Cps*Fso)
[14] To = 280
[15] X = 1-((Fso*Ks)/((mu*V*(Cso^2))-Fso*Cso))
[16] Gt = X*(-dH)*Ycs
[17] Rt = Cps*(T-To)+UA*(T-Ta)/Fso

Independent variable
 variable name : t
 initial value : 0
 final value : 30
```



P8-15 (b)

To maximize the exiting cell concentration, we want to maximize the conversion of substrate. If we look at G(T) from part A, we see that it is at a maximum at about 310 K. This corresponds to the highest conversion that can be achieved. By changing the values of UA and m_c we can change the slope of the R(T). What we are looking to do is get R(T) to intersect with G(T) at 310 K.

Since we now have a limited coolant flow rate we will use a different value for Q.

$$Q = m_C C_{PC}(T - T_a)\left(1 - \exp\left(\frac{-UA}{m_C C_{PC}}\right)\right)$$

and so,

$$R(T) = m_C C_{PC}(T - T_a)\left(1 - \exp\left(\frac{-UA}{m_C C_{PC}}\right)\right) + C_{PS}(T - T_0)$$

Now we set R(T) equal to the maximum value of G(T) which is 15600 J/h

$$G(T) = 15600F_{S0} = m_C C_{PC}(T - T_a)\left(1 - \exp\left(\frac{-UA}{m_C C_{PC}}\right)\right) + F_{S0}C_{PS}(T - T_0)$$

And now plug in the known values. Assume the maximum coolant flow rate and that will give the minimum heat exchange area.

$$15600\frac{J}{g}\left(100\frac{g}{hr}\right) =$$

$$\left(60000\frac{g}{hr}\right)\left(74\frac{J}{g\,K}\right)(310K - 290K)\left(1 - \exp\left(\frac{-UA}{\left(60000\frac{g}{hr}\right)\left(74\frac{J}{g\,K}\right)}\right)\right) + \left(100\frac{g}{h}\right)\left(74\frac{J}{g\,K}\right)(310K - 288K)$$

$$1560000\ \frac{J}{hr} = \left(88800000\ \frac{J}{hr}\right)\left(1 - \exp\left(\frac{-UA}{\left(4440000\ \frac{J}{hr\ K}\right)}\right)\right) + \left(162800\ \frac{J}{hr}\right)$$

$$UA = 70415\frac{J}{hr\,K}$$

A=1.4 m^3

P8-15 (c)

There are two steady states for this reaction. There is an unstable steady state at about 294.5 K and a stable steady state at 316 K.

P8-15 (d)

Increasing T_0 enough will eliminate the lower temperature steady state point. It will also lower the outlet concentration of cells. Decreasing T_0 will increase the outlet concentration of cells.

Increasing m_C increases the slope of R(T) and will increase the exit concentration of cells.

Increasing T_a will lower the exit concentration of cells.

P8-16 (a)

$$G(T) = \Delta H_R X$$

$$X = \frac{\tau k}{1+\tau k} \quad \tau = 6.6\times10^{-3}\exp\left[\frac{E}{R}\left(\frac{1}{350} - \frac{1}{T}\right)\right]$$

$$R(T) = C_{p0}(1+\kappa)(T - T_C)$$

$$C_{p0} = \Sigma\theta_i C_{pi} = \theta_A C_{pA} + \theta_I C_{pI} = 20 + 30 = 50$$

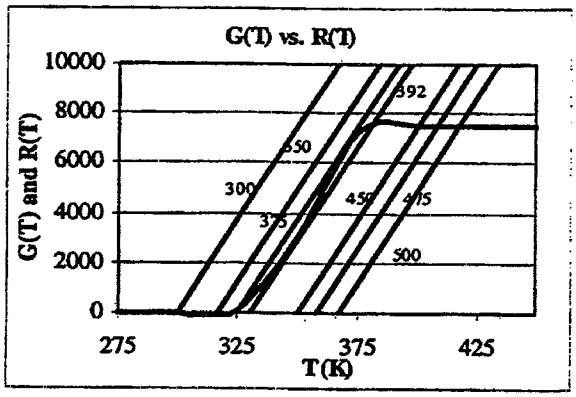
$$\kappa = \frac{UA}{C_{po}F_{A0}} = \frac{8000}{(50)(80)} = 2$$

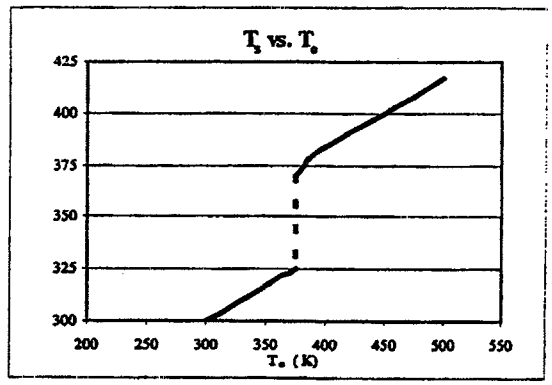
$$T_C = \frac{T_0 F_{A0} C_{p0} + UAT_a}{UA + C_{p0}F_{A0}} = \frac{\kappa T_a + T_0}{1+\kappa} = 350$$

To find the steady state T, we must set G(T) = R(T). This can be done either graphically or solving the equations. We find that for T_0 = 450 K, steady state temperature 358 K.

P8-16 (b)

First, we must plot G(T) and R(T) for many different T_0's on the same plot. From this we must generate data that we use to plot T_s vs T_o.





P8-16 (c)

For high conversion, the feed stream must be pre-heated to at least 390 K. At this temperature, X = .98 and T = 380 K in the CSTR. Any feed temperature above this point will provide for higher conversions.

P8-16 (d)

For a temperature of 375 K, the conversion is .968

P8-16 (e)

The inlet extinction temperature is 375 K.

P8-17

The energy balance for a CSTR:

$$-F_{A0}X\Delta H_{Rx}(T) = F_{A0}[\Sigma\theta_i C_{pi}(T-T_0)+\frac{UA}{F_{A0}}(T-T_0)]$$

$$F_{A0}X = -r_A V$$

C_{ps} is independent of T.

$$C_{p0}(T-T_0) = C_{ps}$$

$$G(T) = (-\Delta H_{Rx})\left(\frac{-r_A V}{F_{A0}}\right)$$

$$R(T) = F_{A0}C_{pS} + UAT_r - UAT$$

Differentiating: $\frac{dR(T)}{dT} = UA$

$$\frac{dG(T)}{dT} = \frac{-\Delta H_{Rx}}{F_{A0}}\frac{d(-r_A)}{dT}$$

where $\frac{d(-r_A)}{dt} = \frac{E}{RT^2}(-r_A)$

Setting these two equations equal to each other and manipulating,

$$\ln\frac{1.421}{1.127}=\left[\frac{E}{R}\left(\frac{323-313}{323*313}\right)\right]$$

$$E=19474$$

$$\frac{F_{A0}C_{ps}}{UA}+(T_r-T_a)>\frac{RT_r^2}{E}$$, and it will be runaway reaction

At A < 2.5 m^2 it will become a runaway.

P8-18 (a)

Mol Balance:

$$V=\frac{F_{A0}X}{-r_A}=\frac{v_0C_{A0}X}{k\left[C_A-C_B/K_e\right]}$$

$$\left(\frac{v}{v_0}\right)k\left[(1-X)-X/K_e\right]$$

$$X\left[1+\tau k(1+1/K_e)\right]=\tau k$$

$$X=\frac{\tau k}{1+\tau k(1+1/K_e)}$$

$$G(T)=-\Delta H_{Rx}X=80000X$$

$$k=1\,\text{min}^{-1}$$

$$\tau=10\,\text{min}$$

$$K_e=100$$

$$X=\frac{10}{1+10(1.01)}=.901$$

$$G(400)=72080\ cal/mol$$

P8-18 (b)

$$\kappa=\frac{UA}{F_{A0}C_{pA}}=\frac{3600}{10*40}=9$$

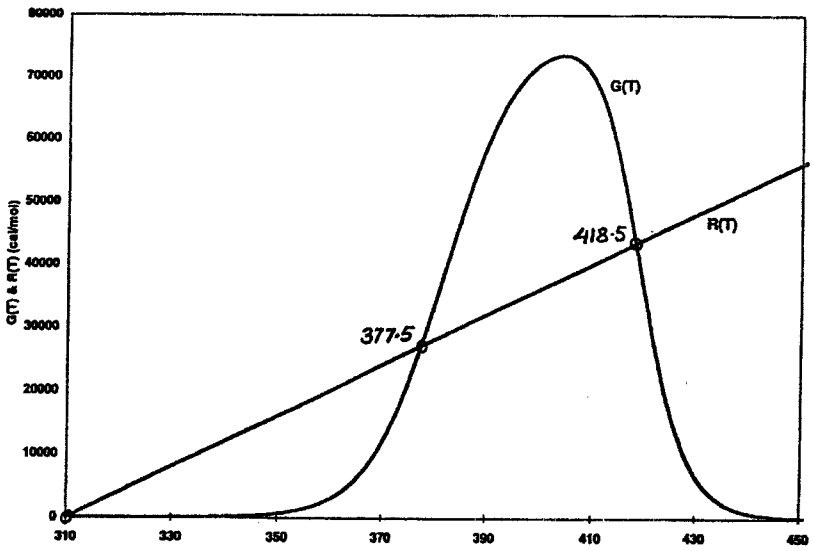
$$R(T)=C_{pA}(1+\kappa)(T-T_C)=400(T-T_C)$$

$$T_C=\frac{T_0+\kappa T_a}{1+\kappa}=310$$

$$R(T)=400(T-310)$$

The following plot gives us the steady state temperatures of 310, 377.5 and 418.5 K

See Polymath program P8-18-b.pol.



P8-18 (c)

310K and 418.5 K are locally stable steady-state points

P8-18 (d)

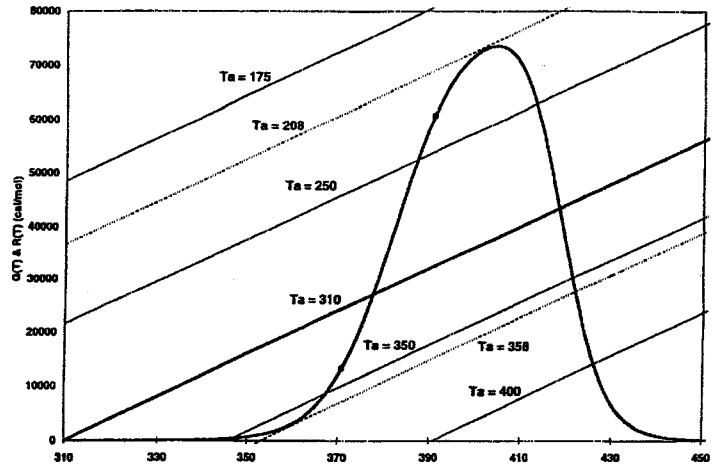
$$R(418.5) = 400(418.5 - 310) = 43400$$

$$G(418.5) = 43400 = 80000 * x$$

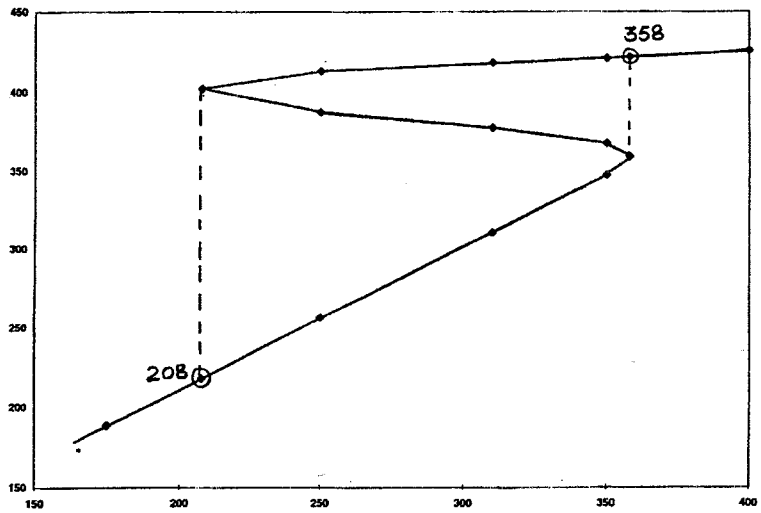
$$x = \frac{43400}{80000} = .54$$

P8-18 (e)

The plot below shows T_a varied.

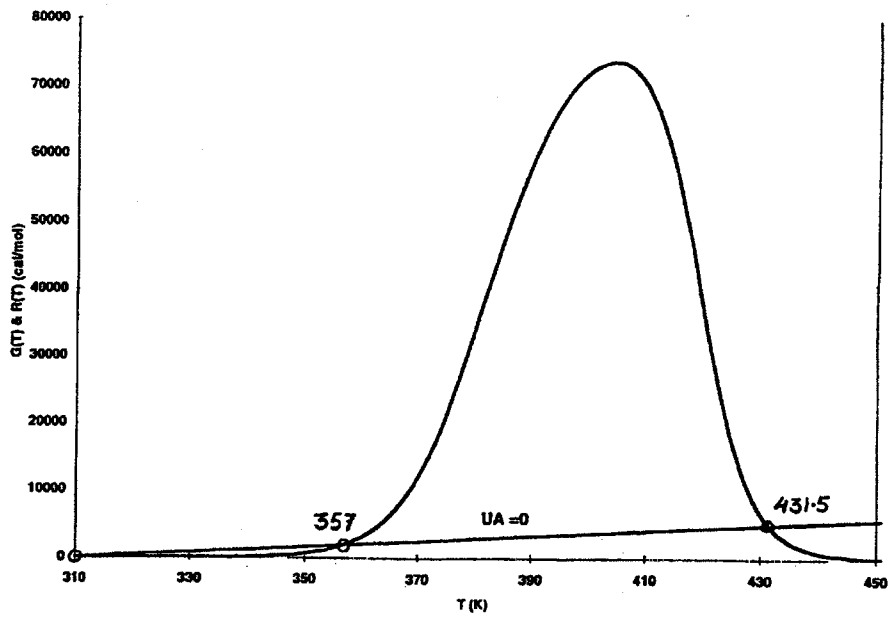


The next plot shows how to find the ignition and extinction temperatures. The ignition temperature is 358 K and the extinction temperature is 208 K.



P8-18 (f)

This plot shows what happens if the heat exchanger quits. The upper steady-state temperature now becomes 431.5 K.



P8-18 (g)

At the maximum conversion G(t) will also be at its maximal value. This occurs at approximately T = 404 K. G(404 K) = 73520 cal. For there top be a steady state at this temperature, R(T) = G(T). See Polymath program P8-18-g.pol.

$$\kappa = \frac{UA}{F_{A0}C_{pA}}$$

$$R(T) = C_{pA}(1+\kappa)(T - T_C) = 73520$$

where $T_C = \frac{T_0 + \kappa T_a}{1+\kappa}$

If we plug in the values and solve for UA, we get:
UA = 7421 cal/min/K

P8-18 (h) Individualized solution

P8-18 (i)

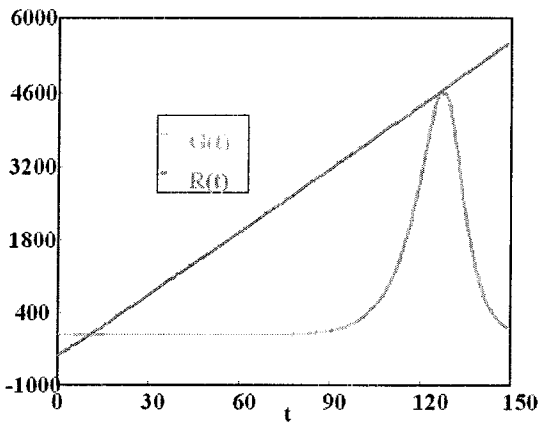
The adiabatic blowout flow rate occurs at $\tau = 0.0041s$

$$\tau = 0.0041s = \frac{V}{v_0}$$

$$v_0 = \tau V = 0.0041*10$$

$$v_0 = 0.041\frac{dm^3}{\text{min}}$$

See Polymath program P8-18-i.pol.



P8-18 (j)

Lowing T_0 or Ta or increasing UA will help keep the reaction running at the lower steady state.

P8-19

Given the first order, irreversible, liquid phase reaction:

$$A \rightarrow B$$

$UA = 1.0 cal/\text{min}/°C$ $\qquad$ $T_A = 100°C$

$Pure\ A\ Feed = 0.5 g\ mol/\min$ $\quad C_{p_A} = C_{p_B} = 2 cal/g-mol/°C$

$\Delta C_p = \Delta C_{pA} - \Delta C_{pB} = 0$ $\quad \Delta H_R = -200 \frac{cal}{g\ mol\ A} = const$

$Design\ Eqn: \quad V = \frac{F_{A0} X}{-r_A} = \frac{v_0}{k(1-X)}$

$Rate\ Law: \quad -r_A = kC_A$

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

$Energy\ Balance \quad -UA(T-T_A) - F_{A0} X \Delta H_R = F_{A0} \Sigma \theta_i C_{pi} (T-T_0)$

Simplifying,

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

$$Q_g = F_{A0} X(-\Delta H_R) = \frac{F_{40}(-\Delta H_R)}{1+\frac{1}{\tau k}}$$

This is the curve plotted in the problem statement From the equation for heat generation curve, we get

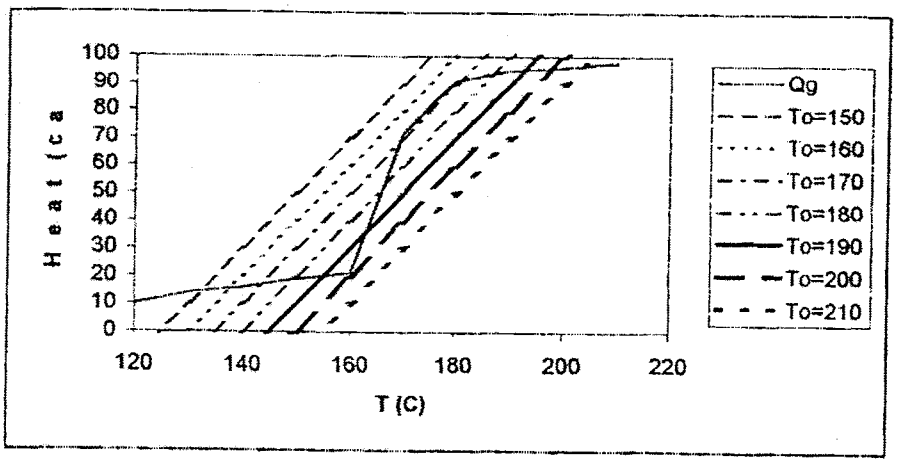
$$X = \frac{Q_g}{F_{40}(-\Delta H_R)} = \frac{Q_g}{5*200} = \frac{Q_g}{100}$$

The equation for heat removal curve is

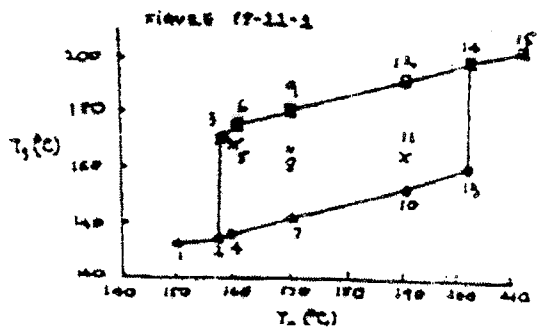
$$Q_R = F_{A0} C_{pA}(T-T_0) + UA(T-T_A) = .5*2*(T-T_0) + 1\ 0*(T-T_1)$$

$$Q_R = 2T - T_0 - 100$$

Plot this along with the heat generation curve for various T_0. This is shown in the figure



The intersection between Qg and QR can be used to prepare the ignition - extinction curve shown in figure P8-22-2 The values for Ts as a function of inlet temperature, T_0, are tabulated below.



T_o (degree C)	T_S (degree C)
150	132
157	135, 172
160	137, 168,176
170	142.5, 167, 181
190	154.5, 165, 193.5
202	162, 199
210	204.5

P8-19 (a)

To obtain high conversion, the reactor must operate at or beyond point 14 in figure. So the minimum inlet temperature for high conversion is To 2 202 °C.

P8-19 (b)

The temperature of the fluid in the reactor corresponding to temperature in part 1 is Ts > 199 °C (point 14 in figure).

P8-19 (c)

The inlet temperature of the fluid is To = 202 + 5 = 207 °C. This will be somewhere between points 14 and 15 in figure. Once the fluid is cooled from this temperature, it will follow the line formed by points 15, 14, 12, 9, etc.. Now To = 207 - 10 = 197 °C. From figure, Ts = 195.5 °C. From equation (5),

$$Q_S = 2*196.5 - 19 - 100 = 95 cal/mol$$

$$Q_R = Q_g = 96 cal/mol$$

$$So,\ X = \frac{Q_g}{100} = 0.96$$

P8-19 (d)

Extinction temperature is the temperature corresponding to point 3 in the figure = 157 ^{O}C

P8-19 (e) Individualized solution

P8-20 (a)

The following are the explanations for the unexpected conversion and temperature profiles
Case 1: Broken preheater or ineffective catalyst
Case 2: The equilibrium conversion was reached due to a problem with the heat exchanger
Case 3: Broken preheater or ineffective catalyst
Case 4: The equilibrium conversion was reached due to a problem with the heat exchanger
Case 5: Ineffective catalyst
Case 6: The equilibrium conversion was reached due to a problem with the heat exchanger

P8-20 (b)

The following are the explanations for the unexpected conversion and temperature profiles
Case 1: Broken preheater or ineffective heat exchanger
Case 2: Ineffective catalyst
Case 3: Broken preheater or ineffective heat exchanger
Case 4: Ineffective catalyst

P8-21

Below is the FEMLAB solution.

1. Parameters in simulation on the tubular reactor in Problem 8-6:

Reaction: $A + B \rightarrow C$

(1) operating parameters

Reactants

- Inlet concentration of A $C_{A0} = 100$ mol/m^3
- Inlet concentration of B $C_{B0} = 100$ mol/m^3
- Inlet total flow rate $v_0 = 2\times10^{-3}$ m^3/s
- Inlet temperature of the reactant $T_0 = 300K$

(2) properties of reactants

- Heat of reaction, ΔH_{Rx}, dHrx = -41+20+15=-6 kcal/mol=-25100 J/mol
- Activation energy, E = 41840 J/mol
- Specific reaction rate $k_0 = 0.01\times10^{-3}$ m^3/mol.s @300K
- Reaction rate $k = k_0 \exp\left[\frac{E}{R}(\frac{1}{T_0} - \frac{1}{T})\right]$
- Gas constant, R = 8.314 J/mol·K
- Rate law $-r_A = kC_AC_B$

Assumption:

- Thermal conductivity of the reaction mixture, ke = 0.68 W/m·K
  (needed in the mass balance and the energy balance)
- Average density of the reaction mixture, ρ, rho = 1000 kg/m^3
  (needed in the energy balance)
- Heat capacity of the reaction mixture, Cp = 4200 J/kg·K
  (needed in the energy balance)
- Diffusivity of all species, $Diff$ = 10^{-9} m^2/s

2. Size of the Tubular Reactor

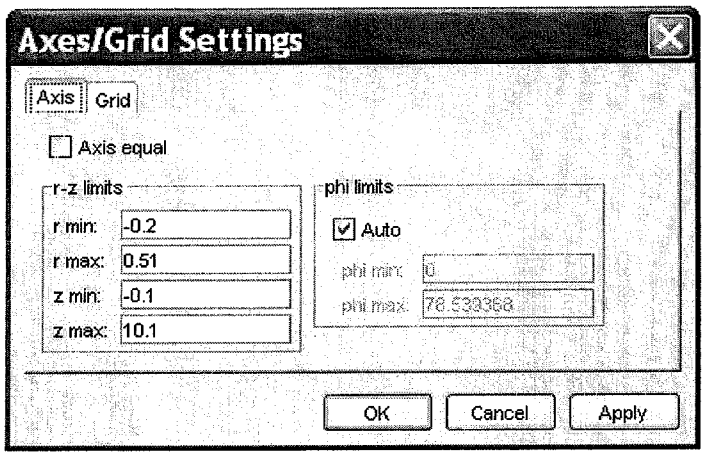
(1) Volume of reactor sized by a PFR = 0.317 m^3

(2) From FEMLAB

- Reactor radius, Ra = 0.1 m
- Reactor length, L = 10.0 m

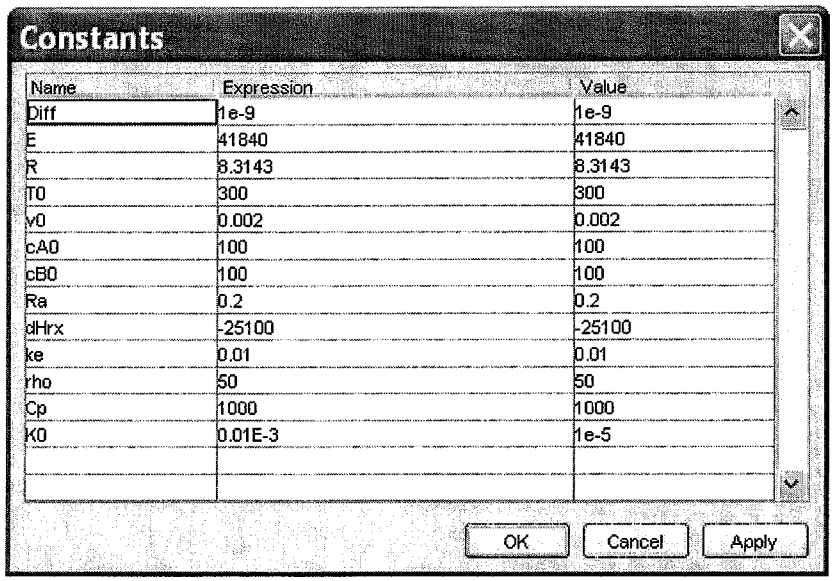
3. Femlab Screen Shots

(1) Domain

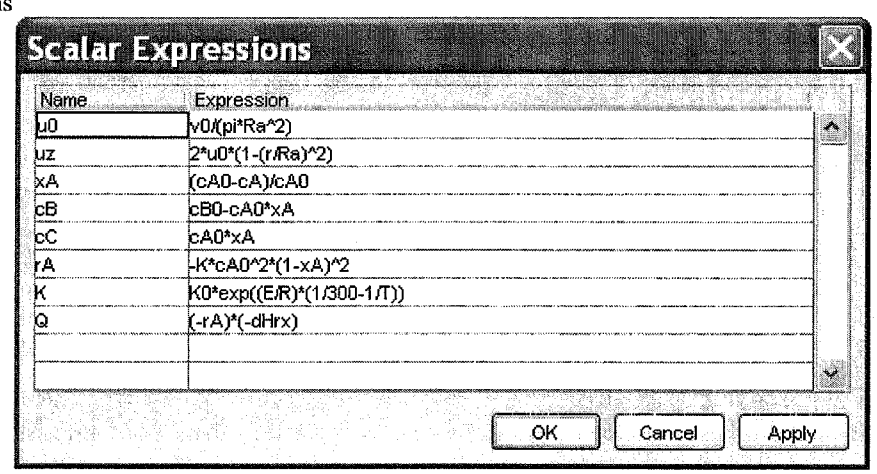


(2) Constants and Scalar Expressions

- Constants



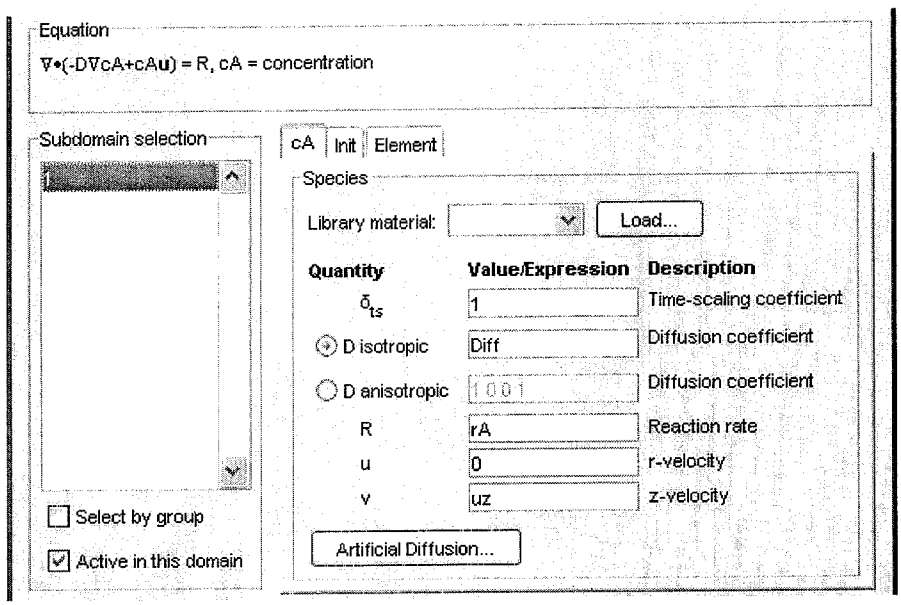
- Scalar Expressions



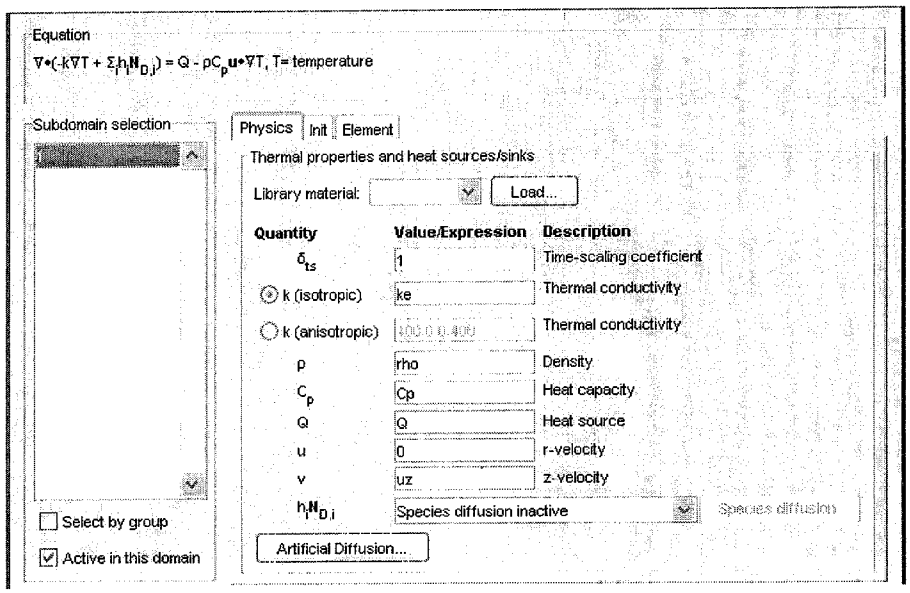
(3) Subdomain Settings

- Physics

(Mass balance)



(Energy balance)



- Initial Values

(Mass balance) cA(t0) = cA0

(Energy Balance) T(t0) = T0

- Boundary Conditions

@ r = 0, Axial symmetry

@ inlet, cA = cA0 (for mass balance)

T = T0 (for energy balance)

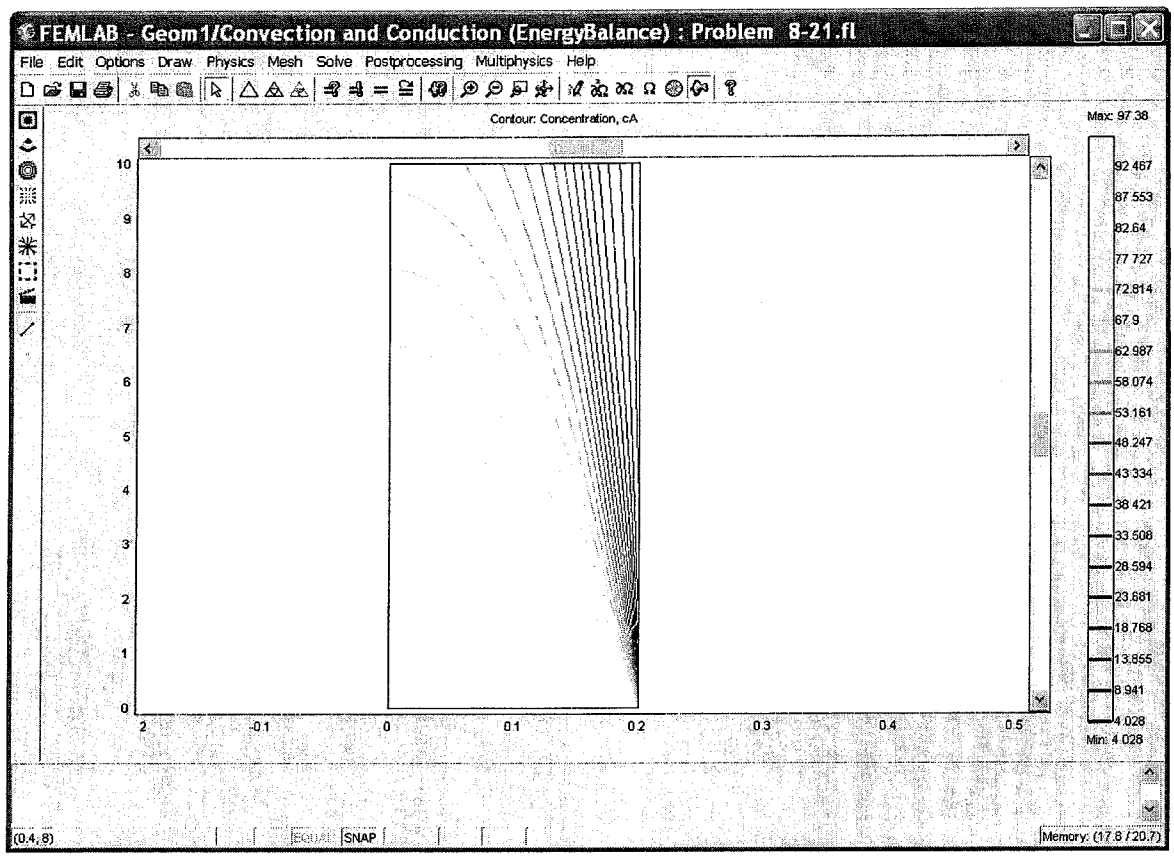
@ outlet, Convective flux

@ wall, Insulation/Symmetry (for mass balance)

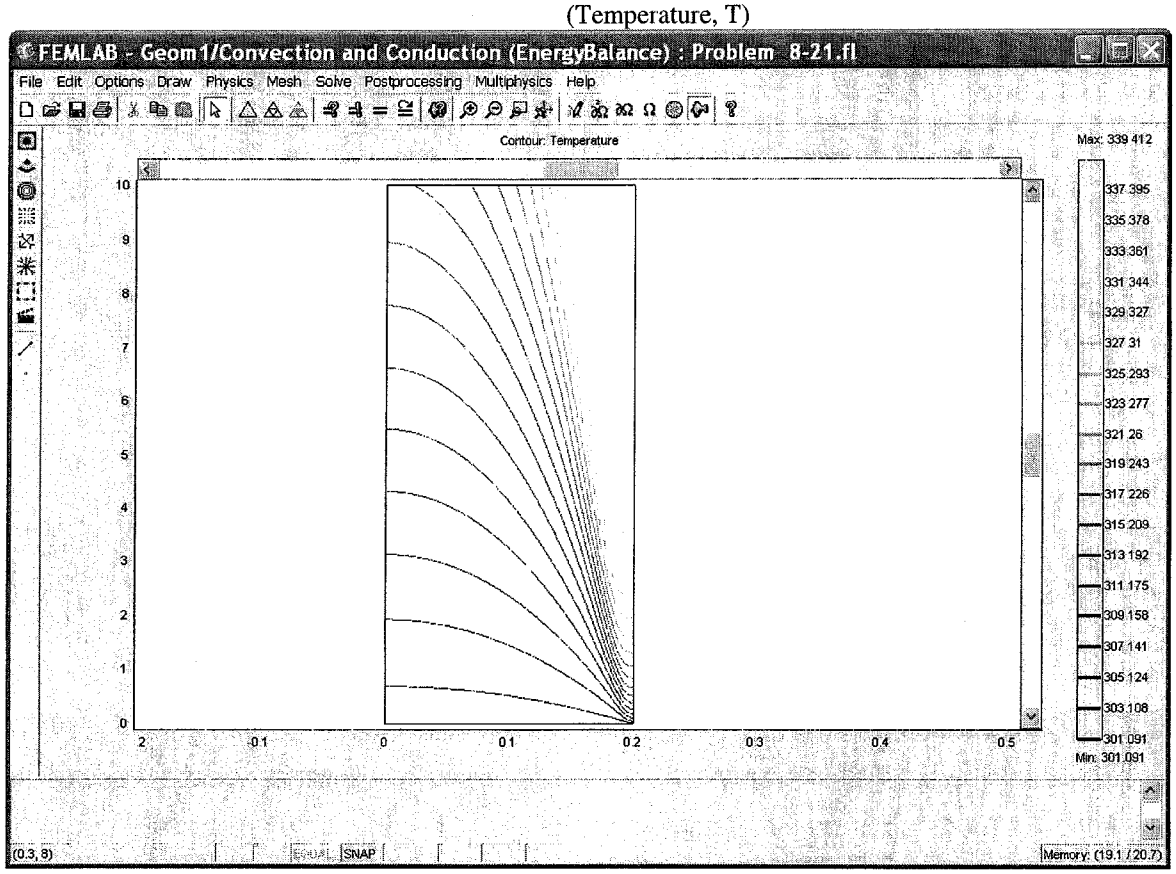
Thermal Insulation (for energy balance)

(4) Results

(Concentration, cA)



(Temperature, T)



P8-22 (a)

$$Liquid\ Phase: A + B \rightarrow C$$

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

$$-r_A = kC_AC_B$$

$$k = .01*\exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{300}\right)\right]$$

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

The energy Balance:

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)(-\Delta H_R)}{F_{A0}\left[C_{p_A} + C_{p_B}\right]}$$

$$a = \frac{4}{D}$$

$$Assume\ D = 4$$

$$U = \frac{5J}{m^2Ks} \times \frac{1cal}{4.184J} \times \frac{1m^2}{10dm^2} = .0120\frac{cal}{dm^2Ks}$$

See Polymath program P8-22-a.pol.

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	V	0	0	1000.	1000.
2	T	300.	300.	434.7779	348.2031
3	X	0	0	0.9620102	0.9620102
4	Ta	300.	300.	300.	300.
5	R	1.988	1.988	1.988	1.988
6	E	10000.	10000.	10000.	10000.
7	cao	0.1	0.1	0.1	0.1
8	ca	0.1	0.003799	0.1	0.003799
9	cb	0.1	0.003799	0.1	0.003799
10	k	0.01	0.01	1.808628	0.1018746
11	ra	-0.0001	-0.0010427	-1.47E-06	-1.47E-06
12	cpb	15.	15.	15.	15.
13	cpa	15.	15.	15.	15.
14	fao	0.2	0.2	0.2	0.2
15	Dhr1	-6000.	-6000.	-6000.	-6000.

16	a	1.	1.	1.	1.
17	U	0.012	0.012	0.012	0.012

Differential equations

1 d(T)/d(V) = (U * a * (Ta - T) + (-ra) * (-Dhr1)) / (fao * (cpa + cpb))

2 d(X)/d(V) = -ra / fao

Explicit equations

1 Ta = 300

2 R = 1.988

3 E = 10000

4 cao = .1

5 ca = cao * (1 - X)

6 cb = cao * (1 - X)

7 k = .01 * exp(-E / R * (1 / T - 1 / 300))

8 ra = -k * ca * cb

9 cpb = 15

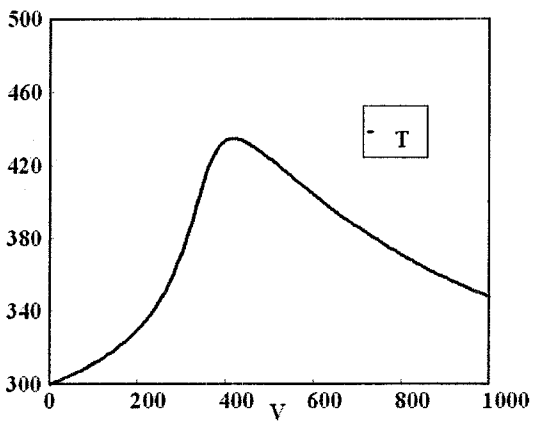
10 cpa = 15

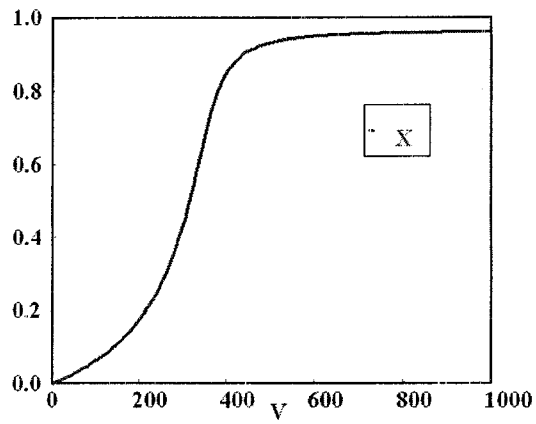
11 fao = .2

12 Dhr1 = -6000

13 a = 1

14 U = .0120





P8-22 (b)

$$Gas\ Phase: A \rightleftarrows B + C$$

$$\frac{dX}{dW} = \frac{-r_A}{F_{A0}}$$

$$-r_A = k_f C_A - k_r C_B C_C$$

$$C_B = C_C = C_{A0}\frac{X}{1+X}\frac{T_0}{T}$$

$$k = .133 * \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{450}\right)\right]$$

$$k_r = .2\exp\left[\frac{E_r}{R}\left(\frac{1}{450} - \frac{1}{T}\right)\right], E_r = 51.4\,kJ/mol$$

The energy Balance:

$$\frac{dT}{dW} = \frac{Ua(T_a - T) + (-r_A)(-\Delta H_R)}{F_{A0}C_{p_A}}$$

$$\Delta H_R = -40 - 50 + 70 = -20\ \text{kJ/mol}$$

$$U = 5$$

See Polymath program P8-22-b.pol.

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	W	0	0	50.	50.
2	X	0	0	0.0560855	0.0560855
3	T	400.	371.902	400.	371.902
4	T0	400.	400.	400.	400.
5	k	0.133	0.0651696	0.133	0.0651696
6	v0	20.	20.	20.	20.
7	kr	0.2	0.0622149	0.2	0.0622149
8	Uarho	5.	5.	5.	5.
9	Ta	323.	323.	323.	323.
10	P0	1.013E+06	1.013E+06	1.013E+06	1.013E+06
11	CA0	304.6819	304.6819	304.6819	304.6819
12	CA	304.6819	292.8948	304.6819	292.8948
13	CC	0	0	17.40323	17.40323
14	CB	0	0	17.40323	17.40323
15	rA	-40.52269	-40.52269	-0.2446624	-0.2446624

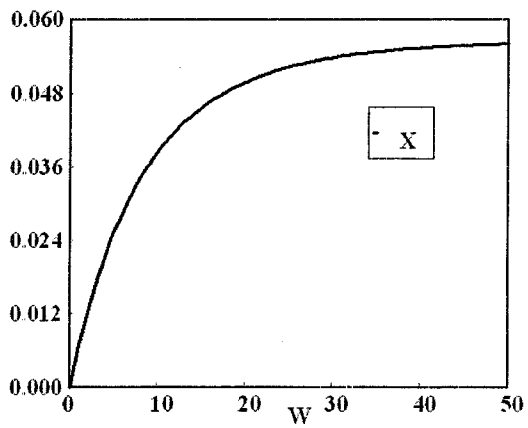
Differential equations

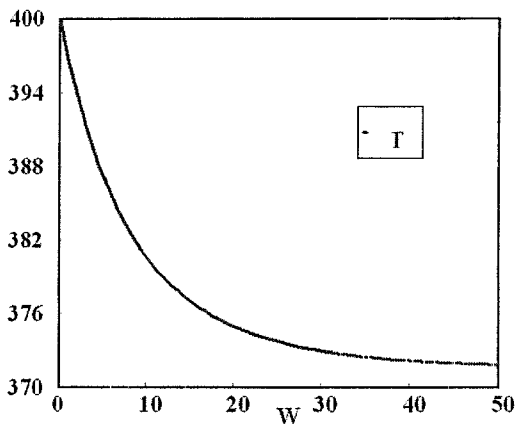
1 d(X)/d(W) = -rA / v0 / CA0

2 d(T)/d(W) = (Uarho * (Ta - T) + rA * 20000) / v0 / CA0 / 40

Explicit equations

1 T0 = 400
2 k = 0.133 * exp(31400 / 8.314 * (1 / T0 - 1 / T))
3 v0 = 20
4 kr = 0.2 * exp(51400 / 8.314 * (1 / T0 - 1 / T))
5 Uarho = 5
6 Ta = 323
7 P0 = 1013250
8 CA0 = P0 / 8.314 / T0
9 CA = CA0 * (1 - X) / (1 + X) * T0 / T
10 CC = CA0 * X / (1 + X) * T0 / T
11 CB = CA0 * X / (1 + X) * T0 / T
12 rA = -(k * CA - kr * CB * CC)





P8-23

First note that $\Delta C_P = 0$ for both reactions. This means that $\Delta H_{Rx}(T) = \Delta H_{Rx}°$ for both reactions.

Now start with the differential energy balance for a PFR;

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + \sum r_{ij}\left(-\Delta H_{Rxij}\right)}{\sum F_j C_{Pj}} = \frac{Ua(T_a - T) + r_{1C}\left(-\Delta H_{Rx1C}\right) + r_{2D}\left(-\Delta H_{Rx2D}\right)}{\sum F_j C_{Pj}}$$

If we evaluate this differential equation at its maximum we get

$$\frac{dT}{dV} = 0 \text{ and therefore, } Ua(T_a - T) - r_{1C}\Delta H_{Rx1C} - r_{2D}\Delta H_{Rx2D} = 0$$

We can then solve for r_{1C} from this information.

$$r_{1C} = \frac{Ua(T_a - T) - r_{2D}\Delta H_{Rx2D}}{\Delta H_{Rx1C}} = \frac{Ua(T_a - T) - k_{2D}C_B C_C \Delta H_{Rx2D}}{\Delta H_{Rx1C}}$$

$$r_{1C} = \frac{10(325-500) - 0.4(0.2)(0.5)(5000)}{-50000} = 0.039$$

$$r_{1C} = 0.039 = k_{1C}C_A C_B = k_{1C}(0.1)(0.2)$$

$$k_{1C} = 1.95$$

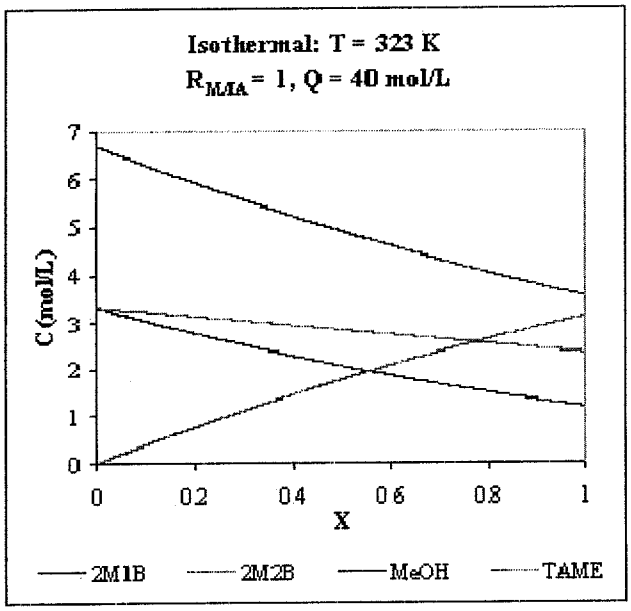
$$k_{1C(500)} = k_{1C(400)} \exp\left[\frac{E}{R}\left(\frac{1}{400} - \frac{1}{500}\right)\right]$$

$$\frac{E}{R} = \frac{\ln\left(\frac{k_{1C(500)}}{k_{1C(400)}}\right)}{\left(\frac{1}{400} - \frac{1}{500}\right)} = 7628$$

$$E = 15{,}158 \frac{\text{cal}}{\text{mol K}}$$

P8-24 (a)

See the additional homework problems in chapter 8 at http://www.engin.umich.edu/~cre for the full solution.

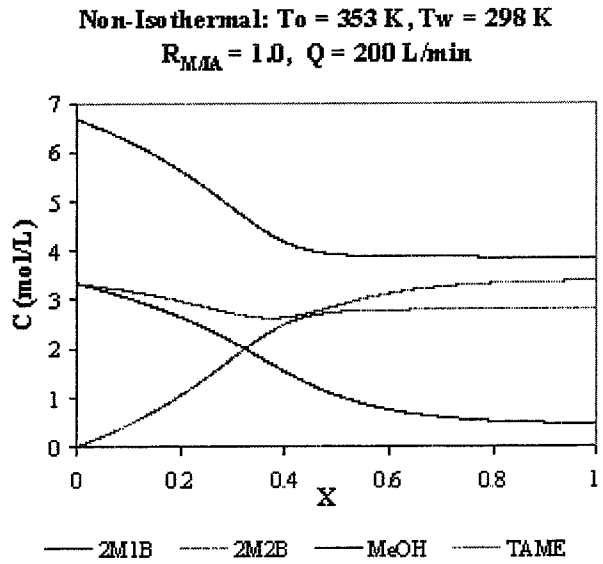


P8-24 (b)

See the additional homework problems in chapter 8 at http://www.engin.umich.edu/~cre for the equations to enter into Polymath. Then vary to see its effect.

P8-24 (c)

See the additional homework problems in chapter 8 at http://www.engin.umich.edu/~cre for full solution



P8-24 (d) No solution will be given

P8-25

Mole balance:

$$\frac{dF_A}{dW} = r_A \qquad \frac{dF_B}{dW} = r_B \qquad \frac{dF_C}{dW} = r_C$$

Rate Laws:

$$r_A = -r_{2B} + r_{1A} + r_{3A}$$

$$r_B = -r_{1A} + r_{2B}$$

$$r_C = -r_{3A}$$

$$-r_{1A} = k_1 C_A$$

$$-r_{2B} = k_B C_B$$

$$-r_{3A} = k_3 C_C$$

Stoichiometry:

$$C_A = C_T \frac{F_A T_0}{F_T T}$$

$$C_B = C_T \frac{F_B T_0}{F_T T}$$

Energy balance:

$$\frac{dT}{dW} = \frac{Ua(T_a - T) + (-r_{1A})(-\Delta H_{R1A}) + (-r_{R2B}) + (-r_{3A})(-\Delta H_{R3A})}{F_A C_{pA} + F_B C_{pB} + F_C C_{pC}}$$

$$\frac{dT}{dW} = \frac{16(500-T)+(-r_{1A})1800+(-r_{R2B})1800+(-r_{3A})1100}{100(F_A+F_B+F_C)}$$

$$k_1 = 0.5\exp[2(1-320/T)]$$

$$k_2 = \frac{k_1}{K_C}$$

$$k_3 = 0.005\exp[4.6(1-460/T)]$$

$$K_C = 10\exp[4.8(430/T-1.5)]$$

See Polymath program P8-25.pol.

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	w	0	0	100.	100.
2	fb	1.	0.9261241	1.368476	0.9261241
3	fa	1.	0.6296429	1.	0.8694625
4	fc	0	0	0.2044134	0.2044134
5	T	330.	330.	416.3069	416.3069
6	Ua	16.	16.	16.	16.
7	Ta	500.	500.	500.	500.
8	Dhr1a	-1800.	-1800.	-1800.	-1800.
9	Dhr3a	-1100.	-1100.	-1100.	-1100.
10	cpa	100.	100.	100.	100.
11	cpb	100.	100.	100.	100.
12	cpc	100.	100.	100.	100.
13	k1	0.5312401	0.5312401	0.7941566	0.7941566
14	k3	0.0008165	0.0008165	0.0030853	0.0030853
15	ct	2.	2.	2.	2.
16	ft	2.	2.	2.	2.
17	To	330.	330.	330.	330.
18	Kc	3.885029	1.062332	3.885029	1.062332
19	k2	0.1367403	0.1367403	0.74756	0.74756
20	ca	1.	0.5682599	1.	0.6892094
21	cb	1.	0.7341242	1.253213	0.7341242
22	r1a	-0.5312401	-0.5748799	-0.362406	-0.5473402
23	r3a	-0.0008165	-0.002138	-0.0007594	-0.0021264
24	rc	0.0008165	0.0007594	0.002138	0.0021264
25	r2b	-0.1367403	-0.5770243	-0.1367403	-0.5488019
26	rb	0.3944998	-0.0522707	0.3944998	-0.0014617
27	ra	-0.3953164	-0.3953164	0.0510521	-0.0006647

Differential equations

1 d(fb)/d(w) = rb

2 d(fa)/d(w) = ra

3 d(fc)/d(w) = rc

4 d(T)/d(w) = (Ua * (Ta - T) + (-r1a) * (-Dhr1a) + (-r2b) * (Dhr1a) * (-r3a) * (-Dhr3a)) / (fa * cpa + fb * cpb + fc * cpc)

Explicit equations

1 Ua = 16

2 Ta = 500

3 Dhr1a = -1800

4 Dhr3a = -1100

5 cpa = 100

6 cpb = 100

7 cpc = 100

8 k1 = .5 * exp(2 * (1 - 320 / T))

9 k3 = .005 * exp(4.6 * (1 - (460 / T)))

10 ct = 2

11 ft = 2

12 To = 330

13 Kc = 10 * exp(4.8 * (430 / T - 1.5))

14 k2 = k1 / Kc

15 ca = ct * fa / ft * To / T

16 cb = ct * fb / ft * To / T

17 r1a = -k1 * ca

18 r3a = -k3 * ca

19 rc = -r3a

20 r2b = -k2 * cb

21 rb = -r1a + r2b

22 ra = -r2b + r1a + r3a

P8-25 (a) As seen in the above table, the lowest concentration of o-xylene (A) = .568 mol/dm^3

P8-25 (b) The maximum concentration of m-xylene (B) = 1.253 mol/dm^3

P8-25 (c) The maximum concentration of o-xylene = 1 mol/dm^3

P8-25 (d) The same equations are used except that $F_{B0} = 0$.

The lowest concentration of o-xylene = 0.638 mol/dm3. The highest concentration of m-xylene = 1.09 mol/dm3. The maximum concentration of o-xylene = 2 mol/dm3.

P8-25 (e)

Decreasing the heat of reaction of reaction 1 slightly decreases the amount of E formed. Decreasing the heat of reaction of reaction 3 causes more of C to be formed. Increasing the feed temperature causes less of A to react and increases formation of C. Increasing the ambient temperature causes a lot of C to be formed.

P8-25 (f) Individualized solution

P8-26 (a)

$A \leftrightarrow B + C$

$A \rightarrow D + E$

$A + C \rightarrow F + G$

We want the exiting flow rates B, D and F

Start with the mole balance in PFR:

$$\frac{dF_A}{dV} = ra \qquad \frac{dF_B}{dV} = r_B \qquad \frac{dF_C}{dV} = r_C \qquad \frac{dF_D}{dV} = r_D$$

$$\frac{dF_E}{dV} = r_E \qquad \frac{dF_F}{dV} = r_F \qquad \frac{dF_G}{dV} = r_G$$

Rate Laws:

$$r_A = -r_{1s} - r_{2B} - r_{3T}$$

$$r_B = r_{1s}$$

$$r_C = r_{1s} - r_{3T}$$

$$r_D = r_{2B}$$

$$r_E = r_{2B}$$

$$r_F = r_{3T}$$

$$r_{1s} = \rho(1-\phi)\exp\left(-0.08359 - \frac{10925}{T}\right)\left(P_A - \frac{P_B P_C}{K}\right)$$

$$r_{2B} = \rho(1-\phi)\exp\left(13.2392 - \frac{25000}{T}\right)(P_A)$$

$$r_{3T} = \rho(1-\phi)\exp\left(0.2961 - \frac{11000}{T}\right)(P_A P_C)$$

Stoichiometry:

$$P_A = \frac{F_A}{F_T} P_{T0}$$

$$P_B = \frac{F_B}{F_T} P_{T0}$$

$$P_C = \frac{F_C}{F_T} P_{T0}$$

$$F_T = F_A + F_B + F_C + F_D + F_E + F_F + F_G + F_I$$

$$F_I = steamratio \times .0034$$

Energy Balance:

$$\frac{dT}{dV} = \frac{-\left(r_{1s}\Delta H_{R1A} + r_{2B}\Delta H_{R2A} + r_{3T}\Delta H_{R3A}\right)}{F_A * 299 + F_B * 283 + F_C * 30 + F_D * 201 + F_E * 90 + F_F * 249 + F_G * 68 + F_I * 40}$$

$$K_{p1} = \exp\left(b_1 + \frac{b_2}{T} + b_3 \ln(T) + \left[(b_4 T + b_5)T + b_6\right]T\right)$$

See Polymath program P8-26.pol.

For T0 = 800K

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	v	0	0	10.	10.
2	fa	0.00344	0.002496	0.00344	0.002496
3	fb	0	0	0.0008974	0.0008974
4	fc	0	0	0.0008615	0.0008615
5	fd	0	0	1.078E-05	1.078E-05
6	fe	0	0	1.078E-05	1.078E-05
7	ff	0	0	3.588E-05	3.588E-05
8	fg	0	0	3.588E-05	3.588E-05
9	T	800.	765.237	800.	765.237
10	Hla	1.18E+05	1.18E+05	1.18E+05	1.18E+05
11	H2a	1.052E+05	1.052E+05	1.052E+05	1.052E+05
12	H3a	-5.39E+04	-5.39E+04	-5.39E+04	-5.39E+04
13	p	2137.	2137.	2137.	2137.
14	phi	0.4	0.4	0.4	0.4
15	Kl	0.0459123	0.0196554	0.0459123	0.0196554
16	sr	14.5	14.5	14.5	14.5
17	fi	0.04988	0.04988	0.04988	0.04988
18	ft	0.05332	0.05332	0.0542282	0.0542282
19	Pa	0.1548387	0.1104652	0.1548387	0.1104652
20	Pb	0	0	0.0397155	0.0397155
21	Pc	0	0	0.0381277	0.0381277
22	r2b	2.991E-06	5.16E-07	2.991E-06	5.16E-07
23	rd	2.991E-06	5.16E-07	2.991E-06	5.16E-07

24	re	2.991E-06	5.16E-07	2.991E-06	5.16E-07
25	r3t	0	0	4.196E-06	4.151E-06
26	rf	0	0	4.196E-06	4.151E-06
27	rg	0	0	4.196E-06	4.151E-06
28	rls	0.0002138	2.481E-05	0.0002138	2.481E-05
29	rb	0.0002138	2.481E-05	0.0002138	2.481E-05
30	rc	0.0002138	2.066E-05	0.0002138	2.066E-05
31	ra	-0.0002167	-0.0002167	-2.948E-05	-2.948E-05

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(fe)/d(v) = re

6 d(ff)/d(v) = rf

7 d(fg)/d(v) = rg

8 d(T)/d(v) = -(rls * Hla + r2b * H2a + r3t * H3a) / (fa * 299 + fb * 273 + fc * 30 + fd * 201 + fe * 90 + ff * 68 + fi * 40)

Explicit equations

1 Hla = 118000

2 H2a = 105200

3 H3a = -53900

4 p = 2137

5 phi = .4

6 Kl = exp(-17.34 - 1.302e4 / T + 5.051 * ln(T) + ((-2.314e-10 * T + 1.302e-6) * T + -0.004931) * T)

7 sr = 14.5

8 fi = sr * .00344

9 ft = fa + fb + fc + fd + fe + ff + fg + fi

10 Pa = fa / ft * 2.4

11 Pb = fb / ft * 2.4

12 Pc = fc / ft * 2.4

13 r2b = p * (1 - phi) * exp(13.2392 - 25000 / T) * Pa

14 rd = r2b

15 re = r2b

16 r3t = p * (1 - phi) * exp(.2961 - 11000 / T) * Pa * Pc

17 rf = r3t

18 rg = r3t

19 rls = p * (1 - phi) * exp(-0.08539 - 10925 / T) * (Pa - Pb * Pc / Kl)

20 rb = rls

21 rc = rls - r3t

22 ra = -rls - r2b - r3t

$F_{styrene} = 0.0008974$
$F_{benzene} = 1.078E-05$
$F_{toluene} = 3.588E-05$

$S_{S/BT} = 19.2$

P8-26 (b)

$T_0 = 930K$

$F_{styrene} = 0.0019349$
$F_{benzene} = 0.0002164$
$F_{toluene} = 0.0002034$

$S_{S/BT} = 4.6$

P8-26 (c)

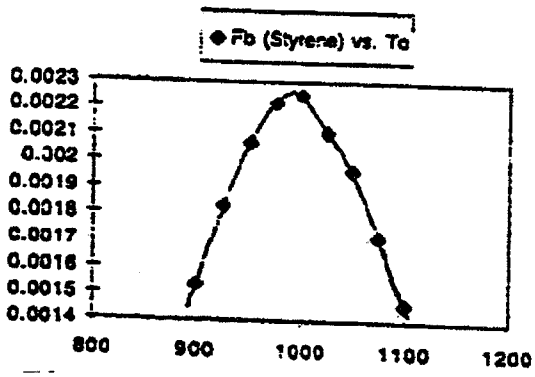
$T_0 = 1100$ K

$F_{styrene} = 0.0016543$
$F_{benzene} = 0.0016067$
$F_{toluene} = 0.0001275$

$S_{S/BT} = 0.95$

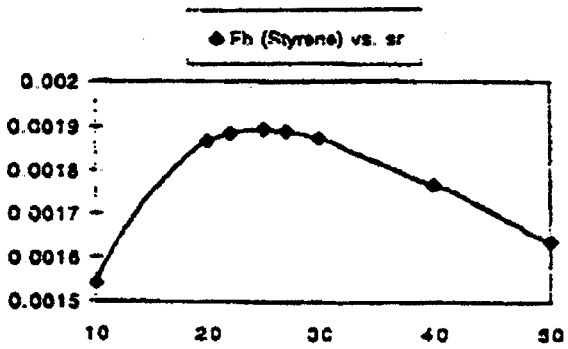
P8-26 (d)

Plotting the production of styrene as a function of To gives the following graph. The temperature that is ideal is 995K



P8-26 (e)

Plotting the production of styrene as a function of the steam gives the following graph and the ratio that is the ideal is 25:1



P8-26 (f)

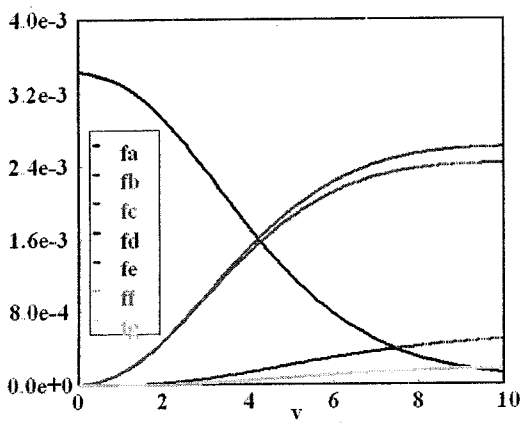
When we add a heat exchanger to the reactor, the energy balance becomes:

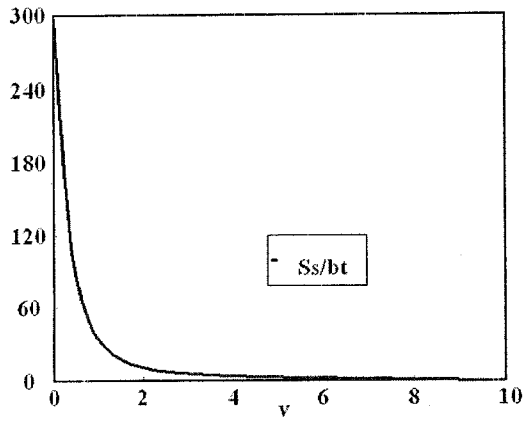
$$\frac{dT}{dV} = \frac{Ua(T_a - T) - (r_{1s}\Delta H_{R1A} + r_{2B}\Delta H_{R2A} + r_{3T}\Delta H_{R3A})}{F_A * 299 + F_B * 283 + F_C * 30 + F_D * 201 + F_E * 90 + F_F * 249 + F_G * 68 + F_I * 40}$$

With T_a = 1000 K

Ua = 100 kJ/min/K = 1.67 kJ/s/K

The recommended entering temperature would be T_0 = 440 K. This gives the highest outlet flow rate of styrene.





P8-26 (g) Individualized solution

P8-26 (h) Individualized solution

P8-27 (a)

Adiabatic exothermic, adiabatic endothermic, exothermic with cooling, endothermic with heating.

All the profiles show the rate of reaction dropping toward the end of the reactor.

P8-27 (b)

The non-adiabatic profiles show an increase and a decrease in temperature profile, and the adiabatic profiles do go from increasing temperature to decreasing temperature (or decreasing to increasing).

P8-27 (c)

Figure E8-5.3 shows a decrease in temperature while the reaction rate is large because the reaction is endothermic. Once the reaction rate drops, the heat exchanger increases the temperature profile because the reaction is no longer removing much heat.

Figure E8-3.1 shows a steady increase in temperature until the reaction rate drops to near zero. The reaction rate increases at the beginning of the reactor because of the increase in temperature affecting the specific reaction rate. At too high a temperature the equilibrium constant gets vbery small and the reverse reaction becomes more prominent and thus the rate decreases as the temperature rises above 350 K.

P8-27 (d)

In Figure E8-10.1, the temperature increases quickly until the reactants are used up. Then there is no more heat generated from the reaction, and the heat exchanger lowers the temperature. Figure E8-10.2 shows that the flow rate of A drops to about zero at about the same time the temperature reaches a maximum. Once there is no reactant, the reaction ceases and the flow rates of the products remains constant.

P8-28 (a)

$2A \longrightarrow B$

a) Design equation:

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

Rate law:

$$-r_A = kC_A^2$$

Stoichiometry:

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

Energy balance:

$$\frac{dT}{dV} = \frac{Ua(T_A - T) + (-r_A)(-\Delta H_{RX})}{F_{A0}C_{pA}}$$

$$\frac{dT}{dV} = \frac{5(700-T) + (231 + .012(T-298))(-r_A)}{5 * .122}$$

Plugging those into POLYMATH gets the following program and the following graphs. The conversion achieved is 0.36.

See Polymath program P8-28-a.pol.

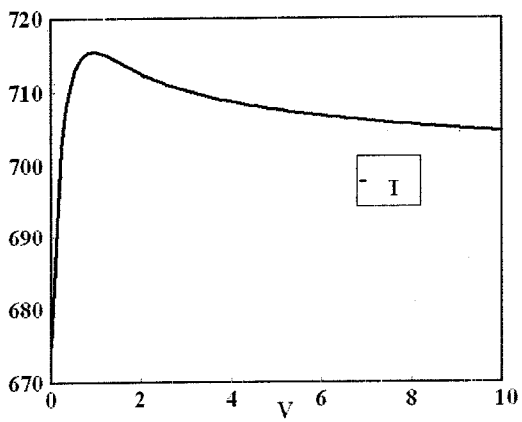
POLYMATH Results
Calculated values of the DEQ variables

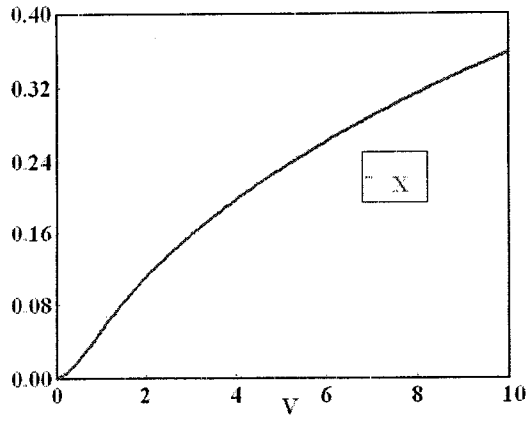
Variable	initial value	minimal value	maximal value	final value
V	0	0	10	10
T	675	675	715.55597	704.76882
X	0	0	0.3580882	0.3580882
Fao	5	5	5	5
Ua	5	5	5	5
Ta	700	700	700	700
dHr	-235.524	-236.01067	-235.524	-235.88123
Cpa	0.1222	0.1222	0.1222	0.1222
k	0.0734336	0.0734336	0.3658299	0.243008
Cao	1	1	1	1
Ca	1	0.6419118	1	0.6419118
ra	-0.0734336	-0.3335975	-0.0734336	-0.1001316

ODE Report (RKF45)

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

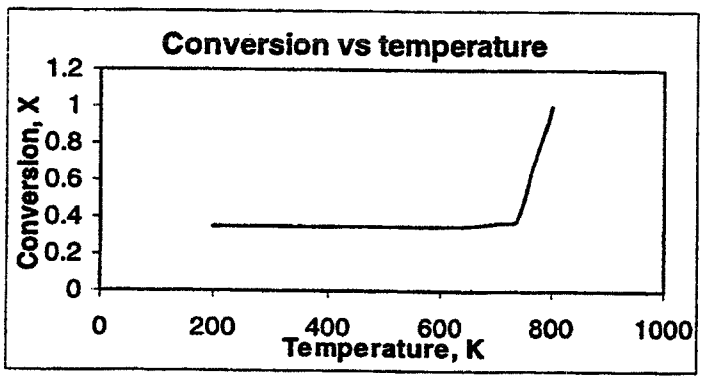
Explicit equations as entered by the user
[1] Fao = 5
[2] Ua = 5
[3] Ta = 700
[4] dHr = -231-0.012*(T-298)
[5] Cpa = .1222
[6] k = 1.48e11*exp(-19124/T)
[7] Cao = 1
[8] Ca = Cao*(1-X)
[9] ra = -k*Ca^2





P8-28 (b)

Using the same POLYMATH program we were able to change the entering temperature and come up with this graph.



P8-28 (c)

Again using the same POLYMATH program, we can vary the ambient temperature until the reaction runs away. As the following summary table will show the maximum temperature is 708 K.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	10	10
T	675	675	758.02032	712.2666
X	0	0	0.4862844	0.4862844
Fao	5	5	5	5
Ua	5	5	5	5
Ta	708.2	708.2	708.2	708.2
dHr	-235.524	-236.5196	-235.524	-235.9712
Cpa	0.1222	0.1222	0.1222	0.1222
k	0.0734336	0.0734336	1.6320169	0.3233503
Cao	1	1	1	1
Ca	1	0.5137156	1	0.5137156
ra	-0.0734336	-1.078707	-0.0734336	-0.0853333

P8-28 (d)

When the reaction becomes adiabatic the energy balance will then become:

$$T = T_0 + \frac{(-r_A)(-\Delta H_R)}{C_{pA}}$$

However, the heat of reaction is a function of temperature. This is a circular reference, so we need to find T as a function of just X.

$$T = \frac{T_0 C_{pA} - 231X - 3.576X}{C_{pA} - 0.012X}$$

Plugging that into POLYMATH gets the following program and graphs.

See Polymath program P8-28-d.pol.

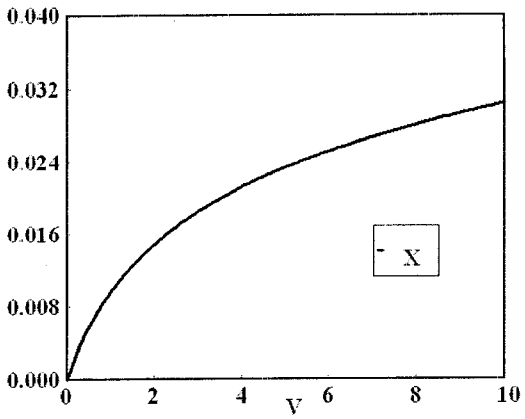
POLYMATH Results
Calculated values of the DEQ variables

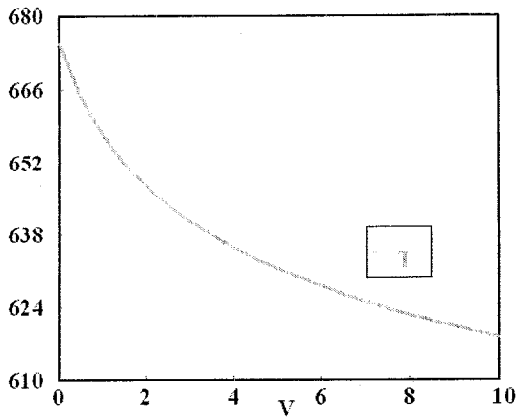
Variable	initial value	minimal value	maximal value	final value
V	0	0	10	10
X	0	0	0.0304837	0.0304837
Fao	5	5	5	5
Ua	5	5	5	5
Ta	708.2	708.2	708.2	708.2
To	675	675	675	675
Cpa	0.1222	0.1222	0.1222	0.1222
T	675	618.33416	675	618.33416
Cao	1	1	1	1
Ca	1	0.9695163	1	0.9695163
dHr	-235.524	-235.524	-234.84401	-234.84401
k	0.0734336	0.0054738	0.0734336	0.0054738
ra	-0.0734336	-0.0734336	-0.0051452	-0.0051452

ODE Report (RKF45)

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

Explicit equations as entered by the user
[1] Fao = 5
[2] Ua = 5
[3] Ta = 708.2
[4] To = 675
[5] Cpa = .1222
[6] T = (To*Cpa-231*X-3.576*X)/(Cpa-0.012*X)
[7] Cao = 1
[8] Ca = Cao*(1-X)
[9] dHr = -231-0.012*(T-298)
[10] k = 1.48e11*exp(-19124/T)
[11] ra = -k*Ca^2





P8-28 (e)

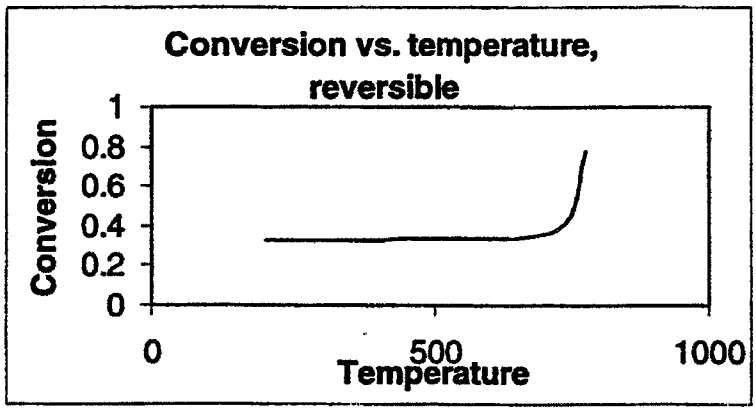
When it becomes reversible with inerts the two equations that change are the rate law and the energy balance.

$$-r_A = k\left(C_A^2 - \frac{C_B}{K}\right)$$

$$\frac{dT}{dV}=\frac{Ua(T_A-T)+(-r_A)(-\Delta H_R)}{F_{A0}(C_{pA}+\Theta_I C_{pI})}$$

$$K=100000\exp\left[\frac{\Delta H_R}{R}\left(\frac{1}{675}-\frac{1}{T}\right)\right]$$

We can use those equations in POLYMATH and the following graph is made:



There is no maximum because the reaction is a runaway at a certain temperature and the conversion goes to close to one at that point.

P8-28 (f) No solution will be given

P8-29

The elementary, reversible, gas phase reaction $A + B \Leftrightarrow 2C$

Feed: $F_{A0} = F_{B0} = 20$ mol/s = 1200 mol/min.

$P_O = 580.5$ kmol = 5.74 atm.

$T_O = 77°C = 350°K$

$Y_{A0} = Y_{B0} = 0.5$

$$C_{A0}=\frac{Y_{A0}P_O}{RT_O}=\frac{(0.5)\ (5.74\ \text{atm.})}{\left(0.082\ \frac{1\ \text{atm}}{\text{g mol°K}}\right)(350°K)}=0.1\ \text{gmol/l}$$

Rate constant: $k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T}\right)\right]$

$$= 0.035 \exp\left[\frac{70{,}000}{8.314}\left(\frac{1}{273}-\frac{1}{T}\right)\right]$$

$$= 0.035 \exp\left[8419.5\left(\frac{1}{273}-\frac{1}{T}\right)\right] \qquad (1)$$

Equilibrium constant:

$$\Delta H_R(T_R) = 2H_C - H_A - H_B = 2(-45{,}000) + 40{,}000 + 30{,}000 = -20{,}000 \text{ J/mole}$$

$$\Delta C_p = 2C_{pC} - C_{pA} - C_{pB} = 2(20) - 25 - 15 = 0$$

So $\Delta H_R(T)$ = constant = -20,000 J/mole (2)

$$K_C = K_{C1} \exp\left[\frac{\Delta H_R}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

$$K_C = 25{,}000 \exp\left[\frac{-20{,}000}{8.314}\left(\frac{1}{298} - \frac{1}{T}\right)\right]$$

$$K_C = 25{,}000 \exp\left[-2405.6\left(\frac{1}{298} - \frac{1}{T}\right)\right] \quad (3)$$

k and K_C can be calculated by equation (1) and (3) if T is given.

$$K_C = \frac{C_C^2}{C_A C_B}$$

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

$$C_B = C_{A0}(1 - X)\, f \qquad \text{where } f = \frac{T_O}{T}$$

$$C_C = 2C_{A0}\, X\, f$$

Substitute C_A, C_B, and C_C into K_C

$$K_C = \frac{4C_{A0}^2 X^2 f^2}{C_{A0}^2 (1 - X)^2 f^2} = \frac{4X^2}{(1 - X)^2} \quad (4)$$

$$\sqrt{K_C} = \frac{2X}{1 - X} \quad \text{or} \quad X_{eq} = \frac{\sqrt{K_C}}{2 + \sqrt{K_C}} \quad (5)$$

Calculate $\sqrt{K_C}$ as a function of temperature from equation (3), substitute in equation (5) to get $X_{e.g.}$ as a function of T. Energy balance for adiabatic condition:

$$-X\,\Delta H_R = \Sigma\, \theta_i\, C_{p_i}(T - T_O) \quad (6)$$

$$\theta_A = \theta_B = 1\ ,\ \theta_C = 0\ ,\ T_O = 350\text{K}$$

Substitute: $+20{,}000X = (25 + 15)(T - 350) \Rightarrow T = 500X + 350$

or $X = 0.002(T - 350)$ (7)

Equations (3) = (4):

$$\frac{4X^2}{(1 - X)^2} = 25000 \exp\left[-2405.6\left(\frac{1}{298} - \frac{1}{350 + 500X}\right)\right]$$

$$X_{eq} = 0.8667$$

$$0.85X_{eq} = 0.7366 \cong 0.7$$

(a) Plug flow reactor design equation: $$V = F_{A0}\int \frac{dX}{-r_A} \qquad (8)$$

Rate law: $$-r_A = k\left[C_A C_B - \frac{C_C^2}{K_C}\right]$$

$$-r_A = k\,C_{A0}^2\,f^2\left[(1-X)^2 - \frac{(2X)^2}{K_C}\right] \qquad (9)$$

$$\text{So } V = \frac{F_{A0}}{C_{A0}^2}\int_0^{0.7} \frac{dX}{kf^2\left[(1-X)^2 - \frac{4X^2}{K_C}\right]} = \frac{1200}{(0.1)^2}\int_0^{0.7} f(X)\,dX$$

$$V = 1.2\times 10^5 \int_0^{0.7} f(X)\,dX \quad \text{where } f(X) = \frac{1}{kf^2\left[(1-X)^2 - \frac{4X^2}{K_C}\right]} \qquad (10)$$

To evaluate the integral, we need to evaluate f(X) as a function of X. This is done in the table below:

X	T°K (eqn. 7)	K_C (eqn. 3)	k (eqn. 1)	f(X) (eqn. 9)
0	350	7534.8	30.96	0.0323
0.1	400	3191.1	626..1	2.58×10^{-3}
0.2	450	1635.9	6491.5	3.98×10^{-4}
0.3	500	958.5	4.216×10^{4}	9.89×10^{-5}
0.4	550	618.9	1.949×10^{5}	3.53×10^{-5}
0.5	600	429.9	6.978×10^{5}	1.70×10^{-5}
0.6	650	315.8	2.054×10^{6}	1.08×10^{-5}
0.7	700	192.8	1.155×10^{7}	4.98×10^{-6}

The integral can be evaluated using Simpson's rule for the first six segments and trapeziodal rule for the last segment.

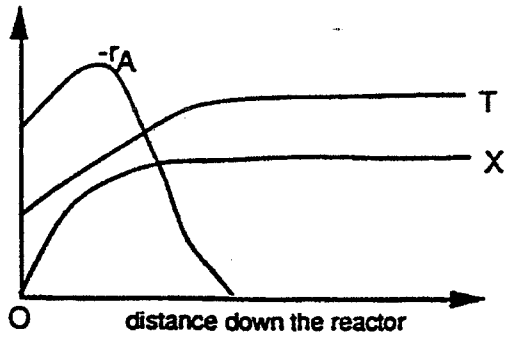
$$I = \int_0^{0.7} f(X)\,dX \cong \frac{0.1}{3}\left[0.0323 + 4(2.58\times 10^{-3}) + 2(3.98\times 10^{-4}) + 4(9.89\times 10^{-5})\right.$$

$$\left. + 2(3.53\times 10^{-5}) + 4(1.70\times 10^{-5}) + 1.08\times 10^{-5}\right] + \frac{0.1}{2}\left[1.08\times 10^{-5} + 4.98\times 10^{-6}\right]$$

$$I = 1.5\times 10^{-3}$$

$$V_{PFR} = (1.2\times 10^5)(1.5\times 10^{-3}) = 180\text{ L}$$

Exothermic, adiabatic



(c) CSTR design equation: $V = \frac{F_{A0} X_A}{-r_A}$

$$V = \frac{F_{A0} X}{k C_{A0}^2 f^2 \left[(1 - X)^2 - \frac{4X^2}{K_C}\right]}$$

$$\frac{X}{k f^2 \left[(1 - X)^2 - \frac{4X^2}{K_C}\right]} = \frac{1500\text{L} \times (0.1)^2 \left(\frac{\text{mol}}{\text{l}}\right)^2}{1200 \frac{\text{mol}}{\text{min}}} = 0.0125$$

$$(1 - X)^2 - \frac{4X^2}{K_C} = 80 \frac{X}{f^2 k}$$

$$1 - 2X + X^2 - \frac{4X^2}{K_C} = \frac{80X}{f^2 k}$$

$$\left(1 - \frac{4}{K_C}\right) X^2 - \left(2 + \frac{80}{f^2 k}\right) X + 1 = 0$$

Let $b_1 = 1 - \frac{4}{K_C}$ and $b_2 = 2 + \frac{80}{f^2 k}$ (11)

$$\Rightarrow X = \frac{b_2 \pm \sqrt{b_2^2 - 4b_1}}{2b_2} \quad (12)$$

Nonadiabatic energy balance:

$$\frac{-UA}{F_{A0}} (T - T_A) - X\Delta H_R = \Sigma \theta_i C_{p_i} (T - T_O)$$

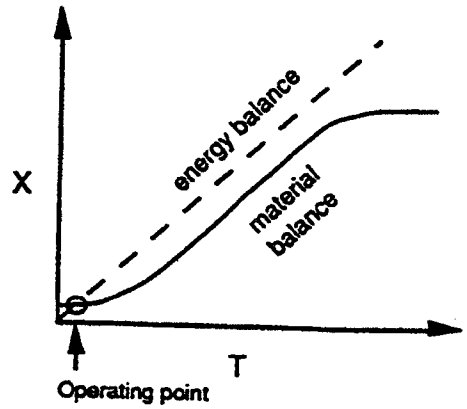
$$\frac{-10 \frac{\text{W}}{\text{m}^2 \text{K}} \times 2}{1200 \frac{\text{mol}}{\text{min}}} \times \frac{1\text{kW}}{1000\text{W}} \times \frac{1\text{hr}}{60\text{min}} \times \frac{3.6 \times 10^6 \text{ J}}{1\text{KW.hr}} (T - 290) + 20000X = 40(T - 350)$$

$$-T + 290 + 20{,}000X = 40T - 14{,}000$$

$$T = 348.5 + 487.8\,X \quad (13)$$

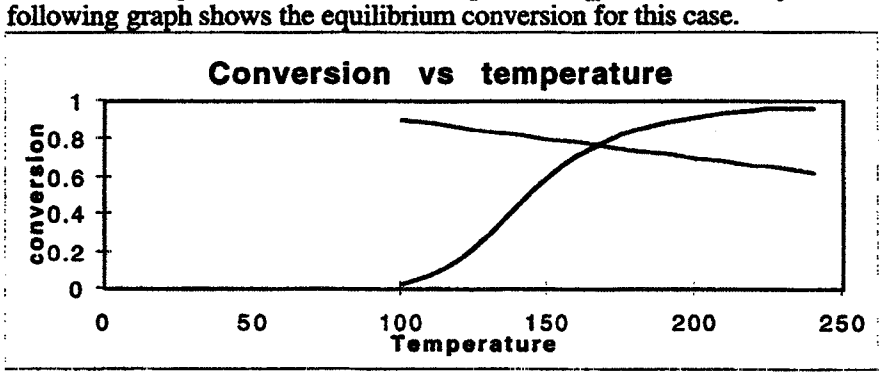
So the procedure to calculate X is as follows:

1. Choose increments in T and calculate X as a function of T from equation (13). This is the value given by energy balance.
2. Choose increments in T and calculate b_1 and b_2 from equation (11). (K_C and k can be calculated from equation (3) and c1) respectively.)
3. Calculate X, discarding X > 1 or X < 0. This is the value of X given by material balance.
4. Plot X vs. T given by equation (13) and (11) on the same graph. The intersection gives the conversion in the reactor. A typical graph looks like the following:



The actual calculation gives: X ≈ 0 which is the conversion in CSTR.

d) The same equations can be used except that $\Delta H_{rx} = 20000$ and $T_0 = 550K$. The following graph shows the equilibrium conversion for this case.



The following POLYMATH program gives the PFR volume necessary to get a conversion of .65.

See Polymath program P8-29.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	1.0E+08	1.0E+08
X	0	0	0.6495463	0.6495463
Fao	1200	1200	1200	1200
T	550	225.22683	550	225.22683

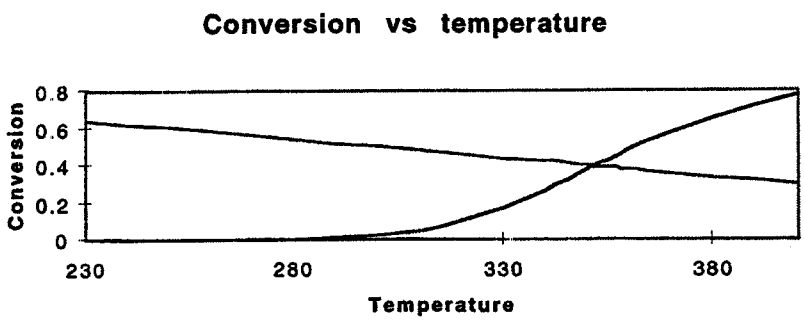
Cao	0.064	0.064	0.064	0.064
To	550	550	550	550
k	1.949E+05	5.047E-05	1.949E+05	5.047E-05
Kc	1.01E+06	1841.4832	1.01E+06	1841.4832
f	1	1	2.4419826	2.4419826
Ca	0.064	0.0547713	0.064	0.0547713
Cb	0.064	0.0547713	0.064	0.0547713
Cc	0	0	0.2030311	0.2030311
ra	-798.17344	-798.17344	-1.503E-07	-1.503E-07

ODE Report (RKF45)

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

Explicit equations as entered by the user
[1] Fao = 1200
[2] T = -500*X+550
[3] Cao = .064
[4] To = 550
[5] k = .035*exp(8419.5*(1/273-1/T))
[6] Kc = 25000*exp(2405.6*(1/298-1/T))
[7] f = To/T
[8] Ca = Cao*(1-X)*f
[9] Cb = Cao*(1-X)*f
[10] Cc = 2*Cao*X*f
[11] ra = -k*(Ca*Cb-Cc^2/Kc)

The CSTR conversion can be found similarly to the equilibrium conversion. The following graph was made to find the conversion.



The graph shows a conversion of .39 at a temperature of 351.8K

e) If the reaction is left in a large enough volume it will "runaway'. If any of the quantities get bigger, then it will run away even faster.

f) The ambient temperature around the CSTR has little effect on the conversion in the CSTR.

P8-30 (a)

P8-6 is adiabatic so the radial reactor has no effect on it.

P8-30 (b)

$$\frac{dX}{dW} = \frac{-r_A}{F_{A0}}$$

$$-r_A = kC_A$$

$$C_A = C_{A0}\frac{1-X}{1+X}\frac{T_0}{T}y$$

$$\frac{dy}{dW} = \frac{-\alpha}{2y}$$

$$\frac{dT}{dW} = \frac{U(r)\frac{2h}{\rho}(T_A - T) + (-r_A)(-\Delta H_R)}{F_{A0}C_{pA}}$$

$$U = U(r_0)\left(\frac{r_0}{r}\right)^{.5}\left(\frac{T}{T_0}\right)^5$$

Since h and ρ are unknown, we will assume that they are both equal to one. We will also assume that r varies as W^5 varies.

so:

$$\frac{dT}{dW} = \frac{U(r)(T_A - T) + (-r_A)(-\Delta H_R)}{F_{A0}C_{pA}}$$

$$U = U(r_0)\left(\frac{W_0^5}{W}\right)^{.5}\left(\frac{T}{T_0}\right)^5$$

See Polymath program P8-30-b.pol.

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
W	0	0	50	50
y	1	0.8062258	1	0.8062258
X	0	0	0.7845538	0.7845538
T	450	450	756.08452	756.08452
Fao	5	5	5	5
alpha	0.007	0.007	0.007	0.007
Ta	300	300	300	300
dHr1	-2.0E+04	-2.0E+04	-2.0E+04	-2.0E+04
Wo	0.01	0.01	0.01	0.01
To	450	450	450	450
E	3.14E+04	3.14E+04	3.14E+04	3.14E+04
R	8.314	8.314	8.314	8.314
Cao	0.2498645	0.2498645	0.2498645	0.2498645
X1	0	0	784.55376	784.55376
y1	1000	806.22577	1000	806.22577
U	5.0E+04	0.9244844	5.0E+04	0.9244844
k	1	1	29.893648	29.893648

Ca	0.2498645	0.0320395	0.2498645	0.0320395
Cc	0	0	0.2333455	0.2333455
Cb	0.2498645	0.0320395	0.2498645	0.0320395
Kc	1635.8981	187.88715	1635.8981	187.88715
ra	-0.0624323	-0.1234947	-0.0220235	-0.0220235

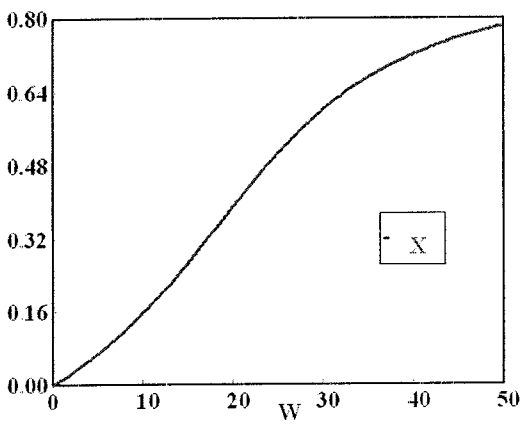
ODE Report (RKF45)

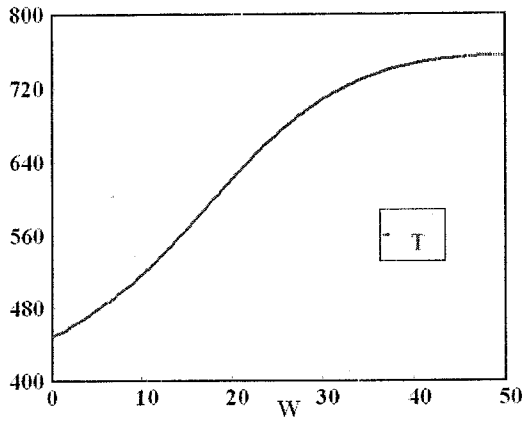
Differential equations as entered by the user

[1] d(y)/d(W) = -alpha/(2*y)
[2] d(X)/d(W) = -ra/Fao
[3] d(T)/d(W) = (U*(Ta-T)+(-ra)*(-dHr1))/(Fao*40)

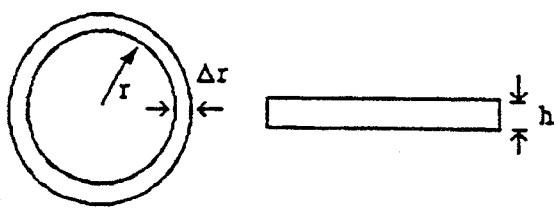
Explicit equations as entered by the user

[1] Fao = 5
[2] alpha = .007
[3] Ta = 300
[4] dHr1 = -20000
[5] Wo = .01
[6] To = 450
[7] E = 31400
[8] R = 8.314
[9] Cao = 9.22/(.082*450)
[10] X1 = 1000*X
[11] y1 = 1000*y
[12] U = 5*(Wo^.5/(W^.5+.000000001))^.5*(T/To)^.5*y^.5*(1+X)^.5
[13] k = exp((E/R)*(1/450-1/T))
[14] Ca = Cao*(1-X)*To/T
[15] Cc = 2*Cao*X*To/T
[16] Cb = Ca
[17] Kc = 25000*exp((dHr1/R)*(1/298-1/T))
[18] ra = -k*(Ca*Cb-Cc^2/Kc)





P8-30 (c)



$$W = \rho V = \rho\pi r^2 h \Rightarrow dW = 2\pi\rho r h dr$$

Material balance: $F_A|_r - F_A|_{r+\Delta r} + r_A \Delta W = 0$

$$F_A|_r - F_A|_{r+\Delta r} + 2\pi\rho r h (r_A)\Delta r = 0$$

Taking the limit as $\Delta r \rightarrow 0$

$$\frac{dF_A}{dr} = (r_A) 2\pi\rho r h$$

$$F_A = F_{AO}(1-X_A) \Rightarrow \frac{dF_A}{dr} = -F_{AO}\frac{dX_A}{dr}$$

$$\text{so: } \frac{dX_A}{dr} = \frac{-2\pi r h \rho (r_A)}{F_{AO}} \qquad (1)$$

$$\text{or: } \frac{dX_A}{dW} = -\frac{r_A}{F_{AO}} \qquad (2)$$

Assuming pressure drop is negligible. The rate equation is:

$$-r_A = k\left(\frac{P_{SO_3}}{P_{SO_3}}\right)^{1/2}\left[P_{O_2} - \left(\frac{P_{SO_3}}{K_P P_{SO_2}}\right)^2\right]$$

The stoichiometry : $SO_2 + \frac{1}{2}O_2 \Leftrightarrow SO_3$

$$A + \frac{1}{2}B \Leftrightarrow C$$

$$\delta = -0.5, y_{AO} = 0.11 \therefore \varepsilon = y_{AO}\delta = -0.055 \; ; \; \theta_C = 0 \; ; \; \theta_B = \frac{10}{11} = 0.91$$

$$P_{SO_2} = P_{SO_{2o}}\frac{1-X_A}{1+\varepsilon X_A} \; ; \; P_{SO_3} = P_{SO_{2o}}\frac{X_A}{1+\varepsilon X_A} \; ; \; P_{O_2} = P_{SO_{2o}}\frac{(0.91-0.5X_A)}{1+\varepsilon X_A}$$

$$\text{Then: } -r_A = k(t)\left(\frac{1-X_A}{X_A}\right)^{1/2}\left[P_{SO_{2o}}\left(\frac{0.91-0.5X_A}{1-0.055X_A}\right) - \frac{X_A^2}{(1-X_A)^2 K_p^2}\right] \qquad (3)$$

Equation (3) is true for $X_A < 0.05$

for $X_A \geq 0.05$

$$-r_A = k(t)(4.35)\left[0.22\left(\frac{0.91-0.025}{1-0.055(0.05)}\right) - \frac{0.0025}{(1-0.05)^2 K_p^2}\right]$$

$$-r_A = k(t)\left[0.848 - \frac{0.01205}{K_p^2}\right] \qquad (4)$$

Energy balance:

$$F_{AO}\left(\Sigma\theta_i\, C_{p_i} + X\,\Delta C_p\right) Tl_r - F_{AO}\left(\Sigma\theta_i\, C_{p_i} + \Delta C_p\, X\right) Tl_{r+\Delta r}$$

$$+ r_A\,\Delta W\left(\Delta H_R\right) - (2)\left(\Delta A\right) U\,(r)\;(T-T_A) = 0$$

or: $$F_{AO}\left(\Sigma\theta_i\, C_{p_i} + X\,\Delta C_p\right) Tl_r - F_{AO}\left(\Sigma\theta_i\, C_{p_i} + \Delta C_p\, X\right) Tl_{r+\Delta r}$$

$$+ r_A\, 2\pi r h\rho\left(\Delta H_R\right)\Delta r - (2)\left(2\pi r\,\Delta r\right) U(r)\;(T-T_A) = 0$$

Taking the limit as $\Delta r \rightarrow 0$:

$$F_{AO}\left(\Sigma\theta_i\, C_{p_i} + X\,\Delta C_p\right)\frac{dT}{dr} = -U(r)\,4\pi r\,(T-T_A) + (-r_A)\left(-\Delta H_R\right) 2\pi r h\rho$$

Rearranging:

$$\frac{dT}{dr} = \frac{-U(r)\,4\pi r\,(T-T_A) + (-r_A)\left(-\Delta H_R\right) 2\pi r h\rho}{F_{AO}\left(\Sigma\theta_i\, C_{P_i} + X\,\Delta C_P\right)} \qquad (5)$$

or: $$\frac{dT}{dW} = \frac{-U(r)\frac{2h}{\rho}(T-T_A) + (-r_A)\left(-\Delta H_R\right)}{F_{AO}\left(\Sigma\theta_i\, C_{P_i} + X\,\Delta C_P\right)} \qquad (6)$$

Assume that: $U(r) = U(r_o)\left(\frac{\upsilon}{\upsilon_o}\right)^{1/2}$; $\upsilon = \frac{\upsilon_o\, r_o}{r}(1+\varepsilon X)\frac{T}{T_o}$

Therefore: $U(r) = U(r_o)\left(\frac{r_o}{r}\right)^{1/2}\left(\frac{T}{T_o}\right)^{1/2}(1 - 0.055X_A)^{1/2}$

From example 8-10, we have:

$$K_P = \exp\left[\frac{42{,}311}{RT} - 11.24\right] \left(K_P \text{ in atm}^{-1/2}\ ,\ T \text{ in } {}^\circ R\right) \qquad (7)$$

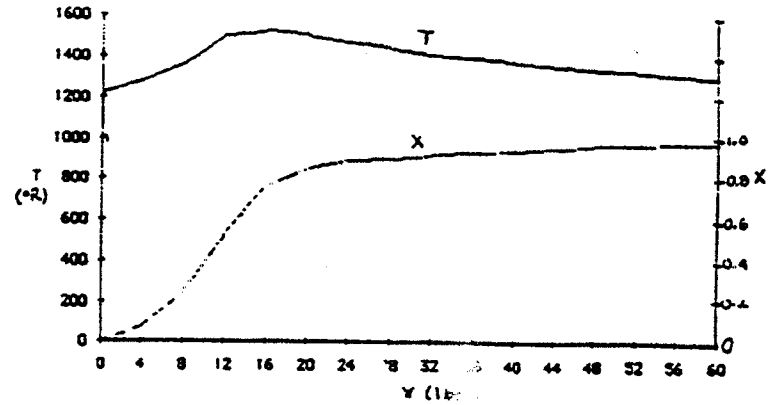
$$k = \exp\left[\frac{-176{,}008}{T} - 110.1 \ln T + 912.84\right] \qquad (8)$$

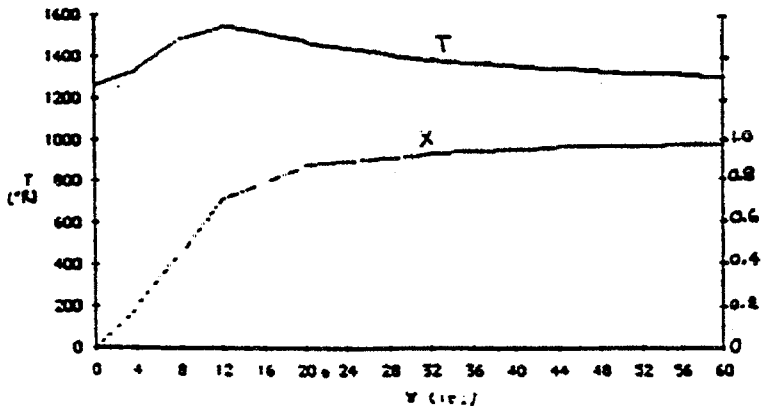
$$\Delta H_R(T) = -42{,}471 - (1.563)(T - 1260) + \left(1.36 \times 10^{-3}\right)\left(\frac{T^2 - 1260^2}{2}\right)$$

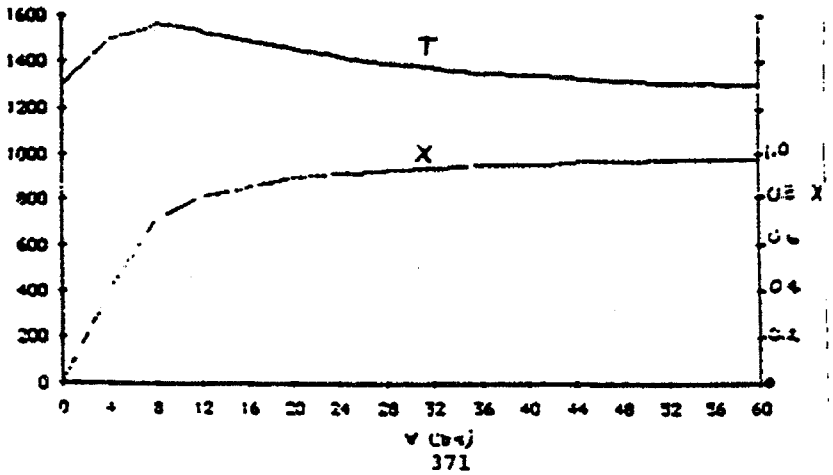
$$-\left(2.459 \times 10^{-7}\right)\left(\frac{T^3 - 1260^3}{3}\right) \text{ where } \Delta H_R \text{ in } \frac{Btu}{lbmole} \qquad (9)$$

$$\Sigma\theta_i C_{p_i} = 57.23 + 0.014T - 1.788 \times 10^{-6} T^2 \qquad (10)$$

Since equations (1) to (10) must be solved together as two pairs of coupled differential equations, they must be solved on a computer, employing numerical methods such as Runge-Kutta. The results follow:







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P8-30 (d)

$$\frac{dX}{dr} = \frac{-2\pi rh\rho(-r_A)}{F_{A0}}$$

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

$$C_A = C_B = C_{A0}(1-X)\frac{T_0}{T}$$

$$C_C = 2C_{A0}X\frac{T_0}{T}$$

$$\frac{dT}{dr} = \frac{U(r)4\pi r(T_A - T) + (-r_A)(-\Delta H_{Rx})}{F_{A0}(C_{PA} + C_{PB})}$$

$$U = U(r_0)\left(\frac{r_0}{r}\right)^{0.5}\left(\frac{T}{T_0}\right)^{0.5}$$

Now put these equations into Polymath to generate the plots.

See Polymath program P8-30-d.pol.

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
r	0.5	0.5	1000	1000
X	0	0	1	1
T	350	350	493.0235	373
Ta	373	373	373	373
dHrx	-2.0E+04	-2.0E+04	-2.0E+04	-2.0E+04
Fao	1200	1200	1200	1200
Cpa	25	25	25	25
Cpb	15	15	15	15
h	0.5	0.5	0.5	0.5
ro	0.5	0.5	0.5	0.5
To	350	350	350	350
E	7.0E+04	7.0E+04	7.0E+04	7.0E+04
R	8.314	8.314	8.314	8.314
Cao	0.1	0.1	0.1	0.1
U	33.3	0.769425	33.3	0.769425
k	30.955933	30.955933	3.398E+04	136.44189
Ca	0.1	-2.608E-10	0.1	-3.125E-17
ra	-3.0955933	-3.0955933	2.09E-06	4.264E-15

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(X)/d(r) = -2*3.1416*h*ra/Fao
[2] d(T)/d(r) = (U*4*3.1415*r*(Ta-T)+(-ra)*(-dHrx))/(Fao*(Cpa+Cpb))

Explicit equations as entered by the user
[1] Ta = 373
[2] dHrx = -20000
[3] Fao = 1200
[4] Cpa = 25
[5] Cpb = 15

```
[6] h = .5
[7] ro = .5
[8] To = 350
[9] E = 70000
[10] R = 8.314
[11] Cao = .1
[12] U = 33.3*(ro/r)^.5*(T/To)^.5
[13] k = .035*exp((E/R)*(1/273-1/T))
[14] Ca = Cao*(1-X)/(1+X)*(To/T)
[15] ra = -k*Ca
```

P8-31 (a)

Mole balances:

$$V = \frac{F_{A0} - F_A}{-r_A}$$

$$V = \frac{F_B}{r_B} = \frac{F_C}{r_C}$$

rate laws:

$$-r_A = k_1 C_A$$

$$r_B = k_1 C_A - k_2 C_B$$

$$r_C = k_2 C_B$$

Stoichiometry:

$$C_i = \frac{F_i}{v_0}\frac{T}{T_0}$$

$$F_B = 10F_C$$

$$.5 = \frac{.05 - F_A}{0.5}$$

$$F_A = .025$$

$$11F_C = .025$$

$$F_C = .023 \qquad F_B = .023$$

From this we can use two of the mole balances to solve for T

$$\frac{F_{A0}-F_A}{k_1F_A}=\frac{F_c}{k_2F_B}$$

$$\frac{1}{A_1e^{-E/RT}}=\frac{0.1}{A_2e^{-E/RT}}$$

$$T=269°F$$

P8-31 (b)

Knowing the temperature we can then solve for the Volume:

$$V=\frac{F_Bv_0}{k_1F_A-k_2F_B}\frac{T_0}{T}=11.9ft^3$$

P8-31 (c)

We then need the energy balance:

$$UA(T_a-T)-F_{A0}C_{pa}(T-T_0)+V\left[(\Delta H_{R1})(r_{1A})+\Delta H_{R2}(r_{2B})\right]=0$$

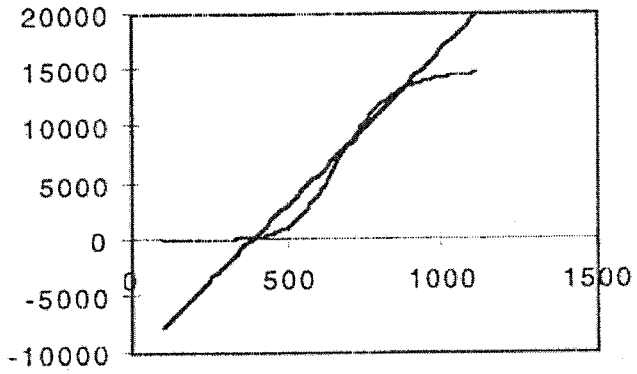
Solve for A and we get:

A = 399 ft^2

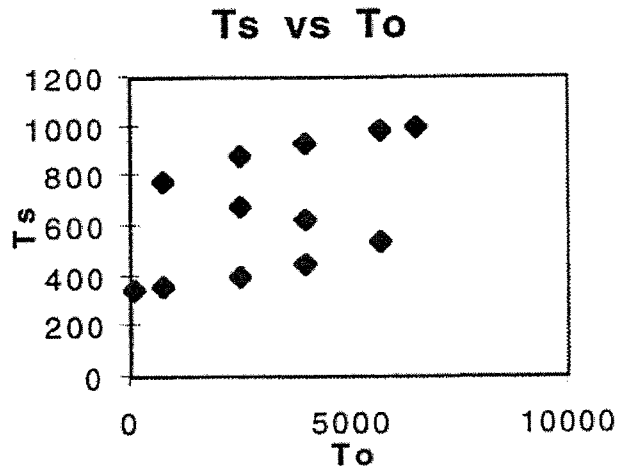
P8-31 (d)

In order to get multiple steady-states, the kappa, tau and feed temperature had to be changed. $\kappa = 0.1$, $\tau = 0.0005$ and T_0 would be changed around.

This first graph is G(T), R(T) vs T at $T_0 = 2000$ °F



As can be seen there are three steady-states.



P8-32 (a)

Energy balance

$$\frac{dT}{dW}=\frac{Ua/\rho_b(T_a-T)+(-r_A)[-\Delta H_R(T_R)]}{F_{A0}\left(\sum\theta_i C_{pi}+X\Delta C_p\right)}$$

$$\frac{dT}{dW}=\frac{Ua/\rho_b(T_a-T)+(-r_A)[-\Delta H_R(T_R)]}{F_{A0}C_{pA}}$$

Mole balance: $\frac{dX}{dW}=\frac{-r_A}{F_{A0}}$

Pressure drop: $\frac{dy}{dW}=\frac{-\alpha}{2y}\frac{T_0}{T}(1+X)$

Rate law: $-r_A=kC_A$

Stoichiometry: $C_A=C_{A0}\left(\frac{1-X}{1+X}\right)\left(\frac{T}{T_0}\right)y$

Evaluating the parameters: $k=\exp\left[\frac{E}{R}\left(\frac{1}{450}-\frac{1}{T}\right)\right]=\exp\left[3776.76\left(\frac{1}{450}-\frac{1}{T}\right)\right]$

Plugging these equations into POLYMATH we get the following plots.

See Polymath program P8-32-a.pol.

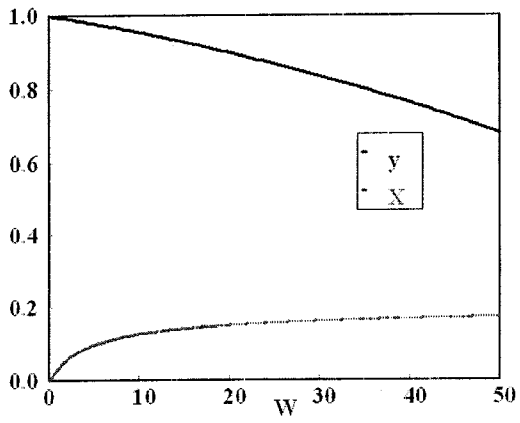
OLYMATH Results
Calculated values of the DEQ variables

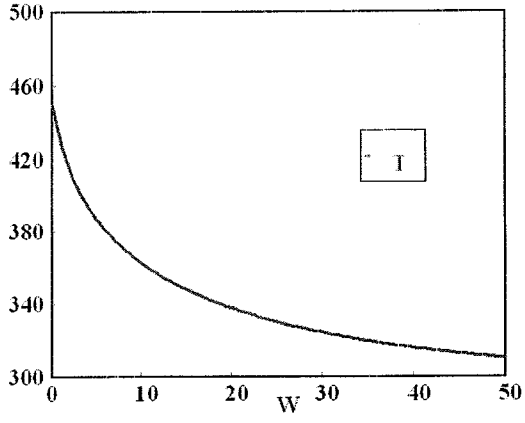
Variable	initial value	minimal value	maximal value	final value
W	0	0	50	50
y	1	0.6823861	1	0.6823861
T	450	310.69106	450	310.69106
X	0	0	0.175758	0.175758
U	5	5	5	5
a	0.007	0.007	0.007	0.007
To	450	450	450	450
Ta	300	300	300	300
dHrx	-2.0E+04	-2.0E+04	-2.0E+04	-2.0E+04
Fao	5	5	5	5
Cpa	40	40	40	40
k	1	0.0232094	1	0.0232094
Cao	0.25	0.25	0.25	0.25
Ca	0.25	0.0825702	0.25	0.0825702
ra	-0.25	-0.25	-0.0019164	-0.0019164

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(y)/d(W) = -a/(2*y)*(To/T)*(1+X)
[2] d(T)/d(W) = (U*(Ta-T)-ra*dHrx)/Fao/Cpa
[3] d(X)/d(W) = -ra/Fao

Explicit equations as entered by the user
[1] U = 5
[2] a = .007
[3] To = 450
[4] Ta = 300
[5] dHrx = -20000
[6] Fao = 5
[7] Cpa = 40
[8] k = exp(3776.76*(1/450-1/T))
[9] Cao = .25
[10] Ca = Cao*((1-X)/(1+X))*(T/450)*y
[11] ra = -k*Ca





P8-32 (b)

From the Polymath summary table, it is apparent that the maximum value for $-r_A$ occurs at the beginning of the reactor.

P8-32 (c)

The maximum value for the temperature also occurs at the beginning of the reactor.

P8-32 (d)

Doubling the heat-transfer coefficient causes a decrease in the temperature, the conversion, and the pressure drop. Halving the heat transfer coefficient casuses all three to increase.

P8-33

Mole balances

$$V = \frac{v_0(C_{A0} - C_A)}{-r_A} \qquad V = \frac{v_o(C_{B0} - C_B)}{-r_B}$$

$$V = \frac{v_0 C_D}{r_D} \qquad V = \frac{v_0 C_U}{r_U}$$

Rate laws:

$$-r_A = k_1 C_A + k_2 C_B \qquad r_D = k_1 C_A$$

$$-r_B = k_1 C_A + k_2 C_B \qquad r_U = k_2 C_B$$

Energy balance:

$$-F_{A0}\left[C_{pA}(T - T_{A0}) + C_{pB}(T - T_{B0})\right] + V(r_{A1})\left(\Delta H_{R1}(T_R) + \Delta C_{p1}(T - T_R)\right) + V(r_{A2})\left(\Delta H_{R2}(T_R) + \Delta C_{p2}(T - T_R)\right)$$

Evaluating the parameters:

T=400K

$$k_1 = 1000\exp\left(-\frac{2000}{T}\right) = 6.73 \qquad k_2 = 2000\exp\left(-\frac{3000}{T}\right) = 1.11$$

$$\Delta C_{p1} = 50 - 20 - 30 = 0 \qquad \Delta C_{p2} = 40 - 30 - 20 = -10$$

$$v_0 = \frac{F_{A0}}{C_{A0}} = \frac{60}{.01} = 6000\frac{dm^3}{min} \qquad C_{B0} = C_{A0}$$

Simplifying:

$$C_A = \tau * r_A + C_{A0} \qquad C_B = \tau * r_B + C_{B0}$$

$$C_D = \tau * r_D \qquad C_U = \tau * r_U$$

$$V = \frac{171000}{20190 * C_A + 6660 * C_B}$$

We can plug those into POLYMATH and find the exit concentrations of U and D and find the volume of the CSTR.

See Polymath program P8-33.pol.

POLYMATH Results
NLES Solution

Variable	Value	f(x)	Ini Guess
Ca	0.0016782	-1.472E-16	0.0017
Cb	0.0016782	-1.472E-16	0.0017
Cd	0.0071436	-1.154E-16	0.0072
Cu	0.0011782	-2.017E-17	0.0012
V	3794.94	1.018E-09	3794
Cao	0.01		
Cbo	0.01		
vo	6000		
k1	6.73		
k2	1.11		
tau	0.63249		
rd	0.0112944		
ru	0.0018628		
ra	-0.0131572		
rb	-0.0131572		

NLES Report (safenewt)

Nonlinear equations

[1] f(Ca) = tau*ra+Cao-Ca = 0
[2] f(Cb) = tau*rb+Cbo-Cb = 0
[3] f(Cd) = Cd-tau*rd = 0
[4] f(Cu) = Cu-tau*ru = 0
[5] f(V) = 171000/(20190*Ca+6660*Cb)-V = 0

Explicit equations

[1] Cao = .01
[2] Cbo = .01
[3] vo = 6000
[4] k1 = 6.73
[5] k2 = 1.11
[6] tau = V/vo
[7] rd = k1*Ca
[8] ru = k2*Cb
[9] ra = -k1*Ca-k2*Cb
[10] rb = ra

P8-33 (a)

$C_U = .0012$
$C_D = .0072$

P8-33 (b)

$V = 3794\ dm^3$

P8-33 (c) Individualized solution

Solutions for Chapter 9 – Unsteady State Nonisothermal Reactor Design

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P9-1 Individualized solution

P9-2 (a) Example 9-1

The new T0 of 20 °F (497 °R) gives a new ΔH_{Rn} and T. With T=497+89.8X the polymath program of example 9-1 gives t= 8920 s for 90 % conversion.

P9-2 (b) Example 9-2

To show that no explosion occurred without cooling failure.

Isothermal operation throughout (T = 175°C)

Maximum cooling rate:

$$Q_r = UA[448 - 298] = 142 * 150$$
$$= 21300 \text{ BTU/min}$$

Maximum Q_g at t = 0 (maximum concentration and reaction rate)

$$Q_g = k\frac{N_{A0}N_{B0}}{V^2} * V(-\Delta H_{Rx})$$
$$= 0.0001167\left[\frac{9.04 * 33}{5.119}\right]2.34 * 10^6$$
$$= 15914.2 \text{ BTU/min}$$

For all t:

$Q_g < Q_r$ No explosion

To show that no explosion occurs with cooling shut down for 10 mi. after 12 hrs.

Isothermal operation for 12 hrs. (at T = 175°C)

$$t = \left[\frac{V}{kN_{A0}}\right]\left(\frac{1}{\theta_B - 2}\right)\ln\frac{\theta_B - 2x}{\theta_B(1-x)}$$

$$\frac{\theta_B - 2x}{\theta_B(1-x)} = 1.276$$

$$3.64 - 2x = 1.276 * 3.64(1-x)$$

$$x = 0.38$$

Q_g at t = 12 hrs.

$$Q_g = k\frac{N_{A0}(1-x)N_{Z0}(\theta_B - 2x)}{V}(-\Delta H_{Rx})$$

$$= 0.0001167\left[\frac{9.04^2(1-.38)(\theta_B - 2*.38)}{5.119}\right]2.34*10^6$$

$$= 77844 \text{ BTU/min.}$$

Adiabatic operation for 10 min. UA = 0

After 10 minutes

x = 0.385, T = 184°C

Q_g = 10000 BTU/min.

When we restart the cooling flow rate

$Q_{r_{max}}$ = 21,300 BTU/min.

Temperature will drop to 175°C

No explosion

P9-2 (c) Example 9-3

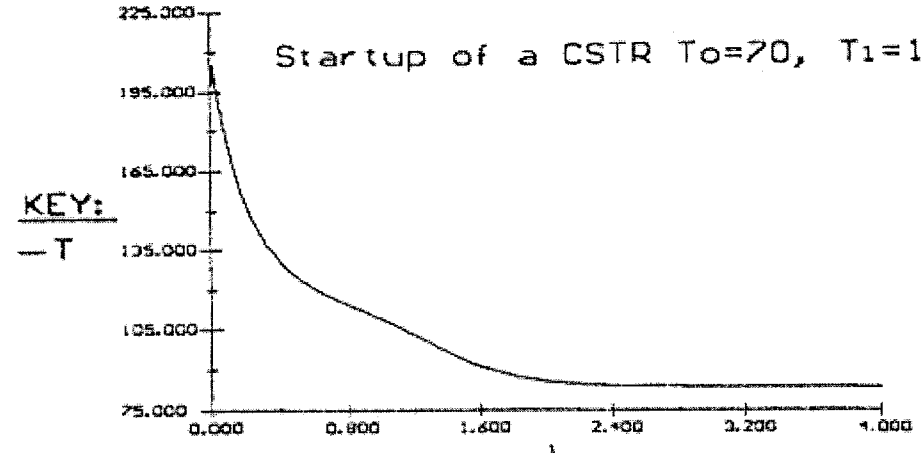
Decreasing the electric heating rate (Tedot in polymath program from example 9-3) by a factor of 10 gives a conversion of 9.72 % at the onset temperature. For a decrease by a factor 10 the conversion is 2.49 %. The higher conversion of a lower heating rate is logical since the time it takes to reach the onset temperature is longer and the reactants have a longer time to react.

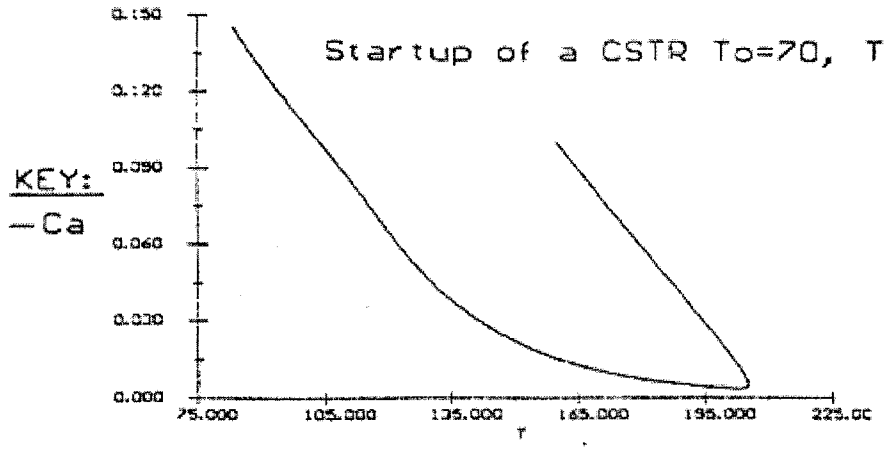
P9-2 (d) Example 9-4

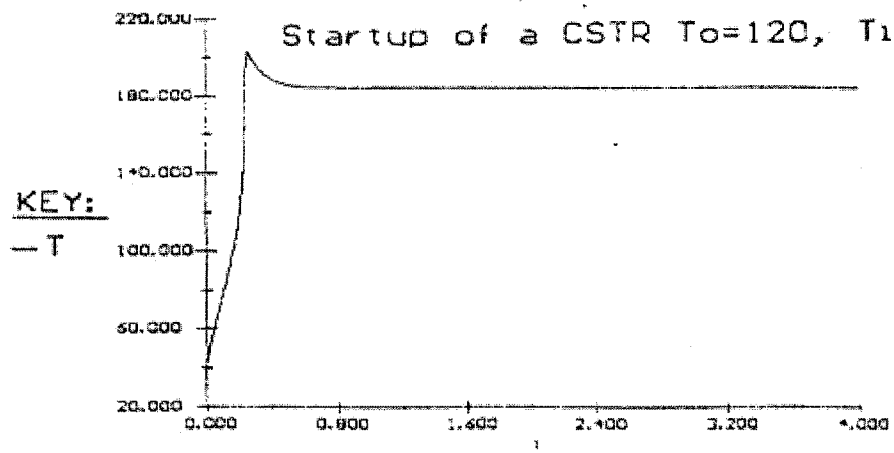
Decreasing the coolant rate to 10 kg/s gives a weak cooling effect and the maximum temperature in the reactor becomes 315 K. An increase of the coolant rate to 1000 kg/s gives a T_{max} of 312 K. A big change to the coolant rate has, in this case, only a small effect on the temperature, and because the temperature does not change significantly the conversion will be kept about the same.

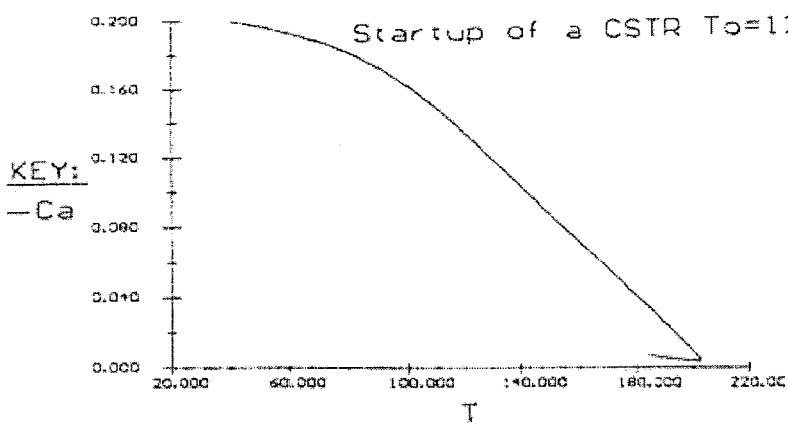
P9-2 (e) Example 9-5

Using the same code as seen in Example 9-4, we were able to change the various parameters. The two graphs we have show T_0 = 70 and 120°C, T_i = 160 and 40°C, and C_{ai} = .1 and .2. Each set of parameters had a Temperature time trajectory and a temperature-concentration phase plane. These are the four graphs.


Startup of a CSTR To=70, T1=160, Ca1=.1
KEY:
—T
225.000
195.000
165.000
135.000
105.000
75.000
0.000
0.800
1.600
2.400
3.200
4.000
t

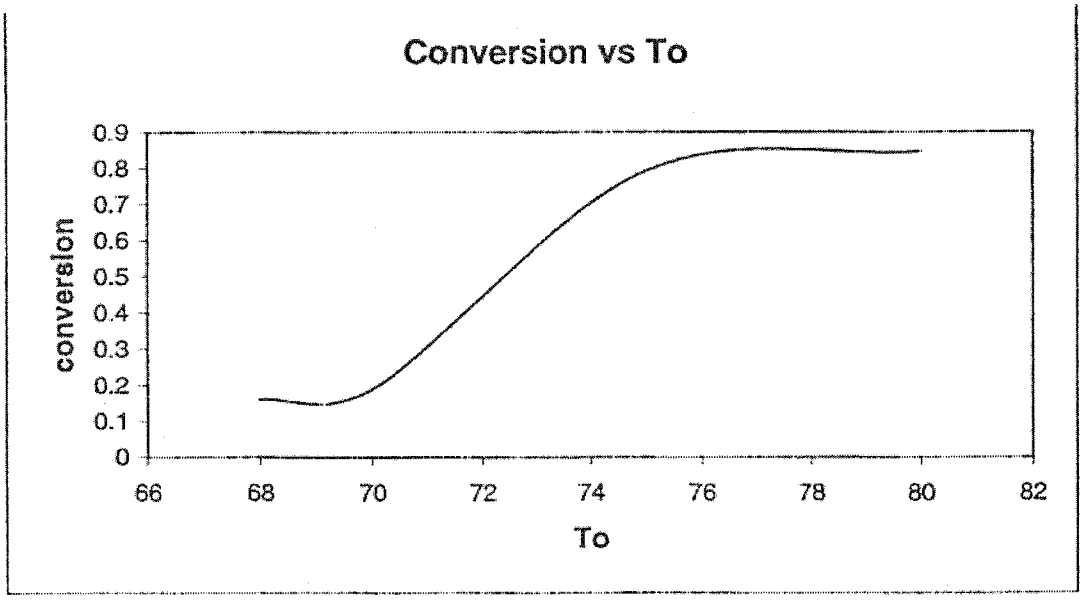

Startup of a CSTR To=70, T1=160, Ca1=.1
KEY:
—Ca
0.150
0.120
0.090
0.060
0.030
0.000
75.000
105.000
135.000
165.000
195.000
225.00
T

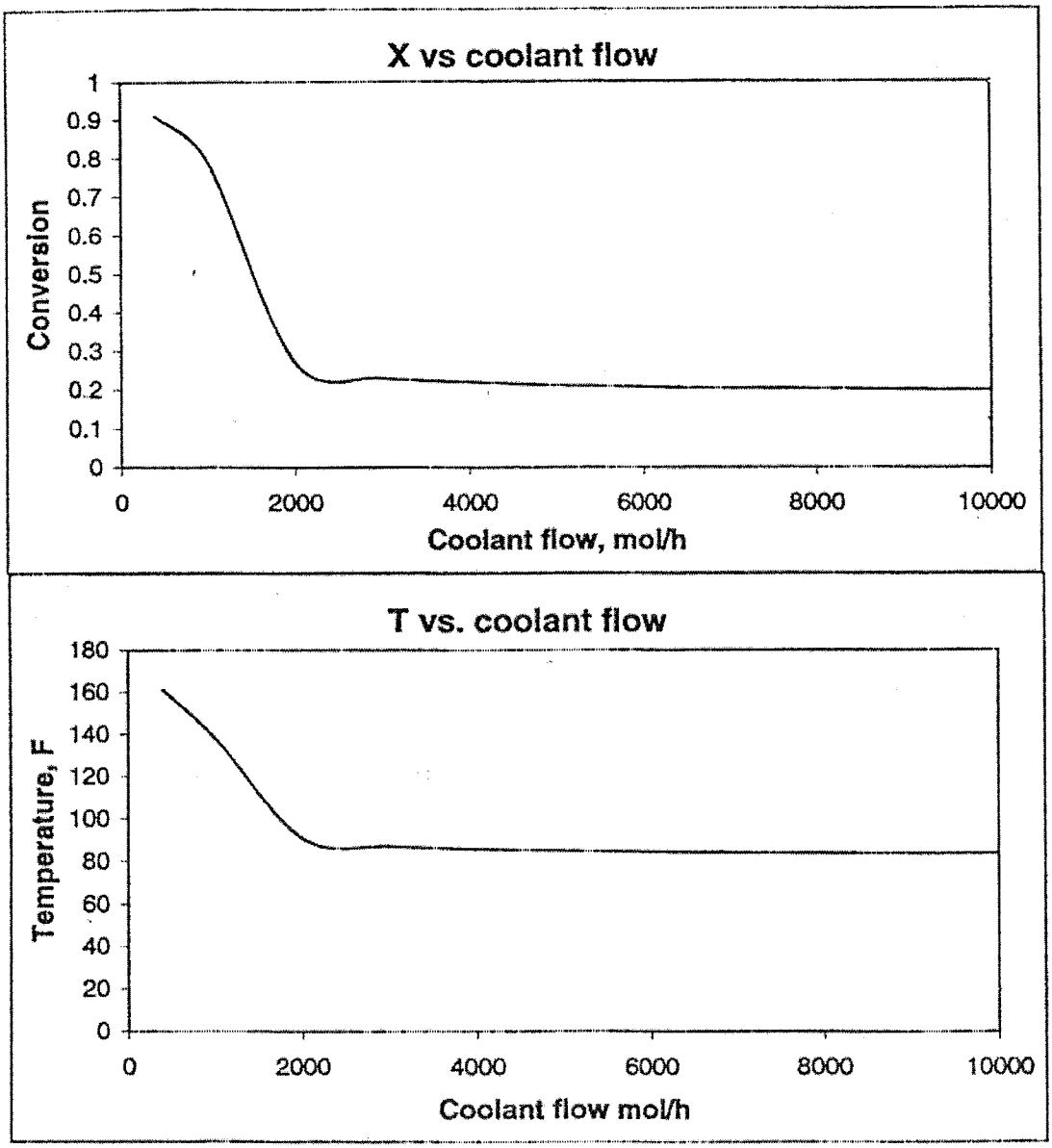

Startup of a CSTR To=120, T1=40, Ca1=.2
KEY:
—T
220.000
180.000
140.000
100.000
60.000
20.000
0.000
0.800
1.600
2.400
3.200
4.000
t



P9-2 (f) Example 9-6

Using the code from Example 9-5, we could produce the following graphs either by changing T_O and finding the steady state conversion or changing the coolant flow rate and finding the steady state conversion and temperature. These are the graphs of those:





P9-2 (g) Example 9-7

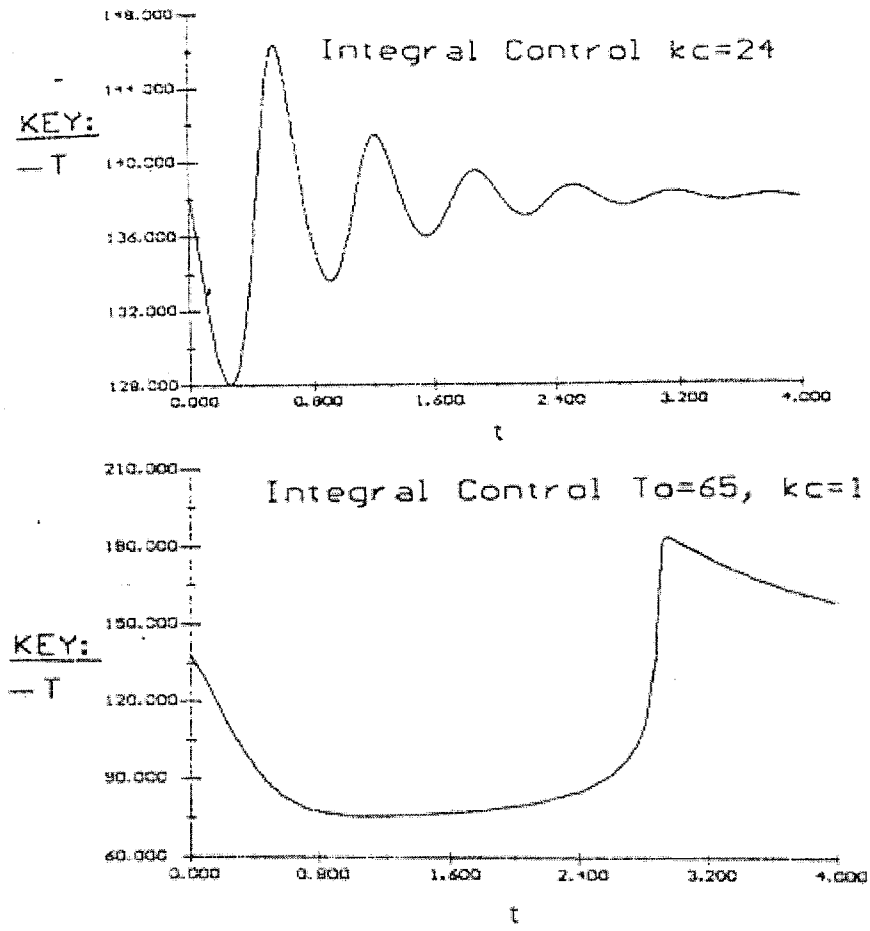
The temperature trajectory changes significantly. Instead of a maximum in temperature, there is now a minimum.

The concentration profiles also change. C_B no longer goes through a maximum and C_C does not rise above 0. It also appears that there is no maximum for C_A.

It appears that because the reactor is kept much cooler with the increase heat transfer and lower coolant temperature the second reaction does not occur.

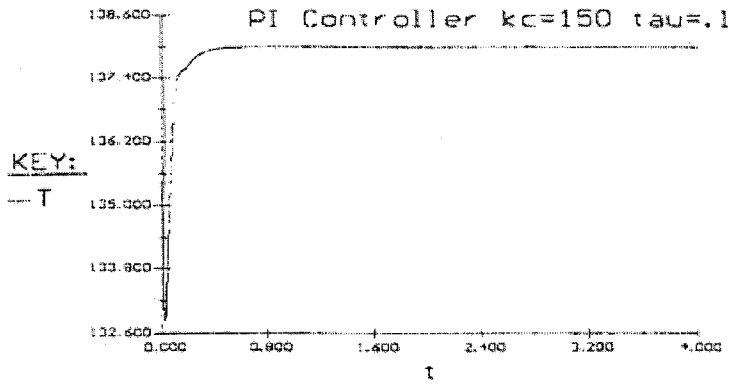
P9-2 (h) Example RE9-1

Using the code from Example RE9-1 , we can determine the value of k_c for which the reactor will fall to the lower steady-state and when it becomes unstable. The following two graphs show those points when k_c = .2 and 24 respectively. The third graph shows what happens when $T_0 = 65$. It becomes unstable at a much lower temperature.



P9-2 (i) Example RE9-2

Using the code from Example RE9-2 , we can change the values of k_c and τ_I and find values that produce the lowest oscillations and the quickest return to steady-state and getting $k_c = 150$ and $\tau_I = .1$. The following graph shows the result.



P9-2 (j) No solution will be given

P9-3

Find time to explosion

For the unsteady-state, we assume the following:

(i) The inlet is closed, but the outlet is not closed

(ii) Operation is adiabatic, and PV terms are negligible so that H ≈ U

Equation 8-61 reduces to:

$$(-\Delta H_R)(-r_A V) = N_A C_{pA} \frac{dT}{dt}$$

$$(-\Delta H_R)(kN_A) = N_A C_{pA} \frac{dT}{dt}$$

$$\frac{dT}{dt} = \frac{\Delta H_{Rxn}}{C_{pA}} k(T)$$

$$k = .53 \exp\left(44499\left(\frac{1}{970} - \frac{1}{T}\right)\right) / 60 \text{ min.}$$

See Polymath program P9-3.pol

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	2.9	2.9
T	970	970	1.119E+23	1.119E+23
dH	-336	-336	-336	-336
Cpa	0.38	0.38	0.38	0.38
k	0.53	0.53	4.438E+19	4.438E+19

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(T)/d(t) = -dH*k/Cpa

Explicit equations as entered by the user
[1] dH = -336
[2] Cpa = .38
[3] k = .53*exp(44498*(1/970-1/T))

P9-4

Mole balance:

$$F_{A0} - F_A + Vr_A = \frac{dN_A}{dt}$$

$$F_{B0} - F_B + Vr_B = \frac{dN_B}{dt}$$

$$F_{C0} - F_C + Vr_C = \frac{dN_C}{dt}$$

There is no A leaving the reactor so $F_A = 0$. There is no B or C entering the reactor so F_{B0} and $F_{C0} = 0$. The amount of B and C leaving is equal to the reaction rate so $F_B = Vr_B$ and $F_C = Vr_C$. Simplifying:

$$F_{A0} + Vr_A = \frac{dN_A}{dt}$$

$$\frac{dN_B}{dt} = 0$$

$$\frac{dN_C}{dt} = 0$$

Rate law:

$$r_A = -kC_A$$

- Stoichiometry:

$$C_A = \frac{N_A}{V}$$

Simplifying:

$$r_A V = kN_A$$

Energy balance:

$$\frac{dT}{dt} = \frac{r_A V \Delta H_{rx} - F_{A0} C_{pA}(T_0 - T)}{N_A C_{pA}}$$

Evaluate the parameters:

$$\ln\left(\frac{.19}{.32}\right) = \frac{E}{R}\left(\frac{1}{800} - \frac{1}{400}\right)$$

$$E = 3467$$

$$k = .19\exp\left[\frac{3467}{8.314}\left(\frac{1}{400} - \frac{1}{T}\right)\right]$$

$$\Delta H(400) = -8kj/mol = \Delta H(800) = \Delta H(1200) = \Delta H(T)$$

Assume a heat capacity for A of 20 J/molK and assume there is no A already in the reactor. We can plug these equations into POLYMATH and get this answer.

See Polymath program P9-4.pol

POLYMATH Results

No Title 08-11-2005, Rev5 1.233

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	100	100
Na	1.0E-09	1.0E-09	326.10947	312.51175
T	400	400	801.376	800
Fao	100	100	100	100
dHr	-8000	-8000	-8000	-8000
Cpa	20	20	20	20

To	400	400	400	400
k	0.19	0.19	0.3202745	0.319988
Vra	-1.9E-10	-101.76832	-1.9E-10	-100

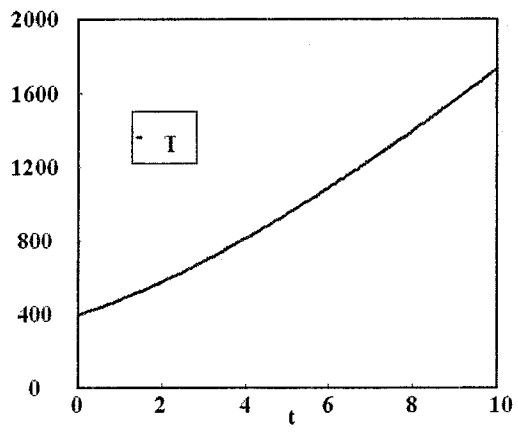
ODE Report (STIFF)

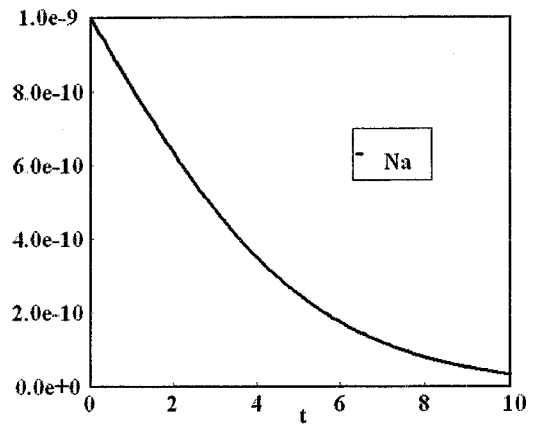
Differential equations as entered by the user
[1] d(Na)/d(t) = Fao+Vra
[2] d(T)/d(t) = ((Vra*dHr)-Fao*Cpa*(T-To))/(Na*Cpa)

Explicit equations as entered by the user
[1] Fao = 100
[2] dHr = -8000
[3] Cpa = 20
[4] To = 400
[5] k = .19*exp(3467/8.314*(1/400-1/T))
[6] Vra = -k*Na

$N_A = 326.125$

When the flow is turned off, $F_{A0} = 0$ and we get this graph of T and N_A.





P9-5 (a)

Mole balance :

$$\frac{dNa}{dt} = r_a.V \qquad \frac{dNb}{dt} = r_a.V + Fbo \qquad \frac{dNc}{dt} = -r_a.V$$

Rate law : $-ra = k(T).Ca.Cb$

Stoichiometry : $Ca = \frac{Na}{V}$ $Cb = \frac{Nb}{V}$ $Cc = \frac{Nc}{V}$

IF (t<50) THEN ($V = V_o + \upsilon.t$) ELSE ($V=V_o + 50$) where $V_0 = 50$ dm^3, $\upsilon = 1$ dm^3/min

Combining :

$$-ra = k(T).\frac{Na}{V}.\frac{Nb}{V}$$

$$k(T) = ko.\exp\left[\frac{E}{R}\left(\frac{1}{To} - \frac{1}{T}\right)\right] \qquad \text{where E = 10000 cal/mol} \quad R = 1.987 \text{ cal/mol.K},$$

ko = 0.01 dm^3/mol.min ,
To = 300 K

Energy balance :

$$\frac{dT}{dt} = \frac{Q - Ws - \sum Fio.Cpi.(T - Tio) + (-\Delta Hrx(T)).(-ra.V)}{\sum Ni.Cpi}$$

where Q = Ws = 0

$\Delta Hrx(T) = \Delta Hrx(Tref) + \Delta Cp(T-Tref)$

$$\Delta Cp = \frac{c}{a}.Cp - \frac{b}{a}.Cpb - Cpa = 30 - 15 - 15 = 0$$

$\Delta Hrx(273) = [(-41)-(-20)-(-15)].10^3 = -6000$ cal/mol

$\Delta Hrx(T) = -6000$ cal/mol

$\sum Fio.Cpi.(T-Tio) = Fbo.(15).(T-323)$

$\sum Ni.Cpi = NaCpa + Nb.Cpb + Nc.Cpc$

$= 15Na + 15Nb + 30Nc$

See Polymath program P9-5-a.pol

POLYMATH Results
08-11-2005, Rev5.1.233

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	120	120
Na	500	0.1396707	500	0.1396707
Nb	0	0	42.43357	0.1397745
Nc	0	0	499.86033	499.86033
T	298	298	510.44411	510.44411
X	0	0	0.9997207	0.9997207
Fbo	10	0	10	0
Nao	500	500	500	500
Cbo	10	10	10	10
k	0.0089352	0.0089352	10.085112	10.085112
vo	1	0	1	0
V	50	50	100	100
ra	0	-0.3365379	0	-1.969E-05

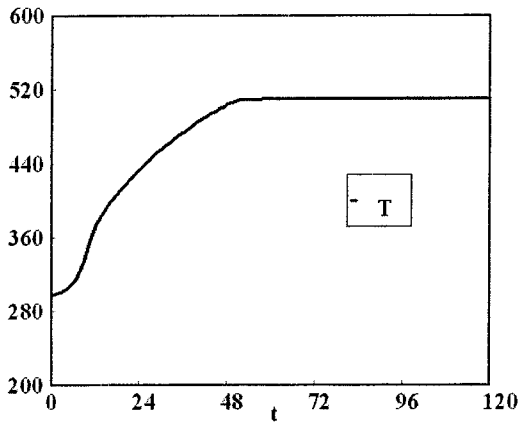
ODE Report (RKF45)

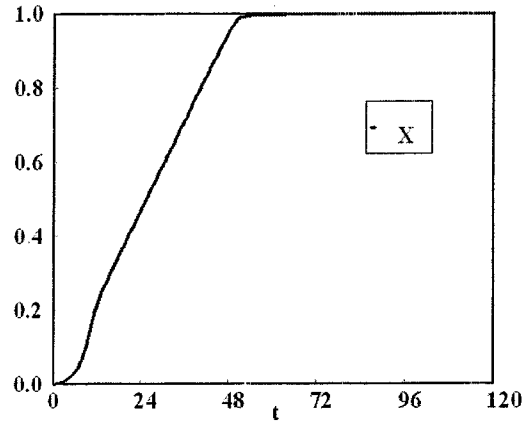
Differential equations as entered by the user

[1] d(Na)/d(t) = ra*V
[2] d(Nb)/d(t) = ra*V+Fbo
[3] d(Nc)/d(t) = -ra*V
[4] d(T)/d(t) = ((6000*(-ra*V))-(Fbo*15*(T-323)))/(15*Na+15*Nb+30*Nc)
[5] d(X)/d(t) = -ra*V/Nao

Explicit equations as entered by the user

[1] Fbo = if(t<50)then(10)else(0)
[2] Nao = 500
[3] Cbo = 10
[4] k = .01*exp((10000/1.987)*(1/300-1/T))
[5] vo = Fbo/Cbo
[6] V = if(t<50)then(50+(vo*t))else(100)
[7] ra = -k*Na*Nb/(V^2)





P9-5 (b)

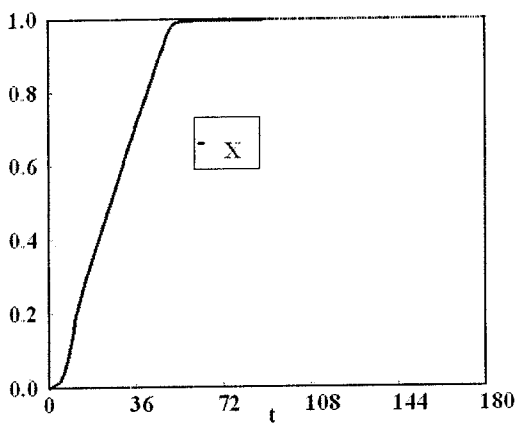
This is the same as part (a) except the energy balance.

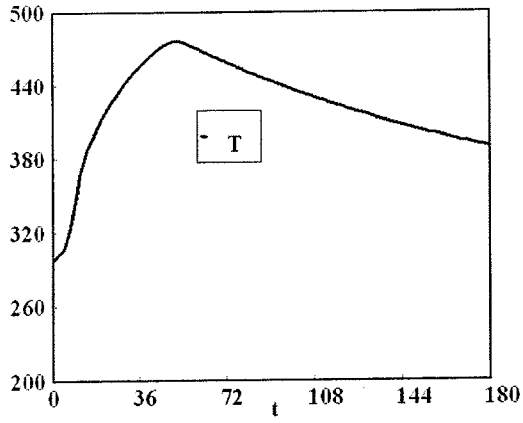
Energy balance :

$$\frac{dT}{dt} = \frac{Q - Ws - \sum Fio.Cpi.(T - Tio) + (-\Delta Hrx(T)).(-ra.V)}{\sum Ni.Cpi}$$

where Q = UA(Ta - T) UA = 100 , Ta = 323

See Polymath program P9-5-b.pol





P9-5 (c)

This is the same as part (b) except the reaction is now reversible.

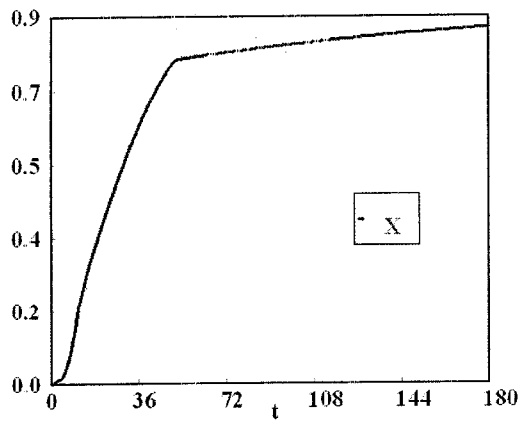
Rate law : $-ra = k1(T).Ca.Cb - k2(T).Cc$

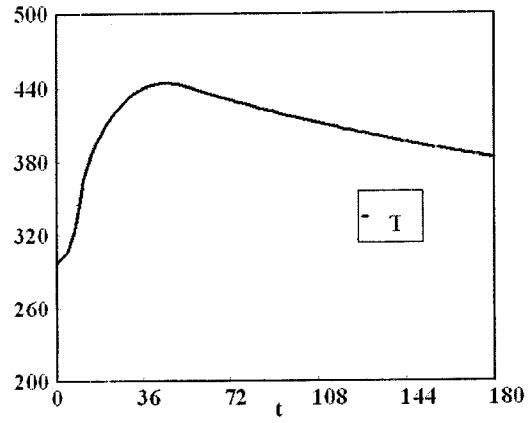
Combining : $$-ra = k1(T).\left(\frac{Na}{V}.\frac{Nb}{V}\right) - k2(T).\left(\frac{Nc}{V}\right)$$

$$k2(T) = ko.\exp\left[\frac{E}{R}\left(\frac{1}{To} - \frac{1}{T}\right)\right]$$ where E = 16000 , R = 1.987 ,

ko = 10 , To = 300

See Polymath program P9-5-c.pol





P9-6 (a)

Mol balance : $$\frac{dNa}{dt} = raV$$

Rate law : $-ra = k.Ca$ But $Ca.V = Na$

$$\frac{dNa}{dt} = -kNa$$

$$\int_{Nao}^{Na} \frac{dNa}{Na} = -k\int_{0}^{t} dt \qquad \ln\frac{Na}{Nao} = -k.t$$

$Na = Nao.e^{-kt}$ where $Nao = 0.5 \times 50 = 25$

Energy balance :

$$\frac{dT}{dt} = \frac{Q - Ws - \sum Fio.Cpi(T - Tio) + (-\Delta Hrx)(-ra.V)}{\sum Ni.Cpi} = 0$$

$Q = Ws = 0$ constant T

$\sum Fi.Cpi(T - Tio) = (-\Delta Hrx)(-ra.V)$

$Fco.Cpc.(T - Tio) = (-\Delta Hrx)(k.Na)$

$= (-\Delta Hrx)(k.Nao.e^{-kt})$

$$Fco = \frac{(-\Delta Hrx).(kNao.e^{-kt})}{Cpc.(T - Tio)}$$

$$= \frac{25000 \times 0.00012 \times 25 \times \exp(-0.00012 \times 2 \times 3600)}{0.5.(100 - 80)}$$

$= 3.16$ lb/s

P9-6 (b)

$\lambda_v = 1000$Btu /lb

$Nao = 25$ lb/mol

$Vo = 300$ ft^3 of which 250 ft^3 is solvent

$$\frac{dT}{dt} = 0$$

Fs. λ_v = = $(-\Delta Hrx)(-ra.V)$

$$Fs = \frac{(-\Delta Hrx).(kNao.e^{-kt})}{\lambda_v} = \frac{25000 \times 0.00012 \times 25 \times \exp(-0.00012 \times 2 \times 3600)}{1000}$$

$Fs = 0.0316$ lb/s

P9-7

Batch problem

Mol balance : $Nao\frac{dX}{dt} = -raV$ $\qquad$ $Cao\frac{dX}{dt} = -ra$

Rate law : $-ra = k1.Ca^{1/2}Cb^{1/2} - k2.Cc$

Stoichiometry : $Ca = Cao(1-X) = 0.1(1-X)$

$Cb = Cao(1.25-X) = 0.1(1.25-X)$

$Cc = Cao(0+X) = 0.1X$

$k1(T) = ko.\exp\left[\frac{E}{R}\left(\frac{1}{To} - \frac{1}{T}\right)\right]$ where E = 100000 J/mol., R = 8.314 J/mol.K ,

ko = 0.002 /s , To = 373 K

$k2(T) = ko.\exp\left[\frac{E}{R}\left(\frac{1}{To} - \frac{1}{T}\right)\right]$ where E = 150000 J/mol., R = 8.314 J/mol.K,

ko = 0.00003 /s, To = 373 K

Energy balance :

$$\frac{dT}{dt} = \frac{(-\Delta Hrx(T)).(-ra.V)}{\sum Ni.Cpi}$$

where $\sum Ni.Cpi = Nao(\sum \theta i Cpi + \Delta CpX)$

$$\Delta Cp = \frac{c}{a}.Cpc - \frac{b}{a}.Cpb - Cpa = 40 - 25 - 25 = -10$$

$$\sum \theta i.Cpi = \frac{Cao}{Cao}.Cpa + \frac{Cbo}{Cao}.Cpb + \frac{Cco}{Cao}.Cpc$$

$$= 25 + {}^{0.125}/_{0.1}\,25 + 0 = 56.25$$

$$\Delta Hrx(T) = \Delta Hrx(Tref) + \Delta Cp(T-Tref)$$

$$= -40000 - 10.(T-298)$$

$$V = \frac{Nao}{Cao}$$

subs $$\frac{dT}{dt} = \frac{[40000 + 10.(T - 298)].\left(-ra.\frac{Nao}{Cao}\right)}{Nao(56.25 - 10X)}$$

cancelling $$\frac{dT}{dt} = \frac{[40000 + 10.(T - 298)].\left(\frac{-ra}{0.1}\right)}{(56.25 - 10X)}$$

See Polymath program P9-7.pol

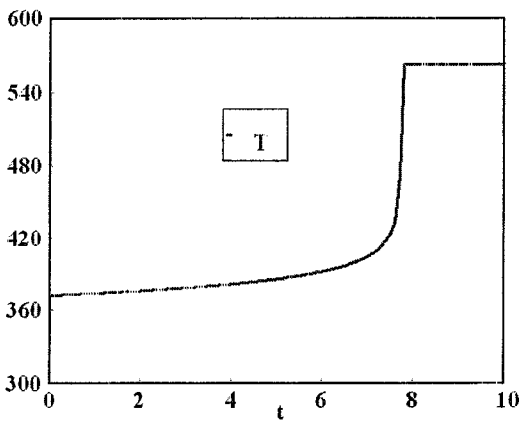
POLYMATH Results
Calculated values of the DEQ variables

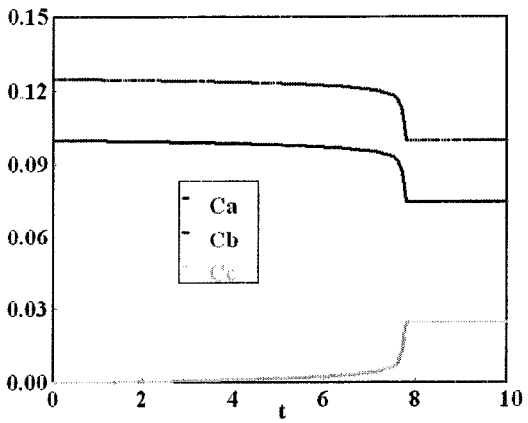
Variable	initial value	minimal value	maximal value	final value
t	0	0	10	10
X	0	0	0.2504829	0.2504829
T	373	373	562.91803	562.91802
k1	0.002	0.002	106.13627	106.13612
Ca	0.1	0.0749517	0.1	0.0749517
Cb	0.125	0.0999517	0.125	0.0999517
k2	3.0E-05	3.0E-05	366.75159	366.75083
Cc	0	0	0.0250483	0.0250483
ra	-2.236E-04	-0.1344598	8.644E-06	1.3E-07

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(X)/d(t) = -ra/.1
[2] d(T)/d(t) = ((40000+(10*(T-298)))*(-ra)*(1/.1))/(56.25-(10*X))

Explicit equations as entered by the user
[1] k1 = .002*exp((100000/8.314)*(1/373-1/T))
[2] Ca = .1*(1-X)
[3] Cb = .1*(1.25-X)
[4] k2 = .00003*exp((150000/8.314)*(1/373-1/T))
[5] Cc = .1*X
[6] ra = -((k1*(Ca^.5)*(Cb^.5))-(k2*Cc))





Check answer : $$\frac{Cc}{\sqrt{Ca}\sqrt{Cb}} = \frac{k1}{k2}$$

$$\frac{0.02504}{\sqrt{0.07495} \times \sqrt{0.09995}} = \frac{1.06}{3.67} = 0.289$$

P9-8 (a)

Use Polymath to solve the differential equations developed from the unsteady state heat and mass balances.
See Polymath program P9-8-a.pol

POLYMATH Results
No Title 08-11-2005, Rev5.1.233

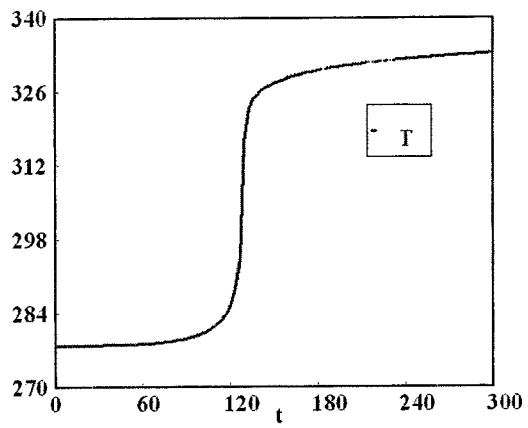
Calculated values of the DEQ variables

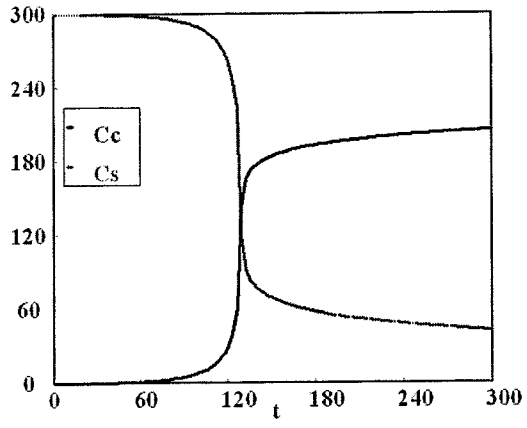
Variable	initial value	minimal value	maximal value	final value
t	0	0	300	300
Cc	0.1	0.1	205.63558	205.63558
Cs	300	43.080524	300	43.080524
T	278	278	333.55016	333.55016
Iprime	0.0866522	6.499E-04	0.3593146	6.499E-04
Km	5	5	5	5
mu1max	0.5	0.5	0.5	0.5
Ycs	0.8	0.8	0.8	0.8
mu	0.0426159	2.912E-04	0.1725264	2.912E-04
Q	0	0	0	0
Cps	74	74	74	74
Hrxn	-2.0E+04	-2.0E+04	-2.0E+04	-2.0E+04
V	25	25	25	25
rho	1000	1000	1000	1000
rg	0.0042616	0.0042616	24.727101	0.0598648
Cpc	74	74	74	74
rs	-0.005327	-30.908876	-0.005327	-0.074831

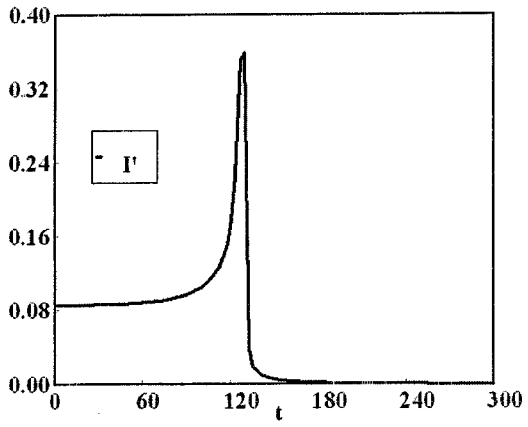
ODE Report (STIFF)

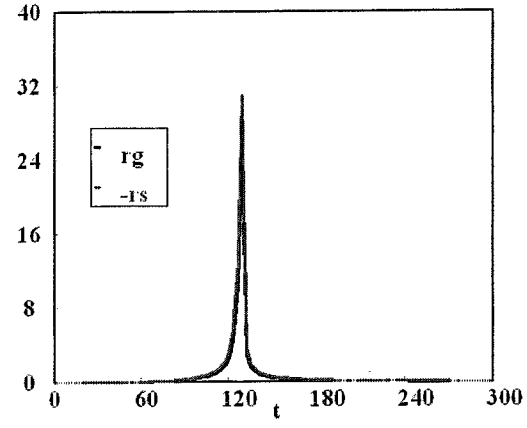
Differential equations as entered by the user
[1] d(Cc)/d(t) = rg
[2] d(Cs)/d(t) = -rg/Ycs
[3] d(T)/d(t) = (Q+(-Hrxn)*(rg))/(rho*Cps)

Explicit equations as entered by the user
[1] Iprime = (0.0038*T*exp(21.6-6700/T))/(1+exp(153-48000/T))
[2] Km = 5.0
[3] mu1max = 0.5
[4] Ycs = 0.8
[5] mu = mu1max*Iprime*(Cs/(Km+Cs))
[6] Q = 0
[7] Cps = 74
[8] Hrxn = -20000
[9] V = 25
[10] rho = 1000
[11] rg = mu*Cc
[12] Cpc = 74
[13] rs = -rg/Ycs



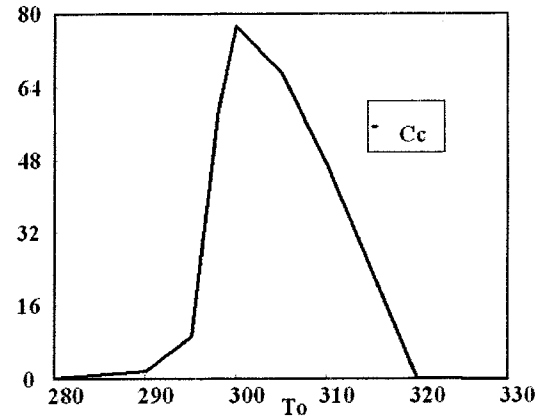






P9-8 (b)

When we change the initial temperature we find that the outlet concentration of species C has a maximum at $T_0 = 300$



P9-8 (c)

Cc can be maximized with respect to T_0 (inlet temp), T_a (coolant/heating temperature), and heat exchanger area. Therefore, if we are to find the optimal heat exchanger area the inlet temperature and coolant/heating temperature needs to be specified. If we take $T_0 = 310$ and $T_a = 290$ we find that the optimal heat exchanger area is an infinite amount of area. As A increases Cc increase without a maximum in 24 hours. Cc = 118.

P9-9

First order liquid phase, CSTR

First solve the steady state problem for the heat exchange area A for normal operation T = 358 K.

Mol balance : $\frac{(C_{AO} - C_A)}{\tau} + r_A = \frac{dC_A}{dt} = 0$ $\qquad$ $\frac{C_B}{\tau} - r_A V = \frac{dC_B}{dt} = 0$

$$Ln\left(\frac{k1}{k2}\right) = \frac{E}{R.T2} - \frac{E}{R.T1}$$

$$E = \frac{Ln\left(\frac{k1}{k2}\right)}{\frac{1}{R.T2} - \frac{1}{R.T1}} = \frac{Ln\left(\frac{1.1}{3.4}\right)}{\frac{1}{8.314(323)} - \frac{1}{8.314(313)}}$$

$$94852 = \text{J/ mol K}$$

$$k = 1.1\exp\left[\frac{94852}{8.314}\left(\frac{1}{313} - \frac{1}{T}\right)\right] = 107.4 \text{ /min} \quad \text{for T} = 358 \text{ K}$$

Steady state solution :

$$\upsilon_o = \frac{F_{AO}}{C_{AO}} = \frac{90000}{90 * 2} = 500 dm^3 / \text{min}$$

$$\tau = \frac{V}{\upsilon} = \frac{200}{500} = 0.4 / \text{min}$$

$C_{AO} = 2\text{ M} = 2*90 = 180 \text{ g/dm}^3$

$C_A = C_{AO} + r_A \tau = 180 + 0.4\, r_A$

$C_B = - r_A \tau = - 0.4\, r_A$

$- r_A = k.C_A$

$C_A = 180 - 107.4\,(0.4)\,C_A$

$$C_A = \frac{180}{1 + (0.4 * 107.4)} = 4.1 g / dm^3$$

$r_A = - 107.4 * 4.1 = - 440 \text{ g/min.dm}^3$

$$C_B = -(-440)\,0.4 = 175.9\ g/dm^3$$

Energy balance :
$$\frac{dT}{dt} = \frac{Q - Ws - \sum Fio.Cpi(T - Tio) + (-\Delta Hrx)(-ra.V)}{\sum Ni.Cpi} = 0$$

$$Q = UA(Ta - T) = (120*60)A(273 - T) \qquad J/min$$

$$F_{AO}.C_{pA}.(T - T_{AO}) = 90000*2*(T - 313) \qquad J/min$$

$$A = \frac{-180000.(358 - 313) + (250)(440x200)}{7200(273 - 358)} = 22.7m^2$$

Use the unsteady state equations to determine what heat exchange area A will give a runaway reaction.

where $\sum Ni.Cpi = Cp_{sol}\,\rho_{sol}\,V = 2 \times 900 \times 200 = 360000\ J/K$

See Polymath program P9-9.pol

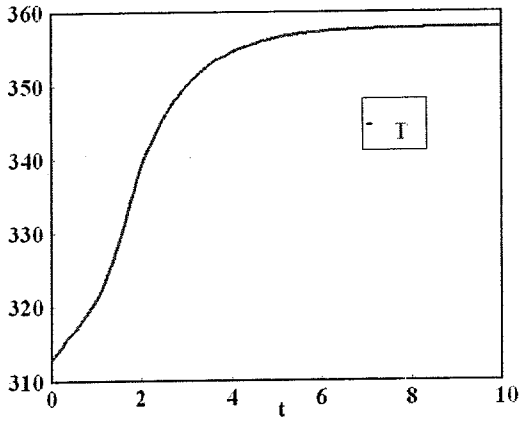
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	10	10
Ca	180	4.1007565	180	4.1007565
Cb	0	0	175.89924	175.89924
T	313	313	357.97719	357.97719
tau	0.4	0.4	0.4	0.4
A	22.696	22.696	22.696	22.696
k	1.1	1.1	107.23721	107.23721
V	200	200	200	200
ra	-198	-439.75367	-198	-439.75367
Na	0.9	0.0205038	0.9	0.0205038
Nb	0	0	0.8794962	0.8794962

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Ca)/d(t) = ((180-Ca)/tau)+ra
[2] d(Cb)/d(t) = -ra-(Cb/tau)
[3] d(T)/d(t) = ((7200*A*(273-T))-(90000*2*(T-313))+((-250)*ra*V))/(2*900*200)

Explicit equations as entered by the user
[1] tau = .4
[2] A = 22.696
[3] k = 1.1*exp(11409*(1/313-1/T))
[4] V = 200
[5] ra = -k*Ca
[6] Na = Ca/V
[7] Nb = Cb/V



A sensitivity analysis for different values of A show that a new steady state is reached at every new A but at an increasingly higher T. The required A depends on the definition of reactor runaway.

P9-10 (a)

$$X = \sum \Theta_i Cp_i [(T - T_0)/(-\Delta H_{Rx})] \qquad (1)$$

X=1 → T=T_f gives

$$1 = \sum \Theta_i Cp_i [(T_f - T_0)/(-\Delta H_{Rx})] \Leftrightarrow$$

$$(T_f - T_0) = \frac{(-\Delta H_{Rx})}{\sum \Theta_i Cp_i}$$

P9-10 (b)

$$C_A = C_{A0}(1 - X) \qquad (2)$$

$$X = \sum \Theta_i Cp_i [(T - T_0)/(-\Delta H_{Rx})]$$

Insert (1) in (2)

$$C_A = C_{A0} - C_{A0} \cdot \frac{\sum \Theta_i Cp_i}{(-\Delta H_{Rx})}(T - T_0) \qquad (3)$$

For X= 1, T_f= T expression (1) becomes

$$-\Delta H_{Rx} = \sum \Theta_i Cp_i \cdot (T - T_0) \Leftrightarrow T_f - T_0 = \frac{-\Delta H_{Rx}}{\sum \Theta_i Cp_i} \qquad (4)$$

Insert the inverse of (4) in (3)

$$C_A = C_{A0} - C_{A0} \cdot \frac{(T - T_0)}{(T_f - T_0)} = \frac{\left[C_{A0}(T_f - T_0) - C_{A0}(T - T_0)\right]}{T_f - T_0} = C_{A0}\left[\frac{T_f - T}{T_f - T_0}\right]$$

$$C_B = C_{A0}(\Theta_B - X) \tag{5}$$

Remember that C_{B0} is not constant here. Similar to C_A, use equations (1) and (4)

$$C_B = C_{B0} - C_{A0} \cdot \frac{\sum \Theta_i Cp_i}{(-\Delta H_{Rx})} \cdot (T - T_0) = C_{B0} - C_{A0} \cdot \frac{(T - T_0)}{(T_f - T_0)} = C_{B0} \cdot \Theta_B \cdot \frac{(T - T_0)}{(T_f - T_0)} - C_{A0} \cdot \frac{(T - T_0)}{(T_f - T_0)} =$$

$$C_{A0}\left[\frac{\Theta_B \cdot T_f - T + (T_0 - \Theta_B \cdot T_0)}{T_f - T_0}\right]$$

For developing $-r_A$ use

$$C_A = C_{A0} \cdot \left[\frac{T_f - T}{T_f - T_0}\right] \tag{6}$$

$$C_B = C_{A0}\left[\frac{\Theta_B \cdot T_f - T + (T_0 - \Theta_B \cdot T_0)}{T_f - T_0}\right] \tag{7}$$

$$-r_A = k \cdot C_A^{\alpha} \cdot C_B^{\beta} \tag{8}$$

Insert (7) and (8) in (9)

$$-r_A = k \cdot \left[C_{A0}\left(\frac{T_f - T}{T_f - T_0}\right)\right]^{\alpha} \cdot \left[C_{A0}\left(\frac{\Theta_B \cdot T_f - T + (T_0 - \Theta_B \cdot T_0)}{T_f - T_0}\right)\right]^{\beta} =$$

$$k \cdot {C_{A0}}^{\alpha} \cdot \frac{(T_f - T)^{\alpha}}{(T_f - T_0)^{\alpha}} \cdot {C_{A0}}^{\beta} \cdot \frac{(\Theta_B \cdot T_f - T + (T_0 - \Theta_B \cdot T_0))^{\beta}}{(T_f - T_0)^{\beta}} =$$

$$\frac{k \cdot {C_{A0}}^{\alpha+\beta} \cdot \left[(T_f - T)^{\alpha} \cdot (\Theta_B \cdot T_f - T + (T_0 - \Theta_B \cdot T_0))^{\beta}\right]}{(T_f - T_0)^{\alpha+\beta}}$$

P9-10 (c)

The unsteady energy balance for a batch reactor is showed in equation 9-11.

$$\frac{dT}{dt} = \frac{\dot{Q} + \dot{W}_s + (-\Delta H_{Rx}) \cdot (-r_A \cdot V)}{\sum N_i Cp_i}$$

Adiabatic operation ($\dot{Q}$ =0), neglecting $\dot{W}_s$ and assuming ΔCp=0 gives the following using the expression for $-r_A$:

$$\frac{dT}{dt}=\frac{(-\Delta H_{Rx})}{N_{A0}\sum\Theta_i Cp_i}(-r_A\cdot V)=$$

$$\left[\frac{(-\Delta H_{Rx})}{\sum\Theta_i Cp_i}\right]\cdot\frac{1}{C_{A0}}\cdot\frac{k\cdot C_{A0}{}^{\alpha+\beta}\cdot\left[(T_f-T)^{\alpha}\cdot(\Theta_B\cdot T_f-T+(T_0-\Theta_B\cdot T_0))^{\beta}\right]}{(T_f-T_0)^{\alpha+\beta}}=$$

$$\left[\frac{(-\Delta H_{Rx})}{\sum\Theta_i Cp_i}\right]\frac{k\cdot C_{A0}{}^{\alpha+\beta-1}}{(T_f-T_0)^{\alpha+\beta}}\left[(T_f-T)^{\alpha}\cdot(\Theta_B\cdot T_f-T+(T_0-\Theta_B\cdot T_0))^{\beta}\right]$$

P9-10 (d)

Put $\alpha = 1$, $\beta = 1$, $\Theta_B = 3$ in the equation from part (c)

$$\frac{dT}{dt}=\left[\frac{(-\Delta H_{Rx})}{\sum\Theta_i Cp_i}\right]\frac{k\cdot C_{A0}{}^{1+1-1}}{(T_f-T_0)^{1+1}}\left[(T_f-T)^1\cdot(3\cdot T_f-T+(T_0-3\cdot T_0))^1\right]=$$

$$\left[\frac{(-\Delta H_{Rx})}{\sum\Theta_i Cp_i}\right]\frac{k\cdot C_{A0}}{(T_f-T_0)^2}\left[(T_f-T)\cdot(3\cdot T_f-T-2\cdot T_0)\right]$$

P9-10 (e)

Use the reaction constant expression from the great Swedish chemist Arrhenius and develop expression from 9-10d.

$$\frac{dT}{dt}=\left[\frac{(-\Delta H_{Rx})}{\sum\Theta_i Cp_i}\right]\frac{k\cdot C_{A0}}{(T_f-T_0)^2}\left[(T_f-T)\cdot(3\cdot T_f-T+(T_0-3\cdot T_0))\right]\Leftrightarrow$$

$$\frac{\frac{dT}{dt}}{(T_f-T)\cdot(3\cdot T_f-T+(T_0-3\cdot T_0))}=\frac{C_{A0}}{(T_f-T_0)^2}\cdot k_1\cdot\exp\left[\frac{E}{R\cdot T_1}-\frac{E}{R\cdot T}\right]\Leftrightarrow$$

$$\ln\left(\frac{\frac{dT}{dt}}{(T_f-T)\cdot(3\cdot T_f-T+(T_0-2\cdot T_0))}\right)=\ln\left(\frac{k_1\cdot C_{A0}}{(T_f-T_0)^2}\right)+\frac{E}{R\cdot T_1}-\frac{E}{R\cdot T}$$

P9-10 (f)

First use a plot of T vs. t to get T_0 (329 K) and T_f (439 K). Checking the concentration of species B gives Θ_B=3. Make a table showing t, T, dT/dt, left hand side of equation P9-10.7 and 1/T. Plot left hand side of equation P9-10.7 vs. 1/T in Polymath and use linear regression to get E from the slope and k_1 from the intercept.
Regression equation as shown in Polymath:

$$y = a0 + a1\cdot T_inverse = -8944.2\cdot T_inverse + 17.534$$

Activation energy and Arrhenius constant from slope and intercept:

$$slope = -E/R \Rightarrow E = -8944.2\cdot 8.314 = -74.36 \text{ kJ/mol}$$

$$a0 = 17.534 = \ln\left(\frac{k_1 \cdot C_{A0}}{\left(T_f - T_0\right)^2}\right) + \underbrace{\frac{E}{R \cdot T_0}}_{neglect} = \ln\left(\frac{k_1 \cdot 6.7}{12100}\right) \Rightarrow k_1 = \frac{12100}{6.7} \cdot \exp^{17.534} = 1.298 \bullet 10^{11}$$

P9-10 (g)

Follow the procedure from example 9-3 gives heat of reaction.

X=1 and $T=T_f$ gives

$$-\Delta H_{Rx} = \sum \Theta_i C_{p_i} \cdot (T - T_0) = \left(C_{p_A} + \Theta_B \cdot C_{p_B}\right)\left(T_f - T_0\right)$$

$$= \left(189.7 + 3 \cdot 75.4 \frac{J}{mol \cdot K}\right)(439 - 329K) = -45.75kJ / mol$$

P9-11 (a)

Mol balance : $\frac{dNa}{dt} = raV$ $\qquad Nao\frac{dX}{dt} = -raV$

$\frac{dNb}{dt} = 2.ra.V + Fbo$ $\qquad Fbo = Cbo.\upsilon_o = 4.\upsilon_o$

$\frac{dNc}{dt} = -raV$ $\qquad V = V_o + \upsilon_o .t$

Rate law : $-ra = k.Ca.Cb^2$

$$k(T) = 0.0005 \exp\left[\frac{8000}{1.987}\left(\frac{1}{300} - \frac{1}{T}\right)\right]$$

Stoichiometry : $Ca = \frac{Na}{V}$ $\qquad Cb = \frac{Nb}{V}$ $\qquad Cc = \frac{Nc}{V}$

Energy balance :

$$\frac{dT}{dt} = \frac{Q - Ws - \sum Fio.Cpi.(T - Tio) + (-\Delta Hrx(T)).(-ra.V)}{\sum Ni.Cpi}$$

where $Q = UA.(Ta - T) = 250.(390 - T)$

$Ws = 0$ $\qquad \Delta Hrx(T) = -55000$

$\sum Fio.Cpi = Fbo.Cpb = Cbo.\ \upsilon_o.Cpb = 4*\upsilon_o*20 = 80\upsilon_o$

- $\sum Ni.Cpi = NaCpa + Nb\ Cpb + Nc.Cpc = 35Na + 20Nb + 75Nc$

$$\frac{dT}{dt} = \frac{250.(290 - T) - 80.\upsilon_{..}.(T - 325) + (-55000).(-ra.V)}{35.Na + 20.Nb + 75.Nc}$$

See Polymath program P9-11-a.pol

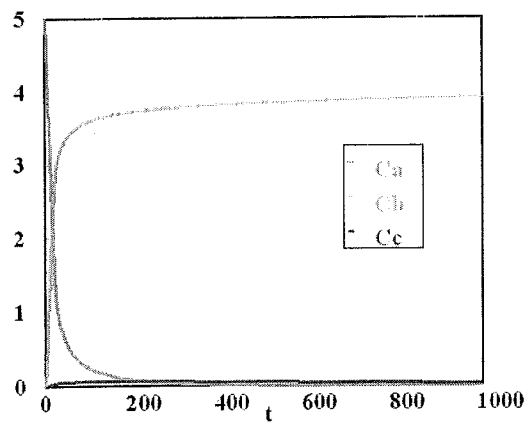
POLYMATH Results
Calculated values of the DEQ variables

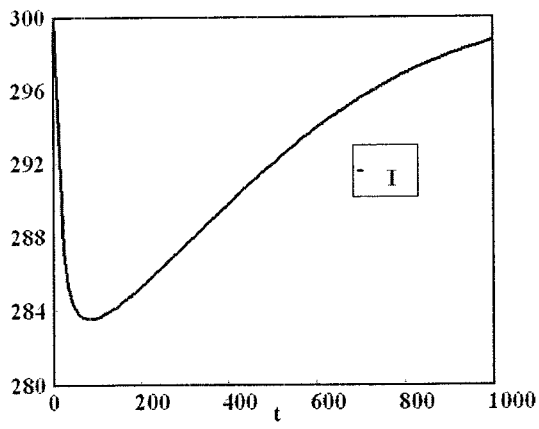
Variable	initial value	minimal value	maximal value	final value
t	0	0	1000	1000
Na	50	0.3324469	50	0.3324469
Nb	0	0	5900.6649	5900.6649
Nc	0	0	49.667553	49.667553
X	0	0	0.9933511	0.9933511
T	300	283.60209	300	298.76383
vb	1.5	1.5	1.5	1.5
k	5.0E-04	2.3E-04	5.0E-04	4.73E-04
V	10	10	1510	1510
Fbo	6	6	6	6
Ca	5	2.202E-04	5	2.202E-04
Cb	0	0	3.9077251	3.9077251
Cc	0	0	0.0718765	0.0328924
ra	0	-0.0028611	0	-1.59E-06

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Na)/d(t) = ra*V
[2] d(Nb)/d(t) = 2*ra*V+Fbo
[3] d(Nc)/d(t) = -ra*V
[4] d(X)/d(t) = -ra*V/50
[5] d(T)/d(t) = ((250*(290-T))-(80*vb*(T-325))+(-55000*(-ra*V)))/(35*Na+20*Nb+75*Nc)

Explicit equations as entered by the user
[1] vb = 1.5
[2] k = .0005*exp((8000/1.987)*(1/300-1/T))
[3] V = 10+(vb*t)
[4] Fbo = 4*vb
[5] Ca = Na/V
[6] Cb = Nb/V
[7] Cc = Nc/V
[8] ra = -k*Ca*Cb^2





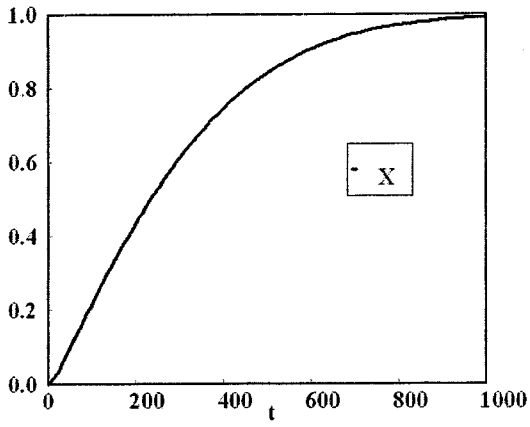


Table 1 Iterating wrt υ_0 for X=0.8 and T<403K and daily Nc = 120 molC

υ_0 dm^3/min	T (X=0.8) K	t (X=0.8) min	Nc (X=0.8) mol	Daily Nc Nc(24*60/t+30) mol
1	289	521	40	104
5	300	262	40	197
2	293	400	40	134
1.5	291	450	40	120

A flowrate of 1.5 mol B/min would produce 120 mol C/ day , with X = 80 % and T<130°C at all times.

P9-11 (b)

If the max. coolant rate falls to 200 mol/min, then it may not be prudent to assume that the coolant leaves at the entering ambient temperature, Ta. It should be assumed that the coolant temperature varies spatially along the heat exchanger pipes and the required term for the heat exchange would be :

$Q = m_c\, Cp_{cool}\, (Ta1 - Ta2)$ where Ta1 = ambient T coolant entering
Ta2 = ambient T coolant leaving

$$Ta2 = T - (T - Ta1).\exp\left(-\frac{UA}{m_c Cp_{coll}}\right)$$

The reduced flowrate and hence heat exchange, may increase the reactor temperature to approaching 130°C, the upper limit, at conversions approaching 80 %, and so more caution is required. The incorporation of temperature control would be prudent.

P9-12

CSTR startup

Need steady-state values at To = 75°F

Mol balance : $\frac{dNa}{dt} = Fao - Fa + ra.V$

$$\frac{dCa}{dt} = \frac{(Cao - Ca).\upsilon_0}{V} + ra$$

$$\frac{dCb}{dt} = \frac{(Cbo - Cb)\upsilon_0}{V} + ra$$

$$\frac{dCc}{dt} = \frac{(Cco - Cc)\upsilon_0}{V} - ra$$

$$\frac{dC_M}{dt} = \frac{(C_{MO} - C_M)\upsilon_0}{V}$$

$$Cio = \frac{Fio}{\upsilon_0} \qquad Cao = \frac{Fao}{\upsilon_0} = 0.18157 \text{ lb mol/ ft}^3$$

$$Cbo = \frac{Fbo}{\upsilon_0} = 2.2696 \text{ lb mol/ ft}^3$$

$$Cco = 0$$

$$C_{MO} = \frac{F_{MO}}{\upsilon_0} = 0.22696 \text{ lb mol/ ft}^3$$

$$V = \frac{1}{7.484} \times 500$$

$$\upsilon_0 = \frac{Fao}{\rho ao} + \frac{Fbo}{\rho bo} + \frac{F_{MO}}{\rho_{MO}} = \frac{80}{0.932} + \frac{1000}{3.45} + \frac{100}{1.54} = 440.6 \text{ ft}^3/\text{ hr}$$

Rate law : $-ra = k.Ca$ (Cb in excess)

$$k = 16.96e12.\exp\left(-\frac{32400}{1.987(T + 460)}\right)$$

Energy balance :

$$\frac{dT}{dt} = \frac{Q - Ws - \sum Fio.Cpi(T - Tio) + (-\Delta Hrx)(-ra.V)}{\sum Ni.Cpi}$$

$$Ws = 0$$

$$Q = m_c.Cp_{cool}.(Ta1 - Ta2) = 1000 \times 18 \times (60 - Ta2)$$

$$\sum Fio.Cpi.(T - Tio) = [Fao.Cpa + Fbo.Cpb + F_Mo.Cp_M].(T - 75)$$

$$\Delta Hrx = -36000 \text{ Btu/lb mol}$$

$$\sum Ni.Cpi = Na.Cpa + Nb.Cpb + Nc.Cpc + N_M.Cp_M$$

$$= 53Ca.V + 18Cb.V + 46Cc.V + 19.5C_M.V$$

$$Ta2 = T - (T - Ta1).\exp\left(-\frac{UA}{m_c Cp_{cool}}\right)$$

$$= T - (T - 60).\exp\left(-\frac{16000}{1000 \times 18}\right)$$

$$Ta2 = T - 0.41111(T - 60)$$

$$\frac{dT}{dt} = \frac{18000(60 - (T - 0.41111(T - 60) - 22750(T - 75) + (36000)(-ra.V)}{35Ca.V + 18Cb.V + 46Cc.V + 19.5C_M.V}$$

Initial conditions : To = 75, T = 138.5 °F, Ca = 0.03780 , Cb = 3.3062 ,
Cc = 0.0144 , C_M = 0.2269 lb mol / ft^3

If To drops from 75 to 70 °F

P9-12 (a)

P-control only : manipulated variable = m_c

controlled variable = T

$$m_c = m_{co} + kc.(T - Tsp)$$ where m_{co} = 1000lb mol/h
Tsp = 138.5 °F
kc = 10

See Polymath program P9-12-a.pol

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	4	4

Ca	0.03789	0.03789	0.0584442	0.053671
Cb	2.12	2.12	2.1423214	2.1376461
Cc	0.143	0.1227539	0.143	0.1275442
Cm	0.2265	0.2265	0.226519	0.226519
T	138.53	125.70694	138.53	128.49299
I	0	-39.636625	0	-39.636625
Fa0	80	80	80	80
T0	70	70	70	70
V	66.809193	66.809193	66.809193	66.809193
Tsp	138.5	138.5	138.5	138.5
UA	1.6E+04	1.6E+04	1.6E+04	1.6E+04
Ta1	60	60	60	60
kc	10	10	10	10
k	24.990212	13.770535	24.990212	15.702753
Fb0	1000	1000	1000	1000
Fm0	100	100	100	100
mc0	1000	1000	1000	1000
ra	-0.9468791	-0.9468791	-0.7913918	-0.8427832
NCp	3372.5882	3372.5882	3385.3399	3383.2355
ThetaCp	284.375	284.375	284.375	284.375
v0	441.46403	441.46403	441.46403	441.46403
Ca0	0.1812152	0.1812152	0.1812152	0.1812152
Cb0	2.2651902	2.2651902	2.2651902	2.2651902
Cm0	0.226519	0.226519	0.226519	0.226519
tau	0.1513355	0.1513355	0.1513355	0.1513355
X	0.7909116	0.6775218	0.7909116	0.703827
mc	1000.3	872.17351	1000.3	899.92991
Ta2	106.23674	102.00022	106.23674	102.98479
Q	8.325E+05	6.594E+05	8.325E+05	6.963E+05

ODE Report (RKF45)

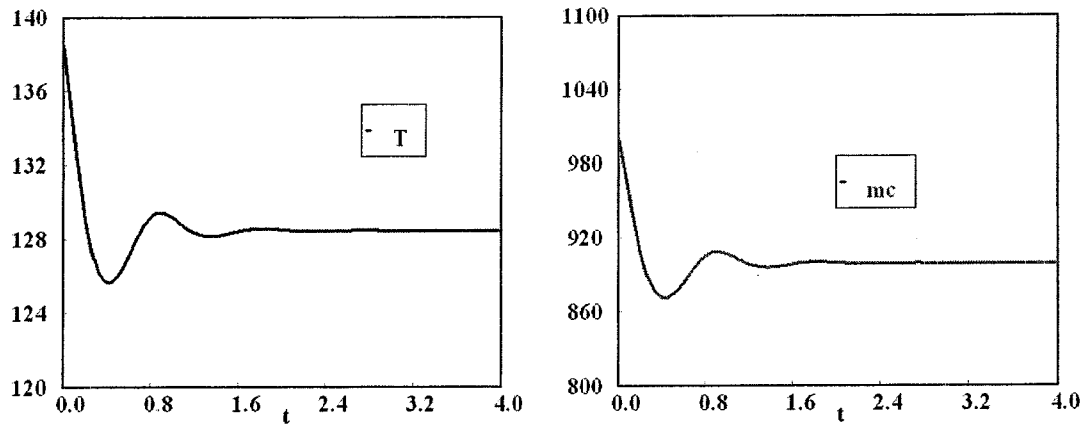
Differential equations as entered by the user

[1] d(Ca)/d(t) = 1/tau*(Ca0-Ca)+ra
[2] d(Cb)/d(t) = 1/tau*(Cb0-Cb)+ra
[3] d(Cc)/d(t) = 1/tau*(0-Cc)-ra
[4] d(Cm)/d(t) = 1/tau*(Cm0-Cm)
[5] d(T)/d(t) = (-Q-Fa0*ThetaCp*(T-T0)+(-36000)*ra*V)/NCp
[6] d(I)/d(t) = T-Tsp

Explicit equations as entered by the user

[1] Fa0 = 80
[2] T0 = 70
[3] V = (1/7.484)*500
[4] Tsp = 138.5
[5] UA = 16000
[6] Ta1 = 60
[7] kc = 10
[8] k = 16.96e12*exp(-32400/1.987/(T+460))
[9] Fb0 = 1000
[10] Fm0 = 100
[11] mc0 = 1000
[12] ra = -k*Ca
[13] NCp = Ca*V*35+Cb*V*18+Cc*V*46+Cm*V*19.5
[14] ThetaCp = 35+Fb0/Fa0*18+Fm0/Fa0*19.5
[15] v0 = Fa0/0.923+Fb0/3.45+Fm0/1.54
[16] Ca0 = Fa0/v0
[17] Cb0 = Fb0/v0
[18] Cm0 = Fm0/v0
[19] tau = V/v0
[20] X = (Ca0-Ca)/Ca0
[21] mc = mc0+kc*(T-Tsp)
[22] Ta2 = T-(T-Ta1)*exp(-UA/(18*mc))

[23] Q = mc*18*(Ta2-Ta1)



P9-12 (b)

I-control only : manipulated variable = m_c

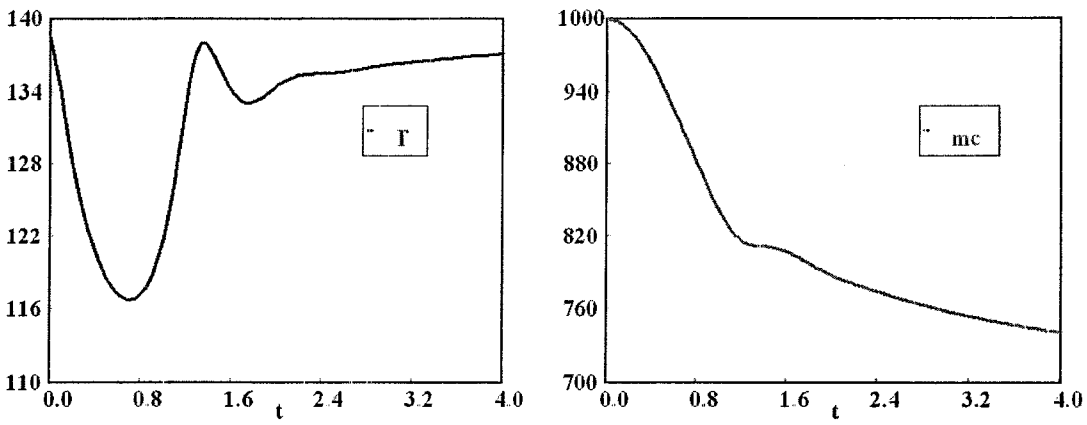
controlled variable = T

$$m_c = m_{co} + \frac{kc}{\tau_I} I$$ where m_{co} = 1000 lb mol/h

kc = 10, τ_I = 1

$$\frac{dI}{dt} = (T - Tsp)$$ Tsp = 138.5 °F

See Polymath program P9-12-b.pol



P9-12 (c)

PI-control only : manipulated variable = m_c

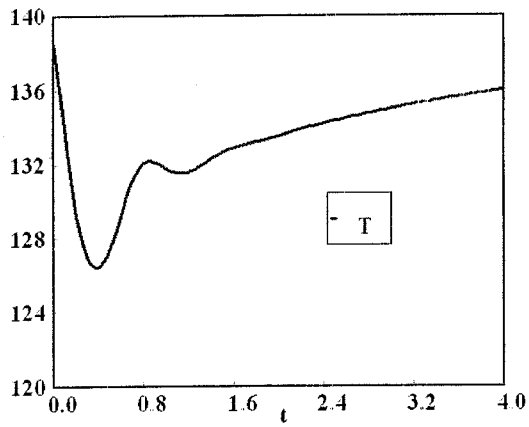
controlled variable = T

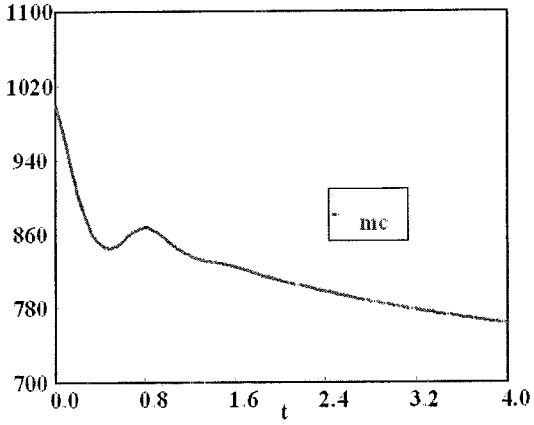
$$m_c = m_{co} + kc(T - Tsp) + \frac{kc}{\tau_I} I$$ where m_{co} = 1000 lb mol/h

kc = 10, τ_i = 1

$$\frac{dI}{dt} = (T - Tsp)$$ Tsp = 138.5 °F

See Polymath program P9-12-c.pol





P9-13

Mol balance : $$\frac{dCa}{dt} = \frac{(Cao - Ca)}{\tau} + ra$$ Cao = 0.1 kmol/m^3

Cao = 0.1 mol/dm^3

$$\frac{dCb}{dt} = \frac{(Cbo - Cb)}{\tau} + ra$$ Cbo = Cao

$$\frac{dCc}{dt} = \frac{(0 - Cc)}{\tau} - ra$$ τ = 50 s

Rate law : $-ra = k.Ca.Cb$

$$k(T) = 0.01 \exp\left[\frac{10000}{1.987}\left(\frac{1}{300} - \frac{1}{T}\right)\right]$$

Energy balance : $$\frac{dT}{dt} = \frac{Q - Ws - \sum Fio.Cpi(T - Tio) + (-\Delta Hrx)(-ra.V)}{\sum Ni.Cpi}$$

$V = \upsilon_o \,.\, \tau = 2 \times 50 = 100 \text{ dm}^3$

$Fao = Cao \,.\, \upsilon_o = 0.1 \times 2 = 0.2 \text{ mol/s} = Fbo$ (equimolar feed)

$\Sigma Fio.Cpi.(T - Tio) = 2 \times 0.2 \times (15)(T - 300) = 6(T - 300)$

$\Delta Hrx(T) = \Delta Hrx(To) + \Delta Cp.(T - To)$ but $\Delta Cp = 0$

$= -41000 - (-20000) - (-15000)$

$= -6000$ cal/mol

$$\frac{dT}{dt} = \frac{6(T - 300) + (6000).(-ra.V)}{15.Ca.v + 15.Cb.V + 30.Cc.V}$$

No control: See Polymath program P9-13-a.pol

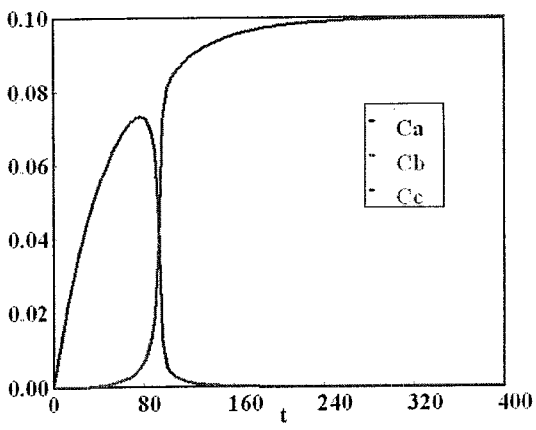
POLYMATH Results
Calculated values of the DEQ variables

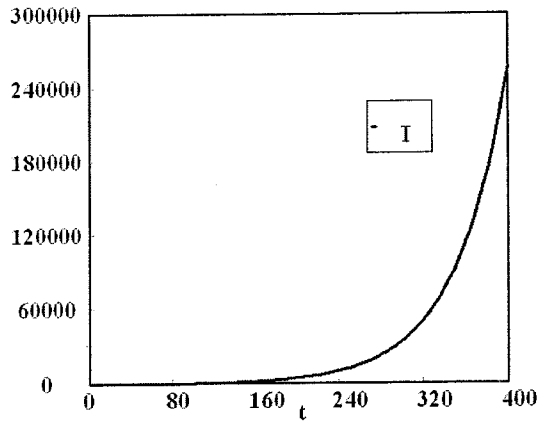
Variable	initial value	minimal value	maximal value	final value
t	0	0	400	400
Ca	0.001	1.027E-04	0.0732572	1.027E-04
Cb	0.001	1.027E-04	0.0732572	1.027E-04
Cc	0	0	0.099864	0.099864
T	300	300	2.574E+05	2.574E+05
V	100	100	100	100
k	0.01	0.01	1.893E+05	1.893E+05
ra	-1.0E-08	-0.0088037	-1.0E-08	-0.001998

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Ca)/d(t) = ((.1-Ca)/50)+ra
[2] d(Cb)/d(t) = ((.1-Cb)/50)+ra
[3] d(Cc)/d(t) = (-Cc/50)-ra
[4] d(T)/d(t) = ((6*(T-300))+(6000*(-ra*V)))/(15*Ca*V+15*Cb*V+30*Cc*V)

Explicit equations as entered by the user
[1] V = 100
[2] k = .01*exp((10000/1.987)*(1/300-1/T))
[3] ra = -k*Ca*Cb





The results without control, indicate a runaway reaction, as T continues to increase after the concentrations have approached their steady-state values

Control aspects : assume that the operating T should not exceed 550K, the boiling point of the liquid.

Without given data for heat exchange :

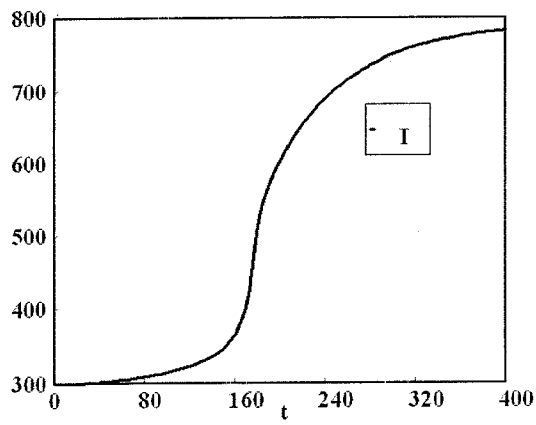
Try manipulated variable = Tio (inlet feed T)
controlled variable = T

P-control : Tio = IF (T<550)THEN (300) ELSE (Tioo + kc.(T - Tsp))

where Tsp = 550 K, Tioo = 300 K, kc = -10

⇒ Tio manipulation not feasible for T control for any kc (requires Tio -- - 2000 K)

See Polymath program P9-13-b.pol

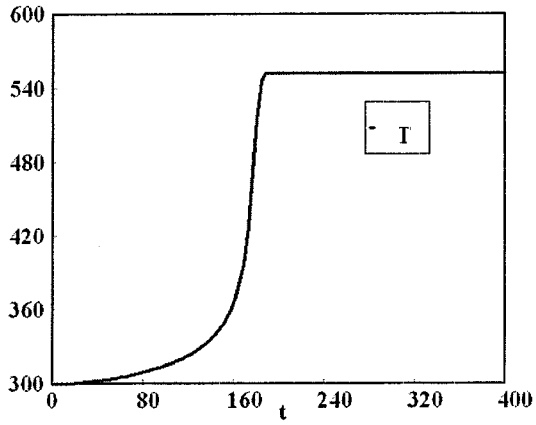


Try manipulated variable = υ_o (inlet volumetric flowrate)
controlled variable = T

P-control : υ_o = IF (T<550) THEN (2) ELSE (υ_{oo} + kc.(T - Tsp))

where Tsp = 550 K, υ_{oo} = 2 dm^3, kc = 10

See Polymath program P9-13-c.pol



P9-14 (a)

CSTR startup

Initial conditions : To = 75, T = 138.5 °F, Ca = 0.03780 , Cb = 2.12 ,
Cc = 0.0144 , C_M = 0.2269 lb mol / ft^3

If T drops from 138.5 to 133.5 °F

As in P9-12_B except :

$$\frac{dCa}{dt} = \frac{Fao - Ca.\upsilon_0}{V} + ra$$

$$\upsilon_0 = \frac{Fao}{0.932} + \frac{1000}{3.45} + \frac{100}{1.54}$$

$$\frac{dT}{dt} = \frac{18000(60 - (T - 0.41111(T - 60) - (35Fao + 19950).(T - 75) + (36000)(-ra.V)}{35Ca.V + 18Cb.V + 46Cc.V + 19.5C_M.V}$$

I-control only : manipulated variable = Fao

controlled variable = T

$Fao = Faoo + \frac{kc}{\tau_I} I$ where Faoo = 80 lb mol/h,

say kc = -0.2 , τ_I = 0.1

$$\frac{dI}{dt} = (T - Tsp) \qquad Tsp = 138.5\ °F$$

See Polymath program P9-14-a pol

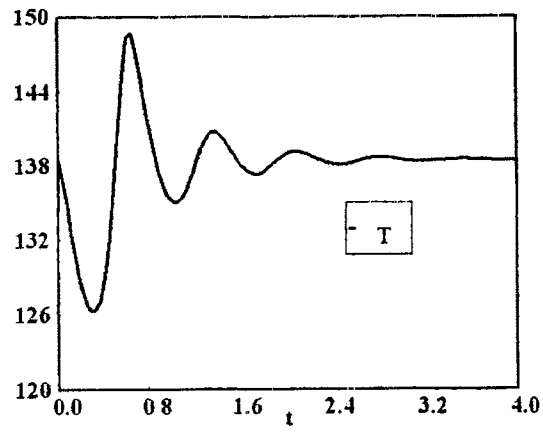
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	4	4
Ca	0.03789	-27.922973	0.0898852	-27 922973
Cb	2.12	2.12	95.168593	95.168593
Cc	0.143	-1.7469378	0.143	-1.7469378
Cm	0.2265	0.2265	9.3421656	9.3421656
T	138.53	17.999228	138.53	17.999228
I	0	-307.34656	0	-307.34656
Fa0o	80	80	80	80
T0	70	70	70	70
V	66.809193	66.809193	66.809193	66.809193
Tsp	138.5	138 5	138 5	138.5
UA	1.6E+04	1.6E+04	1.6E+04	1 6E+04
Ta1	60	60	60	60
kc	0.2	0.2	0.2	0.2
k	24.990212	0.0260082	24.990212	0.0260082
Fb0	1000	1000	1000	1000
Fm0	100	100	100	100
mc0	1000	1000	1000	1000
ra	-0.9468791	-0.9468791	0.723285	0.723285
NCp	3372.5882	3372.5882	5.574E+04	5.574E+04
Fa0	80	-534.4229	80	-534.4229
ThetaCp	284 375	-3993.8255	9.686E+04	-2.3299873
v0	441.46403	-224.21625	441 46403	-224 21625
Cb0	2.2651902	-183.76896	364.28299	-4.45998
Cm0	0.226519	-18 376896	36.428299	-0.445998
tau	0.1513355	-12 277456	24.337453	-0.2979677
Ca0	0.1812152	-118 36922	61.10206	2 3835154
mc	1000	938.55771	1000	938.55771
Ta2	106.24535	34.305432	106.24535	34.305432
Q	8.324E+05	-4.341E+05	8.324E+05	-4.341E+05
X	0.7909116	-65.857622	12.667586	12.667586

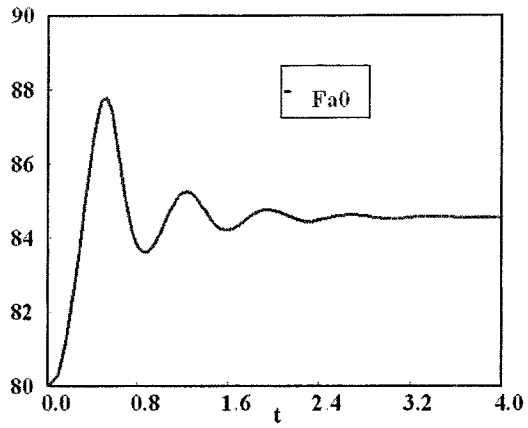
ODE Report (STIFF)

Differential equations as entered by the user
[1] d(Ca)/d(t) = 1/tau*(Ca0-Ca)+ra
[2] d(Cb)/d(t) = 1/tau*(Cb0-Cb)+ra
[3] d(Cc)/d(t) = 1/tau*(0-Cc)-ra
[4] d(Cm)/d(t) = 1/tau*(Cm0-Cm)
[5] d(T)/d(t) = (-Q-Fa0*ThetaCp*(T-T0)+(-36000)*ra*V)/NCp
[6] d(I)/d(t) = T-Tsp

Explicit equations as entered by the user
[1] Fa0o = 80
[2] T0 = 70
[3] V = (1/7 484)*500
[4] Tsp = 138.5
[5] UA = 16000
[6] Ta1 = 60
[7] kc = .2
[8] k = 16 96e12*exp(-32400/1.987/(T+460))
[9] Fb0 = 1000



```
[10] Fm0 = 100
[11] mc0 = 1000
[12] ra = -k*Ca
[13] NCp = Ca*V*35+Cb*V*18+Cc*V*46+Cm*V*19.5
[14] Fa0 = Fa0o+(kc/.1)*I
[15] ThetaCp = 35+Fb0/Fa0*18+Fm0/Fa0*19.5
[16] v0 = Fa0/0.923+Fb0/3.45+Fm0/1.54
[17] Cb0 = Fb0/v0
[18] Cm0 = Fm0/v0
[19] tau = V/v0
[20] Ca0 = Fa0/v0
[21] mc = mc0+kc*I
[22] Ta2 = T-(T-Ta1)*exp(-UA/(18*mc))
[23] Q = mc*18*(Ta2-Ta1)
[24] X = (Ca0-Ca)/Ca0
```



P9-14 (b)

$T_{a1} = 55°F$

I-control only : manipulated variable = T_o

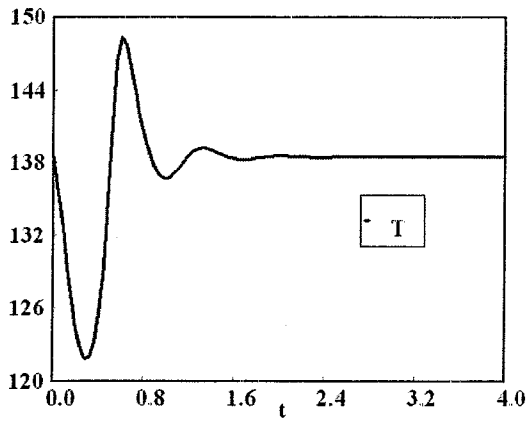
controlled variable = T

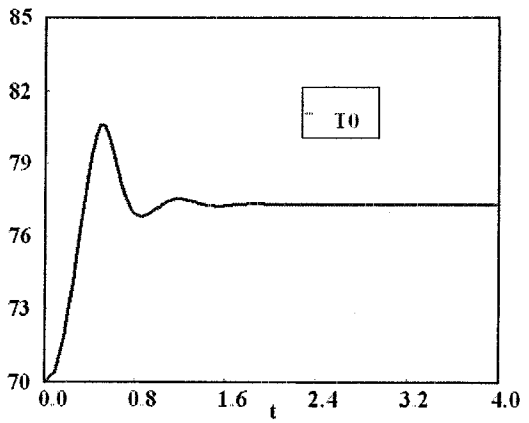
$$To = Too_o + \frac{kc}{\tau_I} I$$ where Too = 75 °F ,

say kc = -0.2 , $\tau_I = 0.1$

$$\frac{dI}{dt} = (T - Tsp)$$ Tsp = 138.5 °F

See Polymath program P9-14-b.pol





P9-14 (c) No solution will be given

P9-15

$$NH_4NO_3 \rightarrow N_2O + 2\,H_2O_g$$

ammonium nitrate	nitrous oxide	steam
A	B	C

Feed , mo = mao + mco = 0.83 mo + 0.17 mo (mco = 17% liquid water in feed)

Mol balance : $\frac{dMa}{dt} = mao - 0 + ra.V$ Ma = lb A, mao = lb/h A

$$\frac{dMb}{dt} = 0 - mb - ra.V$$

leaving : $mb = mao.\left(\theta b + \frac{b}{a}X\right) = mao$; $\theta_b = 0$, b/a = 1

(X = 1, i.e. all of A entering reacts, but there is some initially inside)

$$\frac{dMc}{dt} = mco - mc - 2.ra.V$$

leaving : $mc = mao.\left(\theta c + \frac{c}{a}X\right) = mco + 2mao$; $\theta_c \neq 0$, c/a = 2

assuming all water entering with the ammonium nitrate leaves as steam.

Rate law : -ra.V = k.Ca.V = k.Ma

$$Ln\left(\frac{k1}{k2}\right) = \frac{E}{R.T2} - \frac{E}{R.T1}$$

$$E = \frac{Ln\left(\frac{k1}{k2}\right)}{\frac{1}{R.T2} - \frac{1}{R.T1}} = \frac{Ln\left(\frac{0.53}{5.03}\right)}{\frac{1}{1.987(560+460)} - \frac{1}{1.987(510+460)}}$$

$$= 88500 \text{ Btu /lb mol}$$

$$k = 0.53.\exp\left[\frac{88500}{1.987}\left(\frac{1}{510+460} - \frac{1}{T+460}\right)\right]$$

Energy balance :

$$\frac{dT}{dt} = \frac{Q - Ws - \sum mio.Cpi(T - Tio) - mco.(Hi - Hio) + (-\Delta Hrx)(-ra.V)}{\sum Mi.Cpi}$$

where Ws = 0

Q = UA.(Ta - T)

$$\Sigma mio.Cpi.(T - Tio) = mao.Cpa.(T - Tio)$$
$$= 0.83 \times 310 \times 0.38 \times (T - 200)$$

$$mco.(Hi - Hio) = mco.[H_g(T) - H_l(Tio)]$$
$$= 0.17 \times 310 \times [(1202 + 0.47(T - 500)) - 168]$$

assumes all liquid water in feed leaves as steam.

$$H_g(T) = H_g(Tref) + Cpc.(T - Tref) = 1202 + 0.47.(T - 500)$$
$$H_l(200) = 168 \text{ Btu /lb}$$

$$\Sigma Mi.Cpi = 0.38\ Ma + Cpb.Mb + 0.47\ Mc$$

From ChemCAD III physical properties systems:

$$Cpb\ (N_2O, 516°F) = 1065 \text{ J/kg.K} \left(\frac{1}{1055} Btu\right).\left(0.454 \frac{1}{kg}\right).\left(\frac{516F}{542K}\right)$$
$$= 0.44 \text{ Btu/lb } N_2O.\ K$$

P9-15 (a)

at t = 0 Ca = 500 lb, T = 516 °F

$$\frac{dT}{dt} = \frac{10000.(515 - T) - 97.77(T - 200) - 52.7[(1202 + 0.47(T - 500)) - 168] + 336.(-ra\ V)}{0.38Ma + 0.44.Mb + 0.47Mc}$$

See Polymath program P9-15-a.pol

POLYMATH Results
Calculated values of the DEQ variables

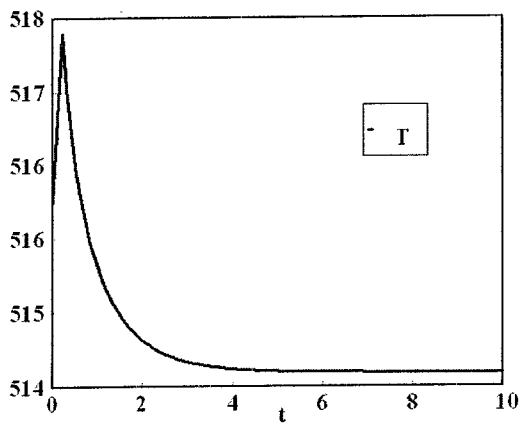
Variable	initial value	minimal value	maximal value	final value
t	0	0	10	10
Ma	500	399.06704	500	399.06704
Mb	0	0	100.93296	100.93296
Mc	0	0	201.86591	201.86591
T	516	514.15817	517.83877	514.15817
mco	52.7	52.7	52.7	52.7
mao	257.3	257.3	257.3	257.3
k	0.7028594	0.6447579	0.7677849	0.6447579
raV	-351.4297	-366.56963	-257.30162	-257.30162
mb	257.3	257.3	257.3	257.3
mc	567.3	567.3	567.3	567.3

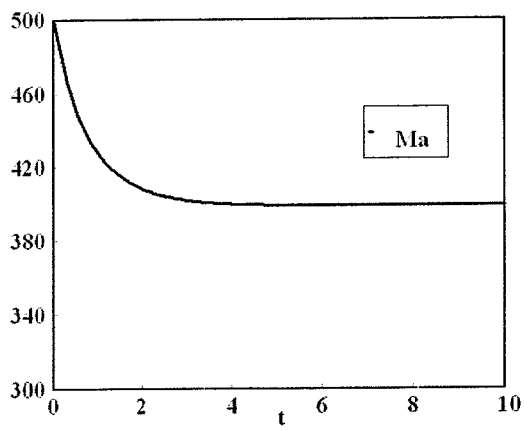
ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Ma)/d(t) = 310*.83+raV
[2] d(Mb)/d(t) = -mb-raV
[3] d(Mc)/d(t) = mco-mc-2*raV
[4] d(T)/d(t) = ((10000*(515-T))-(99.77*(T-200))-(52.7*(1202+(.47*(T-500)))-168)+(336*(-raV)))/(.38*Ma+.44-Mb+.47*Mc)

Explicit equations as entered by the user
[1] mco = 310*.17
[2] mao = 310*.83
[3] k = .53*exp(44540*(1/970-1/(T+460)))

[4] raV = -k*Ma
[5] mb = mao
[6] mc = mco+2*mao





P9-15 (b)

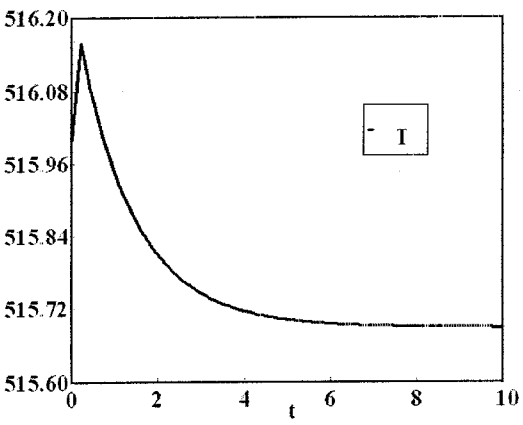
$UA = 10000$ Btu /h.ft^2

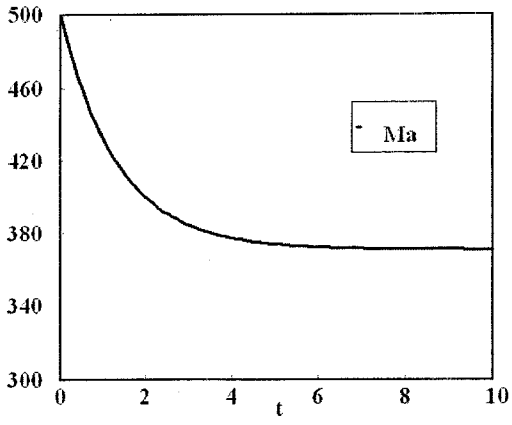
P-control only : manipulated variable = Ta
controlled variable = T

$$Ta = Tao + kc.(T - Tsp)$$

where Tsp = 516 °F, kc = -5, Tao = 975 °R = 515 °F

See Polymath program P9-15-b.pol





P9-15 (c)

UA = 10000 Btu /h.ft^2

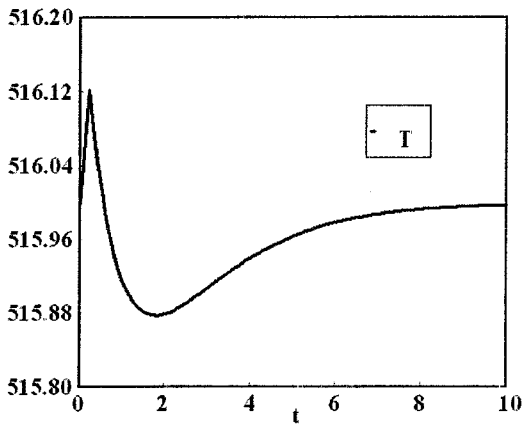
PI-control : manipulated variable = Ta
controlled variable = T

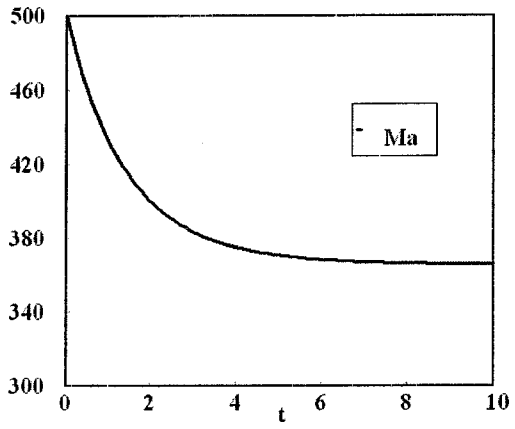
$$Ta = Tao + kc.(T - Tsp) + \frac{kc}{\tau_I}.I$$

$$\frac{dI}{dt} = (T - Tsp)$$

where Tsp = 516 °F, kc = -5, τ_I = 1, Tao = 975 °R = 515 °F

See Polymath program P9-15-c.pol





P9-15 (d)

UA = 10000 Btu /h.ft^2

PI-control loop 1 : manipulated variable = Ta
controlled variable = T

$$Ta = Tao + kc1.(T - Tsp) + \frac{kc1}{\tau_I 1}.I1$$

$$\frac{dI1}{dt} = (T - Tsp)$$

where Tsp = 516 °F, kc1 = -5, τ_I1 = 1, Tao = 975 °R = 515 °F

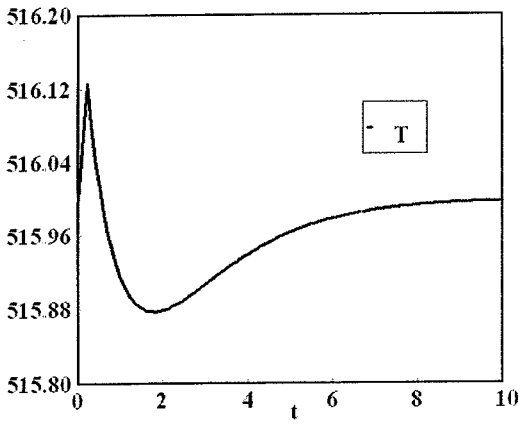
PI-control loop 2 : manipulated variable = mao
controlled variable = M (= Ma + Mb + Mc)

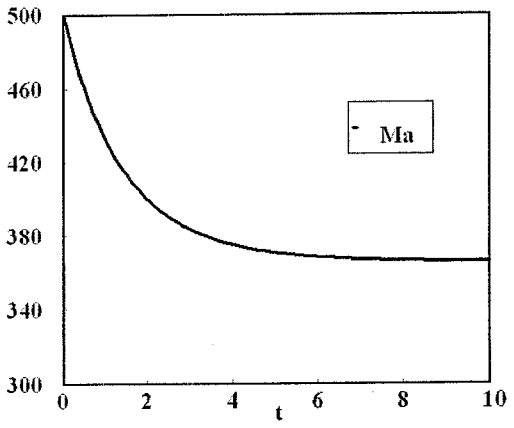
$$mao = maoo + kc2.(M - Msp) + \frac{kc2}{\tau 2}.I2$$

$$\frac{dI2}{dt} = (M - Msp)$$

where Msp = 500 lb, kc2 = 25, $\tau_I 2 = 1$, maoo = 310 lb/h

See Polymath program P9-15-d.pol





P9-16 (a)

Plot R(T) vs G(T):

$$R(T) = UA(T - T_a) + \rho v_0 C_p (T - T_0)$$

$$G(T) = -\Delta H_{Rx} V k C_A$$

Evaluate the parameters in those equations:

$$k = 2 * 7.08 * 10^{11} \exp(-30000/1.987/T)$$

$$\Delta H_{RX} = -30000\, BTU/lbmol$$

$$\rho = 50 lb/ft^3$$

$$UA = 150 * 250 = 37500$$

See Polymath program P9-16-a.pol

POLYMATH Results
Calculated values of the DEQ variables

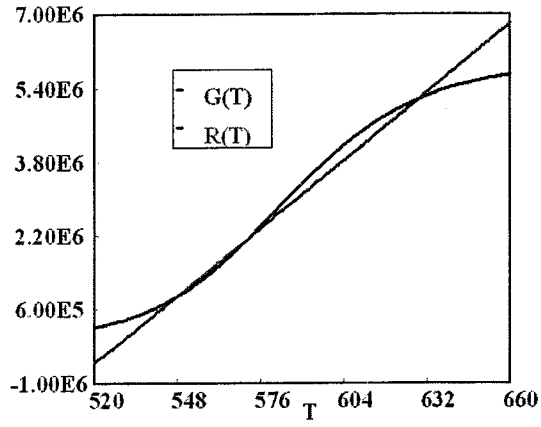
Variable	initial value	minimal value	maximal value	final value
t	0	0	140	140
T	520	520	660	660
dHr	-3.0E+04	-3.0E+04	-3.0E+04	-3.0E+04
V	48	48	48	48
Cao	0.5	0.5	0.5	0.5
vo	400	400	400	400
UA	3.75E+04	3.75E+04	3.75E+04	3.75E+04

Ta	530	530	530	530
rho	50	50	50	50
To	530	530	530	530
E	3.0E+04	3.0E+04	3.0E+04	3.0E+04
k	0.3478362	0.3478362	164.49672	164.49672
tau	0.12	0.12	0.12	0.12
Ca	0.479966	0.0241085	0.479966	0.0241085
Cp	0.75	0.75	0.75	0.75
Gt	2.404E+05	2.404E+05	5.711E+06	5.711E+06
Rt	-5.25E+05	-5.25E+05	6.825E+06	6.825E+06

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(T)/d(t) = 1

Explicit equations as entered by the user
[1] dHr = -30000
[2] V = 48
[3] Cao = .5
[4] vo = 400
[5] UA = 250*150
[6] Ta = 530
[7] rho = 50
[8] To = 530
[9] E = 30000
[10] k = 2*7.08e11*exp(-E/1.987/T)
[11] tau = V/vo
[12] Ca = Cao/(1+tau*k)
[13] Cp = .75
[14] Gt = -dHr*V*k*Ca
[15] Rt = UA*(T-Ta)+rho*vo*Cp*(T-To)



P9-16 (b)

From part (a), we find the concentration and temperatures at the points where G(T) and R(T) intersect.

$C_A = 0.425 \quad T = 547.1°R$

$C_A = 0.319 \quad T = 571.3°R$

$C_A = 0.068 \quad T = 628.6°R$

The extinction temperature is $T_0 = 506°R$. At this point R(T) is tangent to G(T) at the upper steady state.

P9-16 (c)

Using the unsteady-state equations for a CSTR we get the following
Mole balance:

$$\frac{dC_A}{dt} = \frac{v_0(C_{A0} - C_A)}{V} - kC_A$$

Energy balance:

$$\frac{dT}{dt} = \frac{UA(T_a - T) - \rho v_0 C_p(T - T_0) - \Delta H_{Rx} kC_A V}{\rho V C_p}$$

See Polymath program P9-16-c.pol

POLYMATH Report

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	t	0	0	6.	6.
2	Ca	0.0681	0.04847	0.4290427	0.4253139
3	T	628.	542.6046	638.1791	547.0711
4	Ca0	0.5	0.5	0.5	0.5
5	Fa0	200.	200.	200.	200.
6	T0	530.	530.	530.	530.
7	Ar	1.416E+12	1.416E+12	1.416E+12	1.416E+12
8	R	1.987	1.987	1.987	1.987
9	U	150.	150.	150.	150.
10	A	250.	250.	250.	250.
11	v0	400.	400.	400.	400.
12	Ta	530.	530.	530.	530.
13	V	48.	48.	48.	48.
14	E	3.0E+04	3.0E+04	3.0E+04	3.0E+04
15	k	51.27669	1.165967	75.24179	1.463353
16	tau	0.12	0.12	0.12	0.12
17	rA	-3.491943	-3.971954	-0.4433316	-0.6223844
18	delH	-3.0E+04	-3.0E+04	-3.0E+04	-3.0E+04
19	Na0	24.	24.	24.	24.
20	Cpa	75.	75.	75.	75.

Differential equations

1 d(Ca)/d(t) = rA + Ca0 / tau - Ca / tau

2 d(T)/d(t) = (U * A * (Ta - T) - Fa0 * Cpa * (T - T0) + (rA * V) * delH) / (Na0 * Cpa)

Explicit equations

1 Ca0 = 0.5

2 Fa0 = 200

3 T0 = 530

4 Ar = 1.416 * 10 ^ 12

5 R = 1.987

6 U = 150

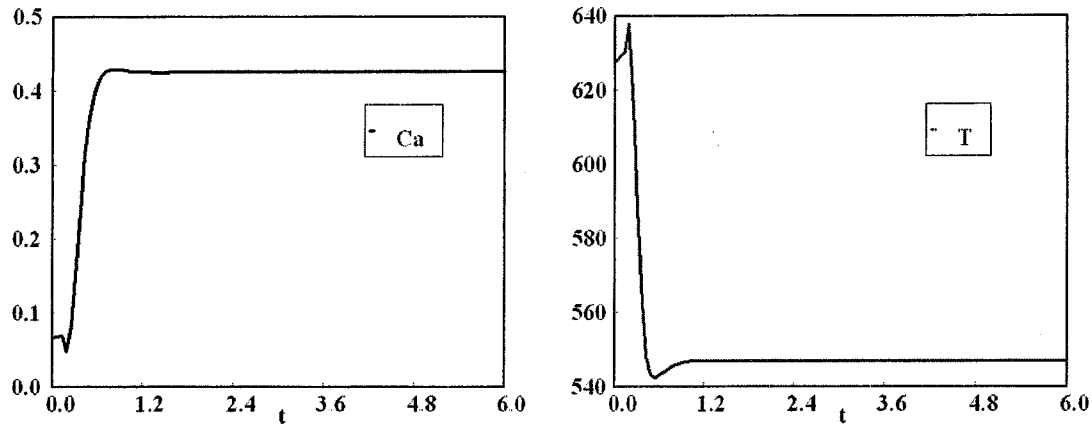
7 A = 250

8 v0 = 400

9 Ta = 530

10 V = 48

```
11 E = 30000
12 k = Ar * exp(-E / R / T)
13 tau = V / v0
14 rA = -k * Ca
15 delH = -30000
16 Na0 = Ca0 * V
17 Cpa = 37.5 * 2
```



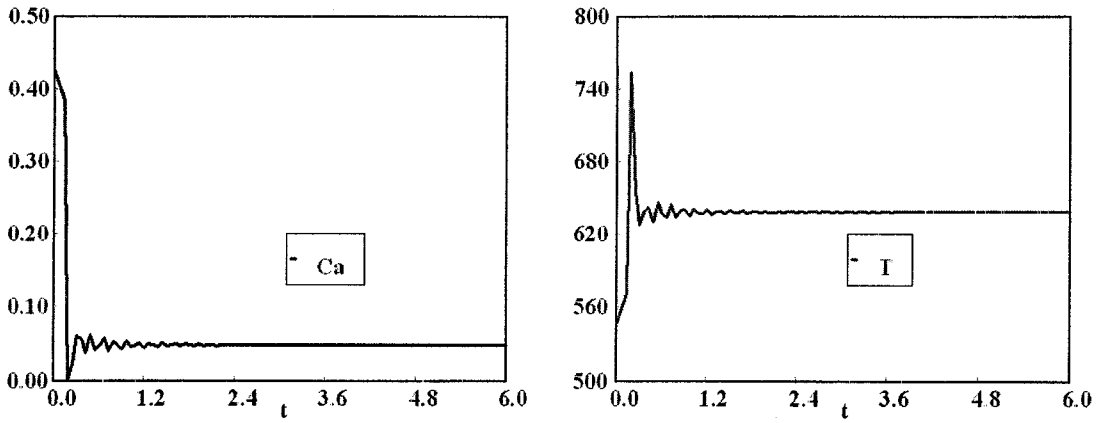
When the upper steady state is used as the initial conditions, the unsteady-state mole balance shows that this steady state is actually unstable. The concentration increases and the temperature drops to the lower stable steady state.

P9-16 (d)

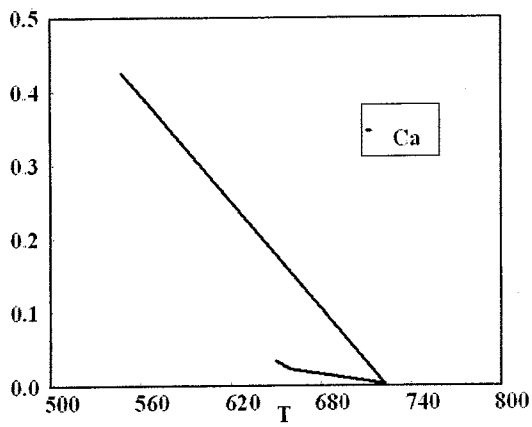
When T_0 or T_a is increases slightly, the upper steady state becomes stable. At these elevated inlet and coolant temperatures, the lower steady state is no longer stable.

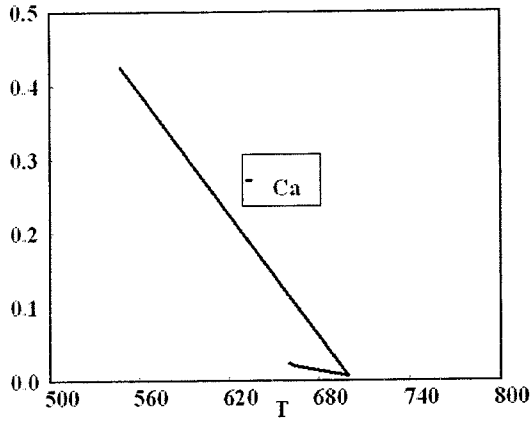
P9-16 (e)

Starting at the lower steady state, if T_0 is increased to 550 °R, the lower steady state is no longer stable, but the upper steady state is



If we plot the concentration-temperature phase-plane trajectory, we see that increasing T_a will shift the trajectory to the left. However, the final steady state is shifted to the right. This means that from the initial conditions, at any temperature C_A is lower for the larger T_a until the minimum in C_A is reached.





P9-16 (f) Individualized solution

P9-16 (g)

The following Polymath program gives the linear analysis of the problem
A = 1.175, B = 6.03, J = 1600, τ = .12

See Polymath program P9-16-g.pol

POLYMATH Report

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	t	0	0	6.	6.
2	y	2.	0.0176788	4.159719	0.0176788
3	x	0.2	-0.0225558	0.2	-0.0001258
4	Ca	0.0681	0.04847	0.4290427	0.4253139
5	T	628.	542.6046	638.1791	547.0711
6	Cpa	75.	75.	75.	75.
7	Ca0	0.5	0.5	0.5	0.5
8	Fa0	200.	200.	200.	200.
9	T0	530.	530.	530.	530.
10	Ar	1.416E+12	1.416E+12	1.416E+12	1.416E+12
11	R	1.987	1.987	1.987	1.987
12	U	150.	150.	150.	150.
13	Area	250.	250.	250.	250.
14	v0	400.	400.	400.	400.
15	Ta	530.	530.	530.	530.
16	V	48.	48.	48.	48.
17	E	3.0E+04	3.0E+04	3.0E+04	3.0E+04
18	k	51.27669	1.165967	75.24179	1.463353
19	tau	0.12	0.12	0.12	0.12

20	rA	-3.491943	-3.971954	-0.4433316	-0.6223844
21	delH	-3.0E+04	-3.0E+04	-3.0E+04	-3.0E+04
22	Na0	24.	24.	24.	24.
23	J	800.	800.	800.	800.
24	C	6.	6.	6.	6.
25	B	6.03	6.03	6.03	6.03
26	A	1.175	1.175	1.175	1.175

Differential equations

1 d(y)/d(t) = (-J * (1 - A) * x + (B - C) * y)

2 d(x)/d(t) = (-A * x - B * y / J) / tau

3 d(Ca)/d(t) = rA + Ca0 / tau - Ca / tau

4 d(T)/d(t) = (U * Area * (Ta - T) - Fa0 * Cpa * (T - T0) + (rA * V) * delH) / (Na0 * Cpa)

Explicit equations

1 Cpa = 37.5 * 2

2 Ca0 = 0.5

3 Fa0 = 200

4 T0 = 530

5 Ar = 1.416 * 10 ^ 12

6 R = 1.987

7 U = 150

8 Area = 250

9 v0 = 400

10 Ta = 530

11 V = 48

12 E = 30000

13 k = Ar * exp(-E / R / T)

14 tau = V / v0

15 rA = -k * Ca

16 delH = -30000

17 Na0 = Ca0 * V

18 J = -delH/Cpa / Ca0

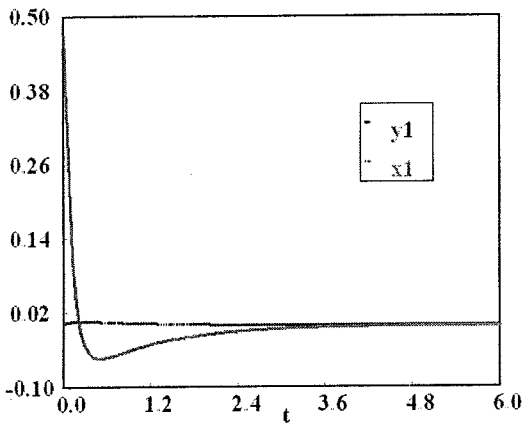
19 C = 6

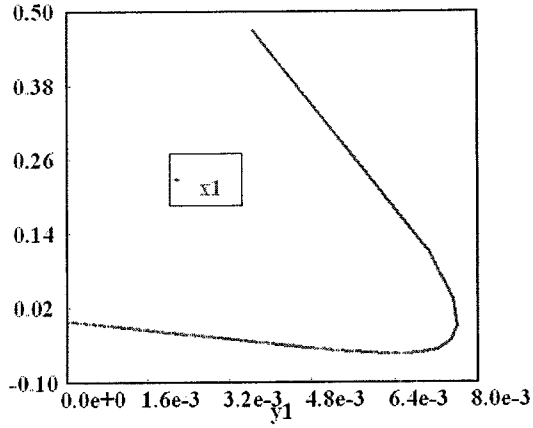
20 B = 6.03

21 A = 1.175

P9-16 (f)

Only the lower steady state plot of x1 and y1 will be shown.





P9-17

Batch reactor - series reaction

Mol balance on A : $\frac{dCa}{dt} = ra1$

$-ra1 = k1.Ca \qquad Ca = Cao.\exp(-k1.t)$

Mol balance on B : $\frac{dCb}{dt} = rb1 + rb2$

$rb1 = -ra1 = k1.Ca \quad \text{and} \quad -rb2 = k2.Cb$

$$\frac{dCb}{dt} = k1.Cao.\exp(-k1.t) - k2Cb$$

Mol balance on C : $\frac{dCc}{dt} = -rb2$

$$k1 = 3.03.\exp\left(\frac{9900}{1.987}\left(\frac{1}{300} - \frac{1}{T}\right)\right)$$

$$k2 = 4.58.\exp\left(\frac{27000}{1.987}\left(\frac{1}{500} - \frac{1}{T}\right)\right)$$

Energy balance : $$\frac{dT}{dt} = \frac{Q + (-\Delta Hrxa1)(-ra1.V) + (-\Delta Hrxb2)(-rb2.V)}{\sum Ni.Cpi}$$

$$Q = UA.(Ta - T)$$

$$\sum Ni.Cpi = Ca.V.Cpa + Cb.V.Cpb + Cc.V.Cpc$$

$$\frac{dT}{dt} = \frac{UA.(330 - T) + 55000(-ra1.V) + 71500(-rb2.V)}{200.V.(Ca + Cb + Cc)}$$

P9-17 (a)

$UA = 0$

$$\frac{dT}{dt} = \frac{V[55000(-ra1.) + 71500(-rb2.)]}{200.V.(Ca + Cb + Cc)}$$

See Polymath program P9-17-a.pol

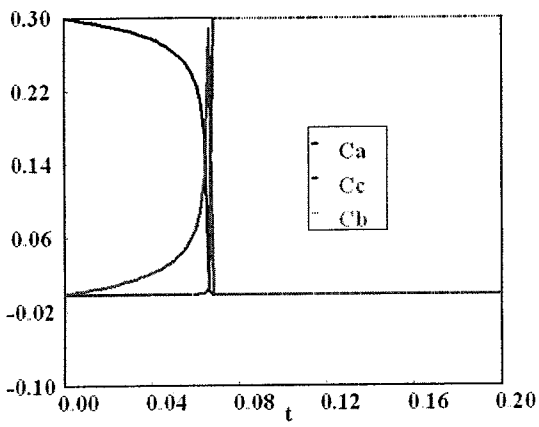
POLYMATH Results
Calculated values of the DEQ variables

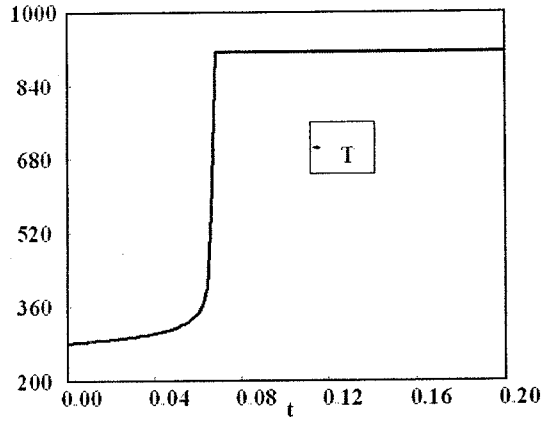
Variable	initial value	minimal value	maximal value	final value
t	0	0	0.2	0.2
Ca	0.3	1.34E-65	0.3	1.34E-65
Cc	0	0	0.3	0.3
Cb	0	-2.02E-44	0.2895784	-1.864E-65
T	283	283	915.5	915.5
UA	0	0	0	0
V	10	10	10	10
k1	1.1172964	1.1172964	2.141E+05	2.141E+05
k2	4.081E-09	4.081E-09	1.041E+06	1.041E+06
ra1	-0.3351889	-35.016552	6.345E-60	6.345E-60
rb2	0	-27.963241	2.103E-38	-3.974E-59
rb1	0.3351889	-6.345E-60	35.016552	-6.345E-60

ODE Report (STIFF)

Differential equations as entered by the user
[1] d(Ca)/d(t) = ra1
[2] d(Cc)/d(t) = -rb2
[3] d(Cb)/d(t) = rb1+rb2
[4] d(T)/d(t) = ((UA*(330-T))+(55000*(-ra1*V))+(71500*(-rb2*V)))/(200*V*(Ca+Cb+Cc))

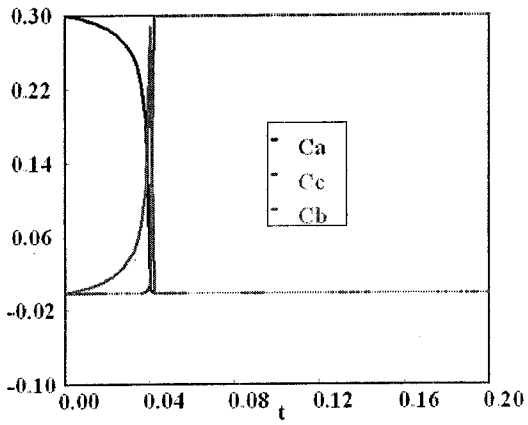
Explicit equations as entered by the user
[1] UA = 0
[2] V = 10
[3] k1 = 3.03*exp((9900/1.987)*(1/300-1/T))
[4] k2 = 4.58*exp((27000/1.987)*(1/500-1/T))
[5] ra1 = -k1*Ca
[6] rb2 = -k2*Cb
[7] rb1 = -ra1

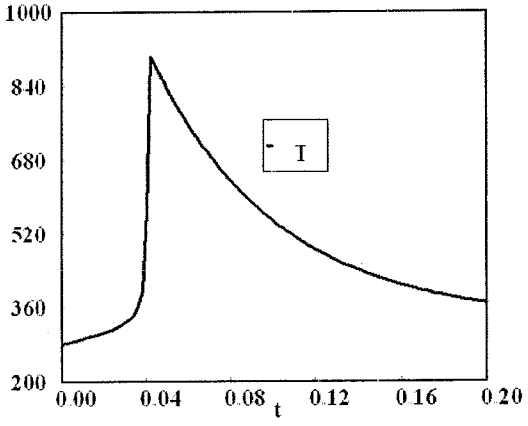




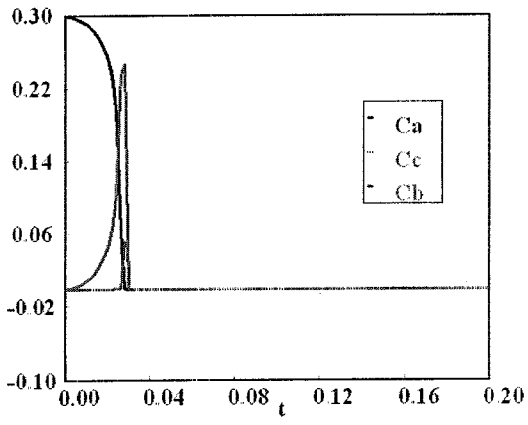
P9-17 (b)

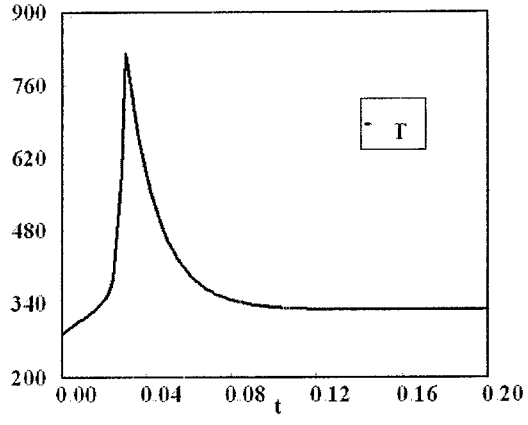
UA = 10000 J/min.K V = 10 dm^3



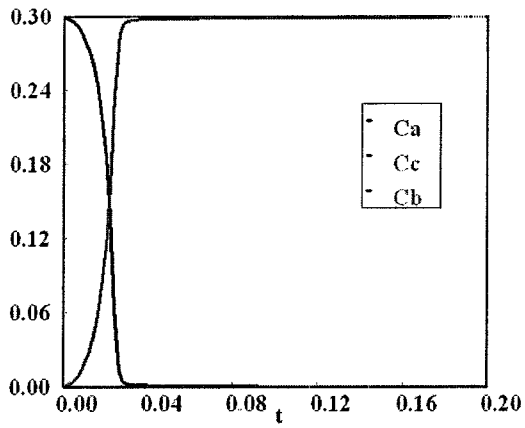


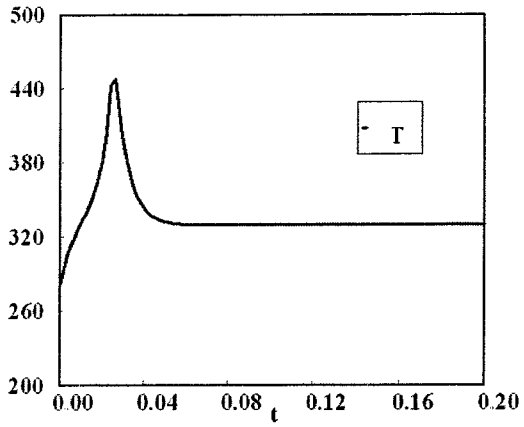
UA = 40000 J/min.K V = 10 dm^3





UA = 100000 J/min.K V = 10 dm^3

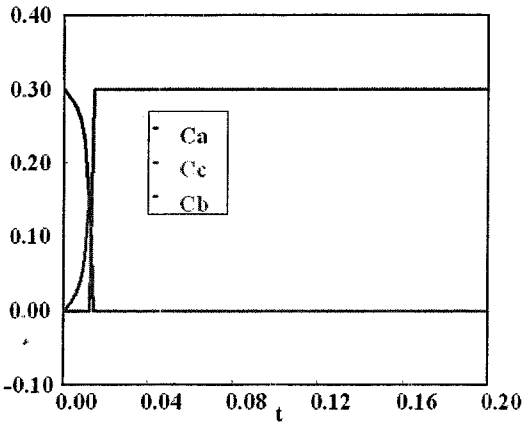


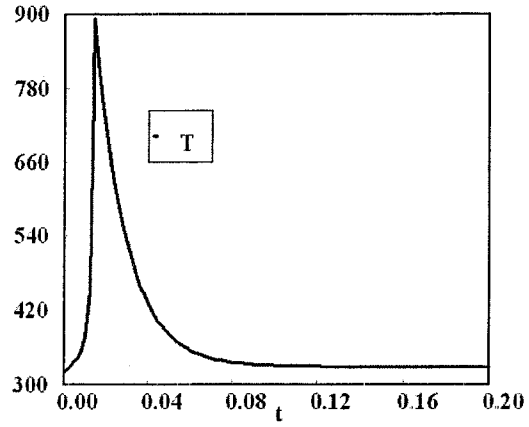


At UA = 10 0000 J/min.K the 2nd reaction for C is totally suppressed

P9-17 (c)

UA = 40000 J/min.K To = 320 K





P9-18

Semibatch with parallel reactions

Mol balance : $\frac{dNa}{dt} = Fao + (r1 + r2).V$ $\frac{dNb}{dt} = Fbo + (r1 + r2).V$

$$\frac{dNd}{dt} = -r1.V \qquad \frac{dNu}{dt} = -r2.V$$

Rate laws : $-r1 = k1.Ca$ $-r2 = k2.Cb$

$$k1 = 1000.\exp\left(-\frac{2000}{T}\right) \qquad k1 = 2000.\exp\left(-\frac{3000}{T}\right)$$

Stoichiometry : $Ca = \frac{Na}{V}$ $Cb = \frac{Nb}{V}$

$Cd = \frac{Nd}{V}$ $Cu = \frac{Nu}{V}$

$V = Vo + \upsilon a.t + \upsilon b.t$ assume Vo = 0

$\upsilon a = \frac{Fao}{Cao}$ $\upsilon b = \frac{Fbo}{Cbo}$

Cao = 5 mol/dm^3 Cbo = 4 mol/dm^3

V = υo.t where $\upsilon o = \frac{Fao}{Cao} + \frac{Fbo}{Cbo}$

But Fao = Fbo (equimolar feed) υo = 0.45.Fao

V = 0.45Fao.t

Energy balance : $\frac{dT}{dt} = \frac{Q - Ws - \sum Fio.Cpi.(T - Tio) + (-\Delta Hrx(T)).(-ra.V)}{\sum Ni.Cpi}$

where Q = Ws = 0

ΔHrx(T) = ΔHrx(Tref) + ΔCp(T-Tref)

$\Delta Cp1 = \frac{d}{a}.Cpd - \frac{b}{a}.Cpb - Cpa = 50 - 20 - 30 = 0$

ΔHrx1(T) = - 3000 cal/mol A

$\Delta Cp2 = \frac{u}{a}.Cpu - \frac{b}{a}.Cpb - Cpa = 40 - 20 - 30 = -10$

ΔHrx2(T) = - 5000 - 10.(T - 300)

ΣFio.Cpi.(T-Tio) = 20.Fa0.(T-Tao) + 30.Fbo.(T-Tbo)

ΣNi.Cpi = NaCpa + Nb.Cpb + Nd.Cpd + Nu.Cpu

$\frac{dT}{dt} = \frac{20.Fao(T - Tao) + 30.Fbo.(T - Tbo) + 3000.(-r1.V) + [5000 + 10(T - 300)](-r2.V)}{20.Na + 30.Nb + 50.Nd + 40.Nu}$

Selectivity $S = \frac{r1}{r2}$

P9-18 (a)

The selectivity is proportional to C_A/C_B and therefore a small concentration of B in the reactor is preferable. To maintain a low concentration of B it would be beneficial to run a semibatch reactor where B is slowly added to A.

P9-18 (b)

Let the rate laws be : $-r1 = k1.Cb$ $-r2 = k2.Ca$

Now it would be best to slowly add A to B in a semibatch reactor.

Let the rate laws be :

$-r1 = k1.Ca.Cb$	$-r2 = k2.Ca.Cb$
$-r1 = k1.Ca$	$-r2 = k2.Ca$
$-r1 = k1.Cb$	$-r2 = k2.Cb$

For these rate law combinations a semibatch reactor will not improve selectivity.

Let the rate laws be :

$-r1 = k1.Ca.Cb$	$-r2 = k2.Ca$
$-r1 = k1.Cb$	$-r2 = k2.Ca.Cb$

Now it would be best to slowly add A to B in a semibatch reactor to maintain high concentrations of B and low concentrations of A.

Let the rate laws be :

$-r1 = k1.Ca$	$-r2 = k2.Ca.Cb$
$-r1 = k1.Ca.Cb$	$-r2 = k2.Cb$

Now it would be best to slowly add B to A in a semibatch reactor to maintain high concentrations of A and low concentrations of B.

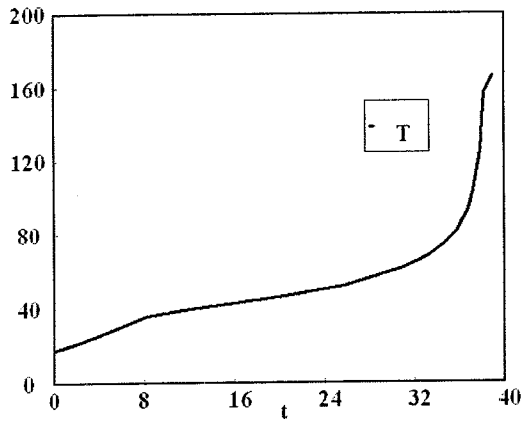
P9-18 (c)

ΔHrx1 cal/mol A	ΔHrx2(300K) cal/mol A	Temp. K	Selectivity S
3000	5000	362	7.9
5000	5000	399	6.1
10000	5000	484	3.9
1000	5000	323	11.0
3000	1000	354	8.5
3000	10000	375	7.2

If ΔHrx2 is constant , then if ΔHrx1 increases, T increases and S decreases.
If ΔHrx1 is constant , then if ΔHrx2(300K) increases, T increases and S decreases.
S is dependent on r1 and r2, which depend on k1 and k2, which depend on the temperature. The greater the temperature in the reactor the smaller the ratio between k1 and k2, hence reduced S.

P9-19

Plotting the data of t vs. T gives the initial and final temperature of the reaction, $T_0 = 52.5$ °C and $T_f = 166.8$ °C.



Recalling equation (8-29) with $\Delta Cp = 0$, $X = 1$ and $T = T_f$ gives:

$$-\Delta H_{Rx} = \sum \Theta_i Cp_i \cdot (T_f - T_0)$$

$$\sum \Theta_i Cp_i = 18 \frac{cal}{mol \cdot K}$$

$$\Delta H_{Rx} = -18 \frac{cal}{mol \cdot K}(166.8 - 52.5)K = -2057.4 \frac{cal}{mol}$$

Make a table of t (min), T (°C), dT/dt, 1/T (K^{-1}), ln(dT/dt) and plot ln(dT/dt) vs 1/K (K) in Polymath. According to equation (E9.3-14) the slope of the curve is E over R. Linear regression gives:

See Polymath program P9-19.pol

POLYMATH Report

Model: lnTdot = a0 + a1*T_inverse_kelvin

Variable	Value	95% confidence
a0	18.88162	2.425175
a1	-6224.846	880.596

Statistics

R^2	0.9755663
R^2adj	0.9720758
Rmsd	0.0597988
Variance	0.0413783

Remember that T_S is the self-heating rate, which occurs after the onset temperature is reached.

$$\ln \dot{T}_s = \frac{-6224}{T} + 18.88$$

$$6224 = \frac{E}{R}$$

$$E = 6224K \cdot 1.987 \frac{cal}{mol \cdot K} = -12367 \frac{cal}{mol}$$

P9-20 No solution will be given

CDP9-A

CDP9-B

CDP9-C

Adiabatic, batch, reversible.

Design equation : $N_{AO}\frac{dX}{dt} = -r_A V$

Rate law : $-r_A = k_1\left[C_A - \frac{C_B^2}{Ke}\right]$

Stoichiometry : $C_A = C_{AO}(1 - X), \qquad C_B = -2.C_{AO}.X$

Combining : $C_{AO}\frac{dX}{dt} = k_1\left[C_{AO}(1-X) - \frac{4C_{AO}^2(1-X)^2}{Ke}\right]$

$$\frac{dX}{dt} = k_1\left[(1-X) - \frac{4C_{AO}(1-X)^2}{Ke}\right]$$

Parameter evaluation : $E = \frac{Ln\frac{k_1}{k_2}}{\frac{1}{R.T_2} - \frac{1}{R.T_1}} = \frac{Ln\frac{0.217}{0.324}}{\frac{1}{8.314(340)} - \frac{1}{8.314(300)}} = 8498 J/mol$

$$k_1 = 0.217 \exp\left[\frac{8498}{8.314}\left(\frac{1}{340} - \frac{1}{T}\right)\right]$$

$$Ln\frac{Ke(T)}{Ke(300)} = \frac{\Delta Hrx}{R}\left(\frac{1}{300} - \frac{1}{T}\right)$$

$\Delta Cp = 2\ Cp_B - Cp_A = 20 - 12 = 8$ J/mol.K

$\Delta Hrx = \Delta Hrx\ (300) + \Delta Cp(T - 300) = -75000 + 8\ (T - 300)$

$N_{AO} = 0.6667 * 900 * 254 = 272\ 127$ mol A

$N_{IO} = 0.3333 * 900 * 454 = 136\ 064$ mol I

$C_{AO} = N_{AO} / V = 272127 / (50 * 28.12) = 192$ mol / dm^3

$Cps = \sum \theta_i Cp_i = \theta_A Cp_A + \theta_B Cp_B + \theta_I Cp_I$

$= (1)(12) + 0 + (136064 / 272027)*(15) = 19.5$ J/mol

Energy balance : $$T = To + \frac{[-\Delta Hrx(300).X]}{Cp_A + \Delta Cp.X} = 300 + \frac{(-75000).X}{19.5 + 8.X}$$

$\Rightarrow$ POLYMATH

Equations:

```
d(x)/d(t)=kl*((1-x)-(4*cao*(x^2)/Ke))
To=300
cao=192
T=To+(75000*x/(19.5+(8*x)))
kl=.217*exp(1022*(1/340-1/T))
Dhrx=-75000+(8*(T-300))
Ke=70000*exp(Dhrx/8.314*(1/300-1/T))
```

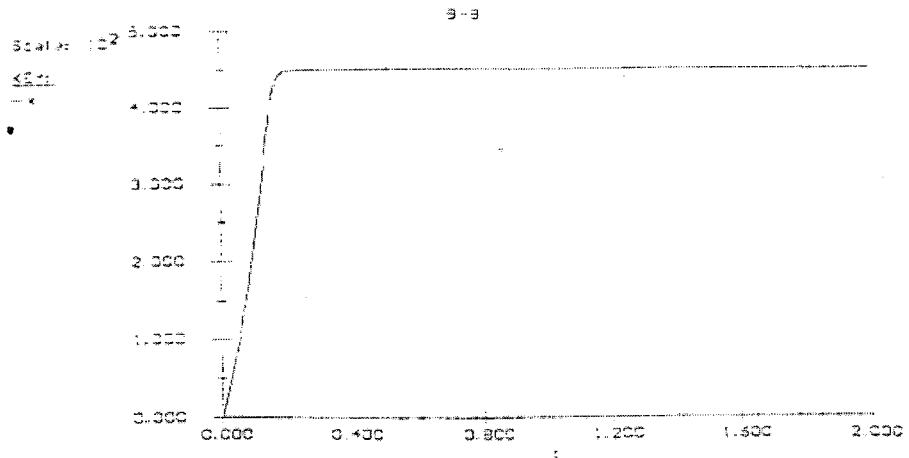
$t_0 = 0, \quad t_f = 2$

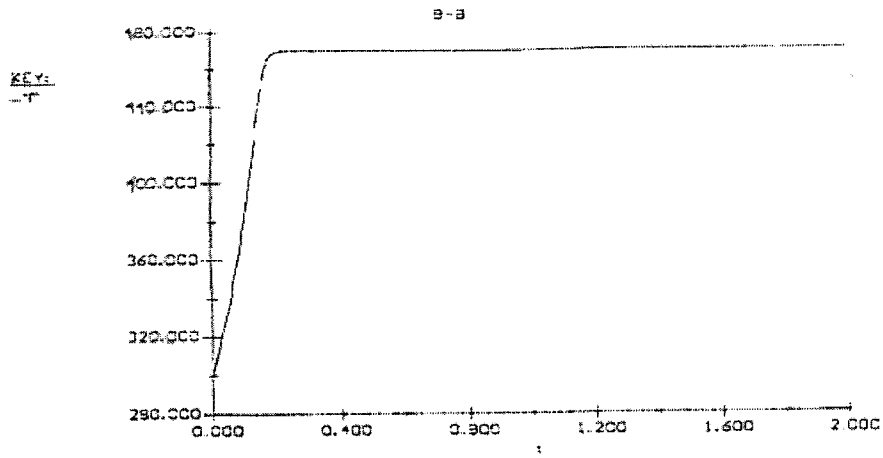
Initial value

0

9-8

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	2	0	2
x	0	0.0449573	0	0.0449573
To	300	300	300	300
cao	192	192	192	192
T	300	469.781	300	469.781
kl	0.145345	0.49785	0.145345	0.49785
Dhrx	-75000	-73641.8	-75000	-73641.8
Ke	70000	70000	1.62532	1.62532





Equilibrium conversion , Xe = 4.5 %

90 % of Xe = 0.9 * 4.5 = 4.05 % conversion

Time for this conversion = 0.11 min = 6.6 s

Check :

at equilibrium : $$C_{A0}(1 - Xe) = \frac{4.C_{A0}^2 X^2}{Ke}$$

$$(4.C_{A0}^2).Xe^2 + (Ke.C_{A0}).Xe - Ke.C_{A0} = 0$$

using the solution to a quadratic : $$Xe = \frac{-Ke.C_{A0} \pm \sqrt{Ke^2.C_{A0}^2 - 16.Ke.C_{A0}^3}}{8.C_{A0}^2}$$

where at T = Te = 470 K, Ke = 1.625 mol / dm^3

$$Xe = \frac{-(1.625*192) + \sqrt{(1.625)^2(192)^2 - [16*(1.6*(192)^3]}}{8*(192)^2} = 0.045$$

From POLYMATH , Xe = 0.045

CDP9-D

CSTR startup

Part (a) CSTR startup, gas phase, isobaric - no pressure drop

Mol balance : $\frac{dFa}{dt} = (Fao - Fa) + ra.V$

$$\frac{dFb}{dt} = (0 - Fb) - 2.ra.V$$

$$Ca = \frac{Fa}{\upsilon_T} \qquad Cb = \frac{Fb}{\upsilon_T} \qquad \upsilon_T = \upsilon a + \upsilon b$$

$$F_T = C_T.\upsilon_T = \frac{P}{R.T}.\upsilon_T \qquad F_{TO} = C_{TO}.\upsilon_{TO} = \frac{P}{R.To}.\upsilon_{TO}$$

$$\upsilon_T = \upsilon_{TO}\frac{F_T}{F_{TO}}.\frac{T}{To}$$

$$F_T = Fa + Fb \qquad F_{TO} = Fao + Fbo$$

$$V = \upsilon_T.\tau \qquad \tau = 500 \text{ s}$$

Energy balance : $\frac{dT}{dt} = \frac{Q - \sum Fio.Cpi.(T - Tio) + (-\Delta Hrx)(-ra.V)}{\sum Ni.Cpi}$

$$\frac{UA}{\rho cat} = 5J / kgcat.s.K \qquad \text{but kg catalyst} = 50 \text{ kg}$$

$$UA = 5 \times 50 = 250 \text{ J / s.K}$$

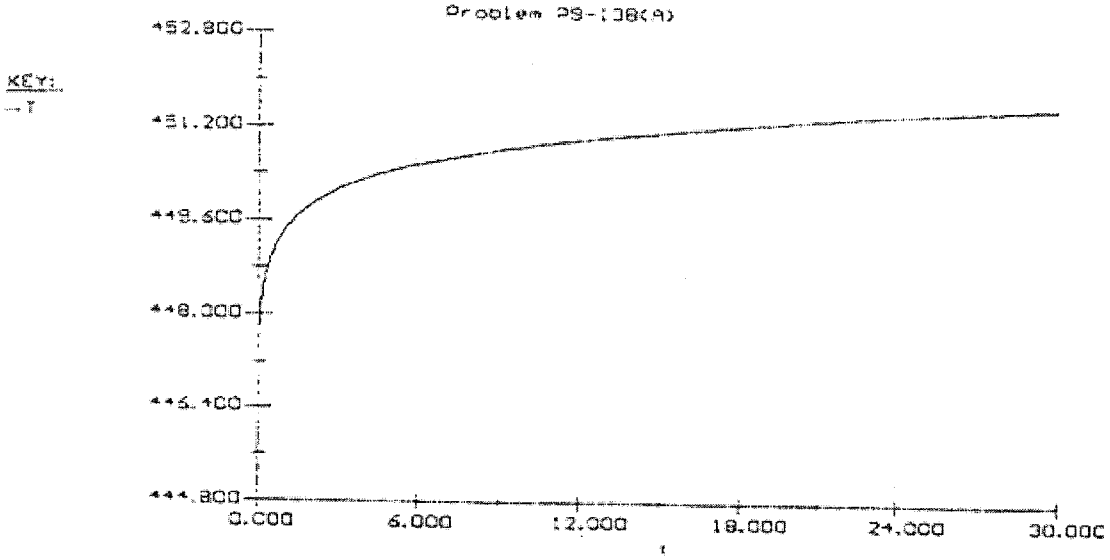
$$\Delta Cp = 0$$

$$\frac{dT}{dt} = \frac{250.(Ta - T) - 40.Fao.(T - Tio) + 20000.(-ra.V)}{40.Ca.V + 20.Cb.V}$$

No control : Ta = 300 K, Tio = 450 K, Fao = 5 mol/s

Equations:	Initial value
d(fa)/d(t)=(fao-fa)+(ra*V)	1e-08
d(fb)/d(t)=(-fa)-(2*ra*V)	0
d(T)/d(t)=((250*(Ta-T))-(40*fao*(T-Tio))+(20000*(-ra*V)))/((	450
40*Ca*V)+(20*Cb*V))	
fao=5	
Ta=300	
Tio=450	
ft=fa+fb	
To=450	
tau=500	
Tau=500	
k=exp((31400/8.314)*((1/450)-(1/T)))	
cao=0.25	
fto=fao	
vo=fao/cao	
v=vo*ft*T/(fto*To)	
Ca=fa/v	
Cb=fb/v	
V=v*tau	
ra=-k*Ca	
$t_0 = 0$, $t_f = 30$	

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	30	0	30
fa	1e-08	0.0106221	1e-08	0.00969749
fb	0	299.098	0	299.098
T	450	451.548	445.634	451.548
fao	5	5	5	5
Ta	300	300	300	300
Tio	450	450	450	450
ft	1e-08	299.107	1e-08	299.107
To	450	450	450	450
tau	500	500	500	500
Tau	500	500	500	500
k	1	1.0292	0.921054	1.0292
cao	0.25	0.25	0.25	0.25
fto	5	5	5	5
vo	20	20	20	20
v	4e-08	1200.55	4e-08	1200.55
Ca	0.25	0.251187	8.07756e-06	8.07756e-06
Cb	0	0.250078	0	0.249135
V	2e-05	600273	2e-05	600273
ra	-0.25	-8.31339e-06	-0.25	-8.31339e-06



Part (b)

Mol balance : $$\frac{dCa}{dt} = \frac{(Cao - Ca)}{\tau} + ra \qquad Cao = 0.1 \text{ kmol/m}^3 = 0.1 \text{ mol/dm}^3$$

P9-10 **cont'd**

$$\frac{dCb}{dt} = \frac{(Cbo - Cb)}{\tau} + ra \qquad Cbo = Cao$$

$$\frac{dCc}{dt} = \frac{(0 - Cc)}{\tau} - ra \qquad \tau = 50 \text{ s}$$

Rate law : $-ra = k.Ca.Cb$

$$k(T) = 0.01\exp\left[\frac{10000}{1.987}\left(\frac{1}{300} - \frac{1}{T}\right)\right]$$

Energy balance :
$$\frac{dT}{dt} = \frac{Q - Ws - \sum Fio.Cpi(T - Tio) + (-\Delta Hrx)(-ra.V)}{\sum Ni.Cpi}$$

$V = \upsilon_o \,.\, \tau = 2 \text{ x } 50 = 100 \text{ dm}^3$

$Fao = Cao \,.\, \upsilon_o = 0.1 \text{ x } 2 = 0.2 \text{ mol/s} = Fbo$ (equimolar feed)

$\sum Fio.Cpi.(T - Tio) = 2 \text{ x } 0.2 \text{ x } (15)(T - 300) = 6(T - 300)$

$\Delta Hrx(T) = \Delta Hrx(To) + \Delta Cp.(T - To)$ but $\Delta Cp = 0$
$= -41000 - (-20000) - (-15000)$
$= -6000$ cal/mol

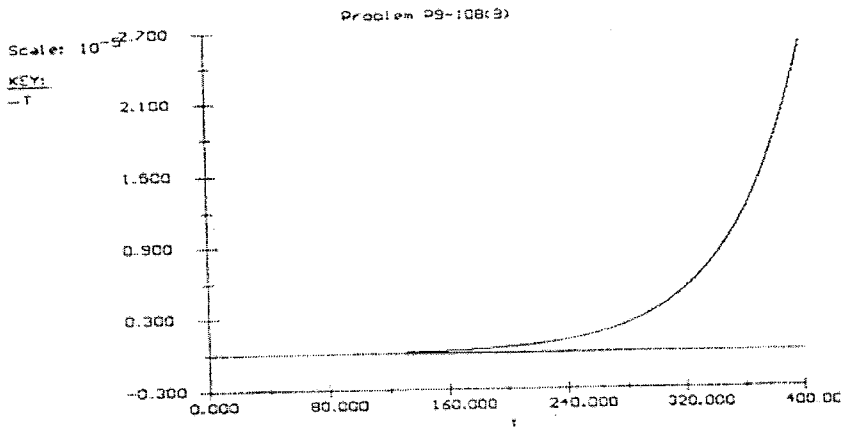
$$\frac{dT}{dt} = \frac{6(T - 300) + (6000).(-ra.V)}{15.Ca.v + 15.Cb.V + 30.Cc.V}$$

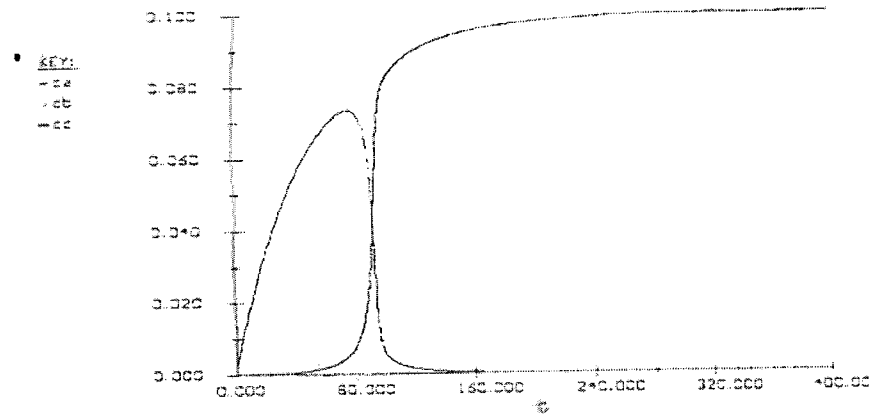
Equations:

	Initial value
d(ca)/d(t)=((0.1-ca)/50)+ra	0.001
d(cb)/d(t)=((0.1-cb)/50)+ra	0.001
d(cc)/d(t)=((0-cc)/50)-ra	0
d(T)/d(t)=((6*(T-300))+(6000*(-ra*V)))/((15*ca*V)+(15*cb*V)+(30*cc*V))	300
V=100	
k=0.01*exp((10000/1.987)*((1/300)-(1/T)))	
ra=-k*ca*cb	

$t_0 = 0, \quad t_f = 400$

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	400	0	400
ca	0.001	0.0732615	0.00010274	0.00010274
cb	0.001	0.0732615	0.00010274	0.00010274
cc	0	0.099864	0	0.099864
T	300	257380	300	257380
V	100	100	100	100
k	0.01	189280	0.01	189280
ra	-1e-08	-1e-08	-0.0110871	-0.00199796


Problem 99-108(3)
Scale: 10^{-5}
KEY:
T
2.700
2.100
1.500
0.900
0.300
-0.300
0.000
80.000
160.000
240.000
320.000
400.00
t


KEY:
0.080
0.060
0.040
0.020
0.000
0.000
80.000
160.000
240.000
320.000
400.00
t

Solutions for Chapter 10 – Catalysis and Catalytic Reactors

P10-1 Individualized solution

P10-2 (a) Example 10-1

(1) Pentane isomerization $nP \xrightarrow[Pt]{} iP$

Assume that Pt is the catalyst used.
Maximum f = 5 molecules/site/sec
Minimum f = 3e-3 molecukes/site/sec

Maximum rate:

$$-r_P = fD\left(\frac{1}{MW_{Pt}}\right)\frac{\%Pt}{100}$$

$$-r_P = 5(0.5)\left(\frac{1}{195}\right)\frac{1}{100} = 1.28*10^{-4}\frac{mol}{s\ gcat}$$

Minimum:

$$-r_P = 3*10^{-3}(0.5)\left(\frac{1}{195}\right)\frac{1}{100} = 7.69*10^{-7}\frac{mol}{s\ gcat}$$

(2) $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$

No turnover frequency is given so this rate law cannot be determined by this method

(3) $H_2 + C_2H_4 \rightarrow C_2H_6$

Assume Cobalt is the catalyst.

$$-r_{H_2} = fD\left(\frac{1}{MW_{Co}}\right)\frac{\%Co}{100}$$

Maximum:
f = 100 molecules/site/sec

$$-r_{H_2} = 100(0.5)\left(\frac{1}{58.9}\right)\frac{1}{100} = 0.00849\frac{mol}{s\ gcat}$$

Minumum:
f = 0.01

$$-r_{H_2} = 0.01(0.5)\left(\frac{1}{58.9}\right)\frac{1}{100} = 8.49*10^{-7}\frac{mol}{s\ gcat}$$

P10-2 (b) Example 10-2

(1) $\frac{C_V}{C_T} = \frac{1}{1 + K_T P_T + K_B P_B}$

$K_B = 1.39 \qquad K_T = 1.038$

$P_{T0} = y_{T0} P_{Total} = 0.3 * 40 = 12$

For 60% conversion

$P_T = P_{T0}(1 - X) = 12 * 0.4 = 4.8\,atm$

$P_B = P_{T0} X = 12 * 0.6 = 7.2\,atm$

$$\frac{C_V}{C_T} = \frac{1}{1 + (1.038)(4.8) + (1.39)(7.2)} = \frac{1}{15.99} = 0.063$$

6.3% of the sites are vacant

(2) X = 0.8

$$\frac{C_{T \bullet S}}{C_T} = \frac{C_V K_T P_T}{C_T} = \frac{K_T P_T}{1 + K_T P_T + K_B P_B}$$

$$\frac{C_{T \bullet S}}{C_T} = \frac{(1.038)(1)(1 - 0.8)}{1 + (1.038)(1)(1 - 0.8) + (1.39)(1)(0.8)} = \frac{0.2076}{2.3196} = 0.09$$

9% of the sites are covered by toluene

(3) Linearize the rate law to:

$$\frac{P_{H_2} P_T}{-r_T} = \frac{1}{k} + \frac{K_B P_B}{k} + \frac{K_T P_T}{k}$$

P10-2 (c) Example 10-3

Increasing the pressure will increase the rate law.

$$-r_A \sim \frac{P_T^2}{1 + K_T P_T} \sim P_T$$

If the flow rate is decreased the conversion will increase for two reasons: (1) smaller pressure drop and (2) reactants spend more time in the reactor.

From figure E10-3.1 we see that when X = 0.6, W = 5800 kg.

P10-2 (d) Example 10-4

With the new data, model (a) best fits the data

(a)

POLYMATH Results

Nonlinear regression (L-M)

Model: ReactionRate = k*Pe*Ph/(1+Kea*Pea+Ke*Pe)

Variable	Ini guess	Value	95% confidence
k	3	3.5798145	0.0026691
Kea	0.1	0.1176376	0.0014744
Ke	2	2.3630934	0.0024526

Precision

R^2	= 0.9969101
R^2adj	= 0.9960273
Rmsd	= 0.0259656
Variance	= 0.0096316

(b)

POLYMATH Results

Nonlinear regression (L-M)

Model: ReactionRate = k*Pe*Ph/(1+Ke*Pe)

Variable	Ini guess	Value	95% confidence
k	3	2.9497646	0.0058793
Ke	2	1.9118572	0.0054165

Precision

R^2	= 0.9735965
R^2adj	= 0.9702961
Rmsd	= 0.0759032
Variance	= 0.0720163

(c)

POLYMATH Results

Nonlinear regression (L-M)

Model: ReactionRate = k*Pe*Ph/((1+Ke*Pe)^2)

Variable	Ini guess	Value	95% confidence
k	3	1.9496445	0.319098
Ke	2	0.3508639	0.0756992

Precision

R^2	= 0.9620735
R^2adj	= 0.9573327
Rmsd	= 0.0909706
Variance	= 0.1034455

(d)

POLYMATH Results

Nonlinear regression (L-M)

Model: ReactionRate = k*Pe^a*Ph^b

Variable	Ini guess	Value	95% confidence
k	3	0.7574196	0.2495415
a	1	0.2874239	0.0955031
b	1	1.1747643	0.2404971

Precision

R^2	= 0.965477
R^2adj	= 0.9556133
Rmsd	= 0.0867928
Variance	= 0.107614

Model (e) at first appears to work well but not as well as model (a). However, the 95% confidence interval is larger than the actual value, which leads to a possible negative value for K_a. This is not possible and the model should be discarded. Model (f) is the worst model of all. In fact it should be thrown out as a possible model due to the negative R^2 values.

(e)

POLYMATH Results

Nonlinear regression (L-M)

Model: ReactionRate = k*Pe*Ph/((1+Ka*Pea+Ke*Pe)^2)

Variable	Ini guess	Value	95% confidence
k	3	2.113121	0.2375775
Ka	1	0.0245	0.030918
Ke	1	0.3713644	0.0489399

Precision

R^2	= 0.9787138
R^2adj	= 0.9726321
Rmsd	= 0.0681519
Variance	= 0.0663527

(f)

POLYMATH Results

Nonlinear regression (L-M)

Model: ReactionRate = k*Pe*Ph/(1+Ka*Pea)

Variable	Ini guess	Value	95% confidence
k	3	44.117481	7.1763989
Ka	1	101.99791	16.763192

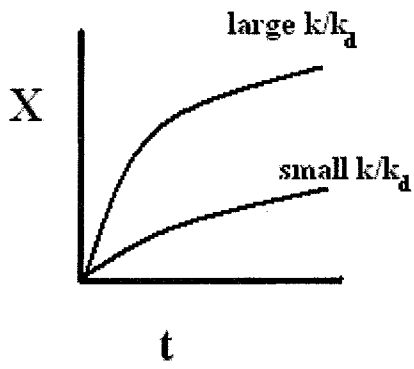
Precision

R^2	= -0.343853
R^2adj	= -0.5118346
Rmsd	= 0.5415086
Variance	= 3.6653942

P10-2 (e) Example 10-5

(1) $$X = 1 - \frac{1}{\left(1 + k_d t\right)^{k/k_d}}$$

As t approaches infinity, X approaches 1.



(2) Second order reaction with first order decay.

$$\frac{dX}{dt} = -r_A' \frac{W}{N_{A0}}$$

$$-r_A' = ak' C_A^2$$

$$a = \exp[-k_d t]$$

$$\frac{dX}{dt} = \frac{Wk'}{N_{A0}} C_{A0}^2 (1-X)^2 \exp[-k_d t]$$

$$\frac{dX}{dt} = k(1-X)^2 \exp[-k_d t]$$

$$\frac{X}{1-X} = \frac{k}{k_d}\left(1-\exp[-k_d t]\right)$$

as t → infinity $\frac{X}{1-X} = \frac{k}{k_d}$

$$X = \frac{k/k_d}{1+k/k_d}$$

(3) First order reaction with first order decay

$$\frac{dX}{dt} = \frac{Wk'}{N_{A0}} C_{A0}(1-X)\exp[-k_d t]$$

$$\frac{dX}{dt} = k(1-X)\exp[-k_d t]$$

$$\ln\left(\frac{1}{1-X}\right) = \frac{k}{k_d}\left(1-\exp[-k_d t]\right)$$

t → infinity $X = 1-\exp\left[-\frac{k}{k_d}\right]$

P10-2 (f) Example 10-6

Increasing the space time makes the minimum disappear. Decreasing the space time moves the minimum to the left and the concentration is higher.

Increasing the temperature so that the rate constants are higher will cause the catalyst lifetime to be shorter.

If tau = 0.005 the minimum C_A= 0.607
If tau = 0.01the minimum C_A= 0.5088

P10-2 (g) Example 10-7

(1) If the solids and reactants are fed from opposite ends,

$$\frac{da}{dW}=\frac{k_d a}{U_S} \quad \text{at W = W}_e\text{, a = 1}$$

$$\ln a=\frac{k_d}{U_S}W+C_1 \qquad C_1=\frac{k_d W_e}{U_S}$$

$$a=\exp\left[\frac{k_d}{U_S}(W-W_e)\right]$$

$$F_{A0}\frac{dX}{dW}=kC_{A0}^2(1-X)^2 a$$

$$\frac{X}{1-X}=\frac{kC_{A0}^2}{F_{A0}}\exp\left[\frac{-k_d W_e}{U_S}\right]\frac{U_S}{k_d}\exp\left[\frac{k_d W}{U_S}\right]\Bigg|_0^{We}$$

$$\frac{X}{1-X}=\frac{kC_{A0}^2 U_S}{k_d F_{A0}}\left(1-\exp\left[\frac{-k_d W_e}{U_S}\right]\right)$$

This gives the same expression for conversion as in the example.

(2) Second order decay

$$a=\frac{1}{1+\frac{k_d W}{U_S}}$$

$$\frac{X}{1-X}=\frac{kC_{A0}^2 U_S}{k_d F_{A0}}\ln\left(1+\frac{k_d W}{U_S}\right)$$

$$1.24=\frac{(0.6)(0.075)^2 U_S}{(0.72)(30)}\ln\left(1+\frac{(0.72)22000}{U_S}\right)$$

Solve for U_S by trial and error or a non-linear equation solver.
U_S = 0.902

(3) If ε = 2

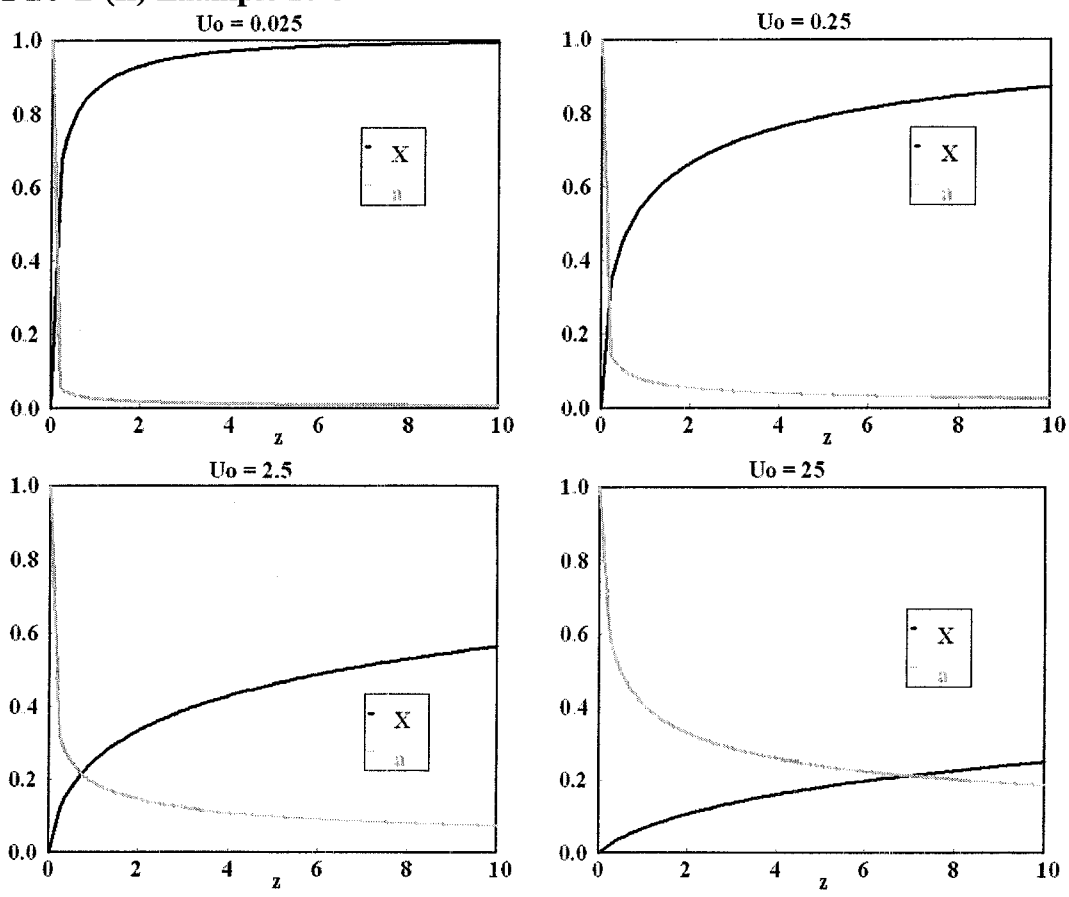
$$F_{A0}\frac{dX}{dW}=kC_{A0}^2\frac{(1-X)^2}{(1+\varepsilon X)^2}a$$

$$2\varepsilon(1+\varepsilon)\ln(1-X)+\varepsilon^2 X+\frac{(1+\varepsilon)^2 X}{1-X}=\frac{kC_{A0}^2 U_S}{k_d F_{A0}}\left(1-\exp\left[\frac{-k_d W_e}{U_S}\right]\right)$$

$$12\ln(1-X)+4X+\frac{9X}{1-X}=1.24$$

X = 0.372

P10-2 (h) Example 10-8



P10-2 (i)

For E_A = 10 and E_d = 35, for first order decay we rearrange Eq 10-120 to:

$$\ln\left(1-\frac{k_{d0}tE_d}{E_A}\right)=\frac{E_d}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)$$

$$\ln\left(\frac{1}{1-\frac{k_{d0}tE_d}{E_A}}\right)=\frac{E_d}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)$$

$$\frac{R}{E_d}\ln\left(\frac{1}{1-\frac{k_{d0}tE_d}{E_A}}\right)=\frac{1}{T_0}-\frac{1}{T}$$

$$T=\frac{T_0}{1-\frac{T_0R}{E_d}\ln\left(\frac{1}{1-\frac{k_{d0}tE_d}{E_A}}\right)}=\frac{400}{1+0.07948\ln\left(\frac{1}{1-0.00286t}\right)}$$

P10-2 (j) Individualized solution

P10-3 Solution is in the decoding algorithm given with the modules

---

P10-4

$I + S \leftrightarrow I \bullet S \qquad r_{ADI} = k_{AI}\left[C_I C_V - \frac{C_{I\bullet S}}{K_I}\right]$

$W + S \leftrightarrow W \bullet S \qquad r_{ADW} = k_{AW}\left[C_W C_V - \frac{C_{W\bullet S}}{K_W}\right]$

$W \bullet S + I \bullet S \leftrightarrow TBA \bullet S + S \qquad r_S = k_S\left[C_{W\bullet S}C_{I\bullet S} - \frac{C_V C_{TBA\bullet S}}{K_S}\right]$

$TBA\bullet S \leftrightarrow TBA + S \qquad r_D = K_D\left[C_{TBA\bullet S} - \frac{C_{TBA}C_V}{K_D}\right]$

P10-4 (a)

Surface Rxn Limited

$\frac{r_{ADI}}{k_A} = 0 \qquad C_{I\bullet S} = K_I C_I C_V \qquad C_{W\bullet S} = K_W P_W C_V \qquad \frac{r_{ADW}}{k_W} = 0$

$\frac{r_D}{k_D} = 0 \qquad C_{TBA\bullet S} = \frac{C_{TBA}C_V}{K_D} = K_{TBA}C_{TBA}C_V, \text{ since } \frac{1}{K_D} = K_{TBA}$

$r_S = \overbrace{k_S K_I K_W}^{k} C_V^2\left[C_I C_W - \frac{C_{TBA}}{K_P}\right] \qquad K_P = \frac{K_S K_I K_W}{K_{TBA}}$

$C_T = C_V + C_{I\bullet S} + C_{W\bullet S} + C_{TBA\bullet S} = C_V(1 + K_I C_I + K_W C_W + K_{TBA} C_{TBA})$

$$-r_I' = -r_W' = r_S = \frac{\overbrace{k_S K_I K_W C_T^2}^{k}\left[C_I C_W - \frac{C_{TBA}}{K_P}\right]}{\left(1+K_I C_I + K_W C_W + K_{TBA} C_{TBA}\right)^2}$$

P10-4 (b)

Adsorption of isobutene limited

$$r_{ADI} = k_{AI}\left[C_I - \frac{C_{TBA}}{C_W K_P}\right] C_V \quad , \quad \left(\frac{r_{ADW}}{k_{AW}}\right) = 0 \quad , \quad \left(\frac{r_D}{k_D}\right) = 0$$

$$C_{W \bullet S} = C_W C_V K_W \quad , \quad C_{TBA \bullet S} = C_{TBA} C_V K_{TBA}$$

$$\left(\frac{r_S}{k_S}\right) = 0 \quad C_{I \bullet S} = \frac{C_V C_{TBA \bullet S}}{C_{W \bullet S} K_S} \qquad C_{I \bullet S} = \frac{C_{TBA} K_{TBA} C_V}{C_W K_W K_S}$$

$$r_{ADI} = k_{AI}\left[C_I - \frac{C_{TBA}}{C_W K_P}\right] C_V \qquad K_P = \frac{K_W K_S}{K_{TBA}}$$

$$-r_I' = \frac{k_{AI} C_T \left[C_I - \frac{C_{TBA}}{C_W K_P}\right]}{\left[1 + C_W K_W + K_{TBA} C_{TBA} + \frac{C_{TBA}}{C_W K_P}\right]}$$

P10-4 (c)

Eley Rideal Kinetics

$$r_S = k_S\left[C_W C_{I \bullet S} - \frac{C_{TBA \bullet S}}{K_S}\right]$$

$$C_{I \bullet S} = K_I C_I C_V$$

$$C_{TBA \bullet S} = K_{TBA} C_{TBA} C_V$$

$$-r_I' = \frac{k\left[C_W C_I - \frac{C_{TBA}}{K_H}\right]}{1 + K_I C_I + K_{TBA} C_{TBA}}, \text{ where } k = k_S K_I C_T \text{ and } K_H = \frac{K_I K_S}{K_{TBA}}$$

P10-4 (d)

$$W \bullet S_2 + I \bullet S_1 \leftrightarrow TBA + S_2 + S_1$$

$$r_S = k_S\left[C_{W\bullet S2}C_{I\bullet S1} - \frac{C_{TBA}C_{V1}C_{V2}}{K_S}\right]$$

$$C_{T1} = C_{V1} + C_{I\bullet S1}$$

$$C_{T2} = C_{V2} + C_{W\bullet S2}$$

$$C_{I\bullet S1} = K_I C_I C_{V1}\ ,\ C_{T1} = C_{V1}\left(1+K_I C_I\right)$$

$$C_{W\bullet S2} = K_W C_W C_{V2}\ ,\ C_{T2} = C_{V2}\left(1+K_W C_W\right)$$

$$r_I = \frac{k\left[C_I C_W - \frac{C_{TBA}}{K_S}\right]}{\left(1+K_I C_I\right)\left(1+K_W C_W\right)},\ \text{where } k = k_S K_W K_I C_{T1} C_{T2}$$

P10-4 (e) Individualized solution

P10-4 (f) Individualized solution

P10-5 (a)

$$H_2 + C_2H_4 \xrightarrow[Cat]{} C_2H_6$$

$$H + E \rightarrow A$$

Eley Rideal

$$E \bullet S \leftrightarrow A + S$$

$$E + S \leftrightarrow E \bullet S\ ,\ C_{E\bullet S} = K_E P_E C_V$$

$$r_S = k_S\left[C_{E\bullet S} P_H\right]$$

$$C_T = C_V + C_{E\bullet S}$$

$$r_A = \overbrace{k_S K_E C_T}^{k}\left[\frac{P_E P_H}{1+K_E P_E}\right]$$

P10-5 (b) Individualized solution

P10-5 (c)

$O_2 + 2S \rightleftarrows 2O \bullet S$

$C_3H_6 + O \bullet S \rightarrow C_3H_5OH \bullet S$

$C_3H_6OH \bullet S \rightleftarrows C_3H_5OH + S$

$-r_B = r_S = k_3 P_B C_{A\bullet S}$

$$r_{AD} = k_A\left[P_{A_2}C_V^2 - \frac{C_{A\bullet S}^2}{K_A}\right]$$

$A_2 + 2S \rightleftarrows 2A \bullet S$

$B + A \bullet S \rightarrow C \bullet S$

$C \bullet S \rightarrow C + S$

$$\frac{r_{AD}}{k_A} = 0$$

$$C_{A\bullet S} = C_V \sqrt{K_A P_A}$$

$$-r_B = r_S = k_3 P_B C_V \sqrt{K_A P_A}$$

$$r_{C\bullet S} = k_D \left[C_{C\bullet S} - \frac{P_C C_V}{K_D} \right] = k_D \left[C_{C\bullet S} - K_C P_C C_V \right]$$

$$\frac{r_{C\bullet S}}{k_D} = 0$$

$$C_{C\bullet S} = K_C P_C C_V$$

$$C_T = C_V + C_{A\bullet S} + C_{C\bullet S} = C_V \left[1 + \sqrt{K_A P_A} + K_C P_C \right]$$

$$-r_B = r_S = \frac{k_3 C_T P_B \sqrt{K_A P_A}}{1 + \sqrt{K_A P_A} + K_C P_C}$$

P10-6 (a)

A (butanol) $\rightleftarrows$ B (butene) + C (water)

Possible mechanism:

$A + S \rightleftarrows A \cdot S$	$r_{AA} = K_{AA}\left(P_A C_S - \frac{C_{AS}}{K_{AA}} \right)$
$A \cdot S + S \rightleftarrows B \cdot S + C \cdot S$	$r_S = k_S (C_{A\text{-}S} C_S - C_{B\text{-}S} C_{C\text{-}S} / K_S)$
$B \cdot S \rightleftarrows B + S$	$r_{DB} = k_{DB} (C_{B\text{-}S} - P_B C_S / K_{DB})$
$C \cdot S \rightleftarrows C + S$	$r_{DC} = k_{DC} (C_{CS} - P_C C_S / K_{DC})$

Assume surface reaction controlling:

$\frac{-r_{AA}}{k_{AA}} \equiv 0$	$C_{A\text{-}S} = P_A K_{AA} C_S$
$\frac{-r_{DB}}{k_{DB}} \equiv 0$	$C_{B\text{-}S} = \frac{P_B C_S}{K_{DB}} = P_B K_{AB} C_S$
$\frac{-r_{DC}}{k_{DC}} \equiv 0$	$C_{C\text{-}S} = \frac{P_C C_S}{K_{DC}} = P_C K_{AC} C_S$

$$-r_A' = r_S = k_S\left(P_A K_{AA} C_S^2 - \frac{P_B P_C C_S^2}{K_S K_{DB} K_{DC}}\right) = k_S K_{AA} C_S^2\left(P_A - \frac{P_B P_C}{K_{eq}}\right) \text{ where } K_{eq} = K_S K_{AA} K_{DC} K_{DB}$$

site balance: $C_T = C_S + C_{AS} + C_{BS} + C_{CS} = C_S\,(1 + K_{AA}\,P_A + K_{AB}\,P_B + K_{AC}\,P_C)$

$$\therefore -r_A' = \frac{k_S\,K_{AA}\,C_T^2\,(P_A - P_B\,P_C/K_{eq})}{(1 + P_A\,K_{AA} + P_B\,K_{AB} + P_C\,K_{AC})^2}$$

If $P_{BO} = 0$ and $P_{CO} = 0$, then

$$-r_{A0}' = \frac{k_S\,K_{AA}\,C_T^2\,P_{A0}}{(1 + P_{A0}\,K_{AA})^2} = \frac{k_1\,P_{A0}}{1 + k_2\,P_{A0}^2 + k_3\,P_{A0}} \qquad \text{where } \begin{cases} k_1 = k_3\,K_{AA}\,C_T^2 \\ k_2 = K_{AA}^2 \\ k_3 = 2\,K_{AA} \end{cases}$$

This is consistent with the observation.

P10-6 (b)

From the figure,

Point number	1	2	3	4	5	6
$-r_{A0}'\left(\frac{\text{lbmoles}}{\text{hr} \cdot \text{lb cat}}\right)$	0	0.275	0.5	0.77	0.77	0.5
P_{A0} (atm)	0	4.5	27	54	112	229
$\sqrt{\frac{P_A}{-r_{A0}}}$	--	4.05	6.45	8.14	12.06	21.4

At large P_{A0} : $-r'_{A0} = \frac{k_1 P_{A0}}{k_2 P_{A0}^2} = \frac{k_1}{k_2}\left(\frac{1}{P_{A0}}\right)$; using point 6 : $\frac{k_1}{k_2} = (229)\ (0.5) = 114$

At small P_{A0} : $-r'_{A0} = k_1 P_{A0}$; using point 2 : $k_1 = 0.061 \Rightarrow k_2 = 5.34\times10^{-4}$

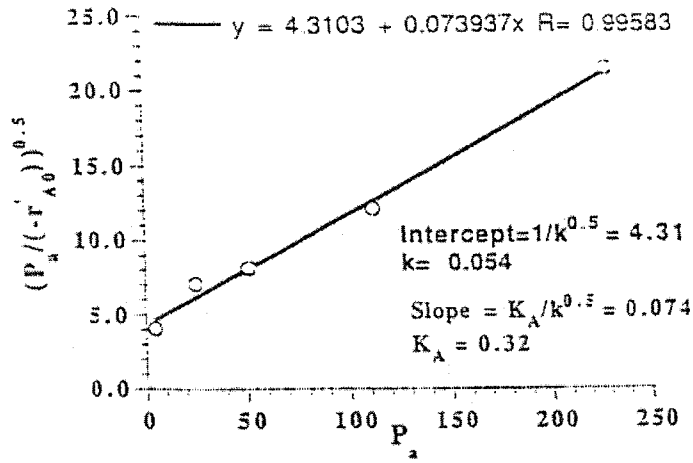
$$-r'_{A0} = \frac{0.061\ P_{A0}}{1 + 5.34\times10^{-4}\ P_{A0}^2 + k_3 P_{A0}} \quad ; \text{ so } \quad k_3 = \frac{0.061}{-r'_{A0}}\cdot\frac{1}{P_{A0}} - 5.34\times10^{-4}\ P_A$$

Using point 3: $k_3 = 7.05\times10^{-2}$

Using point 4: $k_3 = 3.19\times10^{-2}$

Using point 5: $k_3 = 1.05\times10^{-2}$

$\Rightarrow k_3 = 3.19\times10^{-2}$
(The reason for the different values of k_3 is from reading the graph)



P10-6 (c)

Find the percent of vacant sites.

$$\%\text{vacant} = \frac{C_s}{C_T} = \frac{C_S}{C_S(1 + K_{AA}P_A + K_{AB}P_B + K_{AC}P_C)}$$

P_b and $P_C = 0$ so that reduces to:

$$\%\text{vacant} = \frac{1}{1 + K_{AA}P_{A0}} = \frac{1}{1 + 0.01596 * 90} = 0.41$$

Find the percent of sites occupied by A and B. No B will have occupied any sites at X = 0. So:

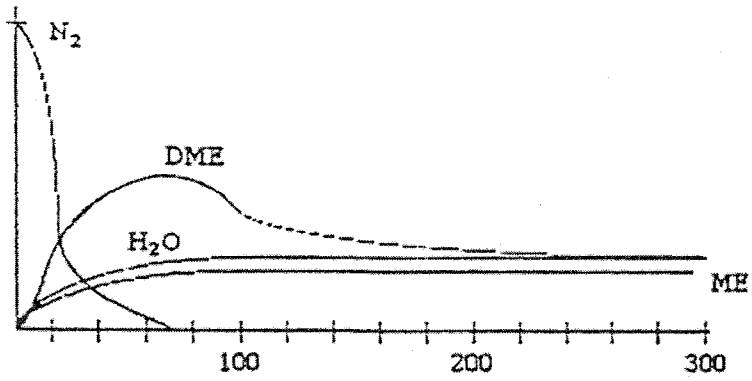
$$\%A = \frac{K_{AA}P_A}{1 + K_{AA}P_A} = \frac{0.01595 * 90}{1 + 0.01595 * 90} = 0.59$$

P10-6 (d) Individualized solution

P10-6 (e) Individualized solution

P10-7

$$ME \rightarrow DME + H_2O$$



The rate of formation of DME is greater initially. This is a result of more vacant sites being initially available for reaction because water is not adsorbed on the sites. As time goes on the equilibrium concentration of water sites is reached. Water is strongly adsorbed on this catalyst.

Probable Mechanism

$$ME + S \rightleftarrows ME \cdot S$$

$$2ME \cdot S \rightarrow W \cdot S + DME + S$$

$$W \cdot S \rightleftarrows W + S$$

Assume Surface Reaction Controls

$$r_S = k_S C^2_{ME\text{-}S}$$

$$C_{ME\text{-}S} = K_{ME} P_{ME} C_V$$

$$C_{W\text{-}S} = K_W P_W C_V$$

$$r'_{ME} = r_S = \frac{kP^2_{ME}}{\left(1 + K_W P_W + K_{ME} P_{ME}\right)^2} \quad \text{where } k = k_S K^2_{MS} C_t^2$$

P10-8

Given: Kinetic rate expression for the reduction of NO over a solid catalyst:

$$r = \frac{k\, P_N\, P_C}{(1 + K_1\, P_N + K_2\, P_C)^2}$$

P_N = partial pressue NO

P_C = partial pressure CO

Assume that overall reaction is of the form

$$NO + CO \rightarrow \frac{1}{2} N_2 + CO_2$$

P10-8 (a)

It is seen that neither N_2 or CO_2 appear in the denominator. This infers that neither is adsorbed on the catalyst. On the other hand, it can be infered that both NO and CO are adsorbed on the surface. The squared denominator suggests a dual site surface reaction of the adsorbates of NO and CO. Therefore the following mechanism is proposed.

$$NO(g) + S \underset{}{\overset{k_{AN}}{\rightleftarrows}} NO \cdot S \qquad P_N = P_{NO} \quad P_C = P_{CO} \qquad -r_{AN} = k_{AN}[P_N C_S - C_{NO\text{-}S}/K_{AN}]$$

$$CO(g) + S \overset{k_{CN}}{\rightleftarrows} CO \cdot S \qquad -r_{CN} = k_{CN}[P_C C_S - C_{CO\text{-}S}/K_{CN}]$$

$$NO \cdot S + CO \cdot S \overset{k_S}{\rightarrow} \tfrac{1}{2} N_2 + CO_2 + 2S \qquad -r_S = k_S C_{NO\text{-}S} C_{CO\text{-}S}$$

With the surface reaction controlling

$$\frac{-r_{AN}}{k_{AN}} \equiv 0 \quad C_{NO\text{-}S} = K_{AN} P_N C_S$$

$$\frac{-r_{CN}}{k_{CN}} \equiv 0 \quad C_{CO\text{-}S} = k_{CN} P_C C_S$$

Then $C_T = C_S + C_{NO\text{-}S} + C_{CO\text{-}S} = C_S [1 + K_{AN} P_N + K_{CN} P_C]$

and therefore reaction is $-r_S = k_S C_{NO\text{-}S} C_{CO\text{-}S} = k_S C_S^2 P_N P_C K_{AN} K_{CN}$

$$\text{or} \quad -r_S = \frac{k_S K_{AN} K_{CN} P_N P_C C_T^2}{[1 + K_{AN} P_N + K_{CN} P_C]^2} \quad \text{with} \quad \begin{aligned} k_1 &= k_S C_T^2 K_{AN} K_{CN} \\ K_1 &= K_{AN} \\ K_2 &= K_{CN} \end{aligned}$$

$$-r_S = \frac{k_1 P_C P_N}{[1 + K_1 P_N + K_2 P_C]^2}$$

P10-8 (b)

Assume that $P_C >> P_N$. Then P_C changes very little during the course of the reaction and remains constant. A maximum in $(-r_S)$ then occurs, for a fixed value of P_N at:

$$\frac{\partial(-r_S)}{\partial P_C} = \frac{k_1 P_N}{[1 + K_1 P_N + K_2 P_C]^2} - \frac{2 k_1 P_C P_N K_2}{[1 + K_1 P_N + K_2 P_C]^3} = 0$$

$$\text{or at } P_C = \frac{1 + K_1 P_N}{K_2}$$

The rate of reaction will increase with an increase in P_C until the above value is reached, after which it will decrease. It appears that there is an excess pressure which will minimize reactor volume. Operating at excess pressure greater than this value will decrease ($-r_S$), and hence increase V. This analysis is exact if the catalytic reactor is a CSTR. If the reactor is treated as PFR, the critical value of P_C is only approximate, but the general observation is qualitatively the same.

This analysis further assumes that the excess CO can be eliminated easily and economically downstream from the NO converter.

P10-8 (c)

The conditions for which the rate law and mechanism are consistent are the following. The CO S surface reaction must be the rate limiting. P_{CO}/P_{NO} must be small. The mechanism must be a dual site mechanism (which it is).

P10-9

Methyl ethyl ketone (MEK) is an important industrial solvent that can be produced from the dehydrogenation of butan-2-ol (Bu) over a zinc oxide catalyst.

$$Bu \rightarrow MEK + H_2$$
$$A \rightarrow B + C$$

The following data giving the reaction rate for MEK were obtained in a differential reactor at 490°C.

Data Set	1	2	3	4	5	6
P_{Bu} *(atm)*	2	0.1	0.5	1	2	1
P_{MEK} *(atm)*	5	0	2	1	0	0
P_{H_2} *(atm)*	0	0	1	1	0	10
r'_{MEK} *(mol/h x g cat)*	0.044	0.040	0.069	0.060	0.043	0.059

P10-9 (a)

Suggest a rate law that is consistent with the experimental data

From data sets 2 and 5

Data Set	2	5
P_{Bu} *(atm)*	0.1	2
P_{MEK} *(atm)*	0	0
P_{H_2} *(atm)*	0	0
r'_{MEK} *(mol/h x g cat)*	0.040	0.043

we can say that an increase in Bu partial pressure slightly increases the reaction rate.

From data sets 1 and 5

Data Set	1	5
P_{Bu} *(atm)*	2	2
P_{MEK} *(atm)*	5	0
P_{H_2} *(atm)*	0	0
r'_{MEK} *(mol/h x g cat)*	0.044	0.043

we can see that the MEK partial pressure has little if no effect on the rate law.

From data sets 4 and 6

Data Set	4	6
P_{Bu} *(atm)*	1	1
P_{MEK} *(atm)*	1	0
P_{H_2} *(atm)*	1	10
r'_{MEK} *(mol/h x g cat)*	0.060	0.059

Is seems that the partial pressure of H_2 has no effect on the reaction rate.

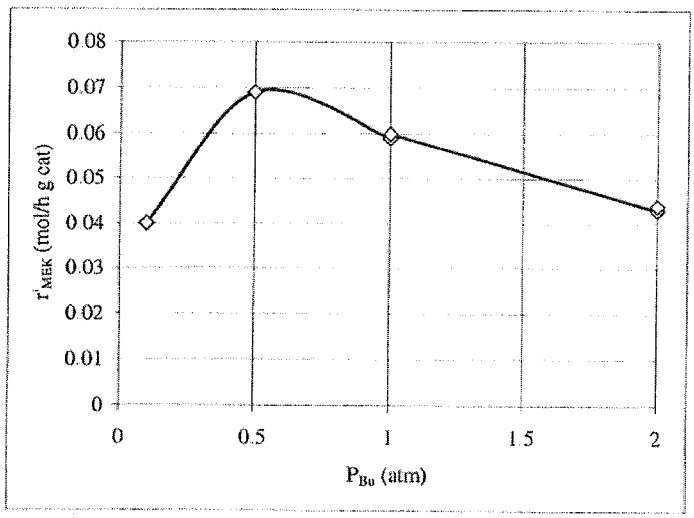
If MEK and H_2 are weakly adsorbed (or not adsorbed at all) we can proposed initially the following

$$-r'_A = r'_B = \frac{k_1 P_A}{1 + k_2 P_A}$$

But, from the complete data set

Data Set	1	2	3	4	5	6
P_{Bu} *(atm)*	2	0.1	0.5	1	2	1
r'_{MEK} *(mol/h x g cat)*	0.044	0.040	0.069	0.060	0.043	0.059

We can see that the reaction rate goes through a maximum



$$-r'_A = r'_B = \frac{k_1 P_A}{(1 + k_2 P_A)^2}$$

P10-9 (b)

Suggest a reaction mechanism and rate-limiting step consistent with the rate law.

One possible mechanism is the following one

$$(1)\ A + S \leftrightarrow A \cdot S$$
$$(2)\ A \cdot S + S \leftrightarrow B \cdot S + C \cdot S$$
$$(3)\ B \cdot S \leftrightarrow B + S$$
$$(4)\ C \cdot S \leftrightarrow C + S$$

If the limiting step is #2 (irreversible surface reaction) and the others are at Pseudo Steady State (#1, 3and 4)

$$-r'_A = k_2 C_{AS} C_V$$

$$P_A C_V = \frac{C_{A\cdot S}}{K_1}$$

$$C_{BS} = \frac{P_B C_V}{K_3}$$

$$C_{C\cdot S} = \frac{P_C C_V}{K_4}$$

A site's balance will yield

$$C_T = C_V + C_{AS} + C_{B\cdot S} + C_{C\cdot S}$$

Therefore,

$$C_T = C_V + C_V P_A K_1 + \frac{C_V P_B}{K_3} + \frac{C_V P_C}{K_4}$$

Solving for C_V

$$C_V = \frac{C_T}{1 + P_A K_1 + \frac{P_B}{K_3} + \frac{P_C}{K_4}}$$

Substituting the expressions for C_V and $C_{A\cdot S}$ into the equation for $-r'_A$

$$-r'_A = k_2 C_{AS} C_V = k_2 K_1 P_A C_V^2 = \frac{k_2 K_1 P_A C_T^2}{\left(1 + P_A K_1 + \frac{P_B}{K_3} + \frac{P_C}{K_4}\right)^2}$$

which for the case of weak adsorption of MEK and H_2 reduces to

$$-r'_A = \frac{k_2 K_1 P_A C_T^2}{(1 + P_A K_1)^2}$$

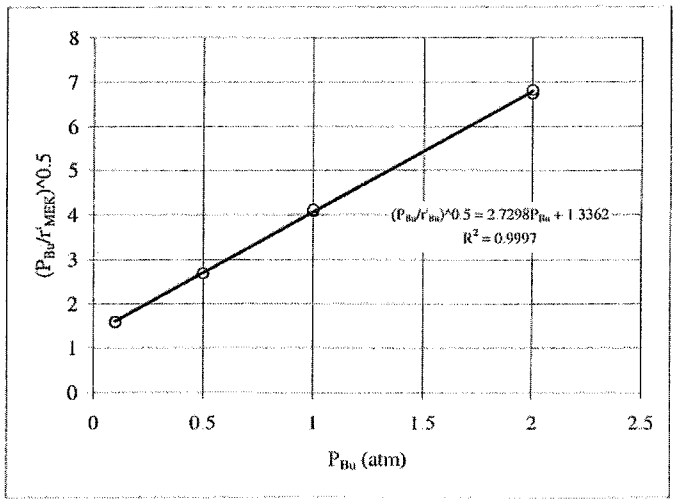
P10-9 (c) Individualized solution

P10-9 (d)

First we need to calculate the rate constants involved in the equation for $-r'_A$ in part (a). We can rearrange the equation to give the following

$$\sqrt{\frac{P_A}{r'_{MEK}}} = \frac{1}{\sqrt{k_1}} + \frac{k_2}{\sqrt{k_1}} P_A$$

which is a linear equation with slope equal to $k_2/\sqrt{k_1}$ and intercept equal to $1/\sqrt{k_1}$. Shown below is the linear regression we did using the problem data



Thus from the slope and intercept data

$$k_1 = 0.56 \frac{mol}{h \cdot gcat \cdot atm} \qquad \text{and} \qquad k_2 = 2.04 \frac{1}{atm}$$

Thus,

$$-r'_A = r'_B = \frac{0.56 P_A}{(1 + 2.04 P_A)^2}$$

The design equation for the PBR is

$$F_{A0} \frac{dX}{dW} = -r'_A$$

From stoichiometry (gas phase)

$$C_A = C_{A0} \left(\frac{1 - X}{1 + \epsilon X} \right) \frac{T_0}{T} \frac{P}{P_0}$$

From the reaction $\epsilon = 1 + 1 - 1$. Assuming isobaric and isothermal operation and using ideal gas law

$$P_A = P_{A0} \left(\frac{1 - X}{1 + X} \right)$$

Using equations 10-8-13,10-8-14 and 10-8-16 together with Polymath we can solve for W at X = 90%.

See Polymath program P10-9-d.pol.

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
W	0	0	23	23
X	0	0	0.9991499	0.9991499
e	1	1	1	1
Pao	10	10	10	10
Pa	10	0.0042521	10	0.0042521
k1	560	560	560	560
k2	2.04	2.04	2.04	2.04
Fao	600	600	600	600
ra	-12.228142	-68.5622	-2.3403948	-2.3403948
rate	12.228142	2.3403948	68.5622	2.3403948

ODE Report (RKF45)

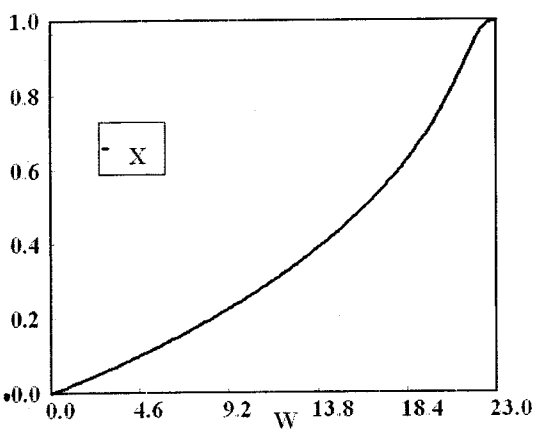
Differential equations as entered by the user

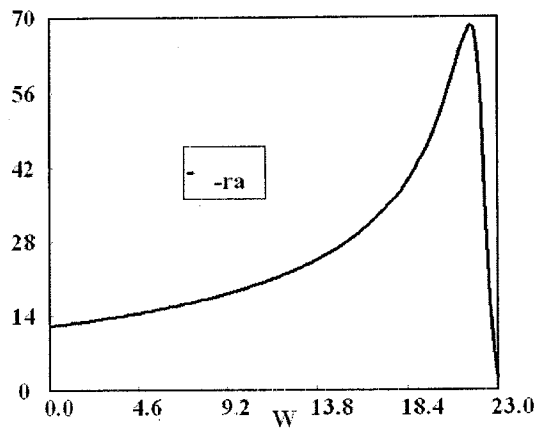
[1] d(X)/d(W) = -ra/Fao

Explicit equations as entered by the user

[1] e = 1
[2] Pao = 10
[3] Pa = Pao*(1-X)/(1+e*X)
[4] k1 = 560
[5] k2 = 2.04
[6] Fao = 600
[7] ra = -k1*Pa/((1+(k2*Pa))^2)
[8] rate = -ra

It should be mentioned that $F_{A0} = 10\dfrac{mol}{\min} = 600\dfrac{mol}{hr}$.





P10-9 (e) Individualized solution

P10-9 (f)

Now consider the change in pressure:

Stoichiometry: $$P_A = C_A RT = C_{Ao}\left(\frac{1-X}{1+\varepsilon X}\right)\frac{P}{P_o}RT \quad \Rightarrow \quad P_A = P_{Ao}\left(\frac{1-X}{1+X}\right)y$$

Pressure: $$\frac{dy}{dW} = \frac{-\alpha}{2y}(1+X)$$

Use these new equations in the Polymath program from part (d).

See Polymath program P10-9-f.pol.

POLYMATH Results

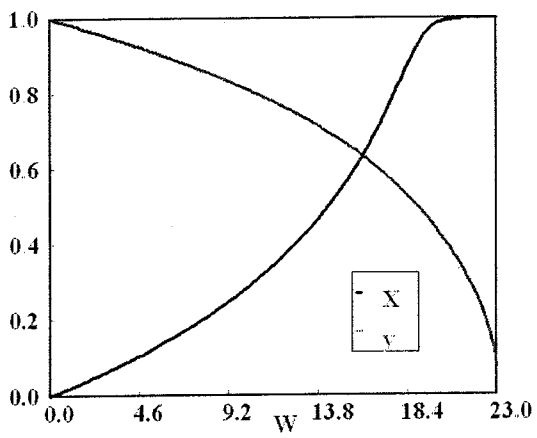
Calculated values of the DEQ variables

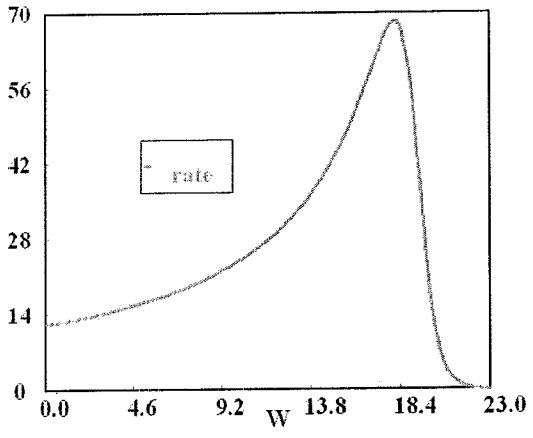
Variable	initial value	minimal value	maximal value	final value
W	0	0	23	23
X	0	0	0.9997919	0.9997919
y	1	0.0746953	1	0.0746953
e	1	1	1	1
Pao	10	10	10	10
Pa	10	7.771E-05	10	7.771E-05
k1	560	560	560	560
k2	2.04	2.04	2.04	2.04
Fao	600	600	600	600
ra	-12.228142	-68.584462	-0.0435044	-0.0435044
rate	12.228142	0.0435044	68.584462	0.0435044
alpha	0.03	0.03	0.03	0.03

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(X)/d(W) = -ra/Fao
[2] d(y)/d(W) = -alpha*(1+X)/2/y

Explicit equations as entered by the user
[1] e = 1
[2] Pao = 10
[3] Pa = y*Pao*(1-X)/(1+e*X)
[4] k1 = 560
[5] k2 = 2.04
[6] Fao = 600
[7] ra = -k1*Pa/((1+(k2*Pa))^2)
[8] rate = -ra
[9] alpha = .03





P10-10 (a)

Iso-octene + Hydrogen → iso-octane

A + B → C

Discrimination of models:

Assume $-r_A = k C_A^{\alpha} C_B^{\beta} C_C^{\gamma}$

For runs 2 and 3, $0 < \alpha < 1$; 2 and 4 , $0 < \beta < 1$; and 2 and 5 , $-1 < \gamma < 0$. From

Perry's handbook, 5th ed., p. 4-8; the reaction is probably surface reaction rate controlling.

Mechanism I (H. Alvord):

$$A + S \rightleftarrows A \cdot S$$

$$B_2 + 2S \rightleftarrows 2B \cdot S$$

$$A \cdot S + 2B \cdot S \rightleftarrows C \cdot S + 2S$$

$$C \cdot S \rightleftarrows C + S$$

Hence, $$-r_A = \frac{k[P_A P_B - P_C/K_{eq}]}{[1 + K_A P_A + K_B^{0.5} P_B^{0.5} + K_C P_C]^3}$$

Mechanism II (S. L. Mullick):

$$A + S \rightleftarrows A \cdot S$$

$$B + S \rightleftarrows B \cdot S$$

$$A \cdot S + B \cdot S \rightleftarrows C \cdot S + S$$

$$C \cdot S \rightleftarrows C + S$$

Hence, $$-r_A = \frac{k[P_A P_B - P_C/K_{eq}]}{[1 + K_A P_A + K_B P_B + K_C P_C]^2}$$

From runs 2, 9 11, 12, $P_A = P_B = P_C = P$, a plot of $-r_A$ vs. P shows a parabollic behavior, therefore we will drop the second term in the denominator for easy linearization. The readers can calculate K_{eq} value by Gibbs free energy change in this equation (up to 650 K, the reverse reaction is negligible)

The linearized regression model is:

$$\left(\frac{P_A P_B}{-r_A}\right)^{0.5} = \frac{1}{k^{0.5}} + \frac{K_A P_A}{k^{0.5}} + \frac{K_B P_B}{k^{0.5}} + \frac{K_C P_C}{k^{0.5}} = y$$

Using given 12 data points to solve for these four unknowns:

$$y = 3.0 + 1.42 P_A + 0.97 P_B + 1.42 P_C$$

The final results are:

$$-r_A = \frac{0.1113 P_A P_B}{(1 + 0.475 P_A + 0.322 P_B + 0.414 P_C)^2}$$

The comparison of the percentage error between the model and the experimental data are:

Run	P_A	P_B	P_C	r (exp.)	$\left(\frac{P_A P_B}{r_{exp.}}\right)^{0.5}$	r (calc.)	% error
1	1	1	0	0.0362	5.26	0.0345	-4.8
2	1	1	1	0.0239	6.47	0.0227	-4.7
3	1	3	1	0.0390	8.77	0.0410	+5.0
4	3	1	1	0.0351	9.25	0.0334	-4.8
5	1	1	3	0.0114	9.37	0.0120	+5.7
6	1	10	0	0.0534	13.69	0.0505	-5.4
7	10	1	0	0.0310	17.96	0.0302	-2.6
8	1	1	10	0.0033	10.41	0.00315	-4.5
9	2	2	2	0.0380	10.26	0.0380	0
10	0.2	0.2	0.2	0.0032	3.54	0.00288	-9.8
11	0.1	0.1	0.1	0.0008	3.54	0.00089	+10.7
12	5	5	5	0.0566	21.02	0.0599	-1.2
							lsuml = 59.2
							avg. = 4.9

P10-10 (b)

Discussion: The readers may check the validity of mechanism I. To reduce the accumulation of error in calculations, the readers should have used all data points and solved all unknowns simultaneously. To get the maximum information of complex kinetics of a reaction from the least runs, it is advantageous to do planned experiments such as factorial design. (W. G. Hunter, and A. C. Atkinson, Chemical Engineering, p. 159, June 6, 1966).

A paper discussing chemical reaction rate equations from experimental data is in: C. H. Ware Jr., Summer Computer Simulation Conference, Proceedings, 1975, Part I, p. 368.

P10-10 (c)

$$-r_A' = \frac{0.2223\, C_{A0}^2 (RT)^2 (1-X)^2 / (1-0.5X)^2}{\left[1 + \frac{C_{A0} RT}{1-0.5X}\left((0.475 + 0.322\,(1-X)) + 0.414X\right)\right]^2}$$

$$-r_A' = \frac{0.1113\, (RT\, C_{A0})^2 (1-X)^2 / (1-0.5X)^2}{\left[1 + \frac{C_{A0} RT}{1-0.5X}(0.797 - 0.383\, X)\right]^2}$$

$$P_{A0} = C_{A0} RT = 1.5 \text{ atm}$$

$$F_{A0} = 2.5 \frac{\text{mol}}{\text{min}} = 150 \frac{\text{mol}}{\text{hr}}$$

CSTR :

$$W = \frac{150 \times 0.8}{\frac{0.1113\, (1.5)^2 (1 - 0.8)^2 / (1 - 0.5 \times 0.8)^2}{\left[1 + \frac{1.5}{1 - 0.5 \times 0.8}(0.797 - 0.383 \times 0.8)^2\right]}}$$

$$W = 21{,}380 \text{ g} = 21.4 \text{ kg}$$

PFR :

$$W = F_{A0} \int_0^X \frac{dX}{-r_A'}$$

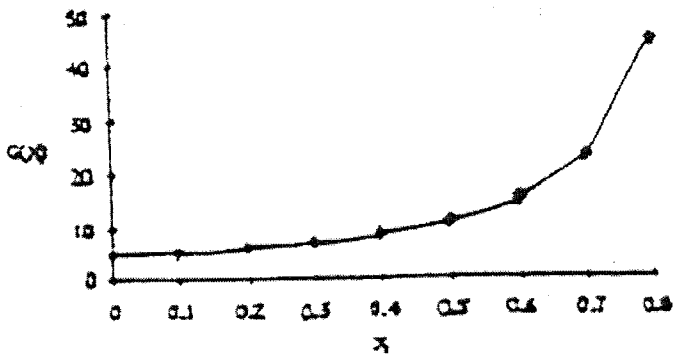
$$W = 150 \int_0^X \frac{dX}{\frac{0.1113\, (1.5)^2 (1 - X)^2 / (1 - 0.5\, X)^2}{\left[1 + \frac{1.5}{1 - 0.5\, X}(0.797 - 0.383\, X)\right]^2}}$$

$$W = \frac{150}{0.1113 \times 2.25} \int_0^X G(X)\, dX$$

where $$G(X) = \frac{\left[1 + \frac{1.5\,(0.797 - 0.383\,X)}{1 - 0.5\,X}\right]^2 (1 - 0.5\,X)^2}{(1 - X)^2}$$

$$G(X) = \left(\frac{2.1955 - 1.0745\,X}{1 - X}\right)^2$$

X	G(X)
0	4.82
0.1	5.38
0.2	6.13
0.3	7.16
0.4	8.66
0.5	11.00
0.6	15.03
0.7	23.15
0.8	44.62



Using Simpson's rule,

area under the curve = 10

$$W = \frac{150}{0.1113 \times 2.25} \times 10 = 6000\ g = 6\ kg$$

P10-10 (d)

Consider the differential section between L and L + dL

In - Out + Generation = Accumulation

$$r_A(C_A, L)\, A_T\, \rho_C (1 - \phi)\, dL = -dL\left[\frac{d}{dL} A_T v(L) C_A(L)\right]$$

But: $A_T v(L) C_A(L) = N_A(L) = F_{A0}(1 - X)$

$$\therefore F_{A0}\frac{dX}{dL} = TA\ \rho_C\,(1 - \phi)\, r_A(P_i)$$

Relating the expression r_A to X and L :

$$F_A = F_{A0}(1\text{-}X) = \frac{1}{2} F_o (1\text{-}X)$$

$$F_B = F_{B0}(1\text{-}X) = \frac{1}{2} F_o (1\text{-}X)$$

$$F_C = F_{A0}\, X = \frac{1}{2} F_o\, X$$

$$F_T = \frac{1}{2}(2 - X)$$

$$P_A = \frac{F_A}{F_T} = \frac{1 - X}{2 - X}$$

$$P_A = P_A = \frac{1\text{-}X}{2\text{-}X} P_T \ ; \ P_C = \frac{X}{2\text{-}X} P_T$$

Let $P = P_T$,

$$\frac{dX}{dL} = \frac{TA\,\rho_C\,(1-\phi)}{F_{A0}}\, r_A\left[\frac{1-X}{2-X}P,\ \frac{1-X}{2-X}P,\ \frac{X}{2-X}P\right]$$

From the Ergun equation, we have:

$$\frac{dP}{dL} = \frac{G}{\rho g_o D_P}\left(\frac{1-\phi}{\phi^3}\right)\left[\frac{150\,(1-\phi)\,\mu}{D_P} + 1.75\,G\right]$$

All the things on RHS are constant, except for ρ

$$\rho = \rho_0\left(\frac{P}{P_0}\right)\left(\frac{2}{2-X}\right)$$

- $$\frac{dP}{dL} = \frac{2-X}{2}\left(\frac{P_o}{\rho_o}\right)\left(\frac{1}{P}\right)\frac{G}{g_C D_P}\left(\frac{1-\phi}{\phi^3}\right)\left[\frac{150\,(1-\phi)\,\mu}{D_P} + 1.75\,G\right]$$

$$\frac{dP}{dL} = \frac{2-X}{2P}\ \beta_o \text{ where } \beta_o = \frac{P_o\,G}{\rho_o\,g_C\,D_P}\frac{(1-\phi)}{\phi^3}\left[\frac{150\,(1-\phi)\,\mu}{D_P} + 1.75\,G\right]$$

$$\text{Let } L^* = \frac{L}{L_{des}}\ ;\ P^* = \frac{P}{P_o}\ ,\ \text{then}: \frac{dP}{dL} = \frac{2-X}{2P^*}\ \beta_o^*$$

$$\text{where } \beta_o^* = \frac{L_{des}}{P_o^2}\ \beta_o$$

$$\beta_o^* = \frac{LG\,(1-\phi)}{P_o\,\rho_o\,g_c\,D_P\,\phi^3}\left[\frac{150\,(1-\phi)\,\mu}{D_P} + 1.75\,G\right]$$

$$\phi = 0.4$$

$$D_P = \left(\frac{1}{16}\text{ in}\right)\left(\frac{1\text{ ft}}{12\text{ in}}\right) = \frac{1}{192}\text{ ft}$$

$$g_c = 32.174\ \frac{\text{lbm}\ \text{ft}}{\text{lb}_f\ \text{sec}^2}$$

$$G = \frac{(F_{A0}\,m_A + F_{B0}\,m_B)}{AT} = \frac{\left(150\ \frac{\text{gmol}}{\text{hr}}\right)(2+112)\ \frac{\text{g}}{\text{gmol}}\left(\frac{\text{lb}}{453.6\text{ g}}\right)}{T\ \frac{\pi}{4}\left(\frac{0.957}{12}\right)^2\text{ ft}^2}$$

$$G = \frac{7546.9}{T}\ \frac{\text{lbm}}{\text{ft}^2\,\text{hr}}$$

$$P_o = (3\text{ atm})\left(\frac{14.7\text{ psi}}{1\text{ atm}}\right)\left(\frac{144\text{ in}^2}{1\text{ ft}^2}\right) = 6348.7\ \frac{\text{lb}}{\text{ft}^2}$$

$$\rho_o = C_T\,\overline{m} = \left(\frac{57\text{ lb}}{\text{lbmol}}\right)\frac{P}{RT} = \frac{\left(57\ \frac{\text{lb}}{\text{lbmol}}\right)(3\text{ atm})}{\left(0.7301\ \frac{\text{ft}^3\,\text{atm}}{\text{lbmol}°\text{R}}\right)[(200+273.15)(1.8)]\,°\text{R}}$$

$$\beta_o^* = \frac{LG(1-\phi)}{P_o \rho_o g_c D_P \phi^3}\left[\frac{150(1-\phi)\mu}{D_P} + 1.75\,G\right]$$

$\phi = 0.4$

$$D_P = \left(\frac{1}{16}\text{ in}\right)\left(\frac{1\text{ ft}}{12\text{ in}}\right) = \frac{1}{192}\text{ ft}$$

$$g_c = 32.174\ \frac{\text{lbm}\ \text{ft}}{\text{lb}_f\ \text{sec}^2}$$

$$G = \frac{(F_{A0}\,m_A + F_{B0}\,m_B)}{AT} = \frac{\left(150\ \frac{\text{gmol}}{\text{hr}}\right)(2+112)\ \frac{\text{g}}{\text{gmol}}\left(\frac{\text{lb}}{453.6\text{ g}}\right)}{T\,\frac{\pi}{4}\left(\frac{0.957}{12}\right)^2\text{ ft}^2}$$

$$G = \frac{7546.9}{T}\ \frac{\text{lbm}}{\text{ft}^2\,\text{hr}}$$

$$P_o = (3\text{ atm})\left(\frac{14.7\text{ psi}}{1\text{ atm}}\right)\left(\frac{144\text{ in}^2}{1\text{ ft}^2}\right) = 6348.7\ \frac{\text{lb}}{\text{ft}^2}$$

$$\rho_o = C_T\,\overline{m} = \left(\frac{57\text{ lb}}{\text{lbmol}}\right)\frac{P}{RT} = \frac{\left(57\ \frac{\text{lb}}{\text{lbmol}}\right)(3\text{ atm})}{\left(0.7301\ \frac{\text{ft}^3\,\text{atm}}{\text{lbmol}^\circ\text{R}}\right)[(200+273.15)(1.8)]^\circ\text{R}}$$

$$\rho_o = 0.2750\ \frac{\text{lbm}}{\text{ft}^3}$$

$$\left.\begin{aligned}\mu(3\text{ atm}, 200^\circ\text{C}) &= 9.4719\times10^{-3}\text{ cp}\quad \left(\tfrac{1}{2}\,C_8\,,\ \tfrac{1}{2}\,H_C\right)\\ &= 8.6211\times10^{-3}\text{ cp}\quad (\text{all } C_8)\end{aligned}\right\}\ \text{PPROP}$$

$$\Rightarrow \mu = \frac{\left(9.4719\times10^{-3} + 8.6211\times10^{-3}\right)}{2}\text{ cp}\ 6.7197\times10^{-4}\ \frac{\text{lbm}}{\text{ft sec cp}}$$

$$\times\ \frac{3600\text{ sec}}{\text{hr}}$$

$$\mu = 0.02188\ \frac{\text{lbm}}{\text{ft hr}}$$

$$\beta_o^* = \frac{(35\text{ ft})\left(\frac{7546.9}{T}\ \frac{\text{lbm}}{\text{ft}^2\,\text{hr}}\right)(1-0.4)\left(\frac{1\text{ hr}}{3600\text{ sec}}\right)^2}{\left(6348.7\ \frac{\text{lb}_f}{\text{ft}^2}\right)\left(0.2750\ \frac{\text{lbm}}{\text{ft}^2}\right)\left(82.174\ \frac{\text{lbm ft}}{\text{lb}_f\,\text{sec}^2}\right)\left(\frac{1\text{ ft}}{192}\right)(0.4)^3}$$

$$\times\left[\frac{150(1-0.4)\left(0.02188\ \frac{\text{lbm}}{\text{ft hr}}\right)}{\left(\frac{1}{192}\text{ ft}\right)} + 1.75\left(\frac{7546.9}{T}\right)\frac{\text{lbm}}{\text{ft}^2\,\text{hr}}\right]$$

$$\frac{dX}{dL^*} = \left[\frac{L_d A T \rho_C (1-\phi)}{F_{A0}}\right] R_A(X_1 P^*)$$

where $$R_A = \frac{k P_A P_B}{(1 + K_A P_A + K_B P_B + K_C P_C)^2}$$

$$R_A = \frac{K P_o^2 \left(\frac{1-X}{2-X}\right)^2 P^{*2}}{\left[1 + (K_A P_o + K_B P_o)\left(\frac{1-X}{2-X}\right) P^* + K_C P_o \left(\frac{X}{2-X}\right) P^*\right]^2}$$

$$R_A = \frac{K P_0^2 (1-X)^2}{P_0^2\left[\frac{1}{P_0^2 P^{*2}} + (K_A + K_B)\left(\frac{1-X}{2-X}\right) + K_C\left(\frac{X}{2-X}\right)\right]^2}$$

$$R_A = \frac{K P_0^2 (1-X^2)}{\left[\frac{2-X}{P^{*2}} + (K_A + K_B) P_0 (1-X) + K_C P_0 X\right]^2}$$

Let: $\alpha^* = \dfrac{LAT \rho_\beta (1-\phi) K P_o^2}{F_{A0}}$; $K_1^* = (K_A + K_S) P_o$; $K_2^* = (K_C - K_A - K_B) P_o$

Then: $\dfrac{dX}{dL} = \alpha^* \dfrac{(1-X)^2}{\left[\frac{2-X}{P^*} + K_1^* + K_2^* X\right]^2}$

For a given T, we can solve the two ODE's to get X(L*). We need to guess T until X = 0.8.

For the rate constants, we use the solution of 6.10 (a)

$$K = 0.1118 \frac{\text{gmol}}{\text{gcat} \cdot \text{hr} \cdot \text{atm}^2} \quad ; \quad K_A = 0.475 \text{ atm}^{-1} \quad ; \quad K_B = 0.322 \text{ atm}^{-1}$$

$K_C = 0.414 \text{ atm}^{-1}$

$\therefore \quad K_1^* \cdot (0.475 + 0.322)\, 3 = 2.391$

$K_2 = (0.414 - 0.475 - 0.332)\, 3 = -1.149$

$$\alpha^* = \frac{LAT \rho_\beta (1-\phi) K P_o^2}{F_{A0}} = \frac{T(35 \text{ ft})(3.14/4)\left(\frac{0.957}{12}\right)^2 \text{ft}^2 \left(2.6 \frac{g}{cm^3}\right)}{\left(2.5 \frac{\text{gmol}}{\text{min}}\right)\left(\frac{60 \text{ min}}{1 \text{ hr}}\right)}$$

$$\times \left(0.113 \frac{\text{gmol}}{\text{gcat hr atm}^2}\right)(3 \text{ atm})^2 \left(\frac{30.41 \text{ cm}}{\text{ft}}\right)$$

$\alpha^* = 85.958\, T$

$$\beta_o^* = \left(\frac{6.531}{T} \times 10^{-4}\ \frac{ft^2\ hr}{lbm}\right)\left(378.09 + \frac{13207}{T}\right)\frac{lbm}{ft^2\ hr}$$

$$\beta_o^* = -\frac{0.24693}{T} - \frac{8.6255}{T^2}$$

A FORTRAN program is written to solve the equations. The results show that any numbers of tubes sufficient to allow the given flow rates with a positive pressure provides more than enough catalyst for the desired conversion. The problem as stated, therefore has no solution. However, we can choose a different L, and it only changes the dimensionless parameters. With L = 20, the problem is still unsolvable.

For L = 10 ft , T = 2.16 tubes $\Rightarrow \frac{P}{P_{in}} = 0.46$

Note: Using the modified program with

$D_p = \frac{1}{16}$ in , $\mu = 9.05 \times 10^{-3}$ cp

L = 10 ft , A = 2.15 in^2

$\Rightarrow$ X = 0.80 , P* = 0.7537

Using 1 1/2 in schedule 80 pipe (I.D. = 1.5 in) , A = 1.76715 in^2 and the length to get

X = 0.8 is impossible ($P_f < 0$).

With 2 in schedule 80 pipe (I.D. = 1.939 in) , A = 2.952877 in^2

This gives L = 6.67 ft , X = 0.80 and P = 0.9173

1 1/2 in schedule 40 $\Rightarrow$ A = 2.03580 in^2

L = 10.94857 , X = 0.8 and P = 0.6903

P10-11 (a)

$$A \rightarrow B + H$$

Assume a rate-limiting step; start with surface reaction

$$A \cdot S + S \rightleftarrows B \cdot S + H \cdot S$$

$$B \cdot S \rightleftarrows B + S$$

$$H \cdot S \rightleftarrows H + S$$

Assume a rate-limiting step; start with surface reaction

$$-r_A = r_s = k_s C_v P_{A \cdot S}$$

Come up with ways to find $P_{A \cdot S}$, $P_{B \cdot S}$, and $P_{H \cdot S}$

$$\frac{r_{AD}}{k_{AD}} = 0 \qquad C_{A \cdot S} = K_{AA} P_A C_V$$

$$C_{B \cdot S} = \frac{P_B C_V}{K_{DB}} = K_{AB} P_B C_V$$

$$\frac{r_{BD}}{k_{BD}} = 0$$

$$\frac{r_{HD}}{k_{HD}} = 0 \qquad C_{H \cdot S} = \frac{P_H C_H}{K_{DH}} = K_{DH} P_B C_V$$

Find the expression for C_v

$$C_t = C_v + C_{A \cdot S} + C_{B \cdot S} + C_{H \cdot S}$$

Combine all of those to get the following rate law suggestion.

$$r_s = \frac{k_s K_A P_A C_t^2}{\left(1 + K_A P_A + K_B P_B + K_H P_H\right)^2} = \frac{k P_A}{\left(1 + K_A P_A + K_B P_B + K_H P_H\right)^2}$$

Checking to see if it fits, we see that for high P_A, increases in P_A cause decreases in the rate. We see that if P_B or P_H increase the rate will go down, which is consistent with the rate law.

P10-11 (b)

Now using POLYMATH's non-linear equation regression we can find the values for the parameters. We find that

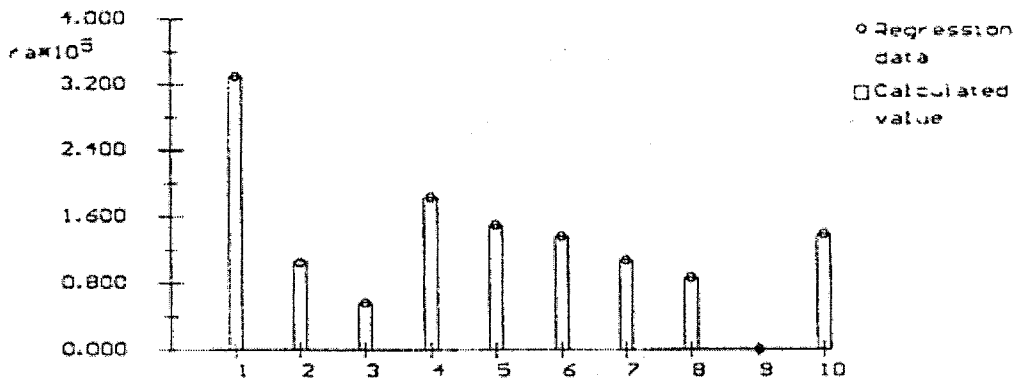
$k = 0.00137$

$K_a = 4.76$

$K_B = 0.259$

$K_C = 0.424$

In the problem it is given that K_A is 1 or 2 orders of magnitude greater than K_B and K_C which is true so this is a good answer.



Model: ra=k*Pa/(1+Ka*Pa+Kb*Pb+Kh*Ph)^2
k = 0.00137022 Kb = 0.259382
Ka = 4.76084 Kh = 0.42359
7 positive residuals, 3 negative residuals. Sum of squares = 5.27033e-15

P10-11 (c)

The estimates of the rate law parameters were given to simplify the search techniques to make sure that it converged on a false minimum. In real life, one should make a number of guesses of the rate lw parameters and they should include a large range of possibilities

---

P10-12 (a)

Assume that the second reaction is the rate-limiting step.

$$r_s = k_2 C_{SiH_4} S$$

Using PSSH, we know that

$$r^*_{SiH_4} S = 0 = k_1 C_{SiH_4} S C_v$$

$$C_{SiH_4\text{-}S} = \frac{k_1 C_{SiH_4} C_V}{k_2} = K C_{SiH_4} C_V$$

$$K = \frac{k_1}{k_2}$$

Perform a site balance:

$$C_t = C_V + C_{SiH_4} S$$

$$C_v = \frac{C_t}{1 + KC_{SiH_4}}$$

Combining all of these we find:

$$r_S = \frac{k_1 C_{SiH_4} C_v}{1 + KC_{SiH_4}} = \frac{kC_{SiH_4}}{1 + KC_{SiH_4}}$$

This rate law is consistent with the data. As the concentration gets larger, the rate change gets smaller which is consistent with the rate law as given.

P10-12 (b)

No answer is right or wrong, but the points will probably be higher than the ones given to see that the change in rate becomes even smaller.

P10-13

Assume the rate law is of the form $r_{Dep} = \frac{kP_{VTIPO}^2}{1 + KP_{VTIPO}^2}$

At high temperatures K ↓ as T ↑ and therefore $KP_{VTIPO}^2 \ll 1$

$$r_{Dep} = kP_{VTIPO}^2$$

$$\frac{r_{Dep}}{P_{VTIPO}^2} = k$$

Run 1 $\frac{0.028}{(0.05)^2} = 11.2$

Run 2 $\frac{0.45}{(0.2)^2} = 11.28$

Run 5 $\frac{7.2}{(0.8)^2} = 11.25$

At low temperature and low pressure

$$r_{Dep} = kP_{VTIPO}^2$$

$$\frac{r_{Dep}}{P_{VTIPO}^2} = k$$

Run 1 $\frac{0.004}{(0.1)^2} = 0.4$

Run 2 $\frac{0.015}{(0.2)^2} = 0.375$

These fit the low pressure data

At high pressure $KP_{VTIPO}^2 \gg 1$

$$r_{Dep} = \frac{kP_{VTIPO}^2}{KP_{VTIPO}^2} = \frac{k}{K}$$

This fits the high pressure data
At $P_{VTIPO} = 1.5$, r = 0.095 and at $P_{VTIPO} = 2$, r = 0.1

Now find the activation energy
At low pressure and high temperature k = 11.2
At low pressure and low temperature k = 0.4

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{E}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\ln\left(\frac{11.2}{0.4}\right) = \frac{E}{R}\left(\frac{473-393}{(473)(393)}\right)$$

$$\frac{E}{R} = 7738$$

$$E = 15375\frac{cal}{mol}$$

P10-14

$$r_{TiO_2} = k_S f_{1*S} \qquad f_{1*S} = P_I K_I f_V$$

$$1 = f_V + f_{1*S} = f_V(1 + K_I P_I) \qquad f_{1*S} = \frac{K_I P_I}{1 + K_I P_I}$$

$$\frac{P_I P_{P1}}{P_{TIP}^2} = K_P \quad , \quad P_I = K_P P_{TIP}^2 / P_{P1}$$

$$r_{TiO_2} = \frac{k_S P_I K_I}{1 + P_I K_I}$$

$$r_{TiO_2} = k_S f_{1*S} \qquad f_{1*S} = P_I K_I f_V$$

$$1 = f_V + f_{1*S} = f_V\left(1 + K_I P_I\right) \qquad f_{1*S} = \frac{K_I P_I}{1 + K_I P_I}$$

$$\frac{P_I P_{P1}}{P^2_{TTIP}} = K_P \quad , \quad P_I = K_P P^2_{TTIP}/P_{P1}$$

$$r_{TiO_2} = \frac{k_S P_I K_I}{1 + P_I K_I}$$

$$r_{TiO_2} = \frac{kP^2_{TTIP} / P_{PI}}{1 + \left(P^2_{TTIP} / P_{PI}\right)K} = \frac{kP^2_{TTIP}}{P_{PI} + P^2_{TTIP}K}$$

Low P_{TTIP}: Rxn is second order

Since $1 >> K P^2_{TTIP}/P_{P1}$

High P_{TTIP}: $1 << K P^2_{TTIP}/P_{P1}$

Reaction is zero order

High Temperature K_I very small such that

$$P^2_{TTIP} K_P K_I << P_{P1}$$

P10-15 (a)

Using Polymath non-linear regression few can find the parameters for all models:

See Polymath program P10-15.pol.

(1)

POLYMATH Results

Nonlinear regression (L-M)

Model: rT = k*PM^a*PH2^b

Variable	Ini guess	Value	95% confidence
k	1	1.1481487	0.1078106
a	0.1	0.1843053	0.0873668
b	0.1	-0.0308691	0.1311507

Precision

R^2	= 0.7852809
R^2adj	= 0.7375655
Rmsd	= 0.0372861
Variance	= 0.0222441

$\alpha = 0.184$ $\beta = -0.031$ $k = 1.148$

(2)

POLYMATH Results

Nonlinear regression (L-M)

Model: rT = k*PM/(1+KM*PM)

Variable	Ini guess	Value	95% confidence
k	1	12.256274	2.1574162
KM	2	9.0251862	1.8060287

Precision

R^2	= 0.9800096
R^2adj	= 0.9780106
Rmsd	= 0.0113769
Variance	= 0.0018638

$k = 12.26 \quad K_M = 9.025$

(3)

OLYMATH Results

Nonlinear regression (L-M)

Model: rT = k*PM*PH2/((1+KM*PM)^2)

Variable	Ini guess	Value	95% confidence
k	1	8.4090333	18.516752
KM	2	2.8306038	4.2577098

Precision

R^2	= -4.3638352
R^2adj	= -4.9002187
Rmsd	= 0.1863588
Variance	= 0.5001061

$k = 8.409 \quad K_M = 2.83$

(4)

POLYMATH Results

Nonlinear regression (L-M)

Model: rT = k*PM*PH2/(1+KM*PM+KH2*PH2)

Variable	Ini guess	Value	95% confidence
k	1	101.99929	4.614109
KM	2	83.608282	7.1561591
KH2	2	67.213622	5.9343217

Nonlinear regression settings
Max # iterations = 300

Precision

R^2	= -3.2021716
R^2adj	= -4.1359875
Rmsd	= 0.1649487
Variance	= 0.4353294

$k = 102 \quad K_M = 83.6 \quad K_{H2} = 67.21$

P10-15 (b)

We can see from the precision results from the Polymath regressions that rate law (2) best describes the data.

P10-16

Using Polymath non-linear regression few can find the parameters for all models:

See Polymath program P10-16.pol.

(1)

POLYMATH Results
Nonlinear regression (L-M)

Model: r = k*KNO*PNO*PH2/(1+KNO*PNO+KH2*PH2)

Variable	Ini guess	Value	95% confidence
k	1	0.0030965	3.702E-05
KNO	1	57.237884	1.0353031
KH2	1	101.9967	2.2870513

Precision

R^2	= 0.9709596
R^2adj	= 0.9645062
Rmsd	= 5.265E-07
Variance	= 4.436E-12

$k = 0.0031 \quad K_{NO} = 57.23 \quad K_{H2} = 102$

(2)

POLYMATH Results
Nonlinear regression (L-M)

Model: r = k*KNO*PNO*KH2/(1+KNO*PNO+KH2*PH2)

Variable	Ini guess	Value	95% confidence
k	0.1	-4.713E-06	1.297E-05
KNO	10	-108.42354	4.9334604
KH2	1	1.046E-05	2.878E-05

Nonlinear regression settings
Max # iterations = 300

Precision

R^2	= -9.6842898
R^2adj	= -12.058576
Rmsd	= 1.01E-05
Variance	= 1.632E-09

$k = -0.00000471 \quad K_{NO} = -108.4 \quad K_{H2} = 0.00001046$

(3)

POLYMATH Results
Nonlinear regression (L-M)

Model: r = k*KNO*PNO*KH2*PH2/((1+KNO*PNO+KH2*PH2)^2)

Variable	Ini guess	Value	95% confidence
k	0.1	5.194E-04	2.242E-04
KNO	10	13.187119	7.659298
KH2	1	18.487727	7.7652667

Nonlinear regression settings
Max # iterations = 300

Precision

R^2	= 0.9809761
R^2adj	= 0.9767486
Rmsd	= 4.262E-07
Variance	= 2.906E-12

$k = 0.000519 \quad K_{NO} = 13.19 \quad K_{H2} = 18.49$

The third rate law best describes the data.

P10-17 (a)

Mole balance:

$$\frac{dX}{dW} = \frac{(-r_A')a}{F_{A0}}$$

Rate law:

$$r_A' = -k'C_A$$

Decay law:

$$\frac{da}{dW} = -\frac{k_d a C_A}{U_S}$$

Stoichiometry:

$$C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}$$

Evaluate the parameters:

$$\varepsilon = .8$$

POLYMATH

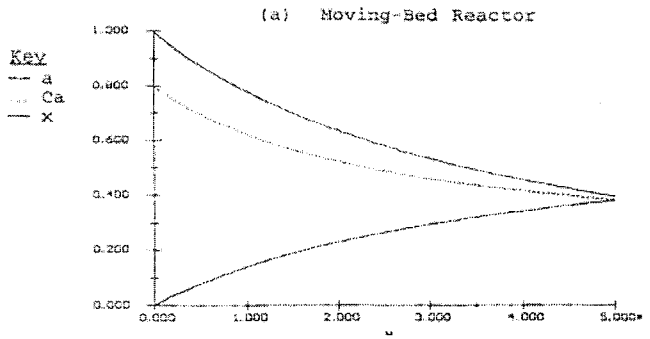
Equations:

```
d(x)/d(w)=a*(-ra)/fao
d(a)/d(w)=-kd*a*ca/Us
kd=9
fao=4000000
```

Initial value

```
0
1
```

```
Us=250000
k=90
cao=.8
eps=.8
ca=cao*(1-x)/(1+eps*x)
ra=-k*ca
W0 = 0,    WE = 50000
```



P10-17 (b)

Mole balance:

$$\frac{dC_{A1}}{dt} = \frac{C_{A0}}{\tau} - \left(\frac{1+y_{A0}}{1+\frac{C_{A1}}{C_{T0}}} + \tau ak\right)\frac{C_{A1}}{\tau}$$

$$\frac{dC_{A2}}{dt} = \frac{C_{A1}}{\tau} - \left(\frac{1+y_{A1}}{1+\frac{C_{A2}}{C_{T0}}} + \tau ak\right)\frac{C_{A2}}{\tau}$$

$$\frac{dC_{A3}}{dt} = \frac{C_{A2}}{\tau} - \left(\frac{1+y_{A2}}{1+\frac{C_{A3}}{C_{T0}}} + \tau ak\right)\frac{C_{A3}}{\tau}$$

$$\frac{dC_{A4}}{dt} = \frac{C_{A3}}{\tau} - \left(\frac{1+y_{A3}}{1+\frac{C_{A4}}{C_{T0}}} + \tau ak\right)\frac{C_{A4}}{\tau}$$

$$\frac{dC_{A}}{dt} = \frac{C_{A4}}{\tau} - \left(\frac{1+y_{A4}}{1+\frac{C_{A}}{C_{T0}}} + \tau ak\right)\frac{C_{A}}{\tau}$$

Everything else is the same and we need to know τ.

$$\tau = \frac{V}{v_0} = 0.004$$

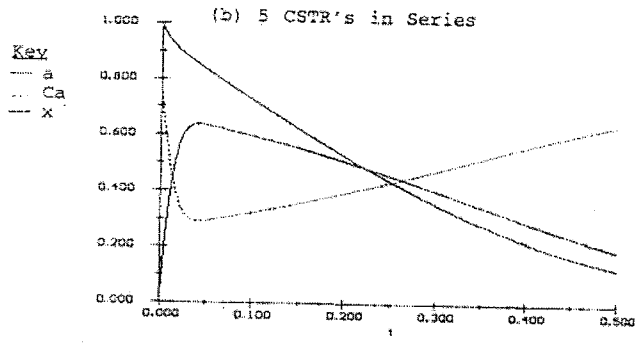
```
5 CSTR's in Series
```

Equations:	Initial value
d(a)/d(t)=-kd*a*ca	1
d(ca)/d(t)=ca4/tau-(((1+ya4)/(1+ca/cto))+tau*a*k)*ca/tau	0.8
d(ca4)/d(t)=ca3/tau-(((1+ya3)/(1+ca4/cto))+tau*a*k)*ca4/t	0.8
d(ca1)/d(t)=cao/tau-(((1+yao)/(1+ca1/cto))+tau*a*k)*ca1/t	0.8
d(ca2)/d(t)=ca1/tau-(((1+ya1)/(1+ca2/cto))+tau*a*k)*ca2/t	0.8
d(ca3)/d(t)=ca2/tau-(((1+ya2)/(1+ca3/cto))+tau*a*k)*ca3/t	0.8

```
kd=9
```

```
tau=0.004
cto=1
k=45
cao=0.8
ya4=ca4/cto
ya1=ca1/cto
ya2=ca2/cto
ya3=ca3/cto
x=(cao-ca)/cao
yao=cao/cto
```

$t_0 = 0, \quad t_f = 0.5$



P10-17 (c)

The only change from part (a) is the decay law:

$$\frac{da}{dt} = -k_d a C_A$$

$$t = \frac{W_{max} - W}{U_s}$$

$$dt = \frac{-dW}{U_s}$$

$$\frac{da}{dW} = \frac{k_d C_A a}{U_s}$$

Integrating:

$$\ln a = \frac{k_d C_A W}{U_s} + k$$

$W = W_{MAX}$ @ $a = 1$

$$k = -\frac{k_d C_A W_{MAX}}{U_s}$$

$$a = \exp\left(\frac{k_d C_A (W - W_{max})}{U_s}\right)$$

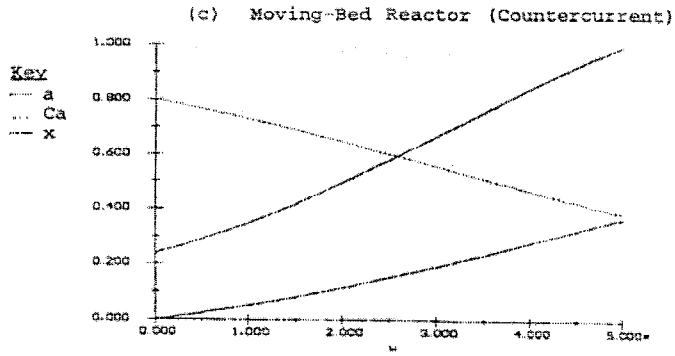
Equations:

```
d(x)/d(w)=a*(-ra)/fao
k=90
fao=4000000
kd=9
Us=250000
wmax=50000
cao=.8
eps=.8
ca=cao*(1-x)/(1+eps*x)
ra=-k*ca
a=exp(kd*ca/Us*(w-wmax))
```

$w_0 = 0, \quad w_f = 50000$

Initial value

0

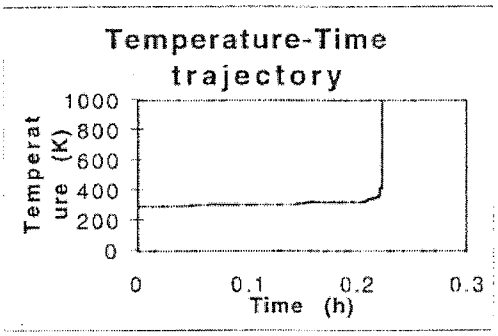


P10-17 (d)

To find the Time-Temperature Trajectory we need to use the following equation for first-order decay.

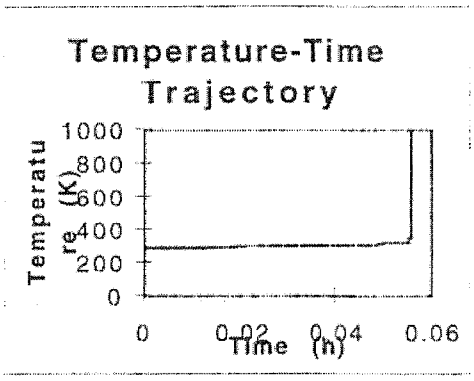
$$t = \frac{E_A}{k_{d0} C_A E_d}\left[1 - \exp\left[\frac{E_d}{R}\left(\frac{1}{T} - \frac{1}{300}\right)\right]\right]$$

Since no initial temperature was given, we assumed one of 300K. This is the graph of that equation.



P10-17 (e)

The two energy of activations are switched and this is the new graph made.



The graph looks the same just the time is much smaller.

P10-18 (a)

For all of the parts, the mole balances and rate laws are the same. They are:

$$\frac{dC_A}{dW} = r_A v_0 \qquad \frac{dC_B}{dW} = r_B v_0$$

$$r_A = -kaC_A \qquad r_B = kaC_A$$

Find the equation needed for a.

$$-\frac{da}{dt} = k_d a C_A$$

$$a = \exp(-k_d C_A t)$$

a=1 when t=0

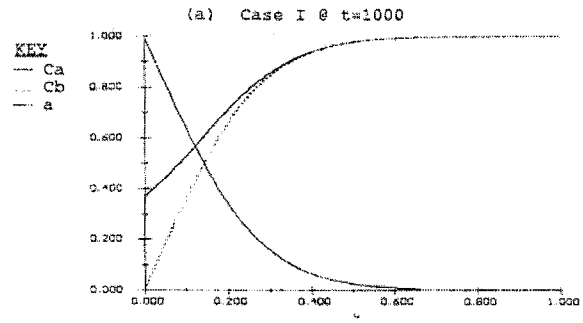
Assuming values for v_0, k, and k_d come up with the following graphs according to the cases described.

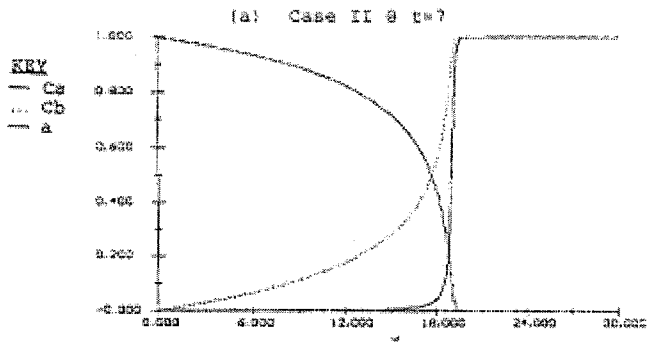
Equations:

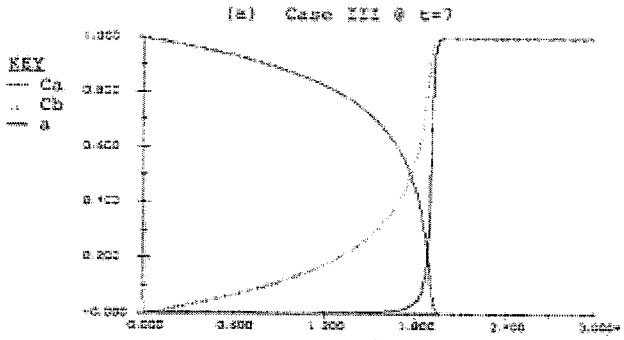
```
d(cb)/d(w)=rb*vo
d(ca)/d(w)=ra*vo
vo=10
a=1
kd=1
t=20
k=1
ra=-k*a*ca
rb=k*a*ca
```

$w_0 = 0, \quad w_f = 50$

Initial value
0
1







P10-18 (b)

- Find the new equation for a:

$$-\frac{da}{dt} = k_d a^2 C_A$$

$$a = \frac{1}{1 + k_d C_A t}$$

Using same values come up with these graphs:

Equations:

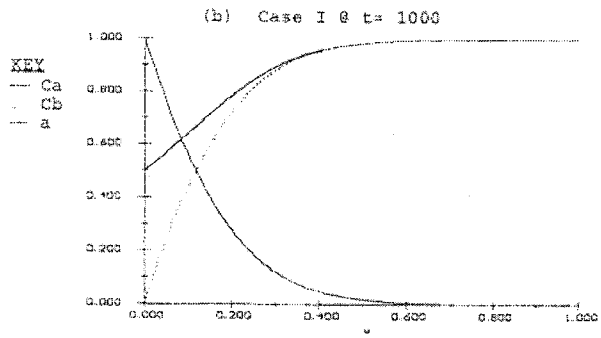
```
d(cb)/d(w)=rb*vo
d(ca)/d(w)=ra*vo
vo=10
kd=.001
t=1000
k=1
a=1/(1+kd*ca*t)
ra=-k*a*ca
rb=k*a*ca
```

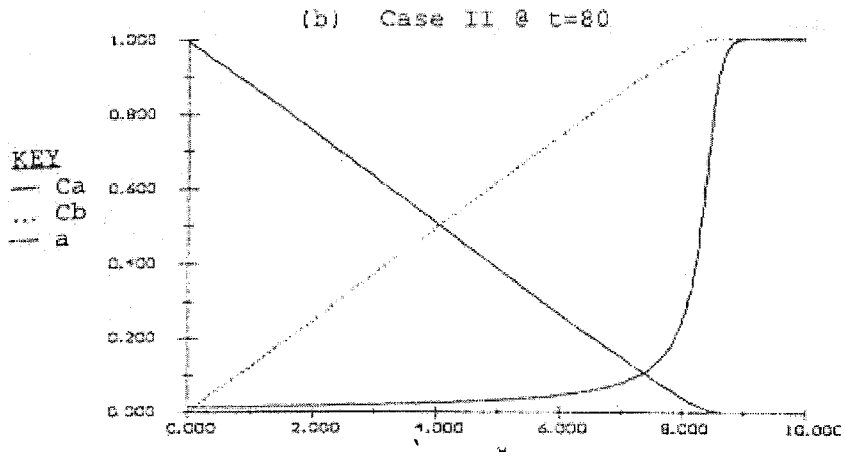
$w_0 = 0, \quad w_f = 1$

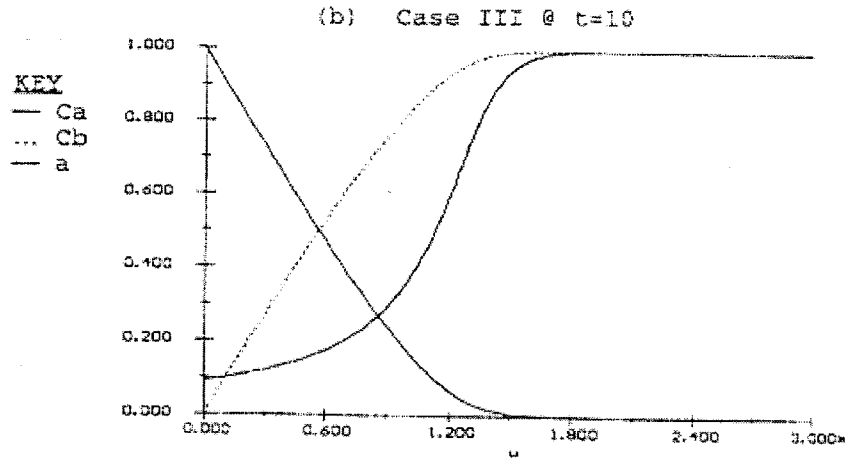
Initial value

0

1







P10-18 (c)

Find the new equation for a:

$$-\frac{da}{dt} = k_d a C_B$$

$$a = \exp(-k_d C_B t)$$

The following graphs are made:

Equations:

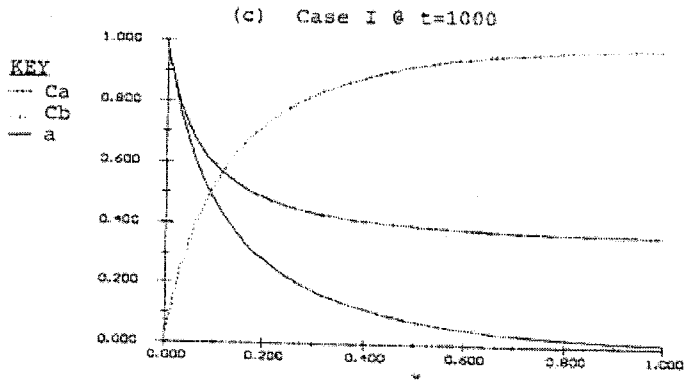
```
d(ca)/d(w)=ra*vo
d(cb)/d(w)=rb*vo
vo=10
kd=.001
t=1000
k=1
a=exp(-kd*cb*t)
rb=k*a*ca
ra=-k*a*ca
```

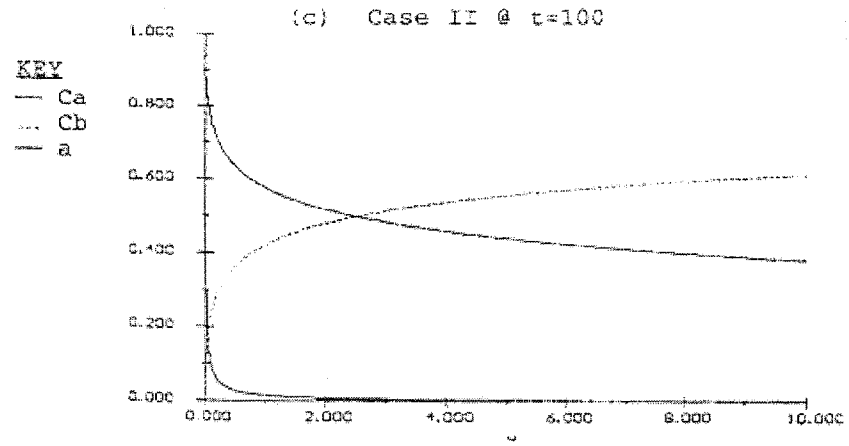
$w_0 = 0, \quad w_f = 1$

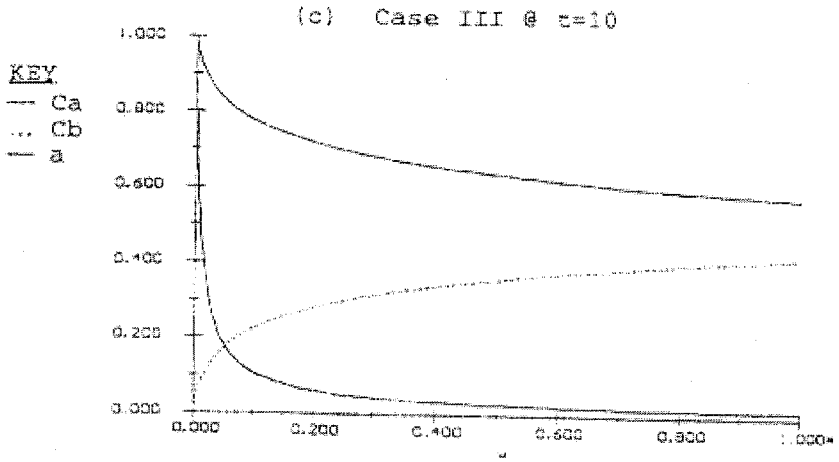
Initial value

1

0







P10-18 (d)

Making a into a differential equation we come up with this:

$$\frac{da}{dt} = k_d C_A a$$

$$t = \frac{W}{U_s}$$

$$\frac{da}{dW} = \frac{k_d C_A a}{U_s}$$

Equations:

d(ca)/d(w)=ra*vo

d(cb)/d(w)=rb*vo

d(a)/d(w)=-kd*a*ca/Us

vo=10

kd=.001

Us=10

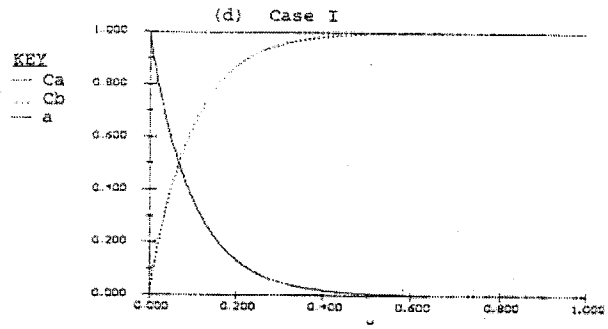
k=1

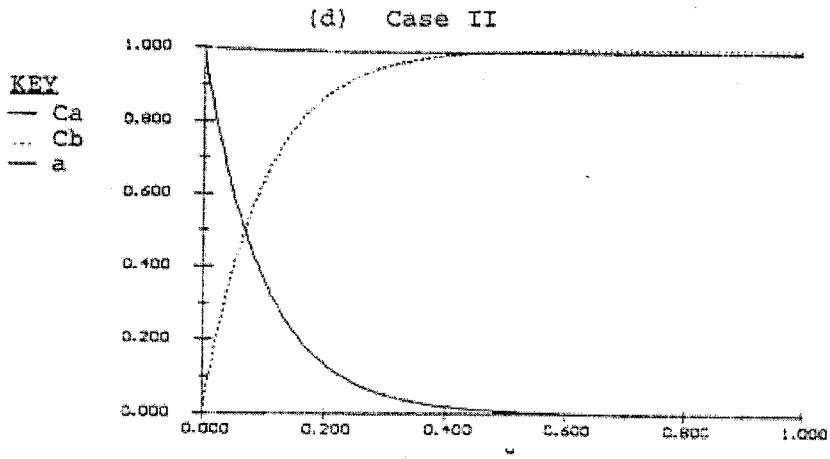
rb=k*a*ca

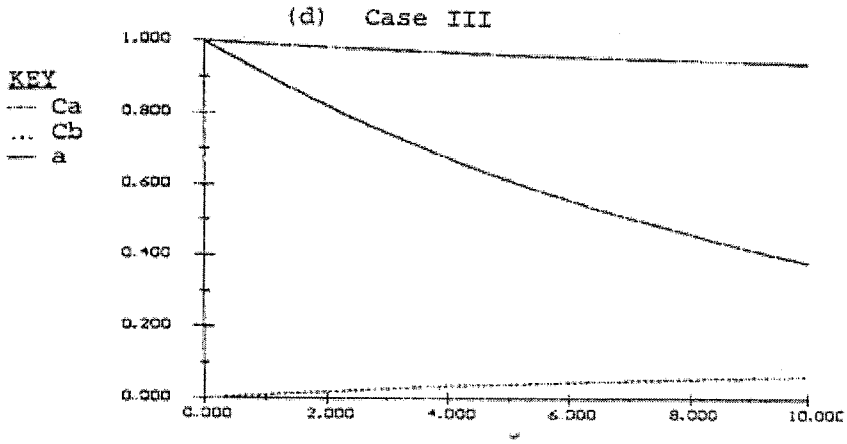
ra=-k*a*ca

$w_0 = 0, \quad w_f = 1$

Initial value
1
0
1







P10-18 (e)

Everything from part (d) is the same except for the decay law.

$$\frac{da}{dt} = -k_d a C_A$$

$$t = \frac{W_{MAX} - W}{U_S}$$

$$dt = -\frac{dW}{U_S}$$

$$\frac{da}{dW} = \frac{k_d C_A a}{U_S}$$

Integrating:

$$\ln a = \frac{k_d C_A W}{U_S} + k$$

$W = W_{MAX}$ @ a = 1

$$k = -\frac{k_d C_A W_{MAX}}{U_S}$$

$$a = \exp\left[\frac{k_d C_A (W - W_{MAX})}{U_S}\right]$$

Equations:

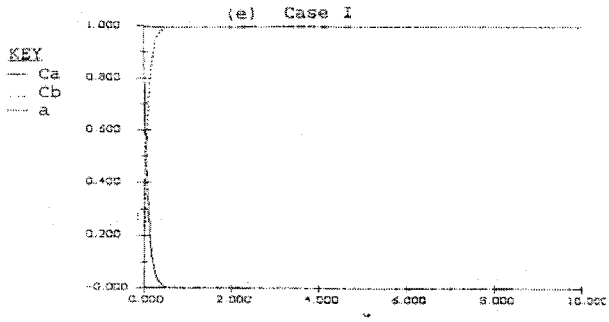
```
d(ca)/d(w)=ra*vo
d(cb)/d(w)=rb*vo
vo=10
kd=1
Us=10
k=.001
wmax=10
a=exp(kd*ca/Us*(w-wmax))
rb=k*a*ca
ra=-k*a*ca
```

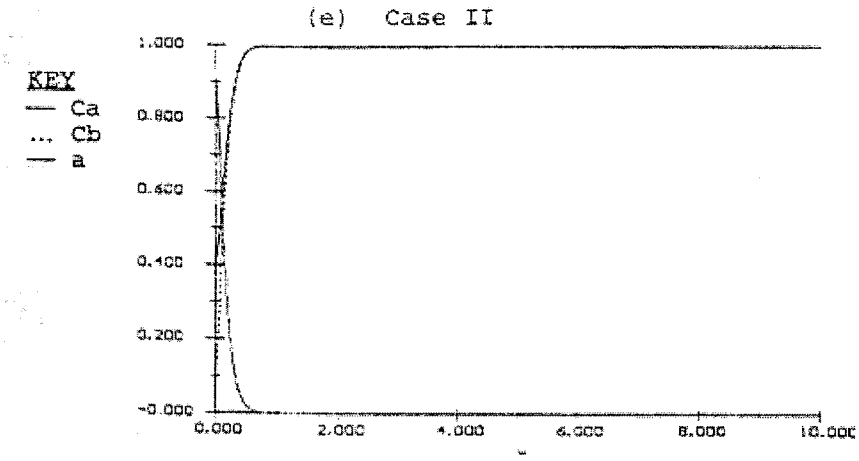
$w_0 = 0, \quad w_f = 10$

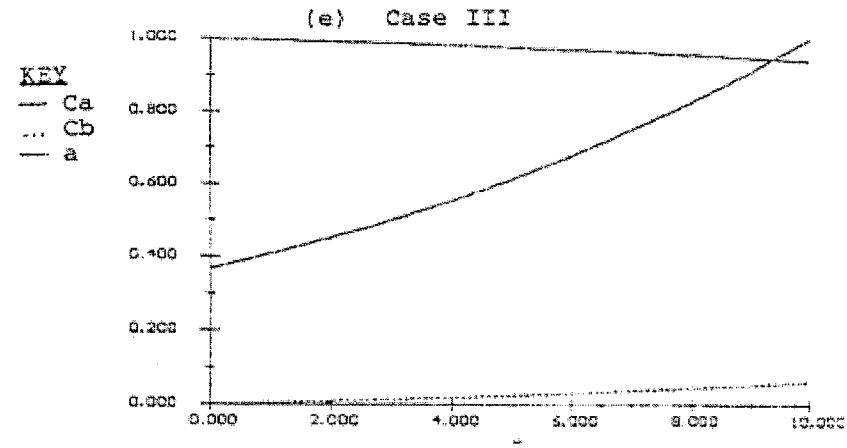
Initial value

```
1
0
```

(e) Case I







P10-19(a)

$$\frac{da}{dt} = -k_D \qquad W = U_S t \qquad dW = U_S dt$$

$$\frac{dt}{dW}\frac{da}{dt} = \frac{-k_D}{U_S} \qquad a = 1 - \frac{k_D W}{U_S}$$

If $0 = 1 - \frac{k_D W}{U_S}$ then $W = \frac{U_S}{k_D} = \frac{.5}{.2} = 2.5\,kg$

$$\frac{dX}{dW} = \frac{-r_A}{F_{A0}} = \frac{a}{F_{A0}}\left(-r_A(0)\right) = \frac{akC_{A0}^2(1-X)^2}{F_{A0}}$$

$$\frac{dX}{dW} = \left(1 - \frac{k_D W}{U_S}\right)\frac{kC_{A0}(1-X)^2}{v_0}$$

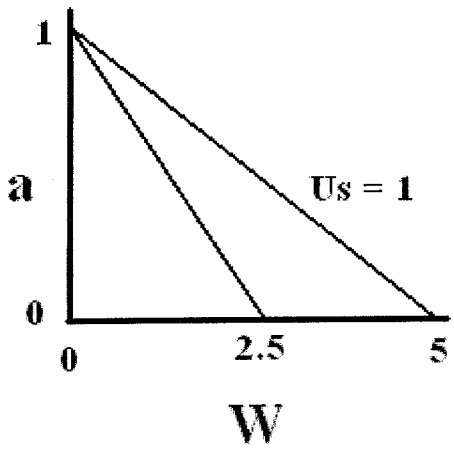
$$\int \frac{dX}{(1-X)^2} = \frac{kC_{A0}}{v_0}\int 1 - \frac{k_D W}{U_S} dW$$

Activity is zero for W > 2.5 kg, so the catalyst weight only goes to the effective weight.

$$\frac{X}{1-X}=\frac{kC_{A0}}{v_0}\left[W_e-\frac{k_D W_e^2}{2U_s}\right]=\frac{1(0.2)}{1}\left[2.5-\frac{0.2(2.5)^2}{2*0.5}\right]=0.25$$

$$X=0.2$$

P10-19(b)



P10-19(c)

For infinite catalyst loading a = 1.

$$\frac{dX}{dW}=\frac{kC_{A0}(1-X)^2}{v_0}$$

$$\frac{X}{1-X}=\frac{kC_{A0}}{v_0}W=1$$

$$X=0.5$$

P10-19(d)

$$\frac{X}{1-X}=\frac{kC_{A0}}{v_0}\left[W-\frac{k_D W^2}{2U_s}\right]$$

$$\frac{0.4}{1-0.4}=0.2\left[5-\frac{0.2*25}{2U_s}\right]$$

$$U_S=1.5\frac{kg}{s}$$

P10-19(e)

$$a=1-\frac{k_D W}{U_S}$$

$$0=1-\frac{k_D W}{U_S}$$

$$U_S = k_D W = 0.2*5 = 1\frac{kg}{s}$$

P10-19(f)

a = 0 means there is no reaction is taking place. Activity can never be less than 0.

P10-19(g)

$$U = -U_S$$

$$\frac{da}{dW} = \frac{k_D}{U_S} \qquad \text{when } W = W_t,\ a = 1$$

$$a = \frac{k_D W}{U_S} + C$$

$$1 = \frac{k_D W_t}{U_S} + C$$

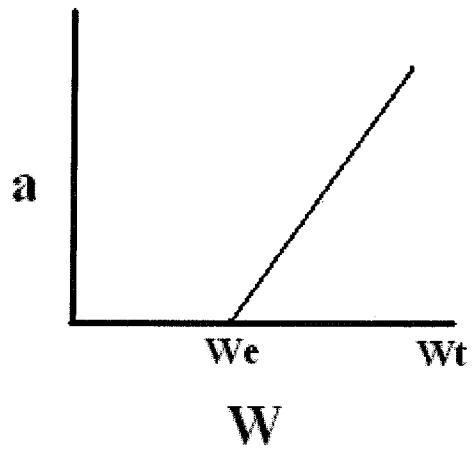
$$a = \frac{k_D W_e}{U_S} + 1 - \frac{k_D W_t}{U_S}$$

Now find W_e.

$$0 = \frac{k_D W_e}{U_S} + 1 - \frac{k_D W_t}{U_S}$$

$$W_e = \frac{U_S}{k_D}\left[\frac{k_D W_t}{U_S} - 1\right] = \frac{.5}{.2}\left[\frac{.2*5}{.5} - 1\right]$$

$$W_e = 2.5$$



$$\frac{dX}{dW} = \left(1 - \frac{k_D W_t}{U_S} + W\right)\frac{kC_{A0}(1-X)^2}{v_0}$$

$$\frac{X}{1-X} = \frac{kC_{A0}}{v_0}\int\left(1 - \frac{k_D W_t}{U_S} + W\right)dW$$

$$\frac{X}{1-X} = \frac{kC_{A0}}{v_0}\left[(W_t - W_e)\left(1 - \frac{k_D W_t}{U_S}\right) + \frac{W_t^2 - W_e^2}{2}\right]$$

$$\frac{X}{1-X} = 0.2\left[(5-2.5)\left(1 - \frac{0.2*5}{0.5}\right) + \frac{25-6.25}{2}\right]$$

$$\frac{X}{1-X} = 1.875$$

$$X = 0.65$$

P10-19(h)

$$\$ = 160F_{A0}X - 10U_S$$

$$a = 1 - \frac{k_D W}{U_S}$$

$$\frac{dX}{dW} = ka = k\left(1 - \frac{k_D W}{U_S}\right)$$

$$X = kW - \frac{kk_D W^2}{2U_S}$$

To maximize profit, a maximum in profit is reached and so we set the differential of profit equal to 0.

$$\frac{d\$}{dU_S} = 0 = 160F_{A0}\frac{dX}{dU_S} - 10$$

$$\frac{dX}{dU_S} = \frac{kk_D W^2}{2U_S^2}$$

$$160F_{A0}\frac{kk_D W^2}{2U_S^2} = 10$$

$$8F_{A0}kk_D W^2 = U_S^2$$

$$U_S = \sqrt{8F_{A0}kk_D W^2} = \sqrt{8(2)(.2)(.2)(25)}$$

$$U_S = 4\frac{kg}{\text{min}}$$

P10-19(i) No solution will be given

P10-20 (a)

Start with the mole balance for a batch reactor:

$$\frac{dX}{dt} = \frac{-r_T' W}{N_{T0}}$$

Rate law:

$$-r_T' = k_T P_T a$$

Decay law:

$$-\frac{da}{dt} = k_d a^2$$

Stoichiometry:

$$P_T = P_{T0}(1 - X)$$

Plugging those into POLYMATH gets the following program and the following graph

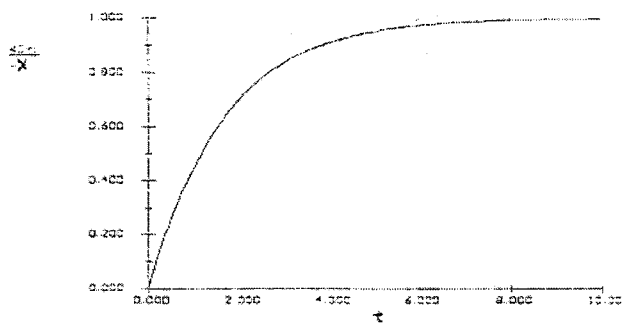
Equations:

```
d(x)/d(t)=-rt*w/nto
d(a)/d(t)=-kd*a^2
w=5
kt=20
kd=1.6
pto=1
v=1
R=.082
T=735
pt=pto*(1-x)
rt=-kt*pt*a
nto=pto*v/(R*T)
```

$t_0 = 0, \quad t_f = 0.001$

Initial value

```
0
1
```



P10-20 (b)

For the moving-bed reactor the mole balance now becomes:

$$\frac{dX}{dW} = \frac{-r_T'}{F_{A0}}$$

The decay law now becomes:

$$-\frac{da}{dW} = \frac{k_d a^2}{U_S}$$

Everything stays the same. Plug into POLYMATH.
The conversion achieved is X = 0.266

Equations:

```
d(x)/d(w)=-rt/fao
d(a)/d(w)=-kd*a^2/Us
kt=20
fao=600
kd=1.6
Us=2
pto=2
pt=pto*(1-x)
rt=-kt*pt*a
```

$w_0 = 0, \quad w_f = 50$

Initial value

```
0
1
```

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	50	0	50
x	0	0.26616	0	0.26616
a	1	1	0.0243902	0.0243902
kt	20	20	20	20
fao	600	600	600	600
kd	1.6	1.6	1.6	1.6
Us	2	2	2	2
pto	2	2	2	2
pt	2	2	1.46768	1.46768
rt	-40	-0.715941	-40	-0.715941

P10-20 (c)

c) Increasing U_S will get us a higher conversion. Looking at this summary table,
U_s = 10 kg/h and X = 0.6

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	50	0	50
a	1	1	0.111111	0.111111
x	0	0.599688	0	0.599688
fao	600	600	600	600
kd	1.6	1.6	1.6	1.6
Us	10	10	10	10
kt	20	20	20	20
pto	2	2	2	2
pt	2	2	0.800625	0.800625
rt	-40	-1.77917	-40	-1.77917

P10-20 (d)

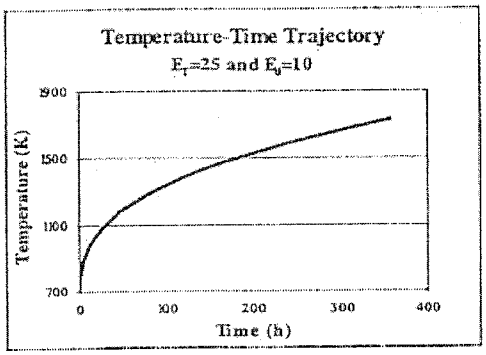
For second-order decay:

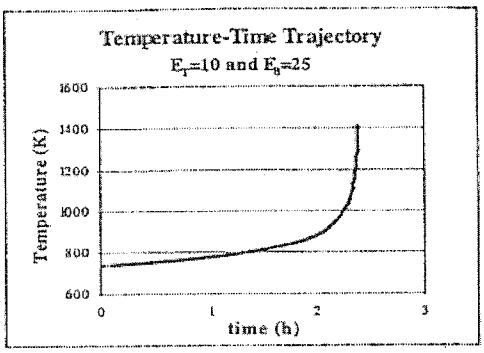
$$t = \frac{1 - \exp\left[\frac{E_T - 2E_T + E_d}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right]}{k_{do}\left(1 - 2 + E_d/E_T\right)} = \frac{1 - \exp\left[\frac{E_d - E_T}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right]}{k_{do}\left(E_d/E_T - 1\right)}$$

For $E_T = 25$ kcal/mol and $E_d = 10$ kcal/mol:

$$t = \frac{1 - \exp\left[\frac{10 - 25}{0.001987}\left(\frac{1}{T} - \frac{1}{735}\right)\right]}{(1.6)(10/25 - 1)} = 0.96\left[1 - \exp\left[-7{,}549\left(\frac{1}{T} - \frac{1}{735}\right)\right]\right]$$

Use this equation in Excel to generate the following graph:





For $E_T = 10$ kcal/mol and $E_d = 25$ kcal/mol:

$$t = \frac{1 - \exp\left[\frac{25 - 10}{0.001987}\left(\frac{1}{T} - \frac{1}{735}\right)\right]}{1.6(25/10 - 1)} = 2.4\left[1 - \exp\left[7{,}549\left(\frac{1}{T} - \frac{1}{735}\right)\right]\right]$$

Use this equation in Excel to generate the above graph.

P10-20 (e)

In part e, the only thing that changes from (b) is the decay law and the decay constant:

$$\frac{da}{dW} = \frac{k_d P_T^2 a^2}{U_S}$$

$$k_d = 0.2$$

Plugging into POLYMATH we get the following summary tables for $U_S = 2$ and 10 kg/h. X = 0.50 and 0.88 respectively. X will again increase as U_S increases.

Equations:

d(x)/d(w)=-ra/fao

d(a)/d(w)=-kd*pt^2*a^2/Us

kd=.2

Us=2

fao=600

kt=20

pto=2

pt=pto*(1-x)

ra=-kt*pt*a

$w_0 = 0, \quad w_f = 50$

Initial value
0
1

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	50	0	50
x	0	0.502431	0	0.502431
a	1	1	0.104635	0.104635
kd	0.2	0.2	0.2	0.2
Us	2	2	2	2
fao	600	600	600	600
kt	20	20	20	20
pto	2	2	2	2
pt	2	2	0.995138	0.995138
ra	-40	-2.08253	-40	-2.08253

10-19e

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	50	0	50
x	0	0.875709	0	0.875709
a	1	1	0.553922	0.553922
kd	0.2	0.2	0.2	0.2
Us	10	10	10	10
fao	600	600	600	600
kt	20	20	20	20
pto	2	2	2	2
pt	2	2	0.248581	0.248581
ra	-40	-2.75389	-40	-2.75389

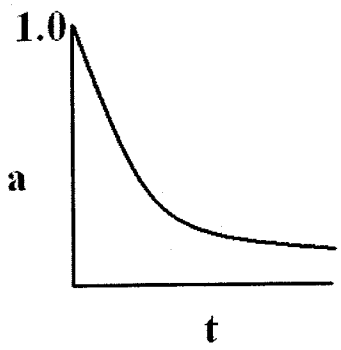
P10-21 (a)

A → B Elementary reaction with 1st order decay.

$$\frac{da}{dt} = -k_D a$$

$$a = \exp(-k_D t)$$

P10-21 (b)



The activity is never zero for first order decay. When $a = \exp(-k_D t)$ there is no t such that a = 0.

P10-21 (c)

Mole balance:

$$\frac{dX}{dt} = \frac{-r'_A W}{N_{A0}} = \frac{-r'_A W}{C_{A0} v_0} = \frac{-r'_A}{C_{A0}} \frac{W}{v_0}$$

Rate Law:

$$r_A' = -a\left[-r_A'(t=0)\right]$$

$$-r_A'(t=0) = k_1 C_A$$

Decay:

$$a = \exp(-k_D t)$$

Stoichiometry:

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

Combine:

$$\frac{dX}{dt} = \exp(-k_D t) k_1 (1-X) \frac{W}{v_0}$$

$$\ln\left(\frac{1}{1-X}\right) = \frac{k_1 W}{k_D v_0}\left[1-\exp(-k_D t)\right]$$

$$X = 1-\exp\left(-\frac{k_1 W}{k_D v_0}\left[1-\exp(-k_D t)\right]\right)$$

P10-21 (d)

$$\frac{k_1 W}{k_D v_0} = \frac{(0.2)(1)}{(0.1)(1)} = 2$$

$$X = 1-\exp\left(-2\left[1-\exp(-1)\right]\right) = 0.97$$

P10-21 (e)

Decay rate increases more rapidly with temperature than does the specific reaction rate. Therefore, conversion decreases with increasing temperature.

P10-21 (f)

$$\frac{k_1 W}{k_D v_0}(T) = 2\exp\left[-1500\left(\frac{1}{310}-\frac{1}{400}\right)\right] = 0.57$$

$$k_D = 0.1\exp\left[2000\left(\frac{1}{300}-\frac{1}{400}\right)\right] = 0.53$$

$$X = 1-\exp\left(-0.57\left[1-\exp(-5.3)\right]\right) = 0.43$$

P10-22 (a)

In order to get a high conversion the entering pressure should be as high as possible since the rate is a second order function of the pressure. U should be kept low since the conversion is an indirect function of the flow rate.

P10-22 (b)

The problem with such a low flow rate is that the activity will remain low.

P10-22 (c)

We can use the same equations that are given in example 10-7 with a few exceptions. For example the rate law, we use the one given in the problem:

$$-r_a' = k' P_A^2$$

The activity will be different because the equation given is different:

$$\frac{da}{dt} = k_D a C_{coke}$$

$$\frac{da}{dz} = \frac{k_D a C_{coke}}{U}$$

To find the concentration of coke we use stoichiometry:

$$P_{coke} = P_{A0}\frac{X}{1+\varepsilon X}$$

$$C_{coke} = \frac{P_{coke}}{RT}$$

We find that the value that gives the best conversion (X = 0.337) and uses the whole reactor is U = 7. See the following POLYMATH program.

Equations:

```
d(a)/d(z)=-kd*a*ccoke/U
d(x)/d(z)=-ra/U/cao
cao=.22
kd=100
kprime=5e-5
Uo=7
eps=1
R=.082
T=673
pao=12
rho=80
U=Uo*(1+eps*x)
pa=pao*(1-x)/(1+eps*x)
pcoke=pao*x/(1+eps*x)
raprime=a*(-kprime*pa^2)
ccoke=pcoke/R/T
ra=rho*raprime
```

$z_0 = 0, \quad z_f = 15$

	Initial value
a	1
x	0

Variable	Initial value	Maximum value	Minimum value	Final value
z	0	15	0	15
a	1	1	0.000254948	0.000254948
x	0	0.336731	0	0.336731
cao	0.22	0.22	0.22	0.22
kd	100	100	100	100
kprime	5e-05	5e-05	5e-05	5e-05
Uo	7	7	7	7
eps	1	1	1	1
R	0.082	0.082	0.082	0.082
T	673	673	673	673
pao	12	12	12	12
rho	80	80	80	80
U	7	9.35712	7	9.35712
pa	12	12	5.95425	5.95425
pcoke	0	3.02288	0	3.02288
raprime	-0.0072	-4.51934e-07	-0.0072	-4.51934e-07
ccoke	0	0.0547762	0	0.0547762
ra	-0.576	-3.61547e-05	-0.576	-3.61547e-05

P10-22 (d)

To find this the only change necessary was the values for the k's because they change with temperature.

$$k_R = 5\times10^{-5}\exp\left[\frac{E_R}{R}\left(\frac{1}{673}-\frac{1}{T}\right)\right]$$

$$k_D = 100\exp\left[\frac{E_D}{R}\left(\frac{1}{673}-\frac{1}{T}\right)\right]$$

The POLYMATH program below shows the results. The temperature is 485K and the conversion is 0.637.

Equations:	Initial value
d(x)/d(z)=-ra/U/cao	0
d(a)/d(z)=-kd*a*ccoke/U	1

cao=.22
Uo=2.5
eps=1
R=.082
T=485
pao=12
rho=80
kd=100*exp(15000/1.987*(1/673-1/T))
kprime=5e-5*exp(3000/1.987*(1/673-1/T))
U=Uo*(1+eps*x)
pa=pao*(1-x)/(1+eps*x)
pcoke=pao*x/(1+eps*x)
ccoke=pcoke/R/T
raprime=a*(-kprime*pa^2)
ra=rho*raprime

$z_0 = 0, \quad z_f = 15$

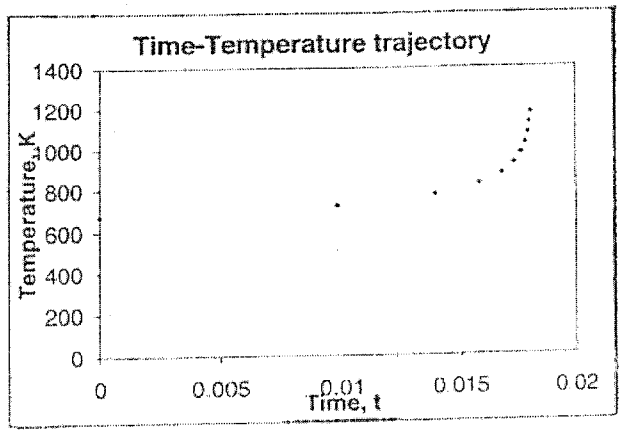
Variable	Initial value	Maximum value	Minimum value	Final value
z	0	15	0	15
x	0	0.637285	0	0.637285
a	1	1	0.605697	0.605697
cao	0.22	0.22	0.22	0.22
Uo	2.5	2.5	2.5	2.5
eps	1	1	1	1
R	0.082	0.082	0.082	0.082
T	485	485	485	485
pao	12	12	12	12
rho	80	80	80	80
kd	1.2932	1.2932	1.2932	1.2932
kprime	2.09558e-05	2.09558e-05	2.09558e-05	2.09558e-05
U	2.5	4.09321	2.5	4.09321
pa	12	12	2.65841	2.65841
pcoke	0	4.6708	0	4.6708
ccoke	0	0.117445	0	0.117445
raprime	-0.00301763	-8.97021e-05	-0.00301763	-8.97021e-05
ra	-0.24141	-0.00717616	-0.24141	-0.00717616

P10-22 (e)

To find the temperature-time trajectory, use equation (10-119) and add C_{coke} where necessary:

$$t = \frac{1 - \exp\left[\frac{E_A - nE_A + E_d}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]}{k_{d0}(1 - n + E_d/E_A)C_{coke}}$$

The following curve is generated from that equation.



P10-23 (a)



Design equation: $r = \frac{F_{A0}X}{W}$

Assume $W = 1g$ $\therefore$ $r = F_{A0}X$

Cumene	$\rightarrow$	Propene	+	Benzene
(A)		(R)		(S)
$F_{A0}(1-X)$		$F_{A0}X$		$F_{A0}X$

The amount of cumene hydroperoxide does not contribute significantly to the total number of moles.

$$y_S = \frac{F_{A0}X}{F_{A0}(1-X) + F_{A0}X + F_{A0}X} = \frac{X}{1+X} \quad \text{or} \quad X = \frac{y_S}{1 - y_S}$$

$$\therefore r = F_{A0}\left(\frac{y_S}{1 - y_S}\right)$$

$$a = \frac{r}{r_o} = \frac{\left(\frac{y_S}{1 - y_S}\right)}{\left(\frac{y_S}{1 - y_S}\right)_{t=0}}$$

X	.0204	.0165	.0133	.0107	.00857	.00563	.00371	.00241
a	1	.809	.652	.5245	.420	.276	.182	.118
t	0	50	100	150	200	300	400	500

ln a vs. t gives the best fit $a = e^{-\alpha t}$

$\alpha = 4.27 \times 10^{-3}$ (sec^{-1})

Therefore, decay is first order with decay constant of 4.27×10^{-3} (sec^{-1})

P10-23 (b)

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon}$$

Assume no ΔP : $\frac{\upsilon}{\upsilon_o} = \frac{n}{n_o} = \frac{F_{A0}(1+X)}{F_{A0}} \Rightarrow \upsilon = (1+X)\,\upsilon_o$

$$C_A = \frac{F_{A0}(1-X)}{\upsilon_o(1+X)} = C_{A0}\frac{(1-X)}{(1+X)}$$

$$P_A = C_A RT = C_{A0}\frac{(1-X)}{(1+X)}RT$$

Mass balance : $F_{A0}\,dX = r dW$

$r = e^{-\alpha t} k P_A$

$t = \frac{W}{U_S}$

$$\therefore\ F_{A0}\,dX = e^{-\left(\frac{\alpha W}{U_s}\right)} k\,P_A\,dW$$

$$\text{or } \frac{F_{A0}}{C_{A0}\,RT}\int_0^X \frac{1+X}{1-X}\,dX = k\int_0^W e^{-\left(\frac{\alpha W}{U_s}\right)}\,dW$$

F_{A0} = 20 mol/min = 1/3 mol/sec

C_{A0} = 0.06 kmol/m^3 = 0.06 mol/l

$R = 0.082\ \frac{\text{atm·l}}{\text{K·mol}}$

T = 273 + 420 = 693 K

k = 3.8×10^{-3} mol/g sec atm

$\alpha = 4.27\times10^{-3}$ sec^{-1}

W = 100 kg

U_S = 10 kg/min = 1/6 kg/sec

Equation (1) becomes:

$$2\ln(1-X) + X = \frac{C_{A0}\,RT\,k\,U_S}{F_{A0}\alpha}\left[e^{-\left(\frac{\alpha W}{U_s}\right)} - 1\right]$$

$$2\ln(1-X) + X = \frac{(0.06)(0.082)(693)(3.8\times10^{-3})\left(\frac{1000}{6}\right)}{\left(\frac{1}{3}\right)(4.27)\times10^{-3}}\left[\exp\left\{-\frac{4.27\times10^{-3}\times1000}{\frac{1}{6}}\right\} - 1\right]$$

$$= -1.4\times10^{3}$$

$\therefore\ X \cong 1.00$

P10-24 (a)

$S \longrightarrow W + CO_2$: first order, irreversible.

$$-\frac{da}{dt} = k_d\,a^n\,C_A^m = k_d\,a^n$$

$$-r_A = Ka\,C_A$$

Assume n=2 : $a = \frac{1}{1+k_d t}$

$$\ln\left(\frac{1}{1-X}\right) = \frac{\tau K}{1+K_d t}$$

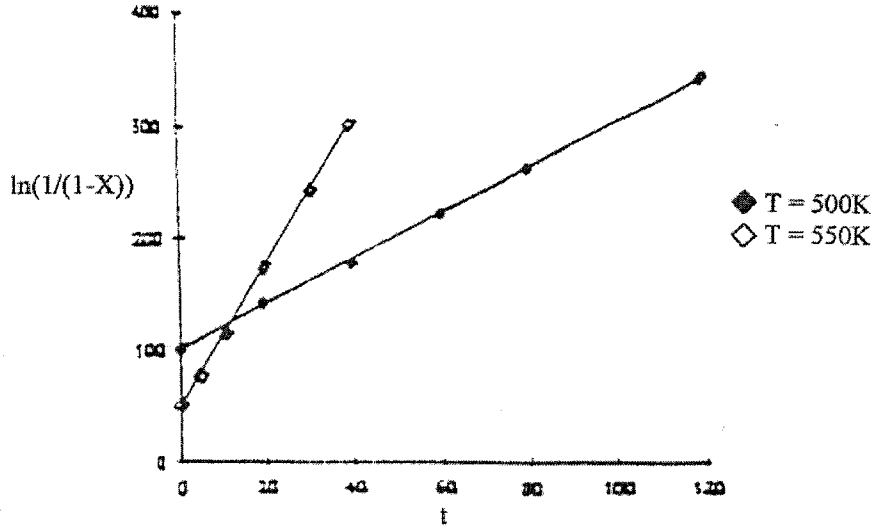
$$\frac{1}{\ln\left(\frac{1}{1-X}\right)} = \frac{1}{\tau K} + \frac{K_d}{\tau K}\,t$$

For T = 500 K

t(min)	0	20	40	60	80	120
X%	1	0.7	0.56	0.45	0.38	0.29
$1/\ln\left(\frac{1}{1-X}\right)$	99.5	142.4	178.1	221.7	262.6	344.3

For T = 550 K

t(min)	0	5	10	15	20	30	40
X%	2	1.2	0.89	0.69	0.57	0.42	0.33
$1/\ln\left(\frac{1}{1-X}\right)$	49.5	82.8	111.8	144.4	174.9	237.6	302.5



They are straight lines ∴ n=2

For $T_1 = 500$ K : slope $= 2.04 \frac{K_{d_1}}{(\tau K)_1}$, [1/intercept] $= 0.01 = (\tau K)_1$ $\Rightarrow$ $K_{d_1} = 0.02$

For $T_2 = 550$ K : slope $= 6.325$, $(\tau K)_2 = 0.02$ $\Rightarrow$ $K_{d_2} = 0.1265$

$$\frac{K_{d_1}}{K_{d_2}} = \frac{0.02}{0.1265} = \exp\left\{\frac{E_d}{8.314}\left(\frac{1}{550} - \frac{1}{500}\right)\right\}$$

$$E_d = 84{,}344 \ \frac{\tau}{\text{mol}}$$

$$K_{d_1} = K_{d_2} \exp\left\{-\frac{E_d}{R}\left(\frac{1}{T_1}\right)\right\} = K_{d_2} \exp\left\{-\frac{84{,}344}{8.314}\left(\frac{1}{500}\right)\right\} = 0.02$$

$$K_{d_2} = 1.296 \times 10^{-3}$$

We want to maintain Ka = constant

$$K\left(\frac{1}{1+K_d t}\right) = K_o$$

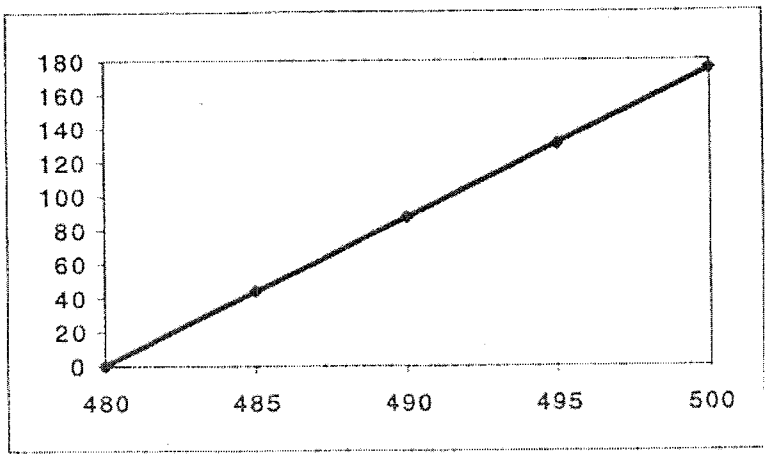
$$K_o \exp\left\{\frac{E}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right\} = K_o (1 + K_d t)$$

$$\exp\left\{\frac{E}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right\} - 1 = K_d t$$

$$t = \frac{\exp\left\{\frac{E}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right\} - 1}{K_d}$$

$$t = \frac{\exp\left\{\frac{150{,}000}{8.314}\left(\frac{1}{480} - \frac{1}{T}\right)\right\} - 1}{1.296 \times 10^7 \exp\left\{-\frac{84{,}344}{8.314\,T}\right\}}$$

T(°K)	t(min)
480	0
485	44.3
490	87.3
495	130.4
500	174.9

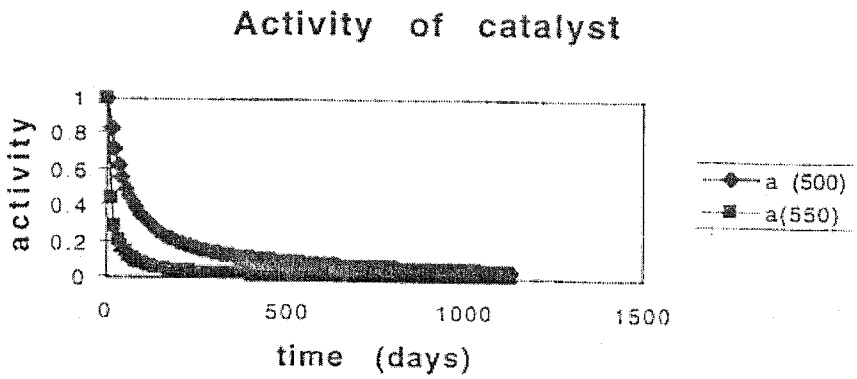


P10-24 (b)

Since the equation for the acivation is:

$$a = \frac{1}{1 + k_d t}$$

we cannot find a time for which a = 0, because it is mathematically impossible. We can, however, find a time at which the activity is small enough that it can be considered to be zero. The following graphs show the activation for the two temperatures given



The graphs show that for 500 K, the lifetime is about 1100 days and for 550 K, the lifetime is about 450 days.

P10-25

First we need to find C_{A0}.

$$\frac{H_2}{ETB} = 10$$

$$y_{ETB} = 0.1$$

$$C_{A0} = \frac{Py_{ETB}}{RT} = \frac{3*10^3(0.1)}{(8.309)553} = 0.065$$

Start by guessing that the decay is first order:

$$k_d t = \ln(k_r) + \ln\frac{C_A^n}{C_{A0} - C_A}$$

We were told that the reaction is zero-order when the conversion is less than 0.75. This is true at any time after 2 hours. We also need to find the denominator as a function of conversion.

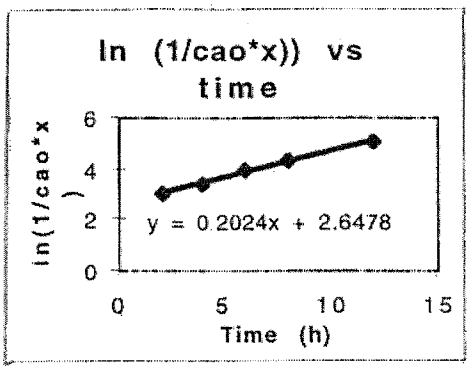
$$X = \frac{C_{A0} - C_A}{C_{A0}}$$

$$C_{A0} - C_A = C_{A0}X$$

So we graph this:

$$\ln\frac{1}{C_{A0}X} \text{ vs. t}$$

This is the graph that we get:



As can be seen this graph is linear which means that the decay is first order. We also know that the slope will be the decay law constant so $k_d = 0.2024$.

P10-26 (a)

Mass balance:

$$\frac{dX}{dW} = \frac{-r_A}{F_{A0}}$$

Rate law:

$$-r_A = kaC_A$$

Decay law:

$$\frac{da}{dW} = \frac{-k_D a}{U_s}$$

Energy balance:

$$\frac{dT}{dW} = \frac{\frac{Ua}{\rho_b}(T_A - T) + (-r_A)(-\Delta H_{Rx})}{U_s C_{ps} + F_{A0} C_{pA}}$$

Stoichiometry

$$C_A = C_{A0}\frac{1 - X}{1 + \varepsilon X}$$

Evaluate the parameters:

$$k = 0.33\exp\left[3777\left(\frac{1}{450} - \frac{1}{T}\right)\right]$$

$$k_D = 0.01\exp\left[7000\left(\frac{1}{450} - \frac{1}{T}\right)\right]$$

Plug that into POLYMATH and get the following program and answers. U_g to get maximum conversion will be 17 kg/s.

Equations:

```
d(a)/d(w)=-kd*a/U
d(x)/d(w)=-ra/fao
d(T)/d(w)=(Ua*(Ta-T)+(-ra)*(-Dhr1))/(U*cps+fao*cpa)
fao=5.42
U=17
Ta=323
Dhr1=-80000
cps=100
cpa=40
Ed=7000
Er=3777
cao=.27
eps=1
Ua=.8
kd=.01*exp(Ed*(1/450-1/T))
k=.33*exp(Er*(1/450-1/T))
ca=cao*(1-x)/(1+eps*x)
ra=-k*a*ca
```

$w_0 = 0.$ $w_f = 50$

Initial value
1
0
450

10-27

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	50	0	50
a	1	1	0.271596	0.271596
x	0	0.887222	0	0.887222
T	450	645.613	450	645.613
fao	5.42	5.42	5.42	5.42
U	17	17	17	17
Ta	323	323	323	323
Dhr1	-80000	-80000	-80000	-80000
cps	100	100	100	100
cpa	40	40	40	40
Ed	7000	7000	7000	7000
Er	3777	3777	3777	3777
cao	0.27	0.27	0.27	0.27
eps	1	1	1	1
Ua	0.8	0.8	0.8	0.8
kd	0.01	1.11401	0.01	1.11401
k	0.33	4.19718	0.33	4.19718
ca	0.27	0.27	0.0161349	0.0161349
ra	-0.0891	-0.0183928	-0.14641	-0.0183928

P10-26 (b)

Using the same program we can see that the maximum conversion is 0.887

P10-26 (c)

Everything is the same except the energy balance:

$$\frac{dT}{dW} = \frac{U\tilde{a}_W(T_a - T) + h\tilde{a}_p(T_s - T) + (r'_A)(\Delta H_{Rx})}{F_{A0}C_{pA}}$$

We also need an energy balance on the catalyst particles.

$$\frac{dT_s}{dW} = \frac{h\tilde{a}_p(T_s - T)}{U_s C_{ps}}$$

Choose values of h and a_p. We find that T_S needs to be slightly higher than T in order to get a large conversion. The maximum conversion will be different for each T_S that is used.

CDP10-A

Given: The catalytic oxidation of ethanol

$$CH_3\,CH_2\,OH + \frac{1}{2}O_2 \rightarrow CH_3\,CHO + H_2O$$

Denote: A [=] $CH_3\,CH_2\,OH$, B [=] $CH_3\,CHO$, W [=] H_2O , A•S [=] $CH_3\,CH_2\,O{\bullet}S$

Mechanism is belived to be the following:

A	+ 2S	$\rightleftarrows$	A•S + H•S	$-r_A = k_A\left[P_A\,C_S^2 - C_{A\bullet S}\,C_{H\bullet S}/K_A\right]$
O_2	+ 2S′	$\rightleftarrows$	2O•S′	$-r_O = k_O\left[P_{O_2}\,C_{S'}^2 - C_{O\bullet S'}^2/K_O\right]$
A•S	+ O•S′	$\rightleftarrows$	B + OH•S′ + S	$-r_{AO} = k_{AO}\left[C_{A\bullet S}\,C_{O\bullet S'} - P_B\,C_{OH\bullet S'}\,C_S/K_{AO}\right]$
OH•S′	+ H•S	$\rightleftarrows$	W + S + S′	$-r_W = k_W\left[C_{OH\bullet S'}\,C_{H\bullet S} - P_W\,C_S\,C_{S'}/K_W\right]$

It is given also that $C_{H\bullet S} = C_{A\bullet S}$

With reaction ($-r_{A0}$) controlling

$$\frac{-r_A}{k_A} \equiv 0 \quad C_{A\bullet S}\,C_{H\bullet S} = K_A\,P_A\,C_S^2 \text{ or } C_{H\bullet S} = C_{A\bullet S} = \sqrt{K_A\,P_A}\,C_S$$

$$\frac{-r_O}{k_O} \equiv 0 \quad C_{OS'}^2 = K_O\,P_{O_2}\,C_{S'}^2 \text{ or } C_{OS'} = \sqrt{K_O\,P_{O_2}}\,C_{S'}^2$$

$$\frac{-r_W}{k_W} \equiv 0 \quad C_{OH\bullet S'}\,C_{H\bullet S} = \frac{P_W\,C_S\,C_{S'}}{K_W} \text{ with } C_{H\bullet S} = \sqrt{K_A\,P_A}\,C_S$$

$$C_{OH\bullet S'} = \frac{P_W\,C_{S'}}{K_W\sqrt{K_A\,P_A}}$$

$$C_T = C_S + C_{H\bullet S} + C_{A\bullet S} = C_S\left[1 + 2\sqrt{K_A\,P_A}\right]$$

$$C_{T'} = C_{S'} + C_{O\bullet S'} + C_{OH\bullet S'} = C_{S'}\left[1 + \sqrt{K_O\,P_{O_2}} + \frac{P_W}{K_W\sqrt{K_A\,P_A}}\right]$$

$$-r_{AO} = k_{AO}\left[C_{AS}\,C_{OS'} - \frac{P_B\,C_{OH\bullet S'}\,C_S}{K_{AO}}\right] = k_{AO}\left[\sqrt{K_A\,P_A\,K_O\,P_{O_2}}\,C_S\,C_{S'} - \frac{P_B\,P_W\,C_S\,C_{S'}}{K_W\,K_{AO}\sqrt{K_A\,P_A}}\right]$$

$$-r_{AO} = \frac{k_{AO}\sqrt{K_A\,K_O}\,C_S\,C_{S'}}{\sqrt{P_A}}\left[P_A\sqrt{P_{O_2}} - \frac{P_B\,P_W}{K_A\,K_W\,K_{AO}\sqrt{K_O}}\right]$$

$$K_{eq} = K_A\,K_W\,K_{AO}\sqrt{K_O}$$

$$-r_{AO} = \frac{k_{AO}\sqrt{K_A\,K_O}\,C_T\,C_{T'}\left[P_A\sqrt{P_{O_2}} - \frac{P_B\,P_W}{K_{eq}}\right]}{\sqrt{P_A}\left[1 + 2\sqrt{K_A\,P_A}\right]\left[1 + \sqrt{K_O\,P_{O_2}} + \frac{P_W}{K_W\sqrt{K_A\,P_A}}\right]}$$

Initially $P_B = P_W = 0$

$$-r_{AO} = \frac{k_{AO}\sqrt{K_A\,P_A\,K_O\,P_{O_2}}\,C_T\,C_{T'}}{\left(1 + 2\sqrt{K_A\,P_A}\right)\left(1 + 2\sqrt{K_O\,P_{O_2}}\right)}$$

(b) With reaction 3 irreversible, $-r_{A0} = k_{A0}\, C_{A\text{-}S}\, C_{OS'}$. Since A-S, H-S, OH-S′ are created (and destroyed) only at the reaction surface. A stoichiometric relationship exists between them:

$$C_{H\text{-}S'} = C_{A\text{-}S'} + C_{OH\text{-}S'} \qquad (a)$$

The same equilibrium expressions for reactions (1), (2) and (4) exist as before:

$$C_{A\text{-}S}\, C_{H\text{-}S} = K_A\, P_A\, C_S^2 \qquad (b)$$

$$C_{OH\text{-}S'}\, C_{H\text{-}S} = \frac{P_W\, C_S\, C_{S'}}{K_W} \qquad (c)$$

$$\therefore (C_{H\text{-}S} - C_{A\text{-}S})\, C_{H\text{-}S} = \frac{P_W\, C_S\, C_{S'}}{K_W} \Rightarrow C_{H\text{-}S}^2 = K_A\, P_A\, C_S^2 + \frac{P_W\, C_S\, C_{S'}}{K_W}$$

$$\text{or } C_{H\text{-}S} = \sqrt{K_A\, P_A\, C_S^2 + \frac{P_W\, C_S\, C_{S'}}{K_W}}$$

$$C_{A\text{-}S} = \frac{K_A\, P_A\, C_S^2}{\sqrt{K_A\, P_A\, C_S^2 + \frac{P_W\, C_S\, C_{S'}}{K_W}}}$$

$$C_{OH\text{-}S'} = \frac{\frac{P_W\, C_S\, C_{S'}}{K_W}}{\sqrt{K_A\, P_A\, C_S^2 + \frac{P_W\, C_S\, C_{S'}}{K_W}}}$$

Expressions for C_T and C_T' become

$$C_T = C_S + C_{H\text{-}S} + C_{A\text{-}S} = C_S + \sqrt{K_A\, P_A\, C_S^2 + \frac{P_W\, C_S\, C_{S'}}{K_W}} + \frac{K_A\, P_A\, C_S^2}{\sqrt{K_A\, P_A\, C_S^2 + \frac{P_W\, C_S\, C_{S'}}{K_W}}}$$

$$C_T' = C_{S'} + \gamma\sqrt{K_O\, P_{O_2}}\, C_{S'} + \frac{P_W\, C_S\, C_{S'}}{\sqrt{K_A\, P_A\, C_S^2 + \frac{P_W\, C_S\, C_{S'}}{K_W}}}$$

$$\text{with } K_A P_A C_S^2 >> \frac{P_W C_{S'} C_S}{K_W}$$

$$C_T = C_S\left[1 + 2\gamma\sqrt{K_A\, P_A}\right]$$

$$C_T' = C_{S'}\left[1 + \sqrt{K_O P_{O_2}} + \frac{P_W}{\sqrt{K_A P_A}}\right]$$

Rate expression becomes:

$$-r_A = k_{AO}\, C_{A\cdot S}\, C_{O\cdot S'} = k_{AO}\, K_O \sqrt{P_{O_2}}\, C_{S'} \sqrt{K_A P_A}\, C_S \left[\frac{1}{\left(1+\frac{P_W C_S'}{K_W K_A P_A C_S}\right)^{1/2}}\right]$$

$$\text{with } \frac{P_W}{\sqrt{K_A P_A}} << \sqrt{K_O P_{O_2}}$$

$$-r_A = \frac{k_{A0} K_O \sqrt{P_O P_A}\, C_T C_T'}{\left[1+2\sqrt{K_A P_A}\right]\left[1+\sqrt{K_O P_{O_2}}+\frac{P_W}{\sqrt{K_A P_A}}\right]}\left[\frac{1}{\left(1+\frac{P_W C_S'}{K_W K_A P_A C_S}\right)^{\frac{1}{2}}}\right] = \frac{-r_{A0}}{\left(1+\frac{P_W C_S'}{K_W K_A P_A C_S}\right)^{\frac{1}{2}}}$$

$$\frac{C_{S'}}{C_S} = \frac{1}{\mu}\left[\frac{1+2\sqrt{K_A P_A}}{1+\sqrt{K_O P_{O_2}}}\right] \quad \text{with} \quad \sqrt{K_A P_A} < 1$$

$$-r_A = \frac{-r_{A0}}{1+\frac{P_W}{\mu K_W K_A P_A}\left[\frac{1}{1+\sqrt{K_O P_{O_2}}}+\frac{P_W}{\sqrt{K_A P_A}}\right]^{\frac{1}{2}}}$$

CDP10-B

We can first try to come up with a rate law for this data. We can see that as P_E increases the rate law also increases but slowly the amount by which it increases becomes smaller this tells us this:

$$-r_A' \sim \frac{P_E}{1+K_E P_E}$$

We can then see a similar thing happens as P_H increases so:

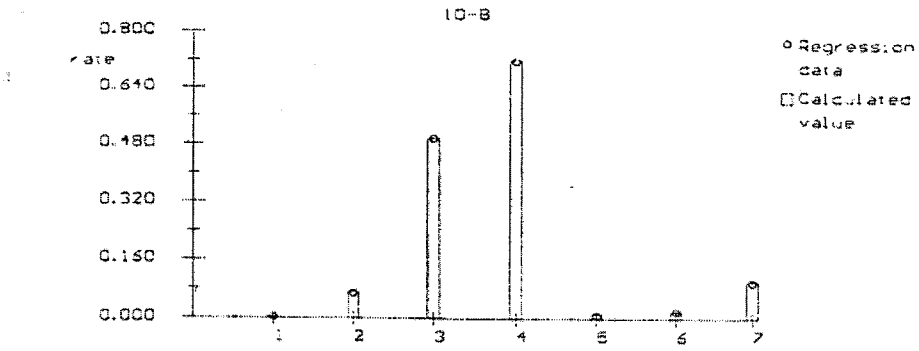
$$-r_A' \sim \frac{P_H}{1+K_H P_H}$$

Since both reactants are adsorbed the mechanism must be a dual site. This makes the rate law:

$$-r_A' = \frac{kP_E P_H}{1+K_E P_E + K_H P_H}$$

We can then plug this into POLYMATH and we then get the following values for k, K_E, and K_H.

k = 14.6
K_E = 2.63
K_H = 1.76



Model: rate=k*Pe*Ph/(1+Ke*Pe+Kh*Ph)^2
k = 14.5344 Kh = 1.75797
Ke = 2.63471
1 positive residuals, 6 negative residuals. Sum of squares = 1.45236e-06

CDP10-C

(1) $N_2O + S \rightleftarrows N_2O \cdot S$

$$SiH_2Cl_2 + 2N_2O \cdot S \rightarrow SiO_2 + 2N_2 + 2HCl + 2S$$

$$r_{SiO_2} = \frac{k\, P_{DCS}\, P_{N_2O}^2}{(1 + K_{N_2O}\, P_{N_2O})^2}$$

(2) $N_2O + S \rightleftarrows N_2O \cdot S$

$$N_2O \cdot S + SiH_2Cl_2\,(g) \rightleftarrows SiO \cdot S + 2HCl + N_2$$

$$N_2O \cdot S + SiO \cdot S \rightarrow SiO_2 + 2S + N_2 \quad \text{(Rapid)}$$

$$r_{SiO_2} = \frac{k\, P_{DCS}\, P_{N_2O}}{1 + K\, P_{N_2O}}$$

(3) $\dfrac{dF_A}{dV} = r_A' a$ (Plug Flow Reactor)

$$F_{A0}\frac{dX}{dV} = -r_A' a$$

$$V = F_{A0}\int_0^X \frac{dX}{-r_A' a}$$

$$\frac{Va}{F_{A0}} = \int_0^X \frac{dX}{-r_A'}$$

$$-r_A' = \frac{k\, P_{N_2O}\, P_{DCS}}{1 + K_{N_2O}\, P_{N_2O}}$$

$$P_{DCS} \equiv P_A = P_{A0}\frac{(1-X)}{(1+\varepsilon X)}$$

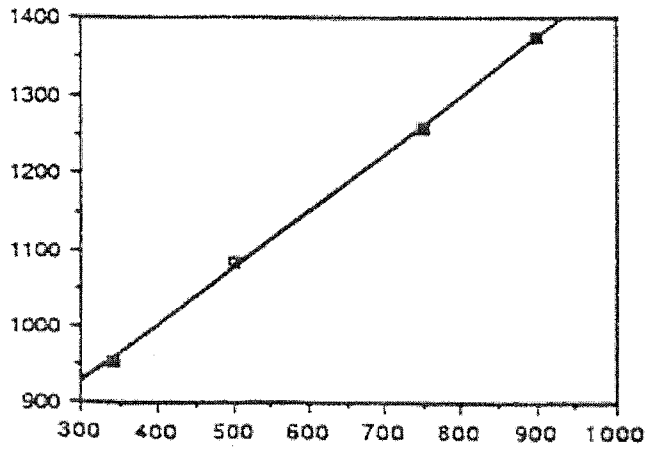
$$P_{N_2O} \equiv P_B = P_{A0}\frac{(\theta_B - 2X)}{(1+\varepsilon X)}$$

$$-r_A' = \frac{k P_{A0}^2 (1-X)(\theta_B-2X)/(1+\varepsilon X)^2}{1 + K_B P_{A0}\frac{(\theta_B-2X)}{(1+\varepsilon X)}}$$

$$= \frac{k P_{A0}^2 (1-X)(\theta_B-2X)}{(1+\varepsilon X)^2 + K_B P_{A0}(\theta_B-2X)(1+\varepsilon X)}$$

$$\theta_B = \frac{11.3}{3.68} = 3.07$$

$$\varepsilon = \left(\frac{3.68}{11.3+3.68}\right)(2+2-1-2) = 0.25$$



$$\text{Slope} = \frac{K}{k'} = 0.7465$$

$$\text{Intercept} = \frac{1}{k'} = 703$$

$$k = 1.49\times10^{-3}\ Å/mTorr^2\text{-}min$$

$$K = 1.1\times10^{-3}\ mTorr^{-1}$$

$K_B = 1.1 \times 10^{-3}$ m Torr^{-1} $K_B P_{A1} = (1.1 \times 10^{-3})(157) = .173$

$k P_{A0}^2 = 1.49 \times 10^{-3} (157)^2 = 36.68$ Å/min

$$-r_A' = 36.7\ Å/min \frac{(3.07 - 2X)(1-X)}{(1+.25X)^2 + .173(3.07-2X)(1+.25X)}$$

$F_{A0} = 3.68 \times 10^{-3}$ gmole/min

$$-r_A' = (Å/min) = 4.4 \times 10^{-6} r_A' \frac{(gmole)}{(m^2\ min)}$$

$a = 250\ m^2/min$

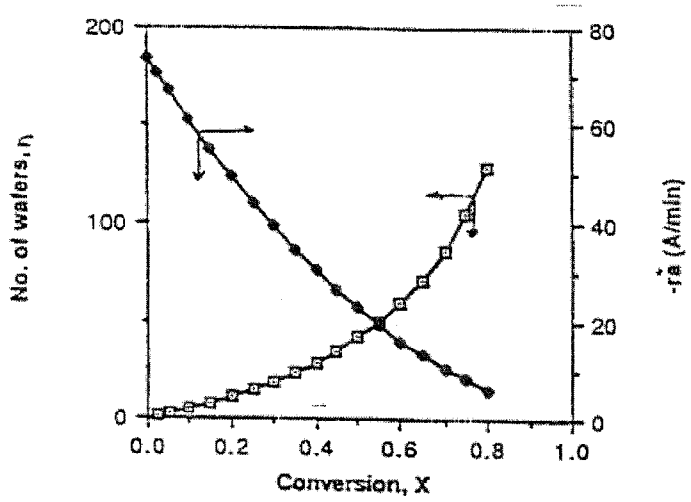
$$\frac{Va}{F_{A0}} = \int_0^X \frac{dX}{r_A'} \Rightarrow \text{Area under curve of X vs. } \frac{1}{r_A'}$$

X	$-r_A'$ (Å/min)	$-1/-r_A'\left(\frac{min}{A}\right)$	$1/-r_A'$ (m^2/gmole)	$\frac{Va}{F_{A0}}$	V(m^3)
0	73.6	0.0136	3091		0
0.025	70.3	0.0142	3235	79.1	0.0012
0.5	67.0	0.0149	3392	82.8	0.0012
0.1	60.8	0.0165	3739	178.3	0.0026
0.15	54.9	0.0182	4139	196.9	0.0029
0.20	49.4	0.020	4545	217.1	0.0032
0.25	44.2	0.0226	5145	242.3	0.0036
0.30	39.3	0.0255	5784	273.2	0.0040
0.35	34.7	0.0288	6547	308.3	0.0045
0.40	30.4	0.0328	7465	350.3	0.0052
0.45	26.5	0.0378	8589	401.4	0.0059
0.50	22.8	0.0439	9983	464.3	0.0068
0.55	19.3	0.0517	11746	543.2	0.0080
0.60	16.2	0.0617	14029	644.4	0.0095
0.65	13.3	0.0751	17067	777.4	0.0114
0.70	10.7	0.0936	21262	958.2	0.0141
0.75	8.3	0.01203	27338	1215	0.0179
0.80	6.2	0.01617	36760	1602	0.0236

Reactor Volume per wafer = 9.8×10^{-4} m^3/wafer

$\therefore$ Number of wafers, n = $V/9.8 \times 10^{-4}$

A plot of conversion X, vs. number. of wafers can be obtained



The thickness on these wafers can be obtained from the same plot.

Wafer #1 : X = 0

$-r_A'' = 73.6$ Å/min

∴ After 30 min: 2208 Å

Wafer #50 : X = 0.52

$-r_A'' = 20$ Å/min

∴ After 30 min: 600 Å

Wafer #110 : X = 0.78

$-r_A'' = 6$ Å/min

∴ After 30 min: 180 Å

CDP10-D (3/e CDP10-E)

CDP10-E

(a) For simplicity, letters were substituted for the species in the problem statement.

$A = TiCl_4 \qquad B = NH_3 \qquad C = TiCl_4(NH_3)_2$

$D = TiCl_4(NH_3)_2 \cdot S$

The rate equations for each of the three steps in the mechanism is given below.

$$-r_A = k_A\left[P_A P_B^2 - \frac{P_C}{K_A}\right] \xrightarrow{\text{at equilibrium}} P_C = K_A P_A P_B^2$$

$$-r_C = k_C\left[P_C f_v - \frac{f_D}{K_C}\right] \xrightarrow{\text{fast step}} f_D = K_C P_C f_v$$

$$-r_{DEP} = k_s(f_D)(f_v)$$

Equations 1 and 2 are substituted into equation 3 because the third step (the deposition step) is assumed to be the rate limiting step, we want to find the rate law of the deposition, and we have data for the deposition rate.

Also, remember that we have the relation below:

$$f_v + f_D = 1$$

$$f_v = \frac{1}{1 + K_C P_C}$$

Substitute everything into the deposition rate law:

$$-r_{DEP} = \frac{k_1 P_A P_B^2}{\left(1 + k_2 P_A P_B^2\right)^2}, \quad \text{where } k_1 \text{ and } k_2 \text{ are constants}$$

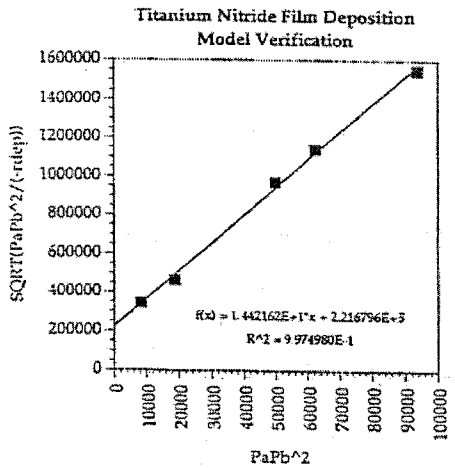
We now have to check if the above rate expression agrees with experimental observations.

- The rate of deposition is independent of Ar and H_2.--YES
- At low partial pressures of $TiCl_4$ and NH_3, the deposition appears to be first order in $TiCl_4$ and second order in NH_3.--YES
- At high partial pressures of NH_3, the rate varies inversely with $TiCl_4$.--YES

(b) To determine the reaction rate parameters, we must rearrange the rate expression to a linear form.

$$\sqrt{\frac{P_A P_B^2}{-r_{DEP}}} = \frac{k_2}{\sqrt{k_1}} P_A P_B^2 + \frac{1}{\sqrt{k_1}}$$

A plot of the experimental data is shown below.



$$\frac{1}{\sqrt{k_1}} = y - \text{intercept} = 2.2168 \times 10^5$$

$$k_1 = 2.035 \times 10^{-11} \frac{\text{mol}}{\text{cm}^3 \cdot \text{min} \cdot \text{mT}^3}$$

$$\frac{k_2}{\sqrt{k_1}} = \text{slope} = 14.42$$

$$k_2 = 6.505 \times 10^{-5} \frac{1}{\text{mT}^3}$$

(c) The experimental data, when plotted with the rate law derived in this problem, form a straight line. Therefore, the proposed mechanism may be used to describe the deposition of titanium nitride films.

CDP10-F

Given: The dehydrogenation of ethyl benzene to styrene:

$$C_8H_{10} \rightarrow C_8H_8 + H_2$$

$$E \rightarrow St + H_2$$

Quantitative data suggests reaction rate is of the form

$$-r_E \propto \frac{A_1 P_E}{1 + A_2 P_E + A_3 P_{St}}$$ where A_1, A_2, A_3 are constants

The fact that $(-r_E)$ is independent of H_2 suggests that the reaction is irreversible, and that H_2 is not adsorbed on the catalyst surface. Also, the above expression for $(-r_E)$ suggests that both E and St are adsorbed on the surface ∴ Try the following reaction scheme.

$E + S \leftrightarrow E \bullet S$

$E \bullet S \leftrightarrow St \bullet S + H_2$

$St \bullet S \leftrightarrow St + S$

$$-r_A = k_A [P_E C_S - C_{E\text{-}S}/K_A]$$

$$-r_S = k_S [C_{E\text{-}S} - C_{St\text{-}S} P_{H_2}/K_S]$$

$$-r_D = k_D [C_{St\text{-}S} - P_{St} C_S/K_D]$$

To insure that P_{H_2} does not appear in the rate expression assume that the surface reaction controls:

$$\frac{-r_A}{k_A} \equiv 0 \quad C_{E\text{-}S} = K_A C_S P_E$$

$$\frac{-r_D}{k_D} \equiv 0 \quad C_{St\text{-}S} = \frac{C_S P_{St}}{K_D}$$

Then: $C_T C_S + C_{E\text{-}S} + C_{St\text{-}S} = C_S \left[1 + K_A P_E + \frac{P_{St}}{K_D}\right]$

And $-r_S = k_S \left[C_{E\text{-}S} - \frac{C_{St\text{-}S} P_{H_2}}{K_S}\right] = k_S K_A C_S \left[P_E - \frac{P_{St} P_{H_2}}{K_A K_S K_D}\right]$

or $-r_S = \frac{k_S C_T K_A \left[P_E - \frac{P_{St} P_{H_2}}{Keq}\right]}{1 + K_A P_E + \frac{P_{St}}{K_D}}$, where $Keq = K_A K_S K_D$

with $K_S >>> 1$, reaction can be considered irreversible, and its dependence on P_{H2} drops.

out: $$-r_S = \frac{k K_A P_E}{1 + K_A P_E + \frac{P_{St}}{K_D}}, \text{ where } k = k_S C_T$$

Evaluation for k, K_A and K_D

Rearranging the rate expression: $\frac{P_E}{-r_S} = \frac{1}{k K_A} + \frac{P_E}{k} + \frac{P_{St}}{K_D k K_A}$

with $P_{St} \rightarrow 0$, a plot of $\frac{P_E}{-r_S}$ vs. P_E should be linear with slope $\left(\frac{1}{k}\right)$ and intercept $\left(\frac{1}{-k K_A}\right)$. Since only two points are given with $P_{St} = 0$, it is easy to solve analytically:

Point	P_E (atm)	$(-r_E)$ gmol/min-gmcat	$P_E/-r_S$
1	1.00	1.415×10^{-3}	706.7
2	0.01	0.214×10^{-3}	46.73

$$\left(\frac{P_E}{-r_S}\right)_1 = \frac{1}{k K_A} + \frac{1}{k}(P_E)_1 \text{ and } \left(\frac{P_E}{r_S}\right)_2 = \frac{1}{k K_A} + \frac{1}{k}(P_E)_2$$

From above : $$\frac{1}{k} = \frac{\left(\frac{P_E}{r_S}\right)_2 - \left(\frac{P_E}{r_S}\right)_1}{(P_E)_2 - (P_E)_1} = \frac{46.73 - 706.7}{0.01 - 1.0} = 666.7 \frac{\text{gmcat-min}}{\text{gmole}}$$

$$k = 1.50 \times 10^{-3} \frac{\text{gmol}}{\text{gmcat-min}}$$

and $\frac{1}{k K_A} = \left(\frac{P_E}{-r_S}\right)_1 - \frac{1}{k}(P_E)_1 = 706.7 - 666.7 = 40 \frac{\text{atm-gmcat-min}}{\text{gmole}}$

$K_A = 16.64 \text{ atm}^{-1}$

Now, taking data points 1 and 3, in which P_E is constant, the value of $K_D k K_A$ and hence

K_D can be determined:

For point 1: $\left(\frac{P_E}{-r_S}\right)_1 = \frac{1}{k K_A} + \frac{1}{k}(P_E)_1 + \frac{(P_{St})_1}{K_D k K_A}$

For point 3: $\left(\frac{P_E}{-r_S}\right)_3 = \frac{1}{k K_A} + \frac{1}{k}(P_E)_3 + \frac{(P_{St})_3}{K_D k K_A}$

Substracting, and solving for $\frac{1}{K_D k K_A}$, noting that $(P_E)_1 = (P_E)_3$

$$\frac{1}{K_D k K_A} = \frac{(P_E)_3\left[\left(\frac{1}{-r_S}\right)_3 - \left(\frac{1}{-r_S}\right)_1\right]}{(P_{St})_3 - (P_{St})_1} = \frac{1.0\left[\frac{1}{0.166\times10^{-3}} - \frac{1}{1.415\times10^{-3}}\right]}{1.0 - 0.0} \frac{\text{gm cat - min}}{\text{gmol}}$$

$$\frac{1}{K_D k K_A} = 5317.3 \frac{\text{gm cat - min}}{\text{gmole}}$$

$K_D = 0.007534$

∴ Rate expression is

$$-r_E = \frac{P_E/40}{1 + 16.64\, P_E + \frac{P_{St}}{0.007534}} = \frac{0.25\, P_E}{1 + 16.64\, P_E + 132.7\, P_{St}} \left(\frac{\text{gmole}}{\text{gm cat - min}}\right)$$

(a) $(MW)_E = 106.1 \frac{g}{\text{gmole}}$, $(MW)_S = 18 \frac{g}{\text{gmole}}$, $(MS)_{St} = 104.1 \frac{g}{\text{gmole}}$

Then $\theta_1 = \frac{1 \text{ gmole } H_2O}{5 \text{ gmole E}} = 0.2$

$y_{E,0} = \frac{1}{1 + \theta_1} = 0.833$; $P = P_o = 0.415$; $X_F = 0.60$; $\delta = 2-1 = 1$; $T = 903°K$

$\therefore \varepsilon = y_{E,0}\,\delta = 0.833$; $F_{St} = \frac{2000 \text{ Kg}}{\text{day}}\left(\frac{1 \text{ kg mol}}{104.1 \text{ kg}}\right) = 19.2 \frac{\text{kg mol}}{\text{day}} = F_{E,0}X_F$

$$P_E = C_E RT = \frac{F_E RT}{\upsilon} = \frac{F_{E,0}(1-X)RT}{\upsilon_o(1+\varepsilon X)} = \frac{C_{E,0}RT(1-X)}{1+\varepsilon X} = \frac{y_{E,0}P_o(1-X)}{1+\varepsilon X}$$

$$P_{St} = C_{St}RT = \frac{F_{St}RT}{\upsilon} = \frac{F_{E,0}\,X\,RT}{\upsilon_o(1+\varepsilon X)} = \frac{y_{E,0}P_o\,X}{1+\varepsilon X}$$

Rate expression for any X is:

$$-r_E = \frac{0.025\left[\frac{y_{E,0}P_o(1-X)}{1+\varepsilon X}\right]}{1+16.64\left[\frac{y_{E,0}P_o(1-X)}{1+\varepsilon X}\right]+\frac{132.7\ y_{E,0}\ P_o\ X}{1+\varepsilon X}}$$

Design expression for a CSTR (fluidized bed) is $W = \frac{F_{E,0}\ X_F}{-r_E}$

$$W = \frac{F_{E,0}\ X_F}{0.025}\left[\frac{1+\varepsilon X_F}{y_{E,0}\ P_o\ (1-X_F)} + 16.64 + \frac{132.7\ X_F}{1-X_F}\right]$$

$$= \frac{F_{St,}\ X_F}{0.025\ X_F}\left[\frac{1+\varepsilon X_F}{y_{E,0}\ P_o\ (1-X_F)} + 16.64 + \frac{132.7\ X_F}{1-X_F}\right]$$

$$= \frac{19.2\times10^3\ \text{gmol}}{\text{day}} \times \frac{1\ \text{day}}{0.025}\left[\frac{1+0.833\ (0.45)}{0.833\ (0.415)(1-.45)} + 16.64 + \frac{132.7\ (0.45)}{1-.45}\right] \times \frac{1\ \text{day}}{24\times60\ \text{min}}$$

$$W = 7.06\times10^4\ \text{g}$$

$$\text{Cost} = 70.6\ \text{kg} \times \frac{\$11}{\text{kg}} = \$777$$

(b) Plug flow reactor, expression for $y_{E,0}$, $F_{St,}$, P_E, P_{St} and $-r_E$ are the same as for the CSTR. The design equation is:

$$W = F_{E,0}\int_0^{X_F}\frac{dX}{-r_E} = \frac{F_{St,}}{.025\ X_F}\int_0^{X_F}\left[\frac{1+\varepsilon X}{y_{E,0}\ P_o\ (1-X)} + 16.64 + \frac{132.7X}{1-X}\right]dX$$

$$W = \frac{F_{St,}}{0.025\ X_F}\left[\frac{1}{y_{E,0}\ P_o}\left(-\varepsilon X - [1+\varepsilon]\ln[1-X]\right) + 16.64X + 132.7\left[-X - \ln(1-X)\right]\right]\Big|_0^{X_F}$$

$$W = \frac{F_{St,}}{0.025\ X_F}\left[\frac{1}{y_{E,0}\ P_o}\left(-\varepsilon X_F - [1+\varepsilon]\ln[1-X_F]\right) + 16.64X_F + 132.7\left[X_F + \ln(1-X_F)\right]\right]$$

$$W = \frac{19.2\times10^3\ \text{gmol}}{\text{day}} \times \frac{1}{0.025\times0.45}\ \frac{\text{gm cat-min}}{\text{gmol}}$$

$$\left[\frac{-.833(.45) + 1.833\ln(1-.45)}{(0.833)(0.415)} + 16.64\,(0.45) - 132.7\left[0.45 + \ln(1-0.45)\right]\right] \times \frac{1day}{24*60\,\text{min}}$$

$$W = 2.71\times10^4$$

$$\text{Cost} = 27.1 \times \frac{\$11}{\text{kg}} = \$298$$

CDP10-G

Given: reduction of CO with hydrogen over Ni catalyst:

$$CO + 3\ H_2 \rightarrow CH_4 + H_2O$$

Kinetic given by: $r = \dfrac{0.0183\ P_{H_2} P_{CO}}{1 + 1.5\ P_{H_2}} \left(\dfrac{\text{gmole } CH_4}{\text{gm cat-min}}\right)$

From the above expression:

1) The appearance of P_{h2} in the denominator suggest that H_2 is adsorbed on the surface.
2) The fact that CO does not appear in the denominator suggests that it reacts as a gas phase species.
3) The square root dependence in the numerator suggests that H_2 splits.

Therefore, suggested mechanism is:

$H_2 + S \underset{\leftarrow}{\overset{k_1}{\rightarrow}} H_2{\cdot}S \qquad -r_1 = k_1 [P_{H_2} C_S - C_{H_2 \cdot S}/K_1]$

$H_2{\cdot}S + S \underset{\leftarrow}{\overset{k_2}{\rightarrow}} 2H{\cdot}S \qquad -r_2 = k_2 \left[C_{H_2 \cdot S} C_S - C_{H \cdot S}^2 / K_2\right]$

$H{\cdot}S + CO \underset{\leftarrow}{\overset{k_3}{\rightarrow}} CHO{\cdot}S \qquad -r_3 = k_3 [C_{H \cdot S} P_{CO} - C_{HO \cdot S}/K_3]$

$CHO{\cdot}S + H{\cdot}S \underset{\leftarrow}{\overset{k_4}{\rightarrow}} C{\cdot}S + H_2O + S \qquad -r_4 = k_4 [C_{CHO \cdot S} C_{H \cdot S} - C_{C \cdot S} P_{H_2O} C_S/K_4]$

$C{\cdot}S + 2H_2 \underset{\leftarrow}{\overset{k_5}{\rightarrow}} CH_4 + S \qquad -r_5 = k_5 [C_{C \cdot S} P_{H_2}^2 - P_{CH_4} C_S/K_5]$

Remarks made in Chapter 5 of the text suggest that reaction 3 is rate controlling:

$\dfrac{-r_1}{k_1} \equiv 0 \quad C_{H_2 \cdot S} = K_1 P_{H_2} C_S$

$\dfrac{-r_2}{k_2} \equiv 0 \quad C_{H \cdot S} = \sqrt{K_2 C_{H_2 \cdot S} C_S} = \sqrt{K_1 K_2 P_{H_2}}\, C_S$

$\dfrac{-r_5}{k_5} \equiv 0 \quad C_{C \cdot S} = \dfrac{P_{CH_4}}{K_5 P_{H_2}^2} \cdot C_S$

$\dfrac{-r_4}{k_4} \equiv 0 \quad C_{CHO \cdot S} = \dfrac{C_{C \cdot S} P_{H_2O} C_S}{K_4 C_{H \cdot S}} = \dfrac{P_{CH_4} P_{H_2O} C_S^2}{K_4 K_5 P_{H_2}^2 C_{H \cdot S}} = \dfrac{P_{CH_4} P_{H_2O} C_S}{K_4 K_5 \sqrt{K_1 K_2}\, P_{H_2}^{5/2}}$

$-r_3 = k_3 \left[C_{H \cdot S} P_{CO} - \dfrac{C_{CHO \cdot S}}{K_3}\right] = k_3 \left[\sqrt{K_1 K_2 P_{H_2}}\, P_{CO} C_S - \dfrac{P_{CH_4} P_{H_2O} C_S}{K_3 K_4 K_5 \sqrt{K_1 K_2}\, P_{H_2}^{5/2}}\right]$

$\text{or } (-r_3) = \dfrac{k_3 \sqrt{K_1 K_2}}{P_{H_2}^{5/2}} C_S \left[P_{H_2}^3 P_{CO} - \dfrac{P_{CH_4} P_{H_2O}}{K_1 K_2 K_3 K_4 K_5}\right]$

$C_T = C_S + C_{H_2S} + C_{C \cdot S} + C_{CHO \cdot S}$

$C_T = C_S \left[1 + K_1 P_{H_2} + \sqrt{K_1 K_2 P_{H_2}} + \dfrac{P_{CH_4}}{K_5 P_{H_2}^2} + \dfrac{P_{CH_4} P_{H_2O}}{P_{H_2}^{5/2} K_4 K_5 \sqrt{K_1 K_2}}\right]$

Kinetic expression becomes

$$-r_3 = \frac{k_3 \sqrt{K_1 K_2}\, C_T \left[P_{H_2}^3 P_{CO} - \dfrac{P_{CH_4} P_{H_2O}}{K_1 K_2 K_3 K_4 K_5} \right]}{\left[P_{H_2}^{1/2} + K_1 P_{H_2}^{1/2} + \sqrt{K_1 K_2}\, P_{H_2}^3 + \dfrac{P_{CH_4} \sqrt{P_{H_2}}}{K_5} + \dfrac{P_{CH_4} P_{H_2O}}{K_4 K_5} \right]}$$

Reaction is irreversible $\therefore$ let $K_5 \to \infty$ Then

$$-r_3 = \frac{k_3 \sqrt{K_1 K_2}\, C_T P_{H_2}^3 P_{CO}}{P_{H_2}^{1/2}\left[1 + K_1 P_{H_2} + \sqrt{K_1 K_2}\, P_{H_2}\right]} = \frac{k_3 \sqrt{K_1 K_2}\, C_T P_{H_2}^{1/2} P_{CO}}{1 + K_1 P_{H_2} + \sqrt{K_1 K_2}\, P_{H_2}^{1/2}}$$

with $K_1 P_{H_2} >> \sqrt{K_1 K_2}\, P_{H_2}^{1/2}$, we get

$-r_3 = \dfrac{k_3 \sqrt{K_1 K_2}\, C_T P_{H_2}^{1/2} P_{CO}}{1 + K_1 P_{H_2}}$. This expression implies that at moderate pressures, most of the active sites are occupied by the H_2 molecules.

(a) Design for a plug flow reactor. Denote A[=] CO, B[=] H_2; then $y_{A0} = 0.25$, $y_{B0} = 0.75$, $\theta_B = \dfrac{F_{B0}}{F_{A0}} = \dfrac{y_{B0}}{y_{A0}} = 3$, $X_F = 0.80$

$\delta = 1 + 1 - 2 - 1 = -1 \quad : \quad \varepsilon = y_{A0}\,\delta = -0.75$

$$F_{A0} X_F = F_{CH_4} = 2000 \frac{\text{lb}}{\text{day}} \times \frac{\text{lbmole}}{16\ \text{lb}} = 125 \frac{\text{lbmol}}{\text{day}}$$

$$F_{A0} = \frac{125}{0.8} \frac{\text{lbmol}}{\text{day}} = 156.25 \frac{\text{lbmol}}{\text{day}}$$

Design equation $F_{A0}\, dX = -r_A\, dW$ or $\dfrac{W}{F_{A0}} = \displaystyle\int_0^{0.80} \frac{dX}{-r_A}$

$$-r_A = \frac{0.0183\, P_A P_B^{1/2}}{1 + 1.5\, P_B}$$

$$P_A = C_A RT = \frac{C_{A0} RT (1-X)}{1 + \varepsilon X} = \frac{y_{A0} P_B (1-X)}{1 + \varepsilon X}$$

$$P_B = C_B RT = \frac{C_{A0} RT(\theta_B - 3X)}{1 + \varepsilon X} = \frac{C_{A0} RT(3 - 3X)}{1 + \varepsilon X} = \frac{3\, y_{A0} P_o (1-X)}{1 + \varepsilon X}$$

$$\therefore -r_A = \frac{0.0183 \left[\dfrac{y_{A0} P_o (1-X)}{1 + \varepsilon X}\right]\left[\dfrac{3\, y_{A0} P_o (1-X)}{1 + \varepsilon X}\right]^{1/2}}{1 + 1.5\left[\dfrac{y_{A0} P_o (1-X)}{1 + \varepsilon X}\right]} = \frac{0.0183 \sqrt{3}\left[\dfrac{y_{A0} P_o (1-X)}{1 + \varepsilon X}\right]^{3/2}}{1 + 1.5\left[\dfrac{y_{A0} P_o (1-X)}{1 + \varepsilon X}\right]}$$

$$\therefore \frac{W}{F_{A0}} = \int_0^{X_F} \left(\frac{1 + 1.5\left[\dfrac{y_{A0} P_o (1-X)}{1 + \varepsilon X}\right]}{0.0183 \sqrt{3}\left[\dfrac{y_{A0} P_o (1-X)}{1 + \varepsilon X}\right]^{3/2}} \right) dX$$

$$\frac{W}{F_{A0}} = \frac{1}{0.0183\sqrt{3}\,(y_{A0}P_o)^{3/2}}\int_0^{X_F}\left\{\left[\frac{1+\varepsilon X}{1-X}\right]^{3/2} + 1.5\,y_{A0}P_o\left[\frac{1+\varepsilon X}{1-X}\right]^{1/2}\right\}dX$$

$$\frac{W}{F_{A0}} = \frac{1}{0.0183\sqrt{3}\,(y_{A0}P_o)^{3/2}}\int_0^{0.8}\left\{\left[\frac{1+(-0.25)X}{1-X}\right]^{3/2} + 3.75\left[\frac{1-0.25X}{1-X}\right]^{1/2}\right\}dX$$

The integral can be solved using Simpson's rule

Let $f(X) = \left[\frac{1-0.25X}{1-X}\right]^{3/2} + 3.75\left[\frac{1-0.25X}{1-X}\right]^{1/2} = \left[\frac{1-0.25X}{1-X} + 3.75\right]\left[\frac{1-0.25X}{1-X}\right]^{1/2}$

Then $\int_0^{X_F} f(X)\,dX \equiv \frac{\Delta X}{3}\left[f(0) + \Delta f(0.2) + 2f(0.4) + 4f(0.6) + f(0.8)\right]$

X	1-X	1-0.25X	$\frac{1-0.25X}{1-X}$	$\frac{1-0.25X}{1-X}+3.75$	$\left(\frac{1-0.25X}{1-X}\right)^{1/2}$	f(X)	W	Wf(X)
0	1	1	1	4.750	1.000	4.750	1	4.750
0.2	0.8	0.95	1.1875	4.974	1.090	5.420	4	21.679
0.4	0.6	0.90	1.500	5.250	1.225	6.430	2	12.860
0.6	0.4	0.85	2.125	5.875	1.458	8.564	4	34.257
0.8	0.2	0.80	4.000	7.950	2.000	15.500	1	15.500

$$\int_0^{0.8} f(X)dX = \frac{0.2}{3}[4.750 + 21.679 + 12.860 + 34.257 + 15.500] = 5.936$$

$$W = \frac{5.936}{0.0183\sqrt{3}\,(0.25\times10)^{3/2}}\frac{\text{gm cat}\cdot\text{min}}{\text{gmol}}\times\frac{156.25\text{ lbmol}}{\text{day}}\times\frac{454\text{ gmol}}{\text{lbmol}}\times\frac{1\text{ day}}{24\times60\text{ min}}$$

$$W = 2334\text{ g}$$

(b) Design of a CSTR

Design equation is $W = \frac{F_{A0}X_F}{-r_A}$

$$W = \frac{F_{A0}X_F}{0.0183\sqrt{3}\,(y_{A0}P_o)^{3/2}}\left[\left(\frac{1+\varepsilon X}{1-X}\right)^{3/2} + 1.5\,y_{A0}P_o\left(\frac{1+\varepsilon X}{1-X}\right)^{1/2}\right]$$

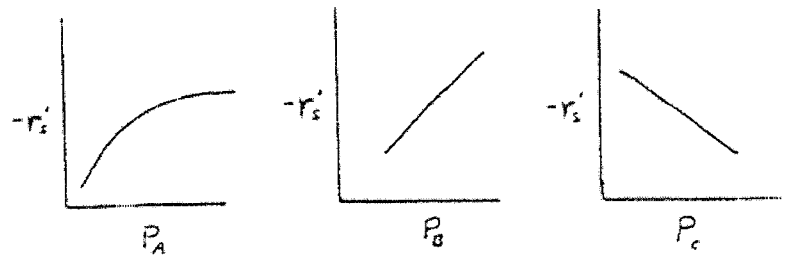
$$W = \frac{125\text{ lbmol/day}\times0.8}{0.0183\sqrt{3}\,(0.25\times10)^{3/2}}\left[\left(\frac{1-(.25)(.8)}{1-.8}\right)^{3/2} + (1.5)(.25)(10)\left(\frac{1-(.25)(.8)}{1-.8}\right)^{1/2}\right]\frac{\text{gmcat}\cdot\text{min}}{\text{gmol}}$$

$$W = 12371\frac{\text{lbmol}}{\text{day}}\times\frac{\text{gm cat}\cdot\text{min}}{\text{gmol}}\times\frac{454\text{ gmol}}{\text{lbmol}}\times\frac{1\text{ day}}{24\times60\text{ min}}$$

$$W = 3900\text{ g}$$

CDP10-H

(a)



Runs 1,3,6,7 $\quad -r_s' = \dfrac{P_A}{1 + K_A P_A + \ldots}$

Runs 1,2,4 $\quad -r_s' = P_B + \ldots$

Runs 4,5 $\quad -r_s' = \dfrac{1}{1 + K_C P_C + \ldots}$

(b) Numerator: P_A and P_B

Denominator: P_A and P_C

Power of Denominator: 1

(c) Proposed Rate Law: $-r_s' = \dfrac{kP_A P_B}{1 + K_A P_A + K_C P_C}$

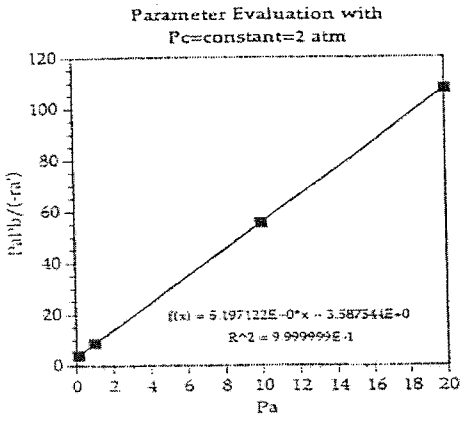
(d) To find the rate law parameters, rearrange the rate law so that it can be plotted as a line with the rate law parameters as the slope and intercept of the line.

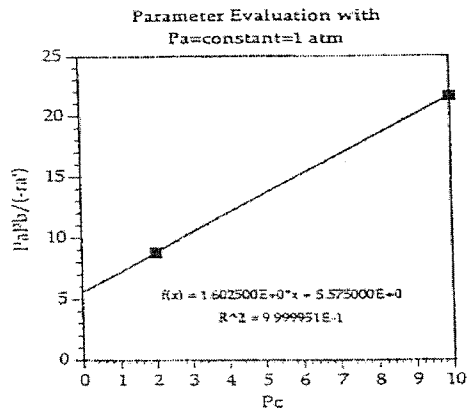
$$\frac{P_A P_B}{-r_s} = \frac{K_A}{k} P_A + \frac{K_C}{k} P_C + \frac{1}{k}$$

First, hold P_C constant and plot $\dfrac{P_A P_B}{-r_s}$ vs. P_A

From the plot

$$\text{Slope} = \frac{K_A}{k} = 5.2, \quad y - \text{Intercept} = \frac{1 + K_C P_C}{k} = 3.59$$





Second, hold P_A constant and plot $\frac{P_A P_B}{-r_S}$ vs. P_C

From plot below,

$$\text{Slope} = \frac{K_C}{k} = 1.6025, \quad \text{y -- Intercept} = \frac{1 + K_A P_A}{k} = 5.575$$

Using the four equations above to solve for k, K_A, and K_C, we get:

$$k = 2.60 \frac{\text{mol}}{\text{gcat} \cdot \text{sec} \cdot \text{atm}^2}, \quad K_A = 13.52\ \text{atm}^{-1}, \quad K_C = 4.1665\ \text{atm}^{-1}$$

(e) A and C are adsorbed on the surface of the catalyst.

(f) Proposed Mechanism:

$$A + S \Leftrightarrow A \cdot S$$

$$A \cdot S + B \Rightarrow B + C \cdot S$$

$$C \cdot S \Leftrightarrow C + S$$

The irreversible reaction step was assumed to be the limiting step. We check this mechanism and rate limiting step by rearranging and combining the rate laws for each step. If the mechanism is correct, we will obtain the rate law proposed in part c.

$$-r_A = k_A\left[P_A C_V - \frac{C_{A\cdot S}}{K_A}\right]$$

$$-r_S = k_S C_{A\cdot S} P_B$$

$$-r_C = k_C\left[C_{C\cdot S} - \frac{P_C C_V}{K_C}\right]$$

k_S is much smaller than k_A and k_C, therefore, $\frac{-r_A}{k_A} = \frac{-r_C}{k_C} = 0$

$$C_{A\cdot S} = K_A P_A C_V \quad \text{and} \quad C_{C\cdot S} = \frac{P_C C_V}{K_C} = K_C P_C C_V, \text{ where } K_C = \frac{1}{K_C}$$

Also, $C_T = C_V + C_{A\cdot S} + C_{C\cdot S}$

After substitution, $C_V = \dfrac{C_T}{1 + K_A P_A + K_C P_C}$

Next, substitute the above equations into the reactions step to get

$$-r_S = \frac{kP_A P_B}{1 + K_A P_A + K_C P_C}$$

Because this is the same as the rate law in part c, the rate law and limiting step assumptions have been verified.

(g) Ratio of sites of A to sites of B at 80% conversion:

$$\frac{C_{A\cdot S}}{C_{C\cdot S}} = \frac{K_A P_A C_V}{K_C P_C C_V} = \frac{K_A P_{A_0}(1-X)}{K_C P_{A_0} X} = \frac{(13.52)(0.20)}{(4.1665)(0.80)} = 0.81$$

Conversion at which the number of sites of A equal the number of sites of C:

$$\frac{C_{A\cdot S}}{C_{C\cdot S}} = \frac{K_A(1-X)}{K_C X} = \frac{(13.52)(1-X)}{(4.1665)(X)} = 1$$

$X = 0.76$

CDP10-I

a) To determine the mechanism and rate-limiting step we must come up with the rate law. Looking at the rate dependence of A we see that between runs 1 and 2, P_A increases from 1 to 1000 atm while the rate law only increases from 1 to 1.5. This tells us that as A gets larger it changes the rate law a good deal less. This tells us that A is both in the numerator and the denominator.

$$-r_A' \sim \frac{P_A}{1+K_A P_A}$$

Looking at the rate dependence of B we see that between runs 1 and 3, P_B increases from 1 to 4.5. This tells us that the rate law is directly related to B.

$$-r_A' \sim P_B$$

Looking at the rate dependence of C we see that between runs 7 and 9 P_C increases from 0 to 4 atm and the rate increases from 4.5 to 4.8. Also in these runs we see that P_A increases from 1 to 4 atm. So one of two things is true either P_C is both in the numerator and denominator or just in the denominator. Since C is a product it will not be in the numerator in an irreversible reaction.

$$-r_A' \sim \frac{\bullet}{1+K_C P_C}$$

So the rate law becomes

$$-r_A' = \frac{kP_A P_B}{1+K_A P_A + K_c P_C}$$

With that rate law the following mechanism exists:

Adsorption

$$A + S \rightarrow A \cdot S$$

Surface reaction

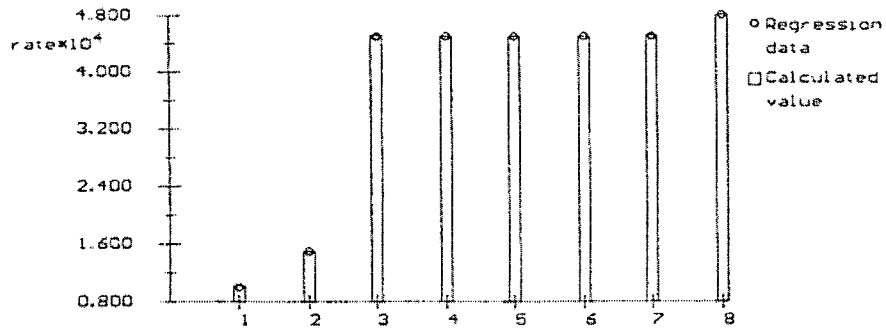
$$A \cdot S + B(g) \rightarrow C \cdot S$$

Dissociation

$$C \cdot S \rightarrow C + S$$

The surface reaction is the rate-limiting step.

b) In evaluating the parameters we can also see if our rate law is a good one. Plugging into POLYMATH we can come up with the parameters.



Model: rate=k*Pa*Pb/(1+Ka*Pa+Kc*Pc)
k = 0.000449997 Kc = 0.5
Ka = 2.99989
4 positive residuals, 4 negative residuals. Sum of squares = 5.26309e-15

We find that the rate law is a good one. $k = 0.00045$
$K_A = 3$
$K_C = .5$

c) The best places to add points would be where P_C is changed, but P_A and P_B are not changed.

d) No solution will be given.

CDP10-J

$$2\,C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + H_2O$$
$$(A) \qquad (E) \qquad (W)$$

$$A + S \rightleftarrows A\cdot S \qquad r_1 = k_1[P_A C_S - C_{A\cdot S}/K_1]$$

$$A\cdot S + A\cdot S \rightleftarrows E\cdot S + W\cdot S \qquad r_2 = k_2[C_{A\cdot S}^2 - C_{E\cdot S} C_{W\cdot S}/K_2]$$

$$E\cdot S \rightleftarrows E + S \qquad r_3 = k_3[C_{E\cdot S} - P_E C_S/K_3]$$

$$W\cdot S \rightleftarrows W + S \qquad r_4 = k_4[C_{W\cdot S} - P_W C_S/K_4]$$

At steady state $r = -\frac{dC_A}{dt} \Rightarrow r = r_1 = 2r_2 = 2r_3 = 2r_4$

If surface reaction is controlling,

$$\frac{r_1}{k_1} \equiv 0 \quad \Rightarrow \quad C_{A\text{-}S} = K_1 P_A C_S$$

$$\frac{r_3}{k_2} \equiv 0 \qquad C_{E\text{-}S} = \frac{P_E C_S}{K_3}$$

$$\frac{r_4}{k_4} \equiv 0 \qquad C_{W\text{-}S} = \frac{P_W C_S}{K_4}$$

$$C_T = C_S + C_{A\text{-}S} + C_{W\text{-}S} = C_S\left[1 + K_1 P_A + \frac{P_E}{K_3} + \frac{P_W}{K_4}\right]$$

$$C_S = \frac{C_T}{1 + K_1 P_A + \frac{P_E}{K_3} + \frac{P_W}{K_4}}$$

$$\therefore\ r = 2r_2 = \frac{2k_2\left[K_1^2 P_A^2 C_T^2 - \frac{P_E P_W C_T^2}{K_2 K_3 K_4}\right]}{\left[1 + K_1 P_A + \frac{P_E}{K_3} + \frac{P_W}{K_4}\right]^2} = \frac{k\left[P_A^2 - \frac{P_E P_W}{K_{eq}}\right]}{\left[1 + K_1 P_A + \frac{P_E}{K_3} + \frac{P_W}{K_4}\right]^2}$$

where $k = 2k_2 C_T^2 K_1^2$

$K_{eq} = K_1^2 K_2 K_3 K_4$

Using points 9 and 13, $P_E = 0$, $P_W = 0$

$$\therefore\ r = \frac{k P_A^2}{(1 + K_1 P_A)^2}$$

$$\sqrt{\frac{1}{r}} = \frac{1}{\sqrt{k}}\frac{1}{P_A} + \frac{K_1}{\sqrt{k}}$$

A plot of $\sqrt{\frac{1}{r}}$ vs. $\frac{1}{P_A}$ produces a straight line with slope $\sqrt{\frac{1}{k}}$ and intercept $\frac{K_1}{k}$

$$\text{slope} = \sqrt{\frac{1}{k}} = 4.945 \qquad \therefore\ k = 0.0409$$

$$\text{intercept} = \frac{K_1}{\sqrt{k}} = 85.59 \qquad \therefore\ K_1 = 17.31$$

Using point 10, $P = 0$ $\qquad \therefore\ K_4 = 0.0399$

Check

Using point 11, $P_E = 0 \Rightarrow K_4 = 0.0368$, close enough

Using point 6 , $P_W = 0 \Rightarrow K_3 = 0.659$

Finally, using point 12 $\Rightarrow K_{eq} = 0.0975$

$$r = \frac{0.0409\,(P_A^2 - 10.256\,P_E P_W)}{[1 + 17.31\,P_A + 1.517\,P_E + 25.05\,P_W]^2}$$

Note: K_{eq} may also be calculated using $RT \ln K_{eq} = -\Delta G^\circ$. Interested readers are encouraged to check the goodness of fit of this rate law with the data.

CDP10-K

CDP10-L

Rate law:

$$-r_{AC} = \frac{kC_{CO}C_{AC}C_{NaOH}}{(1+K_{AC}C_{AC})^2}$$

Proposed Mechanism:

$$Pd + CO \underset{\longrightarrow}{\longleftarrow} Pd \cdot CO$$

$$Pd \cdot CO + NaOH \underset{\longrightarrow}{\longleftarrow} Pd \cdot CO \cdot NaOH$$

$$AC + Pd \rightarrow AC \cdot Pd$$

$$AC \cdot Pd + Pd \cdot CO \cdot NaOH \longrightarrow C_3H_5COOH + NaCl + 2Pd$$

Neither of the first two reactions can be limiting because they are reversible. The rate step must be irreversible because there is no subtraction function in the numerator.

We will first try the third equation as the rate-limiting step:

$$r_A = kC_vP_{AC}$$

Then

$$C_t = C_v + C_{Pd\cdot CO} + C_{Pd\cdot CO\cdot NaOH} + C_{Pd\cdot AC}$$

Find equations for $C_{Pd\cdot CO}$, $C_{Pd\cdot CO\cdot NaOH}$, and $C_{Pd\cdot AC}$.

$$\frac{r_{ACO}}{k_{ACO}} = 0 \qquad C_{Pd\,CO} = C_vC_{CO}K_{CO}$$

$$\frac{r_{ACO\cdot NaOH}}{k_{NaOH}} = 0 \qquad C_{Pd\,CO\,NaOH} = K_{CO}K_{NaOH}C_vC_{NaOH}C_{CO}$$

$$\frac{r_{AC}}{k_{AC}} = 0 \qquad C_{Pd\,AC} = 0$$

Combine to find C_v

$$C_v = \frac{C_t}{1 + C_{CO}K_{CO} + K_{CO}K_{NaOH}C_{CO}C_{NAOH}}$$

This is definitely not what is supposed to be on the bottom of the rate law so reaction 3 can not be rate-limiting.

Trying reaction 4:

$$r_4 = k_4C_{Pd\cdot AC}C_{Pd\cdot CO\cdot NaOH}$$

$C_{Pd\cdot AC}$ cannot be found so therefore this rate law is also not rate-limiting so none of the mechanisms reactions agree with the rate law.

CDP10-M

a) Start with a mole balance:

$$\frac{dX}{dW} = \frac{-r_A'}{F_{A0}}$$

Rate law comes next:

$$-r_A' = k_r a$$

Then the decay law:

$$\frac{da}{dt} = -k_d$$

$$t = \frac{W}{U_s}$$

$$\frac{da}{dW} = -\frac{k_d}{U_s}$$

We then come up with the equation for the profit:

$$P = 160 * (F_B) - 10 * (U_s)$$

Where :

$$F_B = F_{A0} * X$$

Then plug into POLYMATH and get the following program. The feed rate of solids that gives a maximum profit is 4 kg/min.

Equations:

```
d(a)/d(w)=-kd/Us
d(x)/d(w)=-ra/fao
fao=1
kd=2
Us=4
kr=1
ra=-kr*a
fb=fao*x
P=160*fb-10*Us
```

$w_0 = 0, \quad w_f = 1$

Initial value
1
0

10-18a.

Variable	Initial value	Maximum value	Minimum value	final value
w	0	1	0	1
a	1	1	0.5	0.5
x	0	0.75	0	0.75
fao	1	1	1	1
kd	2	2	2	2
Us	4	4	4	4
kr	1	1	1	1
ra	-1	-0.5	-1	-0.5
fb	0	0.75	0	0.75
P	-40	80	-40	80

b) As seen above: X = 0.75 and a =.5

c) The only equation that changes is the rate law:

$$\frac{da}{dt} = -k_d$$

$$t = \frac{W_{MAX} - W}{U}$$

$$dt = \frac{-dW}{U}$$

$$\frac{da}{dW} = \frac{k_d dW}{U}$$

Integrating we get this:

$$a = \frac{k_d W}{U} + k$$

W = W_{MAX} @ a = 1

$$k = 1 - \frac{k_d W}{U}$$

$$a = 1 - \frac{k_d (W_{MAX} - W)}{U}$$

Equations:

```
d(x)/d(w)=-ra/fao
kr=5
fao=1
kd=2
Us=.8
wmax=1
fb=if(x<1)then(fao*x)else(1)
a=if(kd/Us*(wmax-w)<1)then(1-kd/Us*(wmax-w))else(0)
P=150*fb-10*Us
ra=-a*kr
```

$w_0 = 0, \quad w_f = 1$

Initial value
0

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	1	0	1
x	0	1	-6.245e-18	1
kr	5	5	5	5
fao	1	1	1	1
kd	2	2	2	2
Us	0.8	0.8	0.8	0.8
wmax	1	1	1	1
fb	0	1	-6.245e-18	1
a	0	1	0	1
P	-8	142	-8	142
ra	-0	-0	-5	-5

We find U = 0.8 to maximize the profit. X = 1 and a = 0 exiting the reactor.

CDP10-N

(a)

Design Equation : $W = \dfrac{F_{Ao}X}{(-r_A)a(t)} \quad \Rightarrow \quad a(t) = \dfrac{\upsilon_o}{W}\left(\dfrac{C_{Ao} - C_A}{kC_A^n}\right)$ For n^{th} order kinetics.

Assume at $t = 0$, $a(0) = 1$ and $X \approx 1$.

$$\Rightarrow \quad F_B(0) = F_{Ao}X = F_{Ao} = 106 \quad \Rightarrow \quad F_{Ao} = 106$$

Now

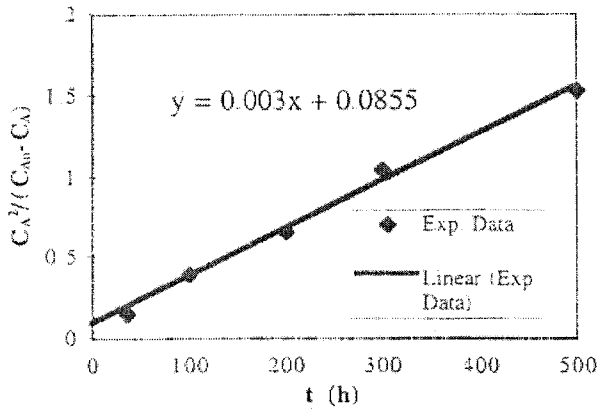
$$F_B(t) = F_{Ao}X(t) = RON(t)$$

$$X(t) = \frac{RON(t)}{106} = \frac{RON(t)}{RON(0)}$$

Second order kinetics and second order decay rate fit the data very well.

$$a'(t) = -k_d a^2 \quad \Rightarrow \quad a(t) = \frac{1}{1 + k_d t} \quad \Rightarrow \quad 1 + k_d t = \frac{kC_A^2}{C_{Ao} - C_A}$$

Plot of $\dfrac{C_A^2}{C_{Ao} - C_A}$ vs. t :



From the graph : intercept $= 1/k = 0.0835 \quad \Rightarrow \quad k = 11.98$

slope $= k_d / k = 0.003 \quad \Rightarrow \quad k_d = 0.00025$

(b) Activation Energies both for rate constant and decay constant can be estimated from the temperature-time trajectory.

CDP10-O

Given $A \longrightarrow R + S$

Batch constant volume reactor, P increases with time

$$N_{A0}\, dX = a\, r_o\, W dt$$

Assume $a = e^{-\alpha t}$

$$r_0 = kP_A$$

$\therefore\ P_A = C_A RT$

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

$\therefore\ N_{A0}\, dX = We^{-\alpha t}\, k\, C_{A0}(1-X)\, RT\, dt$

$$\int_0^X \frac{dX}{1-X} = \frac{W\, k\, C_{A0}\, RT}{N_{A0}} \int_0^t e^{-\alpha t}\, dt = \left(\frac{W}{V_o}\right) k\, RT \int_0^t e^{-\alpha t}\, dt$$

$$= \beta \int_0^t e^{-\alpha t}\, dt \quad \text{where} \quad \beta = \left(\frac{W}{V_o}\right) k\, RT$$

$$-\ln(1-X) = \frac{\beta}{\alpha}\left(1-e^{-\alpha t}\right)$$

Assume that there is very little deactivation in the first 10 sec

$$-\ln(1-X) = \frac{\beta}{\alpha}(\alpha t) = \beta t \quad \text{(for small t)}$$

$$\beta = \frac{1}{t}\ln\left(\frac{1}{1-X}\right) = \frac{1}{10}\ln\left(\frac{1}{1-0.037}\right) = 3.77 \times 10^{-3}\ \text{sec}$$

$$\beta = \left(\frac{W}{V_o}\right) k\, RT \Rightarrow k = \frac{\beta}{\left(\frac{W}{V_o}\right) RT} = \frac{3.77 \times 10^{-3}}{1 \times 0.08205 \times (273+420)}$$

$$k = 6.63 \times 10^{-5}\ \text{sec}^{-1}$$

At t relatively large, $e^{-\alpha t} = 0$

$$\frac{\beta}{\alpha} = -\ln(1-X)$$

$$\alpha = \frac{\beta}{\ln\left(\frac{1}{1-X}\right)} = \frac{3.37 \times 10^{-3}}{\ln\left(\frac{1}{1-0.517}\right)} = 5.18 \times 10^{-3}\ \text{sec}^{-1}$$

$\therefore\ -\ln(1-X) = 0.728\ (1-e^{-5.18\times10^{-3}t})$

t	X	X
0	0	0
10	0.037	0.036
20	0.071	0.069
30	0.102	0.099
40	0.130	0.127
60	0.180	0.177
80	0.223	0.219
100	0.259	0.255
150	0.330	0.325
200	0.379	0.375
300	0.441	0.437
500	0.493	0.490
750	0.512	0.510
1000	0.517	0.515

$\therefore$ The assumption of a first order reaction kinetics and a first order decay kinetics is justified.

CDP10-P

$$\text{cyclopentane} \begin{cases} \text{n - pentane} \\ \text{coke} \end{cases}$$

Batch mole balance : $$-\frac{dN_A}{dt} = -r_A W = k_A C_A^n W$$

$$-\frac{dC_A}{dt} = \frac{k_A}{V} C_A^n W$$

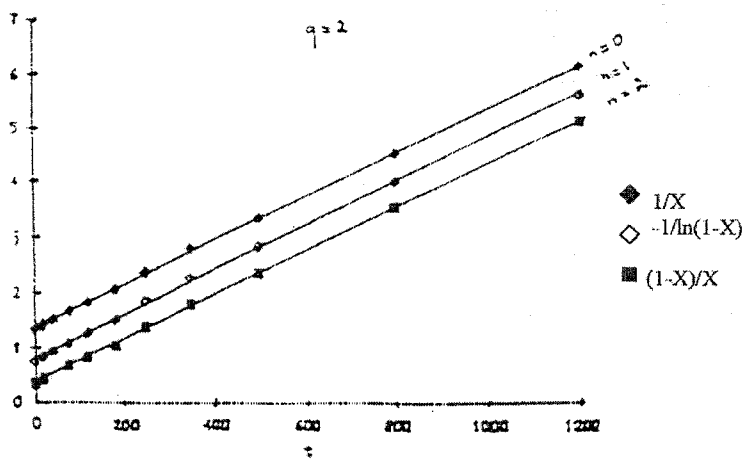
$$-\frac{da}{dt} = k_d a^q C_A^n = k_d a^q, \text{ with } C_A \text{ constant}$$

Assume q = 2 : $$a = \frac{1}{1 + k_d' t}$$

If $n = 0$: $\frac{1}{X} = \frac{1}{k\tau} + \frac{k_d'}{k\tau} t$

If $n = 1$: $\frac{1}{-\ln(1-X)} = \frac{1}{k\tau'} + \frac{k_d'}{k\tau'} t$

t	X(%)	$\frac{1}{X}$	$\frac{1}{-\ln(1-X)}$	$\frac{(1-X)}{X}$
0	75	1.33	0.721	0.333
20	70.7	1.414	0.815	0.415
40	67	1.493	0.902	0.493
80	60.5	1.653	1.076	0.653
120	55.2	1.811	1.245	0.817
180	48.7	2.053	1.498	1.053
250	42	2.381	1.836	1.381
350	36	2.778	2.241	1.777
500	30	3.333	2.804	2.333
800	22	4.545	4.025	3.545
1200	16.3	6.135	5.620	5.135



From the above graph, all lines are straight lines. Therefore, q = 2 is a good assumption.

We need to examine the data to see which value of n having $\frac{\Delta y}{\Delta t}$ = constant. n = 0 and n = 2 will have similar behavior of $\frac{\Delta y}{\Delta t}$ because:

$$\frac{1-X}{X} = \frac{1}{X} - 1$$

$n = 1$; $\Delta y = \Delta\left[\frac{1}{-\ln(1-X)}\right]$ and $\Delta t = 20$ min

$\frac{\Delta y}{\Delta t} = 0.094$; 0.087 ; 0.087 ; 0.084 ; .... ; 0.081 ; .... ; 0.0797

Therefore, $\frac{\Delta y}{\Delta t}$ is decreasing gradually. It is not a constant.

For n = 0, n=2 : $\frac{\Delta Y}{\Delta t} = 4 \times 10^{-3}$ = constant.

If n=0 : $-\frac{dC_A}{dt} = K_R \left(\frac{1}{1 + k_d' t} \right)$

$$\frac{dX}{dt} = \frac{K_R}{C_{A0}} \left(\frac{1}{1 + k_d' t} \right)$$

$$\frac{dt}{dX} = \frac{C_{A0}}{K_R} + \frac{C_{A0} k_d'}{K_R} t$$

If n=2 : $-\frac{dC_A}{dt} = K_R \left(\frac{1}{1 + k_d' t} \right) C_A^2$

$$\frac{1}{(1-X)^2} \frac{dX}{dt} = \frac{K_R C_{A0}}{1 + k_d' t}$$

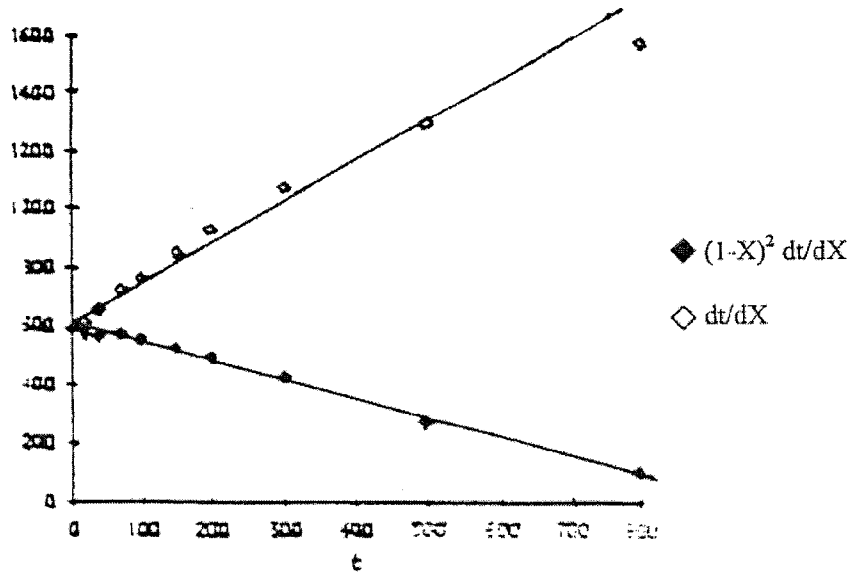
$$(1-X)^2 \frac{dt}{dX} = \frac{1}{K_R C_{A0}} + \frac{k_d'}{K_R C_{A0}} t$$

t	X%	$\frac{\Delta X}{\Delta t}$	$\frac{\Delta t}{\Delta X}$	$\frac{dt}{dX}$	$(1-X)^2 \frac{dt}{dX}$
0	0	1.7×10^{-3}	588	587	587
10	1.7	1.7×10^{-3}	588	600	579
20	3.4	1.6×10^{-3}	625	610	569
40	6.6	1.47×10^{-3}	680	650	567
70	11	1.33×10^{-3}	752	720	570
100	15	1.3×10^{-3}	769	760	549
150	21.5	1.14×10^{-3}	877	850	524
200	27.2	9.9×10^{-3}	1010	930	492
300	37.1	8.4×10^{-3}	1190	1075	425
500	53.9	6.9×10^{-3}	1449	1300	276
800	74.6	3.43×10^{-3}	2919	1580	102
1200	88.3				

n=2 : Slope is negative. It is unreasonable

n=0 : $\frac{dt}{dX}$ vs. t is a straight line.

The reaction is zero-order : $-r_A = k_A a$



$C_{A0} = 0.03 \frac{\text{kmol}}{\text{m}^3}$

$W = 0.01 \text{ kg/m}^3$

$$\tau = \frac{C_{A0}W}{F_{A0}} = \frac{\left(0.03 \frac{\text{kmol}}{\text{m}^3}\right)\left(0.01 \frac{\text{kg}}{\text{m}^3}\right)}{1.5 \times 10^{-5} \text{ kmol/min}} = 20 \frac{\text{kg}}{(\text{m}^3)^2} \text{ min}$$

(b) The order of decay is q=2

$$\frac{k_d'}{k_A} = 4 \times 10^{-3} \implies k_d' \; 3 \times 10^{-3} \text{ min}^{-1}$$

(c) Moving bed reactor: $F_{A0} = \frac{2 \text{ kmol}}{\text{min}}$; $X = 0.80$

$$-\frac{da}{dt} = k_d' a^2$$

$$F_{A0} \frac{dX}{dW} = -r_A = k_A a$$

In moving bed : $t = \frac{W}{u}$ where $u \equiv \frac{\text{mass}}{\text{time}}$

$$dt = \frac{1}{u} dW$$

Substitute into equation (1) : $-\frac{da}{dW} = \frac{k_d}{u} a^2$

$$-\frac{da}{a^2} = \frac{k_d}{u} dW$$

$$1 - \frac{1}{a} = \frac{k_d}{u} W$$

$$a = \frac{1}{1 + \frac{k_d W}{u}}$$

Substitute into equation (2), we have:

$$F_{A0} \int_0^X \frac{dX}{k_A a} = F_{A0} \int_0^X \frac{dX}{k_A \left(\frac{1}{1 + \frac{k_d W}{u}} \right)} = \int_0^W dW$$

$$\frac{F_{A0}}{k_A} \int_0^X dX = \int_0^W \frac{dW}{1 + \frac{k_d W}{u}}$$

$$\frac{F_{A0}}{k_A} X = \frac{u}{k_d} \ln \left(1 + \frac{k_d W}{u} \right)$$

$$W = \frac{u}{k_d} \left\{ \exp \left(X \frac{F_{A0} k_d}{u k_A} \right) - 1 \right\}$$

$$W = \frac{u}{3 \times 10^{-3}} \left\{ \exp \left(\frac{0.8 \times 2 \times 3 \times 10^{-3}}{0.0375 \times} \right) - 1 \right\}$$

If $u = 1 \frac{kg}{min}$ $W = 45.5$ kg

(d) If $u = 0.5 \frac{kg}{min}$ $W = 48.6$ kg

CDP10-Q

a) Mole balance:

$$\frac{dX}{dW} = \frac{-r_A' * a}{F_{A0}}$$

Rate law:

$$r_A' = -kC_A C_B$$

Decay law:

$$\frac{da}{dW} = -\frac{k_d}{U_S} C_B$$

Stoichiometry:

$$C_A = C_{A0}(1 - X)$$
$$C_B = C_{A0}(\theta_B + X)$$

Evaluate the parameters:

$$\theta_B = \frac{C_{B0}}{C_{A0}} = \frac{0.01}{0.1} = 0.1$$

Equations:

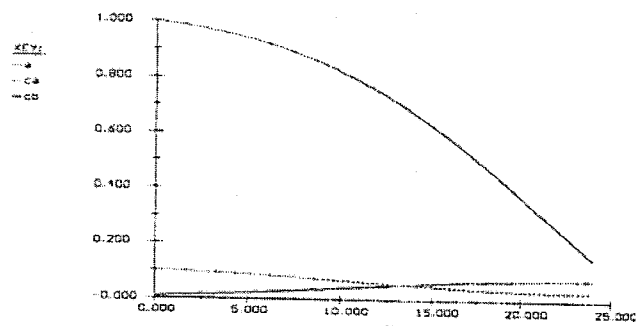
```
d(x)/d(w)=a*(-ra)/fao
d(a)/d(w)=-kd*cb/U
kd=6
fao=20
U=8
k=350
cao=.1
theta=.1
ca=cao*(1-x)
cb=cao*(theta+x)
ra=-k*ca*cb
```

$w_0 = 0, \quad w_f = 24$

Initial value

0

1



b) The only change is in the stoichiometry:

$$C_A = C_{A0}(1-X)(1-\alpha W)^{0.5}$$
$$C_B = C_{A0}(\theta_B + X)(1-\alpha W)^{0.5}$$

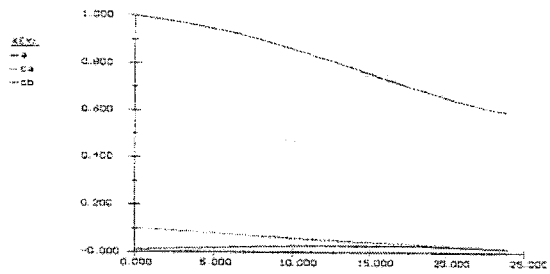
POLYMATH

Equations:

```
d(x)/d(w)=a*(-ra)/fao
d(a)/d(w)=-kd*cb/U
kd=6
fao=20
U=8
k=350
cao=.1
theta=.1
alp=.038
ca=cao*(1-x)*(1-alp*w)^.5
cb=cao*(theta+x)*(1-alp*w)^0.5
ra=-k*ca*cb
w0 = 0,    wf = 24
```

Initial value

```
0
1
```



CDP10-R

$$\underset{(A)}{\text{Cumene}} \rightarrow \underset{(k)}{\text{Propylene}} + \underset{(S)}{\text{Benzene}}$$

$$a \equiv \frac{r}{r_o}$$

(a) We find a relationship between a and C_A

$$r = \frac{F_{A0}X}{W} = \frac{F_R}{W} = F_R \qquad (W = lg)$$

Run 1: P_A = 1 atm

t	0	60	120	180
a	1	0.75	0.594	0.491
C_A	0	0.01	0.018	0.0243

Run 2: P_A = 0.4 atm

t	0	100	200	300	400
a	1	0.833	0.733	0.65	0.583
C_A	0	0.0057	0.0106	0.0148	0.0184

Plot of ln a vs. C_A gives a straight line passing through the origin with slope α

$$a = e^{-\alpha C_A} \quad , \quad \alpha = 28.9$$

$$\therefore \quad r_o = \frac{k_1^{\circ} K_A [P_A - P_R P_S/K_{eq}]}{1 + K_A P_A + K_R P_R} \qquad \text{(single site adsorbed, surface reaction controlling)}$$

I initial rate are used, $P_R = P_S = 0$ and $1 >> K_A P_A$ (adsorption is small at high temperature), then $r_O = k_1^{\circ} K_A P_A$.

Using data at time zero from runs 1 and 2 : $k_1^{\circ} K_A = 3.2 \times 10^{-3}$

Hence, overall apparent rate law is

$$r = k_1^{\circ} K_A e^{-\alpha C_A} P_A \quad ; \quad k_1^{\circ} K_A = 3.2 \times 10^{-3}$$

$$\alpha = 28.9$$

(b) $r = a\, r_o$

$$\frac{da}{dt} = - k_d a^m f(P_A, P_R, P_S) \equiv -k_d a^m P_A^n$$

Try $m = -2$

Since P_A is almost constant, during runs 1 and 2 (low conversion)

$$\frac{1}{a} = 1 + k_d P_A^n t$$

Run 1 : $k_d P_A^n = 5.767 \times 10^{-3}$

Run 2 : $k_d P_A^n = 1.769 \times 10^{-3}$

$P_A = 1$ in run 1 $\Rightarrow$ $k_d = 5.767 \times 10^{-3}$

$P_A = 0.4$ in run 2 $\Rightarrow$ $n = 1.29$

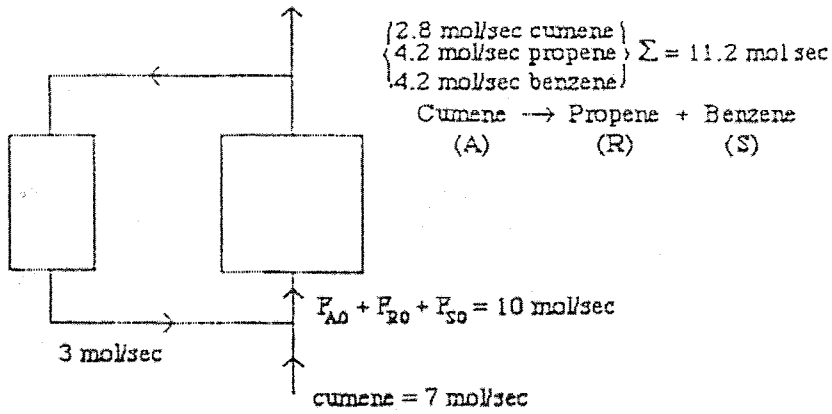
$$r = a r_o = \frac{k_1^{\circ} K_A P_A}{1 + k_d P_A^n t} \quad ; \quad k_1^{\circ} K_A = 3.2 \times 10^{-3}$$

$$k_d = 5.767 \times 10^{-3}$$

$$n = 1.29$$

t in minutes

(c) Overall conversion = 0.60



Composition at reactor outlet

$$y_A = \frac{2.8}{11.2} = 0.25$$

$$y_R = y_S = \frac{4.2}{11.2} = 0.375$$

Composition at reactor inlet, $F_o = 7 + 3 = 10$ mol/sec

$F_{A0} = 7 + 3(0.25) = 7.75$ $\qquad y_A = 0.775$

$F_{R0} = 3(0.375) = 1.125$ $\qquad \Rightarrow \qquad y_R = 0.1125$

$F_{S0} = 3(0.375) = 1.125$ $\qquad y_S = 0.1125$

Let $X_f \equiv$ conversion per pass

Total flow at reactor outlet before the recycle stream is:

$$F_{A0}(1-X_f) + 2F_{A0}X_f + F_{R0} + F_{S0} = F_{A0}(1+X_f) + F_{R0} + F_{S0}$$

$$\therefore y_A = \frac{F_{A0}(1-X_f)}{F_{A0}(1+X_f) + F_{R0} + F_{S0}} = 0.25 \implies X_f = 0.542$$

At any point along the reactor:

$$P_A = y_A P_t = y_A \frac{F_{A0}(1-X)}{F_{A0}(1+X) + F_{R0} + F_{S0}} = \frac{1-X}{\beta+X}$$

when $\beta = \frac{F_{R0} + F_{S0} + F_{A0}}{F_{A0}} = \frac{10}{7.75} = 1.29$

Assume that rate law in (b) is still good for the moving bed operation (may not be true in practice because of the high conversion)

$$\therefore r = a\,k_1^{\circ} K_A P_A = \frac{k_1^{\circ} K_A P_A}{1 + k_d P_A^n t}$$

Moving bed reactor: $t = \frac{W}{U_S}$

$$F_{A0}\,dX = -r_d\,W$$

$$\frac{dW}{dX} = \frac{F_{A0}}{-r} = F_{A0}\left[\frac{1 + k_d P_A^n \frac{W}{U_S}}{k_1^{\circ} K_A P_A}\right] = \frac{F_{A0} k_d}{k_1^{\circ} K_A U_S}\left(\frac{\beta+X}{1-X}\right)^{n-1} W + \frac{F_{A0}}{k_1^{\circ} K_A}\left(\frac{\beta+X}{1-X}\right)$$

$$= \frac{7.75\times5.767\times10^{-3}}{3.2\times10^{-3}\times2000}\left(\frac{1.29+X}{1-X}\right)^{0.29} W + \frac{7.75}{3.2\times10^{-3}}\left(\frac{1.29+X}{1-X}\right)$$

$$= 6.98 \times 10^{-3}\left(\frac{1.29+X}{1-X}\right)^{0.29} W + 2421\left(\frac{1.29+X}{1-X}\right)$$

With $X = 0$, $W = 0$

If $X = 0.542$, using digital computer $W \cong 3.1$ kg

CDP10-S

a) Mole balance:

$$\frac{dX}{dW} = \frac{a^* - r_A'}{F_{A0}}$$

rate law:

$$-r_A' = k' C_A$$

Stoichiometry:

$$C_A = C_{A0}(1 - X)(1 - \alpha W)^{0.5}$$

Decay law:

$$-\frac{da}{dW} = \frac{k_d}{U_S} a$$

Evaluate the parameters:

$$\frac{P}{P_0} = (1 - \alpha W)^{0.5}$$

$$\frac{5}{50} = (1 - 100\alpha)^{0.5}$$

$$\alpha = 0.0099$$

$$-\int_1^{0.1} \frac{da}{a} = \frac{k_d}{U_S}\int_0^{100} dW$$

$$\frac{k_d}{U_S} = 0.023$$

POLYMATH

Equations:

d(x)/d(w)=-ra*a/fao

d(a)/d(w)=-kd*a

kd=.023

fao=4

k=.09

cao=2

alp=.0099

ca=cao*(1-x)*(1-alp*w)^.5

ra=-k*ca

$w_0 = 0, \quad w_f = 100$

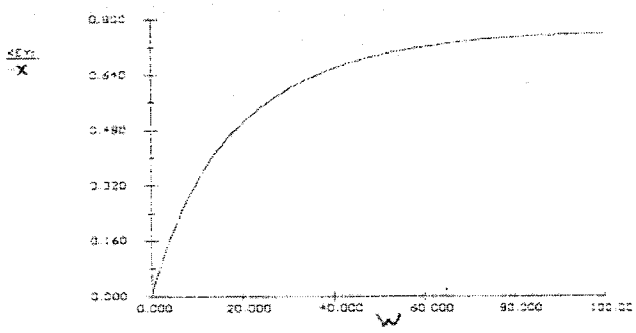
Initial value

0

1

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	100	0	100
x	0	0.757161	0	0.757161
a	1	1	0.100259	0.100259
kd	0.023	0.023	0.023	0.023
fao	4	4	4	4
k	0.09	0.09	0.09	0.09
cao	2	2	2	2
alp	0.0099	0.0099	0.0099	0.0099
ca	2	2	0.0485678	0.0485678
ra	-0.18	-0.0043711	-0.18	-0.0043711

b) POLYMATH



CDP10-T

Design Equation : $F_{Ao}\dfrac{dX}{dW} = a(W)(-r'_A)$

Rate Law : $-r'_A = k'C_A$

Decay Law : (for sintering) $a(W) = \dfrac{1}{1+k_d\left(\frac{W}{U_S}\right)}$

Stoichiometry : $T = T_o \Rightarrow C_A = C_{Ao}(1-X)$

Combine : $\dfrac{dX}{dW} = \dfrac{1}{1+\frac{k_d}{U_S}W}\dfrac{k'}{\upsilon_o}(1-X) \Rightarrow \dfrac{dX}{1-X} = \dfrac{k'}{\upsilon_o}\dfrac{dW}{1+\frac{k_d}{U_S}W}$

$$\ln\left(\frac{1}{1-X}\right) = \frac{k'}{\upsilon_o}\frac{U_S}{k_d}\ln\left(1+\frac{k_d}{U_S}W\right)$$

From the problem statement, $a_{exit} = \dfrac{1}{1+\frac{k_d}{U_S}W} = \dfrac{1}{4}$

Plugging in 100 kg for W, we can solve for $\dfrac{k_d}{U_S}$.

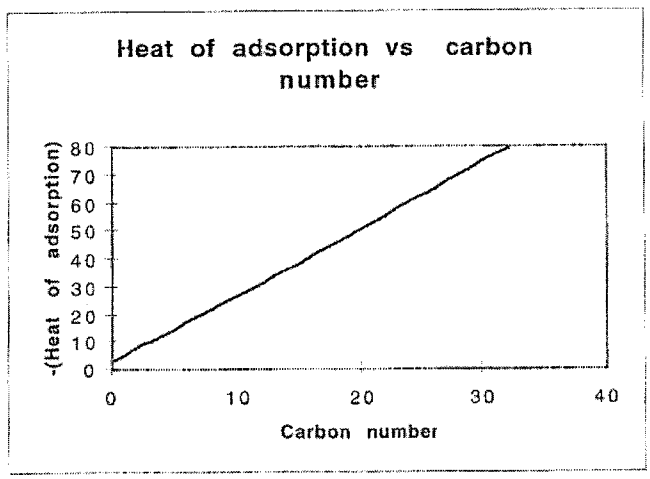
$$\frac{k_d}{U_S} = 0.03$$

$$\ln\left(\frac{1}{1-X}\right) = \frac{(0.10)}{(3.75)(0.03)}\ln(1+(0.03)(100)) = 1.232 \Rightarrow \frac{1}{1-X} = 3.43$$

$$X = 0.708$$

CDP10-U

The heat of activation is given in the problem as a function of the carbon number so we can just graph that:



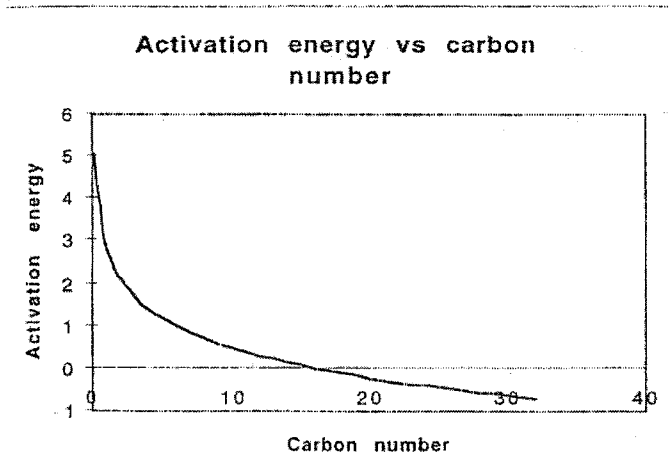
To graph the activation energy we need to find its equation. It is the Arrhenius equation.

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

Solving for E we get:

$$E = -RT\ln\left(\frac{k}{A}\right)$$

We know that as the temperature increases when $n \leq 15$, the rate increases so k still gets larger with greater temperature so E is still positive. When the temperature increases when $n > 15$, the rate decreases so k decreases making E negative. So we can come up with some equation with the above equation that fits this criteria and we can come up with the following graph.



The reason for this unusual temperature dependence is due to the fact that the higher the carbon number the less it wants to add another carbon.

CDP10-V

(a) a = 0 at the end of the reactor:

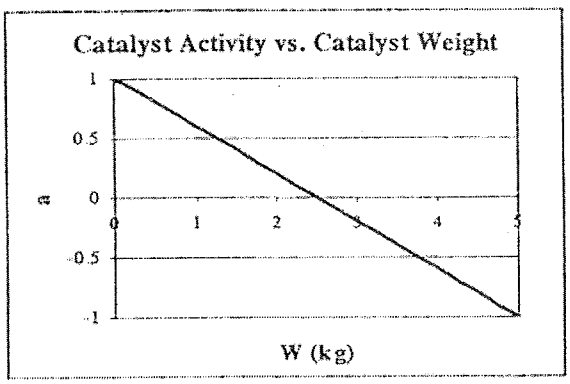
$$-\frac{da}{dW}=\frac{k_D}{U_S}$$

$$\int_1^a -da=\frac{k_D}{U_S}\int_0^W dW \quad\Rightarrow\quad 1-a=\frac{k_D}{U_S}W$$

$$1-0=\left(\frac{0.2\,s^{-1}}{U_S}\right)(5\,kg) \quad\Rightarrow\quad U_S=1\,kg/s$$

(b) For $U_S = 0.5$ kg/s:

$$a=1-\frac{k_D}{U_S}W=1-\left(\frac{0.2\,s^{-1}}{0.5\,kg/s}\right)W=1-(0.4\,kg^{-1})W$$



When a = 0, the catalyst is inactive. In theory a can be negative, but in reality, once the catalyst is inactive there can be no further decrease in activity.

(c) For a catalyst feed rate of $U_S = 0.5$ kg/s:

Mole Balance: $$F_{Ao}\frac{dX}{dW}=a(-r_A')$$

Rate Law: $$-r_A'=kC_AC_B$$

Decay Law: $$-\frac{da}{dW}=\frac{k_D}{U_S}=\frac{0.2\,s^{-1}}{0.5\,kg/s}=0.4\,kg^{-1} \quad\Rightarrow\quad a=1-0.4W$$

Stoichiometry: (Assume $T \approx T_o$, $P \approx P_o$, and $\upsilon \approx \upsilon_o$)

$$C_A=C_B=C_{Ao}(1-X)$$

Combine:

$$F_{Ao}\frac{dX}{dW}=(1-0.4W)\left[kC_{Ao}^2(1-X)^2\right]$$

$$\left(\frac{F_{Ao}}{kC_{Ao}^2}\right)\frac{dX}{(1-X)^2}=\left(1-\frac{k_D}{U_S}W\right)dW \quad\Rightarrow\quad \left(\frac{F_{Ao}}{kC_{Ao}^2}\right)\frac{X}{(1-X)}=\left(W-\frac{k_D}{2U_S}W^2\right)$$

$$\frac{X}{(1-X)}=\frac{kC_{Ao}^2}{F_{Ao}}\left(W-\frac{k_D}{2U_S}W^2\right)$$

From part (b) we know that the maximum catalyst weight (the point where a = 0) is 2.5 kg

We will find the conversion at this point :

$$\frac{X}{(1-X)}=\frac{(1)(0.2)^2}{0.2}\left(2.5-\frac{(0.2)}{2(0.5)}2.5^2\right)=0.25$$

$$X=0.2$$

(d) To achieve 40% conversion:

$$\frac{X}{(1-X)}=\frac{kC_{Ao}^2}{F_{Ao}}\left(W-\frac{k_D}{2U_S}W^2\right)$$

$$\frac{0.40}{(1-0.40)}=0.2\left(5-\frac{0.2}{2U_S}5^2\right) \quad \Rightarrow \quad 0.667=1-\frac{2.5}{U_S}$$

$$U_S=7.5\,\text{kg/s}$$

(e)

For $U_S=\infty$: $\frac{X}{(1-X)}=\frac{kC_{Ao}^2}{F_{Ao}}\left(W-\frac{k_D}{2(\infty)}W^2\right) \Rightarrow \frac{X}{(1-X)}=\frac{kC_{Ao}^2}{F_{Ao}}(W)$

$$\frac{X}{(1-X)}=(0.2)W=(0.2)(5)=1 \quad \Rightarrow \quad X=0.50$$

CDP10-W

Design Equation : $N_{Bo}\frac{dX}{dt}=-r'_A aW$

Rate Law : $-r'_B=k'C_B^2$

Decay Law : $-\frac{da}{dt}=k_D=0.05$

$$\int_1^a da=-0.05\int_0^t dt \quad \Rightarrow \quad a=1-0.05t$$

From this we can see that the maximum reaction time is 20 min. We will find the conversion at this point

Stoichiometry : (Assume constant volume)

$$C_B=C_{Bo}(1-X)=\frac{N_{Bo}}{V}(1-X)$$

Combine :

$$\frac{dX}{dt}=\frac{k'(1-0.05t)N_{Bo}^2(1-X)^2W}{V^2N_{Bo}}=\frac{k'WN_{Bo}}{V^2}(1-0.05t)(1-X)^2$$

$$\frac{dX}{(1-X)^2}=\frac{k'WN_{Bo}}{V^2}(1-0.05t)dt \quad \Rightarrow \quad \frac{X}{1-X}=\frac{k'WN_{Bo}}{V^2}(t-0.025t^2)$$

$$\frac{X}{1-X}=\frac{(0.01)(10)(1)}{(1)}(20-0.025(20)^2)=1$$

$$X=0.50$$

CDP10-X

a) Mole balances:

$$\frac{dF_A}{dW} = r_A \qquad \frac{dF_B}{dW} = r_B \qquad \frac{dF_C}{dW} = r_C$$

rate laws:

$$-r_A' = ak_1C_A \qquad -r_B' = a(k_2C_B - k_1C_A) \qquad r_C' = ak_2C_B$$

stoichiometry:

$$C_A = \frac{F_A}{v} = \frac{F_A(1-\alpha W)^{0.5}}{v_0}$$

$$C_B = \frac{F_B}{v} = \frac{F_B(1-\alpha W)^{0.5}}{v_0}$$

decay law:

$$\frac{da}{dw} = \frac{k_D a}{U_S}$$

Evaluate the parameters:

$$k_1 = 0.02 * \exp\left[\frac{10000}{1.987}\left(\frac{1}{400} - \frac{1}{T}\right)\right]$$

$$k_2 = 0.01 * \exp\left[\frac{20000}{1.987}\left(\frac{1}{400} - \frac{1}{T}\right)\right]$$

$$k_D = 0.08 * \exp\left[\frac{15000}{1.987}\left(\frac{1}{400} - \frac{1}{T}\right)\right]$$

Plugging all of this into POLYMATH we can change values of U_S, T, and v_o (P_{A0}) that will give us the most of product B.

We find that at a temperature of 396K, a solids velocity of 10kg/s and a gas volumetric velocity of 0.633 dm^3/s that corresponds to a partial pressure of 51.3 atm we can the maximum yield for B.

Equations:

```
d(fa)/d(w)=ra
d(fb)/d(w)=rb
d(fc)/d(w)=rc
d(a)/d(w)=kd*a/Us
Us=10
T=396
alp=9.8e-3
vo=.633
kd=.08*exp(15000/1.987*(1/400-1/T))
k2=.01*exp(20000/1.987*(1/400-1/T))
k1=.02*exp(10000/1.987*(1/400-1/T))
ca=fa*(1-alp*w)^.5/vo
cb=fb*(1-alp*w)^.5/vo
ra=-a*k1*ca
rc=a*k2*cb
rb=-a*(k2*cb-k1*ca)
```

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	100	0	100
fa	1	1	0.0813942	0.0813942
fb	0	0.524458	0	0.446634
fc	0	0.471971	0	0.471971
a	1	1.93702	1	1.93702
Us	10	10	10	10
T	396	396	396	396
alp	0.0098	0.0098	0.0098	0.0098
vo	0.633	0.633	0.633	0.633
kd	0.0661149	0.0661149	0.0661149	0.0661149
k2	0.00775554	0.00775554	0.00775554	0.00775554
k1	0.0176131	0.0176131	0.0176131	0.0176131
ca	1.57978	1.57978	0.0181846	0.0181846
cb	0	0.63042	0	0.0997846
ra	-0.0278248	-0.000620403	-0.0278248	-0.000620403
rc	0	0.00641366	0	0.00149902
rb	0.0278248	0.0278248	-0.00217423	-0.000878621

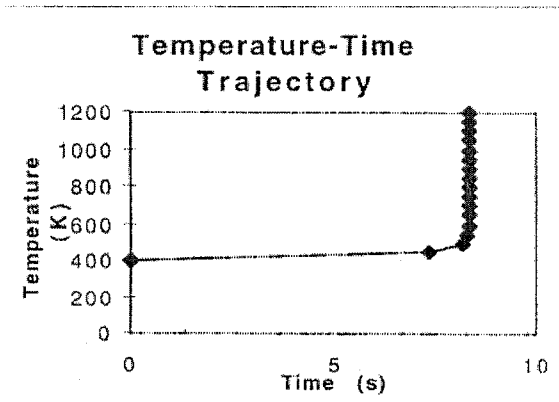
b) Using the same program we can find what it takes to get the most of C possible. We find that at T = 396K, U_s = 10, and v_0 = .03 we can get 1mol C/s. P_{A0} = 1082.4 atm.

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	100	0	100
fa	1	1	1.02629e-23	1.02629e-23
fb	0	0.524487	0	1.35042e-10
fc	0	1	0	1
a	1	1.93702	1	1.93702
Us	10	10	10	10
T	396	396	396	396
alp	0.0098	0.0098	0.0098	0.0098
vo	0.03	0.03	0.03	0.03
kd	0.0661149	0.0661149	0.0661149	0.0661149
k2	0.00775554	0.00775554	0.00775554	0.00775554
k1	0.0176131	0.0176131	0.0176131	0.0176131
ca	33.3333	33.3333	4.83798e-23	4.83798e-23
cb	0	17.2696	0	6.36595e-10
ra	-0.587104	-1.65057e-24	-0.587104	-1.65057e-24
rc	0	0.13615	0	9.56332e-12
rb	0.587104	0.587104	-0.0715782	-9.56332e-12

c) To get the Time-Temperature trajectory we can use the following equation to create it:

$$t = \frac{1 - \exp\left[\frac{E_d}{R}\left(\frac{1}{T} - \frac{1}{400}\right)\right]}{k_{d0}\left(E_d / E_A\right)}$$

This will give us the following graph:



d) For this we just add an energy balance. We have to assume a heat capacity of the catalyst since none is given. Here it is assumed to be 100 J/kgcat

$$\frac{dT}{dW} = \frac{\left(r_A'\right)\left(\Delta H_{Rx}\right) + \left(r_B'\right)\left(\Delta H_{Rx}\right)}{C_{ps}U_S + C_p\left(F_A + F_B + F_C\right)}$$

Plugging this into the POLYMATH gives the following program.

We find that the temperature is 388K, U_s = 10 kg/s and v_o = 0.51 dm^3/s. P_{A0} = 62.4 atm.

Equations:	Initial value
d(fa)/d(w)=ra	1
d(fb)/d(w)=rb	0
d(fc)/d(w)=rc	0
d(a)/d(w)=kd*a/Us	1
d(T)/d(w)=(ra*(-16000)+rb*(-32000))/(cp*(Us+fa+fb+fc))	388

kd=.08*exp(15000/1.987*(1/400-1/T))

Us=10

cp=100

k2=.01*exp(20000/1.987*(1/400-1/T))

k1=.02*exp(10000/1.987*(1/400-1/T))

alp=9.8e-3

vo=.51

ca=fa*(1-alp*w)^.5/vo

cb=fb*(1-alp*w)^.5/vo

ra=-a*k1*ca

rc=a*k2*cb

rb=-a*(k2*cb-k1*ca)

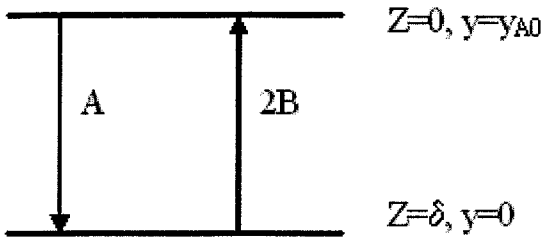
$w_0 = 0, \quad w_f = 100$

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	100	0	100
fa	1	1	0.173516	0.173516
fb	0	0.611156	0	0.611156
fc	0	0.215328	0	0.215328
a	1	1.40401	1	1.40401
T	388	388	381.464	382.242
kd	0.0446269	0.0446269	0.0319753	0.0332906
Us	10	10	10	10
cp	100	100	100	100
k2	0.00459207	0.00459207	0.00294419	0.00310677
k1	0.013553	0.013553	0.0108521	0.0111477
alp	0.0098	0.0098	0.0098	0.0098
vo	0.51	0.51	0.51	0.51
ca	1.96078	1.96078	0.0481154	0.0481154
cb	0	0.783935	0	0.169472
ra	-0.0265744	-0.000753076	-0.0265744	-0.000753076
rc	0	0.00273258	0	0.000739224
rb	0.0265744	0.0265744	1.38516e-05	1.38516e-05

Solutions for Chapter 11 - External Diffusion Effects on Heterogeneous Reactions

P11-1 Individualized solution

P11-2 (a)



$$W_A = cD_{AB}\frac{dy_A}{dz} + y_A(W_A + W_B)$$

$$W_B = -2W_A$$

$$W_A = \frac{cD_{AB}}{(1+y_A)}\frac{dy_A}{dz} = -cD_{AB}d\ln\frac{(1+y_A)}{dz}$$

Integrating with $y_A = 0$ at $z = \delta$

$$W_A = \frac{cD_{AB}}{(\delta - z)}\ln(1+y_A) \qquad (1)$$

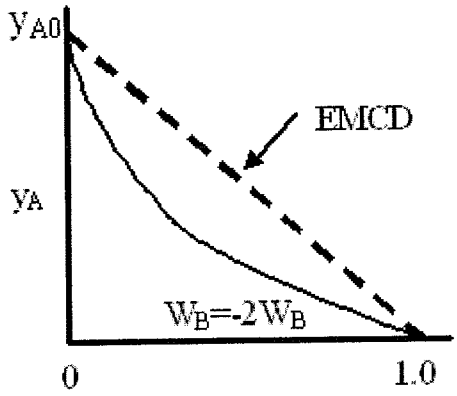
at $z = 0 \quad y_A = y_{A0}$

$$W_A = \frac{cD_{AB}}{\delta}(1+y_{A0}) \qquad (2)$$

Taking the ratio of Equation (1) to Equation (2) to eliminate W_A and solving for y_A

$$\frac{\ln(1+y_A)}{\delta - z} = \frac{\ln(1+y_{A0})}{\delta}$$

$$y_A = 1-(1+y_{A0})^{1-z/\delta}$$



P11-2 (b)

(g) $T_1 = 300K \quad T_2 = 350K$

$$\frac{k_{c2}}{k_{c1}} = \left(\frac{D_{AB2}}{D_{AB1}}\right)^{2/3}\left(\frac{\upsilon_1}{\upsilon_2}\right)^{1/6}\left(\frac{U_2}{U_1}\right)^{1/2}\left(\frac{d_{P1}}{d_{P2}}\right)^{1/2} \qquad (11\text{-}70)$$

As a first approximation assume

$$\frac{D_{AB2}}{D_{AB1}} = \frac{\mu_1}{\mu_2}$$

then

$$\frac{k_{c2}}{k_{c1}} = \left(\frac{\upsilon_1}{\upsilon_2}\right)^{5/6}\left(\frac{d_{P1}}{d_{P2}}\right)^{1/2}\left(\frac{U_2}{U_1}\right)^{1/2}$$

At $T_1 = 300K$ $\mu_1 \approx 0.883cP$

At $T_2 = 350K$ $\mu_2 \approx 0.380cP$

Assume density doesn't change that much, $\upsilon = \frac{\mu}{\rho}$

$$\frac{\upsilon_1}{\upsilon_2} = \frac{\mu_1}{\mu_2} = 2.32$$

$$\frac{U_2}{U_1} = \frac{1}{2}, \frac{d_{P1}}{d_{P2}} = \frac{1}{2}$$

$$k_1 = 4.61\times10^{-6}\ m/s$$

$$k_2 = 4.61\times10^{-6}\ m/s\,[2.32\,]^{5/6}\left[\frac{1}{2}\right]^{1/2}\left[\frac{1}{2}\right]^{1/2}$$

$$= 4.65\times10^{-6}\ m/s$$

$$W_A = -r_A'' = k_{c2}C_{Ab} = \left(4.61\times10^{-6}\ m/s\right)\left(10^3\ mol/m^3\right)$$

$$-r_A'' = 0.00465\ mol/m^2/s$$

P11-2 (c)

(h) A 50-50 mixture of hydrazine and helium would only affect the kinematic viscosity to a small extent. Consequently the complete conversion would be achieved. Increase diameter by a factor of 5

$$k_{c2} = k_{c1}\left(\frac{d_{P1}}{d_{P2}}\right)^{1/2} = 2.9\,\text{m/s}\left(\frac{1}{5}\right)^{1/2}$$

$$= 1.3\,\text{m/s}$$

$$X = 1 - \exp\left[-1.3 \bullet \frac{1063}{15} 0.05\right]$$

$$= 1 - \exp(-4.6)$$

$$X = 1 - 0.01 = 0.99$$

again virtually complete conversion.

P11-2 (d)

Liquid phase : e.g. water $\quad Re = \frac{\rho.u.d}{\mu} = \frac{1000 \times 0.1 \times 0.05}{10e-3} = 5000$

See margin notes on page 786 and 787 for solution.

P11-2 (e)

$$\frac{\upsilon_2}{\upsilon_1} = e^{-4{,}000\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} e^{-4{,}000\left(\frac{1}{773} - \frac{1}{873}\right)}$$

$$= e^{-0.59} = 0.55$$

Assume

$$\frac{D_{A2}}{D_{A1}} \sim \left(\frac{\mu_1}{\mu_2}\right) = \frac{1}{0.55}$$

$$\frac{k_{c2}}{k_{c1}} = \left(\frac{D_{A2}}{D_{A1}}\right)^{2/3}\left(\frac{\upsilon_1}{\upsilon_2}\right)^{1/6} = \left(\frac{\mu_1}{\mu_2}\right)^{4/6}\left(\frac{\mu_1}{\mu_2}\right)^{1/6} = \left(\frac{\mu_1}{\mu_2}\right)^{5/6}$$

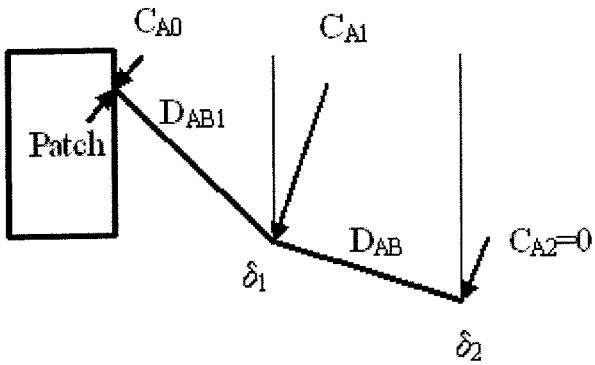
$$\frac{k_{c2}}{k_{c1}} = (0.55)^{5/6} = 0.91$$

$$\frac{U_1 k_{c2}}{U_2 k_1} = (1.059)(0.91) = 0.96$$

$$\ln\frac{1}{1 - X_2} = (0.96)(2) = 1.92$$

$$X_2 = 1 - e^{-1.92} = 0.85$$

P11-2 (f)



Assume concentration in blood is negligible $(C_{A2}=0 \text{ at } \delta_2)$. Assume quasi steady state

$$\frac{d\left(V_P C_{A_P}\right)}{dt} = -W_A A_P$$

$$W_A = \frac{D_{AB1}}{\delta_1}\left[C_A - C_{A1}\right]$$

$$W_A = \frac{D_{AB2}}{\delta_2}\left[C_{A1} - 0\right]$$

adding

$$W_A\left[\frac{\delta_2}{D_{AB2}} + \frac{\delta_1}{D_{AB1}}\right] = C_A$$

$$W_A = \frac{C_A}{\frac{\delta_2}{D_{AB2}} + \frac{\delta_1}{D_{AB1}}}$$

$$C_A = HC_{AP}$$

$$V_P \frac{dC_{AP}}{dt} = \frac{A_P H C_{AP}}{\frac{\delta_1}{D_{AB1}} + \frac{\delta_2}{D_{AB2}}}$$

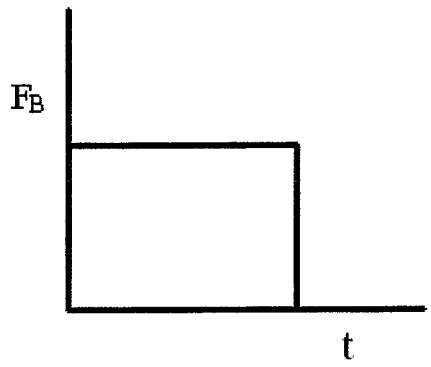
$$R = \left(\frac{\delta_1}{D_{AB1}} + \frac{\delta_2}{D_{AB2}}\right) \Big/ A_P H$$

Flow into the blood

$$F_{AB} = \frac{C_{PA}}{RV} \text{ mol/time}\ ,\ R \equiv [\text{time}]$$

If $C_{PA} = \text{constant} = C_{PA0}$

$$F_{AB} = \frac{C_{PA0}}{R}$$



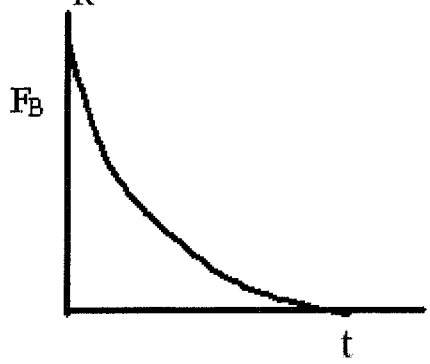
If C_{AD} varies

$$\frac{dC_{AP}}{dt} = \frac{-1}{V}\frac{C_{PA}}{R}$$

$$\ln\frac{C_{PA0}}{C_A} = -\frac{t}{VR}$$

$$C_A = C_{A0}\, e^{-t/VR}$$

$F_B = \frac{C_A}{R}$ δ_1 and δ_2 are given in the side note.



P11-3

Mol balance on oxygen : $Fo_2 - 0 + ro_2 = 0$ constant liquid composition.

$Fo_2 = Co_2 . \upsilon_o$ and $ro_2 = -k.Co_2^n$ where n is the reaction order.

Assuming ideal gas law applies : $Fo_2 = \frac{P.\upsilon_o}{R.T}$ where υ_o = oxygen uptake rate mL/hr

Assuming that $\frac{P}{R.T} = constant$, C by correction of υ_o to some reference,

then $Fo_2 = C.\ \upsilon_o$

Assuming Henry's law applies (low pressures) $Co_2 = H.Po_2$

where H is Henry's constant and Po_2 is the oxygen partial pressure

Substituting into the mol balance : $Fo_2 = - ro_2$

$$C.\ \upsilon_o = k.Co_2^{\ n} = k.(H.Po_2)^n$$

$$\upsilon_o = Po_2^{\ n}.\frac{k.H^n}{C}$$

$$\ln \upsilon_o = n.\ln Po_2 + \ln \frac{k.H^n}{C}$$

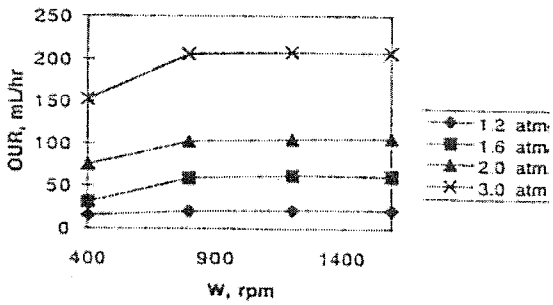
A plot of $\ln \upsilon_o$ vs $\ln Po_2$ will give n as the gradient.

As the system pressure, P, given in the data is absolute : $P = P_x + Po_2$

if in the reactor, the xylene is at boiling point and dissolved oxygen and oxidized xylene are at low levels, then P_x = 1 atm (open to the atmosphere)

In order to deduce the correct kinetics of the oxidation it is necessary to find the partial oxygen pressures for the conditions where the rate is limited only by the reaction kinetics and not by diffusional mass transfer.

Plot of stirrer speed, W, vs oxygen uptake rate, υ_o, for each run will show the conditions at which diffusion is negligible.



It can be seen that at stirrer speeds above 1200 rpm that OUR is insensitive to W and hence the reactor is well mixed i.e. no liquid diffusional limitations.

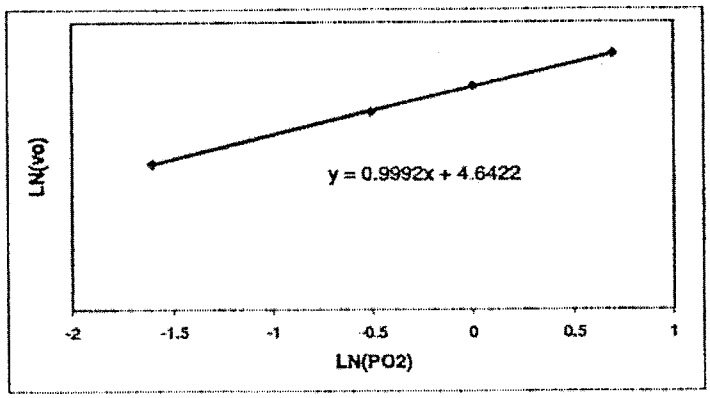
OUR: Oxygen Uptake Rate

Hence using the system pressure data at 1600 rpm for the plot of $\ln \upsilon_o$ vs $\ln Po_2$ will give n uninfluenced by diffusion.

$Po_2 = P - P_x = P - 1$

At 1600 rpm

υ_o ml/hr	$\ln \upsilon_o$	Po_2 atm	$\ln Po_2$
21	3.04	0.2	-1.61
61	4.11	0.6	-0.51
106	4.66	1.0	0.00
207	5.33	2.0	0.69

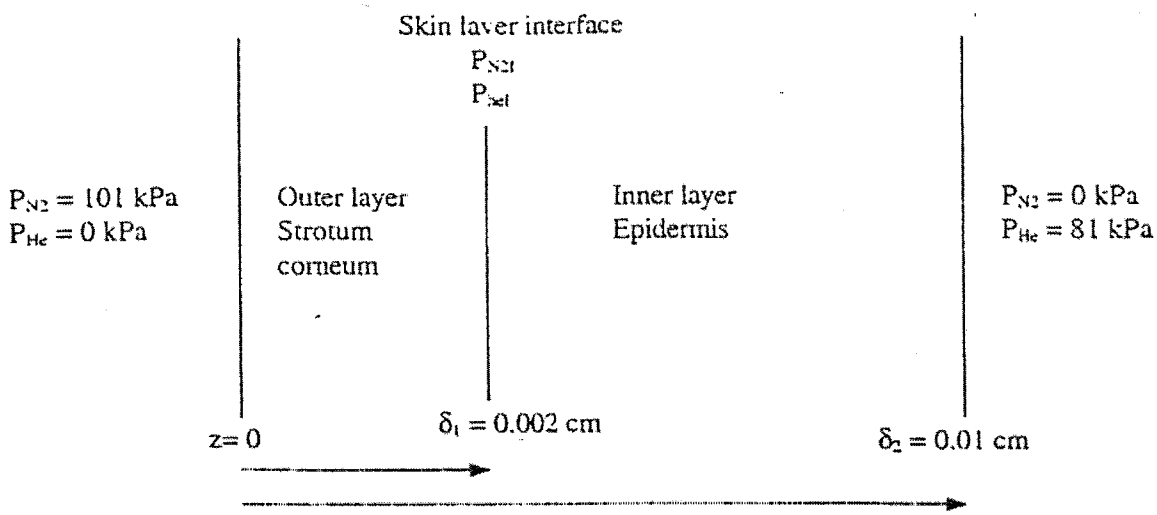


The gradient, n = .999 = 1, so the rate law is:

$$-r_{O2} = k.C_{O2}^{1}$$

P11-4

Diffusion in adjacent skin layers



Assuming dilute solution and constant total concentration in both layers gives:

$$\frac{d^2C_A}{dz^2} = 0 \qquad \frac{d\,C_A}{dz} = K_1 \qquad C_A = K_1.z + K_2$$

for each diffusing component in each layer.

N_2 : Outer layer : boundary conditions $z = 0$, $C_A = C_{AO}$
$z = \delta_1$, $C_A = C_{Ai}$

$$K_1 = \frac{C_{Ai} - C_{AO}}{\delta_1} \qquad K_2 = C_{AO}$$

Profile $C_A = C_{AO} - (C_{AO} - C_{AI}).\frac{z}{\delta_1}$

Inner layer : boundary conditions $z = \delta_1$, $C_A = C_{AI}$
$z = \delta_2$, $C_A = 0$

$$K_1 = -\frac{C_{AI}}{\delta_2 - \delta_1} \qquad K_2 = \frac{C_{AI}.\delta_2}{\delta_2 - \delta_1}$$

Profile $C_A = C_{AI}.\left(\frac{\delta_2 - z}{\delta_2 - \delta_1}\right)$

Total partial pressure profiles

Outer skin layer : $P_A + P_B = P_{AO} - (P_{AO} - P_{AI}).\frac{z}{\delta_1} + P_{BI}\frac{z}{\delta_1}$

$$= 1010 - (1010 - 1008)\frac{z}{0.002} + 10\frac{z}{0.002}$$

$$= 1010 - 1000.z + 5000.z$$

$$= 1010 + 4000.z$$

Inner skin layer :

$$P_A + P_B = P_{AI}.\left(\frac{\delta_2 - z}{\delta_2 - \delta_1}\right) + P_{BO} - (P_{BO} - P_{BI})\left(\frac{\delta_2 - z}{\delta_2 - \delta_1}\right)$$

$$= 1008.\left(\frac{0.01 - z}{0.01 - 0.002}\right) + 810 - (810 - 10)\left(\frac{0.01 - z}{0.01 - 0.002}\right)$$

$$= 810 + 126000(0.01 - z) - 100000(0.01 - z)$$

$$= 810 + 26000(0.01 - z)$$

Check : At interface (z = 0.002 cm) : $outerlayer = innerlayer$

$$P_A + P_B = P_A + P_B$$

$$1010 + 4000.z = 810 + 26000(0.01 - z)$$

$$1018 = 1018 \qquad \text{correct!}$$

Plot these two profiles across the skin from z = 0 to z = 0.01 cm

He : Inner layer : boundary conditons $z = \delta_1$, $C_B = C_{BI}$
$z = \delta_2$, $C_B = C_{BO}$

$$K_1 = \frac{C_{BO} - C_{BI}}{\delta_2 - \delta_1} \qquad K_2 = C_{BO} - \left(\frac{C_{BO} - C_{BI}}{\delta_2 - \delta_1}\right).\delta_2$$

Profile $$C_B = C_{BO} - (C_{BO} - C_{BI})\left(\frac{\delta_2 - z}{\delta_2 - \delta_1}\right)$$

Outer layer : boundary conditons $z = \delta_1$, $C_B = C_{BI}$
$z = 0$, $C_B = 0$

$K_2 = 0$ $$K_1 = \frac{C_{BI}}{\delta_1}$$

Profile $$C_B = C_{BI}\left(\frac{z}{\delta_1}\right)$$

Total concentration profiles :

Outer skin layer : $$C_A + C_B = C_{AO} - (C_{AO} - C_{AI}).\frac{z}{\delta_1} + C_{BI}\frac{z}{\delta_1}$$

Inner skin layer : $$C_A + C_B = C_{AI}\left(\frac{\delta_2 - z}{\delta_2 - \delta_1}\right) + C_{BO} - (C_{BO} - C_{BI})\left(\frac{\delta_2 - z}{\delta_2 - \delta_1}\right)$$

Evaluation of C_{AI} and C_{BI} :

N_2 : Outer layer : $$W_{A1} = \frac{D_{1N2}}{\delta_1}[C_{AO} - C_{AI}]$$

Inner layer : $$W_{A2} = \frac{D_{2N2}}{\delta_2 - \delta_1}[C_{AI} - 0]$$

Assume that flux in inner layer = flux in outer layer i.e. $W_{A1} = W_{A2}$

$$\frac{W_A}{\frac{D_{1N2}}{\delta_1}} = [C_{AO} - C_{AI}] \qquad \frac{W_A}{\frac{D_{2N2}}{\delta_2 - \delta_1}} = [C_{AI} - 0]$$

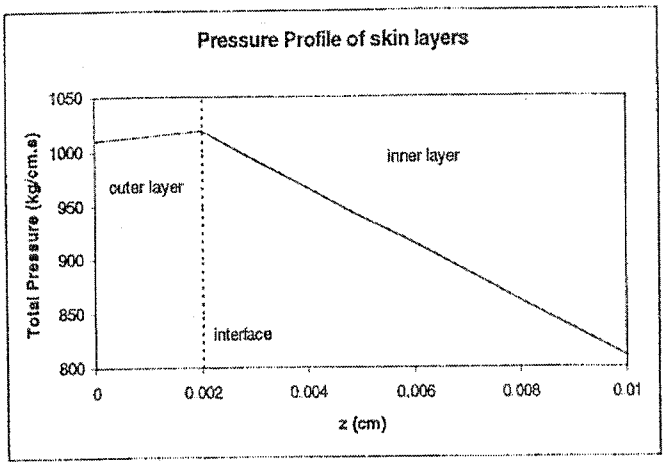
$$W_A\left[\frac{1}{\frac{D_{1N2}}{\delta_1}} + \frac{1}{\frac{D_{2N2}}{\delta_2 - \delta_1}}\right] = C_{AO}$$

Conversion of kPa to kg/cm*s^2
101kPa=101000Pa=101000kg/ms^2=1010kg/cms^2 $\therefore$ 1kPa=10kg/cms^2

$$W_a = \frac{C_{A0}}{\left[\frac{1}{\frac{D_{1He}}{\delta_1}} + \frac{1}{\frac{D_{2He}}{\delta_2 - \delta_1}}\right]} = \frac{810}{\left[\frac{1}{\frac{10*10^{-5}}{0.002}} + \frac{1}{\frac{50*10^{-7}}{0.008}}\right]} = 50*10^{-2}\ \frac{kg}{cm*s^2}$$

He : Outer layer : $W_B = \frac{D_{1He}}{\delta_1}[C_{B1} - 0]$

Inner layer : $W_B = \frac{D_{2He}}{\delta_2 - \delta_1}.[C_{B0} - C_{B1}]$



$$W_B\left[\frac{1}{\frac{D_{1He}}{\delta_1}} + \frac{1}{\frac{D_{2He}}{\delta_2 - \delta_1}}\right] = C_{B0}$$

$$W_B = \frac{C_{B0}}{\left[\frac{1}{\frac{D_{1He}}{\delta_1}} + \frac{1}{\frac{D_{2He}}{\delta_2 - \delta_1}}\right]} = \frac{81x10}{\left[\frac{1}{\frac{10e-5}{0.002}} + \frac{1}{\frac{5x10e-7}{0.008}}\right]} = 5x10e-2kg/cm^2s$$

Hence :

$$P_{A1} = \frac{W_A}{\frac{D_{2N2}}{\delta_2 - \delta_1}} = \frac{1.89x10e-2}{\frac{1.5x10e-7}{0.008}}$$

$$= 1008kg/cm.s^2$$

$$P_{B1} = \frac{W_B}{\frac{D_{2He}}{\delta_1}} = \frac{5x10e-2}{\frac{10e-5}{0.002}}$$

$$= 10kg/cm.s^2$$

The maximum sum of partial pressures occurs at the skin layer interface

$z = 0.002$ cm $\qquad P_{Total} = 1018$ kg/cm.s^2

$P_{sat} = 101$ kPa $= 1010$ kg/cm.s^2 $< P_{Total} = 1018$ kg/cm.s^2

Hence the maximum sum of the partial pressures is slightly greater than the saturation partial pressure and so gas will form bubbles at the skin layer interface causing blisters.

P11-5 (a)

Part (a & b) *Packed bed, mass tranfer limited, gas phase*

Mol balance : $\dfrac{1}{Ac}\dfrac{dFa}{dz} + ra''.a_c = 0$ where $Fa = U.Ca.Ac$

$$\frac{1}{Ac}\frac{FaodX}{dz} = ra''.a_c$$

$$\frac{U.Cao.dX}{dz} = ra''.a_c$$ U = constant superficial gas velocity

Rate law : Mass transfer limited boundary condition

$ra'' = kc.(Ca - Cas)$ but $Cas = 0$, rapid reaction

Stoichiometry : Assume constant T, P, gas phase

$$Ca = \frac{Cao.(1-X)}{(1+\varepsilon.X)}$$ where $\varepsilon = yao.\delta = 0.05 \times 3 = 0.15$

Combining : $\dfrac{U.Cao.dX}{dz} = ra''.a_c$

$$Cao.Uo.\frac{dX}{dz} = a_c.kc.Ca$$

$$\frac{dX}{dz} = \frac{a_c.kc.(1-X)}{Uo.(1+0.15X)}$$

Use Thoenes & Kramers correlation for kc : $Sh' = (Re')^{1/2}(Sc')^{1/3}$

$$\frac{kc.dp}{Dab}\left(\frac{\phi}{1-\phi}\right)\frac{1}{\gamma} = \left[\frac{U.dp.\rho}{\mu.(1-\phi).\gamma}\right]^{1/2}\left[\frac{\mu}{\rho.Dab}\right]^{1/3}$$

Parameter evaluation :

$$d_p = \left[\frac{6}{\pi} V_p\right] = \left[\frac{6(0.5)^2 0.5}{\pi}\right] = 0.238cm$$

Diffusion of cyclohexane in hydrogen (assuming constant T, P)

$$Dab = \frac{0.001T^{1.75}\left[\frac{1}{Ma} + \frac{1}{Mb}\right]^{1/2}}{P\left[\left(\sum Va\right)^{1/3} + \left(\sum Vb\right)^{1/3}\right]^2}$$

Fuller, Schettler, Giddings for binary mixture, low pressure, non polar (Perry's handbook chem.eng.)

Ma , Mc = molecular masses = 84 , 2 respectively
Va , Vb = diffusion volumes = 122 , 7.07 cm^3/mol respectively

$$Dab = \frac{0.001(773)^{1.75}\left[\frac{1}{84} + \frac{1}{2}\right]^{1/2}}{2\left[\left(\sum 122\right)^{1/3} + (7.07)^{1/3}\right]^2} = 0.857cm^2 / s$$

$$\phi = 0.4$$

$$\gamma = \frac{2.\pi.\frac{d^2}{4} + \pi.d.l}{\pi.dp^2} = \frac{\frac{0.5^2}{2} + 0.5(0.5)}{0.572} = 1.146$$

$$Uo = \frac{\upsilon_o}{Ac} = \frac{60000}{\frac{\pi.dt^2}{4}.60} = 50.9cm / s$$

$$U = Uo.(1 + \varepsilon.X) = 50.9(1 + 0.15X)$$

$$\rho = \frac{RMM.P}{R.T} = \frac{(84x0.05x2) + (2x0.95x2)}{0.0821x773} = 0.19gm / l = 0.00019g / cm^3$$

$\mu = 0.00017$ g/cm.s (H_2, 500 K, 2 atm)

$$Re' = \frac{50.9(1+0.15X)0.572x0.00019}{0.00017(1-0.4)1.146} = 47.3(1+0.15X)$$

$$Sc' = \frac{0.00017}{0.00019x0.857} = 1.044$$

$$kc.\frac{0.572}{0.857}\left(\frac{0.4}{1-0.4}\right).\frac{1}{1.146} = 0.388.kc$$

$$kc = \frac{1}{0.388}.\left[47.3(1+0.15X)\right]^{1/2}\left[1.044\right]^{1/3} = 17.98(1+0.15X)^{1/2}$$

$$a_c = \frac{6(1-0.4)}{0.572} = 6.29cm^{-1}$$

$\mu = 0.00017$ g/cm.s (H_2, 500 K, 2 atm)

$$Re' = \frac{50.9(1+0.15X)0.572x0.00019}{0.00017(1-0.4)1.146} = 47.3(1+0.15X)$$

$$Sc' = \frac{0.00017}{0.00019x0.857} = 1.044$$

$$kc.\frac{0.572}{0.857}\left(\frac{0.4}{1-0.4}\right).\frac{1}{1.146} = 0.388.kc$$

$$kc = \frac{1}{0.388}.\left[47.3(1+0.15X)\right]^{1/2}\left[1.044\right]^{1/3} = 17.98(1+0.15X)^{1/2}$$

$$a_c = \frac{6(1-0.4)}{0.572} = 6.29cm^{-1}$$

$$\frac{dX}{dz} = 2.22\frac{(1-X)}{(1+0.15X)^{1/2}}$$ POLYMATH

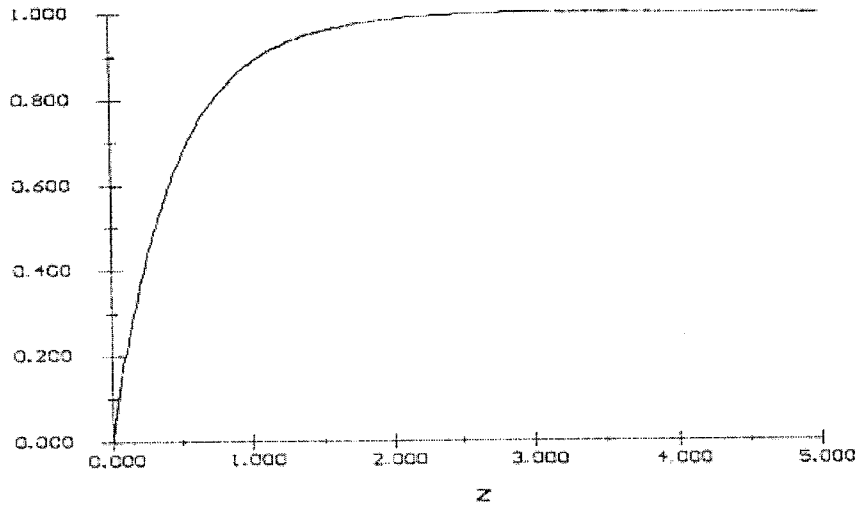
P11-5 (b)

Equations:	Initial value
d(x)/d(z)=2.22*(1-x)/(1+.15*x)^.5	0

$z_0 = 0, \quad z_f = 5$

Variable	Initial value	Maximum value	Minimum value	Final value
z	0	5	0	5
x	0	0.99997	0	0.99997

KEY:
— x



z	x
2.625	0.99591419
2.6875	0.99641018
2.75	0.99684594
2.8125	0.9972288
2.875	0.99756518
2.9375	0.99786072
3	0.99812039
3.0625	0.99834853
3.125	0.99854898
3.1875	0.9987251
3.25	0.99887983
3.3125	0.99901579
3.375	0.99913525
3.4375	0.9992402
3.5	0.99933242
3.5625	0.99941344

The results show that only 3.3 cm of the tube is required for conversion of 99.9%, much less than the full 20 m.

P11-5 (c)

$$\frac{kc \cdot dp}{Dab}\left(\frac{\phi}{1-\phi}\right)\frac{1}{\gamma} = \left[\frac{U \cdot dp \cdot \rho}{\mu(1-\phi)\gamma}\right]^{1/2}\left[\frac{\mu}{\rho \cdot Dab}\right]^{1/3}$$

Assuming the porosity remains the same, factors in the correlation affected by the size of the catalyst pellets are:

$$dp = \left[\frac{6}{\pi} Vp\right]^{1/3} = \left[\frac{6(0.25)^2 0.25}{4}\right]^{1/3} = 0.286cm$$

$$\gamma = \frac{2.\pi.\frac{d^2}{4} + \pi.d.l}{\pi.dp^2} = \frac{\frac{0.25^2}{2} + 0.25(0.25)}{0.286} = 1.145$$

$$\mathrm{Re}' = \frac{50.9(1+0.15X)0.286.x0.00019}{0.00017(1-0.4)1.145} = 23.68(1+0.15X)$$

$$kc.\frac{0.286}{0.857}\left(\frac{0.4}{1-0.4}\right)\frac{1}{1.145} = 0.194.kc$$

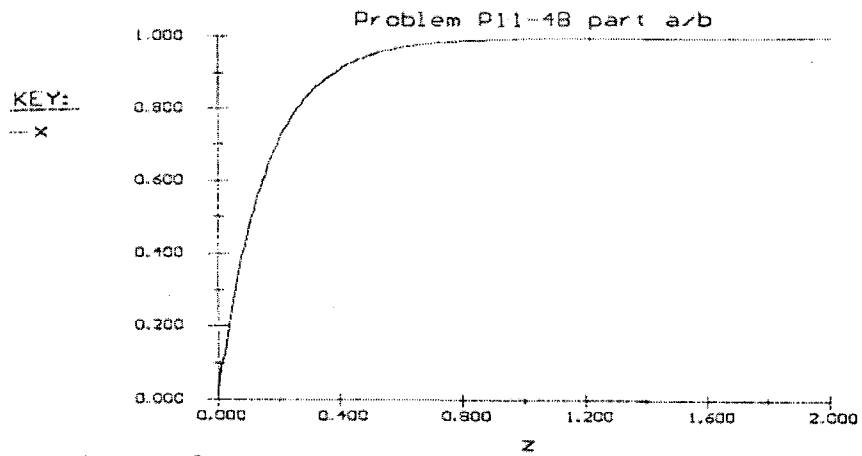
$$kc = \frac{1}{0.194}\left[23.68(1+0.15X)\right]^{1/2}\left[1.044\right]^{1/3} = 25.39(1+0.15X)^{1/2}$$

$$a_c = \frac{6(1-0.4)}{0.286} = 12.59cm^{-1}$$

$$\frac{dX}{dz} = \frac{12.59x25.39(1+0.15X)^{1/2}}{50.9}\cdot\frac{(1-X)}{(1+0.15X)}$$

$$\frac{dX}{dz} = 6.28\frac{(1-X)}{(1+0.15X)^{1/2}}$$

POLYMATH



As can be seen from the above graph, the affect of reducing the dimensions of the pellets by half results in the conversion reaching 99.9 % 1.18 cm from the entrance. This seems reasonable because reducing the size of the catalyst particles is one of the methods for increasing mass transfer and hence kc.

P11-5 (d)

If pure cyclohexane feed were used at the same volumetric flowrate 60 dm^3/min , then the initial bulk concentration would be greater and there would be a greater concentration gradient across the stagnant film on the pellets. However the mass transfer coefficient will be reduced as the products must diffuse away from the surface which will be harder in higher concentrations of cyclohexane.

The equations used in Part (a) do not incorporate Cao, the initial cyclohexane concentration (Cao is cancelled out), so the only affect this change would have is to alter the physical properties of the bulk flow :

$$\rho = \frac{RMM.P}{R.T} = \frac{(84x2)}{0.0821x773} = 2.647 gm/l = 0.00265 g/cm^3$$

μ = ? g/cm.s (cyclohexane , 500 K , 2 atm)

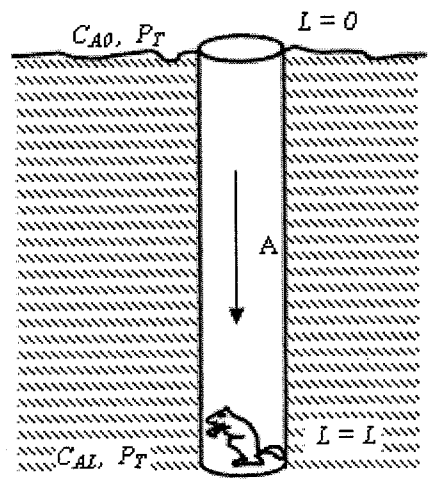
P11-5 (e)

This problem gives an indication as to how changes in parameters may affect a packed bed.

P11-6

Given,

- Minimum respiration rate of chipmunk, F_{AL} = 1.5 µmol O_2/min
- Breathing rate of Chipmunk, v_0 = 0.05 dm^3 gas/min
- Diameter of hole, D = 3cm



Assuming,

- A represents oxygen
- B represents nitrogen
- Chipmunk has a constant breathing rate of 0.05 dm^3 of gas/min

Minimum flow rate of oxygen to the bottom, F_{AL}
= Minimum respiration rate of chipmunk
= 1.5 µmol of O_2/min

•

Flow rate of A down the hole

= Flux of A × Cross - sectional Area

$$\therefore F_{AL} = \mathscr{D}_{AB} \frac{C_{A0} - C_{AL}}{L} \times A_C$$

$$or\ L = \mathscr{D}_{AB} \frac{C_{A0} - C_{AL}}{F_{AL}} \times A_C \qquad \text{----(1)}$$

$$\mathscr{D}_{AB} = 0.18\, cm^2/s = 0.18\times10^{-4}\, m^2/s$$

$$A_C = \frac{\pi D^2}{4} = \frac{\pi\times(0.03m)^2}{4} = 7.069\times10^{-4}\, m^2$$

$$F_{AL} = 1.50\times10^{-6}\, mol/\min = 2.5\times10^{-8}\, mol/s$$

P11-6 (a) At Pasadena, California

$$C_{A0} = \frac{P_T}{RT} \times y_A \qquad \text{(Ideal gas law)}$$

where,

$P_T = 1.013\times10^5\, N/m^2$ at Pasadena, California (situated at sea level)

$R = 8.314\, J/mol.K$

$T = 25^0 C = 298K$

$y_A = 0.21$ (Mole fraction of oxygen in air)

$$C_{A0} = \frac{1.013\times10^5\, N/m^2}{\left(8.314 \frac{J}{mol.K} \times 298K\right)} \times 0.21$$

$$\therefore C_{A0} = 8.59\, mol/m^3$$

Now,

Flow rate of A = (Concentration of A at the bottom) x (Volumetric intake of gas)

$$F_{AL} = C_{AL} \times v_0$$

$$v_0 = 0.05\, dm^3/\min = 0.05\times10^{-3}\, m^3 \text{ gas/min}$$

$$\therefore C_{AL} = \frac{F_{AL}}{v_0} = \frac{2.5\times10^{-8}\, mol/s}{\left(0.05\times10^{-3} \frac{m^3}{\min} \times \frac{1\min}{60s}\right)} = 0.03\, mol/m^3$$

Solving for the length from (1),

$$L = \mathscr{D}_{AB} \frac{C_{A0} - C_{AL}}{F_{AL}} \times A_C$$

$$L = 0.18\times10^{-4} m^2/s \times \left(\frac{(8.59 - 0.030)\, mol/m^3}{2.5\times10^{-8} mol/s}\right)\times 7.069\times10^{-4} m^2$$

$$\therefore L = 4.36m$$

P11-6 (b) At Boulder, Colorado

Boulder, Colorado is 5430 feet above sea-level. The corresponding atmospheric pressure is 0.829 x 10^{-5} N/m^2.

$P_T = 0.829\times10^5 N/m^2$ at Boulder, Colorado

$$C_{A0} = \frac{P_T}{RT}\times y_A$$

$$C_{A0} = \frac{0.829\times10^5 N/m^2}{\left(8.314\frac{J}{mol.K}\times 298K\right)}\times 0.21$$

$$\therefore C_{A0} = 7.03\, mol/m^3$$

Solving for the length from (1),

$$L = \mathscr{D}_{AB}\frac{C_{A0} - C_{AL}}{F_{AL}}\times A_C$$

$$L = 0.18\times10^{-4} m^2/s \times \left(\frac{(7.03 - 0.03)\, mol/m^3}{2.5\times10^{-8} mol/s}\right)\times 7.069\times10^{-4} m^2$$

$$\therefore L = 3.56m$$

P11-6 (c)

During winter at Ann Arbor, Michigan

$T = 0^0 F = -17.78^0 C = 255.37K$

$$C_{A0} = \frac{P_T}{RT}\times y_A$$

$$C_{A0} = \frac{1.013\times10^5 N/m^2}{\left(8.314\ \frac{J}{mol.K}\times 255.37K\right)}\times 0.21$$

$$\therefore\ C_{A0} = 10.02\, mol/m^3$$

Solving for the length from (1),

$$L = \mathscr{D}_{AB}\frac{C_{A0} - C_{Al}}{F_{AL}}\times A_C$$

$$L = 0.18\times10^{-4} m^2/s \times \left(\frac{255}{298}\right)^{1.75} \times \left(\frac{(10.02 - 0.03)\ mol/m^3}{2.5\times10^{-8} mol/s}\right) \times 7.069\times10^{-4} m^2$$

$$\therefore L = 3.87m$$

During winter at Boulder, Colorado

$$T = 0^0 F = -17.78^0 C = 255.37K$$

$$C_{A0} = \frac{P_T}{RT} \times y_A$$

$$C_{A0} = \frac{0.829\times10^5 N/m^2}{\left(8.314\ \frac{J}{mol.K} \times 255.37K\right)} \times 0.21$$

$$\therefore\ C_{A0} = 8.20\ mol/m^3$$

Solving for the length from (1),

$$L = \mathscr{D}_{AB} \frac{C_{A0} - C_{Al}}{F_{AL}} \times A_C$$

$$L = 0.18\times10^{-4} m^2/s \times \left(\frac{255}{298}\right)^{1.75} \times \left(\frac{(8.20 - 0.03)\ mol/m^3}{2.5\times10^{-8} mol/s}\right) \times 7.069\times10^{-4} m^2$$

$$\therefore L = 3.17m$$

P11-6 (d) Individualized solution

P11-7 (a)

Given : P_v = 510 mm Hg @ 35 °C (from plot of ln P_v vs 1/T)

$$\ln P_v = A - \left(\frac{B}{T} + C\right)$$ Antoine Equation

D_{AB} = 0.120 cm^2/sec (from equation of Fuller, et al.)

$$D_{AB} = \frac{0.001T^{1.75}\sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{P(\sqrt[3]{V_A} + \sqrt[3]{V_B})^2}$$ Fuller Equation

where V_A and V_B are the Fuller molecular diffusion volumes which are calculated by summing the atomic contributions. This also lists some special diffusion volumes for simple molecules.

Fuller diffusion volumes

Atomic and structural diffusion volume increments

C	15.9	F	14.7
H	2.31	Cl	21.0
O	6.11	Br	21.9
N	4.54	I	29.8

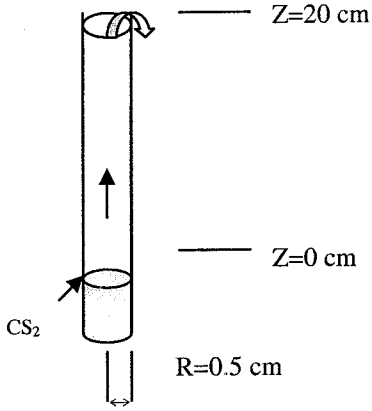
Ring	-18.3	S	22.9

Diffusion volumes of simple molecules

He	2.67	CO	18.0
Ne	5.98	CO2	26.9
Ar	16.2	N2O	35.9
Kr	24.5	NH3	20.7
Xe	32.7	H2O	13.1
H2	6.12	SF6	71.3
D2	6.84	Cl2	38.2
N2	18.5	Br2	69.0
O2	16.3	SO2	41.8
Air	19.7		

P11-7 (b)

By CS_2 molar flow rate balance



$$\frac{dN_A}{dz} = 0$$

And

$$N_A = K_1$$

Fick's First Law (For $N_{AIR} = 0$)

$$N_A = -CD_{AB}\frac{dX_A}{dz} + X_A(N_A + 0)$$

$$= \frac{-CD_{AB}}{1-X_A}\frac{dX_A}{dz}$$

Equating the results of Fick's First Law and molar flow balance, then rearranging and writing in the integral form

$$K_1 \int_0^{z_2} dz = CD_{AB} \int_{X_0}^{X_2} d\ln(1-X_A)$$

$$K_1 = \frac{CD_{AB}}{z_2}\ln\left[\frac{1-X_2}{1-X_0}\right]$$

Evaluating for $z_2 = 20$, $X_2 = 0$

$$C = \frac{P}{RT} = \frac{(1)atm}{(82.6)\frac{atm.cm^3}{gmol.^oK}(308)^0K}$$

$$= 3.95*10^{-5}\, gmol/cm^3$$

$$X_0 = \frac{P_V}{P_{Total}} = \frac{510}{760} = 0.671$$

$$N_A = K_1 = \frac{(3.95*10^{-5})(0.12)}{(20)}\ln\left[\frac{1-0.0}{1-0.671}\right]$$

$$= 2.64*10^{-7}\, gmol/cm^2.\sec$$

P11-7 (c)

For any value of z between z = 0 and z = 20

$$\frac{z}{z_2} = \frac{\ln\left[\frac{1-X_A}{1-X_0}\right]}{\ln\left[\frac{1}{1-X_0}\right]}$$

$$(1-X_A) = (1-X_0)_A\left[\frac{1}{1-X_0}\right]_A^{Z/Z_2} = (1-X_0)_A^{(1-Z/Z_2)}$$

$$X_B = (1-X)_A = (X_{B_0})^{(1-Z/20)}$$

$$C_A = X_A C \qquad C_B = X_B C$$

$$M = X_A M_A + X_B M_B$$

$$C_B = X_B C$$

$$V_A = N_A / C_A \qquad V_B = N_B / C_B = 0$$

$$V^* = \frac{N_A + N_B}{C} = 7.17 * 10^{-3}$$

$$V = \frac{n_A + n_B}{\rho} = n_A / \rho$$

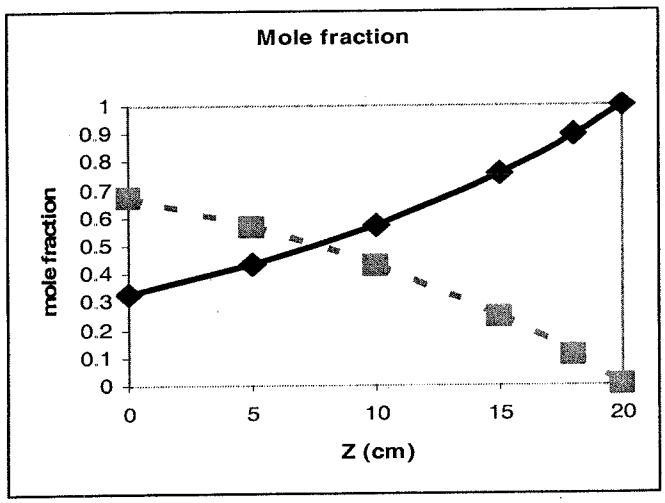
$$J_A = C_A(V_A - V^*) = N_A - X_A N_A = X_B N_A$$

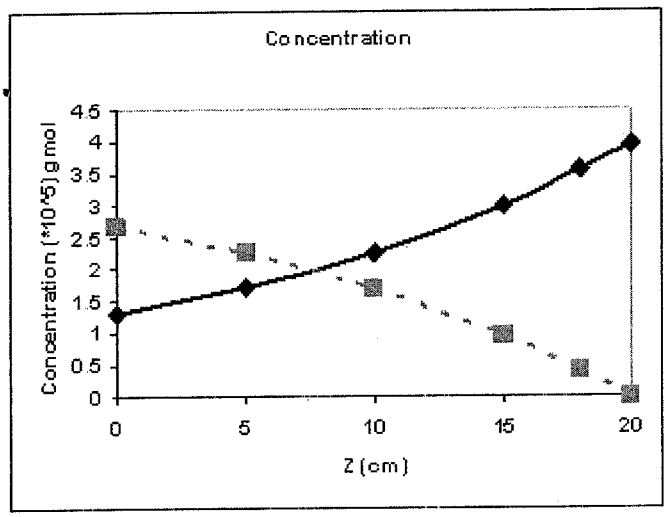
$$J_B = C_B(V_B - V^*) = -X_B N_A = -J_A$$

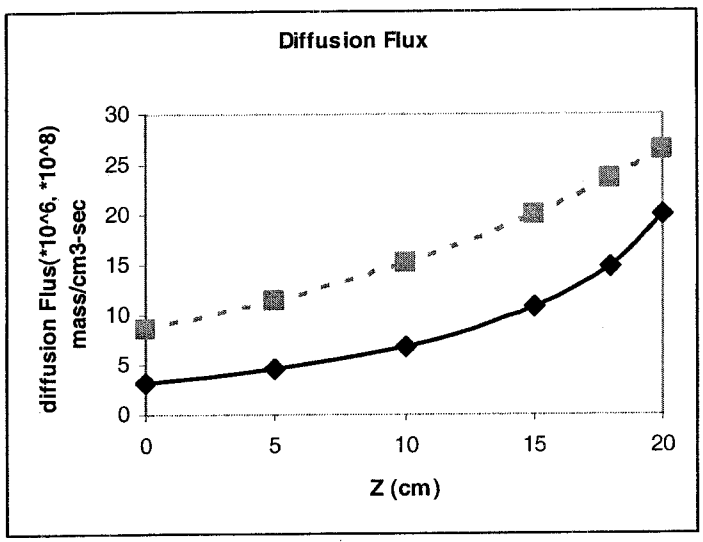
			(*10^5)		(*10^3)					
z	X_B	X_A	C_B	C_A	ρ_B	ρ_A	ρ	ω_B	ω_A	ω
0	0.329	0.671	1.3	2.65	0.376	2.02	2.4	0.158	0.842	60.7
5	0.434	0.566	1.71	2.24	0.495	1.71	2.21	0.226	0.774	56
10	0.573	0.427	2.26	1.69	0.655	1.29	1.95	0.338	0.661	49.4
15	0.757	0.243	2.99	0.96	0.865	0.73	1.6	0.544	0.456	40.5
18	0.895	0.105	3.54	0.415	1.02	0.316	1.34	0.764	0.236	34
20	1	0	3.95	0	1.14	0	1.14	1	0	28.97

	(*10^3)				(*10^6)	(*10^8)
z	V_B	V_A	V^*	V	j_A=-j_B	J_A=-J_B
0	0	9.9	7.17	8.32	3.16	8.7
5	0	11.8	7.17	9.05	4.52	11.45
10	0	15.6	7.17	10.25	6.77	15.15
15	0	27.5	7.17	12.5	10.9	20
18	0	63.5	7.17	14.9	14.9	23.6
20	0	1E+06	7.17	17.5	20	26.4

P11-7 (d)







P11-7 (e)

Evaporation Rate of CS_2 (ρ_{liq} @ 20 °C = 1.26 gm/cc)

$$Q = \frac{n_A A}{\rho_{liq}} t = \frac{(2.0*10^{-5})(\frac{\pi}{4})(3600*24)}{1.26}$$
$$= 1.075 \frac{cm^3 (@\ 20^0 C}{day}$$

P11-7 (f) No solution will be given

P11-7 (g)

Molecular diffusion of air is taking place

$$N_B = J_B + X_B(N_B + N_A)$$
$$0 = J_B + X_B(N_A)$$
$$J_B = -X_B(N_A) = (1 - X_A)N_A$$
$$= -J_A$$

P11-8 (a)

Quasi-steady-state – no accumulation in the capillary tube or in either chamber.

Volume 1:
Accumulation = in – out.

$$\frac{dN_A}{dt} = \frac{d(C_A V_1)}{dt} = 0 - W_A A_C$$

$$W_A = -D_{AB} C_t \frac{dy}{dz} + y_A (W_A + W_B)$$

EMCD: $W_A = -W_B$

$$W_A = -D_{AB} \frac{dC_A}{dt} \rightarrow W_A z\Big|_0^L = -D_{AB} C_A\Big|_{C_{A1}}^{C_{A2}}$$

$$W_A = \frac{D_{AB}}{L}(C_{A1} - C_{A2})$$

Volume 2:

$$\frac{d(C_A V_1)}{dt} = W_A A_C - 0$$

$$\frac{dC_{A1}}{dt} = -\frac{A_C D_{AB}}{V_1 L}(C_{A1} - C_{A2})$$

$$\frac{dC_{A2}}{dt} = \frac{A_C D_{AB}}{V_2 L}(C_{A1} - C_{A2})$$

Subtraction gives us:

$$\frac{d(C_{A1} - C_{A2})}{dt} = -\frac{A_C D_{AB}}{L}\left(\frac{1}{V_1} + \frac{1}{V_2}\right)(C_{A1} - C_{A2})$$

Now integrate:

$$\ln\left(C_{A1}-C_{A2}\right)=-\frac{A_C D_{AB}}{L}\left(\frac{1}{V_1}-\frac{1}{V_2}\right)t+\text{Constant}$$

P11-8 (b)

$$\left(C_{A1}-C_{A2}\right)=k\Delta IC$$

$$\ln k+\ln\Delta IC=-\frac{A_C D_{AB}}{L}\left(\frac{1}{V_1}-\frac{1}{V_2}\right)t+\text{Constant}$$

$$\ln\Delta IC=-\frac{A_C D_{AB}}{L}\left(\frac{1}{V_1}-\frac{1}{V_2}\right)t+\mathrm{C}_2$$

$$\ln\Delta IC=-D_{AB}\left(0.01025\right)t+\mathrm{C}_2$$

if we plot ln(ΔIC) as a function of time and find the slope, that would give us $-D_{AB}$

See Polymath program P11-8-b.pol.

POLYMATH Results
Linear Regression Report

Model: lnDIC = a0 + a1*t

Variable	Value	95% confidence
a0	3.7024708	0.0078035
a1	-0.0107008	9.83E-05

General
Regression including free parameter
Number of observations = 9

Statistics

R^2 =	0.9998944
R^2adj =	0.9998793
Rmsd =	0.0015013
Variance =	2.608E-05

D_{AB} = 0.0107

P11-9

Dissolution of monodisperse solid particles in excess solvent.

$$Di-D+\frac{1}{2D^*}\left(Di^2-D^2\right)=\alpha.t$$

Define conversion in terms of volume dissolved : $$X=\frac{\frac{\rho.\pi}{6}\left(Di^3-D^3\right)}{\frac{\rho.\pi}{6}Di^3}$$

gives $D = Di\,(1-X)^{1/3}$

Substituting for D : $$\underbrace{Di - \mathrm{Di}\,(1 - X)^{1/3}}_{\text{term 1}} + \underbrace{\frac{1}{2D^*}\left(Di^2 - \left[\mathrm{Di}\,(1 - X)^{1/3}\right]^2\right)}_{\text{term 2}} = \alpha.t$$

Surface reaction controls : D* is large, term 2 is small cf term 1

$$Di - \mathrm{Di}\,(1 - X)^{1/3} = \alpha.t$$

$$1 - (1 - X)^{1/3} = \frac{\alpha.t}{Di}$$

Mass transfer controls : D* is small, term 1 is small cf term 2

$$\frac{1}{2D^*}\left(Di^2 - \left[\mathrm{Di}\,(1 - X)^{1/3}\right]^2\right) = \alpha.t$$

$$\frac{Di}{2D^*}\left(1 - (1 - X)^{2/3}\right) = \frac{\alpha.t}{Di}$$

Both regimes apparent : Term 1 and term 2 apply

$$\left[1 - (1 - X)^{1/3}\right] + \left[\frac{Di}{2D^*}\left(1 - (1 - X)^{2/3}\right)\right] = \frac{\alpha.t}{Di}$$

P11-10 (a)

Mass transfer limited $-W_{Ar} = k_C.C_{AO}$ A in excess , $C_A = C_{AO}$

The reaction rate is equal to the mass transfer rate $-r_{As}'' = k_r.C_{As} = k_C.C_{AO}$

For small particles and negligible shear stress : $$kc = \frac{2.De}{D}$$

$$-r_{As}'' = \frac{2.De}{D}.C_{AO}$$

Mol balance on solids : $$r''_{B_s}\pi D^2 = \frac{d\left(\frac{\rho\pi D^3}{6}\right)}{dt} = \frac{\rho\pi D^2}{6}\frac{dD}{dt}$$

For 1 mole A dissolving 1 mole B then $-r_{As}'' = -r_{Bs}'' = k_C.C_{AO}$ as C_{As} is undefined

$$\frac{dD}{dt} = -\left[\frac{2.(-r_{As}'')}{\rho}\right] = \frac{4.De.C_{AO}}{\rho.D}$$

Boundary conditions, t = 0 , D = Di

$$\int_{Di}^{D}(D)dD = \frac{4.De.C_{AO}}{\rho}\int_{0}^{t}dt$$

$$\frac{D^2 - Di^2}{2} = \frac{4.De.C_{AO}.t}{\rho}$$

$$D = \left[Di^2 - \frac{8.De.C_{AO}.t}{\rho}\right]^{1/2}$$

Time for dissolution, tc , at D = 0, and assuming particle density, $\rho = 2000\ kg/m^3$

$$tc = \frac{\rho.Di^2}{8.De.C_{AO}} = \frac{2000\times(10e-5)^2}{8\times(10e-10)\times(2000)} = 0.125s$$

i.e. virtually instantaneous dissolution

P11-10 (b)

Surface reaction limited $-r_{As}'' = k_r.C_{AO}$

Mass transfer effects are not important when the surface reaction rate is limiting.

Mol balance on solids : $$r_{Bs}''.\pi.D^2 = \frac{d\left(\frac{\rho.\pi.D^3}{6}\right)}{dt}$$

For 1 mole A dissolving 1 mole B then $-r_{As}'' = -r_{Bs}''$

$$\frac{dD}{dt} = -\left[\frac{2(-r''_{As})}{\rho}\right] = -\frac{2}{5}k_r.C_{AO}$$

Boundary conditions, t = 0 , D = Di

$$\int_{Di}^{D}dD = \frac{2.kr.C_{AO}}{\rho}\int_{0}^{t}dt$$

$$D - Di = -\frac{2.kr.C_{Ao}.t}{\rho}$$

$$D = Di - \frac{2.kr.C_{Ao}.t}{\rho}$$

Time for dissolution, tc , at D = 0, and assuming particle density, $\rho = 2000$ kg/m^3

$$tc = \frac{\rho.Di}{2.kr.C_{Ao}} = \frac{2000 \times (10e-5)}{2 \times (10e-10) \times (2000)} = 5x10e12s$$

a very long time.

P11-10 (c)

At t = 0, total moles A in tank = 0.1 x 100 = 10 mol A

i.e. there is just enough mols of A to completely dissolve all of B in a well mixed tank.

Acid not in excess and dissolution is mass transfer limited ($C_{As} \neq 0$ and $C_A \neq C_{AO}$)

$W_{Ar} = kc(C_A - C_{As}) = -r_{As}'' = k_r.C_{As}$ assume zero order in B

$$W_{Ar} = kc.(C_A - C_{As}) = -r_{As}'' = \frac{kc.kr}{kc + kr}.C_A \quad \text{and} \quad kc = \frac{2.De}{D}$$

$$-r_{As}'' = \frac{kr}{1 + \frac{D}{D^*}}.C_A \quad \text{where} \quad D^* = \frac{2.De}{kr}$$

Mol balance on solids : $$r_{Bs}''.\pi.D^2 = \frac{d\left(\frac{\rho.\pi.D^3}{6}\right)}{dt}$$

For 1 mole A dissolving 1 mole B then $-r_{As}'' = -r_{Bs}''$

$$\frac{dD}{dt} = -\left[\frac{2.(-r_{As}'')}{\rho}\right] = \frac{2.kr.C_A}{\rho}\left(\frac{1}{1 + \frac{D}{D^*}}\right)$$

$$\frac{dD}{dt} = -\alpha.\left(\frac{1}{1 + \frac{D}{D^*}}\right) \quad \text{where } \alpha = \frac{2.kr.C_A}{\rho}$$

Boundary conditions, t = 0 , D = Di

$$Di - D + \frac{1}{2.D^*}.(Di^2 - D^2) = \alpha.t$$

As a function of radius :

$$\frac{2r^2}{D} - 2r + \alpha t - 2ri - \frac{2ri^2}{D^*} = 0$$

$$r^2 + D^*.r + \left[\frac{D^*.\alpha.t}{2} - D^*.ri - ri^2\right] = 0$$

Using the quadratic solver : $r = \frac{-b \pm \sqrt{b^2 - 4.a.c}}{2.a}$

$$r = \frac{-D^* \pm \sqrt{(D^*)^2 - 4\left(\frac{D^*\alpha t}{2} - D^*ri - ri^2\right)}}{2}$$

Time for complete dissolution, tc, at r = 0 :

$$tc = \frac{1}{\alpha}\left[Di + \frac{Di^2}{2.D^*}\right]$$

assume $\rho = 2000$ kg/m^3 and $\alpha = \frac{2.kr.C_A}{\rho} = \frac{2x(10e-18)x(0.1e3)}{2000} = 10e-19$

$$D^* = \frac{2.De}{kr} = \frac{2x(10e-10)}{10e-18} = 2x10e8$$

gives $tc = \frac{1}{10e-19}\left[(10e-5) + \frac{(10e-5)^2}{2x(2x10e-8)}\right] = 10e14s$

again a very long time.

P11-10 (d)

$$tc = \frac{\rho}{2.kr.C_A}\left[Di + \frac{Di^2}{2.D^*}\right]$$

To reduce tc, increase C_A and / or decrease Di.
To increase tc, decrease C_A and / or increase Di.

P11-11 (a)

Irreversible, gas-phase, adiabatic, no pressure drop, packed bed.

Isothermal

Mol balance : $F_{A0}.\frac{dX}{dW} = -r_A$ mol/gcat s

where $F_{AO} = C_{AO} \cdot \upsilon_o$ = 10e-3 x 10e4 = 10 mol/cm^3

Rate law : $-r_{As} = k'.C_{As}$ But C_{as} is unknown.

Assume reaction rate is mass transfer limited.

$W_A = kc\,(C_A - C_{as}) = k'.C_{As}$

$$C_{As} = \frac{kc.C_A}{kc + k'}$$

$$-r_{As} = \frac{k'.kc.C_A}{kc + k'} \qquad \frac{cm^3}{s.gcat}\,\frac{mol}{cm^3}$$

where k' = 0.01 cm^3/s.gcat at 300 K (constant - isothermal)

$Sh = 100.Re^{1/2}$

$$kc = \frac{De}{dp}100\left(\frac{u.dp}{\nu}\right)^{1/2} = \frac{10e-2}{0.1}100\left(\frac{10x0.1}{0.02}\right)^{1/2} = 70.7cm/s$$

converting : 70.7 x a_{cat} = 70.7 x 60 = 4242 cm^3/s.gcat

$$-r_{As} = \frac{0.01x4242xC_A}{4242 + 0.01}$$

Stoichiometry : gas-phase, constant pressure and temperature

$$C_A = Cao.\left(\frac{1-X}{1+\varepsilon.X}\right)$$

where $\varepsilon = y_{AO}\delta = 0.5(1-1) = 0$

$C_A = C_{AO}(1 - X)$ and C_{AO} = 1 mol/dm^3 = 10e-3 mol/cm^3

POLYMATH

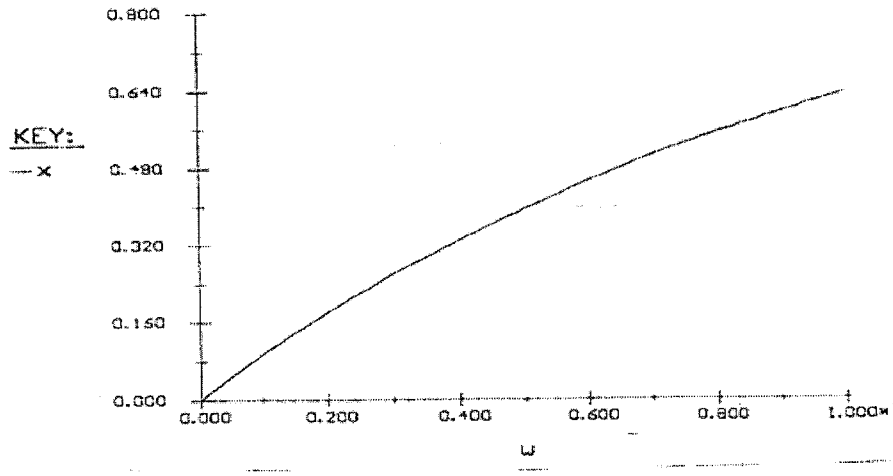
Equations:

```
d(x)/d(w)=-ra/fao
k=0.01
fao=10
kc=4242
cao=0.001
ca=cao*(1-x)
ra=-(k*kc*ca)/(k+kc)
w0 = 0,   wf = 1e+06
```

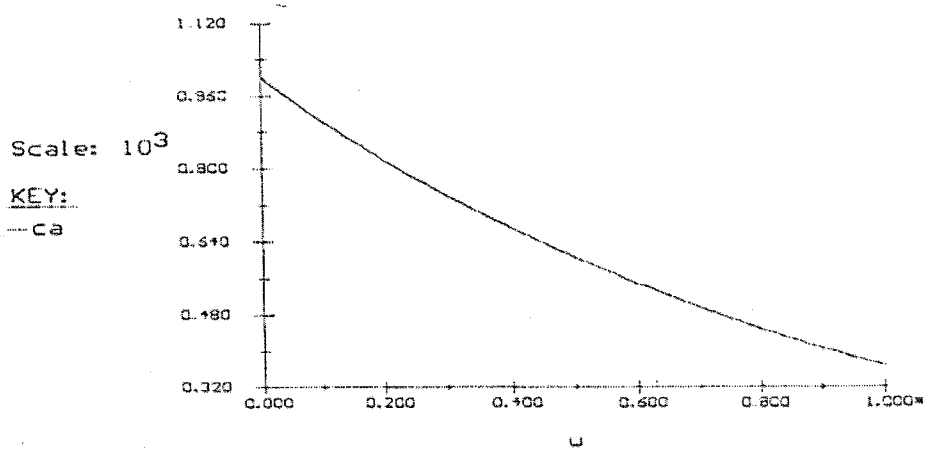
Initial value

```
0
```

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	1e+06	0	1e+06
x	0	0.63212	0	0.63212
k	0.01	0.01	0.01	0.01
fao	10	10	10	10
kc	4242	4242	4242	4242
cao	0.001	0.001	0.001	0.001
ca	0.001	0.001	0.00036788	0.00036788
ra	-9.99998e-06	-3.67879e-06	-9.99998e-06	-3.67879e-06



For a conversion of $X = 60\ \%$, $W_{tot} = 925$ kg



P11-11 (b)

Adiabatic operation

Mol balance and rate law as in Part (a)

$$\text{with} \quad k(T) = 0.01\exp\left[\frac{4000}{1.987}\left(\frac{1}{300} - \frac{1}{T}\right)\right]$$

Stoichiometry : $C_A = C_{Ao}\left(\frac{1-X}{1+\varepsilon X}\right)\frac{To}{T}$ where $\varepsilon = 0$ and To = 300 K

and C_{AO} = 10e-3 mol/cm^3

Energy balance : $$\frac{dF}{dt} = \frac{Q - W_S - \sum F_{io} C_{pi} (T - T_{io}) + F_{A0} X (-\Delta H_{RX}(T))}{\sum N_i C_{pi}} = 0$$

$\sum Fio\ Cpi.(T - Tio)$ = [10 x 25 (T - 300)] + [10 x 75 (T - 750)]

= 1000 (T - 300)

- 1000 (T - 300) + 10.X.(10000) = 0

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Equations:

```
d(x)/d(w)=-ra/fao
k=0.01
fao=10
kc=4242
cao=0.001
To=300
T=(10*x*10000/1000)+To
ca=cao*(1-x)*(To/T)
ra=-(k*kc*ca)/(k+kc)
```

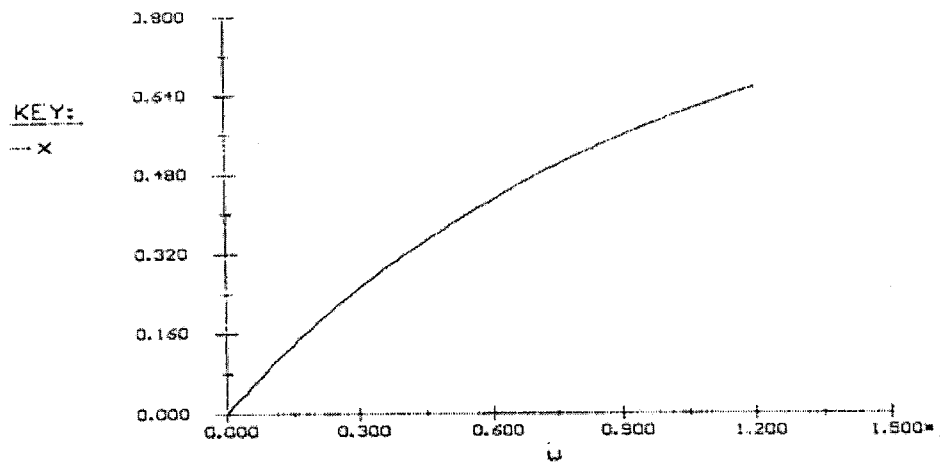
Initial value

0

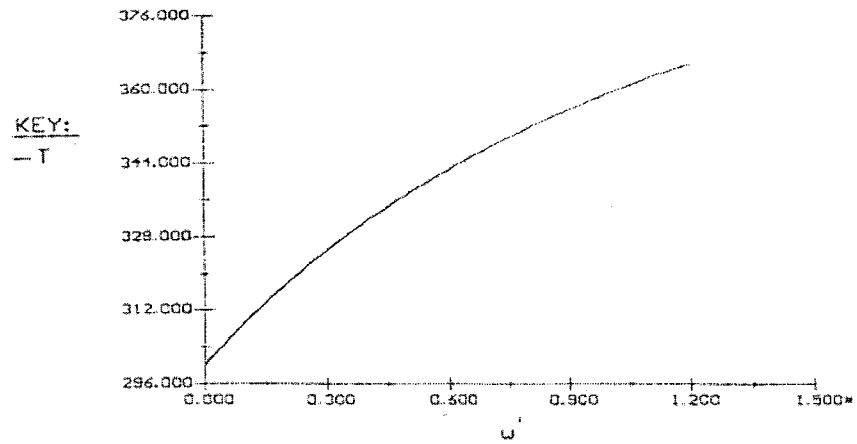
= 300 K

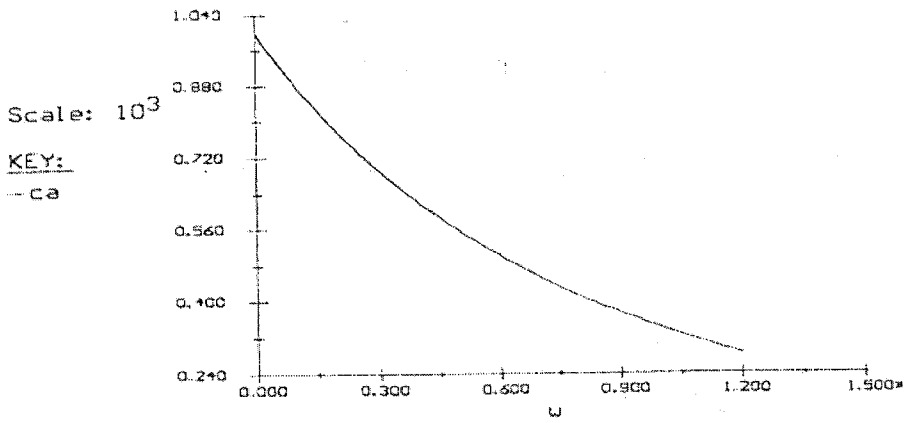
w_0 = 0, w_f = 1.2e+06

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	1.2e+06	0	1.2e+06
x	0	0.654825	0	0.654825
k	0.01	0.01	0.01	0.01
fao	10	10	10	10
kc	4242	4242	4242	4242
cao	0.001	0.001	0.001	0.001
To	300	300	300	300
T	300	365.483	300	365.483
ca	0.001	0.001	0.000283331	0.000283331
ra	-9.99998e-05	-2.8333e-06	-9.99998e-06	-2.8333e-06



For a conversion of X = 60 % , W_{cat} = 1020 kg





P11-11 (c)

It is possible to generalize that the addition of temperature variation in adiabatic operation does not affect the conversion, concentration profiles in form, but the numerical values are slightly different. Because the reaction is exothermic, isothermal operation enhances the conversion profile along the packed bed, so that for a given bed diameter less catalyst is required. It is clear that adiabatic operation inhibits conversion as heat is not removed from the system so more catalyst is needed for the required conversion. The removal of the heat generated in the reaction allows a reduction of 85 kg of catalyst in the bed. More detailed economics will indicate whether isothermal operation is worth it.

P10-12 (a)

Dissolution of pills.

Complete dissolution.

$$C_B = \frac{W_{druginblood}}{W_{body}} \qquad C_A = \frac{W_{druginstomach}}{V_{stomach}}$$

$$\frac{dC_B}{dt} = k_A . C_A . \frac{V_{stomach}}{W_{body}} \qquad \frac{g_{drug}}{g_{body}. \min}$$

Relate C_A to time :

Three pills, each with different thickness outer layers, the inner cores dissolving at different times (but at the same rate) to each other, will each contribute to C_A in the stomach.

Pill 1 $D_2 = 5$ mm, $D_1 = 3$ mm

Time for outer layer to dissolve $t_1 = \frac{0.0354x(0.5^2 - 0.3^2)}{8x(6x10e-4)x1.0} = 1.18 \min$

Pill 2 : $D_2 = 4$ mm, $D_1 = 3$ mm

Time for outer layer to dissolve $t_1 = \frac{0.0354x(0.4^2 - 0.3^2)}{8x(6x10e-4)x1.0} = 0.52 \min$

Pill 3 : $D_2 = 3.5$ mm, $D_1 = 3$ mm

Time for outer layer to dissolve $t_1 = \frac{0.0354x(0.35^2 - 0.3^2)}{8x(6x10e-4)x1.0} = 0.24 \min$

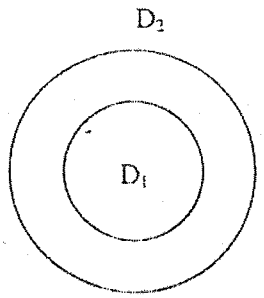
At $t = t_1$ mol balance on drug : $r_A'' . \pi . D_1^2 = \frac{dW_{druginstomach}}{dt}$

where $C_A = \frac{W_{druginstomach}}{V}$ and $r_A'' = k_c . S_{in}$

$$\frac{dC_A}{dt} = \frac{k_c . S_{in} . \pi . D^2}{V} = \frac{2 . D_{AB} . S_{in} . \pi . D^2}{D . V}$$

where W = mass of drug in stomach, g
V = volume stomach fluid , cm^3

and boundary conditions : $t = t_1$, $C_A = 0$
$t = t_2$, $C_A = C_{Ao} = W_o/V = 0.5/1200 = 4.17x10e\text{-}4$ g/cm^3



$D_2 = 4$ mm
$D_1 = 3$ mm

Outer layer :

Mol balance on outer layer : $0 = 0 + r_A''.\pi.D^2 = \dfrac{\left(\frac{1}{6}.\pi.D^3\rho_c\right)}{dt}$

and r_A'' rate of dissolution of outer layer = rate of mass transfer from pill surface W_A

$$W_A = k_c.S_{out} = -r_A''$$

$$Sh = 2,\ k_c = \frac{2.D_{AB}}{D}$$

Assume density of outer layer = inner layer $= \dfrac{500x10e-6}{\frac{\pi.(0.3)^3}{6}} = 0.0354 kg/cm^3$

$$S_{out} = 1.0\ kg/cm^3$$

$$\frac{dD}{dt} = \frac{2.(-r_A'')}{\rho} = \frac{2x2xD_{AB}.S_{out}}{D.\rho}$$

Boundary conditions : $t = 0,\ D = D_2$
$t = t_1,\ D = D_1$

$$\frac{D_2^2 - D_1^2}{2} = \frac{2x2.D_{AB}.S_{out}}{\rho}.t_1$$

where t_1 = time for outer layer to dissolve

$$t_1 = \frac{0.0354x(0.4^2 - 0.3^2)}{8x(6x10e-4)x1.0} = 0.52\ \text{min}$$

Inner core :

Boundary conditions : $t = 0,\ D = D_1$
$t = t_2,\ D = 0$

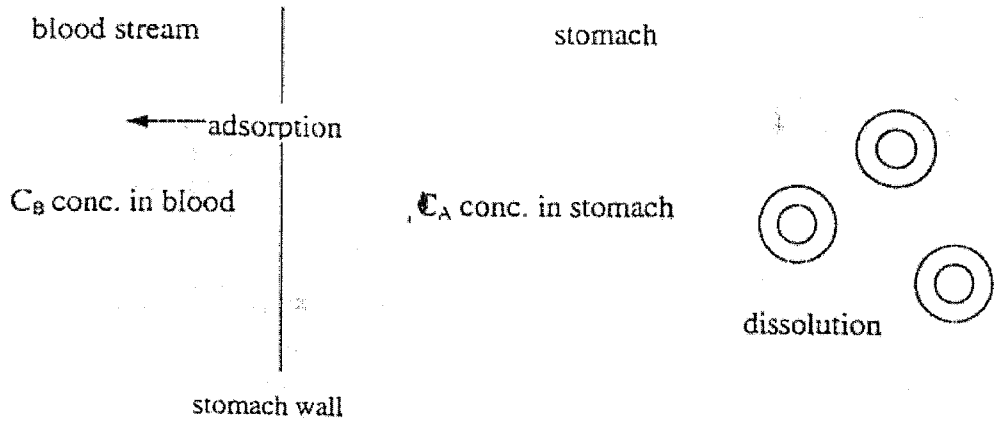
$$\frac{D_1^2}{2} = \frac{2x2.D_{AB}.S_{out}}{\rho}.t_2$$

where t_2 = time for inner core to dissolve

$$t_2 = \frac{0.0354x0.3^2}{8x(6x10e-4)x0.4} = 1.66\,\text{min}$$

time for complete dissolution , $t_T = t_1 + t_2 = 0.52 + 1.66 = 2.18$ min

P10-12 (b)



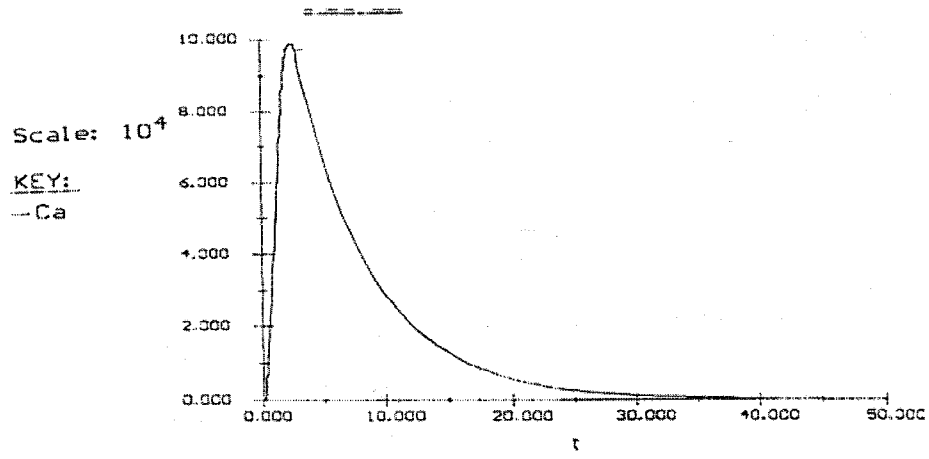
Let rate of adsorption into bloodstream

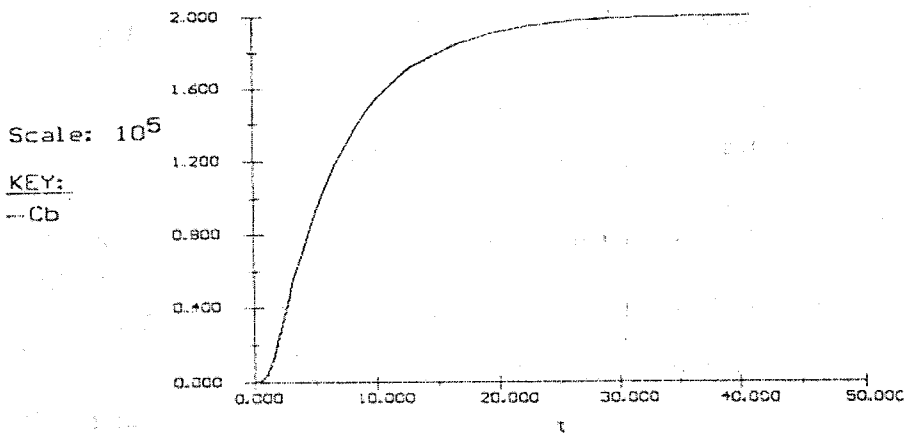
$$-r_A'' = k_A.C_A$$

Relate concentration in stomach C_A , to concentration in blood C_B :

Mol balance on drug in bloodstream : $$-r_A'' = \frac{dC_B}{dt}$$

$$\frac{dC_B}{dt} = k_A.C_A$$





P10-12 (c)

The graph of C_B against time shows how the drug concentration in the bloodstream initially varies with time and then becomes independent of time as all the drug initially in the stomach has absorbed into the blood (consumption of the drug within the bloodstream has not been modelled, unrealistic but no data). If a certain drug level is specified, and assuming a constant size of inner core (drug) and that the pills were to be taken similtaneously, then the way to achieve this would be to use pills of different outer layer thicknesses to maintain an even stomach concentration and hence absorption rate over the whole period.

Relate D with time : $\dfrac{dD}{dt} = \dfrac{2.k_c.S_{in}}{\rho} = \dfrac{4.D_{AB}.S_{in}}{D.\rho}$

and boundary conditions : $t = t_1$, $D = D_1$

$t = t_2$, $D = 0$

Using logic to obtain the correct timing for the drug concentration profiles inside the stomach for each pill, the total profile is used in the relation with the concentration profile in the bloodstream.

P11-12C

Equations:	Initial value
d(D1)/d(t)=if(t>0.24)then(if(D1>0.00001)then(-4*Dab*Sin/(D1*rho))else(0))else(0)	0.3
d(Cb)/d(t)=ka*Ca*V/Wbody	0
d(Ca1)/d(t)=if(t>0.24)then(2*Dab*Sin*3.14*D1/V)else(0)	0
d(Ca2)/d(t)=if(t>0.52)then(2*Dab*Sin*3.14*D2/V)else(0)	0
d(D2)/d(t)=if(t>0.52)then(if(D2>0.00001)then(-4*Dab*Sin/(D2*rho))else(0))else(0)	0.3
d(Ca3)/d(t)=if(t>1.18)then(2*Dab*Sin*3.14*D3/V)else(0)	0
d(D3)/d(t)=if(t>1.18)then(if(D3>0.00001)then(-4*Dab*Sin/(D3*rho))else(0))else(0)	0.3

Dab=0.0006
Sin=400
rho=35.4
ka=0.166667
V=1200
Wbody=75000
Ca=Ca1+Ca2+Ca3-(Cb*Wbody/V)

$t_0 = 0, \quad t_f = 45$

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	45	0	45
D1	0.3	0.3	9.9965e-06	9.9965e-06
Cb	0	2.00164e-05	0	2.00164e-05
Ca1	0	0.000417376	0	0.000417376
Ca2	0	0.000417373	0	0.000417373
D2	0.3	0.3	9.99774e-06	9.99774e-06
Ca3	0	0.000417364	0	0.000417364
D3	0.3	0.3	9.99841e-06	9.99841e-06
Dab	0.0006	0.0006	0.0006	0.0006
Sin	400	400	400	400
rho	35.4	35.4	35.4	35.4
ka	0.166667	0.166667	0.166667	0.166667
V	1200	1200	1200	1200
Wbody	75000	75000	75000	75000
Ca	0	0.00099118	0	1.09044e-06

Relate D with time : $\frac{dD}{dt} = -\frac{2.k_c.S_{in}}{\rho} = -\frac{4.D_{AB}.S_{in}}{D.\rho}$

and boundary conditions : $t = t_1 , D = D_1$

$t = t_2 , D = 0$

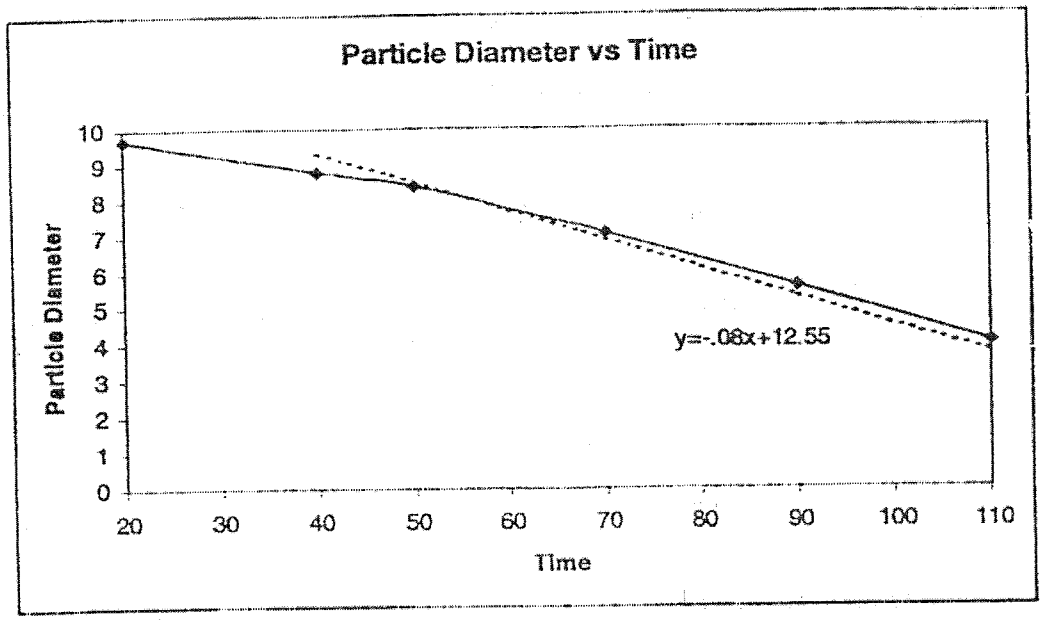
Using logic to obtain the correct timing for the drug concentration profiles inside the stomach for each pill, the total profile is used in the relation with the concentration profile in the bloodstream.

P10-12 (d)

To maintain constant drug level by maintaining a constant stomach concentration, time needs to be allowed for the dissolution of the outer layer. for a given period of say 3 hours, a size distribution of outer layers is needed, with thin layers for initial response and thicker layers for delayed response. This distribution would be back calculated given the necessary stomach concentration for the required bloodstream concentration accounting for bloodstream drug consumption. Optimization of the stomach concentration will indicate the times at which complete dissolution of the outer layer of the 'next' pill is required to maintain this level. The range of pill sizes depends on the number of pills which can be reasonably consumed in one sitting, the period for effect and the limits of practical pill size.

P11-13

The plot of the data is shown below



Initially the rate of incineration of the droplet in terms of diameter, is non-linear, but apparently becomes linear after ~ 50 time units. The linear form of the data indicates that the diameter is directly proportional to time and the rate of decrease in diameter is constant and hence not a function of diameter. This relationship should make it easier to estimate the required incineration time for complete destruction (zero diameter).

Assuming that rate of diameter decrease continues at the linear rate until complete destruction (at time t_d and hence complete decomposition of the POHC's, the equation for the linear relation indicates t_d ~ 160 units.

P11-14

Mol balance on layer of earth control volume:

$$F_{A|_z} - F_{A|_{z+\Delta z}} = A_c \cdot \Delta z \cdot \frac{dC_A}{dt} \qquad \text{but } F_A = A_c \cdot W_A$$

$$\frac{A_c \cdot W_{A|_z} - A_c \cdot W_{A|_{z+\Delta z}}}{A_c \cdot \Delta z} = -\frac{dC_A}{dt}$$

$$z \to 0 \qquad \frac{dW_A}{dz} = -\frac{dC_A}{dt}$$

For dilute solution and constant total concentration : $W_A = -D_{AB} \cdot \frac{dC_A}{dz}$

Gives : $D_{AB} \frac{d^2 C_A}{dz^2} = \frac{dC_A}{dt}$

Let $\psi = \frac{C_A}{C_{AO}}$ gives $D_{AB} \frac{d^2 \psi}{dz^2} = \frac{d\psi}{dt}$

Boundary conditions :

$t = t$ (present day) $z = 0$ (surface), $\psi = 0$

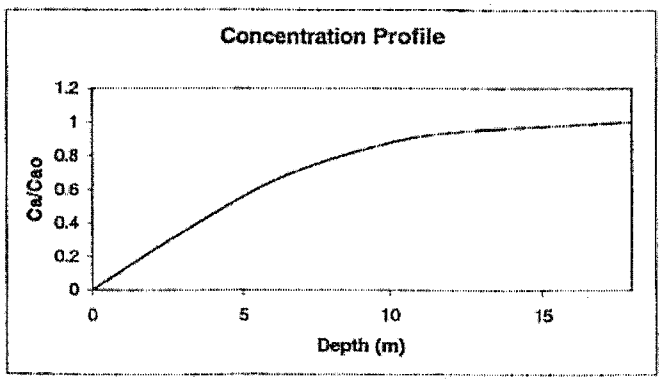
$z = \infty$, $\psi = 1$

$t = 0$ (end of glacial), $z > 0$, $\psi = 1$

Gives the error function : $\psi = erf \frac{z}{\sqrt{4 \cdot D_{AB} t}}$ let $\eta = \frac{z}{\sqrt{4 \cdot D_{AB} \cdot t}}$

It is defined that at $\eta = 1.82$, $C_A = 0.01\ C_{AO}$ and for $\eta > 1.82$, C_A is negligibly small.

This defines the penetration thickness, δ (as a function of time) : $1.82 = \frac{\delta}{\sqrt{4 \cdot D_{AB} \cdot t}}$



But the graph gives at , $C_A = 0.01\ C_{AO}$ $\rightarrow$ $z = 0.4$ hence $\delta = 18 - 0.4$ m , the penetration thickness after time t.

The time taken for δ to reach this thickness, is the time since the diffusion started (i.e. at the end of the last glacial)

$$t = \left(\frac{17.6}{1.82}\right)^2 \frac{1}{2x2.64x10e-10} \frac{1}{3600x24x365} = 5616 years$$

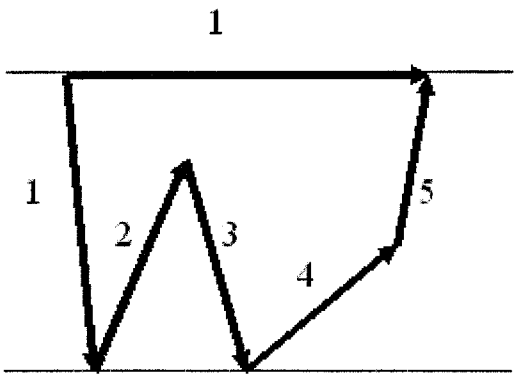
CDP11-A
CDP11-B
CDP11-C
CDP11-D
CDP11-E
CDP11-F
CDP11-G
CDP11-H
CDP11-I
CDP11-J
CDP11-K
CDP11-L
CDP11-M

Solutions for Chapter 12 – Diffusion and Reaction in Porous Catalysts

P12-1 Individualized solution

P12-2 (a)

(i) $\tau = 5$



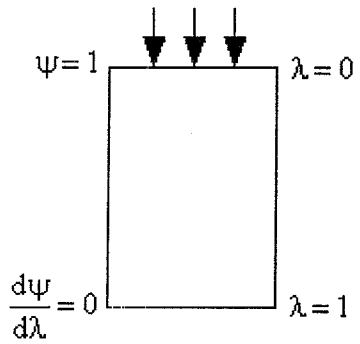
(lines and angles not to scale)

$$D_e \sim D_{AB} \sim \frac{T}{P}$$

$$D_{ex} \sim D_{e1} \sim \frac{P_1}{P}\left(\frac{T_2}{T_1}\right)^{1.75}$$

P12-2 (b)

(1) First Order Reaction Kinetics



$$D_e \frac{d^2C_A}{dz^2} - kC_A = 0\,,\ \psi = \frac{C_A}{C_{A0}}\,,\ \lambda = \frac{z}{b}$$

$$\frac{d^2\psi}{d\lambda^2} - \mathbf{Da}\psi = 0 \qquad \mathbf{Da} = \frac{kb^2}{D_e}$$

$$\psi = A\cosh\sqrt{\mathbf{Da}}\lambda + B\sinh\sqrt{\mathbf{Da}}\lambda$$

$$\frac{d\psi}{d\lambda} = A\sqrt{\mathbf{Da}}\sinh\sqrt{\mathbf{Da}}\lambda + B\sqrt{\mathbf{Da}}\cosh\lambda$$

Symmetry $\frac{d\psi}{d\lambda} = 0$ @ $\lambda = 1$ $\therefore$

$$B = -A\frac{\sinh\sqrt{\mathbf{Da}}}{\cosh\sqrt{\mathbf{Da}}} = -A\,\mathrm{Tanh}\sqrt{\mathbf{Da}}$$

$\psi = 1$ @ $\lambda = 0$

$$1 = A\cosh\sqrt{\mathbf{Da}}$$

$$A = \frac{1}{\cosh\sqrt{\mathbf{Da}}}\ ,\quad B = \frac{\mathrm{Tanh}\sqrt{\mathbf{Da}}}{\cosh\sqrt{\mathbf{Da}}}$$

$$\psi = \frac{\cosh\sqrt{\mathbf{Da}}\ \lambda}{\cosh\sqrt{\mathbf{Da}}} - \frac{\mathrm{Tanh}\sqrt{\mathbf{Da}}}{\cosh\sqrt{\mathbf{Da}}}\sinh\sqrt{\mathbf{Da}}\ \lambda$$

(2) Monod Kinetics

$$D_e\frac{d^2C_A}{dz^2} - \frac{\mu_{max}C_AC_C}{K_S + C_A} = 0$$

$$\frac{dC_C}{dz^2} = \frac{\mu_{max}C_AC_C}{K_S + C_A} = 0$$

Use Quasi Steady State Analysis

No further solution to Monod Kinetics will be given.

(3) Variable Diffusion Coefficient

$$\boxed{\frac{dF_w}{dt} = \upsilon_c W_{O2}|_{z=0} A_c}$$

$$W_A = -D_e\frac{dC_A}{dz} = -\frac{D_eC_{A0}}{L}\frac{d\psi}{d\lambda}\bigg|_{\lambda=0}$$

$$\frac{dF_w}{dt} = \frac{D_eC_{A0}}{L}\frac{d\psi}{d\lambda}\bigg|_{\lambda=0}\upsilon_c A_c/V$$

Mole balance

$$\frac{d\left[D_e\dfrac{dC_A}{dz}\right]}{dz} - k = 0$$

for hindered diffusion

$$D_e = \frac{D_{AB}}{1 + \alpha^2 F_w^2/(1 - F_w)}$$

As a first approximation, assume no variation in D_e with λ

$$\frac{d^2\psi}{d\lambda^2} - \frac{kL^2}{D_eC_{A0}} = 0$$

as before

$$\phi_0 = \frac{kL^2}{2D_eC_{A0}}$$

$$\frac{d^2\psi}{d\lambda^2} - 2\phi_0 = 0$$

Solution the same as before Equation (E12-2.13)

$$\psi = \phi_0\lambda(\lambda-2)+1$$

$$W_A = -D_e\left.\frac{dC_A}{dz}\right|_{z=0} = -\frac{D_eC_{A0}}{L}\left.\frac{d\psi}{d\lambda}\right|_{\lambda=0}$$

$$\left.\frac{d\psi}{d\lambda} = (2\phi_0\lambda - 2\phi_0)\right|_{\lambda=0} = -2\phi_0 = -\frac{2kL^2}{2D_eC_{A0}}$$

$$W_{O_2} = W_A = \left(-\frac{D_eC_{A0}}{L}\right)\left(-\frac{kL^2}{D_eC_{A0}}\right) = kL$$

The flux of O_2 in does not depend upon D_e which is not uprising since this reaction is zero order. For the build up of material that hinders diffusion

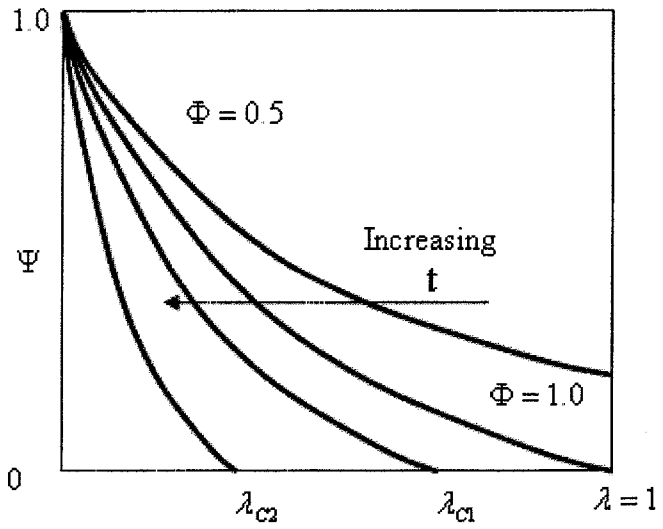
$$\frac{dF_W}{dt} = \upsilon_c A_c kL = A_c Lk = kV$$

$$F_W = kVt$$

From a quasi steady state approximation as time goes on F_W increases D_e decreases and ϕ_0 increases.

However, the point at which the oxygen concentration is equal to zero has to be found. We can parallel the analysis used in P12-10 switching the coordinates of $\lambda = 0$ and $\lambda = 1$ (see solution to P12-10(c) in which the solution manual) we will find

$$\lambda_c = \frac{1}{\phi_0}$$



We see that as t increases λ_c decreases, that is the point at which the oxygen concentration is zero moves toward the top of the gel.

P12-2 (c)

(1) For R_1 $\eta_1 = 0.182$ 18.2% Surface reaction limited and 81.8% Diffusion limited

For R_2 $\eta = 0.856$ 85.6% Surface reaction limited and 14.6% diffusion limited

(2) $$C_{WP} = \frac{-r_A(obs)\rho_c R^2}{D_e C_{As}} = \eta\phi_1^2 \qquad (12\text{-}59)$$

$$= (0.95)(0.9)^2 = 0.77$$

which is less than 1 so there are no significant diffusion limitations.

P12-2 (d)

$$\Omega = \frac{\eta}{1 + \frac{k_1'' S_a \rho_b}{k_c a_c}}$$

$$= \frac{1}{\frac{1}{\eta} + \frac{k'' S_a \rho_b}{k_c a_c}}$$

$\Omega = 0.059$ So 5.9% surface reaction resistance and 94/1% external and internal diffusion limited

$$\%R = \frac{0.941}{\frac{1}{\eta} + \frac{k'' S_a \rho_b}{k_c a_c}} = \frac{0.941}{6.0 + 10.96} == \frac{0.941}{16.96}$$

$$\%\text{ Internal diffusion reaction } 0.941 \times 100 \times \frac{6.0}{16.96} = 33.3\%$$

$$\%\text{ External diffusion resistance} = (0.941)(100) \times \frac{10.96}{16.96} = 60.8\%$$

Summary of Resistances	
External Diffusion	60.8%
Internal Diffusion	33.3%
Surface Reactor	5.9%
	100.0%

Increase temperature significantly. Surface reaction % resistance decreases. Increase gas velocity external resistance decreases decrease pellet size both internal and external resistances decrease. For 99.99% Conversion

$$L_2 = L_1 \ln\frac{1}{1-X_2} \ln\frac{1}{1-X_2} \Big/ \ln\frac{1}{1-X_1} = 0.16 \frac{\ln(10{,}000)}{\ln 500}$$

$$= 0.16 \times \frac{9.2}{6.21} = 0.24\text{m}$$

P12-2 (e)

(j) From Mears's Criterion

$$\left|\frac{-\Delta H_{Rx}(-r'_A)\rho_b RE}{hT^2R_g}\right| < 0.15 \qquad 1)$$

The value from the question

$\Delta H_{Rx} = -25\text{kcal/mol} = -104.6\text{kJ/mol}$

$h = 100\text{BTU/h}\cdot\text{ft}^2\cdot{}^\circ\text{F} = 0.567\text{kJ/s.m}^2\cdot\text{K}$

$E = 20\text{kcal/mol} = 83.682\text{kJ/mol}$

$Rg = 8.3144 * 10^{-3}\text{kJ/mol.K}$

From example 12.3

$-r'_A = kS_aC_{NO}$

$k = 4.42 * 10^{-10}\text{m}^3/\text{m}^2\cdot\text{sec}$

$S_a = 530\text{m}^2/\text{g}$

$\rho_b = (1-\phi)\rho_c = (1-0.5)(2.8*10^6) = 1.4*10^6\text{g/m}^3$

$R = 3*10^{-3}\text{m}$

$T = 1173\text{K}$

At the inlet of the reactor the fraction of NO =0.02

From ideal gas law

$$\frac{n}{V} = \frac{P}{RT}$$

$$= \frac{1.01325*10^5}{8.3144*1173} = 10.39\text{mol/m}^3$$

$C_{NO} = 0.02*10.39 = 0.2078\text{mol/m}^3$

Substituting all value in the first equation

$$\left|\frac{(104.6)((4.42*10^{-10})(530)(0.2078))(1.46*10^6)(3*10^{-3})(83.682)}{(0.567)(1173^2)(8.3144*10^{-3})}\right| = 2.88*10^{-4}$$

As the calculated result is lower than 0.15, there is not the temperature gradient. The bulk fluid temperature will be virtually the same as the temperature at the external surface of the pellet.

P12-2 (f)

(k) For $\gamma = 30$ use Figure 12-7.

If you draw a vertical line up from $\phi_1 = 0.4$ it should be tangent (or very, very close) to the $\beta = 0.4$ curve. Any slight increase in temperature will cause the reaction to go to upper steady state.

P12-2 (g)

(l) $$a = \frac{1}{1+k_0t} \quad , \quad \phi_1 = \underline{R}\sqrt{\frac{k''\rho_c S_a}{D_e}}$$

For large ϕ

$$\eta = \frac{3}{R}\sqrt{\frac{D_e}{k}} = \frac{3}{R}\sqrt{\frac{D_e}{k''\rho_c S_a}}$$

$$S_a' = \frac{S_a}{1+k_D t}$$

(1) Pore closure. Consider D_e As $t \to \infty$ pore throat closes $\beta = \frac{\text{Area 2}}{\text{Area 1}} \to \infty$, $\sigma_c \to 0$, $D_e \to 0$, and $\phi_1 \to \infty$ $-r_A' \to 0$

(2) Loss of surface area S_a. As $t \to \infty$ then $S_a' \to 0$ then $\phi \to 0$ $\eta \to 1$, but $-r_A' = \sqrt{S_a} \to 0$

P12-2 (h)

(m) The activation energy will be larger than that for diffusion control and hence the reaction is more temperature sensitive. If the apparent reaction order is greater than one half, then the rate of reaction will be less sensitive to concentration. If it is less than one half, the true order will be negative and the rate will increase significantly at low concentration.

P12-2 (i)

In example CDR12-1, the reactor is 5 m in diameter and 22 m high, whereas the reactor in CDR12-2 is only 2 m^3 in volume. The charge is much different. In CDR12-1 the charge is 100 kg/m^3 and in CDR12-2 it is only 3.9 kg/m^3

P12-2 (j) No solution will be given at this time

P12-2 (k)

With the increase in temperature, the rate of reaction will increase. This will cause the slope of C_i/R_i vs. 1/m and, therefore, the resistance to decrease.

P12-2 (l) No solution will be given at this time.

P12-3 (a) Yes

P12-3 (b)

All temperatures, F_{T0} = 10 mol/hr. The rate of reaction changes with flow rate and increases linearly with temperature

P12-3 (c) Yes

P12-3 (d)

T < 367 K, F_{T0} = 1000 mol/hr, 5000 mol/hr.
T < 362 K, F_{T0} = 100 mol/hr.

P12-3 (e) Yes

P12-3 (f)

T > 367 K, F_{T0} = 1000 mol/hr, 5000 mol/hr.

T > 362 K, F_{T0} = 100 mol/hr.

P12-3 (g)

$$\Omega = \frac{\text{actual rate of reaction}}{\text{ideal rate of reaction}} = \frac{-r_A\left(at\ 362\,K, F_{T0} = 10\,mol/hr\right)}{-r_A\left(at\ 362\,K, F_{T0} = 5000\,mol/hr\right)}$$

$$\Omega = \frac{0.26}{0.70} = 0.37$$

P12-3 (h)

At F_{T0} = 5000 mol/hr, there is non external diffusion limitation, so the external effectiveness factor is 1.

$$\eta = \frac{\text{actual rate of reaction}\left(\text{at } 362\,\text{K},\ F_{T0} = 5000\,mol/hr\right)}{\text{extrapolated rate of reaction}\left(\text{at } 362\,\text{K},\ F_{T0} = 5000\,mol/hr\right)}$$

$$\eta = \frac{1.2}{1.4} = 0.86$$

P12-3 (i)

$$\eta = \frac{3[\phi\cosh\phi - 1]}{\phi^2} = 0.86$$

by iterative solution $\phi = 1.60$

$$\varphi = \frac{C_A}{C_{AS}} = \frac{1}{\lambda}\frac{\sinh(\phi\lambda)}{\sinh\phi}$$

P12-4 (a)

External mass transfer limited at 400 K and d_P = 0.8 cm. Alos at all F_{T0} < 2000 mol/s

P12-4 (b)

Reaction rate limited at T = 300 K and d_P = 0.3 cm. When T = 400 K: d_P = 0.8, 0.1, and 0.03 cm.

P12-4 (c)

Internal diffusion limited at T = 400 K and 0.1 < d_P < 0.8

P12-4 (d)

$$\eta = \frac{\text{rate with } d_P = 0.8}{\text{rate with } d_P = 0.03} = \frac{10}{16} = 0.625$$

P12-5

Curve A is reaction-rate limited. This is so because of the way the curve bends, implying an exponential function which is the equation form for the specific reaction rate with respect to temperature.

Curve B is inner-diffusion limited. This is because it has a dependence on temperature, but that dependence is small.

Curve C is outer-diffusion limited. This curve has a much larger dependace on temperature than curve B.

P12-6 (a)

$$\text{If } \varphi = \frac{C_A}{C_{AS}},\ \lambda = \frac{r}{R},\ \phi_n^2 = \frac{kn\, R^2\, S_a\, \rho_b\, C_{AS}^{n-1}}{D_e}$$

$$\text{Then } \varphi = \left(\frac{1}{\lambda}\right)\frac{\sin h\, \phi_1 \lambda}{\sin h\, \phi_1}$$

Boundary conditions: $\varphi = (\lambda = 1) = 1$

$\varphi = (\lambda = 0) = \text{finite}$

Effectiveness factor: $\eta = \frac{3}{\phi_1^2}(\phi_1 \cos h\, \phi_1 - 1)$ first order reaction.

At $r = \frac{R}{2}$, $\lambda = \frac{1}{2}$, $C_A = 0.1\, C_{AS}$ where $C_{AS} = 1 \times 10^{-3}\ \frac{\text{mole}}{\text{l}}$

$$\lambda = \frac{7 \times 10^{-4}}{1 \times 10^{-3}} = 0.7$$

$R = 1 \times 10^{-3}$ cm

$D_C = 0.1\ \text{cm}^2/\text{sec}$

$$\varphi = \left(\frac{1}{\lambda}\right)\left(\frac{\sin h\, \phi_1 \lambda}{\sin h\, \phi_1}\right)$$

$$\text{At } \lambda = \frac{1}{2},\ \varphi = 0.1 : 0.1 = 2\left[\frac{\sin h\,(\phi_1/2)}{\sin h\,(\phi_1)}\right] \Rightarrow \phi_1 = 6.0$$

$$\therefore\quad \varphi = \frac{1}{0.7}\left[\frac{\sin h\,(6 \times 0.7)}{\sin h\, 6}\right]$$

$$\frac{C_A}{1 \times 10^{-3}} = \frac{1}{0.7}\left[\frac{e^{4.2} - e^{-4.2}}{e^{6} - e^{-6}}\right]$$

$$C_A = 2.36 \times 10^{-4}\ \frac{\text{g mol}}{\text{l}}$$

P12-6 (b)

$$\eta = \frac{3}{\phi_1^2}\left[\phi_1 \cos h\, \phi_1 - 1\right] = 0.80 \Rightarrow \phi_1 = 2.04$$

$$\phi_1^2 = \frac{k\, R^2\, S_A\, \rho_B}{D_e}$$

$$\text{At } \lambda = \frac{1}{2},\ \varphi = 0.1 : \phi_1 = 6 \text{ (see part (a))}$$

P12-6 (c) Individualized solution

P12-7 (a)

Start with a mole balance:

$$WA|_{z} - WA|_{z+\Delta z} + r_A A\Delta z = 0$$

Divide by AΔz and take the limit as z --> 0.

$$\frac{dW}{dz} - r_A = 0$$

From the flux equation:

$$W = -D_e \frac{dC_A}{dz}$$

Combining the two equations we get:

$$\frac{d\left[-D_e\, dC_A/dz\right]}{dz} + k = 0$$

Dividing by -D_e we get:

$$\frac{d^2C_A}{dz^2} + \frac{k}{D_e} = 0$$

We need boundary conditions

B.C. (1): $\frac{dC_A}{dz} = 0 \;@\; z = L$

B.C. (2): $C_A = C_{A0} \;@\; z = 0$

We can then solve for the concentration profile:

$$\frac{dC_A}{dz} = \frac{kz}{D_e} + C_1$$

Using boundary condition (1):

$$0 = \frac{kL}{D_e} + C_1$$

$$C_1 = -\frac{kL}{D_e}$$

$$\frac{dC_A}{dz} = \frac{kz}{D_e} - \frac{kL}{D_e}$$

Integrating again:

$$dC_A = \left(\frac{kz}{D_e} - \frac{kL}{D_e}\right)dz$$

$$C_A = \frac{k}{2D_e}z^2 - \frac{kL}{D_e}z + C_2$$

From boundary condition 2 $C_{A0} = C_2$

$$C_A = \frac{k}{2D_e}z^2 - \frac{kL}{D_e}z + C_{A0}$$

P12-7 (b)

$$\eta = \frac{\text{rate of reaction with diffusion}}{\text{rate of reaction without diffusion}}$$

$$\eta = \frac{\dfrac{2D(C_A - C_{A0})}{z(z-2L)}}{\dfrac{k}{}} = \frac{2D(C_A - C_{A0})}{k\,z(z-2L)}$$

P12-7 (c)

Boundary conditions: $C_A = 0$ at $z = L$

$$0 = \frac{kL}{D}\left(\frac{L}{2} - L\right) + C_{A0}$$

$$C_{A0} = \frac{kL^2}{2D}$$

$$L = \sqrt{\frac{2D\,C_{A0}}{k}} = \sqrt{\frac{2(3.6\times10^{-6}\ \text{cm}^2/\text{s})(4.36\times10^{-5}\ \text{mol/cm}^3)}{(2.3\times10^{-15}\ \text{mol/s})/(3\times10^{-10}\ \text{cm}^2)(L\ \text{cm})}}$$

$$L^{1/2} = 0.0640$$

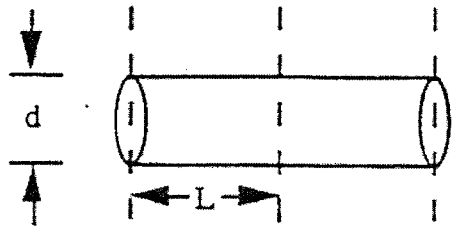
$$L = 0.0041\ \text{cm} = 41\ \mu\text{m}$$

P12-7 (d)

The answer in part (c) is equal to the average tail length.

$\eta = 1$ in this problem. If $\eta = 1$, then it contradicts the assumption of diffusion being rate-limiting.

P12-8



First-order irreversible reaction: $A \rightarrow B$

$$-r_A'' = k C_A$$

$$W_A = -D \frac{dC_A}{dz}$$

Mole balance: $-\frac{\pi}{d} d^2 \left(\frac{dW_A}{dz}\right) + \pi d r_A'' = 0$

$$\frac{d}{4} D \left(\frac{d^2 C_A}{dz^2}\right) - k C_A = 0$$

$$\frac{C_{AS}}{L^2} \left(\frac{d^2 \psi}{d\lambda^2}\right) - \left(\frac{4k}{Dd}\right) C_{AS} \psi = 0$$

$$\Rightarrow \phi^2 = \left(\frac{4k L^2}{Dd}\right)$$

Concentration distribution: $C_A = C_{AS} \left(\frac{\cos h\left[\phi\left(1 - \frac{z}{L}\right)\right]}{\cos h\, \phi}\right)$

$L = 10^{-3}$ cm, $2L = 2 \times 10^{-3}$ cm

$C_{AS} = 10^{-3}$ g mole/l

$D = 0.1$ cm^2/sec

At $z = L$, $C_A = \frac{1}{10} C_{AS} = C_{AS} \left(\frac{\cos h\left[\phi\left(1 - \frac{L}{L}\right)\right]}{\cos h\, \phi}\right)$

$$\frac{1}{10} = \frac{1}{\cos h\, \phi}$$

$\phi = 2.9932$

P12-8 (a)

At z = 1/2 L: $$C_A = C_{AS}\left(\frac{\cos h\left[\phi\left(1 - \frac{0.5L}{L}\right)\right]}{\cos h\,\phi}\right)$$

$$C_A = (0.001)\left(\frac{\cos h\,[2.9932(0.5)]}{\cos h\,(2.9932)}\right)$$

$$C_A = 2.345 \times 10^{-4}\ \text{g mol/l}$$

P12-8 (b)

$$\phi = 2L\sqrt{\frac{k}{Dd}} \Rightarrow \phi \alpha (2L)$$

$$\eta_{old} = \frac{\tan h\,\phi_{old}}{\phi_{old}} = \frac{\tan h\,(2.9932)}{2.9932} = 0.3324$$

$$\eta_{new} = 0.8 = \frac{\tan h\,\phi_{new}}{\phi_{new}} \Rightarrow \phi_{new} = 0.8880$$

$$2L_{new} = 2L_{old}\left(\frac{\phi_{new}}{\phi_{old}}\right) = (2 \times 10^{-3})\left(\frac{0.8880}{2.9932}\right) = 5.993 \times 10^{-4}\ \text{cm}$$

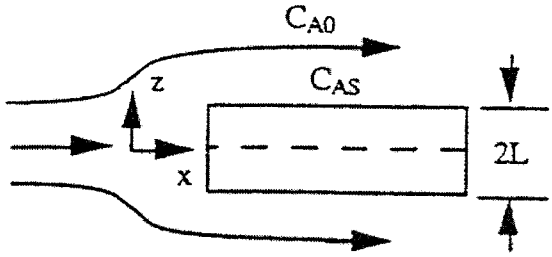
P12-8 (c)

$$\text{At } z = L.\ C_A = \frac{C_{AS}}{\cos h\,\phi_{new}} = \frac{0.001}{\cos h\,(0.8880)} = 7.038 \times 10^{-4}\ \text{g mol/l}$$

Thus minimum C_A is now 70.38% of C_{AS}. Therefore the suggestion is plating entire surface of the inside of the pore.

P12-8 (d) Individualized solution

P12-9 (a)



Define $W_A > 0$ in direction of increasing z.

Material balance:

$$W_A A_P|_z - W_A A_P|_{z+\Delta z} + -\bar{r}_A'' a A_P \Delta_z = 0$$

$-\bar{r}_A'' = k C_A'$; $W_A = -D_e \frac{dC_A}{dz} + C_A V \equiv -D_e \frac{dC_A}{dz}$ for small C_A

Taking $\Delta z \to 0$: $-A_P \frac{dW_A}{dz} + \bar{r}_A'' a A_P = 0$

$$A_P \frac{d}{dz}\left(D_e \frac{dC_A}{dz}\right) - k C_A a A_P = 0$$

For constant D_e; $D_e \frac{d^2 C_A}{dz^2} - k C_A a = 0$

Boundary conditions: $z = L \quad C_A = C_{AS}$

$$z = 0 \quad \frac{dC_A}{dz} = 0 \text{ by symmetry}$$

$\frac{d^2 C_A}{dz^2} - \alpha^2 C_A = 0$ where $\alpha^2 = \frac{k a}{D_e}$

Assume $C_A = e^{rz}$, then $r^2 - \alpha^2 = 0 \qquad r = \pm\alpha$

$$C_A = A_1 e^{-\alpha z} + A_2 e^{\alpha z}$$

At $z = L$: $C_{AS} = A_1 e^{-\alpha L} + A_2 e^{\alpha L}$

$$\frac{dC_A}{dz}\Big|_{z=0} = 0 = -\alpha A_1 + \alpha A_2 = 0$$

$$\therefore \quad A_1 = A_2$$

From above: $A_1 = \frac{C_{AS}}{e^{-\alpha L} + e^{\alpha L}}$

$$C_A = C_{AS}\left\{\frac{e^{-\alpha L} + e^{\alpha L}}{e^{-\alpha L} + e^{\alpha L}}\right\}$$

Therefore, concentration profile can be written as:

$$C_A = C_{AS}\left\{\frac{\cos h\,(\alpha z)}{\cos h\,(\alpha L)}\right\}$$

$$W_A A_P = -D_e\left(\frac{dC_A}{dz}\Big|_{z=L}\right) A_P = -A_P D_e C_{AS}\,\alpha\left(\frac{\sin h\,(\alpha z)}{\cos h\,(\alpha L)}\Big|_{z=L}\right)$$

$$W_A A_P = -A_P D_e\,\alpha\, C_{AS} \tan h\,(\alpha L)$$

By the sign convention: $-W_A A_P = \eta\, r_A'' a A_P L = -\eta\, k\, C_{AS}\, a\, A_P L$

$$\therefore\ \eta\, k\, C_{AS}\, a\, A_P L = A_P D_e\,\alpha\, C_{AS} \tan h\,(\alpha L)$$

$$\eta = \left(\frac{\alpha D_e}{k a L}\right)\tan h\,(\alpha L) = \sqrt{\frac{k a}{D_e}}\left(\frac{D_e}{k a}\right)\frac{1}{L}\tan h\left(\sqrt{\frac{k a}{D_e}}\,L\right)$$

$$\eta = \left(\sqrt{\frac{D_e}{k a}}\,\frac{1}{L}\right)\tan h\,(\alpha L)\left(\sqrt{\frac{k a}{D_e}}\,L\right)$$

Overall effectiveness factor: $-W_A A_P = \Omega\, k\, C_{A0}\, a\, A_P L = \eta\, k\, C_{AS}\, a\, A_P L$

or: $\dfrac{\Omega}{\eta} = \dfrac{C_{AS}}{C_{A0}}$

$$-W_A A_P = k_C A_P (C_{A0} - C_{AS}) = \alpha A_P D_e C_{AS} \tan h\,(\alpha L)$$

$$C_{A0} = C_{AS}\left[1 + \frac{\alpha D_e}{k_C}\tan h\,(\alpha L)\right]$$

$$\frac{C_{AS}}{C_{A0}} = \left[\frac{1}{1 + \dfrac{\alpha D_e}{k_C}\tan h\,(\alpha L)}\right]$$

$$\Omega = \frac{\eta}{1 + \dfrac{\alpha D_e}{k_C}\tan h\,(\alpha L)} = \frac{\left(\sqrt{\dfrac{D_e}{k a}}\,\dfrac{1}{L}\right)\tan h\left(\sqrt{\dfrac{k a}{D_e}}\,L\right)}{1 + \sqrt{\dfrac{k a D_e}{k_C}}\tan h\left(\sqrt{\dfrac{k a}{D_e}}\,L\right)}$$

P12-9 (b)

A → B

$$W_A \pi r L\Big|_r - W_A \pi r L\Big|_{r+\Delta r} + r_A \pi r \Delta r L = 0$$

$$\frac{1}{r}\frac{d}{dr} r W_A r + r_A = 0$$

EMCD therefore, $W_A = -D_e \frac{dC_A}{dr}$

$$\frac{1}{r} D_e \frac{d\frac{rdC_A}{dr}}{dr} = D_e \left(\frac{d^2C_A}{dr^2} - \frac{1}{r}\frac{dC_A}{dr} \right)$$

$$r_A = -kC_A$$

$$\frac{1}{r}\frac{d}{dr} rW_A r + r_A = 0$$

$$D_e \left[\frac{d^2C_A}{dr^2} - \frac{1}{r}\frac{dC_A}{dr} \right] - kC_A = 0$$

$$\psi = \frac{C_A}{C_{A0}} \qquad \lambda = \frac{r}{R}$$

$$\frac{d^2\psi}{d\lambda^2} - \frac{1}{\lambda}\frac{d\psi}{d\lambda} - \frac{kR^2\psi}{D_e} = 0$$

$$\frac{d^2\psi}{d\lambda^2} - \frac{1}{\lambda}\frac{d\psi}{d\lambda} - D_a\psi = 0$$

At $\lambda = 1$, $\psi = 1$ and at $\lambda = 1$, $\frac{d\psi}{d\lambda} = 0$

Bessel Function Solution

(n) P12-10 (a)

(o) EMCD $W_A = -D\frac{dC_A}{dz}$, $r_A = -k$

$$In - Out + Gen = 0$$

$$W_A A_c\big|_z - W_A A_c\big|_{z+\Delta z} + r_A \Delta z A_c = 0$$

$$-\frac{dW_A}{dz} + r_A = 0 \quad , \quad \frac{D_A \tilde{d}C_A}{dz^2} - k = 0$$

$$\psi = \frac{C_A}{C_{As}} \quad , \quad \lambda = \frac{Z}{L} \quad , \quad \frac{d^2\psi}{d\lambda^2}\frac{C_{A0}}{L^2} = \frac{d^2C_A}{dz^2}$$

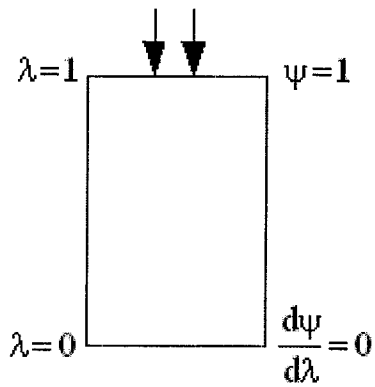
$$\boxed{\frac{d^2\psi}{d\lambda^2} - \frac{kL^2}{D_A C_{As}} = 0} \quad (1)$$

$$\frac{d\psi}{d\lambda} = \frac{kL^2}{D_A C_{As}}\lambda + C_1$$

Using the symmetry B. C.

$$\boxed{\lambda = 0 \quad \frac{d\psi}{d\lambda} = 0}$$

$$C_1 = 0$$



Integrating equation (1)

$$\psi = \frac{kL^2\lambda^2}{2D_A C_{As}} + C_2$$

at $\lambda = 1 \quad \psi = 1$

$$C_2 = 1 - \frac{kL^2}{2D_A C_{As}}$$

$$\psi = 1 + \frac{kL^2}{2DaC_{As}}\left[\left(\lambda^2 - 1\right)\right]$$

$$\phi_0^2 = \frac{kL^2}{2DaC_{As}}$$

$$\boxed{\psi = 1 + \phi_0^2\left[\lambda^2 - 1\right]}$$

P12-10 (b)

(p) Now let's find what value of λ that $\psi = 0$ for different ϕ_0

For $\phi_0^2 = 1$: $0 = 1 + 1\left[\lambda^2 - 1\right] = 1 + \lambda^2 - 1$

$\lambda^2 = 0$

Therefore the concentration is zero (i.e., $\psi = 0$) at

$\boxed{\lambda = 0}$

For $\phi_0^2 = 16$: $0 = 1 + \left[\lambda^2 - 1\right] = 1 + 16\lambda^2 - 16$

$$\lambda^2 = \frac{15}{16} = 0.938$$

Seems okay, but let's look further and calculate the concentration ratio ψ at $\lambda = 0$ for $\phi_0 = 4$.

$$\psi = 1 + 16\left[(0.2)^2 - 1\right] = 1 + 16[0.04 - 1] = -14.9$$

Negative concentration.

(q) **P12-10 (c)**

(r) Let's try again with $\phi_0 = 10$

$$\psi = 1 + (10)^2\left[0.1^2 - 1\right] = 1 - 10^2(0.99)$$

$\psi = 1 - 99 = -99$ not possible

ψ will be negative for any value of ϕ_0 greater than one.

P12-10 (d)

(s) We now need to resolve the problem with the fact that there is a critical value of λ, λ_C, for which both $\psi = 0$ and $\frac{d\psi}{d\lambda} = 0$

$$\frac{d^2\psi}{d\lambda^2} - 2\phi_0^2 = 0$$

$$\frac{d\psi}{d\lambda^2} - 2\phi_0^2\lambda + C_1$$

$$\psi = \phi_0^2\lambda^2 + C_1\lambda + C_2$$

At $\lambda = 1$, $\psi = 1$

$$1 = \phi_0^2 + C_1 + C_2$$

At $\lambda = \lambda_C$, $\psi = 0$

$$0 = \phi_0^2\lambda_C^2 + C_1\lambda_C + C_2$$

Subtracting

$$1 = \phi_0^2 - \phi_0^2\lambda_C^2 + C_1(1 - \lambda_C)$$

Solving for C_1

$$C_1 = \frac{1 - \phi_0^2\left(1 - \lambda_C^2\right)}{1 - \lambda_C}$$

Solving for C_2

$$C_2 = 1 - \phi_0^2 - \frac{\left(1 - \phi_0^2\left(1 - \lambda_C^2\right)\right)}{1 - \lambda_C}$$

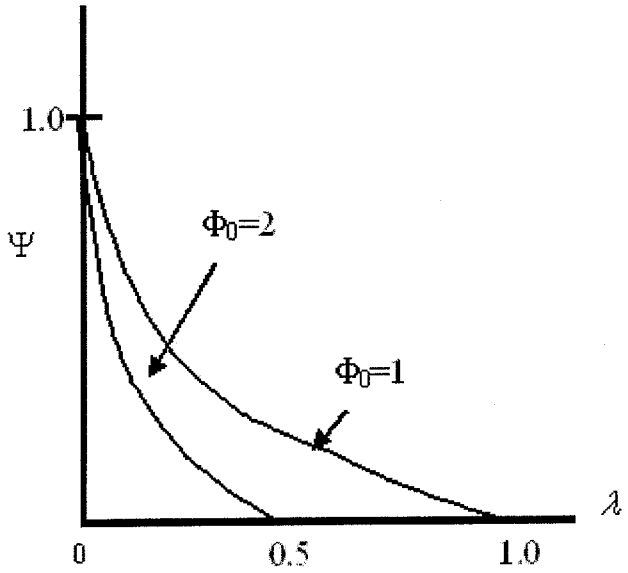
$$\boxed{\psi = \phi_0^2\lambda^2 + \frac{\left(1 - \phi_0^2\left(1 - \lambda_C^2\right)\right)}{1 - \lambda_C}\lambda + 1 - \phi_0^2 - \frac{\left(1 - \phi_0^2\left(1 - \lambda_C^2\right)\right)}{1 - \lambda_C}}$$

At $\lambda = \lambda_C$ then $\frac{d\psi}{d\lambda} = 0 = 2\phi_0^2\lambda_C - \frac{\left(1 - \phi_0^2\left(1 - \lambda_C^2\right)\right)}{1 - \lambda_C}$

$$0 = \phi_0^2\lambda_C^2 - 2\phi_0^2\lambda_C - \left(1 - \phi_0^2\right)$$

$$\lambda_C = 2\phi_0^2 - \frac{\sqrt{4\phi_0^4 - 4\left(\phi_0^2\right)\left(-\left(1 - \phi_0^2\right)\right)}}{2\phi_0^2} = 1 - \frac{\sqrt{4\phi_0^4 + 4\phi_0^2 - 4\phi_0^4}}{2\phi_0^2} = 1 - \frac{\sqrt{4\phi_0^2}}{2\phi_0^2}$$

$$\boxed{\lambda_C = 1 - \frac{1}{\phi_0}}$$



Sketch of concentration profile for different values of ϕ_0

$\phi_0 = 1$ then $\lambda_c = 0$

$\phi_0 = 2$ then $\lambda_c = 0.5$

That is for $\phi_0 = 2$, the concentration of A is zero half way ($\lambda = 0.5$) through the slab.

$$1-\lambda_C = \frac{1}{\phi_0}$$

$$\psi = \phi_0^2\lambda^2 + \left[\phi_0 - \phi_0^2(1+\lambda_C)\right] + 1 - \phi_0^2 - \left[\phi_0 - \phi_0^2(1+\lambda_C)\right]$$

$$= \phi_0^2\lambda^2 + \left[\phi_0 - \phi_0^2 - \phi_0^2 + \phi_0\right]\lambda + 1 - \phi_0^2 - 2\phi_0 + 2\phi_0^2$$

$$\psi = \phi_0^2\lambda^2 + 2\phi_0(1-\phi_0)\lambda + 1 - 2\phi_0 + \phi_0^2$$

For $\lambda > \lambda_c$

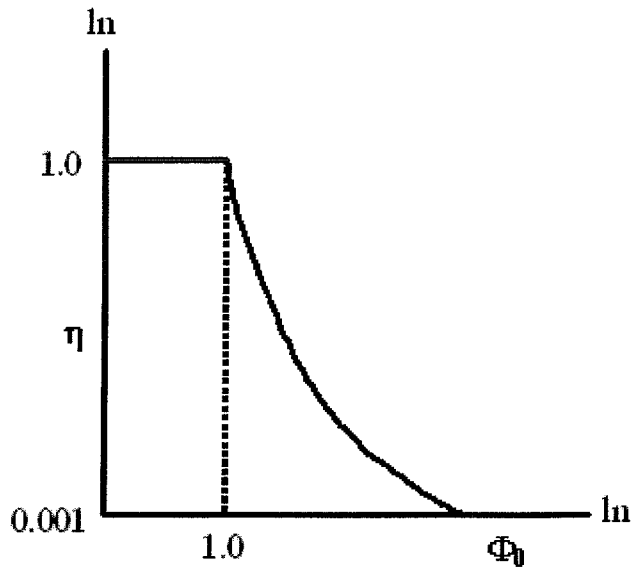
P12-10 (e)

$$\eta = \frac{\int_0^{z_c} -r_A A_c dz + \int_{z_c}^{L} \overbrace{-r_A A_c dz}^{0}}{-r_A A_c dz} = \frac{-r_A A_c z_c + 0}{\int_0^L -r_A A_c dz} = \frac{z_c}{L}$$

$$\boxed{\eta = \frac{z_c}{L} = \lambda_c = 1 - \frac{1}{\phi_0}}$$

$$\boxed{-r_A = 0 \text{ for } z_c < z < L}$$

P12-10 (f)



P12-10 (g) No solution will be given

P12-10 (h) No solution will be given

P12-10 (i) Individualized solution

P12-11

Given: second-order decomposition reaction: $A \rightarrow B + 2C$

$k = 50\ m^6/g\ sec\ mol$; $d_P = 0.4\ cm$; $U = 3\ m/s$; $T = 250°C = 523°K$;

$P = 500\ kP_a = 4.936\ atm$; $X = 0.80$; $D_e = 2.66 \times 10^{-8}\ m^2/s$; $Eb = 0.4$;

$\rho_b = 2 \times 10^6\ g/m^3$; $Sa = 400\ m^2/g$.

$$C_{A0} = \frac{P}{RT} = \frac{4.936\ atm}{\left(0.082 \frac{l\ atm}{g\ mol\ °K}\right) 523\ °K} = 0.115 \frac{g\ mol}{l}$$

Rate law: $-r_A' = k C_A^2$

Mole balance:

$$D_{AB} \frac{d^2 C_A}{dz^2} - U \frac{dC_A}{dz} + r_A' \rho_B = 0$$

$$D_{AB} \frac{d^2 C_A}{dz^2} - U \frac{dC_A}{dz} - \Omega k S_A \rho_B C_A^2 = 0$$

Neglecting axial diffusion with respect to forced axial convection, we have:

$$\frac{dC_A}{dz} = -\left(\frac{\Omega\, k\, S_A\, \rho_B}{U}\right) C_A^2$$

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^2} = \left(\frac{\Omega\, k\, S_A\, \rho_B}{U}\right) \int_0^z dz$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = \left(\frac{\Omega\, k\, S_A\, \rho_B}{U}\right) z$$

At z = L: $\quad \frac{1}{C_{A0}} = \left(\frac{1}{1 - X} - 1\right) = \left(\frac{-2\rho_B\, k\, S_A}{U}\right) L$

$$L = \left(\frac{U}{\Omega\, \rho_B\, k\, S_A\, C_{A0}}\right)\left(\frac{1}{1 - X} - 1\right)$$

Internal effective factor: $\quad \eta = \left(\frac{2}{n+1}\right)^{1/2} \frac{3}{\phi_n}$ where n = 2

$$\phi_2 = R\sqrt{\frac{k\, S_A\, \rho_B\, C_{A0}}{D_e}}$$

$$\phi_2 = 0.2 \times 10^{-2}\, m \sqrt{\frac{\left(50 \frac{m^2}{g\ s\ mol}\right)\left(400 \frac{m^2}{g}\right)\left(2 \times 10^6 \frac{g}{m^2}\right)\left(0.115 \frac{g\ mol}{l}\right)\left(\frac{10^3\, l}{m^3}\right)}{2.66 \times 10^{-8} \frac{m^2}{s}}}$$

$\phi_2 = 2.63 \times 10^7$ very large

$$\eta = \left(\frac{2}{2+1}\right)^{1/2} \frac{3}{2.63 \times 10^7} = 9.313 \times 10^{-8}$$

Internal-diffusion limited: $\quad \Omega = \eta = 9.313 \times 10^{-8}$

Reactor length:

$$L = \frac{3\ m/s\left(\frac{1}{1 - 0.8} - 1\right)}{\left(9.313 \times 10^{-8}\right) 2 \times 10^6 \frac{g}{m^3}\left(50 \frac{m^6}{g\ s\ mol}\right)\left(400 \frac{m^2}{g}\right)\left(115 \frac{g\ mol}{m^3}\right)}$$

$L = 2.80 \times 10^{-5} m$

P12-12 (a)

Start with the mole balance taken on a shell

$$W_{Ar}2\pi rl\Big|_z - W_{Ar}2\pi rl\Big|_{z+\Delta z} + r'_A\rho_c 2\pi rl\Delta r = 0$$

Divide by -2πlΔr and take the limit as Δr approaches zero to get:

$$\frac{d(W_{Ar}r)}{dr} - r'_A\rho_c r = 0$$

Next find the equation for equimolar counterdiffusion and plug it into the above equation:

$$\frac{d\left(r\left(-D_e\, dC_A/dr\right)\right)}{dr} - r'_A\rho_c r = 0$$

Next differentiate to get the following differential equation:

$$\frac{d^2C_A}{dr^2} + \frac{1}{r}\frac{dC_A}{dr} - \frac{k_n\rho_C S_a C_A}{D_e} = 0$$

We can then set the following:

$$\varphi = \frac{C_A}{C_{AS}} \qquad \lambda = \frac{r}{R}$$

$$\frac{d^2\varphi}{d\lambda^2} + \frac{1}{\lambda}\frac{d\varphi}{d\lambda} - \frac{k_n\rho_C S_a R^2}{D_e}\varphi = 0 \qquad \Phi_0^2 = \frac{k_n\rho_C S_a R^2}{D_e}$$

$$\lambda^2\frac{d^2\varphi}{d\lambda^2} + \lambda\frac{d\varphi}{d\lambda} - \Phi_0^2\lambda^2\varphi = 0$$

Solution:

$$\varphi = C_1 I_0(\Phi\lambda) + C_2 K_0(\Phi\lambda)$$

Boundary Conditions:

$$\varphi = 1 @ \lambda = 1$$

$$\frac{d\varphi}{d\lambda} = 0 @ \lambda = 0$$

$$\frac{d\varphi}{d\lambda} = \Phi[C_1 I_1(\Phi\lambda) - C_2 K_1(\Phi\lambda)]$$

$$I_1(0) = 0$$

$$K_1(0) = \infty$$

$$\text{as } \left.\frac{d\varphi}{d\lambda}\right|_{\lambda=0} \to 0 \Rightarrow C_2 = 0$$

$$\varphi = C_1 I_0(\Phi\lambda)$$

$$1 = C_1 I_0(\Phi) \Rightarrow C_1 = \frac{1}{I_0(\Phi)}$$

$$\varphi = \frac{I_0(\Phi\lambda)}{I_0(\Phi)}$$

P12-12 (b)

P12-13 (a)

(t) $$\frac{1}{r^2}\frac{d}{dr}\left(r^2 k_t \frac{dT}{dr}\right) + (\Delta H_{Rx})(-r_A) = 0 \quad (1)$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 D_e \frac{dC_A}{dr}\right) + r_A = 0 \quad (2)$$

Dividing by ΔH_{Rx} and using Equation (2) to substitute for $-r_A$

$$\left(\frac{1}{-\Delta H_{Rx}}\right)\frac{1}{r^2}\left(\frac{d}{dr} r^2 k_t \frac{dT}{dr}\right) + \frac{1}{r^2}\frac{d}{dr}\left(r^2 D_e \frac{dC_A}{dr}\right) = 0$$

$$\frac{d}{dr}\left[r^2\left[\frac{d}{dr}\left[\frac{k_t T}{D_e(-\Delta H_{Rx})} + C_A\right]\right]\right] = 0$$

Integrating

$$r^2 \frac{d}{dr}\left[\frac{k_t T}{D_e(-\Delta H_{Rx})} + C_A\right] + C_1 = 0$$

$$C_A + \frac{k_t T}{D_e(-\Delta H_{Rx})} = -\frac{C_1}{r} + C_2$$

$C_1 = 0$ because T & C must be finite.

$$C_A + \frac{k_t T}{D_e(-\Delta H_{Rx})} = C_2$$

$r = R \quad C_A = C_{As}$ and $T = T_S$

$$C_A + \frac{k_t T}{D_e(-\Delta H_{Rx})} = C_{As} + \frac{kT_S}{D_e \Delta H_{Rx}}$$

$$T = \frac{D_e(-\Delta H_{Rx})}{kT}(C_{As} - C_A) + T_S$$

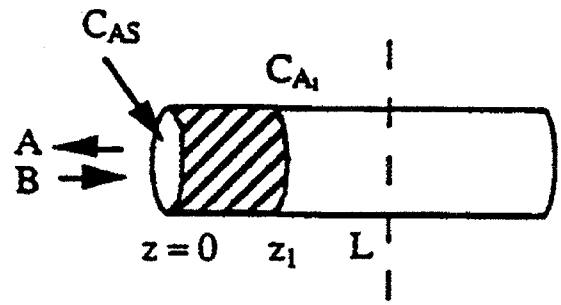
$T = T_{max}$ at $C_{As} = 0$

$$\boxed{T_{max} = T_S + \frac{(-\Delta H_{Rx})D_e C_{As}}{k_t}}$$

P12-13 (b) No solution will be given

P12-14

P12-15 (a)



Given: $A \leftrightarrow B$ on the walls of a cylindrical catalyst pore.

z_1 = length of poisoned section

$-r_A' = k C_A$

In the poisoned section:

$$W_A \pi r^2 |_z - W_A \pi r^2 |_{z+\Delta z} + r_A'' P \Delta z = 0$$

For $0 \le z \le z_1$, $r_A'' = 0$, since this area is poisoned.

$$W_A \pi r^2 |_z - W_A \pi r^2 |_{z+\Delta z} = 0 \quad \text{or} \quad \frac{-dW_A}{dz} = 0$$

$$W_A = -CD_{AB}\frac{dX_A}{dz} + X_A(W_A + W_B)$$

But $W_A = -W_B$, since, for each mole of A consumed, one mole of A is reacted.

$$W_A = -CD_{AB}\frac{dX_A}{dz} \quad \text{and} \quad \frac{d}{dz}\left(CD_{AB}\frac{dX_A}{dz}\right) = 0 \quad \text{or} \quad \frac{d^2X_A}{dz^2} = 0$$

At $z = 0$, $C_A = X_{AS}\,C = C_{AS}$

At $z = z_1$, $C_A = X_{A1} = C_{A1}$

Integrating: $X_{A1} = K_1 z + K_2$

At $z = 0$, $X_A = \frac{C_{AS}}{C}$: $K_2 = \frac{C_{AS}}{C}$

$$\text{at } z = z_1,\ X_A = X_{A1} = \frac{C_{A1}}{C} = k_1 z_1 + \frac{C_{AS}}{C} \Rightarrow k_1 = \frac{C_{A1} - C_{AS}}{C\,z_1}$$

$$X_A = \frac{C_A}{C} = \frac{C_{A1} - C_{AS}}{C\,z_1} z + \frac{C_{AS}}{C}$$

$$C_A = (C_{A1} - C_{AS})\left(\frac{z}{z_1}\right) + C_{AS}$$

The flux is $W_A = -C\,D_{AB}\frac{dX_A}{dz} = -D_{AB}\frac{dC_A}{dz}(C_{A1} - C_{AS})$

P12-15 (b)

Before poisoning, $\eta = \frac{\tan h\,\phi_1}{\phi_1}$ where $\eta = \phi_1 = L\left(\frac{2k''}{r\,D_{AB}}\right)^{1/2}$

After poisoning, the differential equation and boundary conditions are the same for the unpoisoning region of the pore, $z_1 \le z \le L$ if z is replaced by L - z; and if we let $C_A = C_{A1}$ at $z' = 0$ and $\frac{dC_A}{dz} = 0$ at $z = L - z_1$. then, for the unpoisoned section of the catalyst pore η applies if ϕ is replaced by :

$$(L - z)\left(\frac{2k''}{r\,D_{AB}}\right)^{1/2} = \left(1 - \frac{z}{L}\right)\phi_1 \text{ , i.e., } \eta = \frac{\tan h\left[\phi_1\left(1 - \frac{z}{L}\right)\right]}{\phi_1\left(1 - \frac{z}{L}\right)}$$

The effectiveness factor for the unpoisoned section of catalyst pore is defined as :

$$W_A = \eta\,\pi\,r(L - z)\,C_{A1}$$

This can be related to the overall effectiveness factor for the entire pore by

$$W_A = \eta' \pi r L C_{AS} = \eta \pi r L C_{A1}$$

$$\therefore \quad \eta' C_{AS} = \eta C_{A1}\left(1 - \frac{z_1}{L}\right)$$

But $W_A = -\frac{D_{AB}}{z_1}(C_{A1} - C_{AS})$ from part (a)

$$\therefore \quad C_{A1} = C_{AS} - \frac{W_A z_1}{D_{AB}}$$

$$\therefore \quad \eta' C_{AS} = \eta\left(1 - \frac{z_1}{L}\right)\left[C_{AS} - \frac{W_A z_1}{D_{AB}}\right]$$

But $W_A \pi r^2 = \eta' 2\pi r L C_{AS} k''$

$$\eta' = \eta\left(1 - \frac{z_1}{L}\right)\left(1 - \frac{2\eta' L^2 C_{AS} k'' z_1}{r D_{AB} L}\right)$$

$$\eta' = \eta\left(1 - \frac{z_1}{L}\right)\left(1 - \eta'\left(\frac{z_1}{L}\right)\phi^2\right)$$

$$\eta' = \frac{\eta\left(1 - \frac{z_1}{L}\right)}{1 + \phi_1^2 \eta\left(1 - \frac{z_1}{L}\right)\left(\frac{z_1}{L}\right)} = \frac{\left(1 - \frac{z_1}{L}\right)\left[\frac{\tanh\left\{\phi_1\left(1 - \frac{z}{L}\right)\right\}}{\phi_1\left(1 - \frac{z}{L}\right)}\right]}{1 + \phi_1^2 \eta\left(1 - \frac{z_1}{L}\right)\left(\frac{z_1}{L}\right)\left[\frac{\tanh\left\{\phi_1\left(1 - \frac{z}{L}\right)\right\}}{\phi_1\left(1 - \frac{z_1}{L}\right)}\right]}$$

$$\eta' = \frac{\tanh\left\{\phi_1\left(1 - \frac{z}{L}\right)\right\}}{\phi_1 + \phi_1^2\left(\frac{z_1}{L}\right)\tanh\left\{\phi_1\left(1 - \frac{z}{L}\right)\right\}}$$

P12-16

The reaction is $A \rightarrow \frac{1}{2}A_2$

$$\delta = \frac{1}{2} - 1 = -\frac{1}{2}; \quad \varepsilon = y_{A0}\,\delta = -0.5$$

$$C_A = \frac{C_{A0}(1 - X)}{(1 - 0.5X)} \quad \text{where} \quad C_{A0} = \frac{P}{RT} = \frac{8.2 \text{ atm}}{\frac{0.082\ 1 \text{ atm}}{\text{g mol °K}}(227 + 273 \text{ K})} = 0.2\ \frac{\text{g mol}}{\text{l}}$$

$$y_A = \frac{F_A}{F_A + F_{A2}} = \frac{F_A}{F_A + \frac{1}{2}(F_{A0} - F_A)} = \frac{2F_A}{F_A + F_{A0}}$$

$$\frac{1}{y_A} = \frac{1}{2} + \frac{1}{2}\frac{F_{A0}}{F_A}$$

$$\frac{F_{A0}}{F_A} = 2\left(\frac{1}{y_A} - \frac{1}{2}\right) \quad \text{or} \quad \frac{F_A}{F_{A0}} = \frac{1}{\frac{2}{y_A} - 1} = \frac{y_A}{2 - y_A}$$

$$X = 1 - \frac{F_A}{F_{A0}} = 1 - \frac{y_A}{2 - y_A} = \frac{2 - 2y_A}{2 - y_A}$$

$$r_A' = \frac{F_{A0} X}{W} \quad \text{where } W = 4 \times 40\text{g} = 160\text{ g} = 0.16\text{ kg}$$

$$r_A' = k C_A^{\alpha}$$

$$\ln(-r_A') = \ln k_0 + \alpha \ln C_A$$

Let $M = \ln(-r_A')$; $A_0 = \ln k_0$; $A_1 = \alpha$; and $N = \ln C_A$

$$\therefore \quad M = A_0 + A_1 N \qquad (1)$$

$$\sum_i^n M_i = nA_0 + A_1 \sum_i^n N_i \qquad (2)$$

$$\sum_i^n M_i N_i = A_0 \sum_i^n N_i + A_1 \sum_i^n N_i^2 \qquad (3)$$

i	F_{Tn}	y_A	X	C_A	$-r_A'$	M	N	N^2	MN
1	1	0.21	0.88	4.285×10^{-2}	5.5	1.705	-3.150	9.923	-5.371
2	2	0.33	0.80	6.666×10^{-2}	10	2.303	-2.708	7.333	-6.236
3	4	0.40	0.75	8×10^{-2}	18.75	2.931	-2.526	6.381	-7.404
4	6	0.57	0.60	1.143×10^{-1}	22.5	3.114	-2.169	4.704	-6.754
5	11	0.70	0.46	1.403×10^{-1}	31.625	3.454	-1.964	3.857	-6.784
6	20	0.81	0.32	1.619×10^{-1}	40	3.689	-1.821	3.315	-6.717
					$\sum_i^n =$	17.196	-14.338	35.513	-39.266

Equations (2) and (3) become:

$$17.196 = 6A_0 - 14.338\, A_1$$

$$-39.266 = -14.338\, A_0 + 35.513\, A_1$$

$$\therefore \quad A_0 = 6.36 = \ln k_0 \rightarrow k_0 = 578.25$$

$$A_1 = 1.46 \cong 1.5 = \alpha$$

$$\text{At } T_1 = 237\,C = 510\,K: \; k_1 = \frac{-r_A'}{C_A^{1.5}}$$

$$-r_A' = \frac{F_{A0} X}{W} \quad \text{where } X = \frac{2 - 2(0.097)}{2 - 0.097} = 0.9490$$

$$-r_A' = \frac{(9)(0.9490)}{0.16} = 53.38 = k_1 C_A^{1.5} \quad \text{where:}$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{8.2}{0.082(510)} = 0.196 \frac{g\,mol}{l}$$

$$C_A = \frac{0.196\,(1 - 0.9490)}{1 - 0.5(0.9490)} = 0.019 \frac{g\,mol}{l}$$

$$k_1 = \frac{53.38}{(0.019)^{1.5}} = 2.035 \times 10^4$$

$$k_1 = k_0 \exp\left\{\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T_1}\right)\right\}$$

$$2.035 \times 10^4 = 578.25 \exp\left\{\frac{E\,(J/mole)}{8.314}\left(\frac{1}{500} - \frac{1}{510}\right)\right\}$$

$$\therefore \quad E = 7.55 \times 10^5 \frac{J}{g\,mol}$$

P12-16 (b)

$$n_{true} = 2n_{app} - 1 = 2(1.5) - 1 = 2: \text{ second order}$$

$$E_{true} = 2E_{app} = 15.1 \times 10^5 \frac{J}{mol}$$

P12-16 (c)

$$\phi_2 = R\sqrt{\frac{k\,S_a\,\rho_b\,C_{A0}}{D_e}} = \sqrt{\frac{\left(1 \times 10^{-2}\right)^2 \left(2.035 \times 10^4\right) 49 \left(2.3 \times 10^6\right) 0.196}{0.23 \times 10^{-4}}}$$

$$\phi_2 = 1.40 \times 10^6$$

$$\eta = \left(\frac{2}{n+1}\right)^{1/2}\left(\frac{3}{\phi_n}\right) = \left(\frac{2}{2+1}\right)^{1/2}\left(\frac{3}{1.40 \times 10^6}\right) = 1.75 \times 10^{-6}$$

P12-16 (d)

To make the catalyst more effective, we should use a smaller diameter.

P12-16 (e)

$$C_A = 0.01 \frac{\text{g mol}}{\text{l}}; T = 527\,C = 800\,K$$

$$k = k_0 \exp\left\{\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right\} = 578.25 \exp\left\{\frac{7.55 \times 10^5}{8.314}\left(\frac{1}{500} - \frac{1}{800}\right)\right\}$$

$$k = 2.19 \times 10^{32}$$

$$-r_A' = k C_A^{1.5} = 2.19 \times 10^{32}(0.01)^{1.5} = 2.19 \times 10^{29} \frac{\text{g mole}}{\text{l s}}$$

P12-17

(u) $$\frac{d^2y}{d\lambda^2} - \phi_n y^n = 0$$

Multiply by 2 y $\frac{dy}{d\lambda}$

$$2y\frac{dy}{d\lambda}\frac{d}{d\lambda}\left(\frac{dy}{d\lambda}\right) = \phi_n^2 y^n 2\frac{dy}{d\lambda}$$

Manipulating the L.H.S.

$$\frac{d}{d\lambda}\left(\frac{dy}{d\lambda}\right)^2 = 2\frac{dy}{d\lambda}\frac{d^2y}{d\lambda^2}$$

$$\frac{d}{d\lambda}\left(\frac{dy}{d\lambda}\right)^2 = \phi_n y^n 2dy$$

$$\left(\frac{dy}{d\lambda}\right)^2 = 2\phi_n \frac{y^{n+1}}{n+1} + C_1$$

$$y = \psi\lambda = \frac{C_A}{C_{A0}} \quad , \quad \lambda = 0 \;\; y = 0 \;\; \frac{d\psi}{d\lambda} = 0 \text{ therefore } C_1 = 0$$

Taking the derivative of y and evaluating at $\lambda = 1$

$$\left.\frac{dy}{d\lambda}\right|_{\lambda=1} = \left.\sqrt{\frac{2\phi_n^2 y^{n+1}}{n+1}}\right|_{\lambda=1} = \sqrt{\frac{2\phi_n^2}{n+1}}$$

The effectiveness factor is

$$\eta = \frac{\pi R^2 \left(D_A \frac{dC_A}{dr} \right)_{r=k}}{k C_{As}^n \frac{4}{3} \pi R^3}$$

In dimensionless form

$$\eta = \frac{3 \left(\frac{d\psi}{d\lambda} \right)_{\lambda=1}}{\phi_n^2}$$

$\lambda = \psi\lambda$, differentiating gives

$$\frac{dy}{d\lambda} = \lambda \frac{d\psi}{d\lambda} + \psi$$

at $\lambda = 1$

$$\left. \frac{dy}{d\lambda} \right|_{\lambda=1} = \frac{d\psi}{d\lambda} + 1$$

$$\frac{d\psi}{d\lambda} = \sqrt{\frac{2\phi_n^2}{n+1}} - 1$$

$$\boxed{\eta = 3 \left(\frac{\sqrt{\frac{2\phi_n^2}{n+1}} - 1}{\phi_n^2} \right) = \frac{3\sqrt{\frac{2}{n+1}}}{\phi_n} - \frac{3}{\phi_n^2}}$$

For larger ϕ_n

$$\boxed{\eta = 3\sqrt{\frac{2}{n+1}} \frac{1}{\phi_n}}$$

CDP12-A

CDP12-B (a) 3rd ed. 12-19 (a)
CDP12-B (b) 3rd ed. 12-19 (b)
CDP12-B (c) 3rd ed. 12-19 (c)

CDP12-C (a) 3rd ed. 12-20 (a)
CDP12-C (b) 3rd ed. 12-20 (b)
CDP12-C (c) 3rd ed. 12-20 (c)

CDP12-D (a) 3rd ed. 12-21 (a)
CDP12-D (a) 3rd ed. 12-21 (b)
CDP12-D (a) Individualized solution

CDP12-E 2nd ed. 11-18

CDP12-F 2nd ed. 11-19

CDP12-G 2nd ed. 11-20

CDP12-H 2nd ed. 11-21

CDP12-I 2nd ed. 11-22

CDP12-J (a) 2nd ed. 12-7 (a)
CDP12-J (b) 2nd ed. 12-7 (b)
CDP12-J (c) 2nd ed. 12-7 (c)
CDP12-J (d) 2nd ed. 12-7 (d)
CDP12-J (e) 2nd ed. 12-7 (e)

CDP12-K 2nd ed. 12-9

CDP12-L (a) 2nd ed. 12-8 (a)
CDP12-L (b) 2nd ed. 12-8 (b)
CDP12-L (c) 2nd ed. 12-8 (c)
CDP12-L (d) 2nd ed. 12-8 (d)

CDP12-M (a) 3rd ed. CDP12-L (a)
CDP12-M (b) 3rd ed. CDP12-L (b)
CDP12-M (c)
CDP12-M (d)

CDP12-N 3rd ed. CDP12-M

CDP12-O

CDP12-P

CDP12-Q

CDP12-R (a) 3rd ed. CDP12-Q (a)
CDP12-R (b) 3rd ed. CDP12-Q (b)

CDP12-S

CDP12-T

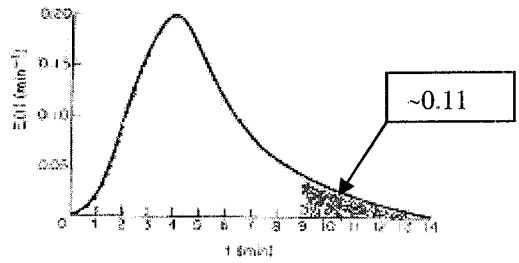
CDP12-U

Solutions for Chapter 13 – Distributions of Residence Times for Chemical Reactors

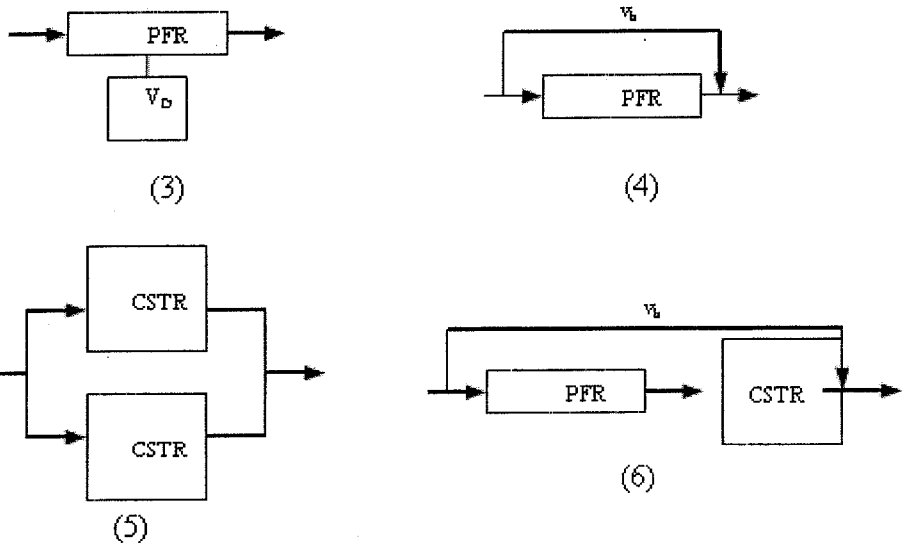
P13-1 No solution will be given.

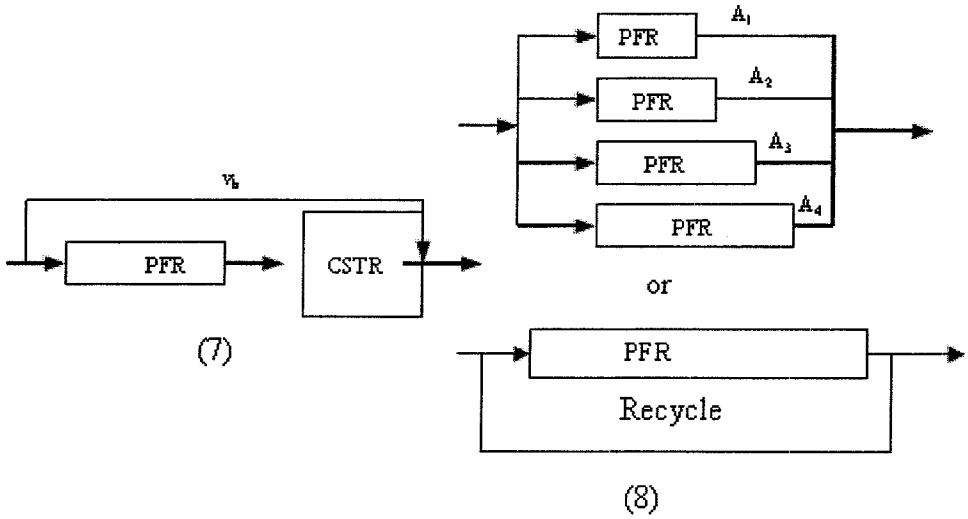
P13-2 (a)

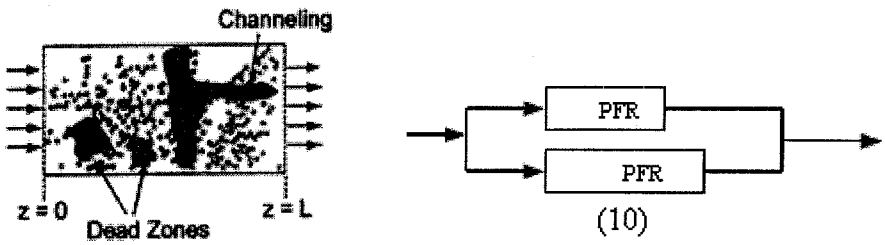
The area of a triangle (h=0.044, b=5) can approximate the area of the tail :0.11

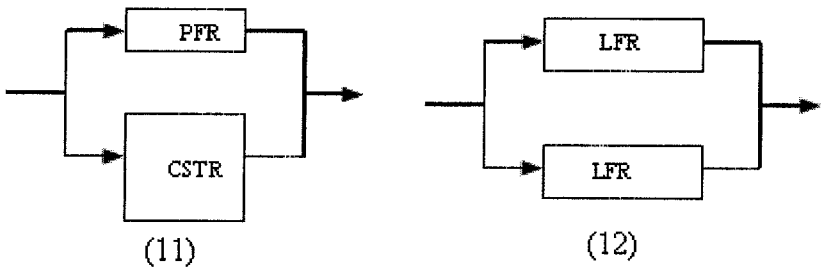


P13-2 (b)



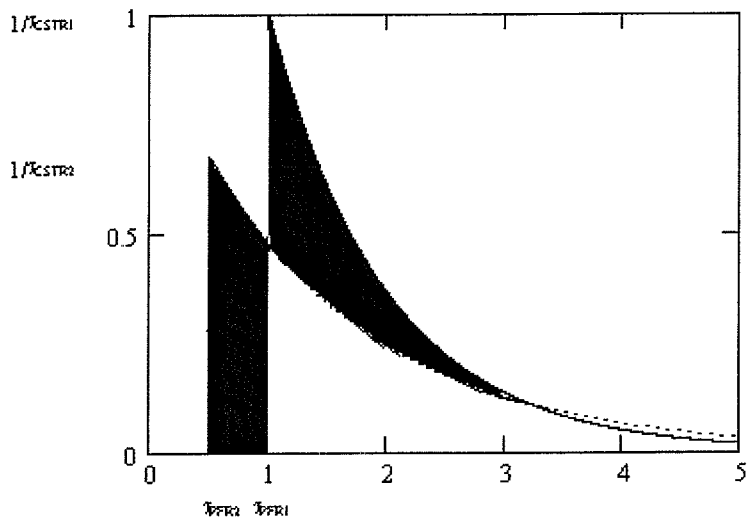






P13-2 (c)

For a PFR/CSTR Series $$E(t) = \begin{cases} 0 & t < \tau_p \\ \dfrac{e^{-(t-\tau_p)/\tau_s}}{\tau_s} & t \geq \tau_p \end{cases}$$



P13-2 (d)

X=0.75

For a PFR first order reaction:

$$Da = \ln\left(\frac{1}{1-X}\right) = \ln(4) = 1.39 \text{ where } Da = k\tau$$

For a CSTR first order reaction:

$$Da = \left(\frac{1}{1-X}\right) - 1 = 3 \text{ where } Da = k\tau$$

For a LFR first order reaction:

Solving iteratively Hilder approximate formula with an initial value Da° (i.e. $Da_{PFR} < Da^{\circ} < Da_{CSTR}$).

$$0.75 = \frac{Da\exp\left(\frac{Da}{2}\right) + Da}{4 + Da\exp\left(\frac{Da}{2}\right) + Da} \text{ where } Da = k\tau$$

Da=2.58

The ratio of the Damköhler numbers is equal to the ratios of the sizes.

Relative sizes: $\frac{V_{PFR}}{V_{CSTR}} = 0.46$, $\frac{V_{LFR}}{V_{CSTR}} = 0.86$;

P13-2 (e)

For a PFR, τ=5.15min, first order, liquid phase, irreversible reaction with k=0.1min^{-1}.

$$X = 1 - e^{-k\tau} = 0.402$$

For a CSTR, τ=5.15min, first order, liquid phase, irreversible reaction with k=0.1min^{-1}.

$$X = \frac{k\tau}{1+k\tau} = 0.402$$

X_{seg}	X_{PFR}	X_{CSTR}
0.385	0.402	0.340

Page 851, only the RTD is necessary to calculate the conversion for a first-order reaction in any type of reactor. Not good when the RTD has a long tail that is difficult to interpret or interpolate.

P13-2 (f)

Decrease of 10 ℃ in temperature
See Polymath program P13-2-f.pol

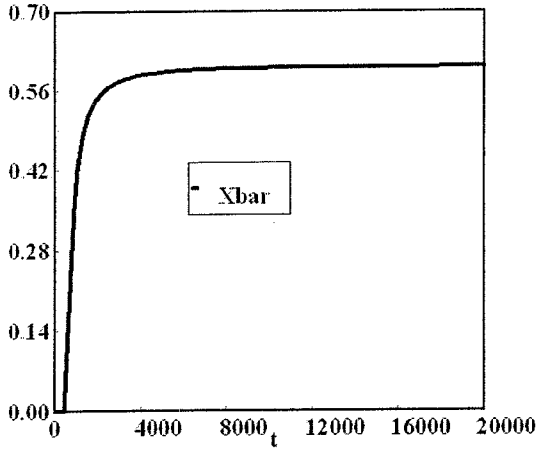
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	2.0E+04	2.0E+04
Xbar	0	0	0.6023837	0.6023837
k	0.0025446	0.0025446	0.0025446	0.0025446
Cao	0.75	0.75	0.75	0.75
X	0	0	0.9744692	0.9744692
tau	1000	1000	1000	1000
t1	500	500	500	500
E2	5.0E+10	6.25E-08	5.0E+10	6.25E-08
E	0	0	0.0023564	6.25E-08

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Xbar)/d(t) = X*E

Explicit equations as entered by the user
[1] k = .00493*exp(13300/1.9872*(1/323.15-1/313.15))
[2] Cao = .75
[3] X = k*Cao*t/(1+k*Cao*t)
[4] tau = 1000
[5] t1 = tau/2
[6] E2 = tau^2/2/(t^3+.00001)
[7] E = if (t<t1) then (0) else (E2)



The decrease of 10°C in temperature has the effect of reducing the mean conversion by 14%.

Decrease in reaction order from 2nd to pseudo 1st
See Polymath program P13-2-f-2.pol

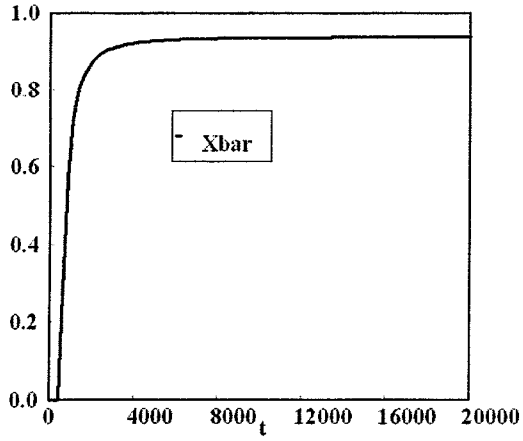
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	2.0E+04	2.0E+04
Xbar	0	0	0.9391084	0.9391084
k	0.004	0.004	0.004	0.004
Cao	0.75	0.75	0.75	0.75
X	0	0	1	1
tau	1000	1000	1000	1000
t1	500	500	500	500
E2	5.0E+10	6.25E-08	5.0E+10	6.25E-08
E	0	0	0.0024915	6.25E-08

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Xbar)/d(t) = X*E

Explicit equations as entered by the user
[1] k = 0.004
[2] Cao = .75
[3] X = 1-exp(-k*t)
[4] tau = 1000
[5] t1 = tau/2
[6] E2 = tau^2/2/(t^3+.00001)
[7] E = if (t<t1) then (0) else (E2)



The decrease in reaction order from 2nd to pseudo 1st has the effect of increasing the exit conversion by 20%. The smaller the dependency of the rate on C_A means that when C_A is below 1 mol/dm^3 then the rate of consumption of A is larger and hence resulting in a larger conversion.

Exothermic reaction in adiabatic reactor:
See Polymath program P13-2-f-3.pol

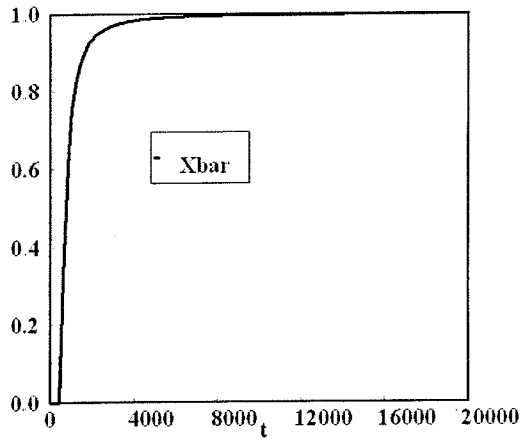
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	2.0E+04	2.0E+04
Xbar	0	0	0.999375	0.999375
X	0	0	1	1
T	323.15	323.15	823.15	823.15
Cao	0.75	0.75	0.75	0.75
tau	1000	1000	1000	1000
t1	500	500	500	500
E2	5.0E+10	6.299E-08	5.0E+10	6.299E-08
E	0	0	0.0022142	6.299E-08
k	0.01	0.01	19.337202	19.337202

ODE Report (STIFF)

Differential equations as entered by the user
[1] d(Xbar)/d(t) = X*E
[2] d(X)/d(t) = k*(1-X)

Explicit equations as entered by the user
[1] T = 323.15+500*X
[2] Cao = .75
[3] tau = 1000
[4] t1 = tau/2
[5] E2 = tau^2/2/(t^3+.00001)
[6] E = if (t<t1) then (0) else (E2)
[7] k = 0.01*exp(8000/1.9872*(1/323.15-1/T))



The mean conversion Xbar, the integral, is estimated to be 99.9%. The reaction is adiabatic and exothermic as the temperature increases to a maximum of 1373.15 K once the batch conversion within the globules has reached 100% which occurs after only – 4 seconds. Hence, the adiabatic increase in temperature considerably increases the rate at which conversions increases with time and hence also the final value.

P13-2 (g)

For a PFR, τ=40min, second order, liquid phase, irreversible reaction with k=0.01 dm^3 /mol·min^{-1}.

$$X = \frac{k\tau C_{Ao}}{1+\kappa\tau C_{Ao}} = 0.76$$

For a CSTR, τ=40min, second order, liquid phase, irreversible reaction with k=0.01 dm^3 /mol·min^{-1}.

$$\frac{X}{(1-X)^2} = k\tau C_{Ao} \rightarrow X = 0.58$$

Maximum Mixedness Model and Segregation model are given in E13-7

Maximum Mixedness Model
See Polymath program P13-2-g.pol

POLYMATH Results
Calculated values of the DEQ variables

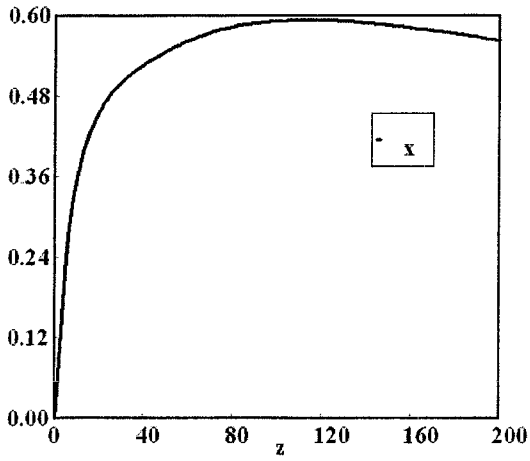
Variable	initial value	minimal value	maximal value	final value
z	0	0	200	200
x	0	0	0.5938635	0.5632738
cao	8	8	8	8
k	0.01	0.01	0.01	0.01
lam	200	0	200	0
ca	8	3.2490705	8	3.4938093
E1	0.1635984	0.0028734	0.1635984	0.028004
E2	2.25E-04	2.25E-04	0.015011	0.015011
F1	5.6333387	0	5.6333387	0
F2	0.9970002	0.381769	0.9970002	0.381769
ra	-0.64	-0.64	-0.1055646	-0.122067
E	2.25E-04	2.25E-04	0.028004	0.028004
F	0.9970002	0	0.9970002	0
EF	0.075005	0.0220689	0.075005	0.028004

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(x)/d(z) = -(ra/cao+E/(1-F)*x)

Explicit equations as entered by the user
[1] cao = 8
[2] k = .01
[3] lam = 200-z
[4] ca = cao*(1-x)
[5] E1 = 4.44658e-10*lam^4-1.1802e-7*lam^3+1.35358e-5*lam^2-.000865652*lam+.028004
[6] E2 = -2.64e-9*lam^3+1.3618e-6*lam^2-.00024069*lam+.015011
[7] F1 = 4.44658e-10/5*lam^5-1.1802e-7/4*lam^4+1.35358e-5/3*lam^3-.000865652/2*lam^2+.028004*lam
[8] F2 = -(-9.30769e-8*lam^3+5.02846e-5*lam^2-.00941*lam+.618231-1)
[9] ra = -k*ca^2
[10] E = if (lam<=70) then (E1) else (E2)
[11] F = if (lam<=70) then (F1) else (F2)
[12] EF = E/(1-F)



X_{MM}	X_{seg}	X_{PFR}	X_{CSTR}
56%	61%	76%	58%

P13-2 (h)

Liquid phase, first order, Maximum Mixedness model

Rate Law: $-r_A = k_1 C_A$ where $k_1 = C_{Ao}k = 0.08\text{min}^{-1}$

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

$$\frac{r_A}{C_{Ao}} = -k_1(1-X)$$

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{Ao}} + \frac{E(\lambda)}{1-F(\lambda)}X$$

$$\frac{dX}{d\lambda} = -k(1-X) + \frac{E(\lambda)}{1-F(\lambda)}X$$

$$\frac{dX}{dz} = k(1-X) - \frac{E(\lambda)}{1-F(\lambda)}X$$

See Polymath program P13-2-h-1.pol

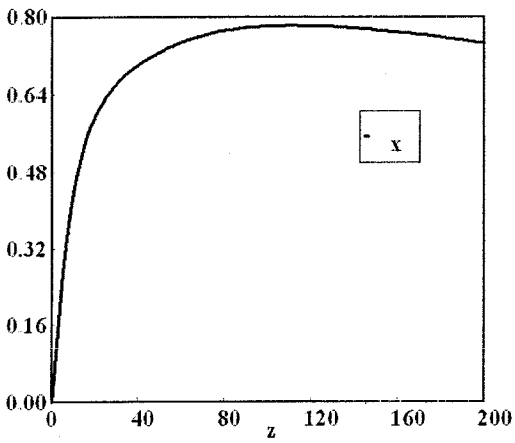
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
z	0	0	200	200
x	0	0	0.7829342	0.7463946
cao	8	8	8	8
k	0.08	0.08	0.08	0.08
lam	200	0	200	0
ca	8	1.7365447	8	2.0288435
E1	0.1635984	0.0028731	0.1635984	0.028004
E2	2.25E-04	2.25E-04	0.015011	0.015011
F1	5.6333387	0	5.6333387	0
F2	0.9970002	0.381769	0.9970002	0.381769
ra	-0.64	-0.64	-0.1389236	-0.1623075
E	2.25E-04	2.25E-04	0.028004	0.028004
F	0.9970002	0	0.9970002	0
EF	0.075005	0.0220691	0.075005	0.028004

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(x)/d(z) = -(ra/cao+E/(1-F)*x)

Explicit equations as entered by the user
[1] cao = 8
[2] k = 0.08
[3] lam = 200-z
[4] ca = cao*(1-x)
[5] E1 = 4.44658e-10*lam^4-1.1802e-7*lam^3+1.35358e-5*lam^2-.000865652*lam+.028004
[6] E2 = -2.64e-9*lam^3+1.3618e-6*lam^2-.00024069*lam+.015011
[7] F1 = 4.44658e-10/5*lam^5-1.1802e-7/4*lam^4+1.35358e-5/3*lam^3-.000865652/2*lam^2+.028004*lam
[8] F2 = -(-9.30769e-8*lam^3+5.02846e-5*lam^2-.00941*lam+.618231-1)
[9] ra = -k*ca
[10] E = if (lam<=70) then (E1) else (E2)
[11] F = if (lam<=70) then (F1) else (F2)
[12] EF = E/(1-F)



At z = 200, i.e. $\lambda = 0$ (exit), conversion X = 75 %.
The decrease in reaction order from 2nd to 1st has the effect of increasing the exit conversion by 19%. Once the concentration of A drops below 1 mol/dm^3 then the rate of consumption of A does not fall as rapidly (as the 2nd order reaction) and hence resulting in a larger conversion.

Liquid phase, third order, Maximum Mixedness model

Rate Law: $-r_A = kC_A^3$

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

$$\frac{r_A}{C_{Ao}} = -k'C_{Ao}{}^2(1-X)^3 \qquad \text{Where } k'C_{Ao}{}^2 = k = 0.08\,\text{min}^{-1}$$

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{Ao}} + \frac{E(\lambda)}{1-F(\lambda)}X$$

$$\frac{dX}{dz} = k'C_{Ao}{}^2(1-X)^3 - \frac{E(\lambda)}{1-F(\lambda)}X$$

See Polymath program P13-2-h-2.pol

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
z	0	0	200	200
x	0	0	0.4867311	0.4614308
cao	8	8	8	8
k	0.08	0.08	0.08	0.08
lam	200	0	200	0
ca	8	4.1061501	8	4.3085534
E1	0.1635984	0.0028733	0.1635984	0.028004
E2	2.25E-04	2.25E-04	0.015011	0.015011
F1	5.6333387	0	5.6333387	0
F2	0.9970002	0.381769	0.9970002	0.381769
E	2.25E-04	2.25E-04	0.028004	0.028004
F	0.9970002	0	0.9970002	0
EF	0.075005	0.0220689	0.075005	0.028004

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(x)/d(z) = -(-k*(1-x)^3+E/(1-F)*x)

Explicit equations as entered by the user
[1] cao = 8
[2] k = 0.08
[3] lam = 200-z
[4] ca = cao*(1-x)
[5] E1 = 4.44658e-10*lam^4-1.1802e-7*lam^3+1.35358e-5*lam^2-.000865652*lam+.028004
[6] E2 = -2.64e-9*lam^3+1.3618e-6*lam^2-.00024069*lam+.015011
[7] F1 = 4.44658e-10/5*lam^5-1.1802e-7/4*lam^4+1.35358e-5/3*lam^3-.000865652/2*lam^2+.028004*lam
[8] F2 = -(-9.30769e-8*lam^3+5.02846e-5*lam^2-.00941*lam+.618231-1)
[9] E = if (lam<=70) then (E1) else (E2)
[10] F = if (lam<=70) then (F1) else (F2)
[11] EF = E/(1-F)

At z = 200, i.e. $\lambda = 0$ (exit), conversion X = 46.1 %.
The increase in reaction order from 2nd to 3rd has the effect of decreasing the exit conversion by 10%. Once the concentration of A drops below 1 mol/dm^3 then the rate falls rapidly and C_A is not consumed so quickly, resulting in a smaller conversion.

Liquid phase, half order, Maximum Mixedness model

Rate Law: $-r_A = k'C_A{}^{1/2}$

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

$$\frac{r_A}{C_{Ao}} = -k'C_{Ao}^{-1/2}(1-X)^{1/2} \qquad \text{Where } k = k'C_{Ao}^{-1/2} = 0.08\,\text{min}^{-1}$$

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{Ao}} + \frac{E(\lambda)}{1-F(\lambda)}X$$

$$\frac{dX}{dz} = kC_{Ao}^{-1/2}(1-X)^{1/2} - \frac{E(\lambda)}{1-F(\lambda)}X$$

See Polymath program P13-2-h-3.pol

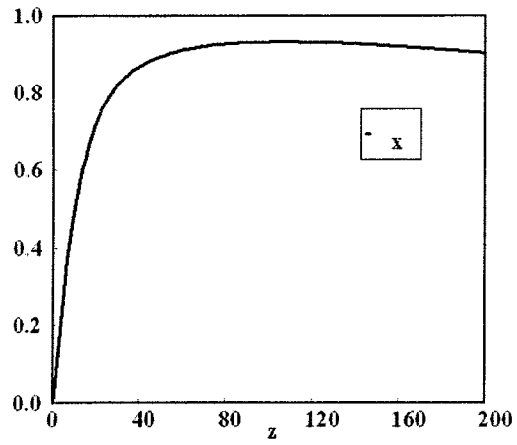
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
z	0	0	200	200
x	0	0	0.9334778	0.9038179
cao	8	8	8	8
k	0.08	0.08	0.08	0.08
lam	200	0	200	0
ca	8	0.532148	8	0.7694568
E1	0.1635984	0.002873	0.1635984	0.028004
E2	2.25E-04	2.25E-04	0.015011	0.015011
F1	5.6333387	0	5.6333387	0
F2	0.9970002	0.381769	0.9970002	0.381769
E	2.25E-04	2.25E-04	0.028004	0.028004
F	0.9970002	0	0.9970002	0
EF	0.075005	0.0220677	0.075005	0.028004

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(x)/d(z) = -(-k*(1-x)^(.5)+E/(1-F)*x)

Explicit equations as entered by the user
[1] cao = 8
[2] k = 0.08
[3] lam = 200-z
[4] ca = cao*(1-x)
[5] E1 = 4.44658e-10*lam^4-1.1802e-7*lam^3+1.35358e-5*lam^2-.000865652*lam+.028004
[6] E2 = -2.64e-9*lam^3+1.3618e-6*lam^2-.00024069*lam+.015011
[7] F1 = 4.44658e-10/5*lam^5-1.1802e-7/4*lam^4+1.35358e-5/3*lam^3-.000865652/2*lam^2+.028004*lam
[8] F2 = -(-9.30769e-8*lam^3+5.02846e-5*lam^2-.00941*lam+.618231-1)
[9] E = if (lam<=70) then (E1) else (E2)
[10] F = if (lam<=70) then (F1) else (F2)
[11] EF = E/(1-F)



At z = 200, i.e. $\lambda = 0$ (exit), conversion X = 90 %.
The decrease in reaction order from 2nd to ½ has the effect of increasing the exit conversion by 34%. The smaller the dependency of the rate on C_A means that when C_A falls below 1 mol/dm^3 then the rate of consumption of A does not fall as rapidly (as the 2nd order reaction) and hence resulting in a larger conversion.

P13-2 (i)

Assymetric RTD:
See Polymath program P13-2-i-1.pol

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	2.52	2.52
ca	1	0.0228578	1	0.0228578
cb	1	0.2840909	1	0.2840909
cc	0	0	0.3992785	0.3992785
cabar	0	0	0.1513598	0.1513306
cbbar	0	0	0.4543234	0.4539723
ccbar	0	0	0.3570959	0.3566073
cd	0	0	0.3178411	0.2612331
ce	0	0	0.3166306	0.3166306
cdbar	0	0	0.3029636	0.3026417
cebar	0	0	0.1782569	0.1778722
T	350	350	350	350
k1	1	1	1	1
k2	1	1	1	1
E1	-0.004	-27.414373	0.958793	-27.414373
E2	-27.402	-27.402	0.9557439	-0.0272502
rc	1	0.0064937	1	0.0064937
k3	1	1	1	1
ra	-2	-2	-0.0293515	-0.0293515
re	0	0	0.1762951	0.0742139
E	-0.004	-0.0272502	0.958793	-0.0272502
rb	-1	-1	-0.0807076	-0.0807076
Scd	0	0	1.5284379	1.5284379
Sde	0	0	42.398031	0.8250406
rd	1	-0.0522659	1	-0.0513561

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(ca)/d(t) = ra
[2] d(cb)/d(t) = rb

[3] d(cc)/d(t) = rc
[4] d(cabar)/d(t) = ca*E
[5] d(cbbar)/d(t) = cb*E
[6] d(ccbar)/d(t) = cc*E
[7] d(cd)/d(t) = rd
[8] d(ce)/d(t) = re
[9] d(cdbar)/d(t) = cd*E
[10] d(cebar)/d(t) = ce*E

Explicit equations as entered by the user
[1] T = 350
[2] k1 = exp((5000/1.987)*(1/350-1/T))
[3] k2 = exp((1000/1.987)*(1/350-1/T))
[4] E1 = -2.104*t^4+4.167*t^3-1.596*t^2+0.353*t-0.004
[5] E2 = -2.104*t^4+17.037*t^3-50.247*t^2+62.964*t-27.402
[6] rc = k1*ca*cb
[7] k3 = exp((9000/1.987)*(1/350-1/T))
[8] ra = -k1*ca*cb-k2*ca
[9] re = k3*cb*cd
[10] E = if(t<=1.26)then(E1)else(E2)
[11] rb = -k1*ca*cb-k3*cb*cd
[12] Scd = cc/(cd+.000000001)
[13] Sde = cd/(ce+.000000000001)
[14] rd = k2*ca-k3*cb*cd

If the temperature is raised, the conversion of A increases. The selectivity $S_{c/d}$ increases with temperature and $S_{d/e}$ decreases with increasing temperature

Bimodal RTD
See Polymath program P13-2-i-2.pol

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
z	0	0	6	6
ca	1	0.2660482	1	0.2660482
cb	1	0.5350642	1	0.5352659
cc	0	0	0.2872257	0.2745726
F	0.99	-0.0033987	0.99	-0.0033987
cd	0	0	0.2692177	0.2692177
ce	0	0	0.1929233	0.1901615
cbo	1	1	1	1
cao	1	1	1	1
cco	0	0	0	0
cdo	0	0	0	0
ceo	0	0	0	0
lam	6	0	6	0
T	350	350	350	350
k2	1	1	1	1
k1	1	1	1	1
rc	1	0.1424065	1	0.1424065
k3	1	1	1	1
E1	346.34561	0.1019474	346.34561	0.20909
E2	6737.4446	0.0742397	6737.4446	925.46463
E3	0.00911	0.0061156	1.84445	1.84445
re	0	0	0.1694414	0.144103
ra	-2	-2	-0.4084547	-0.4084547
rb	-1	-1	-0.28635	-0.2865096
E	0.00911	0.0061156	0.6288984	0.20909
EF	0.911	0.2083818	1.8694436	0.2083818

rd	1	0.1219452	1	0.1219452
Scd	0	0	1.0856272	1.0198908
Sde	0	0	17.698981	1.4157321

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(ca)/d(z) = -(-ra+(ca-cao)*EF)
[2] d(cb)/d(z) = -(-rb+(cb-cbo)*EF)
[3] d(cc)/d(z) = -(-rc+(cc-cco)*EF)
[4] d(F)/d(z) = -E
[5] d(cd)/d(z) = -(-rd+(cd-cdo)*EF)
[6] d(ce)/d(z) = -(-re+(ce-ceo)*EF)

Explicit equations as entered by the user
[1] cbo = 1
[2] cao = 1
[3] cco = 0
[4] cdo = 0
[5] ceo = 0
[6] lam = 6-z
[7] T = 350
[8] k2 = exp((1000/1.987)*(1/350-1/T))
[9] k1 = exp((5000/1.987)*(1/350-1/T))
[10] rc = k1*ca*cb
[11] k3 = exp((9000/1.987)*(1/350-1/T))
[12] E1 = 0.47219*lam^4-1.30733*lam^3+0.31723*lam^2+0.85688*lam+0.20909
[13] E2 = 3.83999*lam^6-58.16185*lam^5+366.2097*lam^4-1224.66963*lam^3+2289.84857*lam^2-2265.62125*lam+925.46463
[14] E3 = 0.00410*lam^4-0.07593*lam^3+0.52276*lam^2-1.59457*lam+1.84445
[15] re = k3*cb*cd
[16] ra = -k1*ca*cb-k2*ca
[17] rb = -k1*ca*cb-k3*cb*cd
[18] E = if(lam<=1.82)then(E1)else(if(lam<=2.8)then(E2)else(E3))
[19] EF = E/(1-F)
[20] rd = k2*ca-k3*cb*cd
[21] Scd = cc/(cd+.0000000001)
[22] Sde = cd/(ce+.0000000001)

If the temperature is raised, the conversion of A increases. The selectivity $S_{c/d}$ increases with temperature and $S_{d/e}$ decreases with increasing temperature

P13-2 (j)

Exothermic Reaction: E=45Kj/mol

See Polymath program P13-2-j-1.pol

POLYMATH Results
Calculated values of the DEQ variables

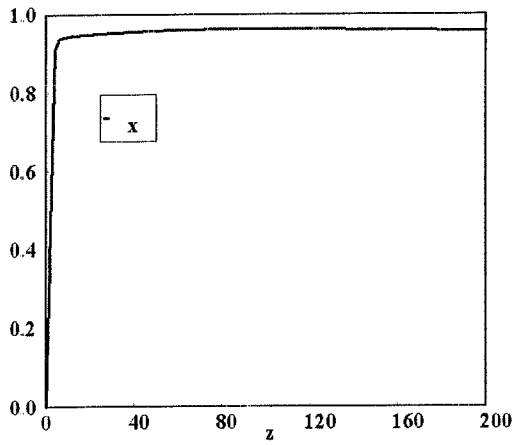
Variable	initial value	minimal value	maximal value	final value
z	0	0	200	200
x	0	0	0.9628524	0.9579239
cao	8	8	8	8
T	320	320	464.4279	463.68858
lam	200	0	200	0
ca	8	0.2971785	8	0.3366089
E1	0.1635984	0.0028744	0.1635984	0.028004
E2	2.25E-04	2.25E-04	0.015011	0.015011
F1	5.6333387	0	5.6333387	0
F2	0.9970002	0.381769	0.9970002	0.381769

k	0.01	0.01	1.924805	1.8893687
E	2.25E-04	2.25E-04	0.028004	0.028004
F	0.9970002	0	0.9970002	0
EF	0.075005	0.0220681	0.075005	0.028004
ra	-0.64	-0.8227063	-0.1699892	-0.2140759

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(x)/d(z) = -(ra/cao+E/(1-F)*x)

Explicit equations as entered by the user
[1] cao = 8
[2] T = 320+150*x
[3] lam = 200-z
[4] ca = cao*(1-x)
[5] E1 = 4.44658e-10*lam^4-1.1802e-7*lam^3+1.35358e-5*lam^2-.000865652*lam+.028004
[6] E2 = -2.64e-9*lam^3+1.3618e-6*lam^2-.00024069*lam+.015011
[7] F1 = 4.44658e-10/5*lam^5-1.1802e-7/4*lam^4+1.35358e-5/3*lam^3-.000865652/2*lam^2+.028004*lam
[8] F2 = -(-9.30769e-8*lam^3+5.02846e-5*lam^2-.00941*lam+.618231-1)
[9] k = .01*exp(45000/8.314*(1/320-1/T))
[10] E = if (lam<=70) then (E1) else (E2)
[11] F = if (lam<=70) then (F1) else (F2)
[12] EF = E/(1-F)
[13] ra = -k*ca^2



Endothermic Reaction: E=45Kj/mol

See Polymath program P13-2-j-1.pol

POLYMATH Results
Calculated values of the DEQ variables

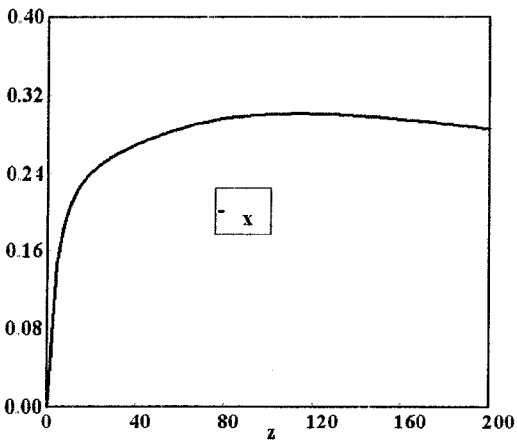
Variable	initial value	minimal value	maximal value	final value
z	0	0	200	200
x	0	0	0.3017158	0.2860515
cao	8	8	8	8
T	320	289.82835	320	291.39485
lam	200	0	200	0
ca	8	5.5862683	8	5.7115879
E1	0.1635984	0.0028739	0.1635984	0.028004
E2	2.25E-04	2.25E-04	0.015011	0.015011
F1	5.6333387	0	5.6333387	0

F2	0.9970002	0.381769	0.9970002	0.381769
k	0.01	0.0017191	0.01	0.0019006
E	2.25E-04	2.25E-04	0.028004	0.028004
F	0.9970002	0	0.9970002	0
EF	0.075005	0.0220679	0.075005	0.028004
ra	-0.64	-0.64	-0.0536459	-0.0620023

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(x)/d(z) = -(ra/cao+E/(1-F)*x)

Explicit equations as entered by the user
[1] cao = 8
[2] T = 320-100*x
[3] lam = 200-z
[4] ca = cao*(1-x)
[5] E1 = 4.44658e-10*lam^4-1.1802e-7*lam^3+1.35358e-5*lam^2-.000865652*lam+.028004
[6] E2 = -2.64e-9*lam^3+1.3618e-6*lam^2-.00024069*lam+.015011
[7] F1 = 4.44658e-10/5*lam^5-1.1802e-7/4*lam^4+1.35358e-5/3*lam^3-.000865652/2*lam^2+.028004*lam
[8] F2 = -(-9.30769e-8*lam^3+5.02846e-5*lam^2-.00941*lam+.618231-1)
[9] k = .01*exp(45000/8.314*(1/320-1/T))
[10] E = if (lam<=70) then (E1) else (E2)
[11] F = if (lam<=70) then (F1) else (F2)
[12] EF = E/(1-F)
[13] ra = -k*ca^2



P13-2 (k)

Base case:

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Ca)/d(t) = ra/vo
[2] d(Cb)/d(t) = rb/vo
[3] d(Cc)/d(t) = rc/vo

Explicit equations as entered by the user
[1] vo = 10
[2] k1 = 1
[3] k2 = 1
[4] tau = 1.26
[5] ra = -k1*Ca
[6] rc = k2*Cb

[7] Cao = 1
[8] x = 1-Ca/Cao
[9] rb = k1*Ca-k2*Cb

PFR	$K_1/K_2=1$	$K_1/K_2=2$	$K_1/K_2=0.5$
C_A	0.284	0.080	0.284
C_B	0.357	0.406	0.203
C_C	0.359	0.513	0.513
X	0.716	0.919	0.716

See Polymath program P13-2-k-2.pol

POLYMATH Results

NLES Solution

Variable	Value	f(x)	Ini Guess
ca	0.4424779	4.704E-10	1
cb	0.2466912	-3.531E-10	0
cc	0.3108309	0	0
cao	1		
tau	1.26		
cbo	0		
cco	0		
k1	1		
k2	1		
ra	-0.4424779		
rc	0.2466912		
rb	0.1957867		

NLES Report (safenewt)

Nonlinear equations
[1] f(ca) = cao+ra*tau-ca = 0
[2] f(cb) = cbo+rb*tau-cb = 0
[3] f(cc) = cco+rc*tau-cc = 0

Explicit equations
[1] cao = 1
[2] tau = 1.26
[3] cbo = 0
[4] cco = 0
[5] k1 = 1
[6] k2 = 1
[7] ra = -k1*ca
[8] rc = k2*cb
[9] rb = k1*ca-k2*cb

CSTR	$K_1/K_2=1$	$K_1/K_2=2$	$K_1/K_2=0.5$
C_A	0.443	0.284	0.443
C_B	0.247	0.317	0.158
C_C	0.311	0.399	0.399
X	0.557	0.716	0.557

See Polymath program P13-2-k-3.pol

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	2.52	2.52
ca	1	0.0804596	1	0.0804596
cb	0	0	0.3678466	0.2027582
cc	0	0	0.7167822	0.7167822
cabar	0	0	0.3050655	0.304964
cbbar	0	0	0.3350218	0.3347693
ccbar	0	0	0.3476989	0.3468313
k1	1	1	1	1
k2	1	1	1	1
cao	1	1	1	1
E1	-0.004	-27.462382	0.9523809	-27.462382
E2	-27.402	-27.402	0.9568359	-0.0272502
ra	-1	-1	-0.0804596	-0.0804596
rc	0	0	0.3678269	0.2027582
x	0	0	0.9195404	0.9195404
rb	1	-0.1353314	1	-0.1222986
E	-0.004	-0.0272502	0.9568359	-0.0272502

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(ca)/d(t) = ra
[2] d(cb)/d(t) = rb
[3] d(cc)/d(t) = rc
[4] d(cabar)/d(t) = ca*E
[5] d(cbbar)/d(t) = cb*E
[6] d(ccbar)/d(t) = cc*E

Explicit equations as entered by the user

[1] k1 = 1
[2] k2 = 1
[3] cao = 1
[4] E1 = -2.104*t^4+4.164*t^3-1.596*t^2+0.353*t-0.004
[5] E2 = -2.104*t^4+17.037*t^3-50.247*t^2+62.964*t-27.402
[6] ra = -k1*ca
[7] rc = k2*cb
[8] x = (cao-ca)/cao
[9] rb = k1*ca-k2*cb
[10] E = if(t<=1.26)then(E1)else(E2)

Asymmetric RTD

Segregation Model	**K_1/K_2=1**	**K_1/K_2=2**	**K_1/K_2=0.5**
C_A	0.306	0.110	0.306
C_B	0.335	0.390	0.195
C_C	0.347	0.486	0.486
X	0.694	0.89	0.694

See Polymath program P13-2-k-4.pol

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	7	7
ca	1	9.119E-04	1	9.119E-04
cb	0	0	0.3678325	0.0063832
cc	0	0	0.9927049	0.9927049
cabar	0	0	0.3879174	0.3879174

cbbar	0	0	0.2782572	0.2782572
ccbar	0	0	0.3271713	0.3271713
k1	1	1	1	1
k2	1	1	1	1
cao	1	1	1	1
E1	0.20909	0.1017293	707.06552	707.06552
E2	925.46463	0.074462	3.072E+04	3.072E+04
ra	-1	-1	-9.119E-04	-9.119E-04
rc	0	0	0.3675057	0.0063832
x	0	0	0.9990881	0.9990881
rb	1	-0.1353022	1	-0.0054713
E4	0	0	0	0
E3	1.84445	0.0061369	1.84445	0.09781
E	0.20909	0	0.628067	0

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(ca)/d(t) = ra
[2] d(cb)/d(t) = rb
[3] d(cc)/d(t) = rc
[4] d(cabar)/d(t) = ca*E
[5] d(cbbar)/d(t) = cb*E
[6] d(ccbar)/d(t) = cc*E

Explicit equations as entered by the user

[1] k1 = 1
[2] k2 = 1
[3] cao = 1
[4] E1 = 0.47219*t^4-1.30733*t^3+0.31723*t^2+0.85688*t+0.20909
[5] E2 = 3.83999*t^6-58.16185*t^5+366.20970*t^4-1224.66963*t^3+2289.84857*t^2-2265.62125*t+925.46463
[6] ra = -k1*ca
[7] rc = k2*cb
[8] x = (cao-ca)/cao
[9] rb = k1*ca-k2*cb
[10] E4 = 0
[11] E3 = 0.00410*t^4-0.07593*t^3+0.52276*t^2-1.59457*t+1.84445
[12] E = if(t<=1.82)then(E1)else(if(t<=2.8)then(E2)else(if(t<6)then(E3)else(E4)))

Bimodal RTD

Segregation Model	$K_1/K_2=1$	$K_1/K_2=2$	$K_1/K_2=0.5$
C_A	0.388	0.213	0.388
C_B	0.278	0.350	0.175
C_C	0.327	0.430	0.430
X	0.612	0.787	0.612

Asymmetric RTD

Maximum Mixedness	$K_1/K_2=1$	$K_1/K_2=2$	$K_1/K_2=0.5$
C_A	0.306	0.110	0.306
C_B	0.335	0.390	0.195
C_C	0.347	0.486	0.486
X	0.694	0.89	0.694

P13-2 (l-r) No solution will be given at this time.

P13-3

Equivalency Maximum Mixedness and Segregation model for first order reaction:

Maximum Mixedness Model: $\frac{dC_A}{d\lambda} = kC_A + \frac{E(\lambda)}{1-F(\lambda)}(C_A - C_{Ao})$

Rearranging: $\frac{dC_A}{d\lambda} - \left[k + \frac{E(\lambda)}{1-F(\lambda)}\right]C_A = -\frac{C_{Ao}E(\lambda)}{1-F(\lambda)}$

Using the integration factor: $\frac{d\left[\frac{C_A}{C_{Ao}} e^{-\int\left[k+\frac{E(\lambda)}{1-F(\lambda)}\right]d\lambda}\right]}{d\lambda} = -\frac{E(\lambda)e^{-\int\left[k+\frac{E(\lambda)}{1-F(\lambda)}\right]d\lambda}}{1-F(\lambda)}$

$$\frac{C_A}{C_{Ao}} e^{-\int\left[k+\frac{E(\lambda)}{1-F(\lambda)}\right]d\lambda} = -\int_{\infty}^{\lambda}\left[\frac{E(\lambda)e^{-\int\left[k+\frac{E(\lambda)}{1-F(\lambda)}\right]d\lambda}}{1-F(\lambda)}\right]d\lambda$$

$$\frac{C_A}{C_{Ao}} e^{-\int\left[k+\frac{E(\lambda)}{1-F(\lambda)}\right]d\lambda} = -\int_{\infty}^{\lambda}\left[\frac{E(\lambda)e^{-k\lambda}e^{-\int\left[\frac{E(\lambda)}{1-F(\lambda)}\right]d\lambda}}{1-F(\lambda)}\right]d\lambda$$

by definition $E(\lambda)d(\lambda) = dF(\lambda)$

gives: $e^{-\int\left[\frac{E(\lambda)}{1-F(\lambda)}\right]d\lambda} = e^{-\int\frac{dF}{1-F(\lambda)}} = e^{d[Ln(1-F(\lambda))]} = (1-F(\lambda))$

changing the variables from λ to t in the RHS integral:

$$\frac{C_A}{C_{Ao}} e^{-k\lambda}(1-F(\lambda)) = \int_{\lambda}^{\infty}\left[\frac{E(t)e^{-kt}(1-F(t))}{1-F(t)}\right]dt$$

$$C_A = C_{Ao}\frac{e^{\lambda k}}{1-F(\lambda)}\int_{\lambda}^{\infty} E(t)e^{-kt}dt \qquad (1)$$

Exit concentration is when λ=0, F(0)=0 hence eqn (1) becomes:

$$C_A = C_{Ao}\int_{0}^{\infty} E(t)e^{-kt}dt$$

This is the same expression as for the exit concentration for the Segregation model.

P13-4 (a)

Mean Residence Time

By definition $\int_0^\infty E(t)dt = 1$. The area of the semicircle representing the E(t) is given by $A = \frac{\pi\tau^2}{2} = 1$ and $\tau = \sqrt{\frac{2}{\pi}}$. For constant volumetric flow $t_m = \tau = \sqrt{\frac{2}{\pi}} = 0.8\,\text{min}$.

P13-4 (b)

Variance

$$\sigma^2 = \int_0^\infty (t-\tau)^2 E(t)dt = \int_0^\infty t^2 E(t)dt - \tau^2$$

$$\int_0^\infty t^2 E(t)dt = \int_0^{2\tau} t^2\sqrt{\tau^2 - (t-\tau)^2}\,dt = -\tau^4 \int_\pi^0 \left[\cos^2(x) + 2\cos(x) + 1\right]\sin^2(x)dx = \frac{5\pi}{8}\tau^4$$

$$\sigma^2 = \frac{5\pi}{8}\tau^4 - \tau^2 = \frac{1}{2\pi} = 0.159$$

Using Polymath:
See Polymath program P13-4-b pol

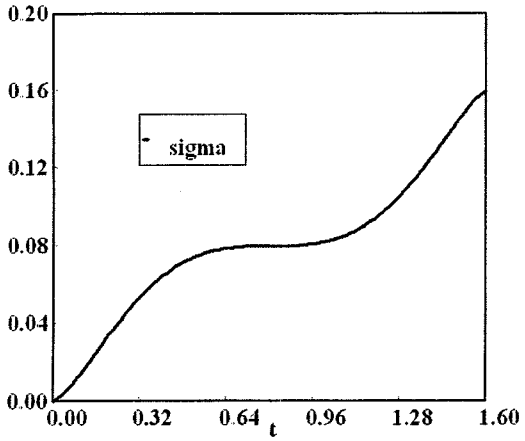
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	1.596	1.596
sigma	0	0	0.1593161	0.1593161
tau	0.7980869	0.7980869	0.7980869	0.7980869
t1	1.5961738	1.5961738	1.5961738	1.5961738
E2	0	0	0.7980614	0.0166534
E	0	0	0.7980614	0.0166534

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(sigma)/d(t) = (t-tau)^2*E

Explicit equations as entered by the user
[1] tau = (2/3.14)^0.5
[2] t1 = 2*tau
[3] E2 = (t*(2*tau-t))^(1/2)
[4] E = if (t<t1) then (E2) else (0)



P13-4 (c)

Conversion predicted by the Segregation model

$$\overline{X} = \int_0^{\infty} X(t)E(t)dt$$

$$X(t) = 1 - e^{-kt}$$

$$\overline{X} = 1 - \int_0^{2\tau} e^{-kt}\left(\tau^2 - (t-\tau)^2\right)^{1/2} dt$$

See Polymath program P13-4-c.pol

POLYMATH Results

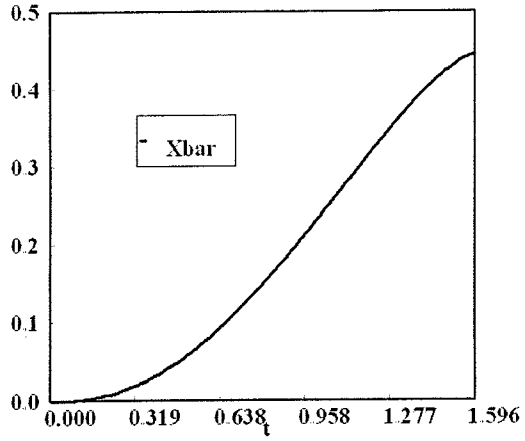
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	1.596	1.596
Xbar	0	0	0.4447565	0.4447565
tau	0.7980869	0.7980869	0.7980869	0.7980869
t1	1.5961738	1.5961738	1.5961738	1.5961738
E2	0	0	0.7980671	0.0166534
E	0	0	0.7980671	0.0166534
k	0.8	0.8	0.8	0.8
X	0	0	0.7210716	0.7210716

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Xbar)/d(t) = X*E

Explicit equations as entered by the user
[1] tau = (2/3.14)^0.5
[2] t1 = 2*tau
[3] E2 = (t*(2*tau-t))^(1/2)
[4] E = if (t<t1) then (E2) else (0)
[5] k = .8
[6] X = 1-exp(-k*t)



$\overline{X} = 44.5\%$

P13-4 (d)

Conversion predicted by the Maximum Mixedness model

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{Ao}} + \frac{E(\lambda)}{1-F(\lambda)}X$$

$$r_A = -kC_A = -kC_{Ao}(1-X)$$

$$\frac{dX}{d\lambda} = -k(1-X) + \frac{E(\lambda)}{1-F(\lambda)}X$$

$$\frac{dX}{dz} = k(1-X) - \frac{E(\lambda)}{1-F(\lambda)}X$$

See Polymath program P13-4-d pol

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
z	0	0	1.596	1.596
x	0	0	0.4445289	0.4445289
F	1	-5.053E-04	1	-5.053E-04
k	0.8	0.8	0.8	0.8
lam	1.596	0	1.596	0
tau	0.7980869	0.7980869	0.7980869	0.7980869
E1	0.0166534	0	0.7980666	0
E	0.0166534	0	0.7980666	0

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(x)/d(z) = -(-k*(1-x)+E/(1-F)*x)

[2] d(F)/d(z) = -E

Explicit equations as entered by the user

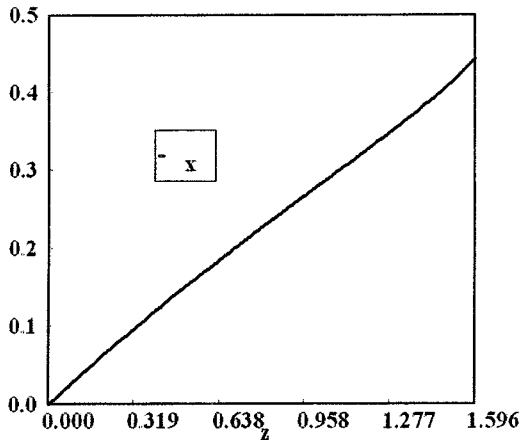
[1] k = .8

[2] lam = 1.596-z

[3] tau = (2/3.14)^0.5

[4] E1 = (tau^2-(lam-tau)^2)^0.5

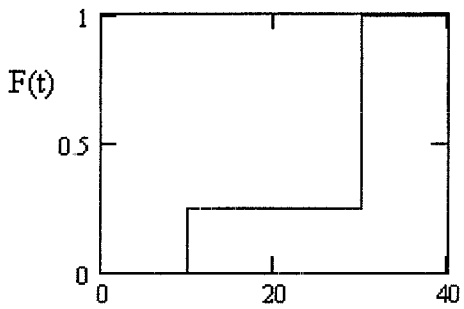
[5] E = if (lam<=2*tau) then (E1) else (0)



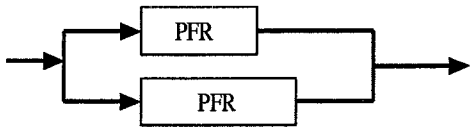
$X = 44.5\%$ as for the Segregation Model, but we knew this because for first order reactions $X_{seg} = X_{MM}$

P13-5 (a)

The cumulative distribution function F(t) is given:



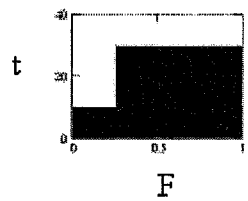
The real reactor can be modelled as two parallel PFRs:



The relative $E(t) = \left\{\frac{1}{4}\delta(t-\tau_1) + \frac{3}{4}\delta(t-\tau_2)\right.$

Mean Residence Time

$$t_m = \int_0^1 t dF = (10\,\text{min} * 1) + (20\,\text{min} * 0.75) = 25\,\text{min}$$



or

$$t_m = \int_0^\infty tE(t)dt = \int t\left[\frac{1}{4}\delta(t-\tau_1)+\frac{3}{4}\delta(t-\tau_2)\right] = \frac{1}{4}\tau_1 + \frac{3}{4}\tau_2 = 25\,\text{min}$$

P13-5 (b)

Variance

$$\sigma^2 = \int_0^\infty (t-\tau)^2 E(t)dt = \int (t-t_m)^2\left[\frac{1}{4}\delta(t-\tau_1)+\frac{3}{4}\delta(t-\tau_2)\right]dt = \frac{1}{4}(\tau_1 - t_m)^2 + \frac{3}{4}(\tau_2 - t_m)^2 =$$

$$= 75\,\text{min}^2$$

P13-5 (c)

For a PFR, second order, liquid phase, irreversible reaction with k = 0.1 dm^3 /mol·min^{-1}, τ = 25 min and C_{Ao} = 1.25 mol/dm^3

$$X = \frac{k\tau C_{Ao}}{1+k\tau C_{Ao}} = 0.758$$

For a CSTR, second order, liquid phase, irreversible reaction with k = 0.1 dm^3 /mol·min^{-1}, τ = 25 min and C_{Ao} = 1.25 mol/dm^3

$$\frac{X}{(1-X)^2} = k\tau C_{Ao} \rightarrow X = 0.572$$

For two parallel PFRs, τ_1 = 10 min and τ_2 = 30 min, Fa_{01} = 1/4Fa_0 and Fa_{02} = 3/4Fa_0 , second order, liquid phase, irreversible reaction with k = 0.1 dm^3 /mol·min^{-1} and C_{Ao} = 1.25 mol/dm^3

$$C_{A1} = C_{Ao} - \frac{k\tau_1 C_{Ao}}{1+k\tau_1 C_{Ao}} C_{Ao} = 0.556 mol/dm^3$$

$$C_{A2} = C_{Ao} - \frac{k\tau_2 C_{Ao}}{1+k\tau_2 C_{Ao}} C_{Ao} = 0.263 mo/dm^3$$

$$X = \frac{vC_{Ao} - \frac{1}{4}vC_{A1} - \frac{3}{4}vC_{A2}}{vC_{Ao}} = 0.731$$

P13-5 (d)

1-Conversion predicted by the Segregation Model

$$\overline{X} = \int_0^\infty X(t)E(t)dt = \int_0^\infty \frac{kC_{Ao}t}{1+kC_{Ao}t}\left[\frac{1}{4}\delta(t-\tau_1)+\frac{3}{4}\delta(t-\tau_2)\right]dt =$$

$$\frac{1}{4}\frac{kC_{Ao}\tau_1}{1+kC_{Ao}\tau_1}+\frac{3}{4}\frac{kC_{Ao}\tau_2}{1+kC_{Ao}\tau_2} = 0.731$$

2-Conversion predicted by the Maximum Mixedness model

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{Ao}} + \frac{E(\lambda)}{1-F(\lambda)}X$$

$$r_A = -kC_A{}^2 = -kC_{Ao}{}^2(1-X)^2$$

$$\frac{dX}{d\lambda} = -kC_{Ao}(1-X)^2 + \frac{E(\lambda)}{1-F(\lambda)}X$$

We need to change the variable such the integration proceeds forward:

$$\frac{dX}{dz} = kC_{Ao}(1-X)^2 - \frac{E(T-z)}{1-F(T-z)}X$$

See Polymath program P13-5-d.pol

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
z	0	0	40	40
x	0	0	0.7125177	0.7061611
F	0.9999	-1.081E-04	0.9999	-1.081E-04
cao	1.25	1.25	1.25	1.25
k	0.1	0.1	0.1	0.1
lam	40	0	40	0
ca	1.25	0.3614311	1.25	0.3672986
t1	10	10	10	10
t2	30	30	30	30
E3	0	0	0	0
ra	-0.15625	-0.15625	-0.0130632	-0.0134908
E2	1.25	1.25	1.25	1.25
E1	1.25	1.25	1.25	1.25
E	0	0	1.25	0
EF	0	0	2.8604931	0

ODE Report (RKF45)

Differential equations as entered by the user

```
[1] d(x)/d(z) = -(ra/cao+E/(1-F)*x)
[2] d(F)/d(z) = -E
```

Explicit equations as entered by the user

```
[1] cao = 1.25
[2] k = .1
[3] lam = 40-z
[4] ca = cao*(1-x)
[5] t1 = 10
[6] t2 = 30
[7] E3 = 0
[8] ra = -k*ca^2
[9] E2 = 0.75/(t2*2*(1-0.99))
[10] E1 = 0.25/(t1*2*(1-0.99))
```

[11] E = if ((lam>=0.99*t1)and(lam<1.01*t1)) then (E1) else(if ((lam>=0.99*t2)and(lam<1.01*t2)) then (E2) else (E3))
[12] EF = E/(1-F)

X_{real}	X_{MM}	X_{seg}	X_{PFR}	X_{CSTR}
0.731	0.706	0.731	0.758	0.572

P13-5 (e)

Adiabatic Reaction E=10000cal/mol and $T = 325 - 500X$

Introducing the enthalpy balance: $T = 325 - 500X$ and the constitutive equation for $k = k_{325} \cdot e^{(45000/8.314*(1/325-1/T))}$ in the MM model.

The conversion is drastically reduced.

P13-5 (f)

Conversion Predicted by an ideal laminar flow reactor
For a LFR, second order, liquid phase, irreversible reaction with k = 0.1 dm^3 /mol·min^{-1}, τ = 25 min and C_{Ao} = 1.25 mol/dm^3

We apply the Segregation model, using Polymath:

$$X = \frac{ktC_{Ao}}{1+ktC_{Ao}} \text{ and } E(t) = \begin{cases} 0 \text{ for } t < 12.5\,\text{min} \\ 625/(2t^3)\,\text{min}^{-1} \text{ for } t \geq 12.5\,\text{min} \end{cases}$$

See Polymath program P13-5-e.pol

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	300	300
xbar	0	0	0.7077852	0.7077852
cao	1.25	1.25	1.25	1.25
k	0.1	0.1	0.1	0.1
tau	25	25	25	25
E1	3.125E+06	1.157E-05	3.125E+06	1.157E-05
t1	12.5	12.5	12.5	12.5
E	0	0	0.0991813	1.157E-05
x	0	0	0.974026	0.974026

ODE Report (RKF45)

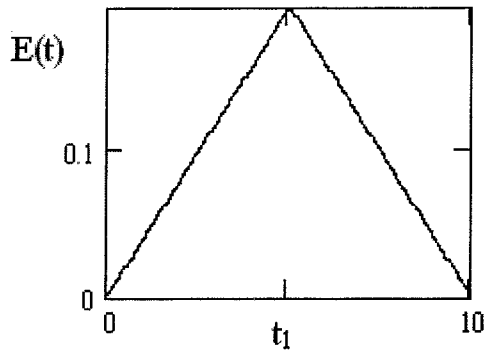
Differential equations as entered by the user
[1] d(xbar)/d(t) = x*E

Explicit equations as entered by the user
[1] cao = 1.25
[2] k = .1
[3] tau = 25
[4] E1 = tau^2/2/(t^3+0.0001)
[5] t1 = tau/2
[6] E = if (t<t1) then (0) else (E1)
[7] x = k*cao*t/(1+k*cao*t)

We can compare with the exact analytical formula due to Denbigh.

$$X = Da\left[1-\left(\frac{Da}{2}\right)\ln(1+2/Da)\right] = 0.709 \text{ with Da= } kC_{Ao}\tau$$

P13-6 (a)



Mean Residence Time

By definition $\int_0^\infty E(t)dt = 1$. The area of the triangle representing the E(t) is given by $A = \frac{2t_1 0.2}{2} = 1$

$t_1 = 5\,\text{min}.$ $\longrightarrow$

$$E(t) = \begin{cases} \frac{t}{t_1^2} \; if\, t < t_1 \\ -\frac{1}{t_1^2}(t-2t_1) if\; t_1 \le t \le 2t_1 \\ 0 \; otherwise \end{cases}$$

$$t_m = \int_0^\infty tE(t)dt = \int_0^{t_1} \frac{t^2}{t_1^2}dt - \int_{t_1}^{2t_1} \frac{(t^2)}{t_1^2}dt + \int_{t_1}^{2t_1} \frac{2t}{t_1}dt = t_1 .$$

P13-6 (b)

Variance

$$\sigma^2 = \int_0^\infty (t-t_m)^2 E(t)dt = \int_0^\infty t^2 E(t)dt - t_m^2$$

$$\int_0^\infty t^2 E(t)dt = \frac{7}{6}t_m^2 \text{ and } \sigma^2 = \frac{7}{6}t_m^2 - t_m^2 = \frac{t_m^2}{6} = \frac{25}{6} = 4.167\,\text{min}^2$$

See Polymath program P13-6-b.pol

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	10	10
sigma	0	0	4.1666667	4.1666667
tau	5	5	5	5
t1	10	10	10	10
E1	0	0	0.4	0.4
E2	0.4	0	0.4	0
E	0	0	0.1989341	0

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(sigma)/d(t) = (t-tau)^2*E

Explicit equations as entered by the user
[1] tau = 5
[2] t1 = 2*tau
[3] E1 = t/tau^2
[4] E2 = -(t-2*tau)/tau^2
[5] E = if (t<tau) then (E1) else (if(t<=t1)then(E2)else(0))

•

σ^2=4.167min^2

P13-6 (c)

For a PFR, second order, liquid phase, irreversible reaction with kC_{Ao} =0.2 min^{-1},τ=5 min

$$X = \frac{k\tau C_{Ao}}{1+k\tau C_{Ao}} = 0.5$$

For a CSTR, second order, liquid phase, irreversible reaction with kC_{Ao} =0.2 min^{-1},τ=5 min

$$\frac{X}{(1-X)^2} = k\tau C_{Ao} \rightarrow X = 0.382$$

P13-6 (d)

1-Segregation model
See Polymath program P13-6-d-1.pol

POLYMATH Results
Calculated values of the DEQ variables

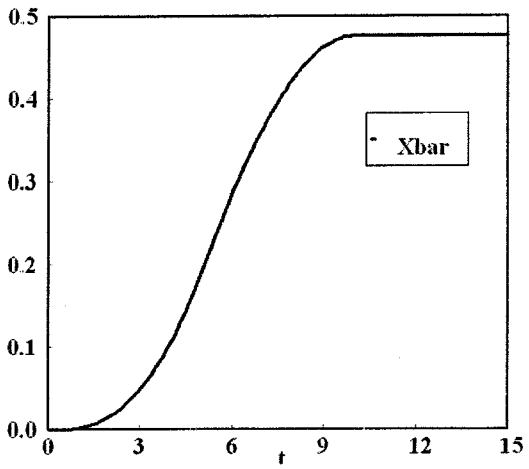
Variable	initial value	minimal value	maximal value	final value
t	0	0	15	15
Xbar	0	0	0.4767547	0.4767547
k1	0.2	0.2	0.2	0.2
X	0	0	0.75	0.75
tau	5	5	5	5
t1	10	10	10	10
E1	0	0	0.6	0.6
E2	0.4	-0.2	0.4	-0.2
E	0	0	0.1978698	0

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Xbar)/d(t) = X*E

Explicit equations as entered by the user

```
[1] k1 = .2
[2] X = k1*t/(1+k1*t)
[3] tau = 5
[4] t1 = 2*tau
[5] E1 = t/tau^2
[6] E2 = -(t-t1)/tau^2
[7] E = if (t<tau) then (E1) else(if(t<=t1)then(E2)else(0))
```



$\overline{X} = 47.7\%$

2-Maximum Mixedness Model

$kC_{Ao} = k'$

$$\frac{dX}{dz} = -\left(\frac{r_A}{C_{Ao}} + \frac{E(T-z)}{1-F(T-z)}X\right)$$

$$r_A = -kC_A{}^2 = -kC_{Ao}{}^2(1-X)^2$$

$$\frac{dX}{dz} = k'(1-X)^2 - \frac{E(T-z)}{1-F(T-z)}X$$

See Polymath program P13-6-d-2.pol

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
z	0	0	20	20
x	0	0	0.6642538	0.4669205
F	1	-7.513E-06	1	-7.513E-06
k	0.2	0.2	0.2	0.2
lam	20	0	20	0
tau	5	5	5	5
E1	0.8	0	0.8	0
t1	10	10	10	10
E2	-0.4	-0.4	0.4	0.4
E	0	0	0.1994823	0

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(x)/d(z) = -(-k*(1-x)^2+E/(1-F)*x)
[2] d(F)/d(z) = -E

Explicit equations as entered by the user
[1] k = 0.2
[2] lam = 20-z
[3] tau = 5
[4] E1 = lam/tau^2
[5] t1 = 2*tau
[6] E2 = -(lam-t1)/tau^2
[7] E = if (lam<tau) then (E1) else(if (lam<=t1) then(E2)else (0))

$X = 46.7\%$

P13-6 (e)

Laminar Flow Reactor
For a LFR, 2nd order, liq. phase, irreversible reaction kC_{Ao} =0.2 min^{-1},τ=5 min.
We apply the segregation model, using Polymath:

$$X = \frac{ktC_{Ao}}{1+ktC_{Ao}} \text{ and } E(t) = \begin{cases} 0 \text{ for } t < 2.5\,\text{min} \\ 25/(2t^3)\,\text{min}^{-1} \text{ for } t \geq 2.5\,\text{min} \end{cases}$$

See Polymath program P13-6-e.pol

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	300	300
xbar	0	0	0.4506243	0.4506243
kcao	0.2	0.2	0.2	0.2
tau	5	5	5	5
E1	1.25E+05	4.63E-07	1.25E+05	4.63E-07
t1	2.5	2.5	2.5	2.5
E	0	0	0.0549822	4.63E-07
x	0	0	0.9836066	0.9836066

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(xbar)/d(t) = x*E

Explicit equations as entered by the user
[1] kcao = 0.2
[2] tau = 5
[3] E1 = tau^2/2/(t^3+0.0001)
[4] t1 = tau/2
[5] E = if (t<t1) then (0) else (E1)
[6] x = kcao*t/(1+kcao*t)

We can compare with the exact analytical formula due to Denbigh.

$$X = Da\left[1-\left(\frac{Da}{2}\right)\ln(1+2/Da)\right] = 0.451 \text{ with Da= } kC_{Ao}\tau$$

X_{LFR}	X_{MM}	X_{seg}	X_{PFR}	X_{CSTR}
0.451	0.467	0.477	0.5	0.382

P13-7

Irreversible Liquid phase, half order, Segregation model

Mean conversion $X = \int_0^\infty X(t)E(t)dt = 0.1$ (1)

Assume a Gaussian distribution for E(t):

$$E(t) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{(t-\tau)^2}{2.\sigma^2}\right] = \frac{1}{3\sqrt{2.\pi}}\exp\left[-\frac{(t-5)^2}{2\cdot 3^2}\right]$$

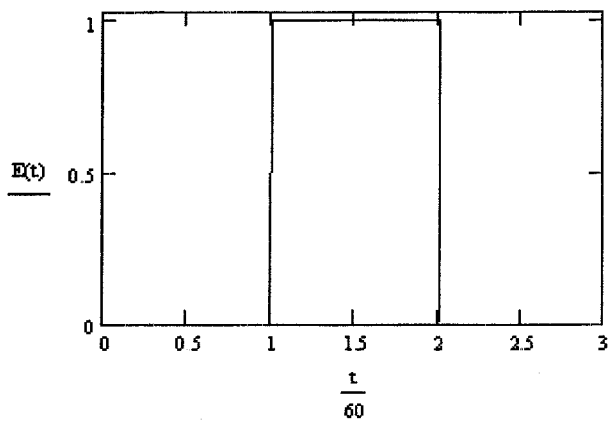
$$\frac{dX}{dt} = k\frac{C_{Ao}^{1/2}}{C_{Ao}}(1-X)^{1/2} \quad \text{and } C_{Ao}=1 \text{ mol/dm}^3$$

The only unknown k1 is estimated solving with a trial and error method Eq(1).

Using POLYMATH: $k_1 = 0.0205$ mol$^{1/2}$/dm$^{3/2}$.s

P13-8 (a)

The E(t) is a square pulse



Third order liquid-phase reaction: $r_A = kC_A^3$ with $C_{Ao} = 2$mol/dm^3 and k = 0.3 dm^6/mol^2/min (Isothermal Operation)

1-Conversions

Segregation Model

$$X(t) = 1 - \frac{1}{\sqrt{(2kC_{Ao}{}^2t+1)}}$$

$$\bar{X} = \int_0^\infty X(t)E(t)dt = \int_1^2\left[1-\frac{1}{\sqrt{2kC_{Ao}^2t+1}}\right]dt = \left|t - \frac{\sqrt{2kC_{Ao}^2t+1}}{kC_{Ao}^2}\right|_1^2 = 0.53$$

See Polymath program P13-8-a-1.pol

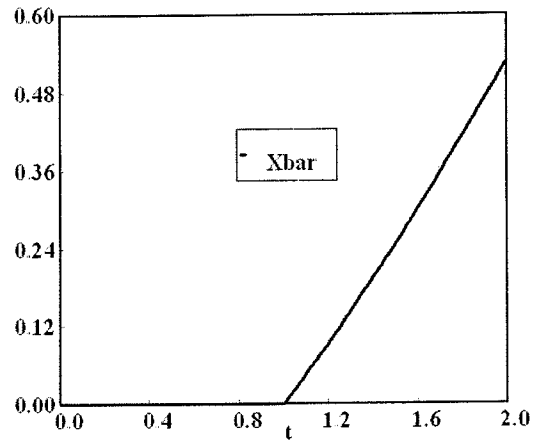
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	2	2
Xbar	0	0	0.5296583	0.5296583
k	0.3	0.3	0.3	0.3
Cao	2	2	2	2
t1	1	1	1	1
E2	1	1	1	1
E	0	0	1	1
X	0	0	0.5847726	0.5847726

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Xbar)/d(t) = X*E

Explicit equations as entered by the user
[1] k = .3
[2] Cao = 2
[3] t1 = 1
[4] E2 = 1
[5] E = if (t>=t1) then (E2) else (0)
[6] X = 1-1/(1+2*k*Cao^2*t)^(1/2)



2-Maximum Mixedness Model

$$\frac{dX}{dz} = -\left(\frac{r_A}{C_{Ao}} + \frac{E(T-z)}{1-F(T-z)}X\right)$$

$$r_A = -kC_A{}^3 = -kC_{Ao}{}^3(1-X)^3$$

$$\frac{dX}{dz} = kC_{Ao}^2(1-X)^3 - \frac{E(T-z)}{1-F(T-z)}X$$

See Polymath program P13-8-a-2.pol

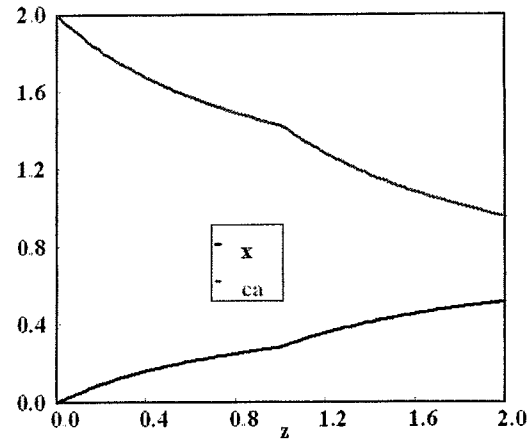
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
z	0	0	2	2
x	0	0	0.5215389	0.5215389
F	0.9999	-9.999E-05	0.9999	-9.999E-05
cao	2	2	2	2
k	0.3	0.3	0.3	0.3
lam	2	0	2	0
ca	2	0.9569223	2	0.9569223
E1	1	1	1	1
ra	-2.4	-2.4	-0.2628762	-0.2628762
t2	2	2	2	2
t1	1	1	1	1
E	1	0	1	0
EF	1.0E+04	0	1.0E+04	0

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(x)/d(z) = -(ra/cao+E/(1-F)*x)
[2] d(F)/d(z) = -E

Explicit equations as entered by the user
[1] cao = 2
[2] k = .3
[3] lam = 2-z
[4] ca = cao*(1-x)
[5] E1 = 1
[6] ra = -k*ca^3
[7] t2 = 2
[8] t1 = 1
[9] E = if ((lam>=t1)and(lam<=t2)) then (E1) else(0)
[10] EF = E/(1-F)



The conversion shows an inflection point in correspondence of z = 1, where start the pulse $\frac{d^2X}{d\lambda^2} = 0$.

P13-8 (b)

Introducing in the Segregated Model and in the MM Model :

$k = k_{300} \cdot e^{(20000*(1/300-1/T))}$

See Polymath program P13-8-b-1.pol and P13-8-b-2.pol

	300K	310K	320K	330K	340K	350K
X_{seg}	0.530	0.82	0.933	0.974	0.989	0.995
X_{MM}	0.521	0.806	0.924	0.97	0.987	0.994

The discrepancy is greatest at 300K

P13-8 (c)

Adiabatic Reaction

Introducing the enthalpy balance:

$$T = T_0 + \frac{(-\Delta H_{RX})}{\sum \theta_i C_{Pi}} X = 305 + \frac{40000}{50} X$$

See Polymath program P13-8-c.pol

POLYMATH Results
Calculated values of the DEQ variables

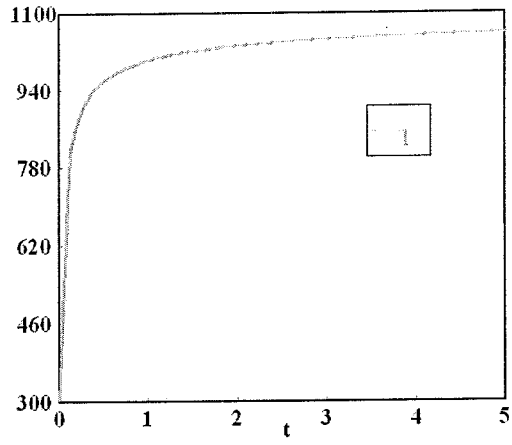
Variable	initial value	minimal value	maximal value	final value
t	0	0	5	5
Xbar	0	0	0.8949502	0.8949502
ko	0.8948702	0.8948702	0.8948702	0.8948702
t1	1	1	1	1
E2	1	1	1	1
t2	2	2	2	2
Cao	2	2	2	2
E	0	0	1	0
k	7.6864651	7.6864651	7.6864651	7.6864651
To	305	305	305	305

X	0	0	0.9430621	0.9430621
T	305	305	1059.4497	1059.4497

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Xbar)/d(t) = X*E

Explicit equations as entered by the user
[1] ko = 0.3*exp(20000*(1/300-1/305))
[2] t1 = 1
[3] E2 = 1
[4] t2 = 2
[5] Cao = 2
[6] E = if((t>=t1) and (t<=t2)) then (E2) else (0)
[7] k = ko*exp(20000*(1/300-1/310))
[8] To = 305
[9] X = 1-1/(1+2*k*Cao^2*t)^.5
[10] T = To+800*X



P13-9 (a)

3rd order, k=175 dm⁶/(mol² min), C_{Bo}=0.0313 dm³/min

(LFR, PFR, CSTR with τ=100s)

PFR

Design equation $v_o C_{Ao}\frac{dX}{dV} = k C_A C_B^{\,2}$

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

$$C_B = C_{Bo}(1-X)$$

$$\int_0^X \frac{dX}{(1-X)^3} = kC_{Bo}^{\,2}\frac{V}{v}$$

$$\int_0^X \frac{dX}{(1-X)^3} = kC_{Bo}^{\,2}\frac{V}{v}$$

$$\frac{1}{(1-X)^2} = 2kC_{Bo}^{\,2}\frac{V}{v}+1$$

Using the quadratic solution $X = 1-\frac{1}{\sqrt{1+2kC_{Bo}^{\,2}\frac{V}{v}}} = 1-0.168 = 0.832$

The conversion for a PFR X=83.2%

CSTR

Design equation $v_o(C_{Ao} - C_A) = -r_A V$

$$-r_A = k C_A C_B^{\,2}$$

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

$$C_B = C_{Bo}(1-X)$$

$$\frac{C_{Ao} - C_A}{C_{Ao}} = X$$

$$X = kC_{Bo}^{\,2}(1-X)^3 \frac{V}{v}$$

The conversion for a CSTR X=66.2 %

LFR (completely segregated)

E(t)=0 for $t<\tau/2$

$=\tau^2/2t^3$ for $t>=\tau/2$

$\tau=V/v=1000/10=100s=1.67min$

$$\overline{X} = \int_0^\infty X(t)E(t)dt$$

$$\frac{dX}{dt} = kC_{Ao}^2(1-X)^3$$

Where $X(t) = 1 - \sqrt{\frac{1}{1+2kC_{Bo}^{\,2}t}}$

See Polymath program P13-9-a.pol

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	1.0E-05	1.0E-05	100	100
xbar	0	0	0.1827616	0.1827616
cbo	0.0313	0.0313	0.0313	0.0313
k	175	175	175	175
tau	1.67	1.67	1.67	1.67
E1	1.394E+15	1.403E-06	1.394E+15	1.403E-06
x	1.714E-06	1.714E-06	0.8315008	0.8315008
E	0	0	0.1480215	1.403E-06

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(xbar)/d(t) = x*E

Explicit equations as entered by the user

[1] cbo = 0.0313

[2] k = 175

[3] tau = 1.67

[4] E1 = tau^2/(2*t^3)
[5] x = 1-(1/(1+2*k*cbo^2*t))^0.5
[6] E = if(t>=tau/2) then (E1) else (0)

The integral $\overline{X} = \int_0^\infty X(t)E(t)dt$ gives mean conversion=18%

P13-9 (b)

(Segregation Model and Maximum Mixedness Model applying RTD of Example 13-1)

Segregation model

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

Batch reactor $N_A = N_{Ao}(1-X)$

$$N_{Ao}\frac{dX}{dt} = kC_A C_B{}^2 V$$

$$C_A = C_{Ao}(1-X)$$
$$C_B = C_{Bo}(1-X)$$

$$\int_0^X \frac{dX}{(1-X)^3} = kC_{Bo}{}^2 t$$

Similarly $$X(t) = 1 - \sqrt{\left[\frac{1}{1+2kC_{Bo}{}^2 t}\right]}$$

$\overline{X} = \int_0^\infty X(t)E(t)dt$ and E(t) from the given data, fitted using Polymath

See Polymath program P13-9-b-regression.pol

POLYMATH Results
Polynomial Regression Report

Model: C02 = a1*C01 + a2*C01^2 + a3*C01^3 + a4*C01^4

Variable	Value	95% confidence
a1	0.0889237	0.0424295
a2	-0.0157181	0.0163712
a3	7.926E-04	0.0019617
a4	-8.63E-06	7.288E-05

General
Order of polynomial = 4
Regression not including free parameter
Number of observations = 13

Statistics

R^2 =	0.8653673
R^2adj =	0.8204897
Rmsd =	0.0065707
Variance =	8.107E-04

See Polymath program P13-9-b-1.pol

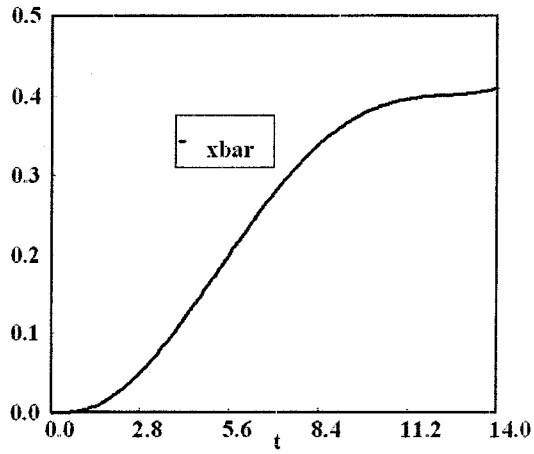
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	14	14
xbar	0	0	0.4106313	0.4106313
F	0	0	1.1137842	1.1137842
cbo	0.0313	0.0313	0.0313	0.0313
k	175	175	175	175
x	0	0	0.5847898	0.5847898
E	0	0	0.1566631	0.0199021

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(xbar)/d(t) = E*x
[2] d(F)/d(t) = E

Explicit equations as entered by the user
[1] cbo = 0.0313
[2] k = 175
[3] x = 1-(1/(1+2*k*cbo^2*t))^0.5
[4] E = 0.0899237*t-0.0157181*t^2+0.000792*t^3-0.00000863*t^4



$\overline{X}$ =41%.

Maximum Mixedness

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{Ao}} + \frac{E(\lambda)}{1-F(\lambda)}X$$

Rate Law : $-r_A = kC_A C_B^{\,2}$

$$C_A = C_{Ao}(1-X) \qquad C_B = C_{Bo}(1-X)$$

$r_A = kC_{Ao}C_{Bo}{}^2(1-X)^3$ where k=175 dm^6/mol^2 min

$$\frac{r_A}{C_{Ao}} = kC_{Bo}{}^2(1-X)^3$$

$$\frac{dF}{dz} = -E(z) \quad \text{where } z=14-\lambda$$

See Polymath program P13-9-b-2.pol

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
z	0	0	14	14
X	0	0	0.3536026	0.3536026
F	0.9999	-0.1138842	0.9999	-0.1138842
Cbo	0.0313	0.0313	0.0313	0.0313
k	175	175	175	175
lam	14	0	14	0
Cao	0.0313	0.0313	0.0313	0.0313
Ca	0.0313	0.0202322	0.0313	0.0202322
E	0.0199021	0	0.156664	0
EF	199.0212	0	199.0212	0
Cb	0.0313	0.0202322	0.0313	0.0202322
ra	-0.0053663	-0.0053663	-0.0014493	-0.0014493

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(X)/d(z) = -(ra/Cao+E/(1-F)*X)
[2] d(F)/d(z) = -E

Explicit equations as entered by the user
[1] Cbo = .0313
[2] k = 175
[3] lam = 14-z
[4] Cao = .0313
[5] Ca = Cao*(1-X)
[6] E = 0.0899237*lam-0.0157181*lam^2+0.000792*lam^3-0.00000863*lam^4
[7] EF = E/(1-F)
[8] Cb = Cbo*(1-X)
[9] ra = -k*Ca*Cb^2

X=35.4%

P13-9 (c)

Exit time(t), internal age(α) and life expectancyλ

$$\int_0 E(t)dt = F(t) \Rightarrow \frac{dF(t)}{dt} = E(t)$$

where E(t) is obtained from the polynomial fit in Part (b).

$$I(\alpha)=\frac{\nu}{V}[1-F(\alpha)]$$

Intensity Function $$\Lambda(\lambda)=\frac{E(\lambda)}{1-F(\lambda)}$$

P13-9 (d)

Adiabatic reaction

Segregation model

$$\frac{dX}{dt}=kC_{Bo}{}^{2}(1-X)^{3}$$

Where $$k(T)=ko\exp\left[\frac{E}{R}\left(\frac{1}{To}-\frac{1}{T}\right)\right]=175\exp\left[\frac{30000}{8.314}\left(\frac{1}{320}-\frac{1}{T}\right)\right]$$

and $$T(K)=To+\left(\frac{-\Delta Hrx}{Cp_A}\right)X=320+150X$$

$\overline{X}=\int_0^\infty X(t)E(t)dt$ and E(t) from the given data.

See Polymath program P13-9-d-1.pol

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	14	14
xbar	0	0	0.7585435	0.7585435
F	0	0	1.1137842	1.1137842
x	0	0	0.8973303	0.8973303
cbo	0.0313	0.0313	0.0313	0.0313
T	320	320	454.59954	454.59954
E	0	0	0.1565966	0.0199021
k	175	175	4931.8727	4931.8727

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(xbar)/d(t) = E*x
[2] d(F)/d(t) = E
[3] d(x)/d(t) = k*cbo^2*(1-x)^3

Explicit equations as entered by the user
[1] cbo = 0.0313
[2] T = 320+150*x
[3] E = 0.0899237*t-0.0157181*t^2+0.000792*t^3-0.00000863*t^4
[4] k = 175*exp(30000/8.314*(1/320-1/T))

$\overline{X}$ =76%

Maximum Mixedness Model

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{Ao}} + \frac{E(\lambda)}{1-F(\lambda)}X$$

$$\frac{r_A}{C_{Ao}} = -kC_{Bo}{}^2(1-X)^3$$

where $k(T) = ko\exp\left[\frac{E}{R}\left(\frac{1}{To}-\frac{1}{T}\right)\right] = 175\exp\left[\frac{30000}{8.314}\left(\frac{1}{320}-\frac{1}{T}\right)\right]$

and $T(K) = To + \left(\frac{-\Delta Hrx}{Cp_A}\right)X = 320 + 150X$

See Polymath program P13-9-d-2.pol

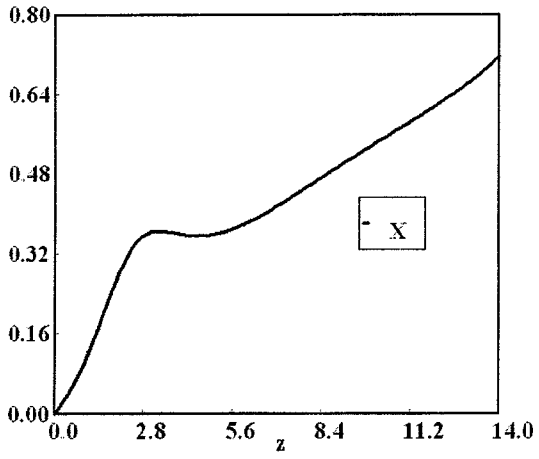
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
z	0	0	14	14
X	0	0	0.7189248	0.7189248
F	0.9999	-0.1138842	0.9999	-0.1138842
Cbo	0.0313	0.0313	0.0313	0.0313
T	320	320	427.83873	427.83873
lam	14	0	14	0
Cao	0.0313	0.0313	0.0313	0.0313
Ca	0.0313	0.0087977	0.0313	0.0087977
E	0.0199021	0	0.1566233	0
EF	199.0212	0	199.0212	0
Cb	0.0313	0.0087977	0.0313	0.0087977
k	175	175	3001.8809	3001.8809
ra	-0.0053663	-0.007411	-0.0020441	-0.0020441

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(X)/d(z) = -(ra/Cao+E/(1-F)*X)
[2] d(F)/d(z) = -E

Explicit equations as entered by the user
[1] Cbo = .0313
[2] T = 320+150*X
[3] lam = 14-z
[4] Cao = .0313
[5] Ca = Cao*(1-X)
[6] E = 0.0899237*lam-0.0157181*lam^2+0.000792*lam^3-0.00000863*lam^4
[7] EF = E/(1-F)
[8] Cb = Cbo*(1-X)
[9] k = 175*exp(30000/8.314*(1/320-1/T))
[10] ra = -k*Ca*Cb^2



gives X=72%

If the reaction is carried out adiabatically the conversions are more than doubled.

P13-10

Irreversible, first order, long tubular reactor, constant volume, isothermal

For a PFR $\dfrac{dF_A}{dV} = -r_A$

$$F_{Ao}\frac{dX}{dV} = kC_{Ao}(1-X)$$

$$\int_0^X \frac{dX}{1-X} = \frac{k}{v_o}\int_0^V dV$$

$$X = 1-e^{-kt}$$

For $X = 0.865 \Rightarrow k\tau = 2.0$

For laminar flow with negligible diffusion (LFR), the mean conversion is given by:

$$\overline{X} = \int_0^\infty X(t)E(t)dt = \int_{\tau/2}^\infty X(t)E(t)dt$$

$$X(t) = 1-e^{-kt}$$

E(t) for laminar flow $= \dfrac{\tau^2}{2t^3}$ where $t \geq \dfrac{\tau}{2}$

Therefore $$\overline{X} = \int_{\tau/2}^\infty \left(1-e^{-kt}\right)\frac{\tau^2}{2t^3}dt = 1-\frac{\tau^2}{2}\int_{\tau/2}^\infty \frac{e^{-kt}}{t^3}dt$$

We can apply the approximated solution due to Hilder:

$$\overline{X} = \frac{(4+Da)e^{0.5Da} + Da - 4}{(4+Da)e^{0.5Da} + Da} = 0.782$$

where Da=kτ=2

$$\overline{X} = 0.782 < X_{PFR} = 0.85$$

P13-11 (a)

First Moment about the mean: by definition is always equal to zero.

$$m_1 = \int_0^\infty (t-\tau)E(t)dt = \int_0^\infty tE(t)dt - \tau\int_0^\infty E(t)dt = \tau - \tau = 0$$

$$m_{1CSTR} = m_{1PFR} = m_{1LFR} = 0$$

P13-11 (b)

Second-order liquid-phase reaction Da= τkC_{Ao}=1.0,τ=2min and kC_{Ao}=0.5min^{-1}.

CSTR

$$F_{Ao} - F_A = -r_A V$$

$$F_{Ao} - F_A = F_{Ao}X$$

$$V = \frac{F_{Ao}X}{(-r_A)_{exit}}$$

Liquid-phase $\tau = \frac{V}{v_o} = \frac{C_{Ao} - C_A}{(-r_A)}$

Second-order $-r_A = kC_A^2$ and $\tau = \frac{C_{Ao} - C_A}{kC_A^2} = \frac{X}{kC_{Ao}(1-X)^2}$

Solved

$$X = \frac{(1+2Da) - \sqrt{1+4Da}}{2Da} = 0.382$$

PFR

$$\frac{-dF_A}{dV} = -r_A$$

$$F_{Ao}\frac{dX}{dV} = -r_A$$

$$V = F_{Ao}\int_0^X \frac{dX}{-r_A}$$

Second-order

$$V = F_{Ao}\int_0^X \frac{dX}{kC_A^2} \text{ where } C_A = C_{Ao}\frac{(1-X)}{(1+\varepsilon X)}$$

Liquid-phase ε = 0 and integrating

$$\tau = \frac{1}{kC_{Ao}}\left[\frac{X}{1-X}\right] \text{ or } X = \frac{Da}{1+Da} = 0.5$$

LFR

In the ring globule of radius r

$$\frac{dC_A}{dt} = r_A \text{ Where } -r_A = kC_A^2$$

$$X = \frac{ktC_{Ao}}{1+ktC_{Ao}} \text{ (2order batch)}$$

$$E(t) = \begin{cases} 0 \; for \; t < 1\min \\ 4/(2t^3)\min^{-1} \; for \; t \geq 1\min \end{cases} \text{ (E(t) LFR)}$$

$$\overline{X} = \int_{\frac{\tau}{2}}^{\infty} X\,E(t)dt = \frac{\tau^2}{2}kC_{Ao}\int_{\tau/2}^{\infty}\frac{dt}{(1+ktC_{Ao})t^2} = \frac{\tau^2}{2}kC_{Ao}\int_{\tau/2}^{\infty}\left[\frac{1}{t^2}+\frac{(kC_{Ao})^2}{(1+ktC_{Ao})}-\frac{kC_{Ao}}{t}\right]dt =$$

$$= \frac{\tau^2 kC_{Ao}}{2}\left[-\frac{1}{t}+kC_{Ao}\ln\left(\frac{1+ktC_{Ao}}{t}\right)\right]_{\tau/2}^{\infty} = Da\left[1-\frac{Da}{2}\ln\left(\frac{1+Da/2}{Da/2}\right)\right]$$

Evaluate for Da=1, $\overline{X} = 0.451$

See Polymath program P13-11-b.pol

CSTR	PFR	LFR
0.382	0.5	0.451

P13-12

$$-r_A = \frac{kC_A}{(1+K_AC_A)^2}$$

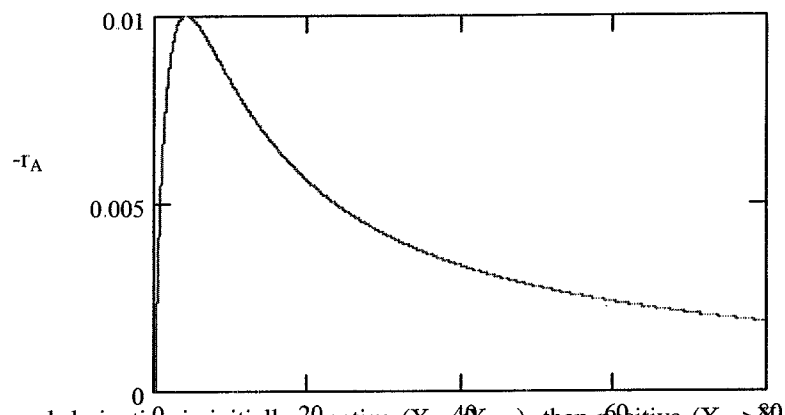
The criteria

$$\frac{\partial^2 -r_A}{\partial C_A^{\,2}} > 0 \quad X_{seg} > X_{MM}$$

$$\frac{\partial^2 -r_A}{\partial C_A^{\,2}} = 0 \quad X_{seg} = X_{MM}$$

$$\frac{\partial^2 - r_A}{\partial C_A{}^2} < 0 \quad X_{seg}<X_{MM}$$

The following figure shows the reaction rate as function of the concentration.



The second derivative is initially negative ($X_{seg}<X_{MM}$), then positive ($X_{seg}>X_{MM}$). The flex point is for C_A=8mol/dm^3 (X_{seg}=XMM).

In the limit of low concentration

$-r_A = kC_A + o(C_A)^2$ (First order) and $X_{seg}=X_{MM}$

in the limit of high concentration

$$-r_A = \frac{k}{K_A{}^2 C_A} + o\left(\frac{1}{C_A{}^2}\right)$$ (Reaction order=-1) and $X_{seg}>X_{MM}$

P13-13 **No solution will be given**

P13-14 (a)

Liquid phase, Segregation Model, second order, non-ideal CSTR, adiabatic

$$\overline{X} = \int_0^\infty X(t,T)E(t)dt = 0.67$$

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)dt} \quad \text{and} \quad \int_0^\infty C(t)dt = 1mg\ \text{min}/dm^3$$

E(t)=IF (t<=1) THEN (t) ELSE (IF (t>=2) THEN (0) ELSE (2-t))

For a batch globule: $C_{Ao}\frac{dX}{dt} = -r_A$

$$-r_A = kC_A{}^2$$

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

$$\frac{dX}{dt} = kC_{Ao}(1-X)^2$$

Where C_{Ao}=2 mol/dm^3

$$k(T) = 0.5\exp\left[\frac{Ea}{8.314}\left(\frac{1}{300}-\frac{1}{T}\right)\right]$$

$$T = To + \frac{-\Delta H_{rx}X}{C_{ps}+\Delta CpX}$$

Where $C_{ps} = \sum \vartheta_i C_{pi} = C_{pa} + 0 = 50J/mol\cdot K$

$$\Delta Cp = 1/2C_{pb} - C_{pa} = 100/2 - 50 = 0$$

T=300+150X

Iterate with Ea, using the ODE solver for values of X(t,T) and substitute these into the polynomial regression to evaluate the integral $\overline{X} = \int_0^\infty X(t,T)E(t)dt = 0.67$

An activation energy Ea of 10000 J/mol gives approximately the correct mean conversion, $\overline{X}$ =0.67. Inaccuracy lies in the polynomial fit and hence the integral area.

See Polymath program P13-14-a.pol

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	3	3
xbar	0	0	0.6673438	0.6673438
x	0	0	0.9198721	0.9198721
cao	2	2	2	2
T	300	300	437.98082	437.98082
E1	0	0	3	3
E2	2	-1	2	-1
E	0	0	0.9933851	0
Ea	1.25E+04	1.25E+04	1.25E+04	1.25E+04
k	0.5	0.5	2.4247011	2.4247011

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(xbar)/d(t) = E*x
[2] d(x)/d(t) = k*cao*((1-x)^2)

Explicit equations as entered by the user
[1] cao = 2
[2] T = 300+150*x

[3] E1 = t
[4] E2 = 2-t
[5] E = if (t<=1) then (E1) else (if (t>=2) then (0) else (E2))
[6] Ea = 12500
[7] k = 0.5*exp(Ea/8.314*((1/300)-(1/T)))

P13-14 (b)

Parallel reactions, isothermal, segregation model

Batch globules

$$\frac{dC_A}{dt} = r_A = r_{A1} + r_{A2} = -k_{1A}C_A{}^2 - k_{2C}C_AC_B$$

$$\frac{dC_B}{dt} = r_B = -r_{A1} + r_{A2} = k_{1A}C_A{}^2 - k_{2C}C_AC_B$$

$$\frac{dC_c}{dt} = r_C = -r_{A2} = k_{2C}C_AC_B$$

Exit concentrations

$$\frac{dC_{Abar}}{dt} = C_A E(t)$$

$$\frac{dC_{Bbar}}{dt} = C_B E(t)$$

$$\frac{dC_{Cbar}}{dt} = C_C E(t)$$

E(t)=IF (t<=1) THEN (t) ELSE (IF (t>=2) THEN (0) ELSE (2-t))

Selectivity $S = \frac{C_{Bbar}}{C_{Cbar}} = 2.38$

Iteration with k_{2C} until S = 2.38 gives k_{2C} = 0.3755 dm^3/mol min
See Polymath program P13-14-b.pol

P13-15

Reactor: fluidised CSTR (V=1m^3; F=10dm^3/s, $C_C{}^0$=2 Kmol/m^3)

τ = 1000dm^3s/10dm^3 = 100s

The system of complex reactions for the Kentucky coal n.9 is given by

$$\frac{dC_C}{d\tau} = -k_1C_P - k_2C_A$$

$$\frac{dC_P}{d\tau} = k_1C_C + k_4C_A - k_3C_P$$

$$\frac{dC_A}{d\tau} = k_2 C_C + k_3 C_P - k_4 C_A - k_5 C_A$$

$$\frac{dC_O}{d\tau} = k_5 C_A$$

P13-15 (a)

Segregation Model

See Polymath program P13-15-a.pol

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	20	20
ca	0	0	900.42918	900.42918
cp	0	0	689.61265	689.61265
cc	2000	1383.5708	2000	1383.5708
cabar	0	0	137.10239	137.10239
cpbar	0	0	46.011527	46.011527
ccbar	2000	2000	3988.5578	3988.5578
co	0	0	466.78696	466.78696
cobar	0	0	9.1391124	9.1391124
k1	0.012	0.012	0.012	0.012
k2	0.046	0.046	0.046	0.046
k3	0.02	0.02	0.02	0.02
k4	0.034	0.034	0.034	0.034
k5	0.04	0.04	0.04	0.04
rc	0	-49.695094	0	-49.695094
ra	92	10.804749	92	10.804749
rp	24	24	37.542445	33.425188
tau	1.667	1.667	1.667	1.667
ro	0	0	36.017167	36.017167
E	0.59988	3.695E-06	0.59988	3.695E-06
Spo	2.4E+08	0.9280349	2.4E+08	0.9280349

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(ca)/d(t) = ra
[2] d(cp)/d(t) = rp
[3] d(cc)/d(t) = rc
[4] d(cabar)/d(t) = ca*E
[5] d(cpbar)/d(t) = cp*E
[6] d(ccbar)/d(t) = cc*E
[7] d(co)/d(t) = ro
[8] d(cobar)/d(t) = co*E

Explicit equations as entered by the user

[1] k1 = 0.012
[2] k2 = 0.046
[3] k3 = 0.020
[4] k4 = 0.034
[5] k5 = 0.04
[6] rc = -k1*cp-k2*ca
[7] ra = k2*cc+k3*cp-k4*ca-k5*ca
[8] rp = k1*cc+k4*ca-k3*cp
[9] tau = 1.667
[10] ro = k5*ca
[11] E = exp(-t/tau)/tau

[12] Spo = rp/(ro+0.0000001)

The exiting selectivity is 0.928

P13-15 (b)

Maximum Mixedness model

See Polymath program P13-15-b.pol

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
z	0	0	20	20
Ca	0	0	875.11273	875.11273
Cp	0	0	631.80972	631.80972
Cc	2000	1463.3111	2000	1463.3111
Co	0	0	408.43732	408.43732
F	1	6.149E-06	1	6.149E-06
k1	0.012	0.012	0.012	0.012
k2	0.046	0.046	0.046	0.046
k3	0.02	0.02	0.02	0.02
k4	0.034	0.034	0.034	0.034
k5	0.04	0.04	0.04	0.04
rc	0	-47.836902	0	-47.836902
ra	92	15.190162	92	15.190162
rp	24	24	37.327161	34.677371
tau	1.667	1.667	1.667	1.667
ro	0	0	35.004509	35.004509
E	0.59988	3.695E-06	0.59988	3.695E-06
Spo	2.4E+08	0.9906544	2.4E+08	0.9906544
EF	5.999E+07	3.695E-06	5.999E+07	3.695E-06
sigma	3	3	3	3
Cao	0	0	0	0
Cpo	0	0	0	0
Cco	2000	2000	2000	2000
Coo	0	0	0	0

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(Ca)/d(z) = -(-ra+(Ca-Cao)*EF)
[2] d(Cp)/d(z) = -(-rp+(Cp-Cpo)*EF)
[3] d(Cc)/d(z) = -(-rc+(Cc-Cco)*EF)
[4] d(Co)/d(z) = -(-ro+(Co-Coo)*EF)
[5] d(F)/d(z) = -E

Explicit equations as entered by the user

[1] k1 = 0.012
[2] k2 = 0.046
[3] k3 = 0.020
[4] k4 = 0.034
[5] k5 = 0.04
[6] rc = -k1*Cp-k2*Ca
[7] ra = k2*Cc+k3*Cp-k4*Ca-k5*Ca
[8] rp = k1*Cc+k4*Ca-k3*Cp
[9] tau = 1.667
[10] ro = k5*Ca
[11] E = exp(-z/tau)/tau
[12] Spo = rp/(ro+0.0000001)
[13] EF = E/(1-F)
[14] sigma = 3

[15] Cao = 0
[16] Cpo = 0
[17] Cco = 2000
[18] Coo = 0

P13-15 (c)

The selectivities are reported in the following table:

SMM_{PFR}	XMM_{CSTR}	Xsm_{PFR}	Xsm_{CSTR}
4.83	0.99	4.174	0.92

P13-15 (d)

Normal Distribution with τ = 5min and σ = 3min

$$E(t)=\frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{(t-\tau)^2}{2.\sigma^2}\right]=\frac{1}{3\sqrt{2.\pi}}\exp\left[-\frac{(t-5)^2}{2\cdot 3^2}\right]$$

Segregation Model

See Polymath program P13-15-d-1.pol

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	2	2
ca	0	0	171.75027	171.75027
cp	0	0	52.879376	52.879376
cc	2000	1991.2989	2000	1991.2989
cabar	0	0	11.116671	11.116671
cpbar	0	0	3.2689487	3.2689487
ccbar	0	0	221.39065	221.39065
co	0	0	7.0306771	7.0306771
cobar	0	0	0.3200147	0.3200147
k1	0.012	0.012	0.012	0.012
k2	0.046	0.046	0.046	0.046
k3	0.02	0.02	0.02	0.02
k4	0.034	0.034	0.034	0.034
k5	0.04	0.04	0.04	0.04
rc	0	-8.5350648	0	-8.5350648
ra	92	79.947816	92	79.947816
rp	24	24	28.677508	28.677508
sigma	3	3	3	3
ro	0	0	6.8700107	6.8700107
tau	5	5	5	5
Spo	2.4E+08	4.1743032	2.4E+08	4.1743032
E1	10	10	10	10
E	0.0331675	0.0331675	0.0806774	0.0806774

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(ca)/d(t) = ra
[2] d(cp)/d(t) = rp
[3] d(cc)/d(t) = rc
[4] d(cabar)/d(t) = ca*E
[5] d(cpbar)/d(t) = cp*E
[6] d(ccbar)/d(t) = cc*E
[7] d(co)/d(t) = ro
[8] d(cobar)/d(t) = co*E

Explicit equations as entered by the user

[1] k1 = 0.012
[2] k2 = 0.046
[3] k3 = 0.020
[4] k4 = 0.034
[5] k5 = 0.04
[6] rc = -k1*cp-k2*ca
[7] ra = k2*cc+k3*cp-k4*ca-k5*ca
[8] rp = k1*cc+k4*ca-k3*cp
[9] sigma = 3
[10] ro = k5*ca
[11] tau = 5
[12] Spo = rp/(ro+0.0000001)
[13] E1 = 1/(tau*2*(1-0.99))
[14] E = exp(-(t-tau)^2/(2*sigma^2))/(sigma*(2*3.14)^0.5)

Maximum Mixedness Model
See Polymath program P13-15-d-2.pol

POLYMATH Results
POLYMATH Report 08-25-2005, Rev5.1.233

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
z	0	0	2	2
Ca	0	0	120.77791	120.77791
Cp	0	0	35.906087	35.906087
Cc	2000	1995.2809	2000	1995.2809
Co	0	0	3.8182818	3.8182818
F	1	0.9770814	1	0.9770814
k1	0.012	0.012	0.012	0.012
k2	0.046	0.046	0.046	0.046
k3	0.02	0.02	0.02	0.02
k4	0.034	0.034	0.034	0.034
k5	0.04	0.04	0.04	0.04
rc	0	-5.986657	0	-5.986657
ra	92	83.563477	92	83.563477
rp	24	24	27.331698	27.331698
lam	2	0	2	0
ro	0	0	4.8311165	4.8311165
tau	5	5	5	5
Spo	2.4E+08	5.6574287	2.4E+08	5.6574287
sigma	3	3	3	3
E	0.0296795	0.0020622	0.0296795	0.0020622
Cao	0	0	0	0
Cpo	0	0	0	0
Cco	2000	2000	2000	2000
Coo	0	0	0	0
EF	2.968E+06	0.089981	2.968E+06	0.089981

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(Ca)/d(z) = -(-ra+(Ca-Cao)*EF)
[2] d(Cp)/d(z) = -(-rp+(Cp-Cpo)*EF)
[3] d(Cc)/d(z) = -(-rc+(Cc-Cco)*EF)
[4] d(Co)/d(z) = -(-ro+(Co-Coo)*EF)
[5] d(F)/d(z) = -E

Explicit equations as entered by the user

```
[1]  k1 = 0.012
[2]  k2 = 0.046
[3]  k3 = 0.020
[4]  k4 = 0.034
[5]  k5 = 0.04
[6]  rc = -k1*Cp-k2*Ca
[7]  ra = k2*Cc+k3*Cp-k4*Ca-k5*Ca
[8]  rp = k1*Cc+k4*Ca-k3*Cp
[9]  lam = 2-z
[10] ro = k5*Ca
[11] tau = 5
[12] Spo = rp/(ro+0.0000001)
[13] sigma = 3
[14] E = exp(-(lam-tau)^2/(2*sigma))/(sigma*(2*3.14)^0.5)
[15] Cao = 0
[16] Cpo = 0
[17] Cco = 2000
[18] Coo = 0
[19] EF = E/(1-F)
```

P13-16

Multiple parallel reactions, isothermal

$E(t)=0.0279693 - 0.0008527t + 1.2778e\text{-}5\ t^2 - 1.0661e\text{-}7\ t^3 + 4.5747e\text{-}10\ t^4 - 7.73108e\text{-}13\ t^5$

K1=5.0 $m^6/kmol^2min$, k2=2.0 $m^3/kmol.min$, k3=10 $m^6/kmol^2min$, k4=5.0 $m^2/kmol^{2/3}min$

P13-16 (a)

Segregation model

$$\frac{dC_A}{dt} = -k_1 C_A C_B^{\,2} - k_2 C_A C_B - \frac{2}{3} k_4 C_C C_A^{\,2/3}$$

$$\frac{dC_B}{dt} = -1.25 k_1 C_A C_B^{\,2} - 0.75 k_2 C_A C_B - k_3 C_B C_C^{\,2}$$

$$\frac{dC_C}{dt} = k_1 C_A C_B^{\,2} - 2k_3 C_C^{\,2} C_B - k_4 C_C C_A^{\,2/3}$$

$$\frac{dC_D}{dt} = 1.5 k_1 C_A C_B^{\,2} + 1.5 k_2 C_A C_B + k_4 C_C C_A^{\,2/3}$$

$$\frac{dC_E}{dt} = 0.5 k_2 C_A C_B + \frac{5}{6} k_4 C_C C_A^{\,2/3}$$

$$\frac{dC_F}{dt} = 2k_3 C_C^{\,2} C_B$$

$$\frac{d\overline{C}_A}{dt} = C_A E(t) \qquad \frac{d\overline{C}_B}{dt} = C_B E(t) \qquad \frac{d\overline{C}_C}{dt} = C_C E(t)$$

$$\frac{d\overline{C}_D}{dt} = C_D E(t) \qquad \frac{d\overline{C}_E}{dt} = C_E E(t) \qquad \frac{d\overline{C}_F}{dt} = C_F E(t)$$

$$S_{CD} = \frac{\overline{C}_C}{\overline{C}_D} \qquad S_{DE} = \frac{\overline{C}_D}{\overline{C}_E} \qquad S_{EF} = \frac{\overline{C}_E}{\overline{C}_F}$$

See Polymath program P13-16-a.pol

Exit concentrations:

$\overline{C}_A = 0.026 mol/dm^3$

$\overline{C}_B = 0.008 mol/dm^3$

$\overline{C}_C = 6.955e-5 mol/dm^3$

$\overline{C}_D = 0.036 mol/dm^3$

$\overline{C}_E = 0.012 mol/dm^3$

$\overline{C}_F = 4.156e-7 mol/dm^3$

Selectivities:

$S_{CD} = 0.00196$

$S_{DE} = 3.009$

$S_{EF} = 28433$

P13-16 (b)

Maximum Mixedness model

$E(t)=0.0279693-0.0008527\lambda+1.2778e\text{-}5\lambda^2-1.0661e\text{-}7\,\lambda^3+4.5747e\text{-}10\,\lambda^4-7.73108e\text{-}13\,\lambda^5$

And $\lambda=t_f-z$ where z=t, t_f=200min (extent of E(t)).

$$\frac{dC_A}{dz} = r_A - \left((C_A - C_{Ao}) \frac{E(\lambda)}{1-F(\lambda)} \right)$$

and $$r_A = \left(-k_1 C_A C_B{}^2 - k_2 C_A C_B - \frac{2}{3} k_4 C_C C_A{}^{2/3} \right)$$

and so on for other species.

$$\frac{dF(\lambda)}{dz} = -E(\lambda)$$ gives F(λ)

See Polymath program P13-16-b.pol

Exit concentrations:

$C_A = 0.028 mol/dm^3$

$C_B = 0.010 mol/dm^3$

$C_C = 2.927e-5 mol/dm^3$

$C_D = 0.033 mol/dm^3$

$C_E = 0.011 mol/dm^3$

$C_F = 7.985e-9 mol/dm^3$

Selectivities:

$S_{CD} = 0.0009$

$S_{DE} = 3.004$

$S_{EF} = 1343110$

P13-16 (c)

Ideal CSTR

$t_m = \tau$ and $E(t) = \frac{e^{-t/\tau}}{\tau}$

Mol balances:

$$\frac{dF_A}{dt} = F_{Ao} - (-r_A) \quad \text{where} \quad r_A = -k_1 C_A C_B{}^2 - k_2 C_A C_B - \frac{2}{3} k_4 C_C C_A{}^{2/3}$$

$F_{Ao} = C_{Ao} v_o = 0.05 \cdot 10 = 0.5 mol/\min = F_{Bo}$

and so on for the other species.

$C_A = C_{To} \frac{F_A}{F_T} \rightarrow etc....$

$C_{To} = C_{Ao} + C_{Bo} = 0.05 + 0.05 = 0.1$

$F_T = F_A + F_B + F_C + F_D + F_E + F_F$

See Polymath program P13-16-c.pol

Exit concentrations:

$C_A = 0.050 mol/dm^3$

$C_B = 0.049 mol/dm^3$

$C_C = 5.639e-5 mol/dm^3$

$C_D = 0.0008 mol/dm^3$

$C_E = 0.0002 mol/dm^3$

Selectivities:

$S_{CD} = 0.068$

$S_{DE} = 3.342$

$S_{EF} = 815844$

$C_F = 3.03e-10 mol/dm^3$

Ideal PFR

$t_m=\tau$ and RTD function $E(t) = \delta(t-\tau)$

$\frac{dF_A}{dV} = (-r_A)$ Where $r_A = -k_1 C_A C_B{}^2 - k_2 C_A C_B - \frac{2}{3} k_4 C_C C_A{}^{2/3}$

and so on for other species.

$C_A = C_{To}\frac{F_A}{F_T} \rightarrow etc....$

$C_{To} = C_{Ao} + C_{Bo} = 0.05 + 0.05 = 0.1$

$F_T = F_A + F_B + F_C + F_D + F_E + F_F$

Exit concentrations:

$C_A = 3.98e-9 mol/dm^3$

$C_B = 0.0065 mol/dm^3$

$C_C = 0.000277 mol/dm^3$

$C_D = 0.068 mol/dm^3$

$C_E = 0.0202 mol/dm^3$

$C_F = 0.0047 mol/dm^3$

Selectivities:

$S_{CD} = 0.004$

$S_{DE} = 3.368$

$S_{EF} = 4.286$

Segregation	Maximum Mixedness	CSTR	PFR
$S_{CD} = 0.00196$	$S_{CD} = 0.0009$	$S_{CD} = 0.068$	$S_{CD} = 0.004$
$S_{DE} = 3.009$	$S_{DE} = 3.004$	$S_{DE} = 3.342$	$S_{DE} = 3.368$
$S_{EF} = 28433$	$S_{EF} = 1343110$	$S_{EF} = 815844$	$S_{EF} = 4.286$

S_{EF} For the PFR is very much smaller than for the others, because C_F is not so small at the exit of the PFR in turn due to exit C_C is not so small either. The conversion of C_A in the PFR is virtually complete at the exit of the PFR, hence greater C_C.

P13-16 (d)

See Polymath program P13-16-d.pol

E(t)=IF (t<=10) THEN (0.01) ELSE (IF(t>=20) THEN (0) ELSE (0.2-0.01 t))

Segregation	Maximum Mixedness	CSTR	PFR
$S_{CD} = 0.004$	$S_{CD} = 0.0035$	$S_{CD} = 0.068$	$S_{CD} = 0.004$
$S_{DE} = 3.109$	$S_{DE} = 3.106$	$S_{DE} = 3.342$	$S_{DE} = 3.368$
$S_{EF} = 24078$	$S_{EF} = 41503$	$S_{EF} = 815844$	$S_{EF} = 4.286$

For the Segregation and Maximum Mixedness models, S_{EF} is much lower than for the CSTR but still far greater than for the PFR. The CSTR and PFR values are unchanged as they do not depend on E(t).

P13-17

Multiple parallel reactions, isothermal

Asymmetric RTD: E=IF (t <=1.26) THEN (E1) ELSE (E2)

E1=-2.104t^4+4.167t^3-1.596t^2-0.353t-0.004
E2=-2.104t^4+17.037t^3-50.247t^2+62.964t-27.402

k_{D1}=0.25 dm^6/mol^2 min, k_{E2}=0.1 dm^3/mol min, k_{F3}=5.0 dm^6/mol^2 min

P13-17 (a)

Segregation model

$$\frac{dC_A}{dt} = -k_{D1}C_A{C_B}^2 - 3k_{E2}C_AC_D$$

$$\frac{dC_B}{dt} = -2k_{D1}C_A{C_B}^2 - k_{F3}C_B{C_C}^2$$

$$\frac{dC_C}{dt} = k_{D1}C_A{C_B}^2 + k_{E2}C_AC_D - 2k_{F3}C_B{C_C}^2$$

$$\frac{dC_D}{dt} = k_{D1}C_A{C_B}^2 - 2k_{E2}C_AC_D + k_{F3}C_B{C_C}^2$$

$$\frac{dC_E}{dt} = k_{E2}C_AC_D$$

$$\frac{dC_F}{dt} = k_{F3}C_B{C_C}^2$$

$$\frac{d\overline{C}_A}{dt} = C_AE(t) \qquad \frac{d\overline{C}_B}{dt} = C_BE(t) \qquad \frac{d\overline{C}_C}{dt} = C_CE(t)$$

$$\frac{d\overline{C}_D}{dt} = C_D E(t) \qquad \frac{d\overline{C}_E}{dt} = C_E E(t) \qquad \frac{d\overline{C}_F}{dt} = C_F E(t)$$

$$S_{CD} = \frac{\overline{C}_C}{\overline{C}_D} \qquad S_{DE} = \frac{\overline{C}_D}{\overline{C}_E} \qquad S_{EF} = \frac{\overline{C}_E}{\overline{C}_F}$$

See Polymath program P13-17-a.pol

Exit concentrations:

$\overline{C}_A = 0.819 mol/dm^3$

$\overline{C}_B = 0.767 mol/dm^3$

$\overline{C}_C = 0.163 mol/dm^3$

$\overline{C}_D = 0.600 mol/dm^3$

$\overline{C}_E = 0.053 mol/dm^3$

$\overline{C}_F = 0.199 mol/dm^3$

Selectivities:

$S_{CD} = 0.272$

$S_{DE} = 11.330$

$S_{EF} = 0.267$

P13-17 (b)

Maximum Mixedness model

As the RTD is asymmetric we can use the same equations for E(λ) as we did for E(t), with : E(λ)=IF (λ<=1.26) THEN (E1) ELSE (E2)

$$\frac{dC_A}{d\lambda} = -\sum r_{iA} + (C_A - C_{Ao})\frac{E(\lambda)}{1-F(\lambda)}$$

$$\frac{dC_A}{d\lambda} = -\left(-k_{D1}C_A C_B{}^2 - 3k_{E2}C_A C_D\right) + (C_A - C_{Ao})\frac{E(\lambda)}{1-F(\lambda)}$$

The same applies to the equations for the other species as in Part (a).

See Polymath program P13-17-b.pol

Exit concentrations:

$C_A = 0.847 mol/dm^3$

Selectivities:

$S_{CD} = 0.281$

$C_B = 0.824 mol/dm^3$ $S_{DE} = 10.7$

$C_C = 0.162 mol/dm^3$ $S_{EF} = 0.280$

$C_D = 0.576 mol/dm^3$

$C_E = 0.054 mol/dm^3$

$C_F = 0.192 mol/dm^3$

P13-17 (c)

Ideal CSTR

$t_m=\tau$ and $E(t) = \dfrac{e^{-t/\tau}}{\tau}$

$\dfrac{dC_A}{dt} = v(C_{Ao} - C_A) + r_A$ Where $r_A = \left(-k_{D1}C_A C_B^2 - 2k_{E2}C_A C_D\right)$, $vo = v$

and so on for the other species.

See Polymath program P13-17-c-1.pol

Exit concentrations:

$C_A = 1.386 mol/dm^3$

$C_B = 1.774 mol/dm^3$

$C_C = 0.095 mol/dm^3$

$C_D = 0.114 mol/dm^3$

$C_E = 0.002 mol/dm^3$

$C_F = 0.008 mol/dm^3$

Selectivities:

$S_{CD} = 0.832$

$S_{DE} = 71.100$

$S_{EF} = 0.198$

Ideal PFR

$t_m=\tau$ and RTD function $E(t) = \delta(t-\tau)$

$\dfrac{dC_A}{dV} = \left(\dfrac{r_A}{v}\right)$ Where $r_A = \left(-k_{D1}C_A C_B{}^2 - 2k_{E2}C_A C_D\right)$, $v_o = v$

and so on for the other species.

See Polymath program P13-17-c-2.pol

Exit concentrations:

$C_A = 0.310 mol/dm^3$

$C_B = 0.338 mol/dm^3$

$C_C = 0.106 mol/dm^3$

$C_D = 0.652 mol/dm^3$

$C_E = 0.180 mol/dm^3$

$C_F = 0.362 mol/dm^3$

Selectivities:

$S_{CD} = 0.162$

$S_{DE} = 3.618$

$S_{EF} = 0.497$

Segregation	Maximum Mixedness	CSTR	PFR
$S_{CD} = 0.272$	$S_{CD} = 0.281$	$S_{CD} = 0.832$	$S_{CD} = 0.162$
$S_{DE} = 11.330$	$S_{DE} = 10.7$	$S_{DE} = 71.100$	$S_{DE} = 3.618$
$S_{EF} = 0.237$	$S_{EF} = 0.280$	$S_{EF} = 0.198$	$S_{EF} = 0.497$

S_{CD} is significantly greater than for the others, because exit C_D is lower.

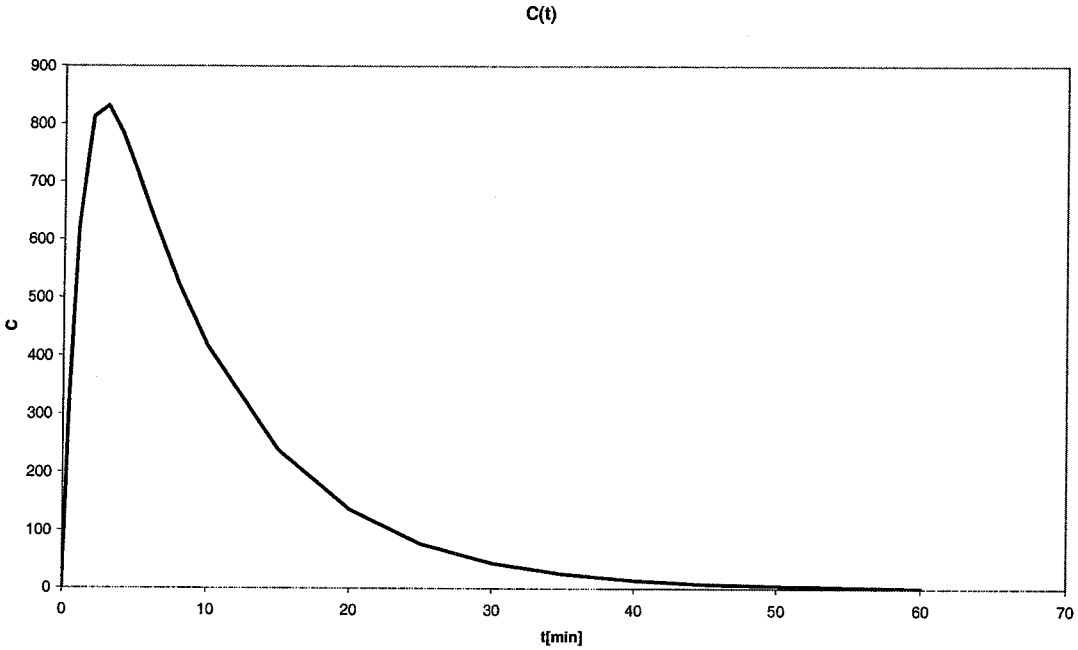
Similarly S_{DE} is much greater in the CSTR than for the others, because exit C_E is so low. This is because the achievable conversion in a CSTR is not so high.

P13-18 (a)
P13-18 (b)
P13-18 (c)
P13-18 (d)

P13-19 (a)

External age distribution E(t)

By plotting C 10^5 as a function of time, the curve shown is obtained



To obtain the E(t) curve from the C(t) curve, we just divide C(t) by the integral

$$\int_0^\infty C(t)dt = \int_0^6 C(t)dt + \int_6^{10} C(t)dt + \int_{10}^{50} C(t)dt + \int_{50}^{60} C(t)dt$$

$$\int_0^6 C(t)dt = \frac{3}{8}(1)[1(0)+3(622)+3(812)+2(831)+3(785)+3(720)+(650)]10^{-5} = 4173.4\cdot 10^{-5}$$

$$\int_6^{10} C(t)dt = \frac{1}{3}(2)[(650)+4(523)+(418)]10^{-5} = 2106.7\cdot 10^{-5}$$

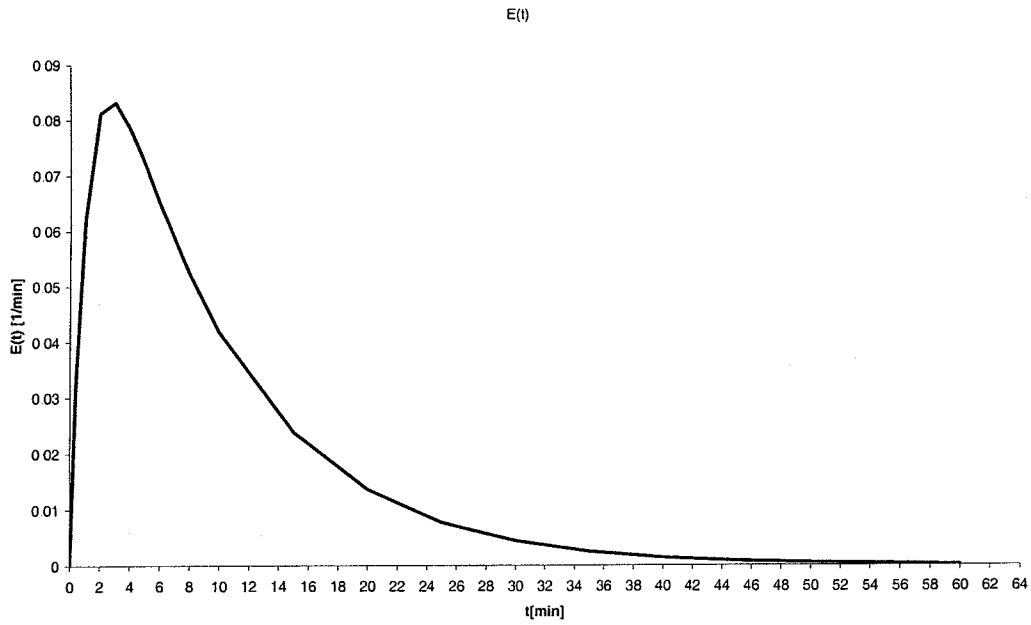
$$\int_{10}^{50} C(t)dt = \frac{1}{3}(5)[418+4(238)+2(136)+4(77)+2(44)+4(25)+2(14)+4(8)+5]10^{-5} = 3671.7\cdot 10^{-5}$$

$$\int_{50}^{60} C(t)dt = \frac{1}{2}(10)[1(5)+1(1)]10^{-5} = 30\cdot 10^{-5}$$

$$\int_0^\infty C(t)dt = 9981.7\cdot 10^{-5} \cong 0.1$$

We now calculate:

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)dt} = \frac{C(t)}{0.1}$$



Using Excel we fit E(t) to a polynomial:

$$E(t)=\begin{cases} for\ 0\le t\le 3\ E_1(t)=-1.1675\cdot 10^{-3}t^4+1.1355\cdot 10^{-2}t^3-4.7492\cdot 10^{-2}t^2 \\ +9.9505\cdot 10^{-2}t \\ for\ 3\le t\le 20\ E_2(t)=-1\cdot 8950\cdot 10^{-6}t^4+8.7202\cdot 10^{-5}t^3-1.1739\cdot 10^{-3}t^2 \\ -1.7979\cdot 10^{-4}t+0.092343 \\ for\ 20\le t\le 60\ E_3(t)=1.2618\cdot 10^{-8}t^4-2.4995\cdot 10^{-6}t^3+1.8715\cdot 10^{-4}t^2- \\ 6.3512\cdot 10^{-3}t+0.083717 \\ for\ t>60 \quad 0 \end{cases}$$

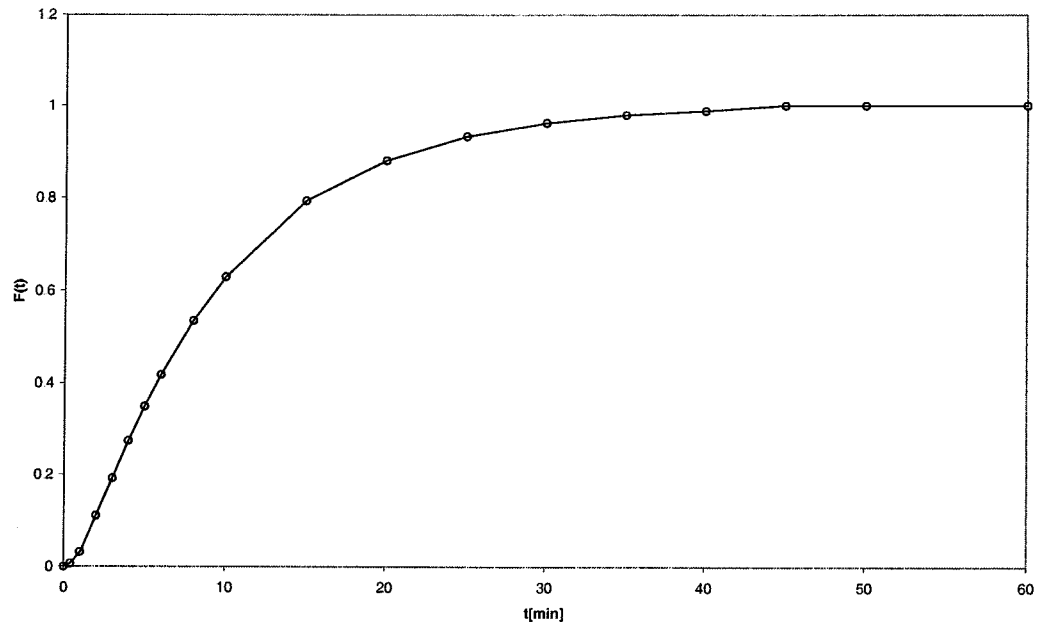
P13-19 (b)

External age cumulative distribution F(t)

$$F(t)=\int_0^t E(t)dt$$

:

Integrating the E(t), we obtain the F(t):

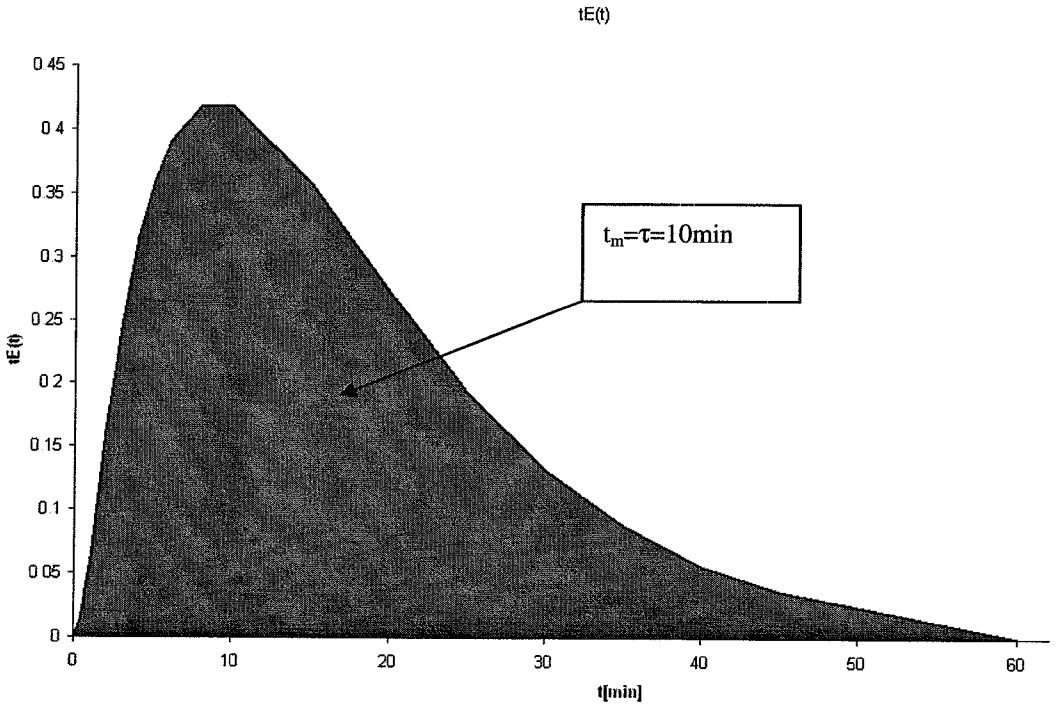


P13-19 (c)

Mean residence time and variance

$$t_m = \int_0^\infty E(t)tdt$$

The area under the curve of a plot tE(t) as a function of t will yield t_m.



t	C(t)	E(t)	tE(t)	$t-t_m$	$(t-t_m)^2E(t)$
0	0	0	0	-10	0

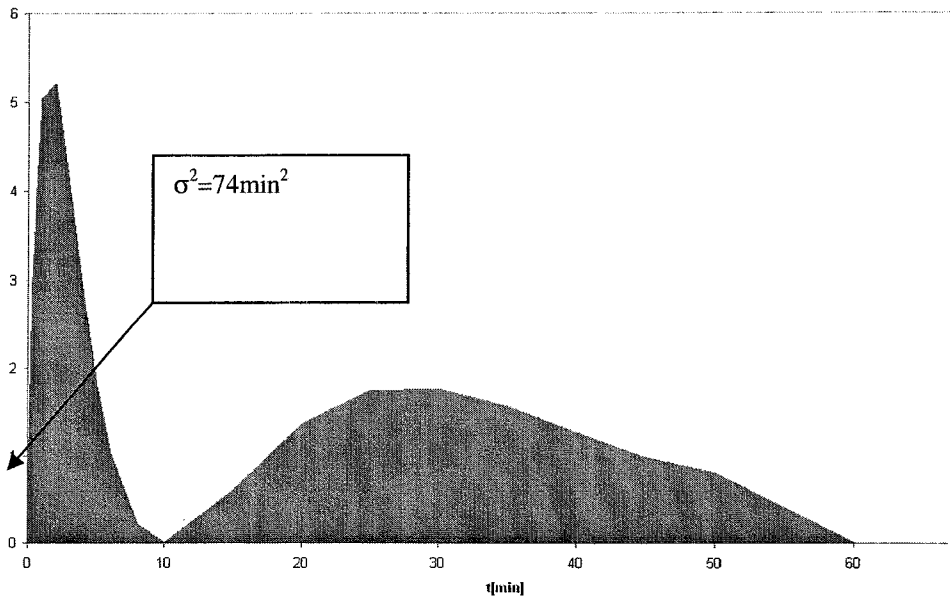
0.4	329	0.0329	0.01316	-9.6	3.032064
1	622	0.0622	0.0622	-9	5.0382
2	812	0.0812	0.1624	-8	5.1968
3	831	0.0831	0.2493	-7	4.0719
4	785	0.0785	0.314	-6	2.826
5	720	0.072	0.36	-5	1.8
6	650	0.065	0.39	-4	1.04
8	523	0.0523	0.4184	-2	0.2092
10	418	0.0418	0.418	0	0
15	238	0.0238	0.357	5	0.595
20	136	0.0136	0.272	10	1.36
25	77	0.0077	0.1925	15	1.7325
30	44	0.0044	0.132	20	1.76
35	25	0.0025	0.0875	25	1.5625
40	14	0.0014	0.056	30	1.26
45	8	0.0008	0.036	35	0.98
50	5	0.0005	0.025	40	0.8
60	1	0.0001	0	50	0.25

$(t-t_m)^2E(t)$

$$t_m = \int_0^{\infty} (t-t_m)^2 E(t)dt = \int_0^{6} E(t)tdt + \int_6^{10} E(t)tdt + \int_{10}^{50} E(t)tdt + \int_{50}^{60} E(t)tdt$$

$$t_m = \tau = 9.88\,\text{min} \cong 10\,\text{min}$$

We can calculate the variance by calculating the area under the curve of a plot of: $(t-t_m)^2E(t)$



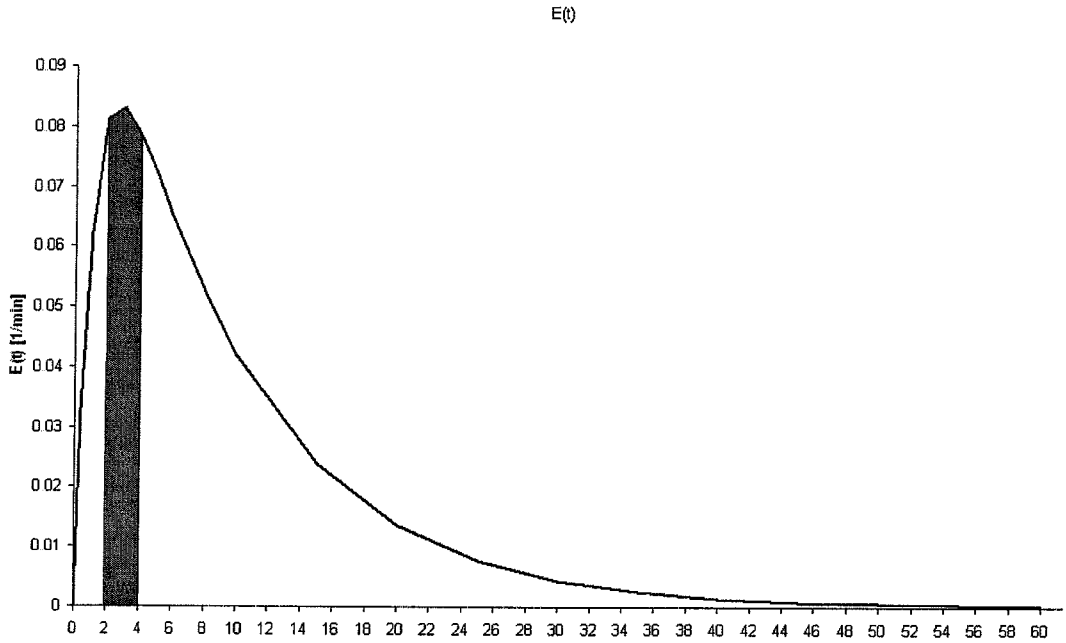
$$\sigma^2 = \int_0^{\infty} (t-t_m)^2 E(t)tdt = \int_0^{6} (t-t_m)^2 E(t)dt + \int_6^{10} (t-t_m)^2 E(t)dt +$$

$$\int_{10}^{50} (t-t_m)^2 E(t)dt + \int_{50}^{60} (t-t_m)^2 E(t)dt$$

$$\sigma^2 = 73.81\,\text{min}^2 \cong 74\,\text{min}^2$$

P13-19 (d)

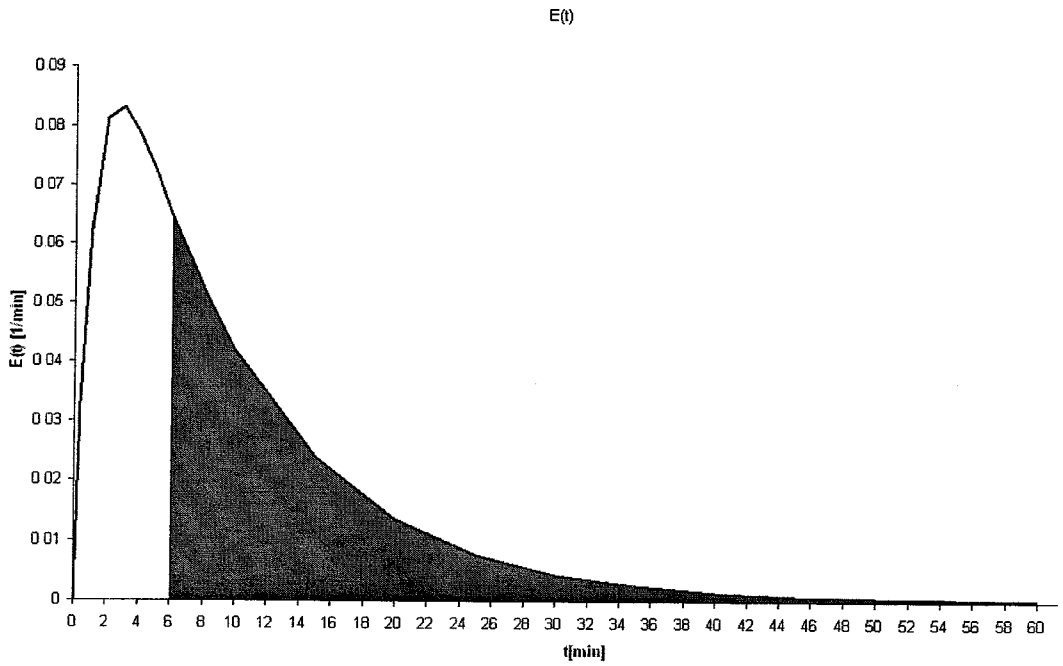
Fraction of the material that spends between 2 and 4min in the reactor



$$\int_2^4 E(t)dt = \text{shaded area} = \frac{1}{3}[1(0.0812) + 4(0.0831) + 1(0.0785)] = 0.16$$

P13-19 (e)

Fraction of the material that spends longer than 6min



$$\int_0^{\infty} E(t)dt = shaded\ area = \int_0^{10} E(t)dt + \int_{10}^{50} E(t)dt + \int_{50}^{60} E(t)dt$$

$$\int_0^{10} E(t)dt = \frac{2}{3}\left(1(0.065) + 4(0.0523) + 1(0.0418)\right) = 0.210$$

$$\int_{10}^{50} E(t)dt = \frac{5}{3}\left(1(0.0418) + 4(0.0238) + 2(0.0136) + 4(0.0077) + 2(0.0044) + 4(0.0025)\right.$$

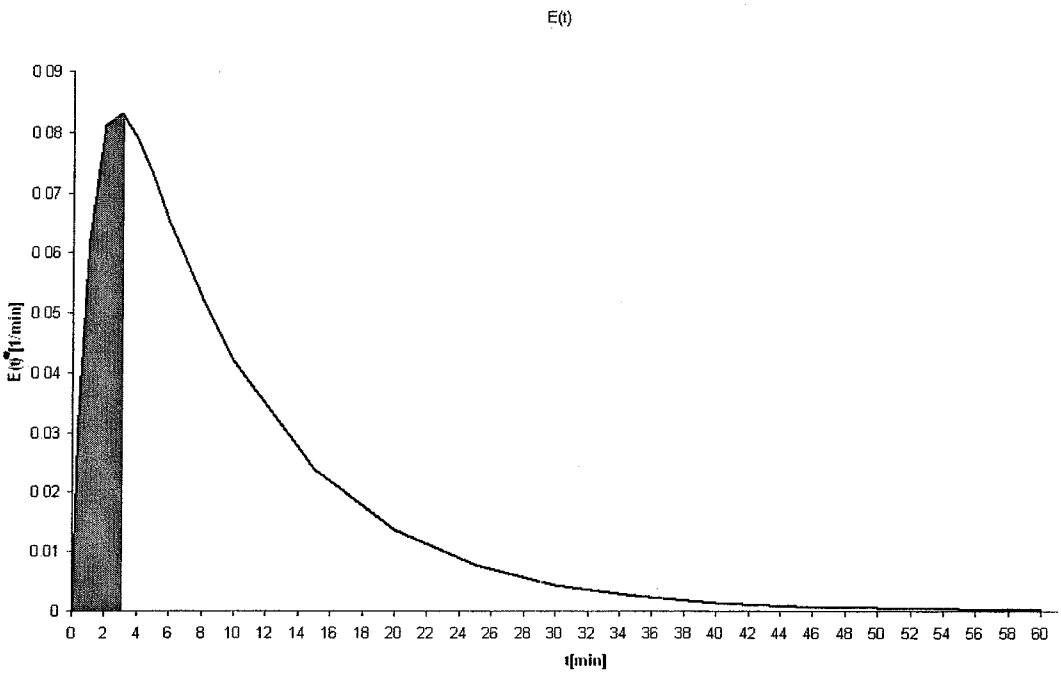
$$\left. + 2(0.0014) + 4(0.0008) + 1(0.0005)\right) = 0.367$$

$$\int_{50}^{60} E(t)dt = tail = \frac{10}{2}\left(0.0005 + 0.0001\right) = 0.003$$

$$\int_0^{\infty} E(t)dt = shaded\ area = 0.581$$

P13-19 (f)

Fraction of the material that spends less than 3min



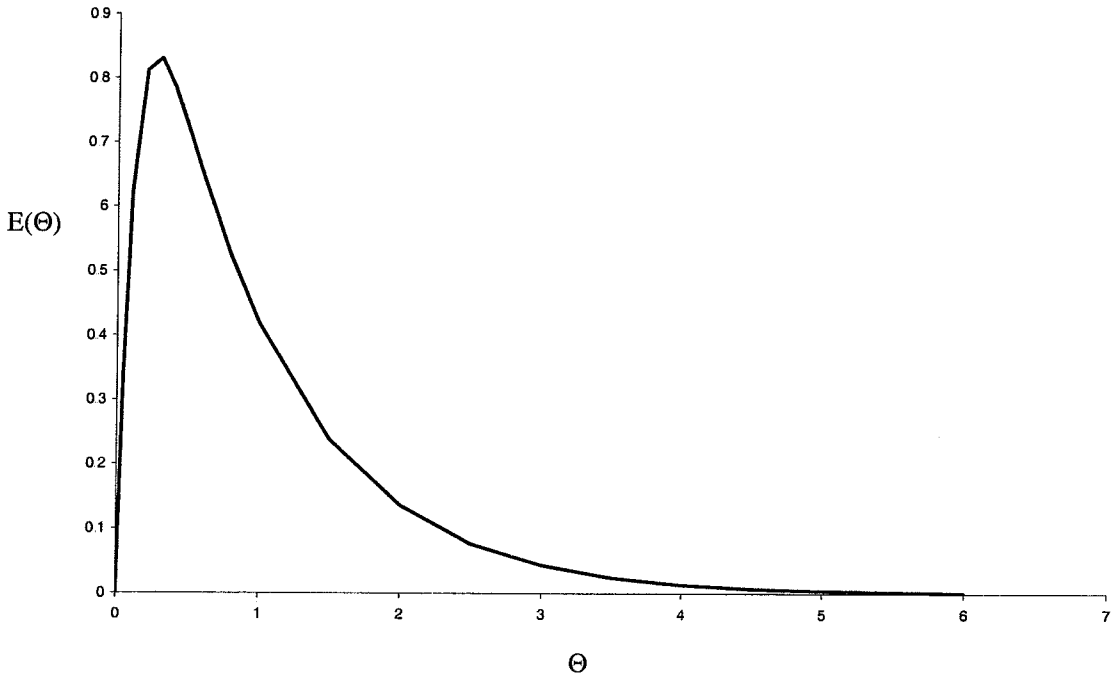
$$\int_0^{3} E(t)dt = shaded\ area = \frac{3}{8}\left[1(0) + 3(0.0622) + 3(0.0812) + 1(0.0831)\right] = 0.192$$

P13-19 (g)

Normalized distributions

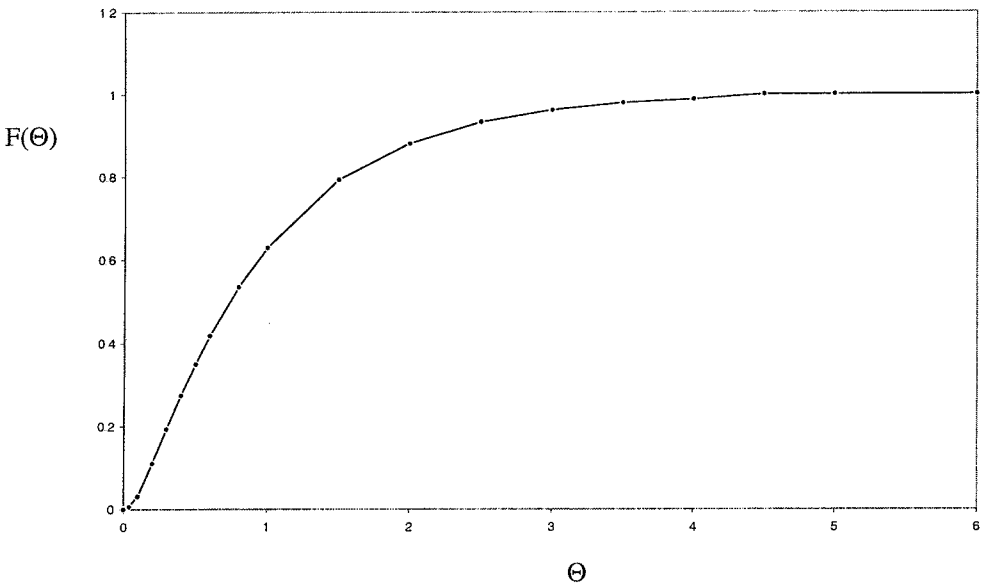
Normalized RTD

$$\Theta = \frac{t}{\tau} \quad E(\Theta) = \tau E(t)$$



Normalized cumulative RTD

$$F(\Theta) = \int_0^{\Theta} E(\Theta) d\Theta = \int_0^{\Theta} E(t) dt$$



P13-19 (h)

Reactor Volume

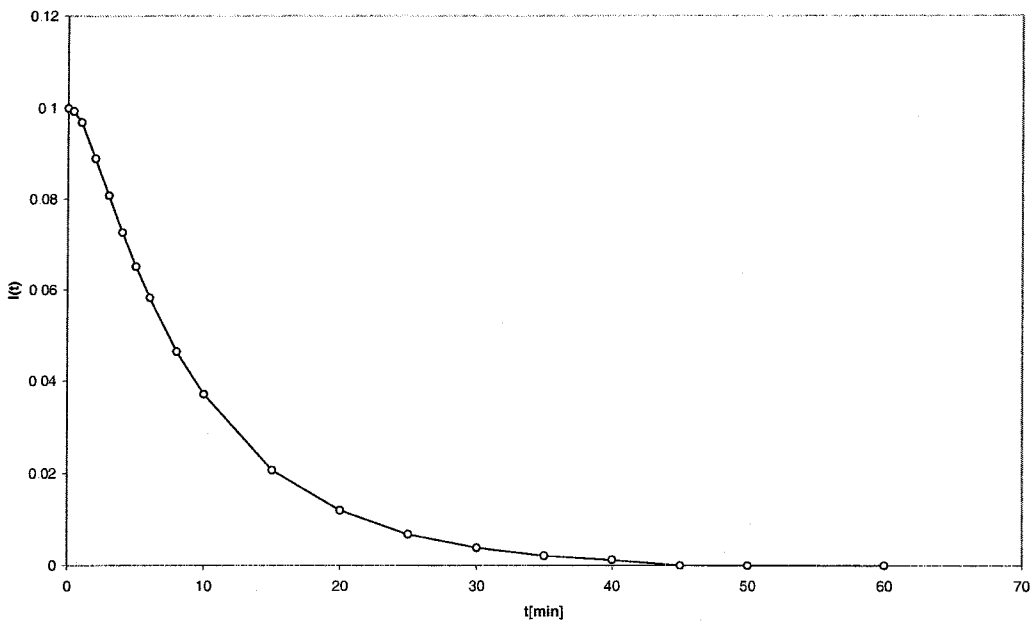
F=10 dm^3/min

$$V = F \cdot \tau = 100 dm^3$$

P13-19 (i)

Internal age distribution

$$I(t) = \frac{1}{\tau}[1 - F(t)]$$



P13-19 (j)

Mean internal age

$$\alpha_m = \int_0^\infty I(t)tdt = \int_0^6 I(t)tdt + \int_6^{10} I(t)tdt + \int_{10}^{50} I(t)tdt + \int_{50}^{60} I(t)tdt = 1\,\text{min}$$

P13-19 (k)

Intensity function

$$\Lambda(t) = \frac{E(t)}{1 - F(t)}$$

P13-19 (l)

Mean catalyst activity

Integrating the decaying rate law: $\int_a^a -\frac{da}{a^2} = \int_0^t k_D dt$

$$a = \frac{1}{1 + k_D t}$$

Applying the Segregation Model with the previous RTD data:

$$a_{mean} = \int_0^\infty aE(t)dt$$

See Polymath program P13-19-l.pol

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	70	70
amean	0	0	0.5778625	0.5778625
kd	0.1	0.1	0.1	0.1
E1	0	-2.436E+04	0.0838847	-2.436E+04
E2	0.092343	-21.261016	0.092343	-21.261016
E4	0	0	0	0
E3	0.083717	1.724E-05	0.083717	0.0017977
E	0	0	0.0838847	0
a	1	0.125	1	0.125

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(amean)/d(t) = a*E

Explicit equations as entered by the user
[1] kd = 0.1
[2] E1 = -0.0011675*t^4+0.011355*t^3-0.047492*t^2+0.0995005*t
[3] E2 = -1.8950*10^(-6)*t^4+8.7202*10^(-5)*t^3-1.1739*10^(-3)*t^2-1.7979*10^(-4)*t+0.092343
[4] E4 = 0
[5] E3 = 1.2618*10^(-8)*t^4-2.4995*10^(-6)*t^3+1.8715*10^(-4)*t^2-6.3512*10^(-3)*t+0.083717
[6] E = if(t<=3)then(E1)else(if(t<=20)then(E2)else(if(t<60)then(E3)else(E4)))
[7] a = 1/(1+kd*t)

P13-19 (m)

Ideal PFR

2nd order, liquid phase, $kC_{Ao}=0.1\text{min}^{-1}$, $C_{Ao}=1\text{mol/dm}^3$

$\tau=10$ min (from P13.19 (c))

$$X=\frac{k\tau C_{Ao}}{1+k\tau C_{Ao}}=0.5$$

P13-19 (n)

LFR

Laminar Flow Reactor

2nd order, liq. phase, irreversible reaction $kC_{Ao}=0.1\ \text{min}^{-1}$, $\tau=10$ min.

We apply the segregation model, using Polymath:

$$X=\frac{ktC_{Ao}}{1+ktC_{Ao}} \text{ and } E(t)=\begin{cases}0 \text{ for } t<5.00\,\text{min}\\ (10)^2/(2t^3)\,\text{min}^{-1} \text{ for } t\geq 5\,\text{min}\end{cases}$$

See Polymath program P13-19-n.pol

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	300	300
xbar	0	0	0.4504221	0.4504221
cao	1	1	1	1
k	0.1	0.1	0.1	0.1
tau	10	10	10	10
E1	5.0E+05	1.852E-06	5.0E+05	1.852E-06
t1	5	5	5	5
E	0	0	0.2284987	1.852E-06
x	0	0	0.9677419	0.9677419

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(xbar)/d(t) = x*E

Explicit equations as entered by the user

[1] cao = 1.0
[2] k = .1
[3] tau = 10
[4] E1 = tau^2/2/(t^3+0.0001)
[5] t1 = tau/2
[6] E = if (t<t1) then (0) else (E1)
[7] x = k*cao*t/(1+k*cao*t)

We can compare with the exact analytical formula due to Denbigh.

$$X=Da\left[1-\left(\frac{Da}{2}\right)\ln(1+2/Da)\right]=0.451 \text{ with Da= } kC_{Ao}\tau=1$$

P13-19 (o)

Ideal CSTR

2nd order, liquid phase, $kC_{Ao}=0.1\ \text{min}^{-1}$, $C_{Ao}=1\text{mol/dm}^3$

$$\frac{X}{(1-X)^2}=k\tau C_{Ao}\rightarrow X=0.382$$

P13-19 (p)

Segregation Model
2nd order, liquid phase, kC_{Ao} =0.1 min^{-1}, C_{Ao}=1mol/dm^3

$$\overline{X} = \int_0^\infty X(t)E(t)dt$$

Where $X(t) = \dfrac{kC_{Ao}t}{1+kC_{Ao}t}$

See Polymath program P13-19-p.pol

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	70	70
Xbar	0	0	0.4224876	0.4224876
kCao	0.1	0.1	0.1	0.1
E1	0	-2.436E+04	0.0836855	-2.436E+04
E2	0.092343	-21.261016	0.092343	-21.261016
E4	0	0	0	0
E3	0.083717	1.949E-05	0.083717	0.0017977
E	0	0	0.0836855	0
X	0	0	0.875	0.875

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Xbar)/d(t) = E*X

Explicit equations as entered by the user
[1] kCao = 0.1
[2] E1 = -0.0011675*t^4+0.011355*t^3-0.047492*t^2+0.0995005*t
[3] E2 = -1.8950*10^(-6)*t^4+8.7202*10^(-5)*t^3-1.1739*10^(-3)*t^2-1.7979*10^(-4)*t+0.092343
[4] E4 = 0
[5] E3 = 1.2618*10^(-8)*t^4-2.4995*10^(-6)*t^3+1.8715*10^(-4)*t^2-6.3512*10^(-3)*t+0.083717
[6] E = if(t<=3)then(E1)else(if(t<=20)then(E2)else(if(t<60)then(E3)else(E4)))
[7] X = kCao*t/(1+kCao*t)

P13-19 (q)

Maximum Mixedness Model
2nd order, liquid phase, kC_{Ao} =0.1 min^{-1}, C_{Ao}=1mol/dm^3

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{Ao}} + \frac{E(\lambda)}{1-F(\lambda)}X$$

Rate Law : $-r_A = kC_A^{\,2}$

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

$r_A = kC_{Ao}{}^2(1-X)^2$ where k=0.1 dm^3/mol min

$$\frac{r_A}{C_{Ao}} = kC_{Ao}(1-X)^2$$

$$\frac{dF}{dz} = -E(z) \quad \text{where } z=60-\lambda$$

See Polymath program P13-19-q.pol

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
z	0	0	60	60
X	0	0	0.4773052	0.4047103
F	0.99	-0.010344	0.99	-0.010344
cao	1	1	1	1
lam	60	0	60	0
E1	-1.284E+04	-1.284E+04	0.0832647	0
E2	-9.8680524	-9.8680524	0.092343	0.092343
E3	2.228E-05	1.806E-05	0.083717	0.083717
E4	0	0	0	0
Ca	1	0.52273	1	0.5952897
k	0.1	0.1	0.1	0.1
ra	-0.1	-0.1	-0.0273247	-0.035437
E	0	0	0.0832647	0

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(X)/d(z) = -(ra/cao+E/(1-F)*X)
[2] d(F)/d(z) = -E

Explicit equations as entered by the user
[1] cao = 1
[2] lam = 60-z
[3] E1 = -0.0011675*lam^4+0.011355*lam^3-0.047492*lam^2+0.0995005*lam
[4] E2 = -1.8950*10^(-6)*lam^4+8.7202*10^(-5)*lam^3-1.1739*10^(-3)*lam^2-1.7979*10^(-4)*lam+0.092343
[5] E3 = 1.2618*10^(-8)*lam^4-2.4995*10^(-6)*lam^3+1.8715*10^(-4)*lam^2-6.3512*10^(-3)*lam+0.083717
[6] E4 = 0
[7] Ca = cao*(1-X)
[8] k = 0.1
[9] ra = -k*Ca^2
[10] E = if(lam<=3)then(E1)else(if(lam<=20)then(E2)else(if(lam<60)then(E3)else(E4)))

X_{LFR}	X_{MM}	X_{seg}	X_{PFR}	X_{CSTR}
0.451	0.405	0.422	0.5	0.382

Solutions for Chapter 14 – Models for Non-ideal Reactors

P14-1 Individualized solution

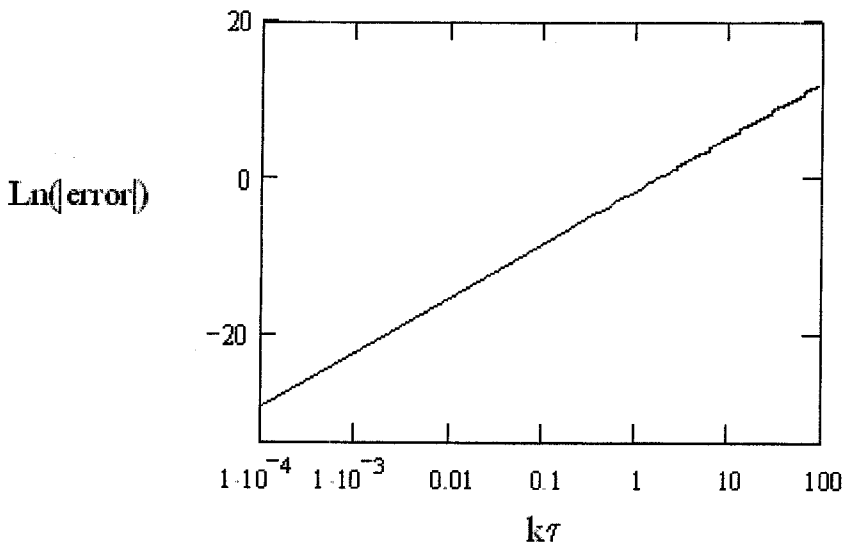
P14-2 (a)

Approximated formula for Segregation Model (1st reaction)

$e^{-kt} = 1 - kt + \frac{k^2 t^2}{2} + Error$. The error is then o((kt)^3).

Approximating the $Error = -\frac{kt^3}{3!}$

$k\tau$	Error
0.1	-0.0001667
1	-0.1667
10	-166.7



P14-2 (b)

Parameters Dispersion Model

Closed-Closed dispersion model

$$X = 1 - \frac{4q\exp(Pe_r/2)}{(1+q)^2\exp(Pe_r q/2) - (1-q)^2\exp(-Pe_r q/2)} \qquad (14\text{-}26)$$

Where

$q = \sqrt{1 + 4Da/Pe_r}$

$Da = k\tau = k\frac{l}{U}$ **Damköhler number**

$$Pe_r = \frac{Ul}{D_a}$$ **Peclet number**

$$Pe_r q = \sqrt{Pe_2^{\ 2} + 4DaPe_r}$$

Where

$$DaPe_r = \frac{kl^2}{D_a} = \frac{Rate\ of\ consumption\ of\ A\ by\ reaction}{Rate\ of\ transport\ by\ diffusion}$$

Numerical example

$$\tau = \frac{L}{U} = const = 5.15\,\mathbf{min}$$

$$L = \tau * U = 5.15\,\text{min} * 0.1 cm/s = 0.309 m$$

$$Sc = \frac{\mu}{D_{AB}} = 1000$$ (Liquids region in Fig. 14.11)

$$Da = k\tau = 1.288$$

d_t	Re	ReSc	L/d_t	$D/(U*d_t)$	D (cm^2/s)
1 cm	10	10^4	30.9	0.18 From Fig14.10	0.018
1 dm	100	10^5	3.09	40 From Fig. 14.11	40
1 m	1000	10^6	0.309	3000 From Fig. 14.11	30000

Pe_r	Q	X
172	1.015	0.721
0.077	8.226	0.567
$1.03 \cdot 10^{-4}$	223.609	0.563

Is there a diameter that would maximize or minimize conversion in this range ?
According Fig.14.10 there will be a radius that maximizes the conversion.

P14-2 (c)

(1) Vary the Damköhler number for a second-order reaction (Example 14-3(b))

For a second order reaction $$Da = \tau k C_{A0} = \frac{L}{U_0} k C_{A0}$$

$R = 0.05m$
$L = 6.36m$
$k = 0.5 dm^3 / mol.\text{min}$
$U_0 = 1.24 m/\text{min}$
$C_{A0} = 0.5 mol/dm^3$
$D_{aris} = 1.05 m^2/\text{min}$

Damköhler number/ Da	Conversion	Parameter
0.1603	0.138	8*U0
0.3205	0.239	4*U0

0.641	0.377	2*U0
1.282	0.523	U0
2.564	0.644	U0/2
5.129	0.732	U0/4
10.258	0.795	U0/8

(2) Vary the Peclet and Damköhler numbers for a second–order reaction in laminar flow (Example 14-3(c))

For a second order reaction $Da = \tau k C_{A0} = \frac{L}{U_0} k C_{A0}$; $Pe = U_0 L / D_{AB}$

$R = 0.05m$

$L = 6.36m$

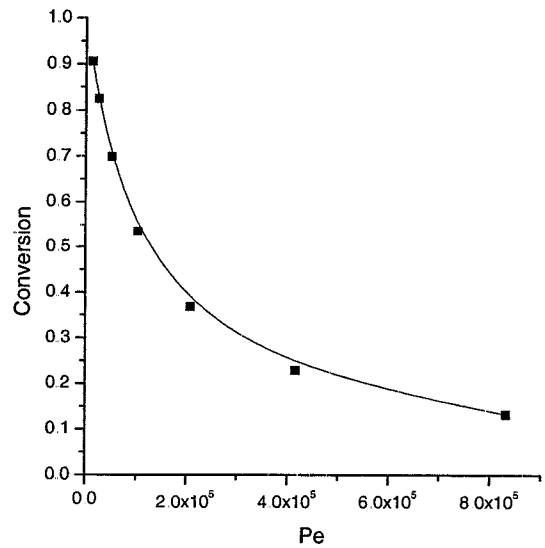
$k = 0.5 dm^3 / mol.\min$

$U_0 = 1.24 m / \min$

$C_{A0} = 0.5 mol / dm^3$

$D_{AB} = 7.6 \times 10^{-5} m^2 / \min$

Da	Pe	Conversion	Parameter
0.1603	8.32×10^5	0.132	8*U0
0.3205	4.16×10^5	0.229	4*U0
0.641	2.08×10^5	0.369	2*U0
1.282	1.04×10^5	0.536	U0
2.564	0.52×10^5	0.699	U0/2
5.129	0.26×10^5	0.825	U0/4
10.258	0.13×10^5	0.906	U0/8



When Peclet Number decreases less than 2×10^5, the conversion is influenced significantly.

Below is a FEMLAB anaylsis of the problem.

(1) Vary the Damköhler number for a second-order reaction (Example 14-3(b))

For a second order reaction $Da = \tau k C_{A0} = \frac{L}{U_0} k C_{A0}$

$R = 0.05m$

$L = 6.36m$

$k = 0.5dm^3 / mol.\min$

$U_0 = 1.24m / \min$

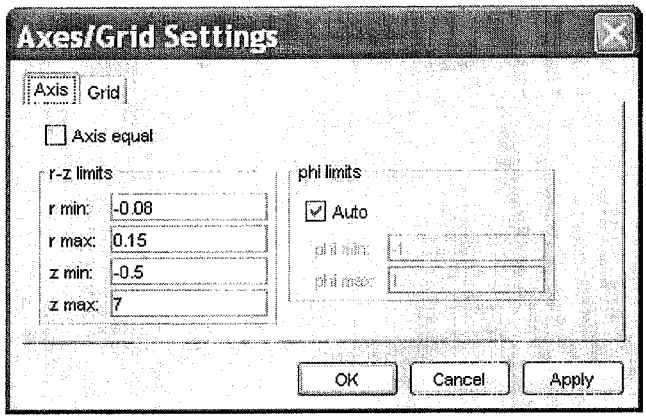
$C_{A0} = 0.5mol / dm^3$

$D_{aris} = 1.05m^2 / \min$

Damköhler number/ Da	Conversion	Parameter
0.1603	0.138	8*U0
0.3205	0.239	4*U0
0.641	0.377	2*U0
1.282	0.523	U0
2.564	0.644	U0/2
5.129	0.732	U0/4
10.258	0.795	U0/8

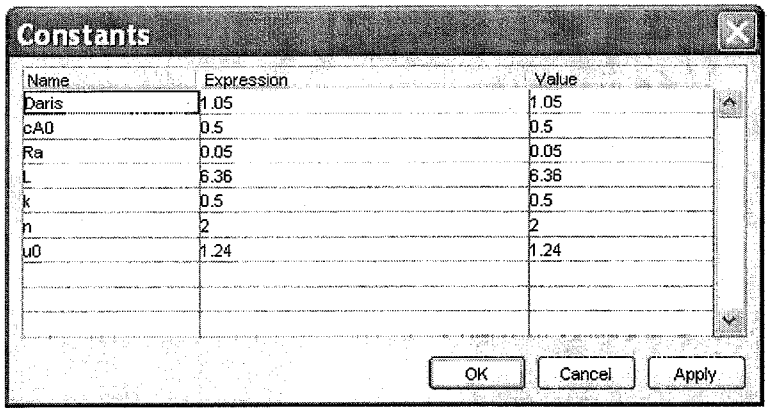
- Femlab Screen Shots

[1] Domain

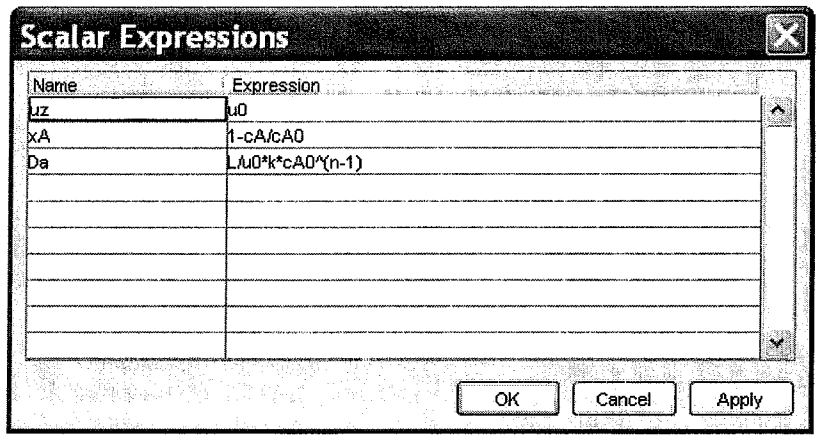


[2] Constants and scalar expressions

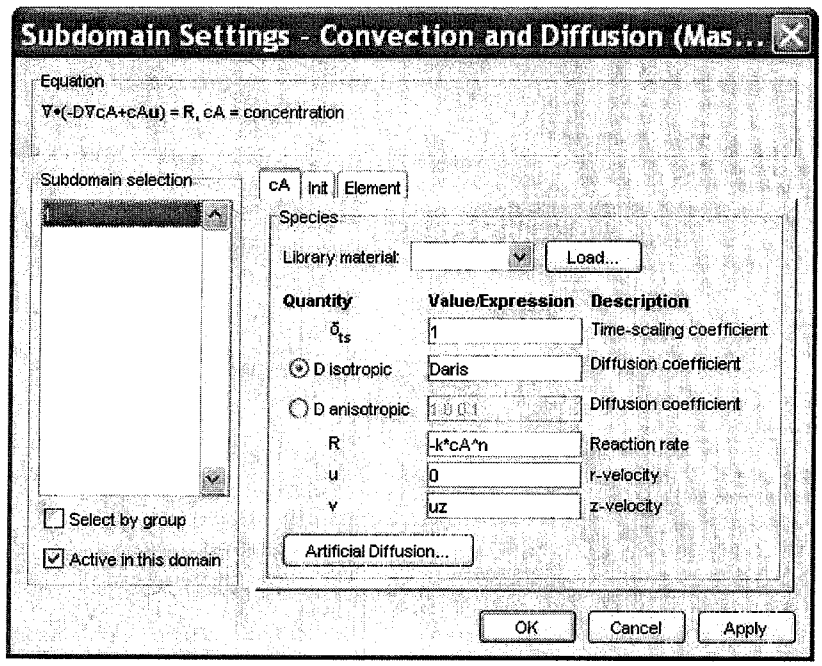
- Constants



- Scalar expressions

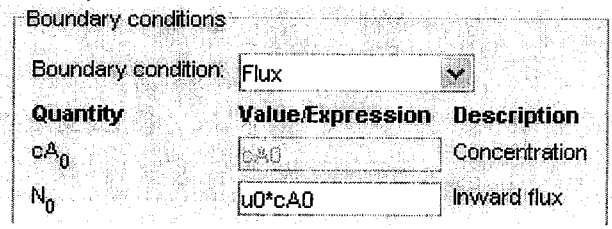


[3] Subdomain Settings
- Physics
(Mass Balance)



- Initial Values
(Mass balance) cA(t0) = cA0

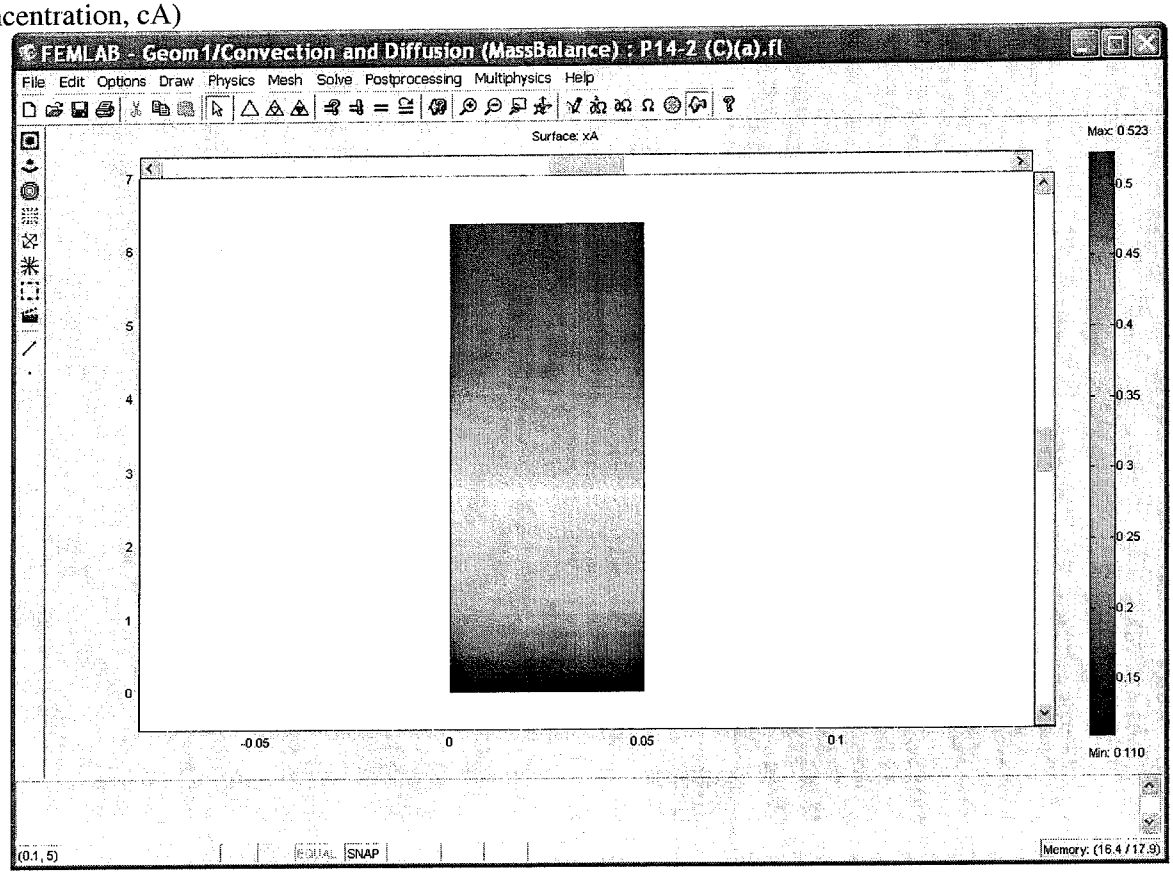
- Boundary Conditions
@ r = 0, Axial symmetry
@ inlet,



@ outlet, Convective flux
@ wall, Insulation/Symmetry

[4] Results

(Concentration, cA)



(2) Vary the Peclet and Damköhler numbers for a second–order reaction in laminar flow (Example 14-3(c))

For a second order reaction $Da = \tau k C_{A0} = \frac{L}{U_0} k C_{A0}$; $Pe = U_0 L / D_{AB}$

$R = 0.05m$

$L = 6.36m$

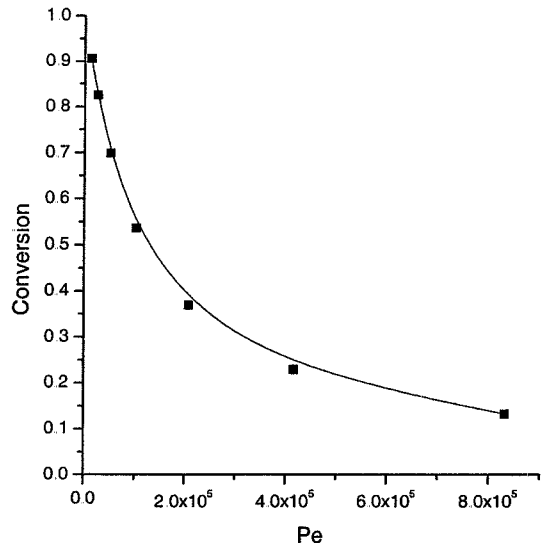
$k = 0.5 dm^3 / mol.\min$

$U_0 = 1.24 m / \min$

$C_{A0} = 0.5 mol / dm^3$

$D_{AB} = 7.6 \times 10^{-5} m^2 / \min$

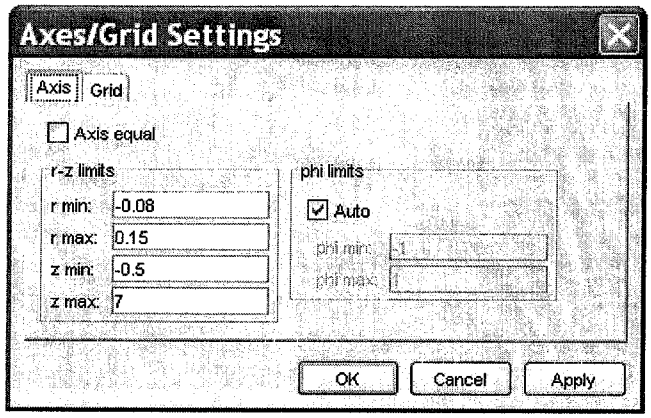
Da	Pe	Conversion	Parameter
0.1603	8.32×10^5	0.132	8*U0
0.3205	4.16×10^5	0.229	4*U0
0.641	2.08×10^5	0.369	2*U0
1.282	1.04×10^5	0.536	U0
2.564	0.52×10^5	0.699	U0/2
5.129	0.26×10^5	0.825	U0/4
10.258	0.13×10^5	0.906	U0/8



When Peclet Number decreases less than 2×10^5, the conversion is influenced significantly.

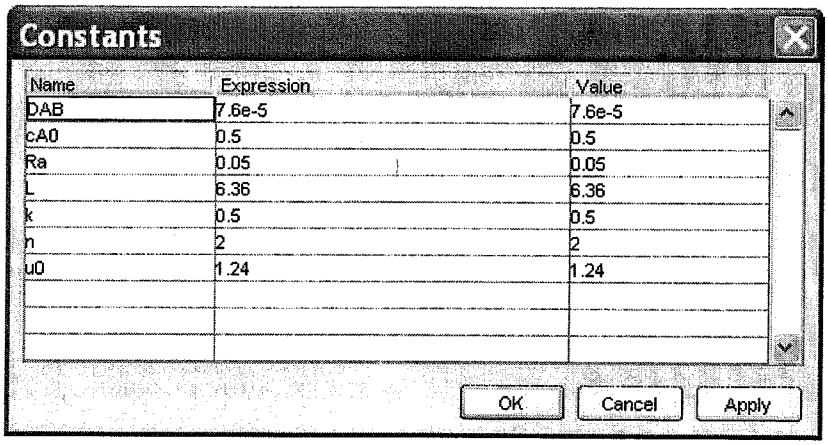
- Femlab Screen Shots

[1] Domain

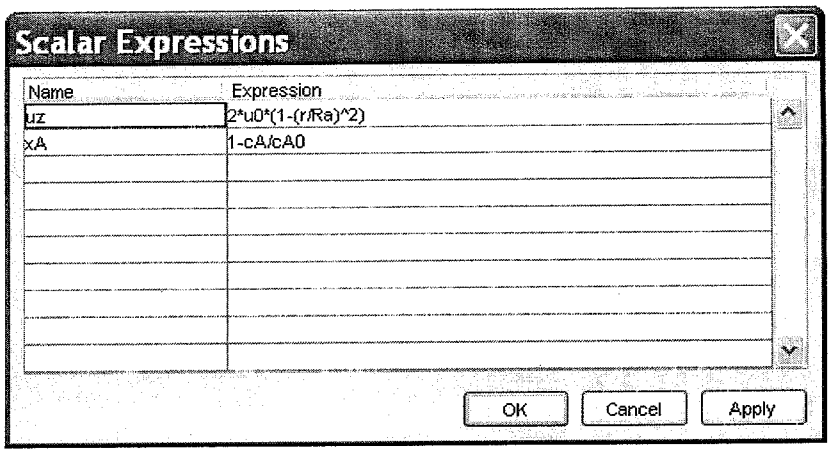


[2] Constants and scalar expressions

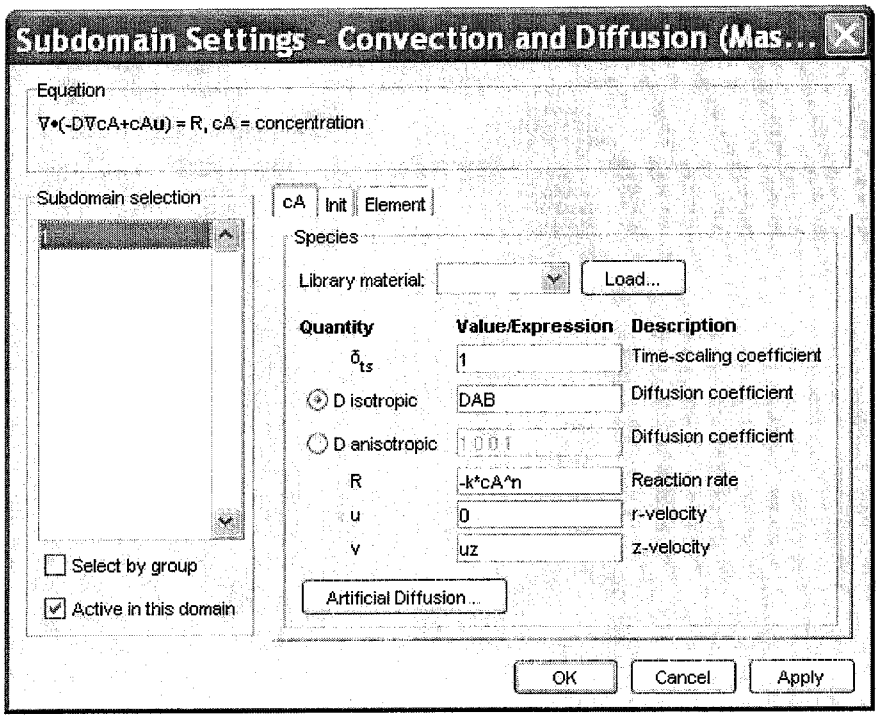
- Constants



- Scalar expressions

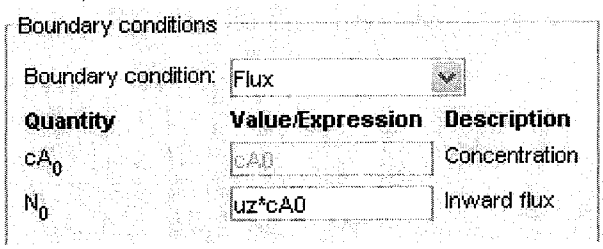


[3] Subdomain Settings
- Physics
(Mass Balance)



- Initial Values
(Mass balance) cA(t0) = cA0

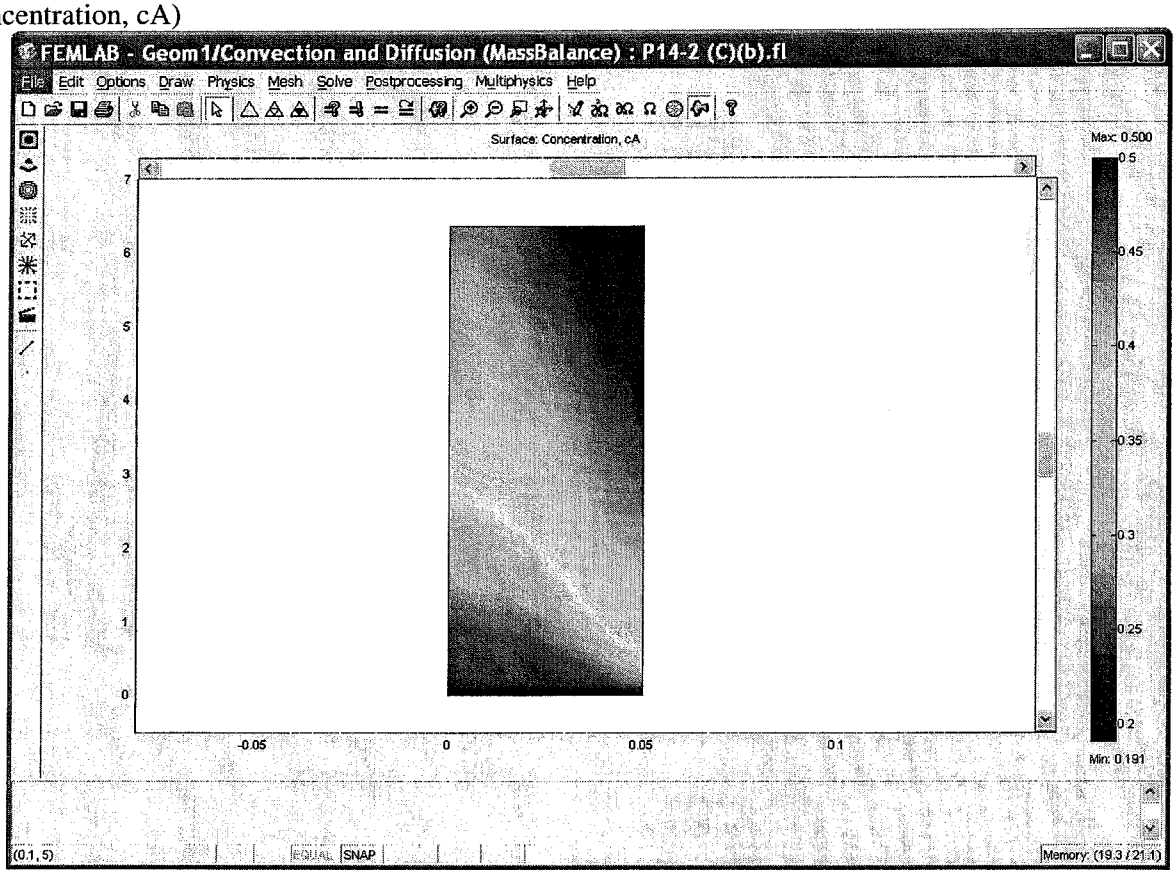
- Boundary Conditions
@ r = 0, Axial symmetry
@ inlet,



@ outlet, Convective flux

@ wall, Insulation/Symmetry

[4] Results
(Concentration, cA)



P14-2 (d)

Two parameters model

$$\tau = \frac{V}{v_o} = 10\,\mathbf{min}$$

I=2 and S=4min^{-1}.

$$\beta = \frac{v_b}{v_o} = \frac{(I-1)}{I} = 0.5$$

$$\alpha = \frac{V_s}{V} = \frac{(1-\beta)}{\tau S} = 0.013$$

$$v_s = (1-\beta)v_o = 0.05\frac{m^3}{\mathbf{min}}$$

$$V_s = (\alpha\tau)v_o = 0.013m^3$$

$$\tau_s = \frac{V_s}{v_s} = 0.25\,\mathbf{min}$$

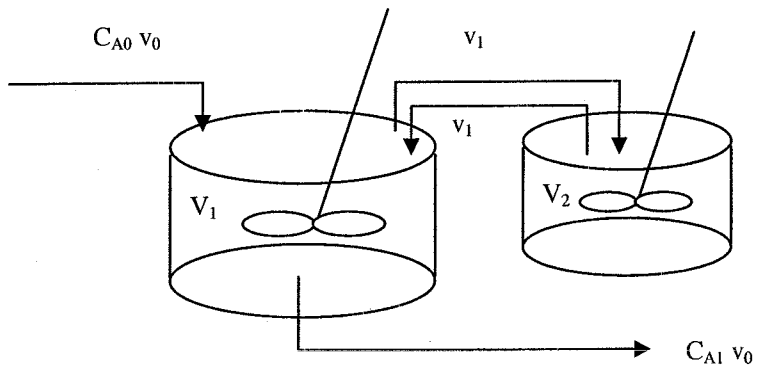
$$C_{As} = \frac{\sqrt{1+4\tau_s k C_{Ao}} - 1}{2\tau_s k} = 1.779 \frac{kmol}{m^3}$$

$$X = 1 - \frac{C_{As}}{C_{Ao}} = 0.111$$

Ideal CSTR	CSTR with Dead Space and Bypass (I=1.25 and S=0.115 min^{-1})	CSTR with Dead Space and Bypass (I=2.0 and S=4 min^{-1})
X=0.66	X=0.51	X=0.111

P14-2 (e)

Two CSTR with interchange (1st order reaction)



$$\alpha = \frac{V_1}{V} \quad \beta = \frac{v_1}{v_o} \quad X = 1 - \frac{C_{A1}}{C_{Ao}}$$

$$X = \frac{(\beta + \alpha\tau k)[\beta + (1-\alpha)\tau k] - \beta^2}{(1-\beta) + \alpha\tau k}$$

See Polymath program P14-2-e.pol

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	200	200
CT1	2000	31.814045	2000	31.814045
CT2	921	164.15831	1048.4628	164.15831
beta	0.15	0.15	0.15	0.15
alpha	0.75	0.75	0.75	0.75
tau	40	40	40	40
CTe1	2000	-1.275E+04	2000	-1.275E+04
CTe2	921	13	921	13
t1	-80	-80	120	120
CTe	2000	13	2000	13
k	0.03	0.03	0.03	0.03
X	0.5134788	0.5134788	0.5134788	0.5134788

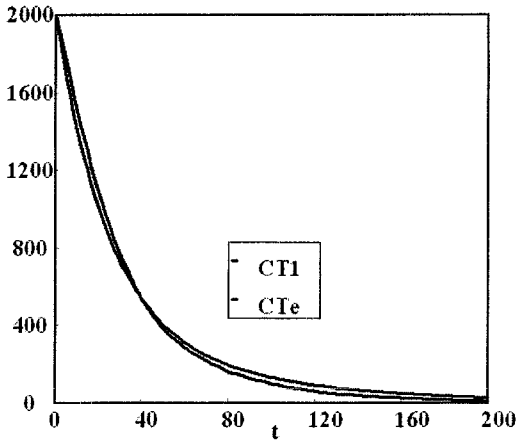
ODE Report (RKF45)

Differential equations as entered by the user

```
[1] d(CT1)/d(t) = (beta*CT2-(1+beta)*CT1)/alpha/tau
[2] d(CT2)/d(t) = (beta*CT1-beta*CT2)/(1-alpha)/tau
```

Explicit equations as entered by the user

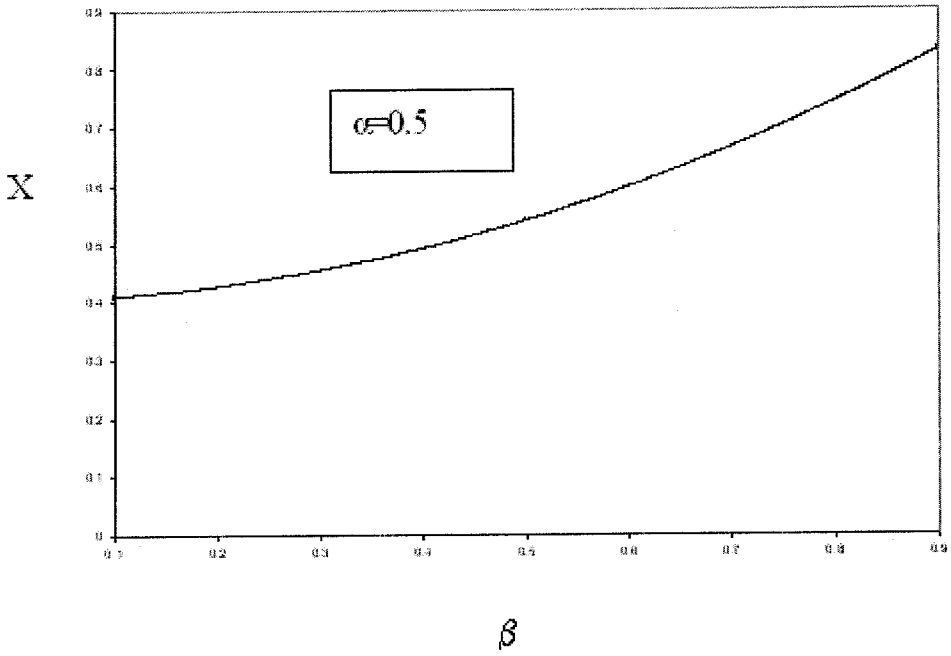
```
[1] beta = 0.15
[2] alpha = 0.75
[3] tau = 40
[4] CTe1 = 2000-59.6*t+0.64*t^2-0.00146*t^3-1.047*10^(-5)*t^4
[5] CTe2 = 921-17.3*t+0.129*t^2-0.000438*t^3+5.6*10^(-7)*t^4
[6] t1 = t-80
[7] CTe = if(t<80)then(CTe1)else(CTe2)
[8] k = 0.03
[9] X = ((beta+alpha*tau*k)*(beta+(1-alpha)*tau*k)-beta^2)/((1+beta+alpha*tau*k)*(beta+(1-alpha)*tau*k-beta^2))
```

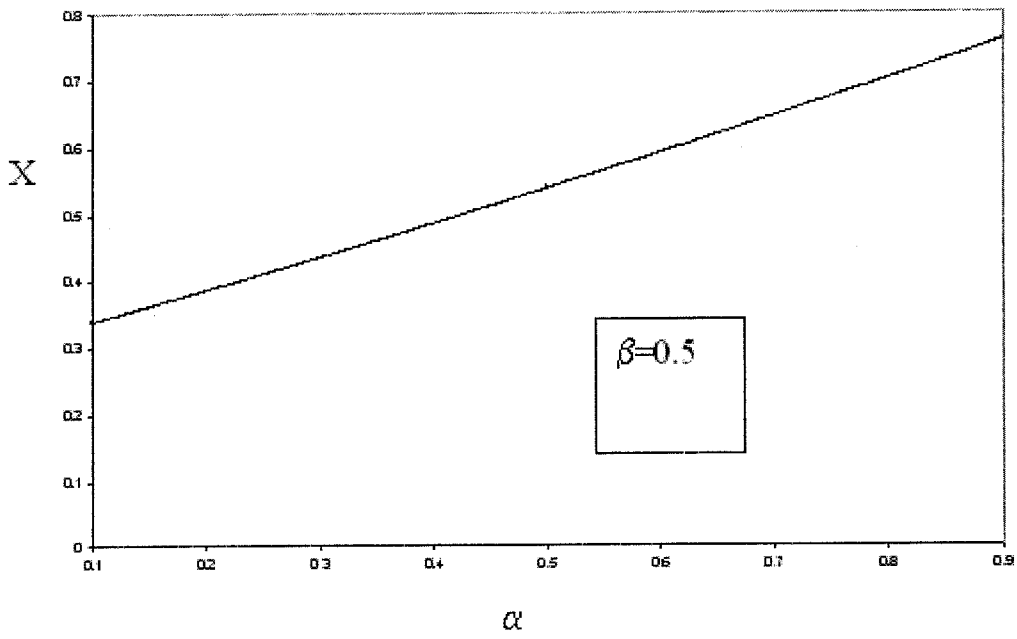


Comparison experimental and predicted (β=0.15 α=0.75) concetration.

For small deviations from the original value of the parameters concentration and conversion are not significantly affected.The following table show the conversion for different combinations of β and α.

α	β	X
0.75	0.15	0.51
0.8	0.1	0.51
0.5	0.5	0.54
0.1	0.8	0.46
0.5	0.1	0.41
0.5	0.9	0.83
0.1	0.5	0.34
0.9	0.5	0.76





Given the interchange flowrate, the conversion is increased with the increasing of the volume of the highly agitated reactor. Given the volume of the highly agitated reactor, the conversion is increased with the increasing of the interchange.

P14-2 (f)

Tubular Reactor Design

The correlations between Re and Da show what flow conditions (characterised by Re) give the greatest or smallest D_a and hence dispersion.

To minimise dispersion a Re number of ~10-20 gives the lowest value for D_a. Because $\mathbf{Re} = \frac{\rho u d}{\mu}$, the design of the vessel could be altered (i.e. diameter) for a given fluid and flowrate.
To maximise dispersion, either a very low Re (<0.1) or Re ~2300 will give the maximum Da values.
For a packed bed, the dispersion also depends on the Schmidt number as well as Re number.

P14-2 (g)

Linearizing non-first-order reactions
May be a good approximation if C_A does not change very much with time, i.e. A is in excess, in which case C_{Ao} should not be divided by anything.
Linearizing the non 1st order reactions may give significantly inaccurate results using Equation 14-27, which can be tested experimentally by recording tracer concentrations with time and using the tanks in series model for a conversion comparison.

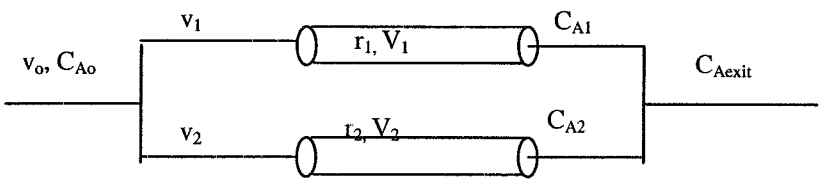
P14-2 (h)

Figures 14.3 and 14.1b
The curves in Fig.14.3 represent the residence time distributions for the Tanks in Series model as function of the number of reactors.
Given a CSTR of volume 1 ($V=V_1$), we divide the CSTR in two CSTRs ($V_2=1/2$). The mean residence time is unchanged (V/F) but the molecules going out of the second reactor will be delayed by the time (distribution) that occur to pass the first reactor (n=2, shift of the maximum). In the limit of infinite division ($V_n=0$), so in the single CSTRs the residence time goes to zero for all the molecules (zero variance), but their summation is the mean residence time (n=∞, PFR behaviour).
The model in Fig. 14.1, assumes a "faster" (channelling) reactor and a "slower" uniform reactor. There is an exit age distribution for the faster reactor which occurs as a distinct pulse clearly before the exit age distribution of the second reactor. The fraction of effluent which has been in the real reactor for less than time t shows a step up from zero when flow leaves from the "faster" reactor. This fraction is the fraction of flow in the "slower" reactor. When the flow leaves the "slower" reactor this fraction becomes one.

The model in Fig. 14.1 is PFR and CSTR in parallel. The exit age distribution for the CSTR is a negative gradient curve, interrupted by the distinct exit age distribution pulse of the PFR. The CSTR will always provide a fraction of effluent which has been inside the reactor for less than time t, which increases with time. But when the effluent exits the PFR at a specified time after zero, this increased effluent is superimposed upon F(t) of the CSTR, giving a combined F(t).
Conversion

$$\theta_1 = \frac{\alpha}{\beta} = 0.5 \quad \theta_2 = \frac{1-\alpha}{1-\beta} = 1.5$$

$$\alpha = \frac{V_1}{V} \quad \beta = \frac{v_1}{v}$$



PFR mol balance: $\frac{dX}{dV} = -\frac{r_A}{F_{Ao}}$

Rate law: $-r_A = kC_A^2$

Stoichiometry: liquid phase $C_A = C_{Ao}(1-X)$

2nd order PFR : $\frac{V}{v} = \frac{1}{kC_{Ao}^{\ 2}}\left[2\varepsilon(1+\varepsilon)\ln(1-X)+\varepsilon^2 X+\frac{(1+\varepsilon^2)X}{1-X}\right]$

$\varepsilon = y_{Ao}\delta$ where $\delta = \frac{c}{a}+\frac{b}{a}-1 = \frac{1}{2}+\frac{1}{2}-1 = 0$

$\varepsilon = 0$

Determining α and β:

$\frac{\alpha}{\beta} = \frac{V_1}{V}\frac{v_o}{v_1} = 0.5 \quad \rightarrow \quad V_1 = 2.5v_1$

$1-\frac{V_1}{V} = 1.5\left(1-\frac{v_1}{v}\right)$

$V = 10v_1$

Gives $\alpha = \frac{2.5}{10}\frac{v_i}{v_1} = 0.25$ and $\beta = \frac{V_1/2.5}{V/5} = \frac{5\alpha}{2.5} = 0.5$

Now $\tau = \frac{\tau_1+\tau_2}{2} = \frac{V_1/v_1+V_2/v_2}{2} = 5\,\text{min}$

Hence $V_1/v_1 + V_2/v_2 = 10$

But $V_1 = 2.5v_1 \quad \rightarrow \quad V_2 = 7.5v_2$

Gives $\tau_1 = 2.5\,\text{min} \qquad \tau_2 = 7.5\,\text{min}$

Substituting into

$\frac{V}{v} = \frac{1}{kC_{Ao}^{\ 2}}\left[2\varepsilon(1+\varepsilon)\ln(1-X)+\varepsilon^2 X+\frac{(1+\varepsilon^2)X}{1-X}\right]$

Reactor 1:

$2.5 = \frac{1}{0.1*2^2}\left[\frac{X_1}{1-X_1}\right]$

$1 = \left[\frac{X_1}{1-X_1}\right] \quad \rightarrow X_1 = 0.5$

$C_{A1} = C_{Ao}(1-X_1) = 2(1-0.5) = 1 mol/dm^3$

Reactor 2:

$7.5 = \frac{1}{0.1*2^2}\left[\frac{X_2}{1-X_2}\right]$

$3 = \frac{1}{0.1*2^2}\left[\frac{X_2}{1-X_2}\right] \rightarrow X_2 = 0.75$

$C_{A2} = C_{Ao}(1-X_2) = 2(1-0.75) = 0.5 mol/dm^3$

$C_{Aexit} = \frac{C_{A1}+C_{A2}}{2} = \frac{1+0.5}{2} = 0.75 mol/dm^3$

$$X = \frac{C_{Ao} - C_A}{C_{Ao}} = \frac{2 - 0.75}{2} = 0.625 mol/dm^3$$

P14-3 (a)

Money for buying reactors
Using the tank in series model:

Second order reaction $X = \frac{2Da + 1 - \sqrt{4Da + 1}}{2Da}$ where Da=kτCao

$$C_A = C_{Ao}(1 - X) \qquad X = \frac{C_{Ao} - C_A}{C_{Ao}}$$

Assume that $\tau = \tau_t$ and that in reactors medelled as more than one tank, that $\tau = \frac{\tau_t}{n}$. Number of tanks $n = \frac{\tau^2}{\sigma^2}$ rounded to the nearest integer.

Reactor	Σ(min)	τ(min)	n	X
Maze & blue	2	2	1	0.50
Green & white	4	4	1	0.61
Scarlet & grey	3.05	4	2	0.69
Orange & blue	2.31	4	3	0.72
Purple & white	5.17	4	1	0.61
Silver & black	2.5	4	3	0.72
Crimson & white	2.5	2	1	0.5

Where
Scarlet & grey: $X_1 = 0.5$, $C_{A1}=0.5 \rightarrow X_2 = 0.38$, $C_{A2}=0.31 \rightarrow X = 0.69$
Orange & blue : $X_1 = 0.43$, $C_{A1}=0.57 \rightarrow X_2 = 0.34$, $C_{A2}=0.38 \rightarrow X_3 = 0.27$,
$C_{A3}=0.28 \rightarrow X=0.72$
Using the combination of maze & blue followed by crimson & white reactor (same overall conversion either way)
$X_1 = 0.5$, $C_{A1}=0.5 \rightarrow X_2 = 0.17$, $C_{A2}=0.41 \rightarrow X=0.59$
The orange & blue or silver & black reactors which both approximate to 3 tanks in series give the greatest conversion.

P14-3 (b)

More money for buying reactors
Try:
Green & white and Maze & blue: $X_1 = 0.61$, $C_{A1}=0.39 \rightarrow X_2 = 0.34$, $C_{A2}=0.26 \rightarrow X = 0.74$
Scarlet & grey and Maze & blue: $X_1 = 0.69$, $C_{A1}=0.31 \rightarrow X_2 = 0.42$, $C_{A2}=0.18 \rightarrow X = 0.82$

Orange & blue and Maze & blue: $X_1 = 0.72$, $C_{A1}=0.28 \rightarrow X_2 = 0.40$, $C_{A2}=0.17 \rightarrow X = 0.83$
The highest conversion is now obtained from the Orange & blue reactor combined with the Maze & blue reactor.

P14-3 (c)

Ann Arbor, MI
East Lansing, MI
Columbus, OH
Urbana, IL

Evanston, IL
West Lafayette, IN
Madison, WI

P14-4

Packed bed reactor with dispersion

1st order, k_1=0.0167/s, ε=0.5, d_p=0.1 cm,

$$\nu = \frac{\mu}{\rho} = 0.01 cm^2/s \quad \text{L=10 cm, U= 1 cm/s}$$

$$\text{Re} = \frac{\rho U d_p}{\mu} = 10 \text{ and } Sc = \frac{\nu}{D_{AB}} \text{ no data concerning } D_{AB}$$

From packed bed correlation for D_a, and liquid phase region of graph,

$$\text{Gives } \frac{D_a \varepsilon}{U d_p} = 2 approx \rightarrow D_a = \frac{2 U d_p}{\varepsilon} = \frac{2*1*0.1}{0.5} = 0.4 cm^2/s$$

$$Pe_r = \frac{UL}{D_a} = \frac{1*10}{0.4} = 25$$

$$X = 1 - \frac{4q \exp(Pe_r/2)}{\left[(1+q)^2 \exp(Pe_r q/2)\right] - \left[(1-q)^2 \exp\left(-Pe_r q/2\right)\right]}$$

$$q = \sqrt{1 + \frac{4Da}{Pe_r}}$$

Da=τκ and $\tau = \frac{L}{U} = \frac{10}{1} = 10s$ → Da=0.167 and q=1.013

$$X = 0.15$$

Conversion X=15%.

P14-5 (a)

Number of tanks in series

Assuming the Peclet-Bodenstein relation: $n = \frac{Bo}{2} + 1$

Where $Bo = \frac{UL}{D_a}$

To estimate Bo, $\text{Re} = \frac{d_t u}{\nu} = \frac{5*2}{0.01} = 1000$ and $Sc = \frac{\nu}{D_{AB}} = \frac{0.01}{0.005} = 2$

From gas phase dispersion correlation chart, $\frac{D_a}{u d_t} = 8$

Gives $D_a = 80 cm^2/s$

$$Bo = \frac{2*200}{80} = 5$$

$$n = \frac{5}{2} + 1 = 3.5$$

P14-5 (b)

Conversion

Using individual reactor material balances:

Reactor 1:

Mol balance: $X = -\frac{r_A V}{F_{Ao}}$

Rate law: $-r_A = kC_A^{\ 2}$

Stoichiometry: $C_A = C_{Ao}(1 - X_1)$ δ=0 and ε=0 hence no volume change

$$X_1 = \frac{kC_{Ao}^{\ 2}(1-X_1)^2}{vC_{Ao}} = \frac{25*0.01}{0.039}(1-X_1)^2$$

$$X_1 = 6.366(1-X_1)^2 \rightarrow 0.674$$

$$C_{A1} = C_{Ao}(1-X_1) = 0.00326 mol/dm^3$$

Reactor 2:

$$X_2 = \frac{kC_{A1}(1-X_2)^2}{v} \rightarrow X_2 = 0.507$$

$$C_{A2} = C_{A1}(1-X_2) = 0.00326(1-0.507) = 0.001607 mol/dm^3$$

Reactor 3:

$$X_3 = \frac{kC_{A2}(1-X_3)^2}{v} \rightarrow X_3 = 0.387$$

$$C_{A3} = C_{A2}(1-X_3) = 0.001607(1-0.387) = 0.000985 mol/dm^3$$

Reactor 4:

$$X_4 = \frac{kC_{A3}(1-X_4)^2}{v} \rightarrow X_4 = 0.305$$

$$C_{A4} = C_{A3}(1-X_4) = 0.000985(1-0.305) = 0.000685 mol/dm^3$$

Bounds on conversion:

3 tanks $X = \frac{C_{Ao} - C_{A3}}{C_{Ao}} = 0.9015$

4 tanks $X = \frac{C_{Ao} - C_{A3}}{C_{Ao}} = 0.9315$

P14-5 (c)

Change of the fluid velocity

Let U=0.1cm/s

Re=50 and Sc=2

From gas phase dispersion correlation chart, $\frac{D_a}{ud_t} = 0.5$

Gives $D_a = 0.5ud_t = 0.5*0.1*5 = 0.25cm^2/s$

$$Bo = \frac{UL}{D_a} = \frac{0.1*200}{0.25} = 80$$

$$n = \frac{Bo}{2} + 1 = 41$$

The conversion is close to the one PFR 2nd order reaction:
k=25dm^3/(mol·s)
τ=l/U=2/0.001=2000s
Da=kτC$_{Ao}$=500

$$X = \frac{Da}{1+Da} = 0.998$$

Let U=100cm/s
Re=50000 and Sc=2

From gas phase dispersion correlation chart, $\frac{D_a}{ud_t} = 0.21$

gives $D_a = 0.21ud_t = 0.21*100*5 = 0.25cm^2/s$

$$Bo = \frac{UL}{D_a} = \frac{100*200}{105} = 190.5$$

$$n = \frac{Bo}{2} + 1 = \frac{190.5}{2} + 1 = 96$$

The conversion is close to the one PFR 2nd order reaction:
k=25dm^3/(mol·s)
τ=l/U=2/1=2s
Da=kτC$_{Ao}$=0.5

$$X = \frac{Da}{1+Da} = 0.333$$

P14-5 (d)

Change of the superficial velocity

$$\mathrm{Re} = \frac{d_t u}{\nu} = \frac{0.2*4}{0.01} = 80$$

From packed bed dispersion correlation chart, $\frac{D_a\varepsilon}{ud_p} = 0.55$

$$D_a = \frac{0.55ud_p}{\varepsilon} = \frac{0.55*4*0.2}{0.4} = 1.1$$

$$Bo = \frac{UL}{D_a} = \frac{4*200}{1.1} = 727$$

$$n = \frac{Bo}{2} + 1 = \frac{727}{2} + 1 = 364.5$$

The conversion is close to the one PFR 2nd order reaction:
check
$k=25dm^3/(mol\cdot s)$
$\tau=l/U=2/1=2s$
$Da=k\tau C_{Ao}=0.5$

$$X=\frac{Da}{1+Da}=0.333$$

P14-5 (e)

Liquid instead of gas

Part (a) $\mathrm{Re}=\frac{d_t u}{\nu}=\frac{5*4*0.001}{0.1}=0.2$

$$Sc=\frac{\nu}{D_{AB}}=\frac{100}{5e-6}=2*10^7$$

This is off the scale of the graph for liquid phase dispersion, hence D_a cannot be evaluated.

P14-6 (a)

Peclet numbers

From Example 13.2 $\sigma^2=6.19min^2$ and $t_m=5.15min$
Closed:

$$\frac{\sigma^2}{tm^2}=\frac{2}{Pe_r}-\frac{2}{Pe_r{}^2}\left(1-e^{-Pe_r}\right)\rightarrow Pe_r=7.414$$

Open:

$$\frac{\sigma^2}{tm^2}=\frac{2}{Pe_r}+\frac{8}{Pe_r{}^2}\rightarrow Pe_r=11.68$$

P14-6 (b)

Space–time and dead volume

$$\tau=\frac{tm}{1+2/\ Pe_r}=4.40$$

$$V_s=\tau*v_o=263.8dm^3$$

$$V_D=V-V_s=156.2dm^3$$

$$\%deadvolume=\frac{156.2}{420}=37.2\%$$

P14-6 (c)

Conversions for 1st order isomerization

Dispersion model
$Da=k\tau=0.927$

$$q = \sqrt{1 + \frac{4Da}{Pe_r}} = 1221$$

$$X = 1 - \frac{4q\exp(Pe_r/2)}{(1+q)^2\exp(Pe_r q/2) - (1-q)^2\exp(-Pe_r q/2)} = 0.570$$

Tanks-in-series

$$n = \frac{\tau^2}{\sigma^2} = 4.35$$

$$X = 1 - \frac{1}{(1+\tau_i K)^n} = 0.568$$

P14-6 (d)

Conversions PFR and CSTR

PFR: $X = 1 - e^{-k\tau}$ X=0.604

CSTR: $X = 1 - \frac{1}{1+\tau k}$ X=0.481

X_{Disp}	$X_{T\text{-}I\text{-}S}$	X_{PFR}	X_{CSTR}
0.570	0.568	0.604	0.481

P14-7

Tubular Reactor

1st order, irreversible, pulse tracer test → $\sigma^2 = 65\ s^2$ and $t_m = 10$ s

For a 1st order reaction, PFR: X =1- $e^{-k\tau}$ = 0.98

We need τ and k. There being no data for diffusivity (Schmidt number) D_a and hence Pe_r cannot be obtained using tubular flow correlations.

Calculate

V= 3 m * 25 dm^2 * (0.1 m/dm)^2 = 0.75 m^3

τ = 0.75 m^3 / (3*10^{-2} m^3/s) = 25 s

This is greater than t_m so channeling is occurring

Calculate, k

$$k = \frac{\ln\frac{1}{1-X}}{\tau} = 3.91/25\ s = 0.156\ s^{-1}$$

Therefore assume closed vessel dispersion model:

$t_m = \tau = 10$ s space-time

Calculate, Pe

$$\frac{\sigma^2}{t_m^{\,2}} = \frac{2}{Pe_r} - \frac{2}{Pe_r^{\,2}}\,(1-e^{-Per}) = 65/10^2 = 0.65$$

Iterating $\rightarrow Pe_r = 1.5$

Calculate, X using the measured V and v_0 giving $\tau = 25$ s

$$X = 1 - \frac{4q\exp\left(\frac{Pe_r}{2}\right)}{\left[(1+q)^2\exp\left(\frac{Pe_r * q}{2}\right)\right] - \left[(1-q)^2\exp\left(\frac{-Pe_r * q}{2}\right)\right]}$$

$Da = \tau k = 25 * 0.156 = 3.9$

$$q = \sqrt{1+\frac{4Da}{Pe_r}} = \sqrt{1+\frac{4*3.9}{1.5}} = 3.376$$

$$X = 1 - \frac{4*3.376\exp\left(\frac{1.5}{2}\right)}{\left[(1+3.376)^2\exp\left(\frac{1.5*3.376}{2}\right)\right] - \left[(1-3.376)^2\exp\left(\frac{-1.5*3.376}{2}\right)\right]} = 0.88$$

Conversion for the real reactor assuming the closed dispersion (X=0.88) model is less than for the ideal PFR (X=0.98)

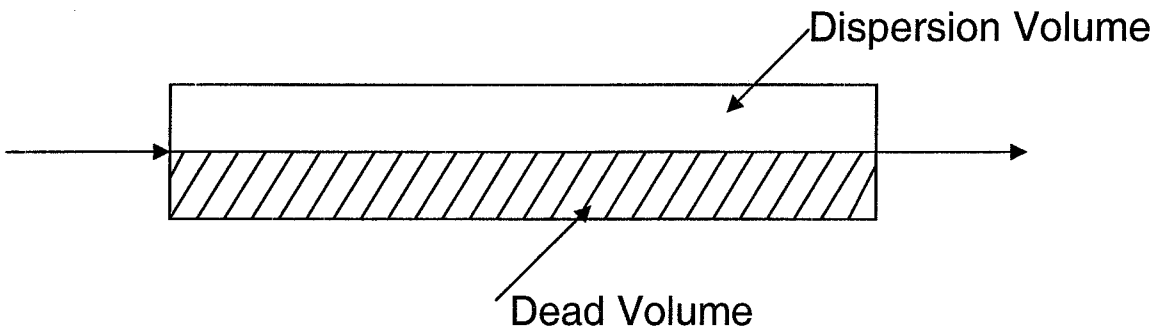
$$\tau_{ideal} = \frac{V}{v_0} = 25 \text{ s}$$

$V = V_D + V_S$

$V_S = \alpha * V$

Note,

$\tau_{RTD} = 10 \text{ s} = \alpha * \tau$, $\alpha = 10/25 = 0.4$



Dead Volume = $(1-\alpha)$ V= 0.6 V, Vs = 0.4V

Use $t_m = 10$s, $Da = t_m * k = 10*0.156 = 1.56$

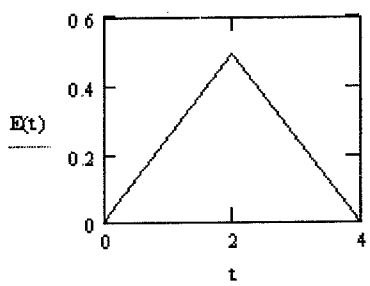
$$q = \sqrt{1+\frac{4*1.56}{1.5}} = 2.27$$

$$X_D = 1 - \frac{4 * 2.27 \exp\left(\frac{1.5}{2}\right)}{\left[(1+2.27)^2 \exp\left(\frac{1.5*2.27}{2}\right)\right] - \left[(1-2.27)^2 \exp\left(\frac{-1.5*2.27}{2}\right)\right]}$$

$X_D = 1 - (19.22/58.38) = 0.67$

P14-8 (a)

E(t):



Conversion T-I-S and Maximum Mixedness Model

$X_{T\text{-}I\text{-}S}=0.5$

For a first order reaction $X_{mm}=X_{T\text{-}I\text{-}S}=1-\frac{1}{\left(1+\frac{\tau}{n}k\right)^n}$

$$\tau = t_m = \int_0^\infty E(t)tdt = \int_0^2 0.25 \cdot t^2 dt + \int_2^4 (1-0.25 \cdot t)t\,dt = 2\,\text{min}$$

$$\sigma^2 = \int_0^\infty E(t)(t-t_m)^2 dt = \int_0^\infty E(t)t^2 dt - \tau^2 = \frac{2}{3}\,\text{min}^2$$

$$n = \frac{\tau^2}{\sigma^2} = 6$$

From the conversion it is possible to determine k at 300K:

$$k = \frac{\left(\frac{1}{\sqrt[n]{1-X}} - 1\right)}{\frac{\tau}{n}} = 0.367\,\text{min}^{-1}$$

The conversion at T=310 K is given by:

$$k_{310} = k_{300}\exp\left(\frac{E}{R300K} - \frac{E}{R\cdot 310K}\right) = 1.422\,\text{min}^{-1}$$

$$R = 1.986\frac{cal}{molK}$$

$$X_{mm}=X_{T\text{-}I\text{-}S}=1-\frac{1}{\left(1+\frac{\tau}{n}k\right)^{n}} = 0.903$$

P14-8 (b)

Complex Reactions

$$\frac{dC_A}{d\tau} = -k_1C_A - k_3C_A$$

$$\frac{dC_B}{d\tau} = k_1C_A - k_2C_B$$

$$\frac{dC_C}{d\tau} = k_2C_B$$

$$\frac{dC_D}{d\tau} = k_3C_A$$

Where $k_1= k_2= k_3=0.1\ \text{min}^{-1}$

$$\frac{dC_A}{d\lambda} = -\sum r_{iA} + (C_A - C_{Ao})\frac{E(\lambda)}{1-F(\lambda)}$$

$$\frac{dC_A}{d\lambda} = -(-k_1C_A - k_3C_A) + (C_A - C_{Ao})\frac{E(\lambda)}{1-F(\lambda)}$$

$$\frac{dC_B}{d\lambda} = -(k_1C_A - k_2C_B) + (C_B - C_{Bo})\frac{E(\lambda)}{1-F(\lambda)}$$

$$\frac{dC_C}{d\lambda} = -(k_2C_B) + (C_C - C_{Co})\frac{E(\lambda)}{1-F(\lambda)}$$

$$\frac{dC_D}{d\lambda} = -(k_3C_A) + (C_D - C_{Do})\frac{E(\lambda)}{1-F(\lambda)}$$

Where $C_{Ao}=1\text{mol/dm}^3$ and $C_{Bo}= C_{Co}= C_{Do}=0$.

Changing variable: λ=z-4
See Polymath program P14-8-b.pol

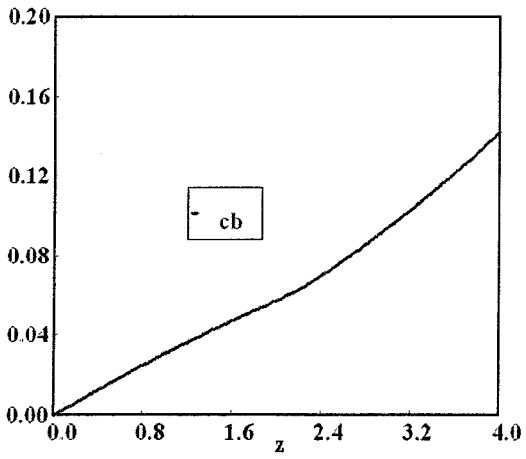
POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
z	0	0	4	4
ca	1	0.6793055	1	0.6793055
cb	0	0	0.142158	0.142158
cc	0	0	0.0181892	0.0181892
cd	0	0	0.1603473	0.1603473
F	0.9999999	2.854E-06	0.9999999	2.854E-06
k1	0.1	0.1	0.1	0.1
k2	0.1	0.1	0.1	0.1
k3	0.1	0.1	0.1	0.1
rc	0	0	0.0142158	0.0142158
ra	-0.2	-0.2	-0.1358611	-0.1358611
rb	0.1	0.0537147	0.1	0.0537147
t2	4	4	4	4
rd	0.1	0.0679305	0.1	0.0679305
cao	1	1	1	1
cbo	0	0	0	0
cco	0	0	0	0
cdo	0	0	0	0
t1	2	2	2	2
lam	4	0	4	0
E1	1	0	1	0
E2	0	0	1	1
E	0	0	0.4965476	0
EF	0	0	25.277605	0

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(ca)/d(z) = -(-ra+(ca-cao)*EF)
[2] d(cb)/d(z) = -(-rb+(cb-cbo)*EF)
[3] d(cc)/d(z) = -(-rc+(cc-cco)*EF)
[4] d(cd)/d(z) = -(-rd+(cd-cdo)*EF)
[5] d(F)/d(z) = -E

Explicit equations as entered by the user
[1] k1 = 0.1
[2] k2 = 0.1
[3] k3 = 0.1
[4] rc = k2*cb
[5] ra = -k1*ca-k3*ca
[6] rb = k1*ca-k2*cb
[7] t2 = 4
[8] rd = k3*ca
[9] cao = 1
[10] cbo = 0
[11] cco = 0
[12] cdo = 0
[13] t1 = 2
[14] lam = 4-z
[15] E1 = 0.25*lam
[16] E2 = 1-0.25*lam
[17] E = if (lam<t1) then (E1) else (if (lam<=t2) then (E2) else (0))
[18] EF = E/(1-F)



P14-8 (c)

Use FEMLAB for the full solution

Complex reactions and Dispersion Model.

$$\frac{dC_A}{d\tau} = -k_1 C_A - k_3 C_A$$

$$\frac{dC_B}{d\tau} = k_1 C_A - k_2 C_B$$

$$\frac{dC_C}{d\tau} = k_2 C_B$$

$$\frac{dC_D}{d\tau} = k_3 C_A$$

P14-9 (a)

From P13-4:

$$t_m = \tau = \sqrt{\frac{2}{\pi}} \text{ min}, \quad \sigma^2 = \frac{1}{2\pi} = 0.159 \text{ min}^2 \text{ and k= 0.8 min}^{-1}$$

Tanks-in-series

For a first order reaction the conversion is given by:

From Example 14-1

$$X_{T-I-S} = X_{seg} = 0.447$$

P14-9 (b)

Closed-closed vessel dispersion model

For a first order reaction the conversion is given:

$$X = 1 - \frac{4q \exp(Pe_r/2)}{(1+q)^2 \exp(Pe_r q/2) - (1-q)^2 \exp(-Pe_r q/2)}$$

$$0.25 = \frac{2}{Pe_r} - \frac{2}{Pe_r^{\,2}}\left(1 - e^{-Pe_r}\right)$$

Pe_r=6.83

$$Da = \tau k = 0.638$$

$$q = \sqrt{1 + \frac{4Da}{Pe_r}} = \sqrt{1 + \frac{4 * 0.638}{6.83}} = 1.885$$

X=0.41

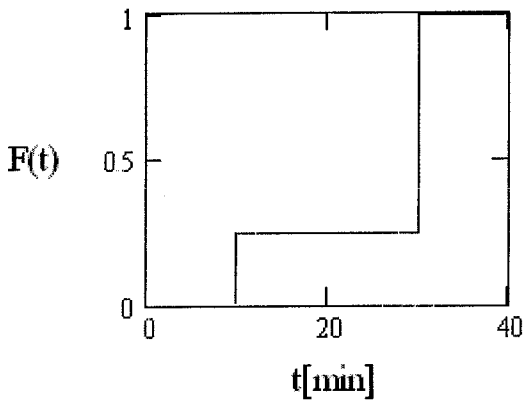
$X_{T\text{-}I\text{-}S}$	$X_{Dispersion}$
0.447	0.41

Referring to P14.2 the approximate formula for the T-I-S is not good approximation.

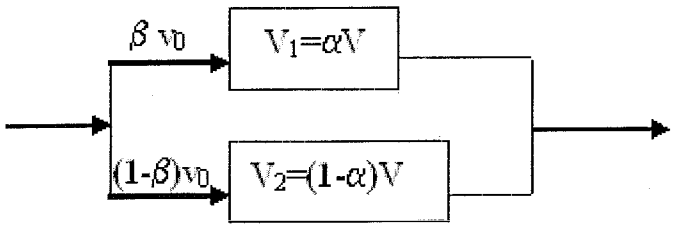
P14-10 (a)

Combination of ideal reactors

The cumulative distribution function F(t) is given:



The real reactor can be modelled as two parallel PFRs:



The relative $E(t) = \left\{\frac{1}{4}\delta(t - \tau_1) + \frac{3}{4}\delta(t - \tau_2)\right.$

P14-10 (b)

Model parameters

For two parallel PFRs, the parameters are τ_1=10 min and τ_2=30 min,

P14-10 (c)

Conversion

Fa_{01} =1/4Fa_0 and Fa_{02}=3/4Fa_0 ,second order, liquid phase, irreversible reaction with k=0.1 dm^3 /mol·min^{-1} and C_{Ao}=1.25 mol/dm^3

$$C_{A1} = C_{Ao} - \frac{k\tau_1 C_{Ao}}{1+k\tau_1 C_{Ao}} C_{Ao} = 0.556 mol/dm^3$$

$$C_{A2} = C_{Ao} - \frac{k\tau_2 C_{Ao}}{1+k\tau_2 C_{Ao}} C_{Ao} = 0.263 mo/dm^3$$

$$X = \frac{vC_{Ao} - \frac{1}{4}vC_{A1} - \frac{3}{4}vC_{A2}}{vC_{Ao}} = 0.731$$

P14-11 (a)

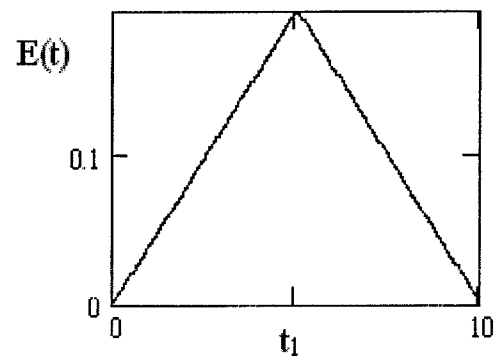
From P13-6

$t_1 = 5\,\text{min}$

$$E(t) = \begin{cases} \frac{t}{t_1^2} \; if \; t < t_1 \\ -\frac{1}{t_1^2}(t - 2t_1) if \; t_1 \le t \le 2t_1 \\ 0 \; otherwise \end{cases}$$

$t_m = t_1$ and

$$\sigma^2 = \frac{t_m^2}{6} = \frac{25}{6} = 4.16$$



Tanks-in-series

$$n = \frac{\tau^2}{\sigma^2} = 6$$ (As in P14.8)

Second order reaction, liquid phase, kC_{Ao}=0.2min^{-1}

$$\frac{C_{Ai} - C_{Aout}}{kC_{Aout}^{\;2}} = \tau$$

Solving for C_{Aout}

$$C_{Aout} = \frac{-1 + \sqrt{1 + 4k\tau C_{Ain}}}{2k\tau}$$

Six-Reactor System: τ_6=τ/6

The Damköhler number is given by Da_0= $kC_{Ao}\tau_6$=0.167

$$Da_i = \frac{-1 + \sqrt{1 + 4Da_{(i-1)}}}{2}$$

with i=1..6

In the following table the exit concentrations for each reactor are reported:

Da_1	0.145
Da_2	0.129
Da_3	0.116
Da_4	0.105
Da_5	0.095
Da_6	0.088

$$X = \frac{C_{A0} - C_{A6}}{C_{A0}} = \frac{Da_0 - Da_6}{Da_0} = 0.473$$

P14-11 (b)

Peclet number

The Peclet number $Pe_r = \frac{Ul}{D_a}$

For Closed-Closed System (no dispersion at the entrance and at the exit of the reactor P13.6)

$$\frac{\sigma^2}{\tau^2} = \frac{1}{6} = \frac{2}{Pe_r} - \frac{2}{Pe_r^{\,2}}\left(1 - e^{-Pe_r}\right)$$

Pe_r=10.875

P14-11 (c)

Conversion

Linearizing the 2st order according 14.2 (g):

$$-r_A = kC_A^2 \cong k\frac{C_{A0}}{2}C_A = k'C_A$$

it is possible to obtain an approximated solution;

$$k' = k\frac{C_{A0}}{2} = 0.1\,\text{min}^{-1}$$

$$Da = \tau k' = 0.5$$

Pe_r=10.875 (from Part(b))

$$q = \sqrt{1 + \frac{4Da}{Pe_r}} = \sqrt{1 + \frac{4*0.5}{10.875}} = 1.088$$

$$X = 1 - \frac{4q\exp(Pe_r/2)}{(1+q)^2\exp(Pe_r q/2) - (1-q)^2\exp(-Pe_r q/2)}$$

X=0.382

Full solution can be obtained with FEMLAB

P14-12 (a)

Remembering the physical meaning of the Peclet number:

$$Pe_r = \frac{rate\,of\,transport\,by\,convection}{rate\,of\,transport\,by\,diffusion\,or\,dispersion} = \frac{Ul}{D_a}$$

$$\lim_{Pe_r \to \infty} X_{Disp} = X_{PFR}$$

For a first order reaction:

$$X = 1 - \frac{4q\exp(Pe_r/2)}{(1+q)^2\exp(Pe_r q/2) - (1-q)^2\exp(-Pe_r q/2)} \quad (1)$$

$$q = \sqrt{1+\frac{4Da}{Pe_r}}$$

$$Da = \tau k$$

For $Pe_r >> 1$ (or for small vessel dispersion number)

$$q = \sqrt{1+\frac{4Da}{Pe_r}} = 1 + 2\frac{Da}{Pe_r} - 2\left(\frac{Da}{Pe_r}\right)^2 + o\left(\frac{Da}{Pe_r}\right)^3 \quad (2)$$

Introducing (2) into (1) and neglecting terms $o\left(\frac{1}{Pe_r}\right)^2$

$$X = 1 - \frac{4\cdot\left(1+\frac{2k\tau}{Pe}\right)e^{\left(\frac{Pe_r}{2}\right)}}{4\cdot\left(1+\frac{2k\tau}{Pe}\right)e^{\left(\frac{Pe_r}{2}\left(1+\frac{2Da}{Pe_r}-\frac{2Da^2}{Pe_r}\right)\right)}}$$

$$X = 1 - e^{\left[-k\tau+\frac{(\tau k)^2}{Pe_r}\right]}$$

P14-12 (b)

$$X_{PFR} = 1 - e^{-k\tau} \text{ and } X_{DisoPe>>1} = 1 - e^{-k\tau+\frac{(k\tau)^2}{Pe_r}}$$

In order to achieve the same conversion:

$$k\tau_{PFR} = k\tau_{Disp} - \frac{(k\tau_{Disp})^2}{Pe_r}$$

$$\frac{\tau_{PFR}}{\tau_{Disp}} = \frac{V_P}{V} = 1 - \frac{(k\tau_{Disp})}{Pe_r} = 1 - \frac{kD_a}{U^2}$$

P14-12 (c)

Defining:

$$Pe_r = \frac{Ul_{PFR}}{D_a} = 0.1$$

$$0.99\left(1-e^{-k\tau}\right) = 1 - \frac{4q\exp\left(Pe_r\left(\frac{l}{l_{PFR}}\right)/2\right)}{(1+q)^2\exp\left(Pe_r\left(\frac{l}{l_{PFR}}\right)q/2\right) - (1-q)^2\exp\left(-Pe_r\left(\frac{l}{l_{PFR}}\right)q/2\right)}$$

$$q = \sqrt{1 + \frac{4\tau_{PFR} k}{Pe_r}}$$

The following figure shows the solution as function of $k\tau_{PFR}$ for different values of l/l_{PFR}.

P14-12 (d)

Starting from 14.12.1 and subtracting the conversion for a PFR:

$$\ln \frac{C_A}{C_{A_{plug}}} = \frac{k\tau}{Pe}$$

For small deviations from the plug flow:

P14-12 (e)

According P12.3 dispersion doesn't affect zero order reaction.

P14-13

From P13.19:

τ=10 min and σ^2=74min^2

$$E(t) = \begin{cases} for\ 0 \le t \le 3\ E_1(t) = -1.1675 \cdot 10^{-3} t^4 + 1.1355 \cdot 10^{-2} t^3 - 4.7492 \cdot 10^{-2} t^2 \\ + 9.9505 \cdot 10^{-2} t \\ for\ 3 \le t \le 20\ E_2(t) = -1 \cdot 8950 \cdot 10^{-6} t^4 + 8.7202 \cdot 10^{-5} t^3 - 1.1739 \cdot 10^{-3} t^2 \\ -1.7979 \cdot 10^{-4} t + 0.092343 \\ for\ 20 \le t \le 60\ E_3(t) = 1.2618 \cdot 10^{-8} t^4 - 2.4995 \cdot 10^{-6} t^3 + 1.8715 \cdot 10^{-4} t^2 - \\ 6.3512 \cdot 10^{-3} t + 0.083717 \\ for\ t > 60 \quad 0 \end{cases}$$

P14-13 (a)

2nd order, kC_{A0}=0.1min^{-1}, C_{A0}=1mol/dm^3, Segregation Model

Segregation Model

$$\overline{X} = \int_0^\infty X(t) E(t) dt$$

Where $X(t) = \dfrac{kC_{Ao} t}{1 + kC_{Ao} t}$

See Polymath program P14-13-a.pol

•

POLYMATH Results

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	70	70
Xbar	0	0	0.4224876	0.4224876

kCao	0.1	0.1	0.1	0.1
E1	0	-2.436E+04	0.0836855	-2.436E+04
E2	0.092343	-21.261016	0.092343	-21.261016
E3	0.083717	1.949E-05	0.083717	0.0017977
E4	0	0	0	0
E	0	0	0.0836855	0
X	0	0	0.875	0.875

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Xbar)/d(t) = E*X

Explicit equations as entered by the user
[1] kCao = 0.1
[2] E1 = -0.0011675*t^4+0.011355*t^3-0.047492*t^2+0.0995005*t
[3] E2 = -1.8950*10^(-6)*t^4+8.7202*10^(-5)*t^3-1.1739*10^(-3)*t^2-1.7979*10^(-4)*t+0.092343
[4] E3 = 1.2618*10^(-8)*t^4-2.4995*10^(-6)*t^3+1.8715*10^(-4)*t^2-6.3512*10^(-3)*t+0.083717
[5] E4 = 0
[6] E = if(t<=3)then(E1)else(if(t<=20)then(E2)else(if(t<60)then(E3)else(E4)))
[7] X = kCao*t/(1+kCao*t)

P14-13 (b)

2nd order, $kC_{A0}=0.1min^{-1}$, $C_{A0}=1mol/dm^3$, Maximum Mixedness Model

$$\frac{dX}{d\lambda}=\frac{r_A}{C_{Ao}}+\frac{E(\lambda)}{1-F(\lambda)}X$$

Rate Law : $-r_A=kC_A{}^2$

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

$r_A=kC_{Ao}{}^2(1-X)^2$ where k=0.1 $dm^3/mol\,min$

$$\frac{r_A}{C_{Ao}}=kC_{Ao}(1-X)^2$$

$$\frac{dF}{dz}=-E(z)$$ where z=60-λ

See Polymath program P14-13-b.pol

POLYMATH Results
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
z	0	0	60	60
X	0	0	0.4773052	0.4047103
F	0.99	-0.010344	0.99	-0.010344
Cao	1	1	1	1
lam	60	0	60	0
Ca	1	0.52273	1	0.5952897
k	0.1	0.1	0.1	0.1
ra	-0.1	-0.1	-0.0273247	-0.035437
E4	0	0	0	0

E1	-1.284E+04	-1.284E+04	0.0832647	0
E2	-9.8680524	-9.8680524	0.092343	0.092343
E3	2.228E-05	1.806E-05	0.083717	0.083717
E	0	0	0.0832647	0

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(X)/d(z) = -(ra/Cao+E/(1-F)*X)
[2] d(F)/d(z) = -E

Explicit equations as entered by the user
[1] Cao = 1
[2] lam = 60-z
[3] Ca = Cao*(1-X)
[4] k = .1
[5] ra = -k*Ca^2
[6] E4 = 0
[7] E1 = -0.0011675*lam^4+0.011355*lam^3-0.047492*lam^2+0.0995005*lam
[8] E2 = -1.8950*10^(-6)*lam^4+8.7202*10^(-5)*lam^3-1.1739*10^(-3)*lam^2-1.7979*10^(-4)*lam+0.092343
[9] E3 = 1.2618*10^(-8)*lam^4-2.4995*10^(-6)*lam^3+1.8715*10^(-4)*lam^2-6.3512*10^(-3)*lam+0.083717
[10] E = if(lam<=3)then(E1)else(if(lam<=20)then(E2)else(if(lam<60)then(E3)else(E4)))

(Check F(t))

P14-13 (c)

Tanks in series and 1st order reaction with k=0.1min^{-1}

$$n = \frac{\tau^2}{\sigma^2} = 1.35$$

For 1st order reaction is acceptable a non integer value of n for calculating the conversion

$$X = 1 - \frac{1}{\left(1 + \frac{\tau}{n}k\right)^n} = 0.527$$

P14-13 (d)

Dispersion models and 1st order reaction with k=0.1min^{-1}

Peclet number open system

$$\frac{\sigma^2}{t_m^2} = \frac{2}{Pe} + \frac{8}{Pe^2} \rightarrow Pe = 4.906$$

FEMLAB application

Peclet number closed system

$$\frac{\sigma^2}{t_m^2} = \frac{2}{Pe} - \frac{2}{Pe^2}\left(1 - e^{-Pe}\right) \rightarrow Pe = 0.98$$

$$X = 1 - \frac{4q\exp(Pe_r/2)}{(1+q)^2\exp(Pe_r q/2) - (1-q)^2\exp(-Pe_r q/2)}$$

$$q = \sqrt{1 + \frac{4Da}{Pe_r}}$$

$$Da = \tau k$$

X=4.59

P14-13 (e)

Dispersion models and 2nd order reaction with k=0.1dm^3/mol·s and C_{A0}=1mol/dm^3
Conversion

Linearizing the 2st order reaction rate according 14.2 (g):

$$-r_A = kC_A^2 \cong k\frac{C_{A0}}{2}C_A = k'C_A$$

it is possible to obtain an approximated solution;

$$k' = k\frac{C_{A0}}{2} = 0.05s^{-1}$$

$$Da = \tau k' = 30$$

Pe_r=0.98 (from Part(b))

$$q = \sqrt{1+\frac{4Da}{Pe_r}} = \sqrt{1+\frac{4*30}{0.98}} = 11.111$$

$$X = 1 - \frac{4q\exp(Pe_r/2)}{(1+q)^2\exp(Pe_r q/2) - (1-q)^2\exp(-Pe_r q/2)}$$

X=0.998

Full solution can be obtained with FEMLAB.

P14-13 (f)

Two parameters model (backflow)

For tracer pulse input

$$V_1\frac{dC_1}{dt} = v_1C_{T2} - v_1C_{T1}$$

$$V_2\frac{dC_2}{dt} = v_1C_{T1} - v_0C_{T2}$$

Defining:

$$\alpha = \frac{V_1}{V}, \beta = \frac{v_1}{v_0} \text{ and } \tau = \frac{V}{v_0}$$

We arrive at two coupled differential equations:
For tracer pulse input

$$\alpha\tau\frac{dC_1}{dt} = \beta(C_{T2} - C_{T1})$$

$$(1-\alpha)\frac{dC_2}{dt} = \beta(C_{T1} - C_{T2})$$

See Polymath program P14-13-f.pol

P14-13 (g)

Two parameters model models and 2nd order reaction with k=0.1dm³/mol·s and C_{A0}=1mol/dm³

$$C_{A0} + \beta C_{A2} - \beta C_{A1} = -k\alpha\tau C_{A1}^2$$

$$\beta C_{A1} - \beta C_{A2} - C_{A2} = -kC_{A2}^2(1-\alpha)\tau$$

$$X = \frac{C_{A0} - C_{A2}}{C_{A0}}$$

P14-13 (h)

Table of the conversions

$X_{I\ I\ S}$	X_{MM}	X_{seg}	$X_{Dispersion}$	$X_{twoparameters}$
0.527	0.405	0.422	0.5	?

P14-13 (i)

Adiabatic reaction with Segregation Model

2nd order, kC_{A0}=0.1min^{-1}, C_{A0}=1mol/dm³, Segregation Model

Segregation Model

$$\frac{\partial X}{\partial t} = kC_{A0}(1-X)^2$$

$$T = 320 + 150X$$

$$k = 0.1 * \exp(45000/8.314 * (1/320 - 1/T))$$

$$\overline{X} = \int_0^\infty X(t)E(t)dt$$

See Polymath program P14-13-i.pol

P14-14 (a)

Product distribution for the CSTR and PFR in series

T	k_2/k_1	$\tau k_1 C_{A0}$
T_1	5.0	0.2
T_2	2.0	2
T_3	0.5	20
T_4	0.1	200

Considering Arrhenius equation and applying the following notation:

$$\ln\frac{k_{rT}}{A_r} = -\frac{E_r}{RT} = -\overline{E}_{rT}$$

We can write this linear system of 5 equations for the 5 unknowns ($\overline{E}_{11}, \overline{E}_{12}, \overline{E}_{13}, \overline{E}_{14}, A_1$):

$$\ln\frac{k_{11}}{k_{12}} = \overline{E}_{12} - \overline{E}_{11} =$$

$$\ln\frac{k_{11}}{k_{13}} = \overline{E}_{13} - \overline{E}_{11} =$$

$$\ln\frac{k_{11}}{k_{14}} = \overline{E}_{14} - \overline{E}_{11} =$$

$$\ln\frac{k_{11}}{k_{21}} = \ln\frac{A_1}{A_2} + \overline{E}_{21} - \overline{E}_{11}$$

$$\ln\frac{k_{12}}{k_{22}} = \ln\frac{A_1}{A_2} + \overline{E}_{22} - \overline{E}_{12}$$

$$\ln\frac{k_{13}}{k_{23}} = \ln\frac{A_1}{A_2} + \overline{E}_{23} - \overline{E}_{13}$$

P14-14 (b-d) No solution will be given at this time.

P14-15 (a)

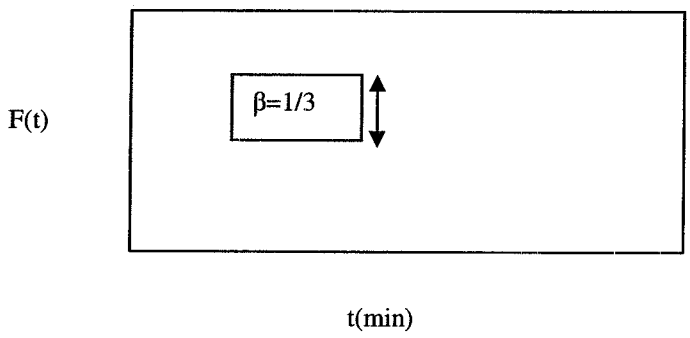
Two parameters model

$0\,\text{min} \le t < 10\,\text{min} \quad C(t) = 10\cdot\left(1-\exp(-0.1t)\right)$

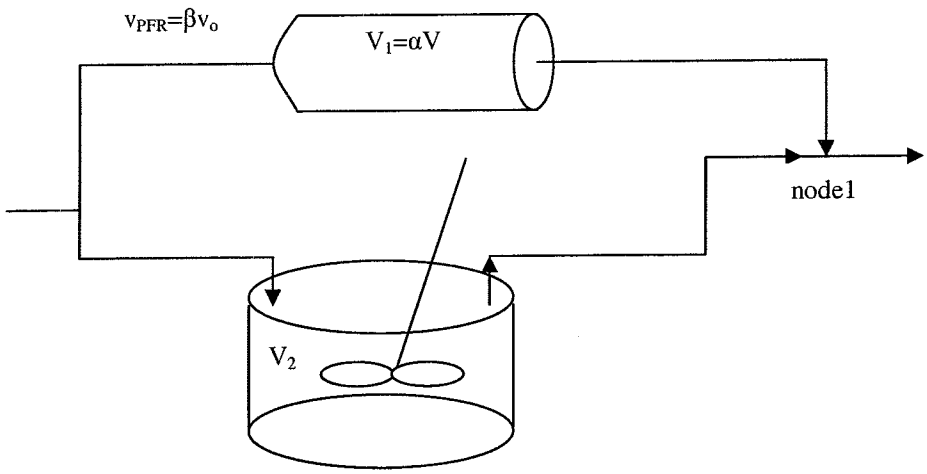
$10\,\text{min} \le t \quad C(t) = 5+10\cdot\left(1-\exp(-0.1t)\right)$

$0\,\text{min} \le t < 10\,\text{min} \quad F_1(t) = \frac{2}{3}\cdot\left(1-\exp(-0.1t)\right)$

$10\,\text{min} \le t \quad F_2(t) = \frac{1}{3}+\frac{2}{3}\cdot\left(1-\exp(-0.1t)\right)$



The F (t) can be representative of the ideal PFR and ideal CSTR in parallel model:



α= Fractional volume
β= Fraction of flow

$$\beta = \frac{1}{3}, \quad \alpha = \frac{1}{3}, \quad \tau = 10\,\text{min}$$

$$\tau_{PFR} = \frac{V_1}{v_{PFR}} = \frac{\alpha}{\beta}\tau = 10\,\text{min} \quad \tau_{CSTR} = \frac{(1-\alpha)}{(1-\beta)}\tau = 10\,\text{min}$$

P14-15 (b)

Conversion

2nd order, v_o=1 dm^3/min, k=0.1dm^3/mol·min, C_{A0}=1.25mol/dm^3

Balance around node 1

$$\beta v_o C_{PFR} + (1-\beta)v_0 C_{CSTR} = v_0 C_A$$

For the PFR:

Second-order

$$X_{PFR} = \frac{C_{A0} - C_{PFR}}{C_{A0}} = \frac{Da_{PFR}}{1 + Da_{PFR}} = 0.556$$

Where $Da_{PFR} = k\frac{\alpha}{\beta}\tau C_{Ao} = 1.25$

$$C_{PFR} = 0.556 mol/dm^3$$

For the CSTR:

$$X_{CSTR} = \frac{C_{A0} - C_{CSTR}}{C_{A0}} = \frac{(1 + 2Da_{CSTR}) - \sqrt{1 + 4Da_{CSTR}}}{2Da_{CSTR}} = 0.42$$

Where $Da_{CSTR} = k\frac{1-\alpha}{1-\beta}\tau C_{Ao} = 1.25$

$$C_{CSTR} = 0.725 mol/dm^3$$

Where $C_A = \beta C_{PFR} + (1-\beta)C_{CSTR} = 0.668 mol/dm^3$

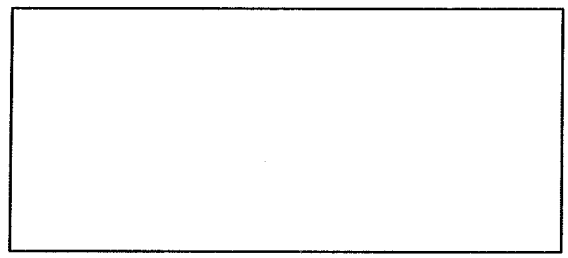
$$X = \frac{C_{A0} - C_A}{C_{A0}} = 0.465$$

P14-15 (c)

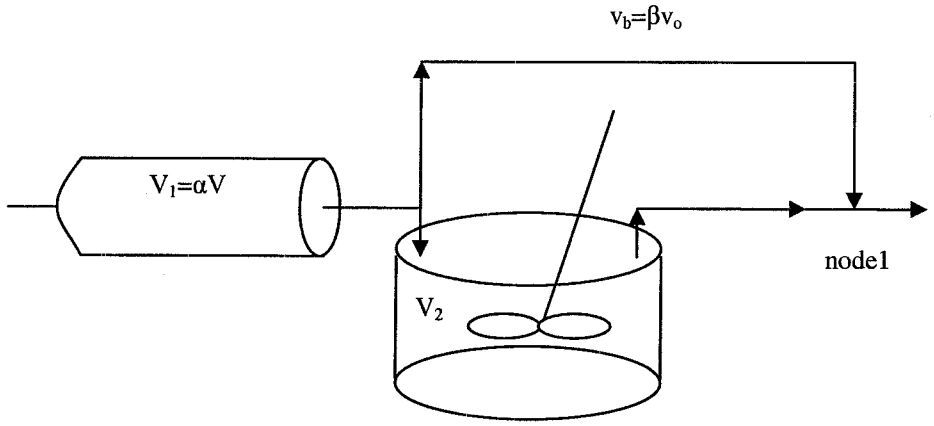
Two parameters model

$0\,\text{min} \le t < 10\,\text{min} \quad F_1(t) = 0$

$10\,\text{min} \le t \quad F_2(t) = \frac{1}{3} + \frac{2}{3} \cdot \{1 - \exp-[0.2(t-10)]\}$



The F (t) can be representative of the ideal PFR and ideal CSTR in series with a bypass between them:



α= Fractional volume

β= Fraction of flow

$$\beta = \frac{1}{3}, \quad \alpha = \frac{3}{4}, \quad \tau = \frac{40}{3}\,\text{min}$$

$$\tau_{PFR} = \frac{V_1}{v_o} = \alpha\tau = 10\,\text{min} \quad \tau_{CSTR} = \frac{(1-\alpha)}{(1-\beta)}\tau = 5\,\text{min}$$

Conversion

2nd order, v_o=1 dm^3/min, k=0.1dm^3/mol·min, C_{A0}=1.25mol/dm^3

Balance around node 1

$$\beta v_o C_b + (1-\beta)v_0 C_{CSTR} = \beta v_o C_{PFR} + (1-\beta)v_0 C_{CSTR} = v_0 C_A$$

For the PFR:

Second-order

$$X_{PFR} = \frac{C_{A0} - C_{PFR}}{C_{A0}} = \frac{Da_{PFR}}{1 + Da_{PFR}} = 0.556$$

Where $Da_{PFR} = k\alpha\tau C_{Ao} = 1.25$

$C_{PFR} = 0.556 mol/dm^3$

For the CSTR:

$$X_{CSTR} = \frac{C_{PFR} - C_{CSTR}}{C_{PFR}} = \frac{(1 + 2Da_{CSTR}) - \sqrt{1 + 4Da_{CSTR}}}{2Da_{CSTR}} = 0.185$$

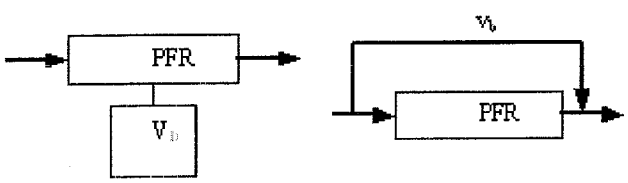
Where $Da_{CSTR} = k\frac{1-\alpha}{1-\beta}\tau C_{PFR} = 0.278$

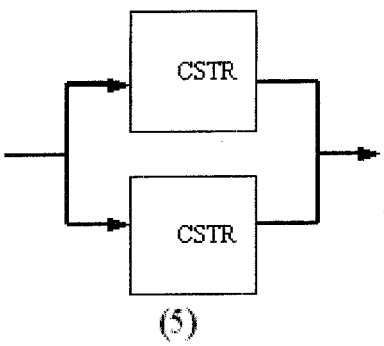
$C_{CSTR} = 0.453 mol/dm^3$

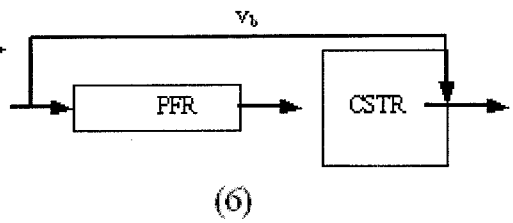
$$X = \frac{C_{A0} - C_A}{C_{A0}} = 0.61$$

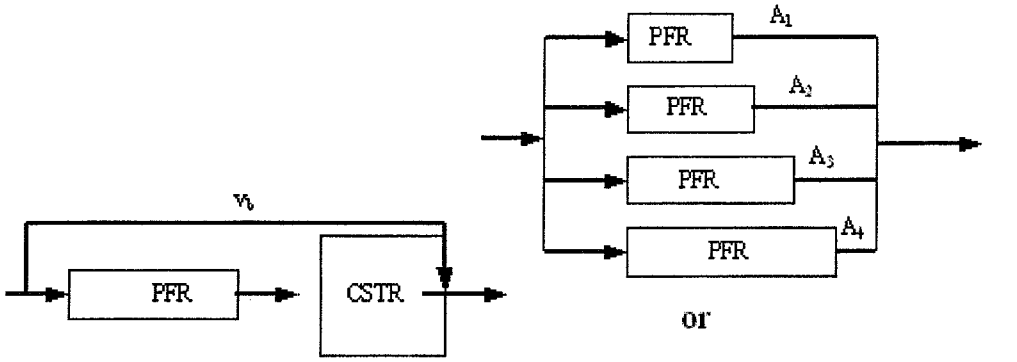
Where $C_A = \beta C_{PFR} + (1-\beta)C_{CSTR} = 0.487 mol/dm^3$

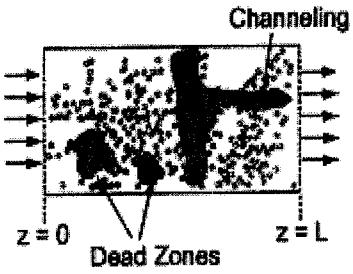
P14-16



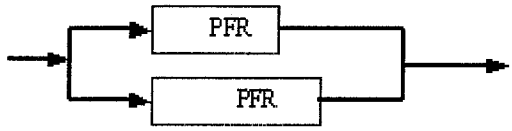




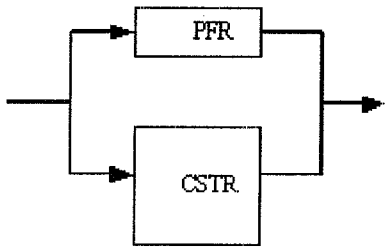




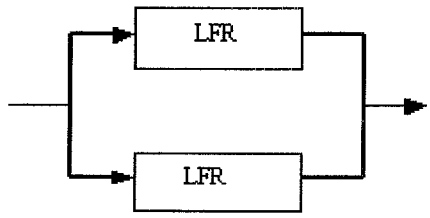
(9)



(10)



(11)



(12)

P14-17

The presence of a minimum (run2) imply the presence of a radial temperature profile that effects the reaction rate and determines the deviation from the concentration profile given by Eq. (14.51).

The enthalpy balance allows the identification of the dimensionless thermal parameters:

Defining

$$\varphi = \frac{r}{R} \quad \lambda = \frac{z}{L} \quad \vartheta = \frac{T}{T_{isot}} \quad \psi = \frac{C_A}{C_{A0}} \quad \overline{U} = \frac{U}{U_0}$$

$$\frac{\lambda_k \tau}{R^2 C_p}\left[\frac{1}{\varphi}\frac{\partial\left(\varphi\dfrac{\partial\vartheta}{\partial\varphi}\right)}{\partial\varphi}+\left(\frac{R}{L}\right)^2\frac{\partial^2\vartheta}{\partial\lambda^2}\right]-\overline{U}\frac{\partial\vartheta}{\partial\lambda}-k(\vartheta)C_{A0}^n\tau\psi^n\frac{\Delta H_{reac}}{C_p T_{isot}}=0$$

$$\varphi=0\quad\frac{\partial\vartheta}{\partial\varphi}=0\quad\varphi=1:\quad-\frac{\partial\vartheta}{\partial\varphi}=Bi(1-\vartheta)$$

where $Bi=\dfrac{hR}{\lambda_k}$ ratio convection-radial conduction

$\dfrac{\lambda_k\tau}{R^2C_p}$ ratio conduction-enthalpy flux

$\dfrac{\Delta H_{reac}}{C_p T_{coolant}}$ dimensionless adiabatic heat

$Da(\vartheta)=k(\vartheta)C_{A0}^n\tau$

A parametric study of the numerical solutions of Eq.(14.51) and the enthalpy balance would give the "exact" conditions for a minimum in the concentration.

P14-17 (a)

A decrease in the thermal conductivity of the reaction mixtures determines an increase of the bulk fluid temperature and can determine a minimum in concentration.

P14-17 (b)

Overall heat transfer coefficient increases:
For a given flux this determines less deviation from the isothermal case: no minimum

P14-17 (c)

Overall heat transfer coefficient decreases:
For a given flux this determines more deviation from the isothermal case
and the possibility of a minimum.

P14-17 (d)

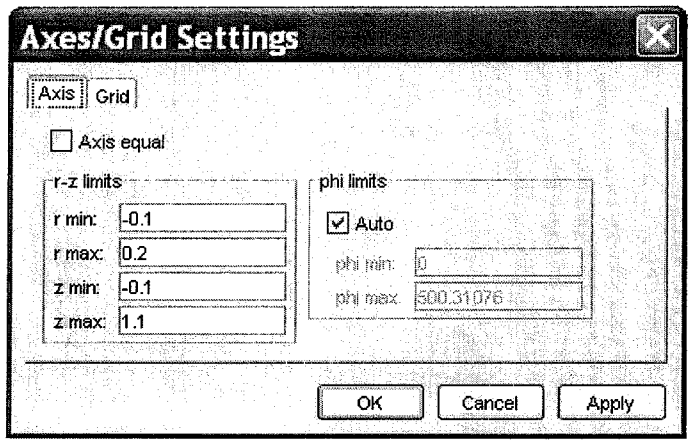
The coolant flow rate increases:
The external heat transfer coefficient increases, this implies a lower wall temperature and a resulting lower temperature in the reacting mixture and less deviation from the isothermal case: no minimum

P14-17 (e)

The coolant flow rate decreases:
The external heat transfer coefficient increases, this implies an increase in the wall temperature and a resulting higher temperature in the reacting mixture that can determine a minimum in the concentration.

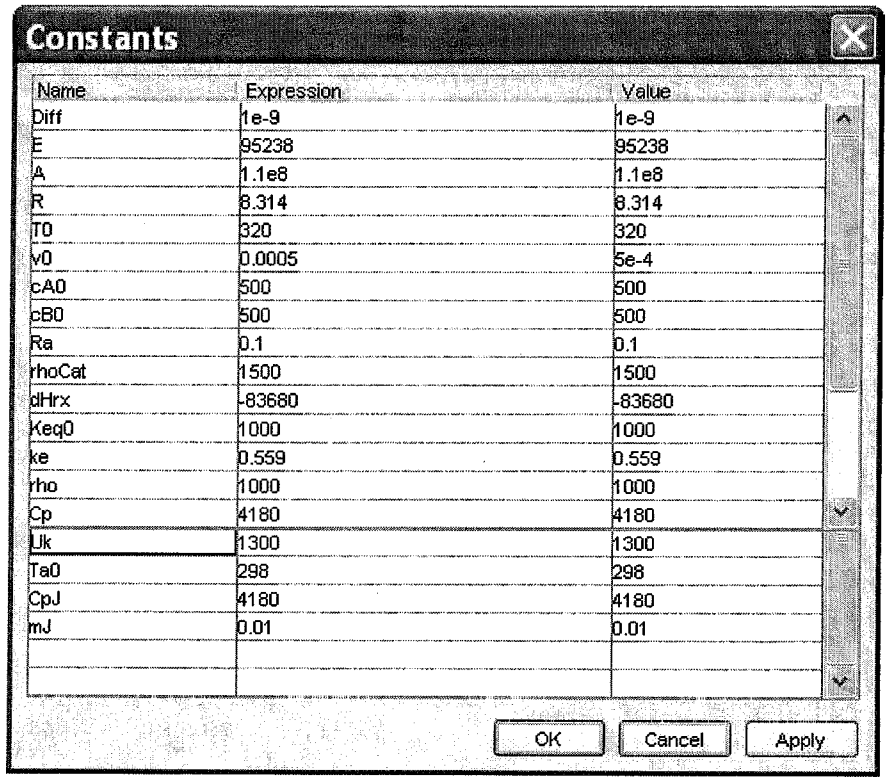
Below shows how to use FEMLAB for this problem.

Femlab Screenshots for the baseline case
(1) Domain

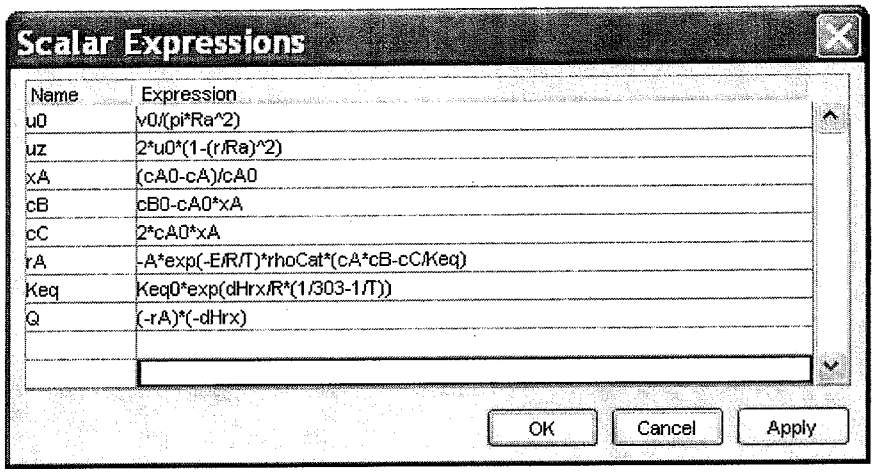


(2) Constants and scalar expressions

- Constants



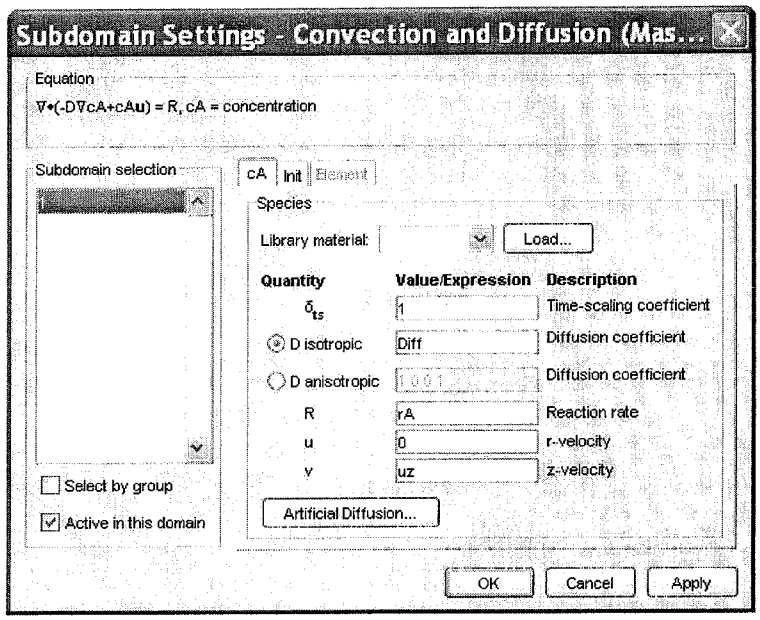
- Scalar expressions



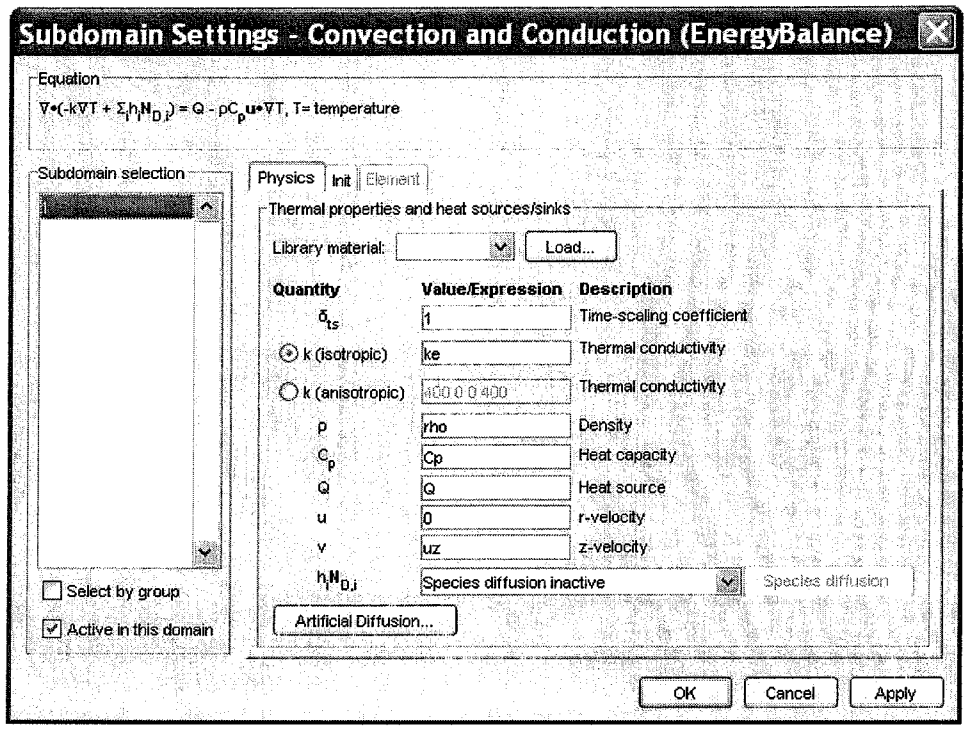
(3) Subdomain settings

- Physics

(Mass balance)



(Energy balance)



- Initial Values

(Mass balance) cA(t0) = cA0

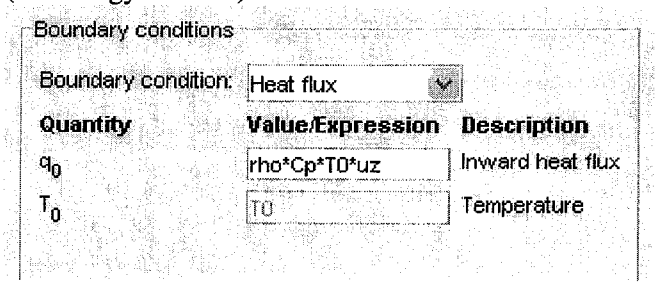
(Energy balance) T(t0) = T0

- Boundary Conditions

@ r = 0, Axial symmetry

@ inlet, cA = cA0 (for mass balance)

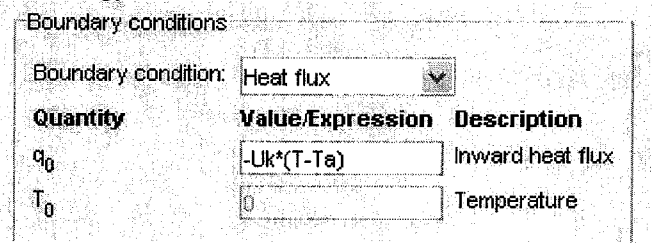
(for energy balance)



@ outlet, Convective flux

@ wall, Insulation/Symmetry (for mass balance)

(for energy balance)



P14-18

Vary the Peclet number and the reaction order in laminar flow (Example 14-3(c))

$$Da = \tau k C_{A0}^{n-1} = \frac{L}{U_0} k C_{A0}^{n-1}$$

$$Pe = U_0 L / D_{AB}$$

$L = 6.36m$

$R = 0.05m$

$k = 0.25 dm^3 / mol.\min$

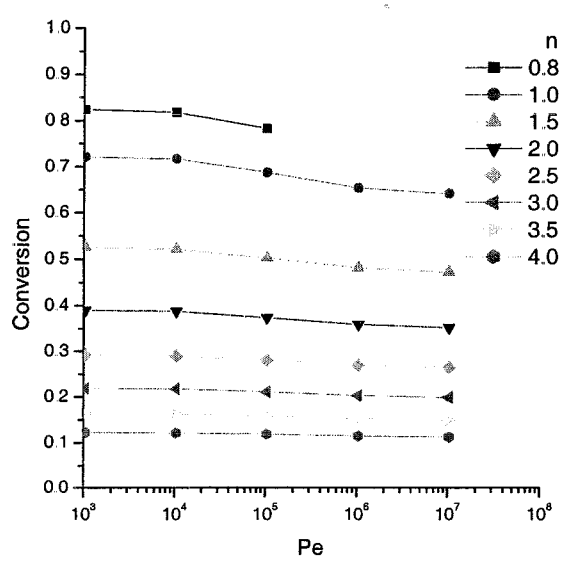
$U_0 = 1.24 m / \min$

$C_{A0} = 0.5 mol / dm^3$

$D_{AB} = 7.6 \times 10^{-5} m^2 / \min$

n	Pe	Conversion	Parameter
0.1 Attempt to evaluate non-integral power of negative number!	1.04×10^3	/	100* D_{AB}
	1.04×10^4	/	10* D_{AB}
	1.04×10^5	/	D_{AB}
	1.04×10^6	/	0.1*D_{AB}
	1.04×10^7	/	0.01*D_{AB}
0.5 Attempt to evaluate non-integral power of negative number!	1.04×10^3	/	100* D_{AB}
	1.04×10^4	/	10* D_{AB}
	1.04×10^5	/	D_{AB}
	1.04×10^6	/	0.1*D_{AB}
	1.04×10^7	/	0.01*D_{AB}
0.8	1.04×10^3	0.824	100* D_{AB}
	1.04×10^4	0.818	10* D_{AB}
	1.04×10^5	0.783	D_{AB}
	1.04×10^6	/	0.1*D_{AB}
	1.04×10^7	/	0.01*D_{AB}
1	1.04×10^3	0.721	100* D_{AB}
	1.04×10^4	0.717	10* D_{AB}
	1.04×10^5	0.687	D_{AB}
	1.04×10^6	0.653	0.1*D_{AB}
	1.04×10^7	0.641	0.01*D_{AB}
1.5	1.04×10^3	0.526	100* D_{AB}
	1.04×10^4	0.522	10* D_{AB}
	1.04×10^5	0.503	D_{AB}
	1.04×10^6	0.481	0.1*D_{AB}
	1.04×10^7	0.472	0.01*D_{AB}
2	1.04×10^3	0.390	100* D_{AB}
	1.04×10^4	0.388	10* D_{AB}
	1.04×10^5	0.374	D_{AB}
	1.04×10^6	0.359	0.1*D_{AB}
	1.04×10^7	0.352	0.01*D_{AB}
2.5	1.04×10^3	0.292	100* D_{AB}
	1.04×10^4	0.290	10* D_{AB}
	1.04×10^5	0.281	D_{AB}

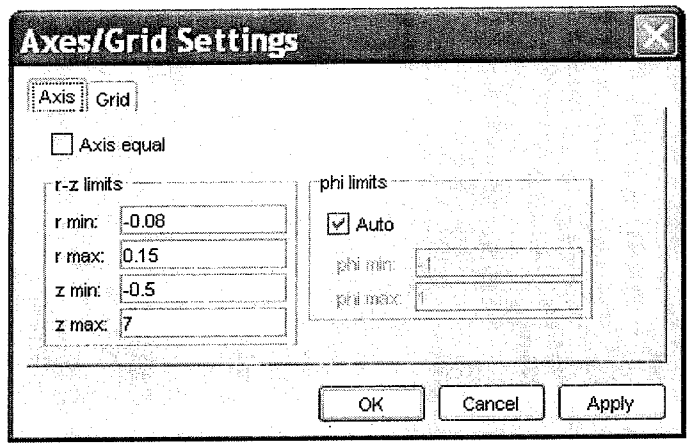
	1.04×10^{6}	0.270	$0.1*D_{AB}$
	1.04×10^{7}	0.265	$0.01*D_{AB}$
3	1.04×10^{3}	0.219	$100* D_{AB}$
	1.04×10^{4}	0.218	$10* D_{AB}$
	1.04×10^{5}	0.211	D_{AB}
	1.04×10^{6}	0.203	$0.1*D_{AB}$
	1.04×10^{7}	0.199	$0.01*D_{AB}$
3.5	1.04×10^{3}	0.164	$100* D_{AB}$
	1.04×10^{4}	0.163	$10* D_{AB}$
	1.04×10^{5}	0.159	D_{AB}
	1.04×10^{6}	0.153	$0.1*D_{AB}$
	1.04×10^{7}	0.150	$0.01*D_{AB}$
4	1.04×10^{3}	0.123	$100* D_{AB}$
	1.04×10^{4}	0.122	$10* D_{AB}$
	1.04×10^{5}	0.119	D_{AB}
	1.04×10^{6}	0.115	$0.1*D_{AB}$
	1.04×10^{7}	0.113	$0.01*D_{AB}$



(1) With the increase of the reaction order n, the conversion will decrease. The conversion will also decrease when the Peclet number increases.
(2) When n is less than 1.5 and Pe is 10^5, the diffusion in the system becomes more important.

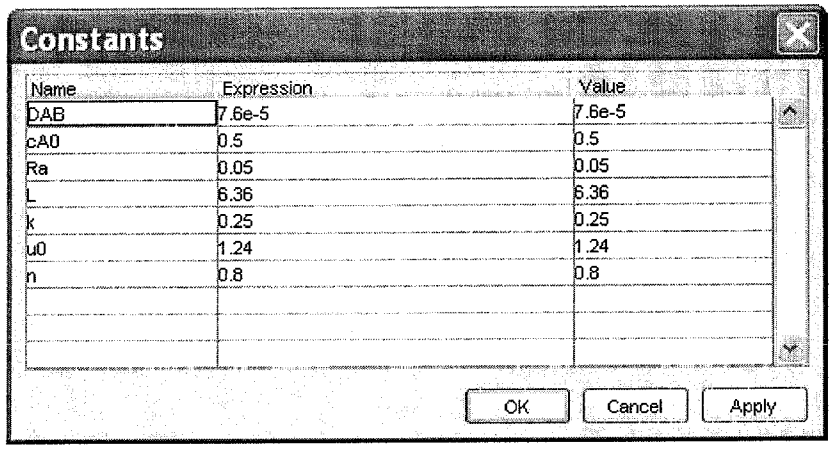
Below show FEMLAB screenshots useful for this problem.

Femlab Screenshots
(1) Domain



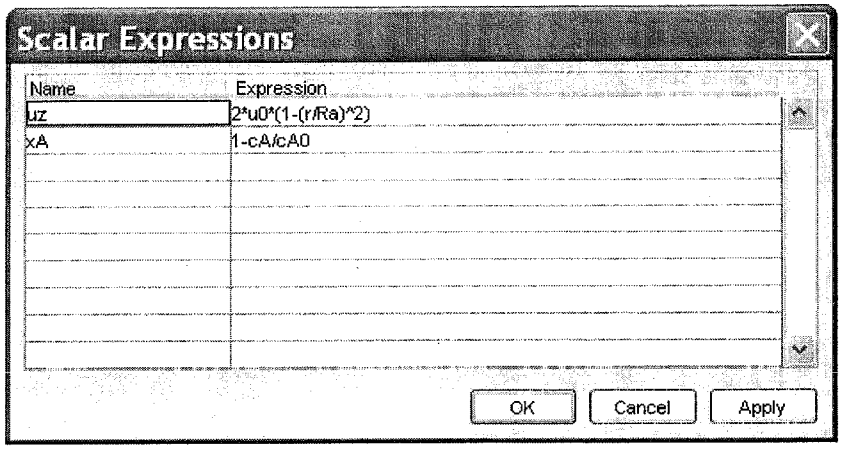
(4) Constants and scalar expressions

- Constants



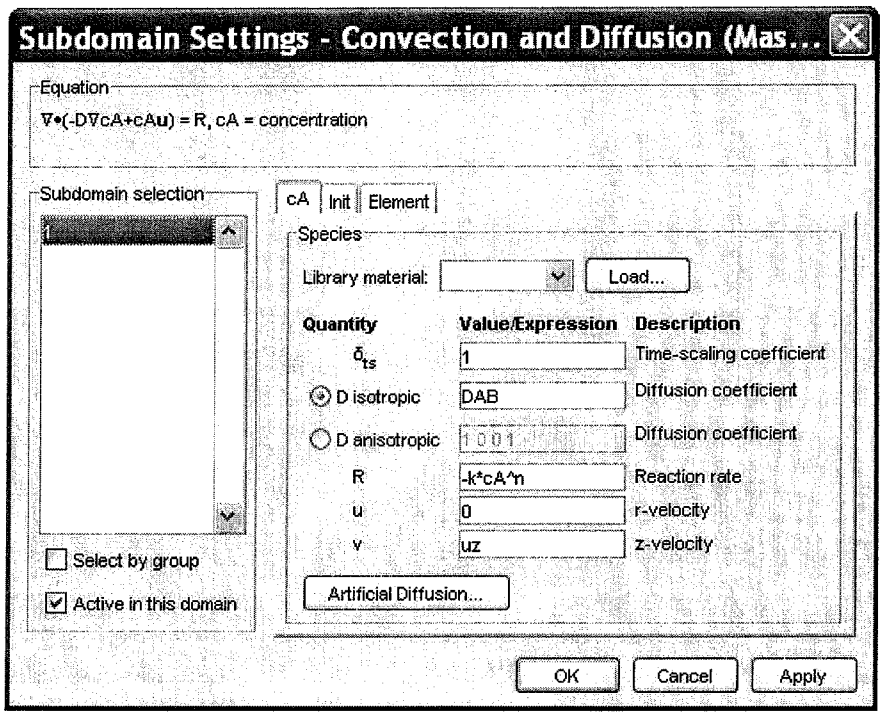
- Scalar expressions

•



(5) Subdomain settings

- **Physics**



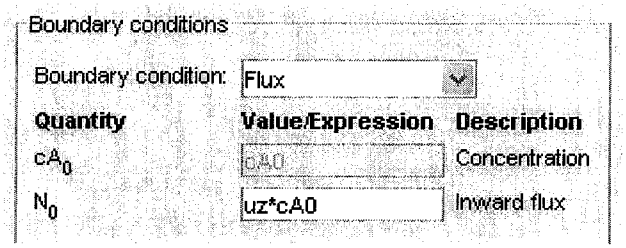
- Initial Values

(Mass balance) cA(t0) = cA0

- Boundary Conditions

@ r = 0, Axial symmetry

@ inlet,



@ outlet, Convective flux

@ wall, Insulation/Symmetry

P14-19 (a)

First order reaction

Input Parameters:

$n = 1$

$R = 0.05m$

$L = 6.36m$

$k = 0.25/\min$

$U_0 = 1.24m/\min$

$C_{A0} = 0.5mol/dm^3$

$D_{AB} = 7.6 \times 10^{-5} m^2 / \min$

Conversion:
xA= 0.687 @ Open-vessel Boundary: –Ni·n =2*U0*(1-(r/Ra)^2)*CA0
xA= 0.726 @ Close-vessel Boundary: –Ni·n =U0*CA0

Conversion:
xA= 0.755 @ Open-vessel Boundary: –Ni·n =2*U0*(1-(r/Ra)^2)*CA0
xA= 0.778 @ Close-vessel Boundary: –Ni·n =U0*CA0

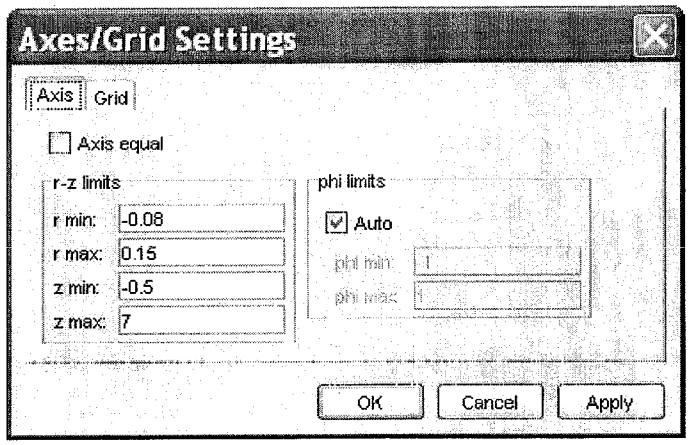
I. Variation of Da number

Damköhler number/ Da	Conversion		Parameter
	Closed-vessel	Open-vessel	
0.449	0.404	0.287	8*U0
0.898	0.527	0.439	4*U0
1.795	0.658	0.606	2*U0
3.59	0.778	0.755	U0
7.18	0.870	0.862	U0/2
14.36	0.930	0.928	U0/4
28.72	0.964	0.964	U0/8

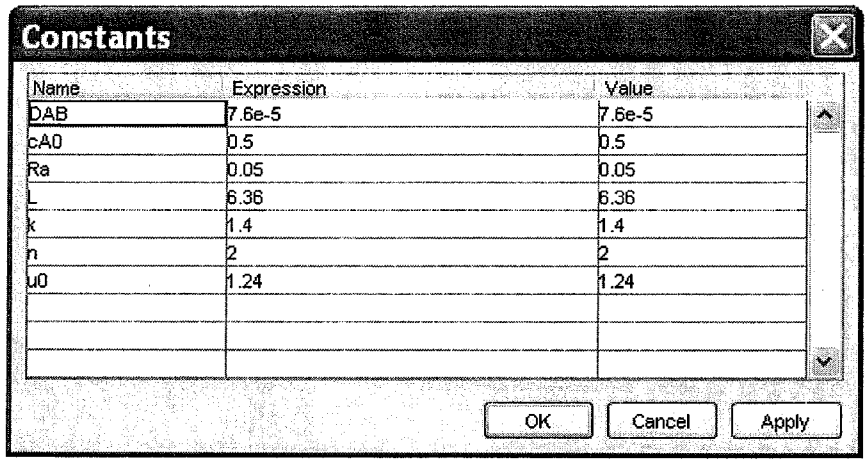
II. Variation of Pe number

Peclet number/Pe	Conversion		Parameter
	Closed-vessel	Open-vessel	
1.04e3	0.781	0.781	100* D_{AB}
1.04e4	0.781	0.776	10* D_{AB}
1.04e5	0.778	0.755	D_{AB}
1.04e6	0.772	0.740	0.1*D_{AB}
1.04e7	0.770	0.737	0.01*D_{AB}

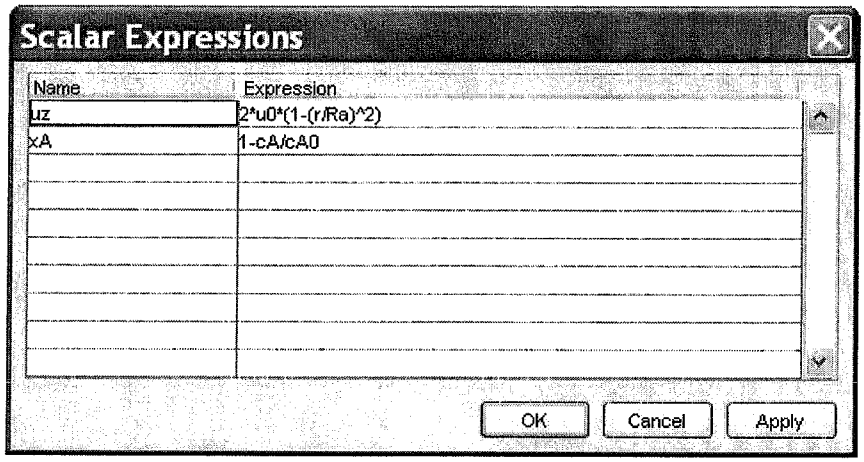
III. Femlab Screen Shots
(1) Domain



(2) Constants and scalar expressions
- Constants

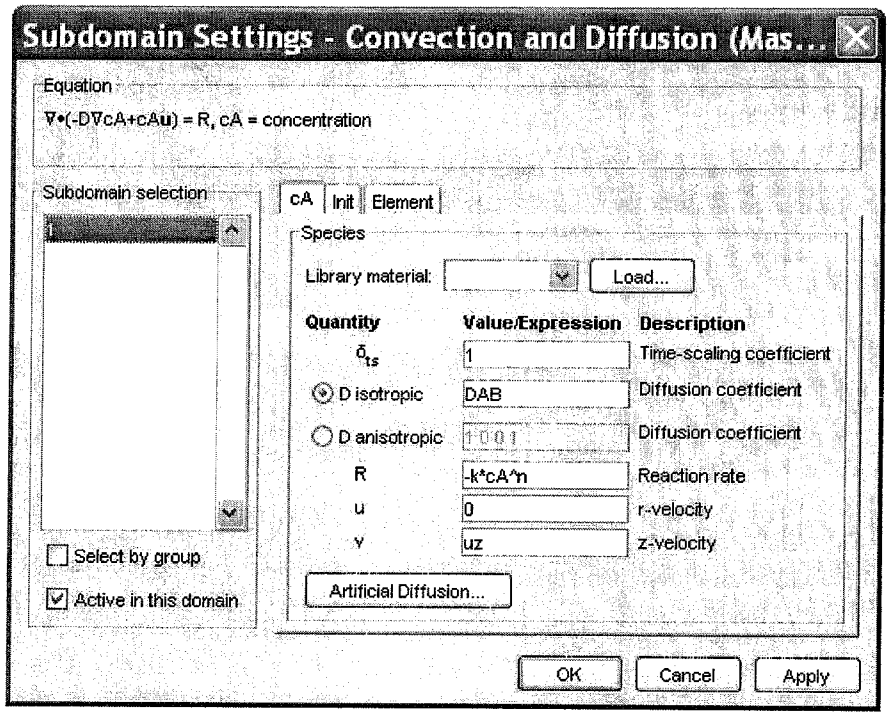


- Scalar expressions



(3) Subdomain settings

- Physics

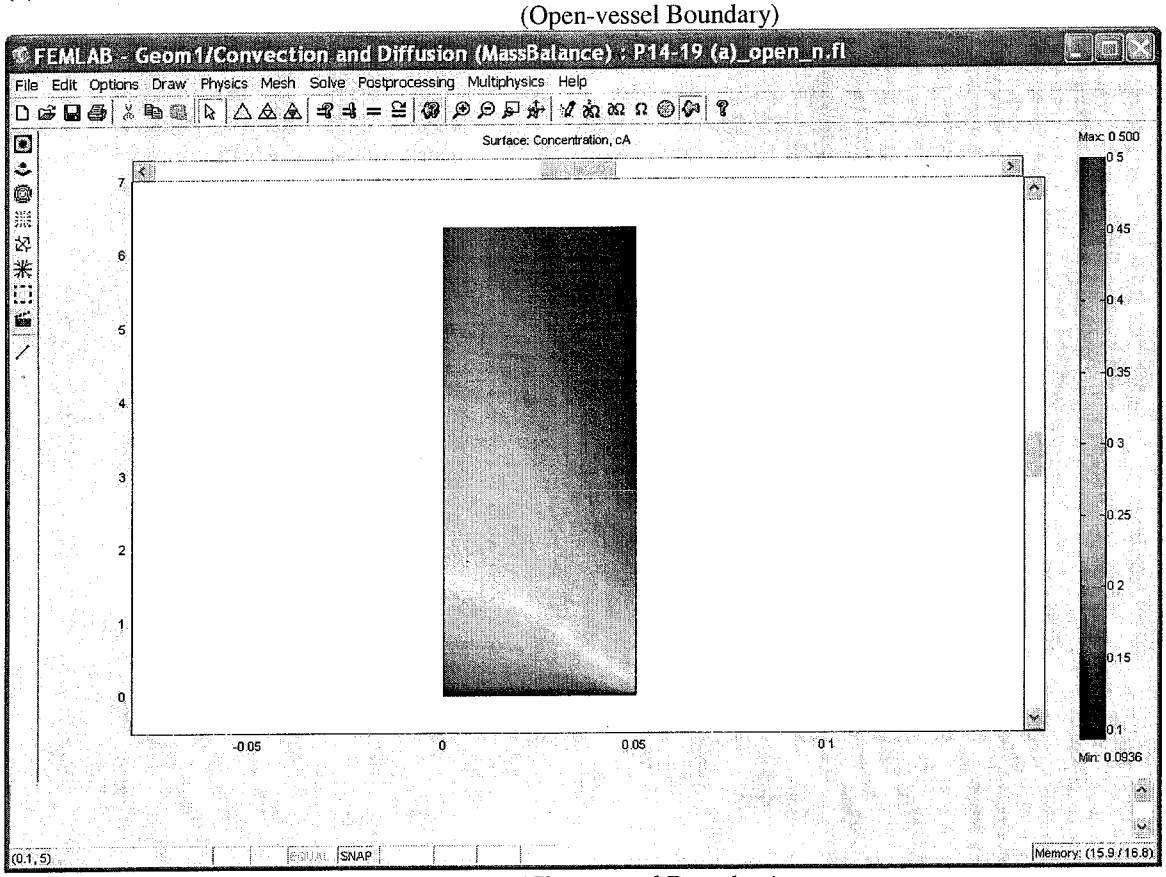


- Initial Values
(Mass balance) cA(t0) = cA0

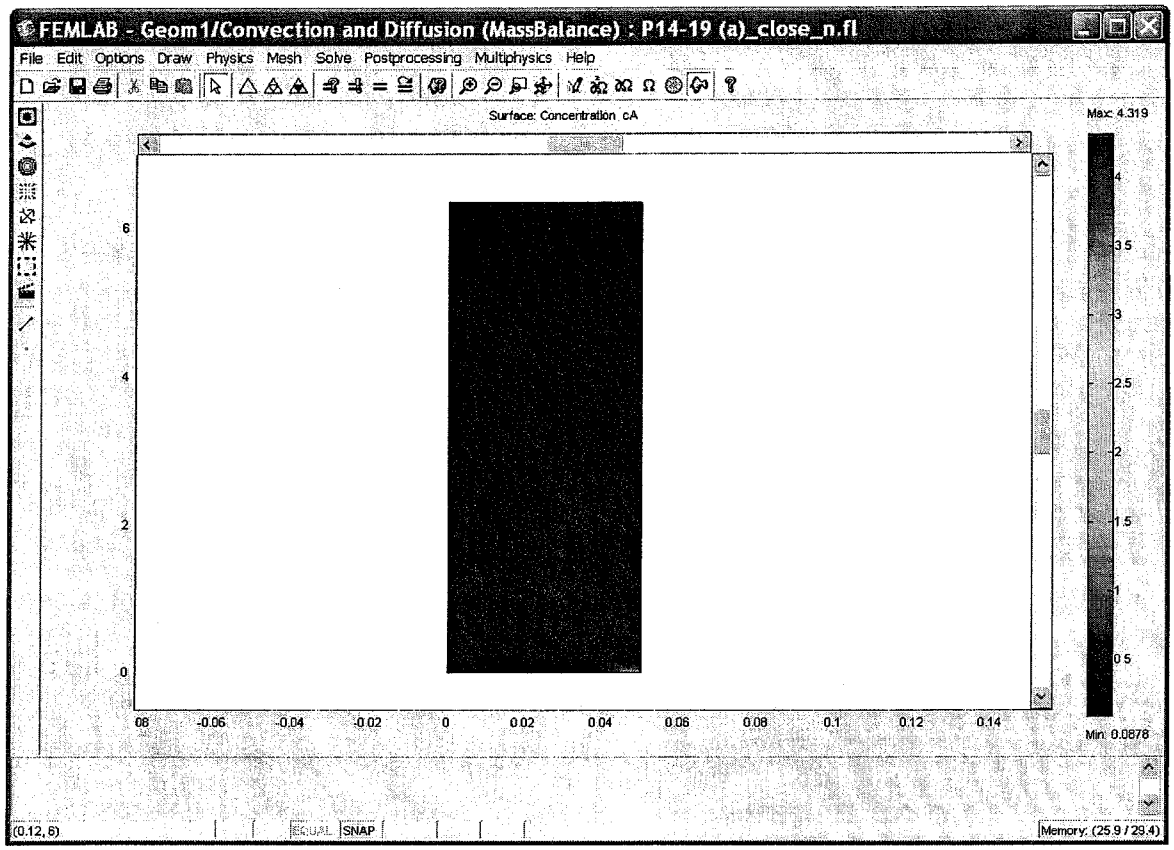
- Boundary Conditions
@ r = 0, Axial symmetry
@ inlet, Flux N_0 = 2*u0*(1-(r/Ra)^2)*cA0 : Open-Vessel Boundary
Flux N_0 = u0*cA0 : Close-Vessel Boundary
@ outlet, Convective flux
@ wall, Insulation/Symmetry

(4) Results

(Open-vessel Boundary)



(Close-vessel Boundary)



P14-19 (b)

Third order reaction with $k*C^2_{A0}= 0.7\ min^{-1}$

$$Da = \tau k C_{A0}^{n-1} = \frac{L}{U_0} k C_{A0}^{n-1}$$

$$Pe = U_0 L / D_{AB}$$

Input Parameters:

$n = 3$

$R = 0.05m$

$L = 6.36m$

$k = 2.8 dm^3 / mol.\min$

$U_0 = 1.24 m / \min$

$C_{A0} = 0.5 mol / dm^3$

$D_{AB} = 7.6 \times 10^{-5} m^2 / \min$

I. Variation of Da number

Damköhler number/ Da	Conversion		Parameter
	Closed-vessel	Open-vessel	
0.255	0.381	0.253	8*U0
0.51	0.466	0.375	4*U0
1.02	0.560	0.506	2*U0
2.03	0.655	0.628	U0
4.06	0.741	0.730	U0/2

8.12	0.813	0.809	U0/4
16.24	0.867	0.865	U0/8

II. Variation of Pe number

Peclet number/Pe	Conversion		Parameter
	Closed-vessel	Open-vessel	
1.04e3	0.650	0.649	100* D_{AB}
1.04e4	0.654	0.645	10* D_{AB}
1.04e5	0.655	0.628	D_{AB}
1.04e6	0.652	0.617	0.1*D_{AB}
1.04e7	0.650	0.615	0.01*D_{AB}

(c) Half order reaction with k= 0.495 $(mol/dm^3)^{1/2}min^{-1}$

$$Da = \tau k C_{A0}^{n-1} = \frac{L}{U_0} k C_{A0}^{n-1}$$

$$Pe = U_0 L / D_{AB}$$

Input Parameters:

$n = 1/2$

$R = 0.05m$

$L = 6.36m$

$k = 0.495(mol/dm^3)^{1/2}\ \min^{-1}$

$U_0 = 1.24m/\min$

$C_{A0} = 0.5mol/dm^3$

$D_{AB} = 7.6\times10^{-5} m^2/\min$

I. Variation of Da number

Damköhler number/ Da	Conversion		Parameter
	Closed-vessel	Open-vessel	
0.69	0.432	0.378	8*U0
1.38	0.713	0.641	4*U0
2.76	0.959	0.911	2*U0
5.52	1	1	U0
11.04	/	/	U0/2
22.08	/	/	U0/4
44.16	/	/	U0/8

II. Variation of Pe number

Peclet number/Pe	Conversion		Parameter
	Closed-vessel	Open-vessel	
1.04e3	1	1	100* D_{AB}
1.04e4	1	1	10* D_{AB}
1.04e5	1	1	D_{AB}
1.04e6	/	0.9995	0.1*D_{AB}
1.04e7	/	0.9994	0.01*D_{AB}

(d) The radial conversion profiles for various order of reaction

(1) First order

$n = 1$

$L = 6.36m$

$R = 0.05m$

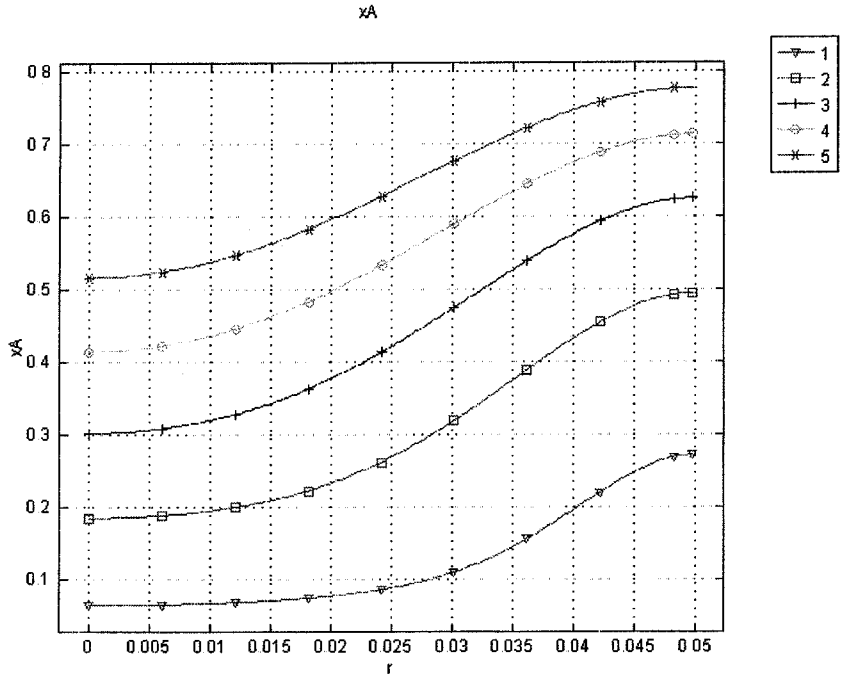
$k = 0.25dm^3 / mol.\min$

$U_0 = 1.24m / \min$

$C_{A0} = 0.5mol / dm^3$

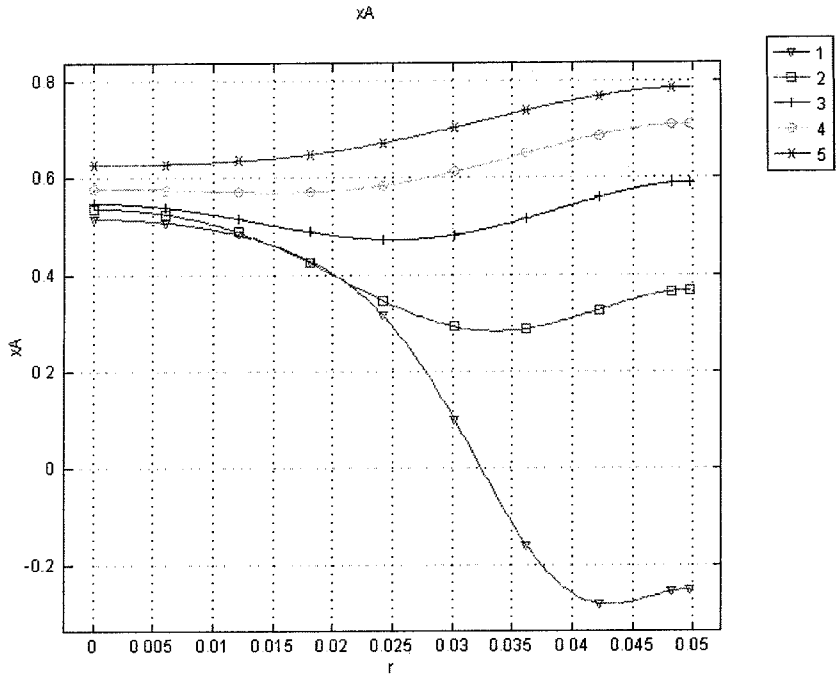
$D_{AB} = 7.6 \times 10^{-5} m^2 / \min$

I. Open–vessel:



Note: 1: z= L/10; 2: z=3L/10; 3: z=L/2; 4: z=7L/10; 5: z=9L/10

II. Closed-vessel:



Note: 1: z= L/10; 2: z=3L/10; 3: z=L/2; 4: z=7L/10; 5: z=9L/10

Something is not correct with z= L/10 because of the FEMLAB!

(2) Second order

$n = 2$

$R = 0.05m$

$L = 6.36m$

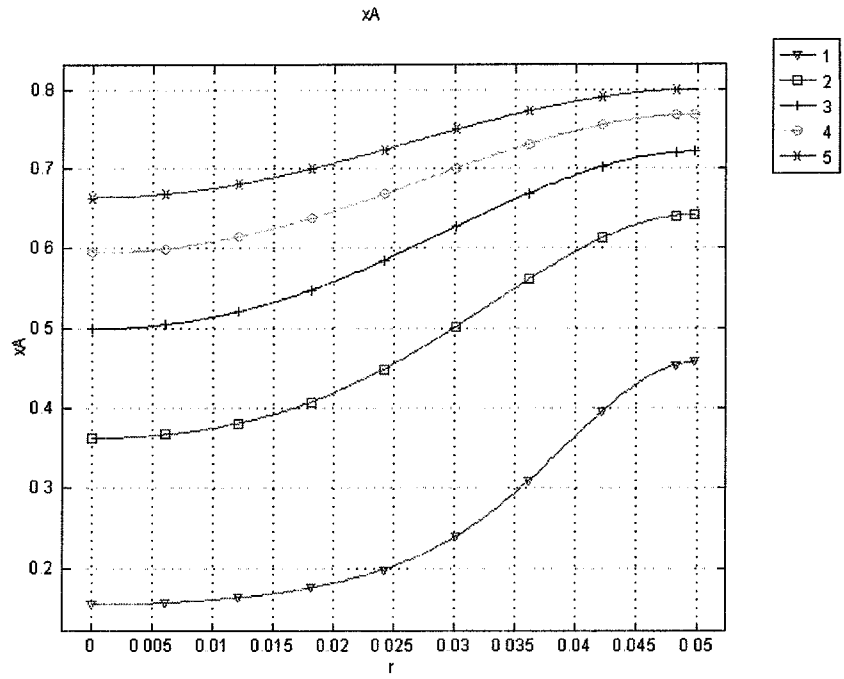
$k = 1.4dm^3 / mol.\min$

$U_0 = 1.24m / \min$

$C_{A0} = 0.5mol / dm^3$

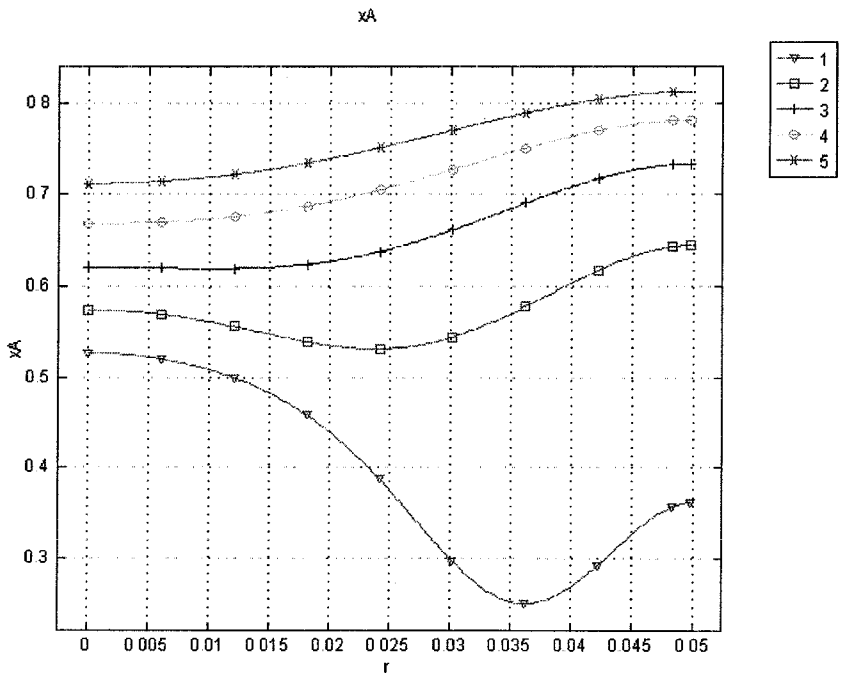
$D_{AB} = 7.6 \times 10^{-5} m^2 / \min$

I. Open–vessel:



Note: 1: z= L/10; 2: z=3L/10; 3: z=L/2; 4: z=7L/10; 5: z=9L/10

II. Closed-vessel:



Note: 1: z= L/10; 2: z=3L/10; 3: z=L/2; 4: z=7L/10; 5: z=9L/10

(3) Third order

$n = 3$

$R = 0.05m$

$L = 6.36m$

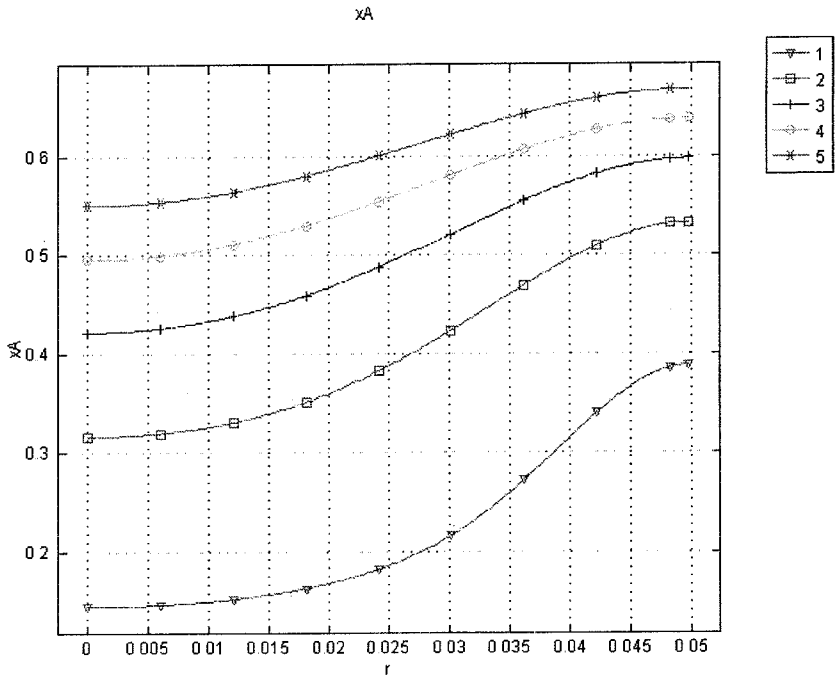
$k = 2.8dm^3 / mol.\min$

$U_0 = 1.24m / \min$

$C_{A0} = 0.5mol / dm^3$

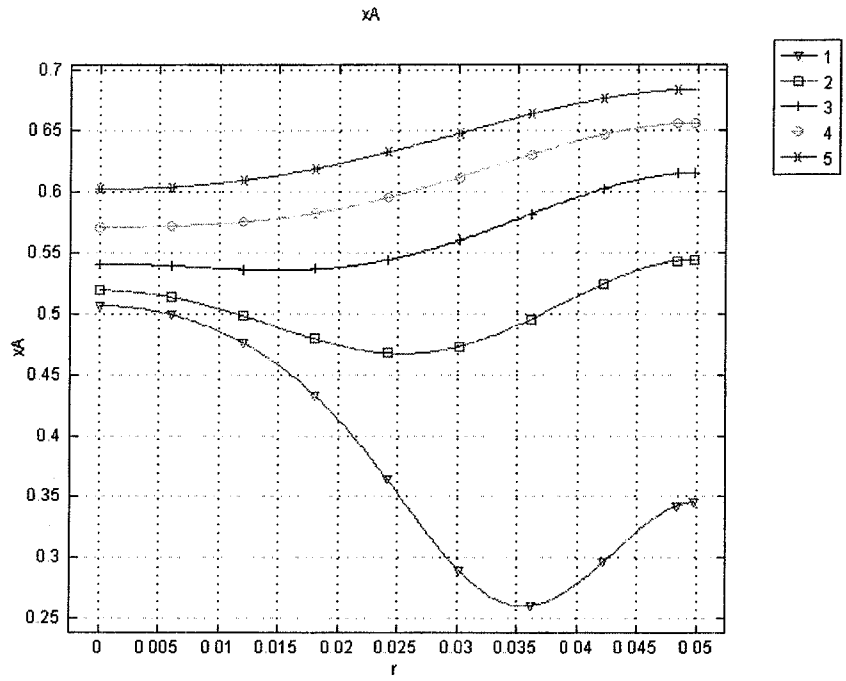
$D_{AB} = 7.6 \times 10^{-5} m^2 / \min$

I. Open vessel:



Note: 1: z= L/10; 2: z=3L/10; 3: z=L/2; 4: z=7L/10; 5: z=9L/10

II. Closed- vessel



Note: 1: z= L/10; 2: z=3L/10; 3: z=L/2; 4: z=7L/10; 5: z=9L/10

P14-20 (a)

Higher Peclet number

Curve 1 ("closer" to the one of an ideal PFR) has a higher Peclet number, because the cumulative distribution is more concentrated around the mean residence time.

P14-20 (b)

Higher dispersion coefficient

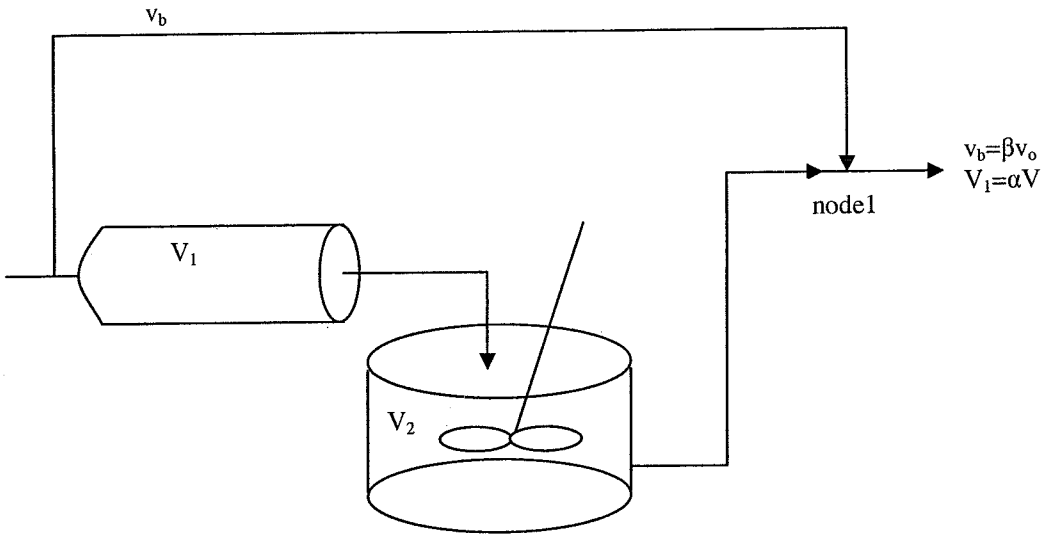
Curve 2 has a higher dispersion coefficient: a higher Peclet number corresponds to a lower dispersion coefficient.

P14-20 (b)

Large number of T-I-S

Curve 1: Increasing the number of T-I-S corresponds to increase the Peclet Number (i.e. Bo=2(n-1)).

P14-21 (a)



F(t) and E(t) curves for $\alpha = \frac{V_1}{V} = 0.4$ *and* $\beta = \frac{v_b}{v_0} = 0.2$

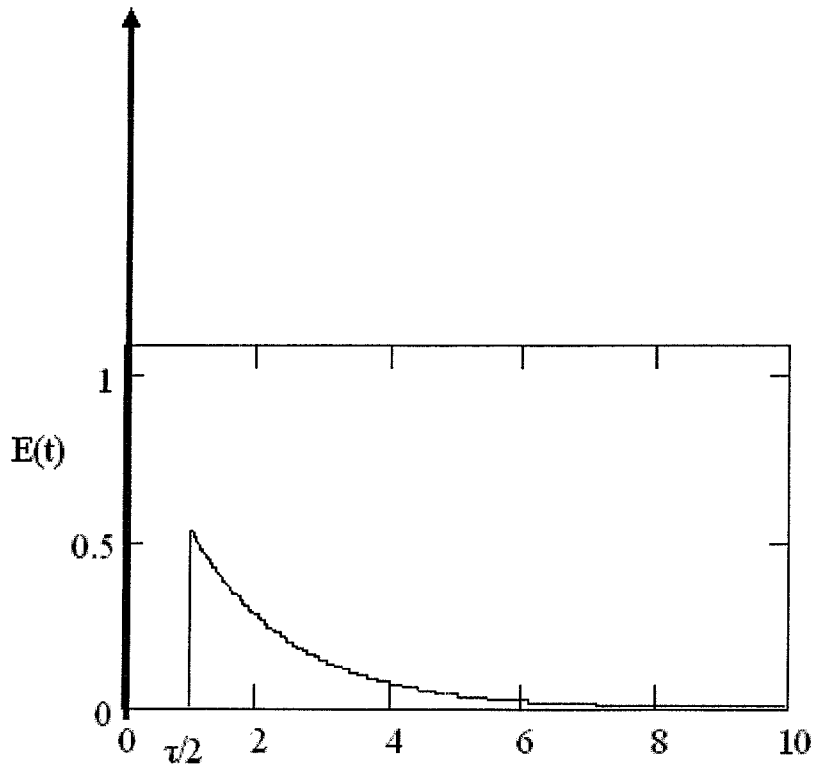
The analytical expression for E (t) is given by:

$$E(t) = \begin{cases} \beta\delta(t) & t < \tau_1 \\ (1-\beta)\dfrac{e^{-(t-\tau_1)/\tau_2}}{\tau_2} & t \geq \tau_1 \end{cases}$$

Where:

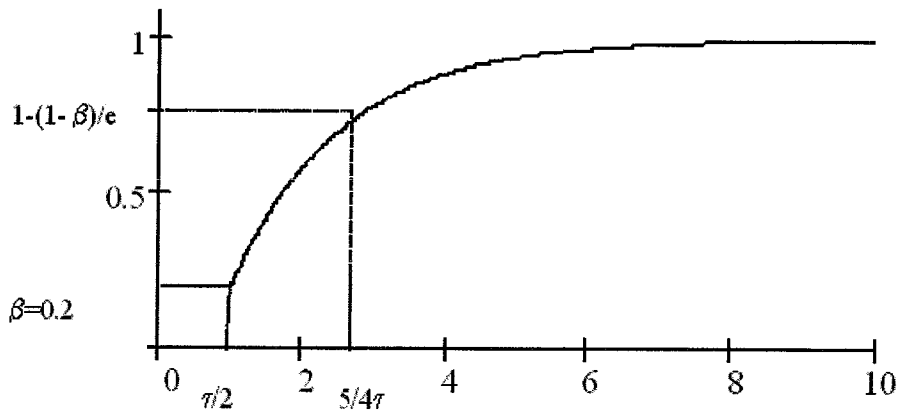
$$\tau_1 = \tau_{PFR} = V_1 \Big/ (v_0 - v_b) = \frac{\alpha V}{(1-\beta)v_0} = \frac{1}{2}\tau$$

$$\tau_2 = \tau_{CSTR} = V_2 \Big/ (v_0 - v_b) = \frac{(1-\alpha)V}{(1-\beta)v_0} = \frac{3}{4}\tau$$



Integrating we can obtain the analytical expression for F (t):

$$F(t)=\begin{cases}\beta & t<\dfrac{\tau}{2}\\ 1-(1-\beta)e^{-\left(t-\frac{\tau}{2}\right)/\left(\frac{3\tau}{4}\right)} & t\geq\dfrac{\tau}{2}\end{cases}$$



P14-21 (b)

Conversion

2nd order, $kC_{Ao}=0.5min^{-1}$, $\tau=2min$

Balance around node 1

$$(1-\beta)v_o C_{CSTR} + \beta v_0 C_b = v_0 C_A$$

For the PFR:

Second-order

$$X_{PFR} = \frac{C_{A0} - C_{PFR}}{C_{A0}} = \frac{Da_{PFR}}{1+Da_{PFR}} = 0.333$$

Where $Da_{PFR} = kC_{Ao}\frac{\alpha}{(1-\beta)}\tau = 0.5$

$$kC_{PFR} = 0.333\,\text{min}^{-1}$$

For the CSTR:

$$X_{CSTR} = \frac{C_{PFR} - C_{CSTR}}{C_{PFR}} = \frac{(1+2Da_{CSTR}) - \sqrt{1+4Da_{CSTR}}}{2Da_{CSTR}} = 0.268$$

Where $Da_{CSTR} = k\frac{1-\alpha}{1-\beta}\tau C_{PFR} = 0.5$

$$kC_{CSTR} = 0.366\,\text{min}^{-1}$$

$$kC_A = (1-\beta)kC_{CSTR} + \beta kC_b = (1-\beta)kC_{CSTR} + \beta kC_{Ao} = 0.393\,\text{min}^{-1}$$

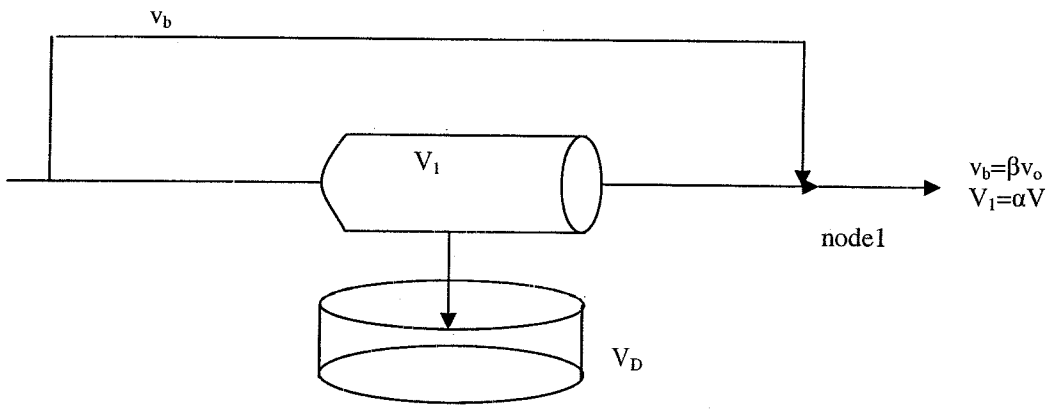
$$X = \frac{kC_{A0} - kC_A}{kC_{A0}} = 0.214$$

In absence of bypass ($\beta=0$) the conversion would be X=0.245

P14-22

Two parameters model

A possible two-parameter model is the PFR with Bypass (v_b) and Dead Volume (V_D)



Where $v_o=1m^3min^{-1}$, $V=2m^3$, $\alpha=V_1/V=0.5$, $\beta=v_b/v_o=0.5$ and $\tau=V/v_o=2min$

To evaluate the conversion we write a balance around node 1on species A:

$$(1-\beta)v_o C_{PFR} + \beta v_0 C_b = v_0 C_A$$

PFR, 2nd order, liquid phase

$$r_A = -kC_A C_B$$

Where k=1.5 m^3/(kmol·min) and $C_{Ao} = C_{Bo} = 2mol/dm^3$

$$X_{PFR} = \frac{C_{A0} - C_{PFR}}{C_{A0}} = \frac{Da_{PFR}}{1 + Da_{PFR}} = 0.857$$

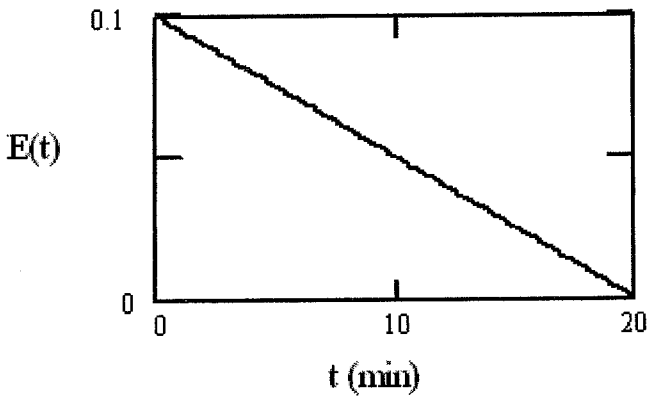
Where $Da_{PFR} = kC_{Ao}\frac{\alpha}{(1-\beta)}\tau = 6$

$$C_{PFR} = C_{Ao} - X_{PFR}C_{Ao} = 0.286mol/dm^3$$

$$C_A = (1-\beta)C_{PFR} + \beta C_b = (1-\beta)C_{PFR} + \beta C_{Ao} = 1.143mol/dm^3$$

$$X = \frac{C_{A0} - C_A}{C_{A0}} = 0.429$$

P14-23



By definition: $\int_0^\infty E(t)dt = 1$

$$\int_0^\infty E(t)dt = \frac{0.1 * t1}{2} = 1 \rightarrow t1 = 20\,\text{min}$$

For a triangular E(t): $t_1 = \frac{2}{E(0)}$

The analytical expression for E(t) is given by:

$For\ 0 \le t \le t_1 \quad E(t) = -\frac{0.1}{t_1}t + 0.1$

$For\ t > t_1 \quad E(t) = 0$

P14-23 (a)

Mean residence time

$$t_m = \int_0^\infty E(t)t\,dt = \int_0^{t_1}\left(-\frac{0.1}{t_1}t + 0.1\right)t\,dt = \left[\frac{-0.1t^3}{3t_1} + \frac{0.1t^2}{2}\right]_0^{t1} = -\frac{0.1}{3}t_1^2 + \frac{0.1t_1^2}{2} = \frac{0.1t_1^2}{6} = 6.67\,\text{min}$$

(For a triangular E(t): $t_m = \frac{t_1}{3}$)

Variance

$$\sigma^2 = \int_0^\infty E(t)(t - t_m)^2\,dt =$$

$$\int_0^{t_1}\left(-\frac{0.1}{t_1}t + 0.1\right)t^2\,dt - t_m^2 = \left[\frac{-0.1t^4}{4t_1} + \frac{0.1t^3}{3}\right]_0^{t1=20\,\text{min}} - t_m^2$$

$$= -\frac{0.1}{4}t_1^3 + \frac{0.1t_1^3}{3} - t_m^2 = \frac{0.1\cdot 20^3}{12} - 6.67^2 = 22.2\,\text{min}$$

Assuming closed-closed system: $\tau = t_m$

P14-23 (b)

Peclet number

$$\frac{\sigma^2}{\tau^2} = 1 = \lim_{Pe\to 0}\frac{2}{Pe_r} - \frac{2}{Pe_r^2}\left(1 - e^{-Pe_r}\right)$$

And $Pe_r = 0$

P14-23 (c)

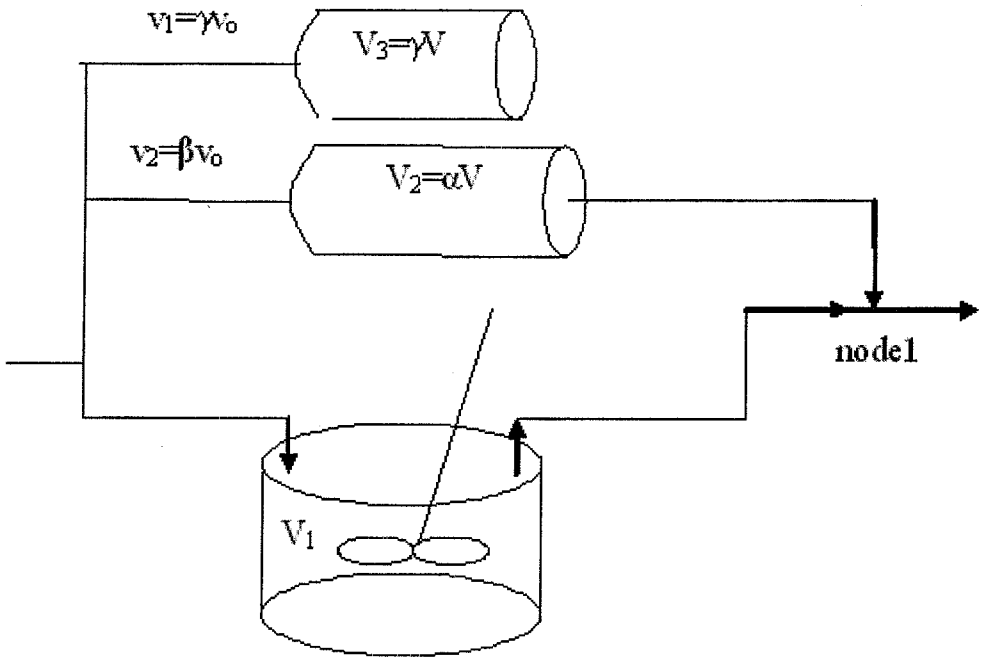
Tanks in series

$$n = \frac{\tau^2}{\sigma^2} = 1$$

The triangular E (t) can be interpreted as an approximation for $t \ll \tau$ of a CSTR where the continuity impose $E(0)*\tau = 2/3$ instead of 1.

P14-24

The F(t) con be representative of a CSTR in parallel with two PFRs:



First order reaction

Ideal PFR	*Ideal CSTR*	*Ideal laminar flow reactor*	*Segregation*	*Maximum Mixedness*	*Dispersion*	*Tanks in series*

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